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Polyester radiation cooling film as well as preparation method and application thereof

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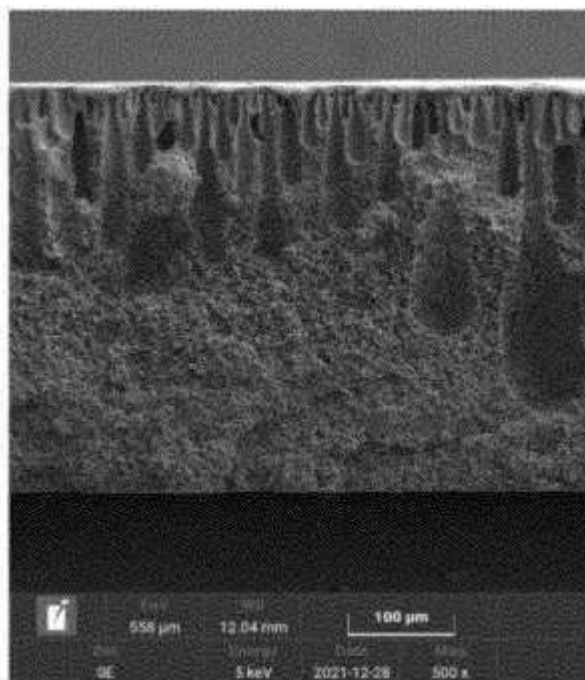
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Abstract of CN114605689 (A)

The invention discloses a polyester radiation cooling film as well as a preparation method and application thereof. The preparation method of the film comprises the following steps: preparing a film casting solution from a polyester polymer, a solvent, a polymer additive and a titanate coupling agent; and coating the membrane casting solution on the surface of a support membrane, standing the obtained wet membrane, and soaking the wet membrane in a non-solvent coagulating bath to obtain the polyester radiation cooling membrane. The polyester radiation cooling film has the advantages of high tensile strength, high interface bonding strength, excellent flexibility, excellent heat insulation and cooling performance and the like, can be bent and curled at will, can be suitable for matrixes



with different properties and shapes, is beneficial to popularization and application of the polyester radiation cooling film, and is high in use value and good in application prospect. The preparation method has the advantages of being simple in process, convenient to operate, low in equipment requirement, capable of recycling the solvent and the non-solvent, low in production cost, high in film forming efficiency and the like, is suitable for large-scale industrial production and has important significance on energy conservation and environmental protection.

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DESCRIPTION CN114605689A

10 A kind of polyester radiation cooling cooling film and its preparation method and application

[0001]

14 technical field

[n0001]

18 The invention belongs to the technical field of heat insulation materials, and in particular relates to a polyester radiation cooling film and its preparation method and application.

[0003]

23 Background technique

[n0002]

27 Under the sun exposure, in order to achieve the purpose of heat insulation and cooling without energy consumption, the surface of the substrate (buildings, tents, parking sheds, cars or other equipment) can be covered with a radiation cooling film or directly placed on the substrate.

30 However, almost all similar products currently on the market can only partially block the entry of sunlight energy, but cannot efficiently dissipate internal heat, such as aluminum foil.

32 Existing heat insulation film products often use aluminum foil to reflect sunlight. Although aluminum foil can reflect infrared heat, it cannot radiate infrared heat. The heat enters the interior; the bonding strength between the aluminum foil and the substrate is poor, and the corrosion resistance and weather resistance are poor. The existence of the above defects limits the service life and heat insulation effect of existing heat insulation film products.

37 Although the introduction of radiant fillers into the heat insulation film can improve the heat dissipation

problem, the performance of the filler type heat insulation film product is easily affected by the uniformity of filler distribution, and the introduced filler will increase the surface density of the film. Therefore, the existence of the above problems makes it difficult for the existing thermal insulation film products to meet higher application requirements, which is not conducive to its promotion and application.

[n0003]

45 Radiative cooling technology is a method of cooling objects by exchanging radiant energy with cold outer space, which can significantly reduce the energy consumption required for cooling, thereby reducing the negative impact on the environment, and has become an emerging research hotspot.

48 In order to achieve the cooling effect, the material is required to have strong radiation ability only in the atmospheric window band of 8-13 μm to realize the full export of heat, and to have strong reflection ability in the sunlight band of 0.3-2.5 μm to prevent the introduction of solar heat. In order to make daytime radiative cooling devices have strict spectral selectivity, researchers have developed and reported a series of metamaterial-based radiative cooling materials and devices, and achieved certain cooling effects in outdoor cooling performance tests, among which Polymer membranes based on disordered porous structures have been intensively studied because of their potential for large-scale preparation, such as fluorocarbon resin PVDF, polysiloxane PDMS, and polyethylene PE-based porous membranes. Although the spectral properties of these porous films show certain spectral selectivity and basically meet the requirements of radiative cooling, there is still much room for improvement in mechanical properties. Polyester film is currently the most widely used thermoplastic polymer film on the market. It is favored by consumers because of its excellent comprehensive properties. It is usually colorless, transparent, shiny, with excellent mechanical properties, rigidity, hardness and toughness. High, puncture resistance, friction resistance, high temperature and low temperature resistance, chemical resistance, oil resistance, air tightness and fragrance retention, it is one of the commonly used composite film substrates. For example, polyethylene terephthalate (PET) is a commercial semi-crystalline aromatic polyester with excellent mechanical, chemical and thermal properties and high cost performance. It is the most important variety of thermoplastic polyesters, and the application market based on PET porous film is also very huge, often used as the support of light reflection film, separation film, light conversion agricultural film and various functional films, but there are almost no reports on the use of PET based porous film in the field of radiation cooling. The development of high-performance PET porous films for radiative cooling not only helps to solve the bottleneck problems of existing materials such as mechanical properties and low-cost large-scale preparation, but also has great significance for expanding the application field of polyester films represented by PET.

[n0004]

74 The commonly used preparation methods of existing PET porous membranes include melt stretching method, microcellular foaming method, track etching method and template method.

76 However, the PET porous films prepared by these methods are difficult to be directly used for radiative cooling, because the pore shape is single and the porosity is low, so it is difficult to realize the coordinated regulation of multi-band light reflection characteristics. In the previous study of the inventors of the present application, a layer of PET porous membrane was prepared on a flexible support membrane by using non-

solvent-induced phase separation method, which showed good sunlight reflection ability and infrared radiation ability in the atmospheric window, but because PET Molecular rigidity is relatively large, and the porous structure with high porosity is more brittle after being prepared, and it is not resistant to bending, and it is very easy to peel off from the bottom support film; at the same time, high solar reflectance depends on the thickness of the porous film, and increasing the thickness will promote the ball The increase of the granular structure further damages the mechanical properties of the porous membrane. At the same time, in the actual research process of the inventors of the present application, it has also been found that: for this class of crystalline polymers such as polyester, the non-solvent/solvent/polyester ternary system is prone to crystallization-induced crystallization in thermodynamics. Solid-liquid phase separation, thus obtaining a spherical structure, is also likely to be accompanied by crystallization and growth in kinetics, which promotes the formation of spherical particles, and the existence of a large number of spherical structures can easily lead to poor mechanical properties of porous membranes. Obviously, the present In the preparation process, the high-porosity porous membrane prepared from polyester polymer still has the defect that the mechanical properties cannot meet the requirements.

[0007]

97 Contents of the invention

[n0005]

101 Aiming at the deficiencies in the prior art, the present invention provides a polyester radiation cooling film with excellent spectral selectivity and mechanical properties as well as its preparation method and application.

[n0006]

106 In order to solve the problems of the technologies described above, the present invention adopts the following technical solutions:

[n0007]

111 A preparation method of polyester radiation cooling film, comprising the following steps:

[n0008]

115 (1) Mix the polyester polymer, solvent, polymer additive, and titanate coupling agent, and stir until completely dissolved to obtain a casting solution; the mass ratio of the polymer additive to the polyester polymer is $\leq 20\%$; The mass ratio of the titanate coupling agent to the polyester polymer is $\leq 4\%$;

[n0009]

121 (2) coating the casting solution obtained in the step (1) on the surface of the support membrane to obtain a

wet film;

[n0010]

¹²⁶ (3) The wet film obtained in step (2) is left to stand, soaked in a non-solvent coagulation bath, washed, and dried to obtain a polyester-based radiation cooling film.

[n0011]

¹³¹ The above preparation method is further improved, in step (1), the mass ratio of the polymer additive to the polyester polymer is 5% to 20%; the titanate coupling agent and the polyester polymer The mass ratio is 0.1% to 2%.

[n0012]

¹³⁷ The above-mentioned preparation method is further improved. In step (1), the polymer additive is at least one of polyethylene glycol, polyvinylpyrrolidone, and polyvinyl alcohol; the titanate coupling agent is KR - At least one of 12, KR-9S, T M C-2, T M C-311, T M C-401.

[n0013]

¹⁴³ The above-mentioned preparation method is further improved. In step (1), the mass ratio of the polyester polymer to the solvent is 3-25: 75-97; the polyester polymer is polyethylene terephthalate At least one of glycol ester, polybutylene terephthalate, polyethylene naphthalate, polycarbonate, polyarylate, polyethersulfone resin; the solvent is hexafluoroisopropanol, at least one of trifluoroacetic acid, dichloromethane and phenol; the stirring is carried out at 40° C to 80° C.

[n0014]

¹⁵¹ The above-mentioned preparation method is further improved. In step (2), the coating method is scraping or spraying; the supporting film is a flexible supporting film; the supporting film is a PET film, a PI film, a PEN film, PC film, PES film; the thickness of the wet film is $\leq 1200 \mu\text{m}$.

[n0015]

¹⁵⁷ The above preparation method is further improved. In step (3), the standing is carried out under an atmosphere; the standing time is $\leq 15\text{min}$; the soaking time is 5h-96h; the non-solvent coagulation bath The temperature is $\leq 50^{\circ}\text{C}$; the non-solvent coagulation bath is at least one of alcohols containing 1 to 8 carbons and their mixtures with water, ethyl propionate and their mixtures with water; the The mass percent content of water in the mixed solution of alcohol containing 1 to 8 carbons and water is $\leq 50\%$; the mass percent content of water in the mixed solution of ethyl propionate and water is $\leq 50\%$.

[n0016]

166 The above preparation method is further improved, in step (2), the thickness of the wet film is 400 μm -1200 μm .

[n0017]

171 The above preparation method is further improved, in step (3), the standing time is 1 min-15 min; the soaking time is 5h-96h; the temperature of the non-solvent coagulation bath is 15° C-50° C.

[n0018]

176 As a general technical idea, the present invention also provides a polyester radiation cooling film, which is prepared by the above-mentioned preparation method.

[n0019]

181 The above-mentioned polyester radiation cooling film is further improved, the polyester radiation cooling film includes a support film and a polyester spectrally selective porous film, and the polyester spectrally selective porous film is supported on the support film Above; the porosity of the polyester-based spectrally selective porous membrane is 55 % to 85 %; the thickness of the polyester-based spectrally selective porous membrane is 100 μm to 600 μm .

[n0020]

189 The above-mentioned polyester-based radiation cooling film is further improved, the surface of the polyester-based spectrally selective porous membrane is dense and smooth; the interior of the polyester-based spectrally selective porous membrane is an asymmetric porous structure; The interior of the above-mentioned polyester spectrally selective porous membrane is sequentially distributed with finger holes with a width of 5 μm to 100 μm , sponge pores with a diameter of less than 5 μm , and double continuous pores or sponge pores with a diameter of 1 μm to 3 μm from the upper surface to the bottom; The sponge holes are filled between the finger holes; the hole walls of the finger holes interpenetrate; the finger holes run through to the bottom of the film and stop at the double continuous holes or sponge holes at the bottom; the hole walls of the sponge holes are distributed with A through hole, the pore diameter of the through hole is below 5 μm ; sponge-like flower clusters are also accumulated on the hole walls of the finger hole and the sponge hole, and the pore diameter of the sponge-like flower cluster is on the order of nanometers.

[n0021]

203 As a general technical idea, the present invention also provides an application of the above-mentioned polyester radiation cooling film, which is to cover the polyester radiation cooling film on the surface of the substrate, or arrange it above the surface of the substrate, Or covered on animal and human skin; The base is

one of houses, cars, tents, pipes, boxes, sunshade products; A sort of.

[n0022]

210 Compared with the prior art, the present invention has the advantages of:

[n0023]

214 (1) In view of the defect that the mechanical properties cannot meet the requirements due to the easy formation of spheroid structure in the existing polyester porous membrane preparation method, the present invention creatively proposes a preparation method of the polyester radiative cooling film, polymer additive modified non-solvent-induced phase separation method, the preparation principle is: dissolve polyester, polymer additive, titanate coupling agent in solvent to obtain a uniform casting solution, and then pass the casting solution through scraping. The wet film is obtained by coating or spraying, and the wet film is immersed in a non-solvent coagulation bath after standing in the air for a period of time to form a porous film.

222 The whole film forming process is divided into two steps: the first step is the phase separation process. After the wet film is immersed in the non-solvent coagulation bath, the solvent in the wet film and the non-solvent in the coagulation bath diffuse each other to form a double diffusion process, the wet film system changes from a thermodynamically stable state to an unstable state, phase separation occurs, and a polymer-rich phase and a polymer-poor phase are obtained; the second step is the film curing process, the double diffusion process continues, and the polymer-rich phase is further solidified into Porous scaffold, the polymer-lean phase forms pores after drying.

229 In the present invention, the polyester polymer is used as the raw material, and the phase separation mechanism of the wet film is completely changed by adding polymer additives and optimizing their dosage, so that the phase separation mechanism is dominated by the solid-liquid phase separation that forms a spherical structure. The liquid-liquid separation phase that transforms into a sponge pore structure dominates, and then realizes the regulation of the pore shape, pore structure and porosity of the porous membrane, and obtains a porous morphology without a spherical structure. The root cause of the above changes is Polymer additives are polar molecules, and polyester molecules are generally weakly polar. Its addition changes the thermodynamic properties and phase separation kinetics of the non-solvent/solvent/polyester ternary system, making the polymer in the polymer-rich phase Esters are not easy to crystallize. Secondly, the molecular weight of the polymer additive is small, and it is easy to enter between the polyester macromolecular chains, which increases the distance between the polyester molecular chains, reduces the regular arrangement of the polyester molecular chains and makes it become It is not easy to crystallize, and the result of inhibited crystallization is to avoid the formation of non-spheroidal structure, thereby greatly improving the intralayer bonding strength of the polyester spectrally selective porous membrane and the interlayer bonding strength between the porous membrane and the support membrane.

244 Second, in the present invention, by adding a titanate coupling agent into the casting solution and optimizing its dosage to make it chemically interact with the support membrane, the bond between the polyester spectrally selective porous surface layer and the flexible support can be improved. The degree of mechanical lock between layers and the bonding strength between layers.

248 Thirdly, the use of titanate coupling agent can also increase the bonding between polyester molecules and improve the overall tensile strength and toughness.

250 Combining the above operations, the mechanical properties can be significantly improved while obtaining a porous morphology that meets the requirements.

252 Moreover, even if the thickness of the porous film is increased, the effect of the polymer additive to inhibit the formation of the spherical structure is still obvious, so that the polyester radiation cooling film prepared by the present invention can meet the requirements of high solar reflectance on the film thickness, thus obtaining A polyester radiation cooling film with excellent spectral selectivity and mechanical properties.

256 The polyester radiation cooling film prepared by the invention has the advantages of high tensile strength, high interface bonding strength, excellent flexibility, excellent heat insulation and cooling performance, etc., can be bent and curled at will, and can be applied to substrates with different properties and shapes, expanding the outdoor application potential of polyester radiation cooling film, which is conducive to the promotion and application of polyester radiation cooling film, with high use value and good application prospect.

262 At the same time, the preparation method of the present invention also has the advantages of simple process, convenient operation, low equipment requirements, recyclable solvent for casting film solution and non-solvent for coagulation bath, low production cost, high film forming efficiency, etc., and is suitable for large-scale industrial production. It is of great significance to energy saving and environmental protection.

[n0024]

269 (2) In the preparation method of the present invention, by optimizing the mass ratio of the polymer additive to the polyester polymer to be 5% to 20%, the phase separation mechanism after the wet film is immersed in the non-solvent coagulation bath can be changed more effectively, and at the same time It will not significantly change the dissolution effect in the casting solution; if the amount of polymer additives is too low, it is difficult to effectively inhibit the preferential formation of internal crystals after the wet film is immersed in a non-solvent coagulation bath; and if the amount of polymer additives is too high, it will be due to the solubility parameter The difference from polyester is too large, and it is difficult to completely dissolve in a solvent tailored for polyester.

277 At the same time, in the present invention, the mass ratio of the titanate coupling agent to the polyester polymer is also optimized to be 0.1% to 4%, which is more conducive to increasing the intralayer bonding strength of the polyester porous membrane and the layer bonding with the support membrane. The bonding strength between them will not significantly affect the viscosity of the casting solution. The principle of improving the mechanical properties of the titanate coupling agent is through its alkoxy functional region (RO—) directly connecting with the carboxyl or The hydroxyl group undergoes chemical action to couple, and at the same time, its -O-functional region can undergo ester exchange reaction with the carboxyl group on the polyester molecule. Further, its long molecular chain functional region can also be entangled with the polyester molecule, so that the polyester, Titanate and polyester are cross-linked; at the same time, the alkoxy functional region (RO—) on the titanate coupling agent can be directly bonded with the support membrane with carboxyl or hydroxyl groups on the surface after chemical modification. Coupling by chemical action, and at the same time, its -O-functional region can undergo transesterification reaction with the carboxyl group on the polyester molecule, so that the support membrane, titanate and polyester are crosslinked, and

the above changes can increase the elongation of the porous membrane And tensile strength, improve impact performance and interfacial bonding strength, but if the amount of titanate coupling agent is too much, it will lead to excessive transesterification reaction, which will lead to a sharp increase in the viscosity of the casting solution, which is not conducive to scraping the film.

[n0025]

297 (3) In the preparation method of the present invention, before the obtained wet film is immersed in the non-solvent coagulation bath, it also includes: placing the wet film in the air for a period of ≤ 15 minutes, so that the titanate acid in the wet film The ester coupling agent can be chemically connected with the support membrane, which is beneficial to improve the bonding strength between the porous membrane and the support membrane.

302 However, if the standing time is too long, it will lead to excessive volatilization of the solvent and the early occurrence of phase separation reaction, and the polymer-rich phase will have sufficient time to crystallize and obtain a spherical structure, resulting in deterioration of the mechanical properties of the radiative cooling film. Decreased significantly.

[n0026]

309 (4) In the preparation method of the present invention, the polyester polymer used is polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyethylene naphthalate At least one of ester (PEN), polycarbonate (PC), polyarylate (PAR), polyethersulfone resin (PES), these polyester polymers have the advantages of low price, easy availability, etc., and by them The prepared polyester-based spectrally selective porous membrane exhibits very excellent mechanical properties and has the advantage of good applicability.

[n0027]

317 (5) The present invention provides a polyester radiation cooling film, which is a two-layer structure composite film formed by carrying a polyester spectrally selective porous film on a support film. It is a kind of strong reflection ability of sunlight The filler-free porous membrane with strong mid-infrared radiation ability has the advantages of good heat insulation effect, good cooling effect, and excellent mechanical properties. It can avoid the use of functional fillers and the resulting problems of agglomeration and increase in surface density. High use value and good application prospect.

[n0028]

326 (6) In the polyester-based radiation cooling film of the present invention, by optimizing the porosity of the polyester-based spectrally selective porous membrane to 55% to 85%, at the same time, the thickness of the polyester-based spectrally selective porous membrane is also optimized to be 100 μm to 600 μm , so that the porous membrane can take into account both excellent spectral properties and mechanical properties.

330 If the porosity is too low and the thickness is too thin, it is difficult to achieve effective light scattering, thereby reducing the ability to reflect sunlight; if the porosity is too high or the thickness is too large, the mechanical

properties of the porous membrane will be seriously reduced.

[n0029]

- 336 (7) In the polyester radiation cooling film of the present invention, the surface of the polyester spectrally selective porous membrane is dense and flat, and the interior is an asymmetric porous structure. From the upper surface to the bottom, there are finger holes with a width of 5-100 μm , Sponge pores below 5 μm , double continuous pores or sponge pores of about 1 ~ 3 μm , large sponge pores are filled between the finger pores, and the walls of the finger pores interpenetrate; the finger pores develop to the bottom of the membrane, and finally terminate at the bottom of the double continuous pores or Sponge pores, from top to bottom, the pore diameter gradually decreases.
- 343 In addition, there are a large number of sponge-like flower clusters piled up on the pore wall, and the pore diameter is extremely small, on the order of nanometers.
- 345 Among them, the micro-holes can reflect long-wave radiation, especially can effectively scatter most wavelengths of sunlight, and the nano-holes can strongly scatter visible light with shorter wavelengths, so that the polyester radiation cooling film shows excellent sunlight reflection ability; The finger hole with larger size can reflect infrared radiation with longer wavelength, so that the sample also has a certain reflection ability to mid-wave infrared (2.5-8 μm).
- 350 In the present invention, the polyester radiation cooling film is a polymer composite film. As a high molecular polymer material, it has a strong absorption capacity for the mid-infrared band and strong infrared radiation characteristics in the window, which is conducive to the realization of thin film efficient heat dissipation.
- 353 Combining the above two factors, the polyester radiation cooling film of the present invention can effectively block the incidence of sunlight, and can effectively radiate heat from the backlight surface, while achieving heat insulation and cooling effects, and can achieve a radiation temperature lower than the ambient temperature. cooling effect.

[n0030]

- 360 (8) The present invention also provides an application of a polyester radiation cooling film, specifically covering the polyester radiation cooling film on the surface of the substrate, or above the surface of the substrate, or covering the skin of animals and humans.
- 363 In the present invention, the polyester radiative cooling film is attached to the surface of the substrate (such as a building, device or device) that needs to be temperature-regulated (such as a building, a device or a device) and the skin surface of an animal or a human body by covering, coating or pasting, which can demonstrate high-efficiency cooling. The heat insulation and cooling effect greatly saves refrigeration energy consumption, high use value, and good application prospects; at the same time, the polyester radiation cooling film of the present invention has excellent mechanical properties, can be bent and curled at will, and can be applied to different properties, The shape of the substrate expands the application range of the polyester radiation cooling film.

[0034]

[n0031]

378 In order to make the purpose, technical solutions and advantages of the embodiments of the present invention more clear, the technical solutions in the embodiments of the present invention will be clearly and completely described below in conjunction with the drawings in the embodiments of the present invention.

[n0032]

384 Fig. 1 is a surface SEM image of the polyester radiation cooling film prepared in Example 1 of the present invention.

[n0033]

389 Fig. 2 is a cross-sectional SEM low magnification view of the polyester radiation cooling film prepared in Example 1 of the present invention.

[n0034]

394 Fig. 3 is a cross-sectional SEM high-magnification view of finger holes in the polyester radiative cooling film prepared in Example 1 of the present invention.

[n0035]

399 Fig. 4 is a high magnification cross-sectional SEM image of double continuous holes in the polyester radiative cooling film prepared in Example 1 of the present invention.

[n0036]

404 Fig. 5 is a graph showing the spectrum of the polyester radiation cooling film prepared in Example 1 of the present invention.

[n0037]

409 Fig. 6 is a mechanical tensile curve of the polyester radiative cooling film prepared in Example 1 of the present invention.

[n0038]

414 Fig. 7 is a cross-sectional SEM low magnification view of the polyester radiation cooling film prepared in Example 2 of the present invention.

[n0039]

419 Fig. 8 is a SE M high magnification view of the section of the sponge hole in the polyester radiative cooling film prepared in Example 2 of the present invention.

[n0040]

424 Fig. 9 is a graph of the spectrum of the polyester radiation cooling film prepared in Example 2 of the present invention.

[n0041]

429 Fig. 10 is a mechanical tensile curve of the polyester radiative cooling film prepared in Example 2 of the present invention.

[n0042]

434 FIG. 11 is a heat insulation curve of the polyester radiation cooling film prepared in Examples 1-3 of the present invention and the heat insulation coating prepared in Comparative Example 1. FIG.

[n0043]

439 FIG. 12 is a low-magnification cross-sectional SE M image of the polyester radiation cooling film prepared in Comparative Example 2.

[n0044]

444 13 is a high magnification cross-sectional SE M image of the spherical structure in the polyester radiation cooling film prepared in Comparative Example 2.

[0049]

449 Detailed ways

[n0045]

453 The present invention will be further described below in conjunction with the accompanying drawings and specific preferred embodiments, but the protection scope of the present invention is not limited thereby.

[n0046]

458 All materials and instruments used in the following examples are commercially available.

[n0047]

462 In the present invention, the polymer is firstly dissolved in a solvent to obtain a uniform casting solution, and then the casting solution is deposited on the surface of the PET support film by scraping or spraying to obtain a wet film, which is evaporated in the air for a period of time and then immersed in non- In the solvent coagulation bath, the solvent-to-phase separation reaction occurs. After the reaction is completed, take it out, wash it, and dry it to obtain the polyester radiation cooling film.

[n0048]

470 Example 1:

[n0049]

478 A preparation method of polyester radiation cooling cooling film, comprising the following steps:

[n0050]

478 (1) According to the mass ratio of 12.5:87.5:1.25:0.125, mix PET powder, hexafluoroisopropanol, polyethylene glycol (PEG2000), titanate coupling agent (KR-12), and stir at 50° C Until it is completely dissolved, a clear and transparent casting solution is obtained.

[n0051]

484 (2) Utilize lye and coupling agent solution to carry out surface modification treatment to support membrane, to increase surface roughness and polarity, be conducive to enhancing the bonding strength of support membrane and porous membrane, and then be beneficial to the mechanical property of composite membrane, Specifically: wash the biaxially oriented polyester film (BOPET) with acetone, dry it, soak it in a mixed aqueous solution containing 15g/L NaOH and 7g/lauryl polyoxyethylene ether at 70° C, take it out after 20 min, and put it in 200g/L NaOH aqueous solution at 60° C, take it out after 30 min, rinse with clean water and dry at 60° C.

491 Prepare a solution with a volume ratio of water to absolute ethanol of 9:1, and dropwise add silane coupling agent KH550 with a mass fraction of 5% to the solution, and after it has been hydrolyzed for 1 hour, immerse the alkali-treated BOPET support membrane in Wherein, it was taken out after 3 hours, fully washed with ethanol and dried to obtain a surface-modified BOPET support membrane.

[n0052]

498 (3) Use a film coater to evenly scrape the casting solution on the surface-modified BOPET support film to obtain a wet film with a thickness of 800 μm. After standing in the air for 2 minutes, transfer it to a non-

woven fabric at 25 ° C. Solvent coagulation bath (ethanol).

501 After soaking for 48 hours, take it out, rinse it repeatedly with absolute ethanol, dry it in a cool place for 24 hours, and then place it in a vacuum oven at 40° C for 5 hours to obtain a polyester radiation cooling film.

[n0053]

506 In this implementation, the prepared polyester-based radiation cooling film includes a support film (BOPET biaxially oriented polyester film) and a polyester-based spectrally selective porous film, wherein the polyester-based spectrally selective porous film is supported on the support film.

[n0054]

512 In this implementation, the porosity of the polyester-based spectrally selective porous membrane is 65.54%, and the thickness is 362.2 μ m.

[n0055]

517 In this implementation, the surface of the polyester-based spectrally selective porous membrane is dense and smooth, and the interior is an asymmetric porous structure; the inner portion of the polyester-based spectrally selective porous membrane is sequentially distributed with fingers with a width of 5-50 μ m from the upper surface to the bottom. Pores, sponge pores with a pore diameter of less than 4 μ m, and double continuous pores with a pore diameter of 1 to 3 μ m. The sponge pores are filled between the finger holes, resulting in interpenetration of the finger hole walls, and the through hole diameter is also below 4 μ m. Finger holes and sponge pores There are also a large number of sponge-like flower clusters accumulated on the pore wall, and the pore diameter of the sponge-like flower cluster is on the order of nanometers; it refers to the double continuous pores that penetrate to the bottom of the membrane and end at the bottom.

[n0056]

529 Fig. 1 is a surface SEM image of the polyester radiation cooling film prepared in Example 1 of the present invention.

531 It can be seen from Figure 1 that the surface of the polyester radiation cooling film is relatively smooth and dense.

[n0057]

536 Fig. 2 is a cross-sectional SEM low magnification view of the polyester radiation cooling film prepared in Example 1 of the present invention.

538 Fig. 3 is a cross-sectional SEM high-magnification view of finger holes in the polyester radiative cooling film prepared in Example 1 of the present invention.

540 Fig. 4 is a high magnification cross-sectional SEM image of double continuous holes in the polyester radiative cooling film prepared in Example 1 of the present invention.

542 It can be seen from Figure 2-4 that the section of the polyester radiation cooling film has an asymmetric structure, and near the upper surface, finger holes with a width of 5-50 μm coexist with sponge holes, and the finger holes are filled with sponge holes, resulting in finger holes. The pore walls interpenetrate, and the through-holes distributed on the pore walls of the sponge pores and finger holes are basically below 4 μm ; the finger holes develop to the bottom of the membrane, and finally terminate at the bottom of the double continuous pores. From top to bottom, the pore diameter gradually decreases, the pore size is about 1-3 μm .

549 In addition, there are a large number of sponge-like flower clusters accumulated on the walls of the finger holes and sponge holes, and the hole diameter is extremely small, on the order of nanometers.

551 The measured porosity is 65.54%.

[n0058]

555 Fig. 5 is a graph showing the spectrum of the polyester radiation cooling film prepared in Example 1 of the present invention.

557 The results show that the polyester radiation cooling film prepared by the present invention has a very high reflectivity (average reflectivity of 95.5%) to the full-band sunlight (0.24~2.5 μm) including ultraviolet and near infrared. The average reflectance from near-infrared to short-wave infrared (0.76-2.5 μm , NIR-SWIR) has also reached 93.7%, and the average emissivity in the atmospheric window (8-13 μm) is 95%, showing a higher performance than commercially available thermal insulation coatings. More excellent sunlight reflection ability and strong infrared radiation characteristics in the window.

563 First of all, the strong infrared radiation capability in the window is due to the strong absorption characteristics in the mid-infrared band of the PET porous film (polyester spectrally selective porous film). Excellent cooling performance.

566 Combined with the SEM results, it can be explained that the excellent sunlight reflection ability and the reflection of near-infrared heat are the result of the combined effect of the multi-level hole structure in the three-dimensional network of the polyester radiation cooling film, specifically: the polyester radiation cooling film The cooling film meets the requirements of full-band reflection of sunlight. It contains double continuous holes with a diameter of 1-3 μm and finger holes with a width of 5-50 μm . The through-holes distributed on the pore walls are basically below 4 μm , and a large number of sponge-like flower clusters are accumulated on the finger holes and sponge pore walls, and the pore diameter is extremely small, on the order of nanometers.

574 Among them, the micro-holes can reflect long-wave radiation, especially can effectively scatter most wavelengths of sunlight, and the nano-holes can strongly scatter visible light with shorter wavelengths, so that the polyester radiation cooling film shows excellent sunlight reflection ability; The finger hole with larger size can reflect infrared radiation with longer wavelength, so that the sample also has a certain reflection ability to mid-wave infrared (2.5-8 μm).

[n0059]

582 Fig. 6 is a mechanical tensile curve of the polyester radiative cooling film prepared in Example 1 of the present invention.

584 It can be seen that the tensile strength of Example 1 reaches 29.46 MPa, and the elongation at break is 57.3%,
which is sufficient to withstand general wind blowing and pulling.

[n0060]

589 Example 2:

[n0061]

593 A preparation method of polyester radiation cooling film, which is basically the same as in Example 1, the only
difference is that in step (1), PET powder, hexafluoroisopropanol, polyethylene glycol (PEG 2000), titanium
Ester coupling agent (KR-12) is mixed in a mass ratio of 12.5:87.5:2:0.125.

[n0062]

599 Fig. 7 is a cross-sectional SEM low magnification view of the polyester radiation cooling film prepared in
Example 2 of the present invention.

601 Fig. 8 is a SEM high magnification view of the section of the sponge hole in the polyester radiative cooling film
prepared in Example 2 of the present invention.

603 It can be seen that after the amount of additives is increased, although the membrane structure from top to
bottom is still the cortex layer, the finger hole structure layer, and the support layer, the finger hole structure
becomes thicker and longer, and develops to the bottom of the membrane, and finally ends at the bottom of
the sponge hole structure.

[n0063]

610 Fig. 9 is a graph of the spectrum of the polyester radiation cooling film prepared in Example 2 of the present
invention.

612 It can be seen that the porosity of the polyester radiation cooling film is 67.48%, and the sunlight reflectance is
93.9%.

[n0064]

617 Fig. 10 is a mechanical tensile curve of the polyester radiative cooling film prepared in Example 2 of the
present invention.

619 The tensile strength reached 60.38 MPa, and the elongation at break was as high as 137.33%.

[n0065]

623 The results show that appropriately increasing the amount of polymer additives will slightly reduce the solar
reflection ability of polyester radiative cooling film, but can significantly improve its mechanical properties.
The reason is that the use of additives changes the thermodynamic properties of the casting solution and The

dynamic process of phase separation changes the pore morphology of the porous membrane, making it change from the coexistence of finger pores, sponge pores, and bicontinuous pores to the coexistence of finger pores and sponge pores, and the bicontinuous pores basically disappear.

629 This change is very beneficial to improve the bonding strength of the porous membrane.

[n0066]

633 Example 3:

[n0067]

637 A preparation method of polyester radiation cooling film, which is basically the same as in Example 1, the only difference is that in step (1), PET powder, hexafluoroisopropanol, polyethylene glycol (PEG 2000), titanium Ester coupling agent (KR-12) is mixed in a mass ratio of 10:90:1:0.1.

[n0068]

643 After testing, the porosity of this polyester radiation cooling film is 82.12% (higher than that of Example 1), the solar reflectance is up to 93.3%, the tensile strength is 28.12 MPa, and the elongation at break is 46.5% (lower than that of Example 1). Example 1).

[n0069]

649 Comparative example 1:

[n0070]

653 Commercially available thermal insulation coating of a certain brand: the coating is scraped directly on the PC board, heated and dried at the bottom of 40° C to obtain a dry film with a thickness of 400 μm.

655 After testing, the solar reflectance of the thermal insulation coating is 81.6%, obviously lower than that of Example 1.

657 At the same time, the coating is suitable for coating on the surface of building walls and does not have tensile properties.

[n0071]

662 The polyester radiative cooling film prepared in Examples 1-3 and the thermal insulation coating prepared in Comparative Example 1 were covered on the surface of the silica aerogel to conduct a thermal insulation test.

[n0072]

667 FIG. 11 is a heat insulation curve of the polyester radiation cooling film prepared in Examples 1-3 of the

present invention and the heat insulation coating prepared in Comparative Example 1. FIG.

669 It can be seen that the temperature on the back of the uncoated PC board under the light is as high as 32.7° C, while the temperature on the back of Example 1 is only 25.0° C, which means that the polyester radiation cooling film has achieved a cooling effect of 7.7° C. Looking at the environment The air temperature is close to 28.8° C, which is higher than the backside temperature of Example 1, which means that Example 1 achieves an absolute cooling effect without energy consumption, and the cooling temperature reaches 3.8° C.

675 Similarly, for the polyester radiation cooling films prepared in Examples 2 and 3, the backside temperatures were 25.7° C and 26.7° C respectively, and the obtained absolute cooling temperatures were 3.1° C and 2.1° C.

678 Under the same lighting conditions, although the backside temperature of the heat-insulating and cooling coating obtained in Comparative Example 1 (average 28.5° C) was 4.2° C lower than that without covering, it was close to the ambient air temperature (28.7° C), almost without absolute cooling effect.

681 Compared with Example 1, the backside temperature is 3.5° C higher.

682 The above results show that the polyester radiative cooling cooling film of the present invention realizes absolute cooling under direct sunlight during the day, and this cooling effect does not require energy consumption, which is a real green cooling method.

[n0073]

688 In the application of the polyester radiation cooling and cooling film of the present invention, the polyester radiation cooling and cooling film can be covered on the surface of the substrate, or placed on the surface of the substrate, or covered on the skin of animals and humans, wherein the substrate can be made according to needs. For example, the substrate can be one of houses, cars, tents, pipes, boxes, and sunshade products, and the sunshade product is at least one of awnings, awnings, sunshades, and parasols.

[n0074]

696 Example 4:

[n0075]

700 A method for preparing a polyester radiation cooling film is basically the same as in Example 1, the only difference being that in step (1), the PET powder is replaced with polybutylene terephthalate (PBT).

[n0076]

705 After testing, the polyester radiation cooling film has a porosity of 63.56%, a solar reflectance of 93.5%, a tensile strength of 27.33 MPa (close to Example 1), and an elongation at break of 52.0%.

[n0077]

710 Example 5:

[n0078]

714 A method for preparing a polyester radiative cooling film is basically the same as in Example 1, except that in step (1), the polymer additive is changed from PEG 2000 to PEG 1000.

[n0079]

719 After testing, the polyester radiation cooling film has a porosity of 57.32%, a solar reflectance of 94.0%, a tensile strength of 27.76 MPa, and an elongation at break of 52.7%.

[n0080]

724 Embodiment 6:

[n0081]

728 A method for preparing a polyester radiative cooling film is basically the same as in Example 1, except that in step (1), the polymer additive is replaced by polyvinyl alcohol (PVA) from PEG 2000.

[n0082]

733 After testing, the polyester radiation cooling film has a porosity of 67.23%, a solar reflectance of 97.4%, a tensile strength of 26.90 MPa, and an elongation at break of 62.7%.

[n0083]

738 Embodiment 7:

[n0084]

742 A method for preparing a polyester radiative cooling film is basically the same as in Example 1, except that in step (2), the thickness of the wet film is 400 μm , and the thickness of the dry film is 193 μm .

[n0085]

747 After testing, the polyester radiation cooling film has a porosity of 68.33%, a solar reflectance of 90.2%, a tensile strength of 64.21 MPa, and an elongation at break of 81.7%.

[n0086]

752 Embodiment 8:

[n0087]

756 A method for preparing a polyester radiation cooling film is basically the same as in Example 1, except that in step (2), the thickness of the wet film is 1000 μm , and the thickness of the dry film is 431 μm .

[n0088]

761 After testing, the polyester radiation cooling film has a porosity of 60.35%, a sunlight reflectance of 96.0%, a tensile strength of 27.57 MPa, and an elongation at break of 50.6%.

[n0089]

766 Embodiment 9:

[n0090]

770 A method for preparing a polyester radiation cooling film is basically the same as in Example 1, the only difference being that in step (2), it is left to stand in the air for 5 minutes.

[n0091]

775 After testing, the porosity of the polyester radiation cooling film is 57.22%, the solar reflectance is 91.2%, the tensile strength is 27.34 MPa, and the elongation at break is 51.2%.

[n0092]

780 Example 10:

[n0093]

784 A preparation method of polyester radiation cooling film is basically the same as Example 1, the only difference is that in step (2), the non-solvent coagulation bath is changed from ethanol to a mixture of ethanol and water, the mass ratio of the two is 1:1.

[n0094]

790 After testing, the polyester radiation cooling film has a porosity of 55.24%, a solar reflectance of 91.3%, a tensile strength of 35.43 MPa, and an elongation at break of 65.2%.

[n0095]

795 Example 11:

[n0096]

799 A method for preparing a polyester radiation cooling film is basically the same as in Example 1, the only difference being that in step (2), the temperature of the non-solvent coagulation bath is 50° C.

[n0097]

804 After testing, the polyester radiation cooling film has a porosity of 72.4%, a solar reflectance of 92.0%, a tensile strength of 27.37 MPa, and an elongation at break of 60.7%.

[n0098]

809 Comparative example 2:

[n0099]

813 A preparation method of polyester radiation cooling film, which is basically the same as in Example 1, the only difference is that in step (1), PET powder, hexafluoroisopropanol, polyethylene glycol (PEG 2000), titanium Ester coupling agent (KR-12) is mixed in a mass ratio of 12.5:87.5:0:0.125, that is, no polymer additives are added.

[n0100]

820 FIG. 12 is a low-magnification cross-sectional SEM image of the polyester radiation cooling film prepared in Comparative Example 2.

822 13 is a high magnification cross-sectional SEM image of the spherical structure in the polyester radiation cooling film prepared in Comparative Example 2.

824 It can be seen that after the non-solvent-induced phase separation of the non-solvent/solvent/PET system, a porous membrane with a dense and smooth surface and an asymmetric cross-section can be obtained, and the overall porosity is relatively large.

827 From top to bottom, the membrane structure is cortex, finger hole structure layer and support layer.

828 The thickness of the cortex is very thin, and the finger pore structure is very narrow, which is difficult to fully develop. In the middle and upper part of the membrane, it terminates in the sponge pore structure and quickly transitions to the spherical structure.

831 After testing, the polyester radiation cooling film has a porosity of 64.81%, a solar reflectance of 91.1%, a tensile strength of 25.76 MPa, and an elongation of only 28.9%.

833 The lower mechanical properties are attributed to the spherulite structure.

[n0101]

837 Comparative example 3:

[n0102]

841 A preparation method of polyester radiation cooling film, which is basically the same as in Example 1, the only difference is that in step (1), PET powder, hexafluoroisopropanol, polyethylene glycol (PEG 2000), titanium Ester coupling agent (KR-12) is mixed in a mass ratio of 12.5:97.5:3.125:0.125.

[n0103]

847 After testing, the polyester radiation cooling film has a porosity of 45.1%, a sunlight reflectance of 89.5%, a tensile strength of 23.41 MPa, and a breaking elongation of 52.3%.

[n0104]

852 Comparative example 4:

[n0105]

856 A preparation method of polyester radiation cooling film, which is basically the same as in Example 1, the only difference is that in step (1), PET powder, hexafluoroisopropanol, polyethylene glycol (PEG 2000), titanium Ester coupling agent (KR-12) is mixed according to the mass ratio of 16:84:1.6:0.16.

[n0106]

862 After testing, the polyester radiation cooling film has a porosity of 53.6%, a solar reflectance of 88.4%, a tensile strength of 26.12 MPa, and an elongation at break of 54.2%.

864 Spectral performance drops significantly.

[n0107]

868 Comparative example 5:

[n0108]

872 A preparation method of polyester radiation cooling film, which is basically the same as in Example 1, the only difference is that in step (1), PET powder, hexafluoroisopropanol, polyethylene glycol (PEG 2000), titanium Ester coupling agent (KR-12) is mixed in a mass ratio of 12.5:87.5:1.25:0.625.

[n0109]

878 After testing, the polyester radiation cooling film has a porosity of 53.6%, a solar reflectance of 88.4%, a tensile strength of 25.36 MPa, and an elongation at break of 56.3%.

880 Spectral performance drops significantly.

[n0110]

884 Comparative example 6:

[n0111]

888 A kind of preparation method of polyester radiation cooling film is basically the same as embodiment 1, the only difference is: in step (1), titanate coupling agent (KR-12) is replaced by silane coupling agent (KH-12) 550).

[n0112]

894 After testing, the polyester radiation cooling film has a porosity of 62.34%, a sunlight reflectance of 95.5%, a tensile strength of 25.62 MPa, and an elongation at break of 27.7%.

896 The mechanical properties are significantly reduced.

[n0113]

900 Comparative example 7:

[n0114]

904 A method for preparing a polyester radiation cooling film is basically the same as that in Example 1, except that in step (2), the thickness of the wet film is 2000 μm .

[n0115]

909 After testing, the polyester radiation cooling film has a porosity of 51.14%, a solar reflectance of 92.2%, a tensile strength of 17.83 MPa, and an elongation at break of 31.6%.

911 The mechanical properties are significantly reduced.

[n0116]

915 Comparative example 8:

[n0117]

919 A method for preparing a polyester radiative cooling film is basically the same as in Example 1, the only

difference being that in step (2), the non-solvent coagulation bath is replaced with water by ethanol.

[n0118]

924 After testing, the polyester radiation cooling film has a porosity of 25%, a sunlight reflectance of 54%, a translucent state, a tensile strength of 52.1 MPa, and an elongation at break of 85.2%.

926 The porosity and spectral performance are severely degraded.

[n0119]

930 Comparative example 9:

[n0120]

934 A method for preparing a polyester radiation cooling film is basically the same as in Example 1, except that in step (2), the temperature of the non-solvent coagulation bath is 60° C.

[n0121]

939 After testing, the polyester radiation cooling film has a porosity of 78.4%, a solar reflectance of 85.2%, a tensile strength of 24.38 MPa, and an elongation at break of 47.3%.

941 Spectral performance drops significantly.

[n0122]

945 It can be seen from the above examples and comparative examples that in the present invention, polyester polymers are used as raw materials, and by adding polymer additives and optimizing their dosage, the thermodynamic properties and phase separation of the non-solvent/solvent/polymer ternary system can be changed. The dynamic process changes the phase separation mechanism from the solid-liquid phase that forms the spheroid structure to the liquid-liquid phase that produces the sponge pore structure, and then realizes the pore shape, pore structure and porosity of the porous membrane. control, to obtain a porous morphology without spherulite structure, and at the same time, polymer additives can be inserted between polyester macromolecular chains to increase the distance between molecular chains to reduce the regular arrangement of polyester molecular chains, which also helps. In order to suppress the appearance of spherulite structure, and finally achieve a significant improvement in mechanical properties while maintaining the advantage of strong reflection of sunlight.

956 At the same time, by adding a titanate coupling agent and optimizing its dosage in the present invention, under the synergistic effect of the titanate coupling agent, the intralayer bonding strength of the polyester-based spectrally selective porous membrane can be improved, and the interlayer bonding strength between the polyester-based spectrally selective porous surface layer and the flexible support film, so by adding polymer additives and titanate coupling agents and optimizing their dosage, not only high solar reflectance is obtained, and significantly improved the bonding strength within the layer of the porous

membrane, and the interlayer bonding strength between the bottom of the porous membrane and the flexible support. At the same time, even if the thickness of the porous membrane is increased, the formation of the spherical structure can be successfully suppressed. The preparation of the present invention The polyester radiative cooling film can also meet the requirements of high solar reflectance for film thickness, thus obtaining a polyester radiative cooling film with excellent spectral selectivity and mechanical properties.

967 The polyester radiation cooling film prepared by the invention has the advantages of high tensile strength, high interface bonding strength, excellent flexibility, excellent heat insulation and cooling performance, etc., can be bent and curled at will, and can be applied to substrates with different properties and shapes, expanding the outdoor application potential of polyester radiation cooling film, which is conducive to the promotion and application of polyester radiation cooling film, with high use value and good application prospect.

973 At the same time, the preparation method of the present invention also has the advantages of simple process, convenient operation, low requirements on equipment, recyclable solvent and non-solvent, low production cost, high film forming efficiency, etc., is suitable for large-scale industrial production, and has great significance for energy saving and environmental protection.

[n0123]

980 The above descriptions are only preferred implementations of the present invention, and the scope of protection of the present invention is not limited to the above examples.

982 All technical solutions under the idea of the present invention belong to the protection scope of the present invention.

984 It should be pointed out that for those skilled in the art, improvements and modifications without departing from the principle of the present invention should also be regarded as the protection scope of the present invention.

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CLAIMS CN114605689A

1.

¹³ A kind of preparation method of polyester radiation cooling cooling film, is characterized in that, comprises the following steps:

(1)

¹⁸ Mix the polyester polymer, solvent, polymer additive, and titanate coupling agent, and stir until completely dissolved to obtain a casting solution; the mass ratio of the polymer additive to the polyester polymer is $\leq 20\%$; The mass ratio of the titanate coupling agent to the polyester polymer is $\leq 4\%$;

(2)

²⁴ coating the casting solution obtained in the step (1) on the surface of the support membrane to obtain a wet film;

(3)

²⁹ The wet film obtained in step (2) is left to stand, soaked in a non-solvent coagulation bath, washed, and dried to obtain a polyester-based radiation cooling film.

2.

³⁴ The preparation method according to claim 1, characterized in that, in step (1), the mass ratio of the polymer additive to the polyester polymer is 5% to 20%; the titanate coupling agent and The mass ratio of the polyester polymer is 0.1%-2%.

3.

40 The preparation method according to claim 2, characterized in that, in step (1), the polymer additive is at least one of polyethylene glycol, polyvinylpyrrolidone, and polyvinyl alcohol; the titanate The coupling agent is at least one of KR-12, KR-9S, T M C-2, T M C-311 and T M C-401.

4.

46 The preparation method according to any one of claims 1 to 3, characterized in that, in step (1), the mass ratio of the polyester polymer to the solvent is 3 to 25:75 to 97; The ester polymer is at least one of polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, polycarbonate, polyarylate, polyethersulfone resin species; the solvent is at least one of hexafluoroisopropanol, trifluoroacetic acid, methylene chloride and phenol; the stirring is carried out at 40° C to 80° C.

5.

54 The preparation method according to any one of claims 1 to 3, characterized in that, in step (2), the coating method is scraping or spraying; the supporting film is a flexible supporting film; The film is PET film, PI film, PEN film, PC film, PES film; the thickness of the wet film is $\leq 1200 \mu\text{m}$;

57 In step (3), the standing is carried out under an atmosphere; the standing time is $\leq 15\text{min}$; the soaking time is 5h to 96h; the temperature of the non-solvent coagulation bath is $\leq 50^\circ\text{C}$; the non-solvent The solvent coagulation bath is at least one of alcohols containing 1 to 8 carbons and their mixtures with water, ethyl propionate and their mixtures with water; The mass percentage of water in the mixture of alcohol and water is $\leq 50\%$; the mass percentage of water in the mixture of ethyl propionate and water is $\leq 50\%$.

6.

65 The preparation method according to claim 5, characterized in that, in step (2), the thickness of the wet film is 400 μm to 1200 μm ;

67 In step (3), the standing time is 1 min to 15 min; the soaking time is 5 h to 96 h; the temperature of the non-solvent coagulation bath is 15° C to 50° C.

7.

72 A polyester radiation cooling film, characterized in that the polyester radiation cooling film is prepared by the preparation method described in any one of claims 1-6.

8.

77 The polyester radiation cooling and cooling film according to claim 7, characterized in that, the polyester radiation cooling and cooling film comprises a support film and a polyester spectrally selective porous membrane, and the polyester spectrally selectively porous The membrane is loaded on the supporting

membrane; the porosity of the polyester spectrum selective porous membrane is 55%-85%; the thickness of the polyester spectrum selective porous membrane is 100 μ m-600 μ m.

9.

⁸⁵ The polyester radiation cooling film according to claim 8, characterized in that, the surface of the polyester spectrally selective porous membrane is compact and smooth; the interior of the polyester spectrally selective porous membrane is asymmetric Porous structure; the inside of the polyester spectrally selective porous membrane is sequentially distributed with finger holes with a width of 5 μ m to 100 μ m, sponge pores with a pore diameter of less than 5 μ m, and double continuous pores with a pore diameter of 1 μ m to 3 μ m. or sponge holes; the sponge holes are filled between the finger holes; the hole walls of the finger holes interpenetrate; the finger holes run through to the bottom of the film and end at the double continuous holes or sponge holes at the bottom; the sponge holes Through holes are distributed on the hole wall, and the pore diameter of the through holes is below 5 μ m; sponge-like flower clusters are also accumulated on the hole walls of the finger hole and the sponge hole, and the pore diameter of the sponge-like flower cluster is nanometer class.

10.

⁹⁹ An application of the polyester radiation cooling film as claimed in any one of claims 7 to 9, wherein the application is to cover the polyester radiation cooling film on the surface of the substrate, or arrange it on the substrate above the surface, or covered on the skin of animals and humans; the substrate is one of houses, cars, tents, pipes, boxes, and sunshade products; at least one of the



Espacenet

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REACTIVE ADHESIVE AGENT, LAMINATE FILM, AND PACKAGING BODY

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Abstract of WO2019188335 (A1)

Provided are: a reactive adhesive agent containing a polyol composition (A) and a polyisocyanate composition (B), wherein the polyol composition (A) contains a polyester polyol (A1) which is the reaction product of the batch charging of a polyethylene terephthalate, a polyhydric alcohol, and a polybasic acid; a laminate film obtained by laminating a reactive adhesive agent layer between a first plastic film and a second plastic film; and a production method for the polyester polyol (A1), said method being characterized in that the polyethylene terephthalate, the polyhydric alcohol, and the polybasic acid are charged and reacted as a batch.

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DESCRIPTION W 02019188335A1

10 Reactive adhesives, laminated films, and packages

[0001]

14 TECHNICAL FIELD The present invention relates to a reactive adhesive, a laminated film and a package using the same.

[0002]

19 Conventionally, various types of plastic films are laminated together, and laminates obtained by laminating plastic films with metal-deposited films or metal foils have been used in various applications, such as packaging materials for foods, pharmaceuticals, and daily necessities, as well as barriers. Materials, roofing materials, solar cell panel materials, battery packaging materials, window materials, outdoor flooring materials, lighting protection materials, automotive parts, signboards, outdoor industrial applications such as stickers, decoration used for injection molding simultaneous decoration methods, etc. It is used for various purposes.

26 For these laminates, various types of plastic films, metal vapor-deposited films, or metal foils are appropriately combined according to the properties required for each application, and an adhesive is selected according to the required properties. For example, in the case of food and daily necessities, functions such as strength, resistance to cracking, retort resistance, heat resistance, and resistance to contents are required to protect the contents from various distributions, storage such as refrigeration, and processing such as heat sterilization. is required. Alternatively, for outdoor industrial applications, weather resistance and hydrolysis resistance are required to maintain long-term adhesiveness even in an open-air environment. Furthermore, these laminates are rarely distributed in the form of sheets, and for example, they are made into bags with heat-sealed ends, or they are sometimes subjected to molding for thermoforming, which requires heat-sealability and molding processability. Sometimes it is.

[0003]

40 Reactive adhesives (also referred to as two-liquid adhesives) that react hydroxyl groups with isocyanate have been conventionally known as adhesives used for such lamination.

42 For example, in food applications, in an adhesive containing a diol compound (A) having two hydroxyl groups and a polyisocyanate (B) having two or more isocyanate groups, the number average of the diol compound (A) A polyisocyanate compound (b1) having a molecular weight (M_n) in the range of 400 to 3000, wherein the polyisocyanate (B) is a trivalent or higher polyisocyanate compound (b1), and a diisocyanate compound (b2) obtained by adding an isocyanate compound to a polyester diol. Adhesives are known which are mixtures of (For example, see Patent Document 1) An adhesive for laminate films of battery packaging materials, containing a polyurethane polyester polyol having a polyol component with a number average molecular weight of 5,000 or more and less than 14,000, the content of urethane bonds, and isocyanate groups It is known that a lamination adhesive having a sum of the contents of within a specific range is excellent in moldability and moist heat resistance (see, for example, Patent Document 2).

[0004]

57 These reactive adhesives are required to have characteristics according to various applications, and in recent years, from the viewpoint of productivity, laminated films that do not cause appearance defects even at coating speeds of 200 m / min or more is required to obtain

60 However, under such high-speed coating (also called high-speed processing) conditions, not only solvent-free reactive adhesives that do not use organic solvents, but also dry-laminate reactive adhesives that can be adjusted in viscosity using organic solvents. Even in this case, there is a problem that depending on the base material, an appearance defect like citrus peel tends to occur.

[0006]

68 The problem to be solved by the present invention is that it can be applied as an adhesive for laminates in which various plastic films, metal vapor deposition films, or metal foils are appropriately combined, and even under high-speed coating conditions, high adhesion and lamination processing To provide a reactive adhesive with which a laminated film having an excellent appearance can be obtained.

[0007]

76 The present inventors have discovered a reactive adhesive containing a polyol composition (A) and a polyisocyanate composition (B), wherein the polyol composition (A) comprises polyethylene terephthalate, a polyhydric alcohol and a polybasic We have found that a reactive adhesive containing a polyester polyol (A1), which is a reaction product obtained by

batch charging with an acid, solves the above problems.

[0008]

84 Adhesives using polyester polyols made from polyethylene terephthalate are known (see, for example, Patent Documents 3 and 4).

86 For example, in Patent Document 3, polyethylene terephthalate is decomposed by a reaction with a low-molecular-weight polyol, and then a polyester polyol obtained by condensation reaction of this decomposition product and a polybasic acid, and a polyisocyanate curing agent. An adhesive is disclosed.

90 However, although Patent Document 3 evaluates a laminate film produced by coating an adhesive at a film speed of 50 m/min, there is nothing about a form produced under high-speed coating conditions at a coating speed of 200 m/min or higher. No mention or suggestion.

94 Further, Patent Document 4 discloses that a polyol compound obtained by depolymerizing a polyester (a) with a polyol (b) having two or more hydroxyl groups in one molecule is used as a raw material for an adhesive. However, in this case, the evaluation of the adhesive is also made on a laminated film obtained by applying the adhesive to a film with a film thickness of 30 μ m with an applicator and then laminating it, and it is prepared under high-speed coating conditions at a coating speed of 200 m/min or more. There is no description or suggestion about the form. That is, a reactive adhesive that uses a polyester polyol made from polyethylene terephthalate as a raw material and has high adhesion and an excellent appearance after lamination even under high-speed coating conditions of 200 m/min or more is now available. The fact is that it is not known.

[0009]

107 The inventors of the present invention have recognized that polyester polyols obtained by the methods disclosed in Patent Documents 3 and 4 have poor appearance during high-speed coating. If the polyester polyol (A1), which is a reaction product obtained by collective charging with a polybasic acid, is used as a component of a reactive adhesive, poor appearance during high-speed coating is less likely to occur, and high adhesion after lamination is achieved. The present inventors have found that a laminate film having adhesiveness, particularly heat resistance and resistance to contents can be obtained, leading to the present invention.

[0010]

118 That is, the present invention provides a reactive adhesive containing a polyol composition (A) and a polyisocyanate composition (B), wherein the polyol composition (A) comprises polyethylene terephthalate, a polyhydric alcohol and a polybasic acid. Provided is a reactive adhesive containing a polyester polyol (A1) which is a reaction product obtained by collective

charging with.

[0011]

126 The present invention also provides a laminated film obtained by laminating an adhesive layer between a first plastic film and a second plastic film, wherein the adhesive layer is the reaction according to any one of claims 1 to 4. A laminated film is provided that is a layer of a flexible adhesive.

[0012]

133 The present invention also provides a package formed by molding the laminate film described above into a bag.

[0013]

148 Moreover, this invention provides the manufacturing method of polyester polyol (A1) which prepares polyethylene terephthalate, a polyhydric alcohol, and a polybasic acid all at once, and makes them react.

[0014]

144 The present invention also provides a method for producing a polyester polyurethane polyol (A2) by reacting a polyester polyol (A1) in which polyethylene terephthalate, a polyhydric alcohol and a polybasic acid are collectively charged and reacted, and a polyisocyanate.

[0015]

150 The reactive adhesive of the present invention can be applied as an adhesive for laminates in which various types of plastic films, metal-deposited films, or metal foils are appropriately combined. A laminated film having an excellent appearance can be obtained.

153 Furthermore, since it is excellent in heat resistance and content resistance, it can be suitably used as a food packaging bag.

[0016]

158 The present invention provides a reactive adhesive containing a polyol composition (A) and a polyisocyanate composition (B), wherein the polyol composition (A) comprises polyethylene terephthalate, a polyhydric alcohol and a polybasic acid. It is characterized by containing a polyester polyol (A1) which is a reaction product by batch charging of.

[0017]

165 (Polyol composition (A)) The polyester polyol (A1) contained in the polyol composition (A) is a reaction product obtained by collectively charging polyethylene terephthalate, polyhydric alcohol and polybasic acid.

[0018]

171 (Polyester polyol (A1)) The polyethylene terephthalate (hereinafter sometimes referred to as PET) used in the present invention is obtained by polycondensation of terephthalic acid or dimethyl terephthalate and ethylene glycol. Those modified with substances such as phthalic anhydride, adipic acid, cyclohexanedicarboxylic acid, 1,3-butanediol and cyclohexanedimethanol can also be used.

176 Furthermore, commercially available unused PET bottles, PET films, other pulverized PET products leftovers from manufacturing, recycled PET collected from waste and washed, and the like can be used.

179 Among them, it is preferable to use recycled PET.

180 They are commercially available washed and pelletized.

[0019]

184 The intrinsic viscosity (IV) of PET is preferably 0.50-0.80 dL/g.

185 Within this range, the polycondensation reaction between PET and other raw materials can be carried out at 250 ° C. or lower.

187 This range is also preferable from the viewpoint of the development of adhesive strength, durability, and heat resistance of the reactive adhesive containing the PET-containing polyester polyol.

[0020]

193 The polyhydric alcohol used in the present invention is not particularly limited, and known polyhydric alcohols can be used.

195 For example, 1,2-propanediol, 1,2,2-trimethyl-1,3-propanediol, 2,2-dimethyl-3-isopropyl-1,3-propanediol, 1,3-butanediol, 2, Aliphatic diols such as 2,4-trimethyl-1,3-pentanediol; 1,3-bis(2-hydroxypropyl)cyclopentane, 1,3-bis(2-hydroxybutyl)cyclopentane, 1,4- Alicyclic diols such as bis(2-hydroxypropyl)cyclohexane, 1,4-bis(2-hydroxybutyl)cyclohexane; 1,4-bis(2-hydroxypropyl)benzene, 1,4-bis(2-hydroxy aromatic diols such as butyl)benzene;

[0021]

203 2,2-bis(4-hydroxyphenyl)propane (hereinafter abbreviated as "bisphenol A"), 2,2-bis(4-hydroxyphenyl)butane (hereinafter abbreviated as "bisphenol B"), bis(4- To bisphenols such as hydroxyphenyl)methane (hereinafter abbreviated as "bisphenol F") and bis(4-

hydroxyphenyl)sulfone (hereinafter abbreviated as "bisphenol S"), 1,2-propylene oxide and 1,2-butylene Alkylene oxide adducts of bisphenol obtained by adding an alkylene oxide having a secondary hydroxyl group such as oxide; ethylene glycol, diethylene glycol, 1,3-propanediol, 1,4-butanediol, 3-methyl-1,3 -butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, 2-butyl-2-ethyl-1,3-propanediol, 1,6-hexanediol, trimethylol Aliphatic polyols such as ethane, trimethylolpropane, glycerin, hexanetriol and pentaerythritol; Ether glycols such as polyoxyethylene glycol and polyoxypropylene glycol;

[0022]

216 Modification obtained by ring-opening polymerization of the aliphatic polyol with various cyclic ether bond-containing compounds such as ethylene oxide, propylene oxide, tetrahydrofuran, ethyl glycidyl ether, propyl glycidyl ether, butyl glycidyl ether, phenyl glycidyl ether, and allyl glycidyl ether Polyether polyols; lactone-based polyester polyols obtained by polycondensation reaction of the aforementioned aliphatic polyols with various lactones such as ϵ -caprolactone; bisphenols such as bisphenol A, bisphenol F and bisphenol S; bisphenol A, bisphenol F and the like and ethylene oxide adducts of bisphenol obtained by adding ethylene oxide to bisphenol.

[0023]

227 Each of these may be used alone, or two or more of them may be used in combination.
228 Among others, ethylene glycol, diethylene glycol, 1,3-propanediol, 1,4-butanediol, 3-methyl-1,3-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, neo Aliphatic polyols such as pentyl glycol, 2-butyl-2-ethyl-1,3-propanediol, 1,6-hexanediol, trimethylolethane, trimethylolpropane, glycerin, hexanetriol, and pentaerythritol are preferred. 6-hexanediol is preferred.

[0024]

236 The polybasic acid used in the present invention is not particularly limited, and known polybasic acids can be used.
238 aromatic dicarboxylic acids such as phthalic acid, phthalic anhydride, terephthalic acid, isophthalic acid, orthophthalic acid; malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, hexahydro Aliphatic dicarboxylic acids such as phthalic acid and 1,4-cyclohexanedicarboxylic acid; maleic acid, maleic anhydride, citraconic acid, dimethylmaleic acid, cyclopentene-1,2-dicarboxylic acid, 1-cyclohexene-1,2-Aliphatic unsaturated dicarboxylic acids such as dicarboxylic acids, 4-cyclohexene-1,2-dicarboxylic acid, fumaric acid, mesaconic acid, itaconic acid, glutaconic acid; 1,2,5-hexanetricarboxylic acid, 1,2, Aliphatic tricarboxylic acids such as 4-cyclohexanetricarboxylic acid; aromatic tricarboxylic acids such as trimellitic acid, 1,2,5-benzenetricarboxylic acid and 2,5,7-naphthalenetricarboxylic acid; and dimer acids.

248 Each of these may be used alone, or two or more of them may be used in combination.

249 Among them, dimer acid is preferred.

[0025]

- 253 The production method of charging and reacting PET, polyhydric alcohol and polybasic acid all at once can be arbitrarily produced by a known polycondensation reaction method. Specifically, PET, polyhydric alcohol and polybasic acid is put into a production apparatus, and the temperature is raised to 180 ° C. or higher while stirring in a nitrogen atmosphere, and any production method such as normal pressure dehydration reaction, reduced pressure and vacuum dehydration reaction, solution polycondensation method, solid phase polycondensation reaction, etc. may be carried out in
- 260 When the PET, polyhydric alcohol and polybasic acid described in the present application are used, dehydration under reduced pressure can be applied at a reaction temperature of 230 ° C. or lower, and the reaction time can be reduced to about 5 hours.
- 263 The progress of the polycondensation reaction can be confirmed by measuring the acid value, hydroxyl value, viscosity or softening point.
- 265 As the production apparatus used at this time, for example, a batch type production apparatus such as a reaction vessel equipped with a nitrogen inlet, a thermometer, a stirrer, a rectification tower, etc. can be suitably used, and a degassing port is provided. An extruder, a continuous reactor, a kneader, etc. can also be used.
- 269 Furthermore, if necessary, an esterification catalyst (a tin compound, a titanium compound, a zirconium compound, etc.) can be used to promote the esterification reaction.
- 271 In addition, the polyol obtained by the method of subjecting PET to a transesterification reaction in a polyhydric alcohol or the method of polycondensing the transesterification reaction product and a polybasic acid has the ethylene terephthalate units decomposed apart, so that the polyol is adhered. Even if it is used as an agent, the appearance, adhesive strength, heat resistance and resistance to inclusions during high-speed coating, which are the objectives of the present application, cannot be achieved.

[0026]

- 280 (Combination of Preferred Raw Materials) The polyester polyol (A1) is preferably a polyester polyol using 1,6-hexanediol as the polyhydric alcohol and dimer acid as the polybasic acid.
- 282 At this time, the weight fraction of 1,6-hexanediol is preferably 5 to 20% by mass, and more preferably 6 to 18% by mass, as a ratio of the polyester polyol (A1) in the starting material.
- 285 Further, the weight fraction of the dimer acid is preferably 5 to 20% by mass, more preferably 6 to 18% by mass, as a proportion of the polyester polyol (A1) in the starting material.

[0027]

290 Further, in the PET, the ratio of the polyester polyol (A1), that is, the total amount of the polyhydric alcohol and the polybasic acid to the total amount of the polyhydric alcohol and the polybasic acid, is 5 to 50% by mass with respect to 100% of the total amount of the polyhydric alcohol and the polybasic acid, is preferred, and more preferably 8 to 48% by mass.

[0028]

298 In the present application, by synthesizing a long-chain unsaturated dibasic acid such as dimer acid, 1,6-hexanediol, and other monomers together with PET as raw materials for the polyester polyol (A1), the adhesion strength to the substrate It is possible to obtain an adhesive that is superior in heat resistance and content resistance.

302 The reason for this is not clear, but with this composition it is possible to carry out the reaction at a temperature of 220 ° C, and the ethylene terephthalate unit in the reaction product thus obtained is less likely to be decomposed by the long-chain unsaturated groups, resulting in a high It is presumed that it remains in the form of a molecular weight, which contributes to the appearance, adhesive strength, heat resistance, and resistance to inclusions during high-speed coating.

308 It should be noted that if a trihydric alcohol (trimethylolpropane) is used as the polyhydric alcohol, the ethylene terephthalate unit in the PET may be sufficiently decomposed, and the reaction temperature must be higher than 220 ° C. to proceed. Therefore, the polyhydric alcohol is preferably a dihydric alcohol such as 1,6-hexanediol.

[0029]

315 (Acid value, hydroxyl value) The polyester polyol (A1) preferably has an acid value of 5.0 or less from the viewpoint of hydrolysis resistance, and more preferably 3.0 or less from the viewpoint of adhesive reactivity. .

318 Moreover, from the viewpoint of high-speed coating properties, the hydroxyl value is preferably 50 or less, more preferably 40 or less. In the present invention, the acid value and hydroxyl value are measured by the following methods, and represent values converted to solid content unless otherwise specified.

[0030]

325 (Acid value) 5 to 10 g of polyester polyol is weighed into a 100 ml Erlenmeyer flask.

326 Let the weighed amount be (S). This is dissolved in 30 ml of tetrahydrofuran. After adding 2 to 3 drops of phenolphthalein as an indicator, titration is performed with a 0.1 mol/L potassium hydroxide alcohol solution. The point at which a slight reddish color persists for 30 seconds is defined as the end point, and the acid value is calculated from the titer (V) at that time by the following formula. The titer of 0.1 mol/L potassium hydroxide alcohol solution is defined as (F). Acid value = $(V \times F \times 5.61) / S$

[0031]

335 (Hydroxyl value) Weigh 6 to 10 g of polyester polyol in a 300 ml Erlenmeyer flask.

336 Let the weighed amount be (S). 25 ml of the acetylating agent prepared in advance is added to this and dissolved. A cooling tube is attached to the mouth of the Erlenmeyer flask, and the acetylation reaction is carried out at 100 ° C. for 1 hour. Add 10 ml of deionized water and cool to room temperature. After adding 2 to 3 drops of phenolphthalein as an indicator, titration is performed with a 0.5 mol/L potassium hydroxide alcohol solution. The point at which a slightly reddish color persists for 30 seconds is defined as the end point, and the hydroxyl value is calculated from the titer (V) at that time by the following formula. At the same time, a blank test is performed and the titration amount at that time is defined as (B). Let (F) be the titer of 0.5 mol/L potassium hydroxide alcohol solution. Separately, measure the acid value. Hydroxyl value = ((B-V) x F x 28.05)/S + acid value

[0032]

349 (Molecular weight) The number average molecular weight of the polyester polyol (A1) is not particularly limited, but from the viewpoint of proper resin viscosity during coating, it is usually adjusted in the range of 2,000 to 12,000, preferably 3,000 to 8,000. is more preferred.

[0033]

356 In the present invention, the number average molecular weight (Mn) and weight average molecular weight (Mw) are values measured by gel permeation chromatography (GPC) under the following conditions.

[0034]

362 Measuring device; Tosoh Corporation HLC-8220GPC column; Tosoh Corporation TSK-GUARD COLUMN SuperHZ-L + Tosoh Corporation TSK-GEL SuperHZM-M x 4 detector; RI (differential refractometer) Data processing; Tosoh Corporation Made by Multistation GPC-8020 model II Measurement conditions; Column temperature 40 ° C Solvent Tetrahydrofuran Flow rate 0.35 ml/min Standard Monodisperse polystyrene Sample;)

[0035]

370 (Polyester polyurethane polyol (A2)) In addition, the polyester polyol (A1) is a polyester obtained by reacting polyethylene terephthalate, a polyhydric alcohol, and a polybasic acid together, and then further reacting with an isocyanate compound described later. It may be a polyurethane polyol (A2).

374 At this time, the isocyanate compound is preferably isophorone diisocyanate.

[0036]

378 The polyester polyurethane polyol (A2) preferably has an acid value of 5.0 or less from the viewpoint of hydrolysis resistance, and more preferably 3.0 or less from the viewpoint of adhesive reactivity.

381 From the viewpoint of heat resistance and content resistance, the hydroxyl value is preferably 30 or less, more preferably 25 or less.

[0037]

386 (Other polyols) In the present invention, in addition to the polyester polyol (A1), polyester polyols, polyether polyols, polyether polyols, polyols, polyether polyols, polyols, polyether polyols, polyhydric alcohols, etc. that do not use the polyhydric alcohol itself or polyethylene terephthalate as a raw material are used within the range that does not impair the effects of the present invention. Polyurethane polyol, polyether ester polyol, polyester (polyurethane) polyol, polyether (polyurethane) polyol, polyester amide polyol, acrylic polyol, polycarbonate polyol, polyhydroxyl alkane, castor oil, or a mixture thereof. good too.

[0038]

396 When other polyols are used in combination, the proportion of the polyester polyol (A1) in the polyol composition (A) is preferably 1 to 50% by mass, more preferably 1 to 40% by mass.

[0039]

402 (Polyisocyanate composition (B)) The polyisocyanate composition (B) used in the present invention is a composition containing a polyisocyanate compound as a main component.

404 As the polyisocyanate compound used in the present invention, known ones can be used without any particular limitation, and they can be used singly or in combination.

406 For example, polyisocyanates having an aromatic structure in the molecular structure such as tolylene diisocyanate, diphenylmethane diisocyanate, polymeric diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate, triphenylmethane triisocyanate, xylylene diisocyanate, and NCO groups of these polyisocyanates A compound in which a portion of is modified with carbodiimide;

[0040]

414 Alphanate compounds derived from these polyisocyanates; polyisocyanates having an alicyclic structure in the molecular structure such as isophorone diisocyanate, 4,4 ' -

methylenebis(cyclohexylisocyanate), 1,3-(isocyanatomethyl)cyclohexane; Linear aliphatic polyisocyanates such as 1,6-hexamethylene diisocyanate, lysine diisocyanate, trimethylhexamethylene diisocyanate, and alphanate compounds thereof; isocyanurate compounds of these polyisocyanates; allophanate compounds derived from these polyisocyanates; Biuret products derived from these polyisocyanates; trimethylolpropane-modified adducts;

[0041]

425 Examples include polyisocyanates which are reaction products of various polyisocyanate compounds described above and polyhydric alcohols.

[0042]

430 In the polyisocyanate which is a reaction product of the various polyisocyanate compounds described above and a polyhydric alcohol, the polyhydric alcohol is a polyhydric alcohol which is a raw material of the polyol composition (A), the polyester polyol (A1), The polyester polyol (A1-2), polyester polyol not using polyethylene terephthalate as a raw material, polyether polyol, polyurethane polyol, polyether ester polyol, polyester (polyurethane) polyol, polyether (polyurethane) polyol, polyester amide polyol, acrylic polyol, polycarbonate polyols, polyhydroxylalkanes, castor oil or mixtures thereof, and the like.

437 Among them, it is preferable to use a polyisocyanate that is a reaction product of the various polyisocyanates described above and the polyester polyol (A1) from the viewpoint of adhesive strength, heat resistance and content resistance.

440 Regarding the reaction ratio of the polyisocyanate compound and the polyhydric alcohol, the equivalent ratio [isocyanate group/hydroxyl group] between the isocyanate group and the hydroxyl group is in the range of 1.0 to 5.0. This is preferable from the point of balance between strength and flexibility.

[0043]

447 The polyisocyanate compound preferably has an average molecular weight in the range of 100 to 1000 from the viewpoint of adhesive strength, heat resistance and content resistance.

[0044]

452 (Solvent) The reactive adhesive used in the present invention is an adhesive that cures through a chemical reaction between an isocyanate group and a hydroxyl group, and can be used as a solvent-type or non-solvent-type adhesive.

455 In addition, the "solvent" of the solvent-free adhesive used in the present invention refers to a highly soluble organic solvent capable of dissolving the polyisocyanate compound and polyol compound used in the present invention. It means that it does not contain these highly

soluble organic solvents.

459 Examples of highly soluble organic solvents include toluene, xylene, methylene chloride, tetrahydrofuran, methanol, ethanol, isopropyl alcohol, methyl acetate, ethyl acetate, n-butyl acetate, acetone, methyl ethyl ketone (MEK), cyclohexanone, toluol, xylol, n-hexane, cyclohexane and the like.

463 Among them, toluene, xylene, methylene chloride, tetrahydrofuran, methyl acetate, and ethyl acetate are known as organic solvents with particularly high solubility.

465 On the other hand, when the adhesive of the present invention is required to have a low viscosity or the like, it may be diluted with the highly soluble organic solvent according to the desired viscosity.

468 In that case, either one of the polyisocyanate composition (B) or the polyol composition (A) may be diluted, or both may be diluted.

470 Examples of organic solvents used in such cases include methanol, ethanol, isopropyl alcohol, methyl acetate, ethyl acetate, n-butyl acetate, acetone, methyl ethyl ketone (MEK), cyclohexanone, toluol, xylol, n-hexane, cyclohexane, and the like. is mentioned.

473 Among these, ethyl acetate and methyl ethyl ketone (MEK) are preferred from the viewpoint of solubility, and ethyl acetate is particularly preferred. Although the amount of the organic solvent used depends on the required viscosity, it is generally used in the range of 20 to 50% by mass.

[0045]

480 In the reactive adhesive used in the present invention, the mixing ratio of the polyisocyanate composition (B) and the polyol composition (A) is The equivalent ratio [isocyanate group/hydroxyl group] between the isocyanate group and the hydroxyl group in the polyol compound contained in the polyol composition (A) is in the range of 0.6 to 5.0. The range of 1.0 to 3.5 is particularly preferred from the viewpoint that these performances become remarkable.

[0046]

489 (Aliphatic cyclic amide compound) As described in detail, the reactive adhesive of the present invention comprises the polyol composition (A) and the polyisocyanate composition (B) as essential components. An aliphatic cyclic amide compound is mixed with either one of the polyol composition (A) and the polyisocyanate composition (B), or is blended as a third component during coating to form a laminate. Elution of harmful low-molecular-weight chemical substances represented by aromatic amines into the contents of the package can be effectively suppressed.

[0047]

499 Aliphatic cyclic amide compounds used here include, for example, δ -valerolactam, ϵ -

caprolactam, ω -enantholactam, η -capryllactam, β -propiolactam and the like.
501 Among these, ϵ -caprolactam is preferable from the viewpoint of being excellent in the effect
of reducing the elution amount of low-molecular-weight chemical substances.
503 Moreover, it is preferable to mix the aliphatic cyclic amide compound in an amount of 0.1 to
5 parts by mass per 100 parts by mass of the polyol component A.

[0048]

508 (Catalyst) By using a catalyst in the present invention, it is possible to effectively suppress the
elution of harmful low-molecular-weight chemical substances represented by aromatic
amines into the contents of the laminate package.
511 The catalyst used in the present invention is not particularly limited as long as it promotes the
urethanization reaction. Examples include metal catalysts, amine catalysts,
diazabicycloundecene (DBU), and aliphatic cyclic amide compounds, a titanium chelate
complex and the like can be used.

[0049]

518 Examples of metal-based catalysts include metal complex-based, inorganic metal-based, and
organic metal-based catalysts. , Th (thorium), Ti (titanium), Al (aluminum), Sn (tin), Zn (zinc),
Bi (bismuth) and Co (cobalt). , for example, iron acetylacetonate, manganese acetylacetonate,
copper acetylacetonate, zirconia acetylacetonate, etc. Among these, iron acetylacetonate
(Fe(acac)₃) or manganese acetylacetonate (Mn(acac)₂).

[0050]

526 Examples of inorganic metal catalysts include catalysts selected from Fe, Mn, Cu, Zr, Th, Ti, Al,
Sn, Zn, Bi and Co.

[0051]

531 Examples of organometallic catalysts include stannus diacetate, stannus dioctoate, stannus
dioleate, stannus dilaurate, dibutyltin oxide, dibutyltin diacetate, dibutyltin dilaurate,
dibutyltin dichloride, dioctyltin dilaurate, nickel octylate, nickel naphthenate, cobalt octylate,
cobalt naphthenate, bismuth octylate, bismuth naphthenate, bismuth neodecanoate and the
like.
536 Preferred among these compounds are organic tin catalysts, and more preferred are stannous
dioctoate and dibutyltin dilaurate.

[0052]

541 The tertiary amine catalyst is not particularly limited as long as it is a compound having the

above structure, and examples thereof include triethylenediamine, 2-methyltriethylenediamine, quinuclidine, and 2-methylquinuclidine.

544 Among these, triethylenediamine and 2-methyltriethylenediamine are preferred because of their excellent catalytic activity and industrial availability.

[0053]

549 Other tertiary amine catalysts include N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylpropylenediamine, N,N,N',N'',N''-pentamethyldiethylenetriamine, N,N,N',N'',N''-pentamethyl-(3-aminopropyl)ethylenediamine, N,N,N',N'',N''-pentamethyldipropylenetriamine, N,N,N',N'-tetramethylhexamethylenediamine, bis(2-dimethylaminoethyl)ether, dimethylethanolamine, dimethylisopropanolamine, dimethylaminoethoxyethanol, N,N-dimethyl-N'-(2-hydroxyethyl)ethylenediamine, N,N-dimethyl-N'-(2-hydroxyethyl)propanediamine, bis(dimethylaminopropyl)amine, bis(dimethylaminopropyl)isopropanolamine, 3-quinuclidinol, N,N,N',N'-tetramethylguanidine, 1,3,5-tris(N,N-dimethylaminopropyl)hexahydro-S-triazine, 1,8-diazabicyclo[5.4.0]undecene-7, N-methyl-N'-(2-dimethylaminoethyl)piperazine, N,N'-dimethylpiperazine, dimethylcyclohexylamine, N-methylmorpholine, N-ethylmorpholine, 1-methylimidazole, 1,2-dimethylimidazole, 1-isobutyl-2-methylimidazole, 1-dimethylaminopropylimidazole, N,N-dimethylhexanolamine, N-methyl-N'-(2-hydroxyethyl)piperazine, 1-(2-hydroxyethyl)imidazole, 1-(2-hydroxypropyl)imidazole, 1-(2-hydroxyethyl)-2-methylimidazole, 1-(2-hydroxypropyl)-2-methylimidazole and the like.

[0054]

567 Aliphatic cyclic amide compounds include, for example, δ -valerolactam, ϵ -caprolactam, ω -enantholactam, η -capryllactam, β -propiolactam and the like.

569 Among these, ϵ -caprolactam is more effective in accelerating hardening.

[0055]

573 The titanium chelate complex is a compound whose catalytic activity is enhanced by irradiation with ultraviolet rays, and a titanium chelate complex having an aliphatic or aromatic diketone as a ligand is preferable from the viewpoint of excellent curing acceleration effect.

577 Further, in the present invention, in addition to aromatic or aliphatic diketones, those having alcohols having 2 to 10 carbon atoms as ligands are preferred from the viewpoint that the effects of the present invention are more pronounced.

580 In the present invention, the above catalysts may be used alone or in combination.

[0056]

585 The mass ratio of the catalyst is preferably in the range of 0.001 to 80 parts per 100 parts of the mixture of the polyisocyanate composition (B) and the polyol composition (A), and more preferably in the range of 0.01 to 70 parts. more preferred.

[0057]

591 The reactive adhesive of the present invention may be used in combination with a pigment, if desired.

593 The pigments that can be used in this case are not particularly limited. Organic and inorganic pigments such as pigments, brown pigments, green pigments, blue pigments, metal powder pigments, luminescent pigments and pearlescent pigments, and plastic pigments can be used.

596 Specific examples of these coloring agents include various ones, and examples of organic pigments include various insoluble azo pigments such as Benzidine Yellow, Hansa Yellow, Laked 4R; soluble pigments such as Laked C, Carmine 6B, and Bordeaux 10; Azo pigments; various (copper) phthalocyanine pigments such as phthalocyanine blue and phthalocyanine green; various chlorine dyeing lakes such as rhodamine lake and methyl violet lake; various mordant pigments such as quinoline lake and fast sky blue; vat dye-based pigments such as thioindigo-based pigments, perinone-based pigments; various quinacridone-based pigments such as Cincasia Red B; various dioxazine-based pigments such as dioxazine violet; pigments; aniline black and the like;

[0058]

608 Examples of inorganic pigments include various chromates such as yellow lead, zinc chromate, and molybdate orange; various ferrocyanic compounds such as Prussian blue; titanium oxide, zinc white, mapico yellow, iron oxide, red iron oxide, and chromium oxide. various metal oxides such as green and zirconium oxide; various sulfides and selenides such as cadmium yellow, cadmium red, and mercury sulfide; various sulfates such as barium sulfate and lead sulfate; various types such as calcium silicate and ultramarine blue various carbonates such as calcium carbonate and magnesium carbonate; various phosphates such as cobalt violet and manganese purple; various metal powders such as aluminum powder, gold powder, silver powder, copper powder, bronze powder and brass powder. pigments; flake pigments of these metals, mica flake pigments; metallic pigments and pearl pigments such as mica flake pigments coated with metal oxides and mica-like iron oxide pigments; graphite, carbon black and the like.

[0059]

623 Extender pigments include, for example, precipitated barium sulfate, rice flour, precipitated calcium carbonate, calcium bicarbonate, Kansui stone, alumina white, silica, hydrous fine silica (white carbon), ultrafine anhydrous silica (Aerosil), silica sand (silica sand), talc,

precipitated magnesium carbonate, bentonite, clay, kaolin, loess, and the like.

[0060]

630 Furthermore, examples of plastic pigments include “ Glandol PP-1000 ” and “ PP-2000S ” manufactured by DIC Corporation.

[0061]

635 As the pigments used in the present invention, inorganic oxides such as titanium oxide and zinc oxide as white pigments, and carbon black as black pigments are more preferable because they are excellent in durability, weather resistance, and design.

[0062]

641 The mass ratio of the pigment used in the present invention is 1 to 400 parts by mass, especially 10 to 300 parts by mass with respect to the total of 100 parts by mass of the isocyanate component B and the polyol component A. Adhesion, blocking resistance, etc. It is more preferable because it is excellent in

[0063]

648 (Adhesion Promoter) In addition, an adhesion promoter can be used in combination with the reactive adhesive used in the present invention.

650 Adhesion promoters include silane coupling agents, titanate-based coupling agents, aluminum-based coupling agents, and epoxy resins.

[0064]

655 Silane coupling agents include, for example, γ -aminopropyltriethoxysilane, γ -aminopropyltrimethoxysilane, N- β (aminoethyl)- γ -aminopropyltrimethoxysilane, N- β (aminoethyl)- γ -aminosilanes such as N-phenyl- γ -aminopropyltrimethoxysilane; β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxysilane; Epoxysilanes such as sidoxypropyltriethoxysilane; Vinylsilanes such as vinyltris(β -methoxyethoxy)silane, vinyltriethoxysilane, vinyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane; hexamethyldisilazane, γ -mercapto Propyltrimethoxysilane and the like can be mentioned.

[0065]

666 Titanate-based coupling agents include, for example, tetraisopropoxytitanium, tetra-n-butoxytitanium, butyl titanate dimer, tetrastearyl titanate, titanium acetylacetonate, titanium

lactate, tetraoctylene glycol titanate, titanium lactate, tetrastearoxy Titanium etc. can be mentioned.

[0066]

673 Examples of the aluminum-based coupling agent include acetoalkoxyaluminum diisopropylate.

[0067]

678 As the epoxy resin, generally commercially available epibis type, novolac type, β -methyl epichloro type, cyclic oxirane type, glycidyl ether type, glycidyl ester type, polyglycol ether type, glycol ether type, epoxidized fatty acid ester type, poly Various epoxy resins such as carboxylic acid ester type, aminoglycidyl type, resorcinol type, triglycidyl tris(2-hydroxyethyl) isocyanurate, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, acryl glycidyl compounds such as ether, 2-ethylhexyl glycidyl ether, phenyl glycidyl ether, phenol glycidyl ether, pt-butylphenyl glycidyl ether, diglycidyl adipate, o-diglycidyl phthalate, glycidyl methacrylate, butyl glycidyl ether; mentioned.

[0068]

689 (Other additives) If necessary, the reactive adhesive used in the present invention may contain additives other than those mentioned above.

691 Additives include, for example, leveling agents, inorganic fine particles such as colloidal silica and alumina sol, polymethyl methacrylate-based organic fine particles, antifoaming agents, anti-sagging agents, wetting and dispersing agents, viscosity modifiers, ultraviolet absorbers, metals Deactivators, peroxide decomposers, flame retardants, reinforcing agents, plasticizers, lubricants, rust inhibitors, fluorescent whitening agents, inorganic heat absorbers, flame retardants, antistatic agents, dehydrating agents, Known and commonly used thermoplastic elastomers, tackifiers, phosphoric acid compounds, melamine resins, or reactive elastomers can be used.

699 The content of these additives can be appropriately adjusted within a range that does not impair the functions of the reactive adhesive used in the present invention.

[0069]

704 These adhesion promoters and additives can be mixed with either the polyisocyanate composition (B) or the polyol composition (A), or used as a third component at the time of coating. can.

707 Usually, a premix is prepared by previously blending the polyol composition (A) with components other than the polyisocyanate composition (B), and the premix and the polyisocyanate composition (B) are added immediately before construction. Mix and prepare.

[0070]

713 (Laminated film) The laminated film of the present invention is formed by laminating an adhesive layer made of the reactive adhesive between a first plastic film and a second plastic film.

716 Specifically, it is obtained by applying the reactive adhesive to a first plastic film, then laminating a second plastic film on the coated surface, and curing the adhesive layer.

718 For example, when the reactive adhesive is a non-solvent type, it may be applied to the first plastic film by a roll coater coating method, and then bonded to another substrate without passing through a drying step.

721 When the reactive adhesive contains a solvent, it may be applied to the first plastic film by a roll coater coating method, passed through a drying oven at 60 ° C., and then laminated with another base material.

724 As for the coating conditions, it is preferable that the viscosity of the mixed liquid of the adhesive is about 300 to 3000 mPa·s at 40 ° C. in a state where the adhesive is heated to 30 ° C. to 90 ° C. in an ordinary roll coater. Since the viscosity is 5000 mPa·s or less after being left in an atmosphere of 40 ° C. for 30 minutes, it can be applied without problems.

728 The coating amount is preferably 0.5 to 5 g/m², more preferably about 0.5 to 3 g/m².

[0071]

732 In addition, gravure or flexographic printing of printing ink may be used on the first plastic film, and even in this case, a good laminate appearance can be exhibited.

734 As the printing ink described above, solvent-based, water-based, or active energy ray-curable inks can be used.

[0072]

739 When the reactive adhesive used in the present invention is used, the adhesive cures in 12 to 72 hours at room temperature or under heat after lamination, and exhibits practical physical properties.

[0073]

745 The first plastic film used here includes PET (polyethylene terephthalate) film, nylon film, OPP (biaxially oriented polypropylene) film, K-coated film such as polyvinylidene chloride, base film such as various vapor deposition films, and aluminum foil. etc., and as the second plastic film, the other substrates include CPP (unstretched polypropylene) film, VMCPP (aluminum-deposited unstretched polypropylene film), LLDPE (linear low-density polyethylene), LDPE (low-density polyethylene), HDPE (high-density polyethylene), VMLDPE (aluminum-deposited non-low-density polyethylene film) films and the like.

[0074]

755 In the present invention, an excellent laminated film appearance can be obtained not only when high-speed lamination is performed using a dry lamination machine having a drying process for the organic solvent in the adhesive, but also when high-speed lamination is performed using a non-solvent type lamination machine. For example, in the case of a PET (polyethylene terephthalate) film / VMCPP (aluminum-deposited unstretched polypropylene film) film configuration, 200 m / min or more, and in the case of an OPP / CPP film configuration, 350 m / min or more. Appearance can be presented.

[0075]

765 (Packaging body) The packaging body of the present invention is formed by molding the laminated film into a bag shape, and specifically, the laminated film is heat-sealed to take the form of the packaging body.

768 In addition, when considering the use as a package, the required performance (easily tearable and hand-cutting), the rigidity and durability required as a package (for example, impact resistance, pinhole resistance, etc.), Other layers may be laminated as desired.

771 It is usually used with a base layer, a paper layer, a second sealant layer, a non-woven fabric layer, and the like.

773 A well-known method can be used as a method of laminating other layers.

774 For example, an adhesive layer may be provided between other layers and laminated by a dry lamination method, a heat lamination method, a heat sealing method, an extrusion lamination method, or the like.

777 As the adhesive, the reactive adhesive may be used, or other one-liquid type urethane-based adhesive, epoxy-based adhesive, aqueous dispersion of acid-modified polyolefin, or the like may be used.

[0076]

783 As a specific laminate structure, a first plastic film layer/adhesive layer/second plastic layer and a first plastic layer, which can be suitably used for general packages, lids, refill containers, etc. A second plastic layer/paper that can be suitably used for a substrate layer/adhesive layer/first plastic film layer/adhesive layer/second plastic layer, paper containers, paper cups, etc., with a barrier layer Layer/adhesive layer/first plastic film layer/adhesive layer/second plastic, second plastic layer/paper layer/polyolefin resin layer/base layer/first plastic layer/adhesive layer/second plastic Layer, paper layer/first plastic film layer/adhesive layer/second plastic layer/adhesive layer/first plastic layer/adhesive layer/second plastic layer/first plastic layer/adhesive layer/second plastic layer that can be suitably used for sealant layers, tube containers, etc. and the like.

793 These laminates may have a printed layer, a topcoat layer, and the like, if necessary.

[0077]

797 The first plastic film layer is, for example, polyester resin films such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and polylactic acid (PLA); polyolefin resin films such as polypropylene; polystyrene resin films; Polyamide resin films such as p-xylylene adipamide (MXD6 nylon); polycarbonate resin films; polyacrylonitrile resin films; polyimide resin films; Ethylene-vinyl alcohol copolymer/nylon 6) and mixtures are used.
802 Among them, those having mechanical strength and dimensional stability are preferable.
803 In particular, among these, films arbitrarily stretched in biaxial directions are preferably used.

[0078]

807 In addition, the first plastic film layer is a soft metal foil such as an aluminum foil in order to impart a barrier function, as well as a vapor deposition layer such as aluminum vapor deposition, silica vapor deposition, alumina vapor deposition, silica-alumina binary vapor deposition; vinylidene chloride resin, denatured polyvinyl alcohol, ethylene-vinyl alcohol copolymer, MXD nylon, or the like.

[0079]

815 A conventionally known sealant resin can be used as the second plastic film layer.
816 For example, polyethylene such as low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE), acid-modified polyethylene, polypropylene (PP), acid-modified polypropylene, copolymerized polypropylene, ethylene-vinyl acetate Copolymers, ethylene-(meth)acrylic acid ester copolymers, ethylene-(meth)acrylic acid copolymers, polyolefin resins such as ionomers, and the like can be mentioned.
822 Among them, polyethylene-based resins are preferable from the viewpoint of low-temperature sealability, and polyethylene is particularly preferable because it is inexpensive.
824 The thickness of the sealant layer is not particularly limited, but is preferably in the range of 10 to 60 μm , more preferably in the range of 15 to 40 μm , in consideration of processability to packaging materials and heat sealability.
827 In addition, by providing the sealant layer with unevenness having a height difference of 5 to 20 μm , it is possible to provide the sealant layer with slipperiness and tearability of the packaging material.

[0080]

833 Examples of the paper layer include natural paper and synthetic paper.
834 The first and second sealant layers can be formed of materials similar to the sealant layers described above.

836 A printed layer may be provided on the outer surface or the inner surface side of the substrate layer and the paper layer, if necessary.

[0081]

841 The "other layer" may contain known additives and stabilizers such as antistatic agents, easy-adhesion coating agents, plasticizers, lubricants and antioxidants.

843 In addition, the "other layers" are pre-treated with corona treatment, plasma treatment, ozone treatment, chemical treatment, solvent treatment, etc. in order to improve adhesion when laminated with other materials. may

[0082]

849 Embodiments of the package of the present invention include a three-side seal bag, a four-side seal bag, a gusset packaging bag, a pillow packaging bag, a gobelet-top type bottomed container, a tetra classic, a Bruck type, a tube container, a paper cup, a lid material, and the like. There are various.

853 Moreover, the package of the present invention may be appropriately provided with an easy-opening treatment or a resealing means.

[0083]

858 Laminates obtained in this manner are used in a variety of applications, such as packaging materials for foods, pharmaceuticals, daily necessities, barrier materials, roofing materials, solar cell panel materials, battery packaging materials, window materials, outdoor flooring materials, and lighting. Protective materials, automobile parts, signboards, outdoor industrial applications such as stickers, decorative sheets used for injection molding simultaneous decoration methods, liquid laundry detergents, liquid kitchen detergents, liquid bath detergents, liquid bath soaps, liquid shampoos, as packaging materials for liquid conditioners and the like.

[0084]

869 EXAMPLES The contents and effects of the present invention will be described in more detail below with reference to examples, but the present invention is not limited to the following examples.

872 In addition, "parts" in the examples indicate "parts by weight".

[0085]

876 (Synthesis Example 1) Synthesis of PET-containing polyester polyol (A1-1) 27.2 g of ethylene glycol was added to a 2-liter four-necked glass flask equipped with a stirring blade,

temperature sensor, nitrogen gas inlet tube, and rectifying column. , 205.0 g of neopentyl glycol, 178.7 g of adipic acid, 164.0 g of isophthalic acid, 64.0 g of recycled PET pellets, and 0.11 g of dibutyltin oxide as a polymerization catalyst are charged.

- 881 The temperature was gradually raised to 230 ° C under a normal pressure nitrogen stream, and the dehydration reaction was carried out while the temperature was raised to 230 ° C. After confirming that the top temperature of the column has reached 80 ° C. or less, the rectifying column is removed, the condenser is switched to a glass condenser, a line is connected from the nitrogen gas introduction pipe to a vacuum pump, and the condensation reaction is carried out under a reduced pressure of 50 Torr for 5 hours.
- 887 When the predetermined acid value and viscosity were reached, the temperature was lowered to 130 ° C., and ethyl acetate was added and diluted using a dropping funnel to obtain PET-containing polyester polyol (A1-1).
- 890 Weight fraction of PET pellets at the time of raw material charging, weight fraction of 1,6-hexanediol, weight fraction of dimer acid, and acid value in terms of solids of the obtained PET-containing polyester polyol (A1-1), in terms of solids Tables 1 and 2 show the hydroxyl value, solid content, and number average molecular weight of

[0086]

- 897 (Synthesis Example 2), (Synthesis Example 6), (Synthesis Example 7) Raw materials shown in Synthesis Tables 1 and 2 of PET-containing polyester polyols (A1-2), (A1-6), and (A1-7) were used. Except for this, it was produced in the same manner as the PET-containing polyester polyol (A1-1).
- 901 Tables 1 and 2 show property values and the like.

[0087]

- 905 (Synthesis Example 3) Synthesis of PET-containing polyester polyol (A1-3) 20.0 g of ethylene glycol was added to a 2-liter four-necked glass flask equipped with a stirring blade, temperature sensor, nitrogen gas inlet tube, and rectifying column. , 150.1 g of neopentyl glycol, 92.0 g of 1,6-hexanediol, 92.0 g of dimer acid, 174.7 g of adipic acid, 160.5 g of isophthalic acid, 76.5 g of PET pellets and 0.14 g of dibutyltin oxide as a polymerization catalyst. prepare the
- 911 The temperature was gradually raised to 220 ° C under a normal pressure nitrogen stream, and the dehydration reaction was carried out while the temperature was raised to 220 ° C. After confirming that the temperature at the top of the column has reached 80 ° C or less, the rectifying column is removed, the condenser is switched to a glass condenser, a line is connected from the nitrogen gas introduction pipe to a vacuum pump, and the condensation reaction is carried out under a reduced pressure of 50 Torr for 4 hours. When the predetermined acid value and viscosity were reached, the temperature was lowered to 130 ° C., and ethyl acetate was added and diluted using a dropping funnel to obtain a PET-containing polyester polyol (A1-3). Weight fraction of PET pellets at the time of raw material

charging, weight fraction of 1,6-hexanediol, weight fraction of dimer acid, and acid value in terms of solids of the obtained PET-containing polyester polyol (A1-3), in terms of solids Tables 1 and 2 show the hydroxyl value, solid content, and number average molecular weight of

[0088]

927 (Synthesis Example 4), (Synthesis Example 5), (Synthesis Example 8), (Synthesis Example 10) PET-containing polyester polyols (A1-4), (A1-5), (A1-8), (A1-10) Synthesis was produced in the same manner as PET-containing polyester polyol (A1-3) except that the raw materials shown in Tables 1 and 2 were used.

931 Tables 1 and 2 show property values and the like.

[0089]

935 (Synthesis Example 9) Synthesis of PET-containing polyester polyol (A1-9) 14.6 g of ethylene glycol was added to a 2-liter four-necked glass flask equipped with a stirring blade, temperature sensor, nitrogen gas inlet tube, and rectifying column. , 109.7 g of neopentyl glycol, 21.0 g of 1,6-hexanediol, 21.0 g of dimer acid, 90.3 g of adipic acid, 83.0 g of isophthalic acid, 690.0 g of PET pellets, and 0.14 g of dibutyltin oxide as a polymerization catalyst. prepare the

941 The temperature was gradually raised to 220 ° C under a normal pressure nitrogen stream, and the dehydration reaction was carried out while the temperature was raised to 220 ° C. After confirming that the top temperature of the column has reached 80 ° C. or less, the rectifying column is removed, the condenser is switched to a glass condenser, a line is connected from the nitrogen gas introduction pipe to a vacuum pump, and the condensation reaction is carried out under a reduced pressure of 50 Torr for 5 hours. When the predetermined acid value and viscosity were reached, the temperature was lowered to 130 ° C., and ethyl acetate was added and diluted using a dropping funnel to obtain a PET-containing polyester polyol (A1-9). PET pellet weight fraction, 1,6-hexanediol weight fraction, dimer acid weight fraction, and the obtained PET-containing polyester polyol (A1-9) acid value in terms of solids, in terms of solids Tables 1 and 2 show the hydroxyl value, solid content, and number average molecular weight of

[0090]

956 (Comparative Synthesis Example 1) Synthesis of PET-decomposed polyester polyol (A1-11) Ethylene glycol 27 was added to a 2-liter glass four-necked flask equipped with a stirring blade, temperature sensor, nitrogen gas inlet tube and glass cooling tube. .2 g, 205.0 g of neopentyl glycol, 372.0 g of recycled PET pellets and 0.60 g of tetraisopropyl titanate as a transesterification catalyst are charged.

961 The temperature was raised to 190 ° C under normal pressure nitrogen stream, and the

decomposition reaction of PET was sufficiently carried out at 190 ° C for 7 hours. After confirming that, the temperature is lowered to 130 ° C., and 157.5 g of adipic acid and 144.7 g of isophthalic acid are charged. The temperature was gradually raised under a normal pressure nitrogen stream to 250 ° C while performing a dehydration reaction, and the reaction was carried out at 250 ° C for 2 hours. Remove the distillation column, switch to a glass condenser, and lower the temperature to 230 ° C. When the temperature reaches 230 ° C., a condensation reaction is carried out for 8 hours under a reduced pressure of 50 Torr by connecting a line from the nitrogen gas introduction pipe to a vacuum pump. When the predetermined acid value and viscosity were reached, the temperature was lowered to 130 ° C., and ethyl acetate was added and diluted using a dropping funnel to obtain a PET-containing polyester polyol (A1-11). Tables 1 and 2 show the weight fraction of the PET pellets when the raw material was charged, and the solid-equivalent acid value, solid-equivalent hydroxyl value, solid content, and number average molecular weight of the obtained PET-decomposed polyester polyol (A1-11).

[0091]

979 (Comparative Synthesis Example 2) Synthesis of PET-decomposed polyester polyol (A1-12)
434 recycled PET pellets were added to a 2-liter four-neck glass flask equipped with a stirring blade, temperature sensor, nitrogen gas inlet tube, and glass cooling tube. Charge .0g.

983 It was immersed in a salt bath at 300 ° C. under normal pressure nitrogen stream, and when PET started to dissolve, stirring was started, and 1.47 g of dibutyltin oxide was charged as a transesterification catalyst. Then, 300.0 g of trimethylolpropane dissolved in advance at 130 ° C. was added little by little while taking care not to solidify the PET, and then the internal temperature was kept at 220 ° C. in an oil bath of 240 ° C. and reacted for 5 hours to decompose PET. A polyester polyol (A1-12) was obtained. Tables 1 and 2 show the weight fraction of the PET pellets when the raw material was charged, and the solid acid value, solid hydroxyl value, solid content and number average molecular weight of the obtained PET decomposed polyester polyol (A1-12).

[0092]

995 (Comparative Synthesis Example 3) Synthesis of PET-decomposed polyester polyol (A1-13)
Into a 2-liter four-necked glass flask equipped with a stirring blade, temperature sensor, nitrogen gas inlet pipe and rectifying column, 61.5 g of neopentyl glycol was added. 6 g, 118.7 g of 1,6-hexanediol, 23.0 g of trimethylolpropane, 157.8 g of adipic acid, 89.4 g of isophthalic acid, 328.2 g of recycled PET pellets, and 0.60 g of monobutyltin oxide as a polymerization catalyst are charged.

1001 The temperature was gradually raised to 230 ° C under a normal pressure nitrogen stream, and the dehydration reaction was carried out while the temperature was raised to 230 ° C. After confirming that the top temperature of the rectifying column became 80 ° C or lower,

the rectifying column was removed, the condenser was switched to a glass condenser, and a line was connected from the nitrogen gas introduction pipe to a vacuum pump, and the pressure was reduced to 50 Torr. The condensation reaction is carried out at rt for 9 hours. When the predetermined acid value and viscosity were reached, the temperature was lowered to 130 ° C., and ethyl acetate was added and diluted using a dropping funnel to obtain a PET-containing polyester polyol (A1-13). Weight fraction of PET pellets at the time of raw material charging, weight fraction of 1,6-hexanediol, weight fraction of dimer acid, and acid value in terms of solids of the obtained PET decomposed polyester polyol (A1-13), in terms of solids Tables 1 and 2 show the hydroxyl value, solid content, and number average molecular weight of

[0093]

1017 In Tables 1 and 2, the unit of charge is g.

[0096]

1021 (Synthesis Example 11) Synthesis of PET-containing polyester polyurethane polyol (A2-1)

PET-containing polyester polyol was added to a 2-liter four-neck glass flask equipped with a stirring blade, temperature sensor, nitrogen gas inlet tube and glass cooling tube. 500.0 g of (A1-1) and 0.10 g of dibutyltin dilaurate as a polymerization catalyst are charged.

1025 When the temperature is raised to 60 ° C under normal pressure nitrogen stream, 15.0 g of isophorone diisocyanate (IPDI) is charged, the temperature is raised to 80 ° C, and urethanization reaction is carried out at 80 ° C for 5 hours.

1028 After confirming that a predetermined viscosity has been reached and that the residual isocyanate content is 0.05% or less, the temperature is lowered to 50 ° C. and the solid content is appropriately adjusted with ethyl acetate to prepare PET-containing urethane-modified polyester polyol (A2-1). Obtained.

1032 Table 3 shows the solid-equivalent acid value, solid-equivalent hydroxyl value, solid content, and number average molecular weight of the obtained PET-containing polyester polyurethane polyol (A2-1).

[0097]

1038 (Synthesis Example 12) to (Synthesis Example 20), (Comparative Synthesis Example 4) to

(Comparative Synthesis Example 5) Synthesis of PET-containing polyester polyurethane polyols (A2-2) to (A2-10) and PET-decomposed polyester polyurethane polyols (A2-11)

Synthesis of (A2-12) A PET-containing polyester polyurethane polyol (A2-1) was produced in the same manner, except that the raw materials shown in Tables 3 and 4 were used.

1043 Tables 3 and 4 show property values and the like.

1044 IPDI in Tables 3 and 4 is an abbreviation for isophorone diisocyanate.

[0100]

1048 (Examples and Comparative Examples) Reactive adhesives for Examples and Comparative Examples were prepared by blending the polyol composition (A) and the polyisocyanate composition (B) shown in Tables 5-7.

1051 The isocyanate (B) is a trifunctional polyisocyanate obtained by adding tolylene diisocyanate (TDI) to commercially available trimethylolpropane (TMP) (product name: Dick Dry KW-75 manufactured by DIC, a TMP-added product of TDI, solid content of 75 %) was used.

1054 Laminated films were prepared and evaluated according to the method of each evaluation item, and evaluated according to the evaluation criteria.

1056 The results are shown in Tables 5-7.

[0101]

1060 (Evaluation) (High-speed processability) A dry laminator (Musashino Machinery Design Office Co., Ltd., dry lamination test coater) is used as the laminator, the processing speed is 250 m/min, and the first plastic film layer is a PET film (After applying the adhesive of Examples or Comparative Examples to a coating amount of 3 g/m² on a commercially available polyethylene terephthalate film), VMCPP (commercially available aluminum-deposited unstretched polypropylene film) was laminated as a second plastic film layer, to obtain a laminated film.

1067 The appearance of the film immediately after lamination (whether there are defects such as wrinkles, floating due to air bubbles, and tunneling caused by misalignment between films) was evaluated visually and using a scale magnifier based on the following evaluation criteria. The evaluation with a scale magnifier was performed based on the number of bubbles within a scale of 1 cm². Evaluation criteria : 0 bubbles, no wrinkles or tunneling
○ : 1 to 4 bubbles, no wrinkles or tunneling ○- : 5 to 9 bubbles, no wrinkles or tunneling
: Partial wrinkles and tunneling with 10 to 16 bubbles × : 17 or more bubbles with wrinkles and tunneling in many places

[0102]

1078 (Heat resistance (high-retardant resistance)) A dry laminator (Musashino Machinery Design Office Co., Ltd., dry lamination test coater) was used as the laminator, the processing speed was 250 m/min, and PET-AL was used as the first plastic film layer. (Commercially available polyethylene terephthalate to which aluminum foil is adhered) was coated with the adhesive of Examples or Comparative Examples in a coating amount of 4.3 g/m², and then CPP (commercially available unstretched polypropylene film) was laminated.

1084 After that, aging was performed under aging conditions of 40 ° C. for 5 days to obtain a laminated film. A pouch having a size of 120 mm × 120 mm was prepared using the obtained laminated film, and 70 g of water/oil=9/1 weight ratio was filled in the pouch as a content. Thereafter, retort treatment was performed at 135 ° C. for 30 minutes in an

autoclave, and evaluation was made by measuring peel strength.

[0103]

1092 For the evaluation method, using a Tensilon universal tester manufactured by Orientec Co., Ltd., a test piece with a width of 15 mm was cut out from the pouch after retort treatment, the contents were wiped off well, and then the atmosphere temperature was 25 ° C. and the peel speed was 300 mm / min., the tensile strength when peeled by the 180 degree peeling method was compared as the adhesive strength.

1097 The unit of adhesive strength was N/15 mm. It can be said that an adhesive strength of 5 N/15 mm or more is practically sufficient. Evaluation criteria : Adhesive strength 12 N/15 mm or more ○: Adhesive strength 7 N/15 mm or more, less than 12 N/15 mm ○ -: Adhesive strength 5 N/15 mm or more, less than 7 N/15 mm : Adhesive strength 1 N/15 mm or more, less than 5 N/15 mm ×: Less than adhesive strength 1N/15 mm

[0104]

1105 (Content resistance) A dry laminator (Musashino Machinery Design Office Co., Ltd., dry lamination test coater) is used as the laminator, the processing speed is 250 m/min, and Nyl (commercially available nylon film) is used as the first plastic film layer.) was coated with the adhesive of Example or Comparative Example at a coating amount of 4.3 g/m², and then laminated with LLDPE (commercially available linear low-density polyethylene film) as a second plastic film layer.

1111 After that, aging was performed under aging conditions of 40 ° C. for 5 days to obtain a laminated film. A pouch having a size of 120 mm × 120 mm was prepared using the obtained laminated film, and 70 g of Supersol pH=13 was filled in the pouch as a content. After that, it was treated in a constant temperature bath at 50 ° C. for 3 days, and evaluated by peel strength measurement.

[0105]

1119 For the evaluation method, using a Tensilon universal testing machine manufactured by Orientec Co., Ltd., a test piece with a width of 15 mm was cut out from the pouch after the content resistance test, and the content was thoroughly wiped off, and then the atmosphere temperature was 25 ° C. and the peel speed was 300 mm. /min, the tensile strength when peeled by the 180 degree peeling method was compared as the adhesive strength.

1124 The unit of adhesive strength was N/15 mm. It can be said that an adhesive strength of 2 N/15 mm or more is practically sufficient. Evaluation criteria : Adhesive strength 7 N/15 mm or more ○: Adhesive strength 5 N/15 mm or more, less than 7 N/15 mm ○ -: Adhesive strength 2 N/15 mm or more, less than 5 N/15 mm : Adhesive strength 1 N/15 mm or more, less than 2 N/15 mm ×: Less than adhesive strength 1N/15 mm

[0109]

1132 (Comparative Example 1) to (Comparative Example 5) Adhesive compounding and evaluation shown in Table 8 were performed in the same manner as in the Examples.

[0111]

1137 According to the reactive adhesive of the present invention, it can be applied as an adhesive for laminates in which various kinds of plastic films, metal-deposited films, or metal foils are appropriately combined. It is possible to obtain a laminated film having excellent adhesiveness and appearance after lamination, as well as excellent heat resistance and resistance to contents.

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CLAIMS WO2019188335A1

1.
13 A reactive adhesive containing a polyol composition (A) and a polyisocyanate composition (B), wherein the polyol composition (A) is obtained by collectively charging polyethylene terephthalate, a polyhydric alcohol and a polybasic acid A reactive adhesive characterized by containing a polyester polyol (A1) which is a reaction product.
2.
20 The reactive adhesive according to claim 1, wherein the proportion of polyethylene terephthalate in the starting material of the polyester polyol (A1) is 5 to 50% by mass.
3.
25 The reactive adhesive according to claim 1, wherein the polybasic acid is a dimer acid, and the dimer acid accounts for 5 to 20% by mass of the starting material of the polyester polyol (A1).
4.
30 The reactive adhesive according to any one of claims 1 to 3, wherein the polyol composition (A) contains a polyester polyurethane polyol (A2) which is a reaction product of a polyisocyanate and the polyester polyol (A).
5.
36 A laminated film obtained by laminating an adhesive layer between a first plastic film and a second plastic film, wherein the adhesive layer is a layer of the reactive adhesive according to

any one of claims 1 to 4. A laminated film characterized by:

6.

42 A laminated film obtained by laminating a first plastic film, a printed layer, an adhesive layer, and a second plastic film in this order, wherein the adhesive layer is the reactive adhesive according to any one of claims 1 to 4. A laminated film characterized by being a layer of an agent.

7.

49 A package formed by molding the laminated film according to claim 5 or 6 into a bag.

8.

53 A method for producing a polyester polyol (A1), characterized in that polyethylene terephthalate, a polyhydric alcohol, and a polybasic acid are charged all at once and reacted.

9.

58 A method for producing a polyester polyurethane polyol (A2), which comprises reacting a polyester polyol (A1) in which polyethylene terephthalate, a polyhydric alcohol, and a polybasic acid are collectively charged and reacted with a polyisocyanate.

1

2,710,848

POLYMERIC LINEAR TEREPHTHALATES DISSOLVED IN A SOLVENT COMPRISING TRIFLUOROACETIC ACID

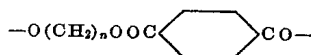
Sterling S. Sweet, Maurice H. Van Horn and Philip T. Newsome, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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Serial No. 364,197

4 Claims. (Cl. 260—31.2)

This invention relates to new compositions of matter containing highly polymeric polymethylene terephthalates dissolved in trifluoroacetic acid; and to the manufacture of synthetic filaments, yarns, sheets, films and other shaped articles therefrom by dry spinning, or other suitable evaporative processes, wherein the solvent is expelled from the shaped article by controlled heated atmospheres, or by contact with a heated surface.

The synthetic polyester component of our new solution composition is highly polymeric linear polymethylene terephthalates with recurring structural units of the general formula:



wherein n is an integer from 2 to 10.

These synthetic polyester compositions may be prepared by heating glycols of the series $\text{HO}(\text{CH}_2)_n\text{OH}$ wherein n is an integer within the range of 2 to 10 with terephthalic acid or with an ester forming derivative thereof as is described in United States Patent 2,465,319 of March 22, 1949.

The polymethylene glycols having from 2 to 10 methylene groups which may be employed include ethylene glycol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, heptamethylene glycol, octamethylene glycol, nonamethylene glycol and decamethylene glycol. It is preferable to employ glycols having 2 to 4 methylene groups since they produce highly polymerized esters with very high melting points and of these glycols, ethylene glycol $\text{HO}(\text{CH}_2)_2\text{OH}$ is favored because of its availability. Mixtures of these glycols can also be employed, if desired.

Suitable ester forming derivatives of terephthalic acid are aliphatic or aromatic esters such as methyl, ethyl, propyl, butyl, amyl, hexyl, and heptyl terephthalates and aryl esters such as those from penol and cresol.

It is well known that these polymers are very slightly or not at all soluble in common low boiling solvents such as acetone, benzene, etc., and that those solvents which are available, such as nitrobenzene, orthochlorophenol, cresylic acid, and mixtures of tetrachloroethane and phenol are high boiling liquids which are difficult to remove after spinning or coating from solvent solutions. Furthermore, the removal of these solvents usually requires such a high temperature that crystallization and embrittlement may occur so as to prevent the cold drawing or rolling of the material. The present invention, however, permits the production of shaped polyesters which have high strength and dimensional and chemical stability.

An object, therefore, of the present invention is to provide a new composition of matter containing a highly polymeric polymethylene terephthalate dissolved in trifluoroacetic acid.

Another object of the invention is to provide a spinning solution containing highly polymeric polymethylene terephthalate in trifluoroacetic acid solvent.

Still another object is to provide a film or sheet con-

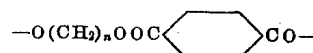
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taining a highly polymeric polymethylene terephthalate and trifluoroacetic acid.

Other objects of the invention are to provide processes for producing filaments, yarn, sheets and film from solutions containing highly polymeric polymethylene terephthalate dissolved in trifluoroacetic acid.

Other objects will appear hereinafter.

We have found, in accordance with our invention, that the linear polyesters which have recurring structural units of the general formula:



wherein n is an integer from 2 to 10 are soluble in trifluoroacetic acid. The use of trifluoroacetic acid as the solvent makes practical the preparation of clear solutions containing as high as 33 grams of polyester to 100 grams of solvent. These solutions can be coated on a moving heated surface to form films of sufficient strength and ductility to permit rolling and stretching. These solutions can also be forced through spinnerets by a suitable dry spinning process and formed into filaments and yarns which can be drawn to result in strong filaments. Our invention, therefore, makes available all the advantages of coating and spinning from solvents to the process of these previously intractable polymers.

The present invention is further illustrated in the following examples:

Example 1

Twenty grams of a high viscosity polyethylene terephthalate were dissolved in 60 grams of trifluoroacetic acid (B. P. 72° C.) at room temperature (20° C.) in an Erlenmeyer flask. Solution is complete in 2-3 hours but may be accelerated by warming at 70° C. for one hour. A clear, practically colorless solution was obtained which was coated on a glass or metal plate. After overcuring at 70° C. for 16 hours, a clear film 0.005 inch thick was obtained and was found to have the following physical properties:

M. I. T. folds	905
Research tear	200
Tensile strength	p. s. i. 4500
Elongation	per cent. 50

The term "research tear" in this table refers to a test commonly employed in paper testing. The machine for making this test is made by the Thwing Albert Instrument Co.

Example 2

Twenty-five grams of a high viscosity polyethylene terephthalate (intrinsic viscosity 0.90) were dissolved in 75 grams of trifluoroacetic acid at 70° C., solution was complete in one hour. A clear, viscous dope was obtained which was then filtered and spun into air at room temperature, i. e. approximately 20° C. through a spinneret under 50 pounds pressure. The resulting filaments were stretched 300%, with a consequent increase in tensile strength from 10,000 to 45,000 pounds per square inch.

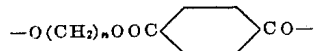
This invention, it will be seen, permits polyethylene terephthalate and its related compounds mentioned herein to be formed by more or less conventional spinning and coating processes into shaped articles. Heretofore the preparation of films and fibers of these polyesters has been impractical except by melt extrusion. Spinning and coating from solvent solutions generally results in more uniformity than is obtainable by melt spinning or coating methods.

We have also found that dichloroacetic acid is a solvent for such above mentioned highly polymeric polymethylene terephthalates. However, for some uses this solvent is held too tenaciously by these polymers so that

3
drying or curing the article formed from such solutions is rather difficult and hence we prefer to employ trifluoroacetic acid as the solvent in such cases.

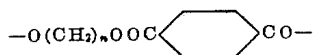
We claim:

1. A new composition of matter comprising a highly polymeric linear terephthalate composed of recurring structural units of the general formula:



wherein n is an integer from 2 to 10 dissolved in a solvent comprising trifluoroacetic acid.

2. A new spinning solution from which filaments and fibers may be dry spun comprising from 5 to 25% by weight a highly polymeric linear terephthalate composed of recurring structural units of the general formula:



4
wherein n is an integer from 2 to 10 dissolved in a solvent comprising trifluoroacetic acid.

3. A new composition of matter consisting of polyethylene terephthalate dissolved in trifluoroacetic acid.

4. A new solution from which filaments and film may be formed consisting of 5 to 25% of polyethylene terephthalate dissolved in trifluoroacetic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,497,376 Swallow ----- Feb. 14, 1950

FOREIGN PATENTS

630,992 Great Britain ----- Oct. 25, 1949

**Espacenet****Bibliographic data: CN106400171 (A) — 2017-02-15**

Preparation method of fiber forming composite material with permeability

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Classification: - international: **C08K3/36; C08K9/06; C08L67/02; D01D5/00; D01F1/10; D01F6/84**
- cooperative: **C08K3/36 (CN); C08K9/06 (CN); D01D5/003 (CN); D01F1/10 (CN); D01F6/84 (CN) more**

Application number: CN201610791068 20160831 [Global Dossier](#)

Priority number(s): CN201610791068 20160831

Abstract of CN106400171 (A)

The invention discloses a preparation method of fiber forming composite material with permeability. The method comprises the following concrete steps: a silane coupling agent solution and nanometer SiO₂ powder are added into a flask, the flask is placed in an electrothermal sleeve and heated till the solution is boiled, a reaction is carried out for 3 hours at a constant temperature, heating is stopped, after vacuum pumping filtration, drying is carried out, grinding and sieving are carried out, the materials are dissolved in a glycol solution, ultrasonic dispersion is carried out, and a modified SiO₂ organic solution is obtained; polyethylene glycol terephthalate is weighed and dissolved in the modified SiO₂ organic solution, the solution is poured into a hydro-thermal reaction vessel and a reaction is carried out for a period of time, after the reaction ends, precipitates are washed, dried, crushed, sieved, and dissolved in a mixed solution of dichloromethane and trifluoroacetic acid in order to prepare a spinning solution, and electrostatic spinning is carried out. SiO₂ is modified by the silane coupling agent, dispersion capability of SiO₂ is improved, at the same time organically modified SiO₂ and PET are selected for generating an inorganic/organic composite material, and electrostatic spinning is carried out for the composite material; and nanometer SiO₂ increases viscosity of melt and reduces molecular weight, and the method is good for melt spinning, processing and stretching.

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DESCRIPTION CN106400171A

10 A kind of preparation method with gas permeable fiber-forming composite material

[0001]

14 technical field

[0002]

18 The invention belongs to the technical field of composite materials, and in particular relates to a preparation method of a gas-permeable fiber-forming composite material.

[0003]

23 Background technique

[0004]

27 Polyethylene terephthalate, referred to as PET, has a chemical formula of $C_{10}H_8O_4$, which is synthesized by transesterification of dimethyl terephthalate and ethylene glycol or by esterification of terephthalic acid and ethylene glycol. Hydroxyethyl ester, and then made by polycondensation reaction.

30 It is a crystalline saturated polyester, a milky white or light yellow, highly crystalline polymer with a smooth and shiny surface.

32 It is a common resin in daily life, which can be divided into APET, RPET and PETG.

33 PET has excellent physical and mechanical properties in a wide temperature range. The long-term use temperature can reach $120^{\circ}C$. It has excellent electrical insulation. Even at high temperature and high frequency, its electrical properties are still good, but its corona resistance is poor. Good creep resistance, fatigue resistance, friction resistance and dimensional stability.

[0005]

40 Silicon dioxide is also called silica, with the chemical formula SiO_2 .

41 There are two kinds of crystalline silica and amorphous silica in nature. Crystalline silica is divided into three types: quartz, tridymite and cristobalite due to different crystal structures. Pure quartz is a colorless crystal, and the large and transparent prismatic quartz is called crystal. If the crystals containing trace impurities have different colors, there are amethyst, tea crystal and so on. Ordinary sand is fine quartz crystals, and there are yellow sand and white sand. In the silicon dioxide crystal, the 4 valence electrons of the silicon atom form 4 covalent bonds with the 4 oxygen atoms, the silicon atom is located in the center of the regular tetrahedron, and the 4 oxygen atoms are located on the 4 vertices of the regular tetrahedron, SiO_2 It is the simplest formula to express the composition, and it only expresses the ratio of the number of atoms of silicon and oxygen in the silicon dioxide crystal. Silica is an atomic crystal.

[0006]

53 Contents of the invention

[0007]

57 The object of the present invention is to provide a kind of preparation method that has gas permeability fiber-forming composite material, by organically modified SiO_2 and PET synthetic composite material, and to composite material electrospinning, synthesize a kind of gas-permeable fiber-forming composite material.

[0008]

63 The present invention is achieved through the following technical solutions:

[0009]

67 A method for preparing a gas-permeable fiber-forming composite material, comprising the following specific steps:

[0010]

72 S1. Add N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane to the mixed solution of diethyl ether and toluene to form a 0.1 g/mL solution of silane coupling agent, and pour it into a flask;

[0011]

77 S2. Add nano- SiO_2 powder to the silane coupling agent solution obtained in S2, place the flask in the electric heating mantle and heat it until the solution boils and react at a constant temperature for 3 hours, then stop heating;

[0012]

83 The SiO₂ solution modified by the coupling agent is vacuum filtered, dried, ground and passed through a 200-mesh sieve to obtain an organically modified SiO₂ powder;

[0013]

88 S3. The organically modified SiO₂ powder obtained by weighing S2 is dissolved in ethylene glycol solution, the mass fraction is 15%, and the modified SiO₂ organic solution is obtained after ultrasonic dispersion;

[0014]

93 S4. Weigh the modified SiO₂ organic solution obtained by dissolving polyethylene terephthalate in S3, and pour the configured solution into the hydrothermal reaction kettle;

[0015]

98 After the reaction is finished, take the precipitate, wash and dry it, and then pulverize it through a 200-mesh sieve to obtain a composite material powder;

[0016]

103 S5, dissolving the composite material powder obtained in S4 in a mixed solution of dichloromethane and trifluoroacetic acid to configure a spinning solution, the solid-to-liquid ratio is 1:10, and magnetically stirred for 30-60 minutes;

[0017]

109 The spinning solution was poured into a syringe for electrospinning.

[0018]

113 Further, the volume ratio of ether to toluene in the mixed solution of ether and toluene in S1 is 1:1.

[0019]

117 Further, the drying temperature in S2 is 105° C., and the drying time is 3 hours.

[0020]

121 Further, the ultrasonic dispersion time in S3 is 20 min-40 min, and the ultrasonic power is 220w.

[0021]

¹²⁵ Further, the mass fraction of polyethylene terephthalate in the polyethylene terephthalate solution in S4 is 3%.

[0022]

¹²⁹ Further, the reaction pressure in the hydrothermal reactor described in S4 is 0.2-0.4 MPa, the reaction temperature is 240-290° C., and the reaction time is 4-6 hours.

[0023]

¹³⁴ Further, the volume ratio of dichloromethane and trifluoroacetic acid in the mixed solution of dichloromethane and trifluoroacetic acid in S5 is 1:1.

[0024]

¹³⁹ Further, in the electrospinning described in S5, the advancing speed of the injector is set to 0.001 m/s, the distance between the spinning hole and the receiving plate is 18 cm, and the spinning voltage is 20 kV.

[0025]

¹⁴⁴ The present invention has the following beneficial effects:

[0026]

¹⁴⁸ The present invention modifies SiO₂ through N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane, enhances the dispersion ability of SiO₂, and simultaneously selects organically modified SiO₂ and polyethylene terephthalate to generate Inorganic/organic composite materials, electrospinning composite materials, because nano-SiO₂ will increase melt viscosity and reduce molecular weight, which is beneficial to melt spinning and processing stretching, and synthesize a fiber-forming composite material with air permeability.

[0027]

¹⁵⁷ Of course, any product implementing the present invention does not necessarily need to achieve all the above-mentioned advantages at the same time.

[0028]

¹⁶² Detailed ways

[0029]

166 The technical solutions in the embodiments of the present invention are clearly and completely described. Obviously, the described embodiments are only some embodiments of the present invention, not all embodiments.

169 Based on the embodiments of the present invention, all other embodiments obtained by persons of ordinary skill in the art without creative efforts fall within the protection scope of the present invention.

[0030]

174 Example 1

[0031]

178 S1. Add N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane to the mixed solution of diethyl ether and toluene to form a 0.1g/mL solution of silane coupling agent, pour it into a flask, wherein diethyl ether and toluene The volume ratio of toluene is 1:1;

[0032]

184 S2. Add nano-SiO₂ powder to the silane coupling agent solution obtained in S2, place the flask in the electric heating mantle and heat it until the solution boils and react at a constant temperature for 3 hours, then stop heating;

[0033]

190 Vacuum filter the SiO₂ solution modified by the coupling agent, place it in an oven at 105° C for 3 hours, and then grind it through a 200-mesh sieve to obtain organically modified SiO₂ powder;

[0034]

195 S3. The organically modified SiO₂ powder obtained by weighing S2 was dissolved in an ethylene glycol solution with a mass fraction of 15%, placed in an ultrasonic oscillator for ultrasonic dispersion for 20 minutes, and the ultrasonic power was 220w, to obtain a modified SiO₂ Organic solution;

[0035]

201 S4. Weigh the modified SiO₂ organic solution obtained by dissolving polyethylene terephthalate in S3, wherein the mass fraction of polyethylene terephthalate is 3%, and pour the configured solution into the hydrothermal reaction In the kettle, set the reaction pressure to 0.2 MPa, the reaction temperature to 240° C, and the reaction time to 4h;

[0036]

208 After the reaction, the precipitate was washed 3 times with deionized water, dried at 80° C, and crushed through a 200-mesh sieve to obtain a composite material powder;

[0037]

213 S5, dissolving the composite material powder obtained in S4 in a mixed solution of dichloromethane and trifluoroacetic acid to configure a spinning solution, the solid-to-liquid ratio is 1:10, and magnetically stirred for 30 minutes, wherein the dichloromethane and trifluoroacetic acid The volume ratio is 1:1;

[0038]

219 The spinning solution was poured into a syringe for electrospinning, wherein the advancing speed of the syringe was 0.001 m/s, the distance between the spinning hole and the receiving plate was 18 cm, and the spinning voltage was 20 kV.

[0039]

225 Example 2

[0040]

229 S1. Add N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane to the mixed solution of diethyl ether and toluene to form a 0.1g/mL solution of silane coupling agent, pour it into a flask, wherein diethyl ether and The volume ratio of toluene is 1:1;

[0041]

235 S2. Add nano-SiO₂ powder to the silane coupling agent solution obtained in S2, place the flask in the electric heating mantle and heat it until the solution boils and react at a constant temperature for 3 hours, then stop heating;

[0042]

241 Vacuum filter the SiO₂ solution modified by the coupling agent, place it in an oven at 105° C for 3 hours, and then grind it through a 200-mesh sieve to obtain organically modified SiO₂ powder;

[0043]

246 S3. The organically modified SiO₂ powder obtained by weighing S2 was dissolved in an ethylene glycol solution with a mass fraction of 15%, placed in an ultrasonic oscillator for ultrasonic dispersion for 40

minutes, and the ultrasonic power was 220w, to obtain a modified SiO₂ Organic solution;

[0044]

²⁵² S4. Weigh the modified SiO₂ organic solution obtained by dissolving polyethylene terephthalate in S3, wherein the mass fraction of polyethylene terephthalate is 3%, and pour the configured solution into the hydrothermal reaction In the kettle, set the reaction pressure to 0.4 MPa, the reaction temperature to 290° C, and the reaction time to 6h;

[0045]

²⁵⁹ After the reaction, the precipitate was washed with deionized water for 5 times, dried at 80° C and crushed through a 200-mesh sieve to obtain a composite material powder;

[0046]

²⁶⁴ S5, dissolving the composite material powder obtained in S4 in a mixed solution of dichloromethane and trifluoroacetic acid to prepare a spinning solution, the solid-to-liquid ratio is 1:10, and magnetically stirred for 30-60 min, wherein dichloromethane and trifluoroacetic acid The volume ratio of acetic acid is 1:1;

[0047]

²⁷⁰ The spinning solution was poured into a syringe for electrospinning, wherein the advancing speed of the syringe was 0.001 m/s, the distance between the spinning hole and the receiving plate was 18 cm, and the spinning voltage was 20 kV.

[0048]

²⁷⁶ Example 3

[0049]

²⁸⁰ S1. Add N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane to the mixed solution of diethyl ether and toluene to form a 0.1g/mL solution of silane coupling agent, pour it into a flask, wherein diethyl ether and The volume ratio of toluene is 1:1;

[0050]

²⁸⁶ S2. Add nano-SiO₂ powder to the silane coupling agent solution obtained in S2, place the flask in the electric heating mantle and heat it until the solution boils and react at a constant temperature for 3 hours, then stop heating;

[0051]

292 Vacuum filter the SiO₂ solution modified by the coupling agent, place it in an oven at 105° C for 3 hours, and then grind it through a 200-mesh sieve to obtain organically modified SiO₂ powder;

[0052]

297 S3. The organically modified SiO₂ powder obtained by weighing S2 was dissolved in an ethylene glycol solution with a mass fraction of 15%, placed in an ultrasonic oscillator for ultrasonic dispersion for 30 minutes, and the ultrasonic power was 220w, to obtain a modified SiO₂ Organic solution;

[0053]

303 S4. Weigh the modified SiO₂ organic solution obtained by dissolving polyethylene terephthalate in S3, wherein the mass fraction of polyethylene terephthalate is 3%, and pour the configured solution into the hydrothermal reaction In the kettle, set the reaction pressure to 0.3 MPa, the reaction temperature to 270° C, and the reaction time to 5h;

[0054]

310 After the reaction, the precipitate was washed 4 times with deionized water, dried at 80° C and crushed through a 200-mesh sieve to obtain a composite material powder;

[0055]

315 S5, dissolving the composite material powder obtained in S4 in a mixed solution of dichloromethane and trifluoroacetic acid to prepare a spinning solution, the solid-to-liquid ratio is 1:10, and magnetically stirred for 30-60 min, wherein dichloromethane and trifluoroacetic acid The volume ratio of acetic acid is 1:1;

[0056]

321 The spinning solution was poured into a syringe for electrospinning, wherein the advancing speed of the syringe was 0.001 m/s, the distance between the spinning hole and the receiving plate was 18 cm, and the spinning voltage was 20 kV.

[0057]

327 The present invention modifies SiO₂ through N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane, enhances the dispersion ability of SiO₂, and simultaneously selects organically modified SiO₂ and polyethylene terephthalate to generate Inorganic/organic composite materials, electrospinning composite materials, because nano-SiO₂ will increase the melt viscosity and reduce the molecular weight, which is beneficial to melt spinning and processing stretching.

[0058]

335 The above content is only an example and description of the present invention. Those skilled in the art will make various modifications or supplements to the described specific embodiments or replace them in similar ways, as long as they do not deviate from the invention or exceed the rights of the present invention. The scope defined in the claims should all belong to the protection scope of the present invention.

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CLAIMS CN106400171A

1.

13 A method for preparing a breathable fiber-forming composite material is characterized in that it comprises the following specific steps:

15 S1. Add N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane to the mixed solution of diethyl ether and toluene to form a 0.1 g/mL solution of silane coupling agent, and pour it into a flask;

17 S2. Add nano-SiO₂ powder to the silane coupling agent solution obtained in S2, place the flask in the electric heating mantle and heat it until the solution boils and react at a constant temperature for 3 hours, then stop heating;

20 The SiO₂ solution modified by the coupling agent is vacuum filtered, dried, ground and passed through a 200-mesh sieve to obtain an organically modified SiO₂ powder;

22 S3. The organically modified SiO₂ powder obtained by weighing S2 is dissolved in ethylene glycol solution, the mass fraction is 15%, and the modified SiO₂ organic solution is obtained after ultrasonic dispersion;

24 S4. Weigh the modified SiO₂ organic solution obtained by dissolving polyethylene terephthalate in S3, and pour the configured solution into the hydrothermal reaction kettle;

26 After the reaction is finished, take the precipitate, wash and dry it, and then pulverize it through a 200-mesh sieve to obtain a composite material powder;

28 S5, dissolving the composite material powder obtained in S4 in a mixed solution of dichloromethane and trifluoroacetic acid to configure a spinning solution, the solid-to-liquid ratio is 1:10, and magnetically stirred for 30-60 minutes;

31 The spinning solution was poured into a syringe for electrospinning.

2.

35 A method for preparing a gas-permeable fiber-forming composite material according to claim 1, wherein the volume ratio of ether to toluene in the mixed solution of ether and toluene in S1 is 1:1.

3.

40 A method for preparing a breathable fiber-forming composite material according to claim 1, characterized in that: the drying temperature in S2 is 105° C., and the drying time is 3 hours.

4.

45 The preparation method of a fiber-forming composite material with air permeability according to claim 1, characterized in that: the ultrasonic dispersion time in S3 is 20 min-40 min, and the ultrasonic power is 220w.

5.

50 A kind of preparation method with gas-permeable fiber-forming composite material according to claim 1, characterized in that: the polyethylene terephthalate mass fraction in the polyethylene terephthalate solution described in S4 3%.

6.

56 A method for preparing a fiber-forming composite material with air permeability according to claim 1, characterized in that: the reaction pressure in the hydrothermal reactor in S4 is 0.2-0.4 MPa, the reaction temperature is 240-290° C, and the reaction The time is 4-6h.

7.

62 A kind of preparation method with air permeability fiber-forming composite material according to claim 1, is characterized in that: the volume ratio of dichloromethane and trifluoroacetic acid in the mixed solution of dichloromethane and trifluoroacetic acid described in S5 is 1:1.

8.

68 A method for preparing a breathable fiber-forming composite material according to claim 1, characterized in that: in the electrospinning described in S5, the advancing speed of the syringe is set to 0.001 m/s, and the distance between the spinning hole and the receiving plate is The distance was 18 cm and the spinning voltage was 20 kV.

**Espacenet****Bibliographic data: JP2006225573 (A) — 2006-08-31**

COVERING MATERIAL OF STEEL STRUCTURE

Inventor(s): BABA TAKASHI; YAMAMOTO MASAHIRO ± (BABA TAKASHI, ; YAMAMOTO MASAHIRO)

Applicant(s): NIPPON STEEL CORP ± (NIPPON STEEL CORP)

Classification: - **international:** *B32B15/09; B32B27/36; C09J121/00; C09J133/00; C09J7/02; C23F11/00*
- **cooperative:**

Application number: JP20050043440 20050221 [Global Dossier](#)

Priority number(s): JP20050043440 20050221

Abstract of JP2006225573 (A)

PROBLEM TO BE SOLVED: To provide a covering material of a steel structure fabricated with materials composed mainly of steel. ;SOLUTION: This covering material of the steel structure is obtained by laminating an adhesive layer comprising an adhesive rubber or an acrylic adhesive onto a surface of a resin sheet mainly comprising polyethylene terephthalate or its derivative to be in contact with a steel material. In an embodiment of the covering material of the steel structure, the resin sheet used for the covering material is obtained by laminating a resin excelling in at least either of adhesivity and weatherability on at least one of surfaces thereof. Further, in another embodiment of the covering material of the steel structure, one or more selected from a UV absorber, an antioxidant and a resin excelling in at least either of adhesivity and weatherability is(are) added to the resin of the resin sheet used for the covering material. ;COPYRIGHT: (C)2006,JPO&NCIPI

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DESCRIPTION JP2006225573A

10 Coating material for steel structures

[0001]

14 TECHNICAL FIELD The present invention relates to a coating material for structures installed outdoors composed of steel-based materials.

[0002]

19 Steel structures installed outdoors, such as distribution boxes made of steel plates, steel towers, and steel bridges, are generally treated with painting, plating, thermal spraying, etc. to prevent corrosion of steel materials. However, after long-term use, the coating film peels off and the anti-corrosion layer formed by zinc or zinc alloy plating on the surface of the steel is worn away, making the steel surface susceptible to corrosion. Conventionally, as a method of on-site anti-corrosion treatment or repair of anti-corrosion coatings of steel structures, physical means such as blasting and grinders are used to remove surface oxide coatings or corrosion products, or anti-corrosion coatings. It was customary to apply paint containing pigments.

[0003]

31 However, repairing with this paint has little anti-corrosion effect, and depending on the location, such as the top of the steel tower, it is necessary to cover it with a sheet to prevent the paint from scattering around. cost.

34 As a method for solving such a problem, various anti-corrosion methods using tapes with excellent workability or repair methods for anti-corrosion films have been developed. For example, Japanese Patent Application Laid-Open Nos. 5-60290 (Patent Document 1), 8-20751 (Patent Document 2), and 10-337804 (Patent Document 3) have been proposed.

[0004]

41 —
42 —
43 —

[0005]

47 However, these methods use nonwoven fabrics for the top layer coating or coating after application, or use porous substrates as a result for coating formation.
49 Therefore, these films have a low function as a barrier against corrosive factors such as water and oxygen.
51 Further, as described above, in the on-site anticorrosion work of steel structures or the repair of anticorrosion coatings, work that uses liquids, such as painting, poses a problem in construction.

[0006]

57 Therefore, even if the workability of the work to attach the anti-corrosion film is improved as in these methods, there are problems such as painting on the film, oxide film on the surface of the steel structure, and deterioration of the anti-corrosion film on the surface of the structure. There is no change in the difficulty of directly adhering a rust preventive (chemical conversion treatment) or adhering it in a form mixed with paint (primer coating) after removing corrosion products.
63 It is well known that even if the metal is directly coated without chemical conversion treatment, primer coating, or the like, the coating film peels off easily.
65 Therefore, these anti-corrosion work and repair methods have limitations in anti-corrosion performance after construction.

[0007]

70 Therefore, in order to solve the above-mentioned problems, the present invention focuses on the function as a barrier against corrosive factors and chemical conversion treatment on the surface of steel structures, and aims to provide a new coating material for steel structures. do.

[0008]

76 In the present invention, attention is paid to oxygen, which is one of the corrosion factors.
77 By using a resin mainly composed of polyethylene terephthalate resin or a derivative thereof, which has low oxygen permeability, it is possible to remarkably improve the anti-corrosion ability of the coating film as a barrier.

80 By subjecting this polyethylene terephthalate resin to an adhesiveness improvement treatment and a weather resistance improvement treatment, and by incorporating an element or compound that has a function of preventing corrosion of steel or zinc-based plating in the adhesive layer of the coating material, The inventors have found that the same effect as primer coating is exerted on the surface from which the oxide film of a steel structure has been removed, the deteriorated anticorrosion film, and the surface after removal of corrosion products, and have completed the present invention.

[0009]

90 That is, the first aspect of the present invention is characterized in that an adhesive layer containing an adhesive rubber or an acrylic adhesive is laminated on a surface of a resin sheet containing polyethylene terephthalate or a derivative thereof as a main component, which is to be in contact with a steel material. It is a coating material for steel structures.

94 Second, the resin sheet used as the coating material is a coating of the steel structure according to the first above, in which a resin having at least one of excellent adhesion and weather resistance is laminated on at least one surface. material.

[0010]

100 Third, one or more selected from ultraviolet absorbers, antioxidants, and resins having at least one of excellent adhesion and weather resistance are added to the resin of the resin sheet used for the coating material. A coating material for a steel structure according to 1 or 2.

103 Fourthly, any one of the above first to thirds, wherein the resin sheet used as the coating material has at least one surface thereof subjected to any one of corona discharge treatment, plasma treatment, ozone treatment and ultraviolet treatment. It is a coating material for steel structures according to the above.

107 Fifth, the coating material for steel structures according to the above first, wherein the adhesive layer used in the coating material contains an element or compound having a metal anticorrosive action.

[0011]

113 By using the coating material for steel structures of the present invention, repair of outdoor steel structures and on-site anti-corrosion coating can be easily carried out at low cost.

115 In addition, the applied film functions as a corrosion-preventing film for structures over a long period of time, especially by cutting off the supply of oxygen, in addition to the corrosion-preventing function of steel materials.

118 In addition, according to the anticorrosion work using the coating material of the present invention, it is possible to eliminate the work of handling liquids such as painting in the on-site anticorrosion film formation work and repair work of steel structures.

121 Therefore, the work can be easily performed with good workability.

[0012]

125 The present invention will be described in detail below.

126 The present invention is characterized in that a polyethylene terephthalate-based resin sheet is subjected, if necessary, to a durability-enhancing treatment and an easy-adhesion treatment, and then a pressure-sensitive adhesive layer containing a metal-corrosion-preventing compound is added to the surface of the sheet. It is a coating material for steel structures.

[0013]

134 The resin sheet used in the present invention is a resin sheet mainly composed of polyethylene terephthalate resin or its derivative.

136 Specifically, pure polyethylene terephthalate (hereinafter referred to as PET) resin, or a PET derivative obtained by copolymerizing PET with 1,4-cyclohexanedimethanol, isophthalic acid, or the like and adjusting the crystallization rate, polyethylene naphthalate, Polybutyterephthalate, etc., or copolymers or polymer alloys containing these resins in an amount of 50% or more of the organic substances in the resin sheet.

[0014]

144 The sheet may be in an amorphous state, a stretched state, or a crystallized state.

145 However, when used in a high-temperature environment, the amorphous PET sheet has a problem in that stress due to crystallization occurs, and the film tends to peel off.

147 Therefore, it is necessary to suppress the crystallization, and for example, it is necessary to devise a method such as blending a 1,4-cyclohexanedimethanol copolymerized PET resin (PET-G) that is difficult to crystallize.

[0015]

153 The thickness of the PET-based resin sheet should be 0.1 mm or more, preferably 0.2 mm or more, in order to function as a barrier against corrosive factors.

155 As for the upper limit, it depends on the shape of the place where it is attached, but from the viewpoint of workability, it is 2 mm or less when attaching to a flat surface. Generally, 1 mm is the upper limit.

158 As for the width of the resin sheet, a wider one is desirable in order to cover a wide area of the steel material without gaps.

160 However, in practice, the limit is about 2 m at most due to manufacturing problems.

161 Further, in consideration of workability, it may be desirable to have a width narrower than that.

163 As long as these basic conditions are satisfied, there is no problem in using a recycled PET

bottle or the like as the resin.

[0016]

168 As the adhesive, natural rubber, synthetic rubber such as styrene-butadiene rubber and butyl rubber, and acrylic adhesive can be used.

170 The type of adhesive is not particularly limited, but the required properties are strong adhesive force and excellent weather resistance.

172 In addition, since it is necessary to absorb the difference in coefficient of thermal expansion between the steel material and the PET resin sheet, flexibility is also required.

174 As a method for increasing the flexibility of the pressure-sensitive adhesive layer, a multi-layer structure may be employed, for example, by applying pressure-sensitive adhesive to both sides of a flexible sheet of rubber or the like.

[0017]

180 As for the thickness of the pressure-sensitive adhesive layer, an extremely thin one is not desirable, considering that flexibility is required as described above.

182 Also, a certain thickness is required in order to allow the pressure-sensitive adhesive layer to contain a compound having an antirust function, as will be described later.

184 Moreover, if the thickness is extremely thick, the internal stress of the adhesive layer itself may become a problem, so the range of 0.1 mm to 1.5 mm is desirable.

186 The properties required of the covering material differ depending on the form of the covered portion of the structure, the work procedure, and the like.

188 When wrapping around a thin steel pipe, or when the ends of the sheet are overlapped and applied over a large area, it is desirable to make it easier to apply or to reduce the gap generated in the overlapped part, so the overall thickness should be reduced. is desirable in some cases, and settings need to be made accordingly.

[0018]

195 Pure PET resin is basically poor in weatherability and adhesiveness.

196 Therefore, it needs to be improved as a long-term anti-corrosion coating.

197 As a method for improving weather resistance, co-extrusion of resin with excellent weather resistance, resin coating, etc. to form an ultraviolet absorbing layer on the surface of the resin sheet. There is a method of adding a resin or the like to PET to improve the weather resistance of the PET resin sheet itself.

[0019]

204 Methods for improving adhesiveness include co-extrusion of a resin with excellent adhesiveness, a method of forming a layer with excellent adhesiveness on the surface of a

resin sheet by resin coating, etc., and adding a resin with excellent adhesiveness to PET. There is a method of improving the adhesiveness of the PET resin sheet itself by using a method of improving the adhesiveness of the PET resin sheet itself, and a method of modifying the PET resin surface by corona discharge treatment, plasma treatment, or the like to improve the adhesiveness.

211 It should be noted that the surface to which the pressure-sensitive adhesive is attached needs only adhesiveness, but the opposite surface may require not only weather resistance but also adhesiveness.

214 This is because it is expected that the repair sheets will be applied while being partially overlapped in the covering operation.

216 In addition, if necessary, after coating the surface of the steel material with this coating material, it is possible to attach a stainless steel foil, titanium foil, etc. with an adhesive sheet or the like to impart even higher weather resistance and corrosion resistance.

[0020]

222 As the antioxidant, known antioxidants such as thioether antioxidants, phenol antioxidants, and carbon black can be used.

224 As the UV absorber, known UV absorbers such as benzotriazole, benzophenone, hindered amine and the like can be used as organic UV absorbers, and titanium oxide and the like can be used as inorganic UV absorbers.

227 These additives are blended in a content of 0.1% by mass to 3.0% by mass at maximum, depending on the type.

229 If it is less than 0.1% by mass, the effect of addition is insufficient, and if it exceeds 3.0% by mass, the effect is saturated, and not only does the cost increase, but the mechanical properties of the resin sheet may be adversely affected. This is because

[0021]

235 One of the simplest ways to improve the adhesiveness and weatherability of both sides of the sheet is to form polymer layers of appropriate thickness on both sides of the resin sheet by co-extrusion, which satisfies both.

238 For example, polyarylate resin (polyester resin composed of aromatic dicarboxylic acid and bisphenols) is very good as an ultraviolet absorbing layer and as an adhesion improving layer.

241 In addition to these, various additives can be used in the PET-based resin sheet.

242 Examples of the colorant include organic azo pigments such as benzimidazolone and diarylide, polycyclic pigments such as phthalocyanine and dioxazine, and inorganic titanium oxide, iron oxide, and cobalt blue pigments. is mentioned.

245 In addition, it is also possible to enhance functionality by adding flame retardants such as phosphoric acid ester amide-based and silicone-based flame retardants.

[0022]

- 250 Compounds added to the adhesive layer include chromates such as strontium chromate, which are generally used as rust preventive pigments, phosphate-based rust preventive pigments such as aluminum phosphate and zinc phosphate, and aluminum molybdate, , molybdic acid-based rust preventive pigments such as barium molybdate, tannates, silane coupling agents, calcium silicate, ferrosilicon and other fine powders.
- 255 It is important that the amount added does not affect the adhesive strength of the adhesive, and the volume fraction is desirably 10% or less.

[0023]

- 260 In carrying out coating work for steel structures, first, oxide films, deteriorated anticorrosion films, and corrosion products such as rust on the surface of the target steel structure are removed by a general method such as sandblasting, and the steel, Exposing the surface of plating, healthy paint film, etc.
- 264 After that, the anticorrosive coating sheet of the present invention is applied.
- 265 In this case, before attaching the anti-corrosion coating sheet, as a chemical conversion treatment, the above-mentioned rust-preventive pigment or the like is directly applied as a chemical conversion treatment, or mixed in the paint and applied to improve the durability after coating. is possible.

[0024]

- 272 However, as mentioned above, it is difficult to use liquids at the installation site of steel structures, especially in situations such as steel tower cladding. An anti-corrosion coating sheet added to the adhesive layer can be used.
- 275 Moreover, even if there are no major problems with the use of liquids, it goes without saying that anti-corrosion work using this coating material is advantageous in terms of work cost, required time, and safety and health.
- 278 As described above, this anticorrosion coating material can also be used as a repair material for a deteriorated anticorrosion coating.

[0025]

- 283 EXAMPLES The present invention will be described in detail below with reference to examples.
- 285 (Example 1) An amorphous PET resin (A-PET) sheet having a total thickness of 1 mm having a polyarylate resin layer having a thickness of 100 μm on both sides, and a polyolefin foam sheet having a thickness of 1 mm on both sides were coated with butyl acrylate and hydroxyethyl. A three-layered pressure-sensitive adhesive sheet to which an acrylic pressure-sensitive adhesive containing methacrylate as a main component was adhered was adhered

to form an anti-corrosion coating sheet.

291 As the polyarylate resin, poly 4,4 ' -isopropylidenediphenylene terephthalate/isophthalate copolymer (trade name: U Polymer, manufactured by Unitika Ltd.) was used.

[0026]

296 In addition, a 1 mm thick A-PET resin sheet containing 0.2% by mass of a phenolic antioxidant and 0.2% by mass of a benzotriazole ultraviolet absorber, and a 1 mm thick A-PET resin sheet containing no additives. - Both surfaces of the PET resin sheet were subjected to corona discharge treatment, and then the above-mentioned 1 mm thick three-layer pressure-sensitive adhesive sheets were attached to each of the PET resin sheets to obtain anti-corrosion coating sheets.

302 As a comparative example, only one side of a 1 mm-thick polyethylene sheet containing carbon black as a stabilizer was subjected to corona discharge treatment. made.

[0027]

307 The performance of the above four coating materials was evaluated by the following methods.
308 (Adhesive strength) According to JIS Z 0237, the peel strength in the direction of 180 ° was measured.

310 The adhesive strength is the adhesive strength to the steel plate (one week after application, one week after application, and 30 days after immersion in hot water at 50 ° C.), and the adhesive strength of the same cover sheet to the cover sheet attached to the steel plate. , were investigated.

314 (Weather resistance) After 1000 hours of sunshine weather meter test (JIS K 5400), the appearance after the test was visually evaluated.

316 Table 1 shows the evaluation results.

[0029]

320 Inventive Example No. Both test results of 1 and 2 are good.

321 Inventive Example No. No. 3 is a PET resin sheet manufactured with 100% recycled resin. Compared to 1, 2, 4, there is no inferior place.

323 On the other hand, Comparative Example No. In No. 5, the adhesiveness is low when the covering sheet is overlaid, and it is expected that problems will occur when the sheet edges are overlaid in actual construction.

326 In addition, in the weather resistance test, invention example No. The yellowing seen in 1 is due to the structural change of the polyarylate resin due to ultraviolet rays, and does not indicate deterioration of the resin.

329 On the other hand, Example No. of the present invention. The rough surface of the PET sheet seen in 4 indicates that the resin has deteriorated mainly due to ultraviolet rays.

331 Also, Comparative Example No. In No. 5, the adhesive strength decreased significantly after

immersion in hot water, and it is highly likely that corrosion of the steel sheet surface progressed due to permeation of oxygen.

[0030]

337 (Example 2) A butyl rubber adhesive with a thickness of 1 mm was adhered to a biaxially stretched PET resin sheet with a total thickness of 0.3 mm having polyarylate resin layers with a thickness of 30 μ m on both sides to form an anti-corrosion coating sheet. .

340 Poly 4,4'-isopropylidene diphenylene terephthalate/isophthalate copolymer (trade name: U Polymer, manufactured by Unitika Ltd.) was used as the polyarylate resin.

342 The pressure-sensitive adhesive used was obtained by kneading fine powder of a 1:1 mixture of tannate and chromate at a volume fraction of 0.5%.

[0031]

347 Further, after subjecting a biaxially stretched PET resin sheet having a thickness of 0.3 mm containing 0.2% by mass of a phenolic antioxidant and 0.2% by mass of a benzotriazole-based ultraviolet absorbent to a corona discharge treatment, the above-mentioned A 1 mm-thick butyl rubber adhesive kneaded with the fine powder of was applied to form an anti-corrosion coating sheet.

352 In addition, a biaxially oriented PET resin sheet with a thickness of 0.3 mm containing no additives was subjected to corona discharge treatment on both sides to improve adhesion, and then a butyl rubber adhesive with a thickness of 1 mm containing no pigment was applied. It was used as an anti-corrosion coating sheet.

[0032]

359 As a comparative example, one side of a polyethylene sheet containing carbon black as a stabilizer was subjected to corona discharge treatment, and a 1 mm-thick butyl rubber adhesive containing no pigment was adhered to prepare a corrosion-resistant coated sheet.

362 In the test, hot-rolled steel sheets of 150 mm x 70 mm x 5 mm were subjected to shot blasting to expose the surface of the steel, and then the four types of anti-corrosion coating sheets described above were attached and evaluated by the following tests.

365 Regarding the anti-corrosion test, after affixing a coating sheet to half of the surface of the steel plate, the sheet was overlapped by about 10 mm and then affixed to the other half of the surface.

[0033]

371 (Adhesive strength) According to JIS Z 0237, the peel strength in the direction of 180 ° was measured.

373 As for the adhesive strength, the adhesive strength to the steel plate (one week after

application, one week after application, and 30 days after immersion in hot water at 50 ° C.) was investigated.

376 (Corrosion resistance) After sealing the back surface and edges of the steel plate (including gaps at the edges of the overlapped portion of the anticorrosion sheet) with resin, a salt water (5% NaCl, 35 ° C) spray test was conducted for 2000 hours.

379 After that, the anticorrosion sheet was peeled off, and the portion where the gap was likely to occur in the overlapped portion of the anticorrosion sheet was observed.

381 Table 2 shows the results.

[0035]

385 Inventive Example No. Both test results of 6 and 7 are good.

386 On the other hand, Example No. of the present invention. In No. 8, red rust is generated in dots in the gaps generated in the overlapping portions.

388 Inventive Example No. 1 was used because no pigment having a metal anticorrosion function was added to the adhesive layer. Compared to 6 and 7, it is clear that the anti-corrosion ability is low, and the adhesion after immersion in hot water is also slightly reduced.

391 Comparative example no. In addition to the absence of a rust preventive agent, sample No. 9 of the present invention had both a decrease in tensile strength and generation of rust because the resin sheet was made of polyethylene having a high permeability to oxygen. Larger than 4, 6-7.

[0036]

398 (Example 3) A 200 mm x 300 mm x 2 mm galvanized steel sheet was coated with a commercially available outdoor acrylic paint to a thickness of 30 μm.

400 A linear scratch reaching the iron surface was made on this test piece with a cutter knife, and then a salt water (5% NaCl, 35 ° C.) spray test was performed for 30 hours.

402 After sandblasting to remove the corrosion products and deteriorated paint film on the scratched part, the four types of anti-corrosion sheets used in Example 2 shown in Table 3 were attached to the entire surface of the test piece, and the back surface and end surfaces were sealed.

406 After further subjecting this test piece to a salt spray test for 2000 hours, the anticorrosion sheet was peeled off and the scratched portion and its surroundings were observed.

408 Table 3 shows the results.

[0038]

412 Inventive Example No. Both Nos. 10 and 11 show a good effect of inhibiting corrosion after repair, and it can be seen that the present invention is useful as a repair material for anticorrosion coatings.

415 Inventive Example No. In No. 12, the acrylic paint peeled off together with the adhesive

material in dots, possibly causing slight corrosion under the paint film. Compared to No. 10 and No. 11, the corrosion inhibitory effect is low.

418 Comparative example no. No. 13 is a PE sheet that easily permeates oxygen, and it can be seen that the corrosion inhibiting effect is clearly lower than that of PET.

[0039]

423 (Example 4) After shot blasting a hot-rolled plated steel sheet of 150 mm x 70 mm x 5 mm, the treatment shown in Table 4 was performed on the entire surface of the test piece.

425 Furthermore, the anti-corrosion sheet used in Example 2 was attached, and the back surface and end surfaces were sealed.

427 A cut with a length of 50 mm reaching the iron surface was made in the anticorrosion coating layer of this test piece using a cutter knife, and then a salt spray test was performed for 2000 hours.

430 After the test, the anticorrosive sheet was peeled off and changes around the scratch were observed.

432 Table 4 shows the results.

[0041]

436 Inventive Example No. All of No. 14, No. 15 and No. 16 are excellent in the effect of suppressing corrosion of the scratched portion. Compared with No. 17, the effect of the antirust pigment is clear.

439 Among these, the present invention sample No. 14 is the invention example No. 14; The reason why the antirust effect is higher than that of Nos. 15 and 16 is due to the difference in the absolute amount of the antirust pigment.

442 Inventive Example No. When the rust-preventive pigment is attached directly to the surface of the steel material as in No. 15, the adhesive strength of the adhesive is expected to be adversely affected, so the amount is naturally limited.

445 Inventive Example No. As in 16, when the rust preventive pigment is contained in the resin and applied, it is possible to increase the amount of the rust preventive pigment.

447 Water or a solvent with a high boiling point requires heating to remove the solvent, and when a solvent with a low boiling point is used, condensation may occur due to the cooling effect.

449 Moreover, it goes without saying that the release of the organic solvent into the atmosphere poses a problem.

451 On the other hand, when a rust-preventive pigment is added to the adhesive layer, it is possible to add a sufficient amount of the pigment for rust-prevention, and it is clear that the application condition is also advantageous.

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CLAIMS JP2006225573A

1.

13 A coating material for steel structures, comprising an adhesive layer containing an adhesive rubber or an acrylic adhesive layered on a surface of a resin sheet containing polyethylene terephthalate or a derivative thereof as a main component, the surface being in contact with the steel material.

2.

20 The coating material for a steel structure according to claim 1, wherein the resin sheet used as the coating material is formed by laminating a resin excellent in at least one of adhesiveness and weather resistance on at least one surface thereof.

3.

26 1 or 2, wherein one or more selected from ultraviolet absorbers, antioxidants, and resins having at least one of excellent adhesion and weather resistance are added to the resin of the resin sheet used as the coating material. 3. Coating material for steel structure according to 2.

4.

32 The resin sheet according to any one of claims 1 to 3, wherein at least one surface of the resin sheet used as the coating material is subjected to one of corona discharge treatment, plasma treatment, ozone treatment, and ultraviolet treatment. Coating material for steel structures.

5.

38 2. A coating material for a steel structure according to claim 1, wherein the adhesive layer used in said coating material contains an element or compound having a metal anti-corrosion action.



Espacenet

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Transferable wearing-resistant flexible super-hydrophobic film and preparation method thereof

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Abstract of CN106366912 (A)

The invention discloses a transferable wearing-resistant flexible super-hydrophobic film and a preparation method thereof. The preparation method comprises the following steps: by using a two-step coating method, coating the surface of a smooth substrate which is subjected to degreasing and decontamination treatment or is coated with a resin film releasing agent with soft and hard compounded resin, further coating the surface of the half-cured compounded resin with a super-hydrophobic nano coating, performing room-temperature or high-temperature curing, and separating from the substrate, or coating the surface of a base film, and curing, thereby obtaining the transferable wearing-resistant flexible super-hydrophobic film directly. The transferable

wearing-resistant flexible super-hydrophobic film has the advantages of being simple in process, simple and easy to operate, low in cost and the like, and has industrial on-scale production prospects. The transferable wearing-resistant flexible super-hydrophobic film disclosed by the invention is relatively good in wearing resistance, good in resistance on external force such as finger friction and sand paper grinding and good in flexibility, and can be adhered to complex substrate surfaces along with shapes after being cut.



图 1 a

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DESCRIPTION CN106366912A

10 A transferable wear-resistant flexible superhydrophobic film and its preparation method

[0001]

14 technical field

[0002]

18 The invention belongs to the field of coating preparation, in particular to a transferable wear-resistant flexible super-hydrophobic film and a preparation method thereof.

[0003]

23 Background technique

[0004]

27 A superhydrophobic material refers to a surface whose water contact angle is greater than 150° and the rolling angle is less than 10° .

29 Studies have found that superhydrophobic surfaces have excellent properties such as antifouling and self-cleaning, and have great applications in daily life.

31 However, as far as the currently prepared superhydrophobic materials are concerned, their fragile mechanical wear resistance has become the main obstacle for their application in actual life production.

33 In 2015, people began to use organic resins as adhesives to bond the superhydrophobic coating to the substrate and successfully broke through the destructibility of the superhydrophobic coating. However, once this superhydrophobic composite coating with high wear resistance is destroyed It will be difficult to repair, and the residual resin adhesive on the surface of the substrate is also difficult to clean, not only losing the anti-fouling and self-cleaning properties of the surface, but making the surface more likely to be polluted. Therefore, the

development of a transferable wear-resistant flexible superhydrophobic film is one of the very important means to apply superhydrophobic materials in actual life production, and its application prospects will be measurable.

[0005]

44 At present, the methods for preparing superhydrophobic surfaces mainly include sol-gel method, etching method, electrospinning method, template method, self-assembly method, coating method, etc., wherein the coating method is to pour the prepared superhydrophobic coating, spraying, dipping, roller coating and other means to form a super-hydrophobic coating on the surface of the substrate. This method has the characteristics of simple operation, low cost, strong designability, etc., and has broad prospects for large-scale production. Good choice in production.

50 However, on the basis of ensuring its wear resistance, there is no relevant report on obtaining a superhydrophobic film that is convenient, repairable, and easy to remove. The various wear-resistant superhydrophobic materials currently prepared mainly have the following problems: First, to directly construct micro-nano rough structures on the surface of materials with low surface energy (such as rare earth oxides, precious metals, PTFE, etc.) to achieve superhydrophobicity, Although it has good wear resistance, its operation is complicated, the conditions are harsh, the cost is too high, and it is difficult to produce on a large scale, and its practicability is insufficient; second, the superhydrophobic composite coating obtained by the coating method is simple to operate, low cost, high wear resistance, but it is not repairable, it is difficult to remove after damage, it is difficult to replace, and it is easy to cause secondary pollution, which greatly limits its application range. Therefore, how to produce a convenient transferable flexible superhydrophobic film on the basis of keeping the equipment process simple, easy to operate, low cost, and has a certain wear resistance is a key step in expanding the wide application of superhydrophobic coatings. and important ways.

[0006]

65 Contents of the invention

[0007]

69 The purpose of the present invention is to provide a transferable wear-resistant flexible super-hydrophobic coating in order to overcome the above-mentioned existing wear-resistant super-hydrophobic coatings that are not repairable, difficult to remove after damage, difficult to replace, and easy to cause secondary pollution. Hydrophobic film and method for its preparation.

73 The technical equipment and process are simple, easy to operate, low in cost, and easy to industrialized large-scale production, and the obtained film can be cut at will, and can be transplanted on the surface of the substrate with complex shapes, which greatly expands the application of superhydrophobic coatings. scope.

[0008]

79 The technical solution of the present invention is: a transferable wear-resistant flexible super-hydrophobic film,

which is a non-fixed and transferable film-type material formed by compounding primer and topcoat. The resin solution is coated on the surface of the smooth substrate to form a primer, and then the super-hydrophobic nano-coating is coated on the surface of the semi-cured primer, and the material obtained after curing is separated from the substrate; or a soft and hard composite resin solution is used to form a primer on the surface of the base film, and then use a super-hydrophobic nano-coating to form a top coat on the semi-cured primer to directly obtain a transferable wear-resistant flexible super-hydrophobic film compounded with the base film; the soft and hard composite resin solution is obtained by mixing 5 to 40 parts by mass of soft resin and hard resin, and 100 to 500 parts by mass of diluent, and the weight ratio of soft resin to hard resin in the soft and hard composite resin solution is 0.1~10.

[0009]

⁹² The soft resin includes any one or more mixed soft resins of polydimethylsiloxane, polyethylene, polypropylene, ethylene-vinyl acetate copolymer, ethylene-acrylic acid copolymer, and acrylic resin.

[0010]

⁹⁷ The hard resin includes any one of polymethyl methacrylate, epoxy resin, polyvinylidene fluoride, fluorocarbon resin, and rigid polyurethane or mixed hard resins.

[0011]

¹⁰² In the soft and hard composite resin solutions, 0-50 parts by mass of micropowder particles are also contained, and the micropowder includes silicon micropowder, diamond powder, hollow microspheres, PTFE, polypropylene powder, sludge powder, clay powder, kaolin powder, fly ash, talcum powder, glass flakes, glass fibers, ceramic fibers, any one or more, the largest dimension of the size of $10 \sim 100 \mu\text{m}$.

[0012]

¹⁰⁹ The smooth and hard substrate includes one of glass, polished metal, glazed ceramic tile, and polytetrafluoroethylene board, and is used after degreasing and decontamination treatment, or coated with a benign release agent.

[0013]

¹¹⁵ The base film includes any one of polyvinyl chloride, polycarbonate, silicone, fluororesin and polyethylene terephthalate.

[0014]

¹²⁰ The soft and hard composite resin solution also includes 0-5 parts by mass of auxiliary agents, and the auxiliary agents include equal mass proportions of leveling agent, defoamer, dispersant and anti-settling

agent.

[0015]

¹²⁶ The superhydrophobic nano-coating is obtained by directly dispersing hydrophobic nanoparticles in a benign solvent, or adding hydrophilic nanoparticles and a hydrophobic treatment agent to a benign solvent to obtain, and the nanoparticles include silicon dioxide, Any one or more mixtures of zinc oxide, titanium dioxide, and polypropylene, the benign solvent includes one or more of alcohols, ketones, and ethers, and the hydrophobic treatment agent includes alkyl siloxane One or more of alkanes or fluoroalkylsiloxanes, the maximum dimension of the nanoparticles is 5-200nm, and the concentration is 10-40mg/mL.

[0016]

¹³⁵ The transferable wear-resistant flexible superhydrophobic film has the following characteristics:

[0017]

¹³⁹ (1) The static contact angle of water droplets of the transferable wear-resistant flexible super-hydrophobic film is greater than 160° , and the rolling angle is less than 5° ; it has been rubbed by fingers 500 times, washed with tap water at 0.1 MPa pressure for 60 minutes, and 1kg of heavy sea sand with a height of 30cm free falling sand, After sanding 100 times with 300-1200 mesh metallographic sandpaper under 0.1 MPa pressure, the film can still maintain super-hydrophobicity;

[0018]

¹⁴⁷ (2) Placed in the outdoor environment for one year, the appearance and color of the film layer have no obvious changes, and still have good super-hydrophobicity;

[0019]

¹⁵² (3) The elongation rate is more than 200%, and it can still maintain superhydrophobicity in the stretched state or when it returns to the natural state;

[0020]

¹⁵⁷ (4) It can be bent and folded in any shape, and after being bent and folded 1000 times, it can still maintain superhydrophobicity and can be cut in any shape;

[0021]

¹⁶² (5) It can be bonded to any substrate surface by glue or solid glue to obtain a super-hydrophobic surface.

[0022]

166 The preparation method of the transferable wear-resistant flexible superhydrophobic film, the steps are as follows:

[0023]

171 (1) Preparation of primer: dissolve the soft and hard resins in the diluent, ultrasonically, and then mechanically stir until the mixed resin is evenly dispersed in the diluent, then add other components and continue stirring to disperse evenly, and let it stand After degassing, a thin film is formed on the surface of the base film or smooth substrate, and the thickness of the film is controlled to be 0.5 μm to 5 mm;

[0024]

178 (2) Topcoat preparation: apply the super-hydrophobic nano-coating on the surface of the semi-cured primer by spraying, and control the coating thickness to 0.5-5 μm by spraying passes;

[0025]

183 (3) Film curing: After the film coated with primer and topcoat is cured, the transferable wear-resistant flexible super-hydrophobic film can be directly obtained for the base film; Transfer wear-resistant flexible superhydrophobic film.

[0026]

189 Beneficial effect:

[0027]

193 (1) Using smooth substrates such as tempered glass, glazed ceramic tiles, polished metal, PTFE boards after degreasing and decontamination, effectively reducing the bonding force between the resin and the substrate, making the bottom surface of the super-hydrophobic film smooth after curing, easy to release the mold, maintain the integrity of the super-hydrophobic film, and realize the transferability and adhesiveness of the super-hydrophobic film.

[0028]

201 (2) After the soft resin solution is sprayed, a rough flexible film can be formed, which can well bond and protect the superhydrophobic nanoparticles, and improve the wear resistance of the superhydrophobic coating, but the resin itself has poor wear resistance and is easy to Wear-through; the film formed after spraying the hard resin solution has good adhesion to the substrate and good wear resistance, but it is difficult to demould, easy to crack or break, and the adhesion and protection of superhydrophobic nanoparticles are

not enough; Combining soft and hard resins can obtain a super-hydrophobic film with rough surface, good flexibility and good wear resistance.

[0029]

211 (3) The present invention not only can obtain a primer film with rough surface, good flexibility and good wear resistance, but also can reduce the binding force between the primer and the base template through the compounding method of the resin, so as to facilitate demoulding.

[0030]

217 (4) The superhydrophobic nano-coating used in the present invention can be obtained only by adding a benign solvent to ordinary commercially available hydrophobic nanoparticles, or by adding the solvent to the nanoparticles and the hydrophobic treatment agent, without complex chemical modification technology, without adding organic binders, and without adding two-dimensional nanomaterials such as chain nano-silica and carbon nanotubes.

[0031]

225 (5) Adding micropowder particles to the soft and hard composite resin can further improve the film strength, surface roughness and wear resistance, and broaden the scope of use.

[0032]

230 (6) Adding additives can effectively improve the uniformity of the primer film, prevent film damage caused by local unevenness, and improve the service life of the super-hydrophobic film.

[0033]

235 (7) The transferable wear-resistant flexible super-hydrophobic film prepared by the method of the present invention can be cut at will, and pasted on any plane, curved surface or heterogeneous surface by means of glue, which can obtain waterproof, anti-fouling, anti-dust, rain-proof, self-sufficiency Clean, anti-corrosion, anti-mildew, anti-snow, anti-dew, anti-frost, anti-icing and other characteristics, can be used in building exterior walls, heat exchangers, transmission lines, wind turbines, aircraft, automobiles, high-speed rail, radar, electronic products and other fields, the application prospect is broad.

[0034]

244 (8) The transferable wear-resistant flexible superhydrophobic film prepared by the method of the present invention has good wear resistance. After scratching the film with fingers for hundreds of times, it still maintains excellent superhydrophobic properties, and the static contact angle of water droplets is greater than 155° , and the water drop rolling angle is less than 5° .

[0035]

251 (9) It is possible to increase the hardness of the film by reducing the proportion of soft resin to obtain a rigid film, and to obtain a highly transparent super-hydrophobic film by reducing the thickness of the film and the amount of powder added in the primer, or by adding pigments to the primer, to obtain superhydrophobic films of various colors.

[0036]

258 (10) The primer and topcoat solution used in the present invention are simple to prepare, do not require special process treatment, and can be used immediately after mixing. There is no problem of micropowder particle settlement, resin phase separation, etc. in the primer, and there is no nanometer in the topcoat. Problems such as particle flocculation and deposition have improved film formation and film uniformity.

[0037]

265 (11) The transferable wear-resistant flexible superhydrophobic film prepared by the method of the present invention has good weather resistance, and after being placed in the natural environment for one year, the superhydrophobicity, appearance and color of the film layer have no obvious changes.

[0038]

271 (12) Increase the content of fluororesin or micropowder particles in the primer, and then use superhydrophobic inorganic nanoparticles as the topcoat, which can further significantly improve the aging resistance of the film, and can reach the service life of the existing fluororesin for more than 25 years.

[0039]

277 (13) The equipment and process used in the method of the present invention are simple, and the wear-resistant superhydrophobic film can be obtained after the primer and the topcoat are film-formed and dried, and the wear-resistant superhydrophobic film can be obtained without using methods such as pressurization and heating to improve the superhydrophobic nanoparticles and the primer film. Excellent bonding force, no need for pressure scratching and gluing, removing weakly bonded coating particles to enhance wear resistance.

[0040]

286 (14) With a smooth roll-and-roll substrate as a mold, the industrial production of the superhydrophobic film of the present invention can be realized through automatic continuous film formation, drying, demoulding and winding.

[0041]

292 (15) The traditional on-site spraying of super-hydrophobic coatings to obtain super-hydrophobic surface
technology has problems such as coating shelf life, powder flocculation and sedimentation, and resin phase
separation. When spraying, irritating solvents often volatilize, material utilization is low, and film layer
uniformity It's also hard to guarantee.

296 During large-scale construction, the requirements for operators and construction equipment are high, the risk
is high, and the difficulty is relatively large.

298 The super-hydrophobic film proposed by the present invention can be produced in a closed assembly line in
the factory, and the super-hydrophobic surface is obtained by gluing on site, which effectively solves the main
technical problems of spraying super-hydrophobic coatings on site. It is environmentally friendly, has super-
hydrophobic effect, and is wear-resistant. The performance and aging resistance are relatively ideal, and the
overall cost of raw materials, equipment and construction is also significantly reduced, making it suitable for
large-scale applications.

304 (16) The soft and hard resins are directly coated on the surface of the base film to separate and obtain a
transferable flexible super-hydrophobic film, or to obtain a transferable flexible super-hydrophobic film by
direct compounding. This composite transferable flexible super-hydrophobic film Its specific functions, such
as improving its mechanical strength, can be enhanced by selecting base films with different functions.

[0042]

311 Description of drawings:

[0043]

315 Figure 1a.

316 Stereo microscope image of the transferable wear-resistant flexible superhydrophobic film; Figure 1b.

317 Water contact angle of transferable wear-resistant flexible superhydrophobic film;

[0044]

321 Figure 2a.

322 The water contact angle of the transferable wear-resistant flexible superhydrophobic film after finger rubbing
500 times; Fig. 2b.

324 The water contact angle of the transferable wear-resistant flexible superhydrophobic film after being washed
by 0.1 MPa pressure tap water for 60 min.

[0045]

329 Figure 3a.

330 The water contact angle of the transferable wear-resistant flexible superhydrophobic film after being impacted
by 1kg heavy sea sand and 30cm high free fall sand; Figure 3b.

332 The water contact angle of the transferable wear-resistant flexible superhydrophobic film after being polished
100 times by 600-mesh metallographic sandpaper under a pressure of 0.1 MPa.

[0046]

337 Figure 4.

338 Optical photographs and hydrophobicity of the transferable wear-resistant flexible superhydrophobic film
placed outdoors for one year.

[0047]

343 Figure 5a.

344 The physical picture of the transferable wear-resistant flexible superhydrophobic film before stretching and its
superhydrophobicity; Figure 5b.

346 The physical picture of the transferable wear-resistant flexible superhydrophobic film after stretching and its
superhydrophobicity.

[0048]

351 Figure 6.

352 The physical picture of the transferable wear-resistant flexible superhydrophobic film after being bent or
folded at any angle for more than 1000 times and its superhydrophobicity.

[0049]

357 Figure 7a.

358 The transferable wear-resistant flexible superhydrophobic film is cut into various sizes and then bonded to the
glass plate and its superhydrophobicity; Figure 7b.

360 Transferable wear-resistant flexible superhydrophobic film attached to the mobile phone screen and its
superhydrophobicity; Figure 7c.

362 Transferable wear-resistant flexible superhydrophobic film attached to display screen and its
superhydrophobicity.

[0050]

367 Figure 8.

368 Optical photographs of a transferable rigid superhydrophobic film after breaking.

[0051]

372 Figure 9.

373 Optical photographs of transferable transparent superhydrophobic films after stretching and fracture.

[0052]

377 Figure 10.

378 Optical photographs of micropowder-reinforced hard superhydrophobic films after fracture.

[0053]

382 Figure 11.

383 Body micrograph of a soft superhydrophobic film after losing its superhydrophobicity by finger rubbing.

[0054]

387 Figure 12.

388 Optical photographs of micropowder-reinforced soft superhydrophobic films damaged by finger rubbing.

[0055]

392 Detailed ways:

[0056]

396 A transferable wear-resistant flexible super-hydrophobic film is a non-fixed and transferable film-like material with good wear resistance, durability and elasticity, which can be bent and folded, and can be cut to any shape as required, and glued Connected to the surface of substrates of various materials and shapes to obtain super-hydrophobicity.

400 The preparation method steps are:

[0057]

404 (1) Primer preparation and preparation: add 5-40 parts by mass of soft and hard composite resin and its curing agent to 100-500 parts by mass of diluent, ultrasonically stir for 30-120 minutes, then mechanically stir for 2-30 minutes, then add 0-50 parts of micro-powder and 0-5 parts of additives, continue stirring for 10-60 minutes to obtain a uniformly dispersed hybrid primer. Form a uniform coating on the surface of the material, adjust the coating thickness to $0.5\ \mu\text{m} \sim 5\text{mm}$, and cure at room temperature for $30 \sim 120$ minutes; the weight ratio of soft resin to hard resin is $0.1 \sim 10$; diluents can choose butyl acetate, acetone, di Corresponding solvents such as toluene.

411 The soft resin includes any of polydimethylsiloxane, polyethylene, polypropylene, ethylene-vinyl acetate copolymer, ethylene-acrylic acid copolymer, acrylic resin, and the like.

413 The hard resin includes any of polymethylmethacrylate, epoxy resin, polyvinylidene fluoride, fluorocarbon resin, rigid polyurethane, and the like.

415 Micropowder can be one of microsilica powder, diamond powder, hollow microspheres, PTFE,

polypropylene powder, sludge powder, clay powder, kaolin powder, fly ash, talcum powder, glass flakes, glass fiber, ceramic fiber, etc. A variety of mixed use, the largest dimension of the size of $10 \sim 100 \mu\text{m}$;

[0058]

421 (2) Topcoat preparation and preparation: disperse hydrophobic nanoparticles with a particle size of 5-200nm in an organic solution at a concentration of 10-40mg/mL, obtain uniform nanoparticles after ultrasonic dispersion and mechanical stirring for 30-60min Suspension, or fluorinating 10-40mg/mL 5-200nm hydrophilic nanoparticles, 0.05-1mg/mL ammonia water, 0.1-2mg/mL deionized water and 0.01-0.1mg/mL hydrophobic treatment agent for 24-36h Finally, the super-hydrophobic topcoat is obtained, and the topcoat is coated on the surface of the semi-cured primer by spraying technology, and the thickness of the coating is adjusted to 0.5-5 μm through the coating pass; the nanoparticles include silicon dioxide, zinc oxide, titanium dioxide, polypropylene Any one or more of them are mixed; good solvents include any one or more of alcohols, ketones, ethers and other volatile solvents;

[0059]

433 (3) Put the composite super-hydrophobic film prepared above at room temperature or $30-150^{\circ}\text{C}$. for 1-48 hours and then separate from the substrate to obtain a transferable wear-resistant flexible super-hydrophobic film.

[0060]

439 The smooth flat mold can be one of glass, polished metal, glazed ceramic tile, polytetrafluoroethylene plate, and can also be a soft polyethylene or polypropylene film, which is treated with degreasing and decontamination, or coated Use after resin release agent.

[0061]

445 Said auxiliary agent includes leveling agent, defoamer, dispersant and anti-sedimentation agent in equal mass proportion.

[0062]

450 The superhydrophobic film refers to a film with a water droplet static contact angle greater than 160° and a rolling angle less than 5° .

[0063]

455 The above-mentioned abrasion resistance means that it can still maintain the ultra-high performance after being rubbed by fingers 500 times, washed by tap water with 0.1MPa pressure for 60 minutes, 1kg heavy sea sand with a height of 30cm free falling sand, and polished with 300-1200 mesh metallographic sandpaper for

100 times. Hydrophobic.

[0064]

462 The durability mentioned above refers to that the appearance and color of the film layer have no obvious changes after being placed in an outdoor environment for one year, and it still has good superhydrophobicity.

[0065]

468 The elasticity means that the elongation rate can reach more than 200%, and the superhydrophobicity can still be maintained in a stretched state or when it returns to a natural state.

[0066]

473 The bending and folding means that the film can be bent and folded in any shape, and can still maintain superhydrophobicity after bending and folding for 1000 times.

[0067]

478 Said cuttable means that the film can be cut into any shape with scissors, utility knife and other tools.

[0068]

482 The bonding means that the film can be bonded to any substrate surface by water, glue, solid glue, etc. to obtain a super-hydrophobic surface.

[0069]

487 Another preparation method is to use a soft and hard composite resin solution to form a primer on the surface of the base film, and then use a super-hydrophobic nano-coating to form a top coat on the semi-cured primer. Transfer wear-resistant flexible superhydrophobic film.

490 The base film includes any one of polyvinyl chloride, polycarbonate, silicone, fluororesin and polyethylene terephthalate.

[0070]

495 Example 1

[0071]

499 Dissolve 5g of dimethylsiloxane and 5g of polymethyl methacrylate in 100g of acetone, ultrasonicate for

30 min, then mechanically stir for 2 min, then add 1g of microsilica powder and 0.1g of additives, which contain fluids of equal mass specific gravity Leveling agent BYK-358, defoamer BYK-555, dispersant BYK-161 and anti-sedimentation agent fumed silica, continue to stir for 30 minutes to obtain a uniformly dispersed hybrid primer, and stand for degassing for 10 minutes to obtain a primer coating; Disperse 1 g of hydrophobic zinc oxide nanoparticles with a particle size of 5-200 nm in 100 mL of acetone solution, and obtain a uniformly dispersed super-hydrophobic coating after ultrasonic dispersion and mechanical stirring for 30 min; A uniform coating is formed on the surface of the toughened glass, and after curing for 30 minutes, the superhydrophobic coating prepared above is sprayed on the surface. Finally, the composite superhydrophobic film prepared above is placed in an oven at 60° C for 12 hours, and is separated from the substrate after cooling. The transferable wear-resistant flexible superhydrophobic film can be obtained, and its surface micro morphology is shown in Figure 1a, with a water contact angle of 168.6° and a rolling angle of 3.2° (Figure 1b).

[0072]

515 Example 2

[0073]

519 Dissolve 10g of polyethylene and 5g of FEVE fluorocarbon resin in 200g of butyl acetate, ultrasonicate for 60 minutes, then mechanically stir for 10 minutes, then add 5g of hollow microspheres, continue stirring for 30 minutes to obtain a uniformly dispersed hybrid primer, and let it stand for degassing for 30 minutes. Finally, the primer coating was obtained; 2 g of silicon dioxide hydrophobic nanoparticles with a particle size of 5 to 200 nm were dispersed in 100 mL of butyl acetate solution, and a uniformly dispersed superhydrophobic coating was obtained after ultrasonic dispersion and mechanical stirring for 30 min; the above primer Spray the lacquer coating on the surface of the degreased and decontaminated glazed tiles to form a uniform coating. After curing for 60 minutes, spray the super-hydrophobic coating prepared above on the surface. Finally, put the composite super-hydrophobic film prepared above in an oven at 150° C. After solidification for 1 hour, the transferable wear-resistant flexible superhydrophobic film can be obtained after being cooled and separated from the substrate. After washing with 0.1 MPa tap water for 60 minutes, the water contact angle is 156.8° , and the rolling angle is 4.3° (Fig. 2b).

[0074]

534 Example 3

[0075]

538 Dissolve 20g of ethylene-vinyl acetate copolymer and 10g of rigid polyurethane in 500g of butyl acetate, ultrasonicate for 120 min, then mechanically stir for 30 min, then add 50g of sludge powder and 1g of additives, and continue stirring for 60 min to obtain a uniformly dispersed hybrid primer , after standing for degassing for 30 min, the primer coating was obtained; 4g of hydrophilic titanium dioxide nanoparticles with

a particle size of 5-200nm were dispersed in 100 mL of absolute ethanol solution, and after ultrasonic dispersion and mechanical stirring for 30 min, a uniform nanoparticle suspension was obtained. Liquid, add 0.1g ammonia water, 0.2g deionized water and 0.01g fluoroalkyl siloxane hydrophobic treatment for 36h to obtain superhydrophobic coating; spray the above primer coating on the smooth polytetrafluoroethylene. A uniform coating is formed on the surface of the board, and after curing for 30 minutes, the superhydrophobic coating prepared above is sprayed on the surface. Finally, the composite superhydrophobic film prepared above is placed in an oven at 80 ° C to cure for 12 hours, and after cooling, it is separated from the substrate. A transferable wear-resistant flexible super-hydrophobic film was obtained. After being impacted by 1kg heavy sea sand and 30cm high free falling sand, the water contact angle was 156.6° , and the rolling angle was 4.7° (Fig. 3a), or 0.1 MPa by 600 mesh metallographic sandpaper. The water contact angle after grinding 100 times under pressure was 159.3° and the rolling angle was 4.7° (Fig. 3b).

[0076]

556 Example 4

[0077]

560 Dissolve 30g of acrylic resin and 10g of epoxy resin in 500g of acetone, ultrasonicate for 60 min, then mechanically stir for 30 min, then add 20g of silicon micropowder and 1g of additives, continue stirring for 60 min to obtain a uniformly dispersed hybrid primer, and let stand for degassing for 30 min. Finally, the primer coating was obtained; 4 g of silicon dioxide hydrophobic nanoparticles with a particle size of 5 to 200 nm were dispersed in 100 mL of absolute ethanol solution, and a uniformly dispersed super-hydrophobic coating was obtained after ultrasonic dispersion and mechanical stirring for 30 min; the above primer. The lacquer coating is sprayed on the surface of the polished stainless steel plate after degreasing and decontamination to form a uniform coating. After curing for 60 minutes, the superhydrophobic coating prepared above is sprayed on the surface, and finally the composite superhydrophobic film prepared above is placed in an oven at 120 ° C. After curing for 8 hours, after cooling and separating from the substrate, a transferable wear-resistant flexible super-hydrophobic film can be obtained. Paste it on a glass substrate and place it in an outdoor environment for 1 year. Observe the surface and find that there is no obvious change in the appearance and color of the film layer, and still have good superhydrophobicity (Figure 4).

[0078]

576 Example 5

[0079]

580 Dissolve 10g of polyethylene resin and 10g of FEVE fluorocarbon resin in 400g of butyl acetate, ultrasonicate for 60 minutes, then mechanically stir for 20 minutes, then add 0.5g of additives, continue stirring for 30 minutes to obtain a uniformly dispersed hybrid primer, and let it stand for degassing. After 30 minutes, the primer coating was obtained; 2 g of silicon dioxide hydrophobic nanoparticles with a particle size of 5-200

nm were dispersed in 100 mL of absolute ethanol solution, and after ultrasonic dispersion and mechanical stirring for 30 minutes, a uniformly dispersed super-hydrophobic coating was obtained; the above Spray the primer paint on the surface of the degreased and decontaminated polytetrafluoroethylene board to form a uniform coating. After curing for 30 minutes, spray the superhydrophobic coating prepared above on the surface, and finally cure the composite superhydrophobic film prepared above at room temperature for 48 hours. , after being cooled and separated from the substrate, a transferable wear-resistant flexible superhydrophobic film can be obtained. After stretching it from the natural state (Figure 5a) to 180% (Figure 5b), its surface remains intact and still possesses superhydrophobicity .

[0080]

595 Example 6

[0081]

599 Dissolve 10g of acrylic resin and 10g of rigid polyurethane in 200g of xylene, ultrasonicate for 30 min, then mechanically stir for 20 min, then add 5g of PTFE powder and 0.5g of additives, continue stirring for 30 min to obtain a uniformly dispersed hybrid primer, and let stand to degas After 30 minutes, the primer coating was obtained; 2g of titanium dioxide nanoparticles with a particle size of 10-500nm were dispersed in 100mL of absolute ethanol solution, and after ultrasonic dispersion and mechanical stirring for 30 minutes, a uniform nanoparticle suspension was obtained, and 0.05g of ammonia water, 0.1g of deionized water and 0.01g of fluorosilane fluorinated for 48 hours to obtain a super-hydrophobic coating; spray the above-mentioned primer coating on the surface of the degreasing and decontaminating PTFE plate to form a uniform coating, and then cure it for 60 minutes. The superhydrophobic coating prepared above is sprayed on its surface, and finally the composite superhydrophobic film prepared above is placed in an oven at 60° C to cure for 12 hours. After cooling, it is separated from the substrate to obtain a transferable wear-resistant flexible superhydrophobic film. The film can be placed at any angle After being bent or folded more than 1,000 times, the surface remained intact without creases and remained superhydrophobic (Figure 6).

[0082]

615 Example 7

[0083]

619 Dissolve 20g of ethylene-vinyl acetate copolymer and 20g of FEVE fluorocarbon resin in 200g of butyl acetate, ultrasonically stir for 60 minutes and then mechanically stir for 60 minutes to obtain a uniformly dispersed hybrid primer, and obtain a primer coating after standing for degassing for 30 minutes; 4g of silicon dioxide hydrophobic nanoparticles with a particle size of 5-200nm were dispersed in 100mL of absolute ethanol solution, and a uniformly dispersed superhydrophobic coating was obtained after ultrasonic dispersion and mechanical stirring for 30 minutes; the above primer coating was sprayed on a flat poly A uniform coating is formed on the surface of the vinyl film, and after curing for 30 minutes, the superhydrophobic coating

prepared above is sprayed on the surface. Finally, the composite superhydrophobic film prepared above is placed at room temperature and cured for 48 hours, and then separated from the base film to obtain a transferable coating. Wear-resistant and flexible super-hydrophobic film, which can be cut into various shapes and bonded to the substrate to obtain a super-hydrophobic surface (Figure 7a), such as water, glue, etc. The self-cleaning superhydrophobic surface (Figure 7b,c) can be used in building exterior walls, heat exchangers, power transmission lines, wind turbines, aircraft, automobiles, high-speed rail, radar, electronic products and other fields.

[0084]

636 Example 8

[0085]

640 Dissolve 10g of polypropylene and 10g of polyvinylidene fluoride in 400g of xylene, ultrasonicate for 60 min, then mechanically stir for 20 min, then add 5g of titanium dioxide, rust red and sludge powder as pigments, and continue stirring for 30 min to obtain a uniformly dispersed hybrid Primer, after standing for degassing for 30 minutes to obtain a primer coating; disperse 1 g of silicon dioxide hydrophobic nanoparticles with a particle size of 5 to 200 nm in 100 mL of xylene solution, and obtain a uniform dispersion after ultrasonic dispersion and mechanical stirring for 30 minutes. Super-hydrophobic coating: Spray the above-mentioned primer coating on the surface of the glazed ceramic tile through degreasing and decontamination to form a uniform coating, after curing for 30 minutes, spray the super-hydrophobic coating prepared above on the surface, and finally apply the composite super-hydrophobic coating prepared above The film was cured in an oven at 60° C for 24 hours, and then separated from the substrate after cooling to obtain white, red and black transferable wear-resistant flexible superhydrophobic films.

[0086]

654 Example 9

[0087]

658 Dissolve 3g of dimethylsiloxane and 30g of rigid polyurethane in 200g of butyl acetate, ultrasonicate for 30 min, then mechanically stir for 20 min, then add 20g of sludge powder and 0.5g of additives, and continue stirring for 30 min to obtain a uniformly dispersed hybrid bottom After standing for degassing for 30 minutes, the primer coating was obtained; 4 g of titanium dioxide hydrophobic nanoparticles with a particle size of 5-200 nm were dispersed in 100 mL of butyl acetate solution, and after ultrasonic dispersion and mechanical stirring for 30 minutes, a uniformly dispersed superhydrophobic Coating; Brush the above-mentioned primer coating on the surface of the polytetrafluoroethylene plate through degreasing and decontamination to form a uniform coating, after curing for 30 min, spray the super-hydrophobic coating prepared above on its surface, and finally apply the composite super-hydrophobic coating prepared above The hydrophobic film was cured at room temperature for 24 hours and then separated from the substrate to obtain a rigid

superhydrophobic film, which was poorly flexible and easy to break (Figure 8).

[0088]

672 Example 10

[0089]

676 Dissolve 30g of FEVE fluorocarbon resin in 100g of butyl acetate, ultrasonically stir for 30 min, then mechanically stir for 30 min to obtain a uniformly dispersed hybrid primer, and stand for degassing for 30 min to obtain a primer coating; Hydrophobic nanoparticles of titanium dioxide were dispersed in 100 mL butyl acetate solution, and a uniformly dispersed superhydrophobic coating was obtained after ultrasonic dispersion and mechanical stirring for 30 min; layer, after curing for 30 minutes, spray the superhydrophobic coating prepared above on its surface, and finally place the composite superhydrophobic film prepared above at room temperature to cure for 48 hours and then separate from the substrate. The obtained superhydrophobic film has high transparency, but poor elasticity, and the fracture is neat after stretching (Figure 9).

[0090]

688 Example 11

[0091]

692 Dissolve 20g of FEVE fluorocarbon resin in 100g of butyl acetate, ultrasonicate for 30 min, then mechanically stir for 20 min, then add 10g of hollow microspheres and 1g of additives, continue stirring for 30 min to obtain a uniformly dispersed hybrid primer, and let it stand for degassing for 30 min. Finally, the primer coating was obtained; 2 g of silica hydrophobic nanoparticles with a particle size of 5 to 200 nm were dispersed in 100 mL of butyl acetate solution, and a uniformly dispersed superhydrophobic coating was obtained after ultrasonic dispersion and mechanical stirring for 30 min; the above primer Brush the lacquer coating on the surface of the polytetrafluoroethylene plate after degreasing and decontamination to form a uniform coating, and then spray the superhydrophobic coating prepared above on the surface after curing for 30 minutes, and finally place the composite superhydrophobic film prepared above at room temperature. After curing for 48 hours, it separated from the substrate, and the obtained superhydrophobic film had high strength, but poor flexibility and easy to break (Figure 10).

[0092]

706 Example 12

[0093]

710 Dissolve 20g of EVA in 100g of xylene, ultrasonicate for 30 min, then mechanically stir for 30 min to obtain a uniformly dispersed hybrid primer, and leave to degas for 30 min to obtain a primer coating; 2g of silicon dioxide with a particle size of 5-200nm Disperse the non-toxic nanoparticles in 100 mL absolute ethanol solution, obtain a uniformly dispersed superhydrophobic coating after ultrasonic dispersion and mechanical stirring for 30 minutes; brush the above-mentioned primer coating on the surface of tempered glass that has been degreased and decontaminated to form a uniform coating After curing for 60 minutes, the superhydrophobic coating prepared above was sprayed on its surface. Finally, the composite superhydrophobic film prepared above was cured at room temperature for 24 hours and then separated from the substrate to obtain a transferable wear-resistant flexible superhydrophobic film. After being rubbed by fingers for 50 times, the film lost its superhydrophobicity, and the surface was seriously damaged when observed by a stereomicroscope (Fig. 11).

[0094]

724 Example 13

[0095]

728 Dissolve 15g of EVA in 100g of xylene, ultrasonically for 30 min, then mechanically stir for 20 min, then add 5g of silicon micropowder and 0.5g of additives, continue stirring for 30 min to obtain a uniformly dispersed hybrid primer, and stand to degas for 30 min to obtain a primer Coating: Disperse 2g of silicon dioxide hydrophobic nanoparticles with a particle size of 5-200nm in 100 mL of absolute ethanol solution, and obtain a uniformly dispersed superhydrophobic coating after ultrasonic dispersion and mechanical stirring for 30 minutes; brush the above primer coating Form a uniform coating on the surface of the tempered glass that has been degreased and decontaminated, and then spray the superhydrophobic coating prepared above on the surface after curing for 60 minutes. Finally, the composite superhydrophobic film prepared above is placed at room temperature for 24 hours and then separated from the substrate. , the transferable wear-resistant flexible super-hydrophobic film can be obtained. Although the addition of micro-powder effectively improves its wear resistance, the film is still easily damaged after being scratched by fingers (Figure 12).

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CLAIMS CN106366912A

1.

¹³ A transferable wear-resistant flexible super-hydrophobic film is characterized in that it is a non-fixed and transferable film-type material formed by compounding primer and topcoat, and a two-step coating method can be used to combine soft and hard composite resin solutions. Coating on the surface of a smooth substrate to form a primer, and then coating the super-hydrophobic nano-coating on the surface of the semi-cured primer, and separating it from the substrate after curing; or using a soft and hard composite resin solution on the base film. A primer is formed on the surface, and then a super-hydrophobic nano-coating is used to form a topcoat on the semi-cured primer. After curing, a transferable wear-resistant flexible super-hydrophobic film compounded with the base film is directly obtained; the soft and hard compounding resin solution is obtained by mixing 5-40 parts by mass of soft resin and hard resin, and 100-500 parts by mass of diluent. The weight ratio of soft resin to hard resin in the soft and hard composite resin solution is 0.1-10.

2.

²⁶ The transferable wear-resistant flexible super-hydrophobic film according to claim 1, wherein said soft resin comprises polydimethylsiloxane, polyethylene, polypropylene, ethylene-vinyl acetate copolymer, ethylene-Any one or more mixed soft resins of acrylic copolymers and acrylic resins.

3.

³² The transferable wear-resistant flexible super-hydrophobic film according to claim 1, wherein the hard resin comprises polymethyl methacrylate, epoxy resin, polyvinylidene fluoride, fluorocarbon resin, rigid polyurethane. Any one or more mixed hard resins.

4.

38 The transferable wear-resistant flexible super-hydrophobic film according to claim 1, characterized in that, in the soft and hard composite resin solutions, 0-50 parts by mass of micropowder particles are also included, and the micropowder includes silicon micropowder, any one or more of diamond powder, hollow microspheres, PTFE, polypropylene powder, sludge powder, clay powder, kaolin powder, fly ash, talc powder, glass flakes, glass fiber, ceramic fiber, the largest dimension The size is 10-100 μm .

5.

46 The transferable wear-resistant flexible super-hydrophobic film according to claim 1, wherein the smooth substrate comprises glass, polished metal, glazed ceramic tile, polytetrafluoroethylene plate, polyethylene film or polypropylene film One, after degreasing and decontamination treatment, or after coating with a benign release agent.

6.

53 The transferable wear-resistant flexible super-hydrophobic film according to claim 1, wherein said base film comprises polyvinyl chloride, polycarbonate, organic silicon, fluoro resin, polyethylene terephthalate any of the

7.

59 The transferable wear-resistant flexible super-hydrophobic film according to claim 1, characterized in that, the soft and hard composite resin solution also includes 0 to 5 parts by mass of additives, and the additives include, etc. Mass proportion of leveling agent, defoamer, dispersant and anti-settling agent.

8.

65 The transferable wear-resistant flexible super-hydrophobic film according to claim 1, wherein the super-hydrophobic nano-coating is obtained by directly dispersing hydrophobic nanoparticles in a benign solvent, or mixing hydrophilic nanoparticles and The hydrophobic treatment agent is added to a benign solvent at the same time, and the nanoparticles include any one or more mixtures of silicon dioxide, zinc oxide, titanium dioxide, and polypropylene. The benign solvents include alcohols, ketones, and ethers. One or more of the class, the hydrophobic treatment agent includes one or more of alkyl siloxane or fluoroalkyl siloxane, the maximum dimension of the nanoparticles is 5-200nm, the concentration 10-40mg/mL.

9.

75 The transferable wear-resistant flexible super-hydrophobic film as claimed in claim 1, is characterized in that, has the following characteristics:

(1)

80 The static contact angle of water droplets of the transferable wear-resistant flexible super-hydrophobic film is greater than 160° , and the rolling angle is less than 5° ; it has been rubbed by fingers 500 times, washed with tap water at 0.1 MPa pressure for 60 minutes, and 1kg of heavy sea sand with a height of 30cm free falling sand, After sanding 100 times with 300-1200 mesh metallographic sandpaper under 0.1 MPa pressure, the film can still maintain super-hydrophobicity;

(2)

88 Placed in the outdoor environment for one year, the appearance and color of the film layer have no obvious changes, and still have good super-hydrophobicity;

(3)

93 The elongation rate is more than 200%, and it can still maintain superhydrophobicity in the stretched state or when it returns to the natural state;

(4)

98 It can be bent and folded in any shape, and after being bent and folded 1000 times, it can still maintain superhydrophobicity and can be cut in any shape;

(5)

103 It can be bonded to any substrate surface by glue or solid glue to obtain a super-hydrophobic surface.

10.

107 The method for preparing a transferable wear-resistant flexible superhydrophobic film according to any one of claims 1 to 9, characterized in that the steps are as follows:

109 (1) Preparation of primer: dissolve the soft and hard resins in the diluent, ultrasonically, and then mechanically stir until the mixed resin is evenly dispersed in the diluent, then add other components and continue stirring to disperse evenly, and let it stand After degassing, a thin film is formed on the surface of the base film or smooth substrate, and the thickness of the film is controlled to be 0.5 μm to 5 mm;

113 (2) Topcoat preparation: apply the super-hydrophobic nano-coating on the surface of the semi-cured primer by spraying, and control the coating thickness to 0.5-5 μm by spraying passes;

115 (3) Film curing: After the film coated with primer and topcoat is cured, the smooth base film is peeled off from the smooth base surface to obtain a transferable wear-resistant flexible super-hydrophobic film; the base film can be obtained directly. Transfer wear-resistant flexible superhydrophobic film.



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Protective tape for photovoltaic module panel as well as preparation method and lamination method thereof

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Abstract of CN107987742 (A)

The invention discloses a protective tape for a photovoltaic module panel. The protective tape sequentially comprises a base material layer, an adhesive layer and a release layer, wherein the base material layer is composed of a high-water resistance aluminum-containing material film, ultra-thin glass, a long-acting weather-resistant anti-fouling film or modified PET (Polyethylene Terephthalate) film material; and the adhesive layer is composed of long-acting weather-resistant cohesion-retaining glue. The protective tape for the photovoltaic module panel disclosed by the invention has the advantages of being weather-resistant (acid-base, damp heat and ultraviolet), hydrolysis resistant, capable of being firmly bound to the photovoltaic module panel for a long time, anti-fouling, highly pervious to light, resistant to mechanical scratch, difficult in chemical corrosion, and capable of preventing from being adhered to dust. The dirt can be smoothly cleaned by virtue of washing and wiping, and even if natural rainwater and wind blows exist, cleaning can be completed.

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DESCRIPTION CN107987742A

10 A kind of protective tape for photovoltaic module panel and its preparation method and bonding method

[0001]

14 technical field

[0002]

18 The invention relates to the technical field of adhesive tapes, in particular to a protective adhesive tape for photovoltaic module panels, a preparation method and a bonding method thereof.

[0003]

23 Background technique

[0004]

27 Photovoltaic modules are composed of panels + encapsulation + batteries + encapsulation + backplane/glass.

The panel is transparent to light, and the backplane/glass can be transparent or impermeable to light. The panel is very important, and the light passes through The panels go into the assembly to generate electricity.

30 Photovoltaic modules are used in a variety of environments, including the use in some harsh environments. A large amount of ash layer, a large amount of acidic and alkaline substances, metal oxides and polymer compounds are diffused in the air, which makes the ash layer on the surface of the module panel, sediment, and sulfur-containing, iron-containing powder and other substances in the air.

34 The cleaning of photovoltaic module panels is mainly carried out by water washing, wind blowing and wiping, etc. The acidic and alkaline rainwater and the metal ions on the surface are often not cleaned, which will reduce the light transmittance of the photovoltaic panel glass. If things go on like this, the power generation efficiency of photovoltaic modules will decrease. More attenuation, and even lead to premature scrapping of

photovoltaic modules, causing huge losses to the owners.

[0005]

42 Contents of the invention

[0006]

46 In view of the above-mentioned defects in the prior art, the object of the present invention is to provide a protective tape for photovoltaic module panels and its preparation method and bonding method.

[0007]

51 In order to achieve the above object, the present invention adopts the following technical solutions:

[0008]

55 A protective tape for a photovoltaic module panel, comprising a substrate layer, an adhesive layer and a release layer arranged in sequence; Film or modified PET film material, the adhesive layer is composed of long-term weather-resistant sticky glue.

[0009]

61 Further, the high water-resistance aluminum-containing material film is a composite film-type high water-resistance aluminum-containing material film composed of aluminum-containing materials, and a co-extruded film-type high water-resistance film composed of polyolefin materials is directly coated on the aluminum-containing surface. Aluminum-containing material films, any of the coating-type high-resistance water-resistance aluminum-containing material films that are directly coated with aluminum-containing materials, or the composite film-type high-water-resistance aluminum-containing material films or co-extruded films A cross-mixed high-water-resistance aluminum-containing material film composed of any two of the high-resistance water-resistance aluminum-containing material film and the coating-type high water-resistance aluminum-containing material film;

[0010]

73 The composite film-type high-resistance water-containing aluminum-containing material film includes a passivated aluminum-containing core layer and a composite film layer arranged on one or both sides of the aluminum-containing core layer, and the composite film layer is pasted on the aluminum-containing core layer. The weather-resistant fluororesin film on the film of the aluminum core layer, or a weather-resistant coating coated on the film containing the aluminum core layer, or an ultraviolet-resistant weather-resistant film; the weather-resistant fluororesin film is made of polyfluorine Any one or more of ethylene, polyvinylidene fluoride, ethylene-tetrafluoroethylene copolymer, polychlorotrifluoroethylene,

polytetrafluoroethylene or ethylene-trifluorochloroethylene copolymer; the weather-resistant coating is composed of Any one or more of fluorocarbon resins, acrylic resins, polyester resins, polyamide resins, polyurethane resins or epoxy resins, and are cured by a curing agent or directly coated on the weather-resistant surface; The UV-resistant and weather-resistant film is composed of any one or more of polyester, polyolefin, polyimide or polyamide;

[0011]

88 The co-extruded film-type high water-resistance aluminum-containing material film includes a passivated aluminum-containing core layer and a weather-resistant fluoro resin layer coated on one or both sides of the aluminum-containing core layer, or a fluorine-free polymer Resin layer; the weather-resistant fluoro resin layer is made of polyvinyl fluoride, polyvinylidene fluoride, ethylene-tetrafluoroethylene copolymer, polytrifluorochloroethylene, polytetrafluoroethylene or ethylene-trifluorochloroethylene copolymer One or more components; the fluorine-free polymer resin layer is composed of any one or more of polyester, polyolefin, polyimide or polyamide;

[0012]

98 The coating-type high water-resistance aluminum-containing material film includes a passivated aluminum-containing core layer and a weather-resistant fluoro resin layer coated on one or both sides of the aluminum-containing core layer, or a fluorine-free polymer resin layer; the weather-resistant fluoro resin layer is made of fluorocarbon resin, and the fluorine-free polymer resin layer is made of any one of acrylic resin, polyester resin, polyamide resin, polyurethane resin or epoxy resin or Various configurations, and are cured by a curing agent or directly coated on the surface of the aluminum-containing core layer.

[0013]

107 Further, the long-term weather-resistant and anti-fouling film is a highly transparent fluorine film selected from one or more of PVF, PVDF, ETFE, PCTFE, PTFE, and ECTFE.

[0014]

112 Further, the modified PET film is a PET film whose surface is hardened, AG-treated or AR-treated.

[0015]

116 Further, the long-term weather-resistant viscous adhesive is any one of silicone pressure-sensitive adhesive, acrylic pressure-sensitive adhesive or polyurethane pressure-sensitive adhesive; the curing agent in the long-term weather-resistant viscous adhesive is selected from epoxy curing One or more in the agent, platinum catalyst, isocyanate curing agent; The ultraviolet absorber in described long-term weather resistance adhesive glue is selected from salicylate ultraviolet absorber.

[0016]

124 A preparation method for a protective tape for a photovoltaic module panel, comprising the steps of:

[0017]

128 S1: Take any one of the raw materials selected from silicone pressure-sensitive adhesive, acrylic pressure-sensitive adhesive or polyurethane pressure-sensitive adhesive, and use organic solvent to mix and stir evenly to obtain the master resin;

[0018]

134 S2: Take the master resin prepared in step S1, add one or more curing agents selected from epoxy curing agents, platinum catalysts, and isocyanate curing agents, and add UV absorbers selected from salicylate esters to carry out After mixing and stirring evenly, an adhesive mixture is obtained;

[0019]

140 S3: apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry glue thickness of the adhesive layer of 20 μm -50 μm , and combine the substrate layer on the side coated with the adhesive mixture with the substrate layer The release layer is attached, placed at 30° C-80° C, and aged for no less than 24 hours.

[0020]

147 A bonding process of a protective tape for a photovoltaic module panel, comprising the following steps:

[0021]

151 Step 1: Clean the surface of the photovoltaic module to be bonded;

[0022]

155 Step 2: Use the protective tape for photovoltaic module panels to fully or segmentally bond the cleaned photovoltaic module panels.

[0023]

160 Further, said step one specifically includes the following:

[0024]

164 Step 1) Place the photovoltaic module panel face up on the working platform, and use vacuum equipment to pre-vacuum the surface of the photovoltaic module panel;

[0025]

169 Step 2) Dedusting the surface of the photovoltaic module panel with a brush;

[0026]

173 Step 3) cleaning the surface of the photovoltaic module panel with an organic solvent;

[0027]

177 Step 4) vacuuming the surface of the photovoltaic module panel with a vacuuming device;

[0028]

181 Described step 2 specifically includes as follows:

[0029]

185 Step 1) cutting the photovoltaic module panel into several sheets with protective tape;

[0030]

189 Step 2) Attach the first sheet to the lower end of the photovoltaic module panel. The short edge of the sheet is laid flat along the long side of the photovoltaic module panel, and the long edge of the sheet is laid flat along the short side of the photovoltaic module panel. Tear off the release layer in the middle, and at the same time stick it with a pressure roller or a scraper, so that the adhesive layer on the half side of the sheet is attached to the photovoltaic module panel, and remove the air bubbles between the adhesive layer and the photovoltaic module panel, repeat The above method completes the lamination of the other half of the sheet, thereby completing the lamination of the first sheet;

[0031]

199 Step 3) Repeat step 2), and attach the remaining sheets in turn until they are attached to the upper end of the photovoltaic module panel;

[0032]

204 Step 4) sealing by silica gel or insulating tape between the edge of the sheet and the edge of the parallel adjacent photovoltaic module panel;

[0033]

209 Adjacent sheets are sequentially overlapped and laminated, and the overlapped width is greater than or equal to 50 m m.

[0034]

214 Further, said step one specifically includes the following:

[0035]

218 Step 1) Place the photovoltaic module panel face up on the working platform, and clean and remove the dust on the surface of the photovoltaic module panel with cleaning solution;

[0036]

223 Step 2) Spray an appropriate amount of water on the surface of the photovoltaic module panel;

[0037]

227 Described step 2 specifically includes as follows:

[0038]

231 Step 1) Cut the protective glue on the photovoltaic module panel into sheets consistent with the size of the photovoltaic module panel;

[0039]

236 Step 2) After tearing off the release layer of the sheet, align the long side of the sheet with the long side of the photovoltaic module panel on which water is sprayed on the surface, and then spray an appropriate amount of water on the tiled surface again, and use a squeeze scraper Drain the moisture from the sheet and photovoltaic module panel, and after the moisture is driven out, let it stand at room temperature for 24-72h;

[0040]

243 Step 3) Sealing between the edges around the sheet and the edges of the photovoltaic module panel with silica gel or insulating tape.

[0041]

248 An application of any one of the above-mentioned protective tape lamination processes for photovoltaic module panels, which is used for on-site lamination or replacement of the protective tape for photovoltaic module panels.

[0042]

254 The outstanding effects of the present invention are:

[0043]

258 A protective tape for a photovoltaic module panel of the present invention and a preparation method and a bonding method thereof have the following advantages:

[0044]

263 1. A protective tape for photovoltaic module panels of the present invention has weather resistance (acid-base, damp heat and ultraviolet rays), hydrolysis resistance, long-term maintenance and reliable combination with photovoltaic module panels, antifouling, high light transmission, mechanical scratch resistance, and is not easy Chemical corrosion, non-stick ash layer, ensure smooth removal by washing and wiping, even when natural rain and wind blow;

[0045]

271 2. The glue used in the adhesive layer of the present invention is highly transparent, highly weather-resistant, and has no residual glue;

[0046]

276 3. The protective tape for photovoltaic module panels of the present invention can be carried out at the factory or at the site of the power station. When the power generation drops significantly, it can be replaced regularly at any time to ensure that the modules are always new;

[0047]

282 4. The bonding process of the protective tape for photovoltaic module panels of the present invention can be comprehensive bonding or segmental bonding, which is simple in operation and convenient in bonding.

[0048]

287 Description of drawings

[0049]

291 Fig. 1 is the structural representation of embodiment 1-14 of the present invention;

[0050]

295 In the figure: 1 substrate layer, 2 adhesive layer, 3 release layer.

[0051]

299 Detailed ways

[0052]

303 The following will clearly and completely describe the technical solutions in the embodiments of the present invention with reference to the accompanying drawings in the embodiments of the present invention.

Obviously, the described embodiments are only some of the embodiments of the present invention, not all of them.

[0053]

310 Example 1

[0054]

314 A protective tape for a photovoltaic module panel of the present embodiment, as shown in Figure 1, includes a substrate layer 1, an adhesive layer 2 and a release layer 3 which are arranged in sequence; the substrate layer 1 is made of ultra-thin glass, The adhesive layer 2 is composed of long-term weather-resistant adhesive glue.

[0055]

320 Among them, the long-term weather-resistant adhesive is a silicone pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from epoxy curing agents; the ultraviolet absorber in the long-term weather-resistant adhesive is selected from salicylates UV absorber.

[0056]

327 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0057]

332 S1: Take the silicone pressure-sensitive adhesive raw material, mix and stir it evenly with an organic solvent, and obtain the master resin;

[0058]

337 S2: Take the master resin prepared in step S1, add a curing agent selected from epoxy curing agents, and add a salicylate UV absorber, mix and stir evenly to prepare an adhesive mixture;

[0059]

342 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 20 μm , and combine the substrate layer coated with the adhesive mixture with the release type. The layers are pasted together, placed at 30° C, and aged for 24 hours.

[0060]

348 Example 2

[0061]

352 A protective tape for a photovoltaic module panel of this embodiment, as shown in Figure 1, includes a substrate layer 1, an adhesive layer 2, and a release layer 3 that are arranged in sequence; It is composed of a thin film, and the adhesive layer 2 is composed of long-term weather-resistant sticky glue.

[0062]

358 Among them, the long-term weather-resistant and anti-fouling film is selected from PVF high-transparency fluorine film.

[0063]

363 The long-term weather-resistant adhesive is silicone pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from epoxy curing agent; the UV absorber in the long-term weather-resistant adhesive is selected from salicylate UV absorbers agent.

[0064]

369 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0065]

374 S1: Take the raw material of silicone pressure-sensitive adhesive, use organic solvent to mix and stir evenly, and obtain the master resin;

[0066]

379 S2: Take the master resin prepared in step S1, add a curing agent selected from epoxy curing agents, and add a salicylate UV absorber, mix and stir evenly to prepare an adhesive mixture;

[0067]

384 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 30 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 40° C, and aged for 36 hours.

[0068]

390 Example 3

[0069]

394 A protective tape for a photovoltaic module panel of this embodiment, as shown in Figure 1, includes a substrate layer 1, an adhesive layer 2, and a release layer 3 that are arranged in sequence; It is composed of a thin film, and the adhesive layer 2 is composed of long-term weather-resistant sticky glue.

[0070]

400 Among them, the long-term weather-resistant and antifouling film is a highly transparent fluorine film selected from PVF and PVDF.

[0071]

405 The long-term weather-resistant adhesive is acrylic pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from epoxy curing agent and platinum catalyst; the UV absorber in the long-term weather-resistant adhesive is selected from salicylate UV absorbers.

[0072]

411 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0073]

416 S1: Take the raw material of acrylic pressure-sensitive adhesive, use organic solvent to mix and stir evenly, and obtain the master resin;

[0074]

421 S2: Take the master resin prepared in step S1, add a curing agent selected from epoxy curing agent and platinum catalyst, and add a UV absorber selected from salicylate, mix and stir evenly to prepare an adhesive mixture ;

[0075]

427 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 40 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 500° C, and aged for 36 hours.

[0076]

433 Example 4

[0077]

437 A protective tape for a photovoltaic module panel of this embodiment, as shown in Figure 1, includes a substrate layer 1, an adhesive layer 2, and a release layer 3 that are arranged in sequence; It is composed of a thin film, and the adhesive layer 2 is composed of long-term weather-resistant sticky glue.

[0078]

443 Among them, the long-term weather-resistant and antifouling film is a highly transparent fluorine film selected from ETFE.

[0079]

448 The long-term weather-resistant adhesive is polyurethane pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from platinum catalyst; the ultraviolet absorber in the long-term weather-resistant adhesive is selected from salicylate ultraviolet absorbers.

[0080]

454 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0081]

459 S1: Take the raw material of polyurethane pressure-sensitive adhesive, mix and stir it evenly with an organic solvent, and obtain the master resin;

[0082]

464 S2: Take the master resin prepared in step S1, add a curing agent selected from platinum catalysts, and add a UV absorber selected from salicylates, and mix and stir evenly to prepare an adhesive mixture;

[0083]

469 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 50 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 60° C, and aged for 50 hours.

[0084]

475 Example 5

[0085]

479 A protective tape for photovoltaic module panels in this embodiment includes a substrate layer 1, an adhesive layer 2 and a release layer 3 arranged in sequence; the substrate layer 1 is composed of a long-lasting weather-resistant and antifouling film, and the adhesive layer 2 Consists of long-term weather-resistant sticky glue.

[0086]

485 Among them, the long-term weather-resistant and antifouling film is a highly transparent fluorine film selected from PCTFE.

[0087]

490 The long-term weather-resistant adhesive is silicone pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from one or more of platinum catalysts and isocyanate curing agents; the ultraviolet absorber in the long-term weather-resistant adhesive Selected from salicylate UV absorbers.

[0088]

497 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0089]

502 S1: Take the raw material of silicone pressure-sensitive adhesive, use organic solvent to mix and stir evenly, and obtain the master resin;

[0090]

507 S2: Take the master resin prepared in step S1, add a curing agent selected from a platinum catalyst and an isocyanate curing agent, and add a UV absorber selected from a salicylate type, and mix and stir evenly to prepare an adhesive mixture;

[0091]

513 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 20 μ m, and combine the substrate layer coated with the adhesive mixture with the release type. The layers are pasted together, placed at 70° C, and aged for 72 hours.

[0092]

519 Example 6

[0093]

523 A protective tape for a photovoltaic module panel of this embodiment, as shown in Figure 1, includes a substrate layer 1, an adhesive layer 2, and a release layer 3 that are arranged in sequence; It is composed of a thin film, and the adhesive layer 2 is composed of long-term weather-resistant sticky glue.

[0094]

529 Among them, the long-term weather-resistant and antifouling film is a highly transparent fluorine film selected from PTFE.

[0095]

534 The long-term weather-resistant adhesive is acrylic pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from isocyanate curing agent; the UV absorber in the long-term weather-resistant adhesive is selected from salicylate UV absorbers.

[0096]

540 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0097]

545 S1: Take the raw material of acrylic pressure-sensitive adhesive, use organic solvent to mix and stir evenly, and obtain the master resin;

[0098]

550 S2: Take the master resin prepared in step S1, add a curing agent selected from isocyanate curing agents, and add a salicylate UV absorber, mix and stir evenly to prepare an adhesive mixture;

[0099]

555 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 25 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 80° C, and aged for 30 hours.

[0100]

561 Example 7

[0101]

565 A protective tape for photovoltaic module panels in this embodiment includes a substrate layer 1, an adhesive layer 2 and a release layer 3 arranged in sequence; the substrate layer 1 is composed of a long-lasting weather-resistant and antifouling film, and the adhesive layer 2 Consists of long-term weather-resistant sticky glue.

[0102]

571 Among them, the long-term weather-resistant and antifouling film is a highly transparent fluorine film selected from ECTFE.

[0103]

576 The long-term weather-resistant adhesive is polyurethane pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from isocyanate curing agent; the UV absorber in the long-term weather-resistant adhesive is selected from salicylate UV absorbers.

[0104]

582 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0105]

587 S1: Take the raw material of polyurethane pressure-sensitive adhesive, mix and stir it evenly with an organic solvent, and obtain the master resin;

[0106]

592 S2: Take the master resin prepared in step S1, add a curing agent selected from isocyanate curing agents, and add a salicylate U V absorber, mix and stir evenly to prepare an adhesive mixture;

[0107]

597 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 30 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 30° C, and cured for 36 hours.

[0108]

603 Example 8

[0109]

607 A protective tape for a photovoltaic module panel of the present embodiment includes a substrate layer 1, an adhesive layer 2 and a release layer 3 arranged in sequence; the substrate layer 1 is made of a modified PET film material, and the adhesive layer 2 Constructed of long-term weather-resistant adhesive.

[0110]

613 Wherein, the modified PET film is a PET film whose surface is hardened.

[0111]

617 The long-term weather-resistant adhesive is silicone pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from epoxy curing agent; the U V absorber in the long-term weather-resistant adhesive is selected from salicylate U V absorbers agent.

[0112]

623 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0113]

628 S1: Take the raw material of silicone pressure-sensitive adhesive, use organic solvent to mix and stir evenly, and obtain the master resin;

[0114]

633 S2: Take the master resin prepared in step S1, add a curing agent selected from epoxy curing agents, and add a salicylate UV absorber, mix and stir evenly to prepare an adhesive mixture;

[0115]

638 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 35 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 80° C, and aged for 48 hours.

[0116]

644 Example 9

[0117]

648 A kind of protective tape for photovoltaic module panel of the present embodiment, as shown in Figure 1, comprises substrate layer 1, adhesive layer 2 and release layer 3 that are provided with successively; Substrate layer 1 is made of modified PET film material Composition, the adhesive layer 2 is composed of long-term weather-resistant sticky glue.

[0118]

655 Wherein, the modified PET film is a PET film with AG treatment on the surface.

[0119]

659 The long-term weather-resistant sticky adhesive is an acrylic pressure-sensitive adhesive; the curing agent in the long-term weather-resistant sticky adhesive is selected from platinum catalysts; the ultraviolet absorber in the long-term weather-resistant sticky adhesive is selected from salicylate ultraviolet absorbers.

[0120]

665 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0121]

670 S1: Take the raw material of acrylic pressure-sensitive adhesive, use organic solvent to mix and stir evenly, and obtain the master resin;

[0122]

675 S2: Take the master resin prepared in step S1, add a curing agent selected from platinum catalysts, and add a UV absorber selected from salicylates, and mix and stir evenly to prepare an adhesive mixture;

[0123]

680 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 40 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 50° C, and aged for 48 hours.

[0124]

686 Example 10

[0125]

690 A kind of protective tape for photovoltaic module panel of the present embodiment, as shown in Figure 1, comprises substrate layer 1, adhesive layer 2 and release layer 3 that are provided with successively; Substrate layer 1 is made of modified PET film material Composition, the adhesive layer 2 is composed of long-term weather-resistant sticky glue.

[0126]

697 Wherein, the modified PET film is a PET film subjected to AR treatment on the surface.

[0127]

701 The long-term weather-resistant adhesive is polyurethane pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from epoxy curing agent and isocyanate curing agent; the ultraviolet absorber in the long-term weather-resistant adhesive is selected from salicylic acid Esters UV absorbers.

[0128]

708 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0129]

713 S1: Take the raw material of polyurethane pressure-sensitive adhesive, mix and stir it evenly with an organic solvent, and obtain the master resin;

[0130]

718 S2: Take the master resin prepared in step S1, add a curing agent selected from epoxy curing agent and isocyanate curing agent, and add a salicylate UV absorber, mix and stir evenly to prepare an adhesive mixture liquid;

[0131]

724 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 50 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 60° C, and aged for 72 hours.

[0132]

730 Example 11

[0133]

734 A protective tape for a photovoltaic module panel of the present embodiment, as shown in Figure 1, comprises a base material layer 1, an adhesive layer 2 and a release layer 3 which are provided in sequence; The material film is formed, and the adhesive layer 2 is formed of long-term weather-resistant sticky glue.

[0134]

740 Among them, the high water-resistance aluminum-containing material film is a composite film-type high water-resistance aluminum-containing material film composed of aluminum-containing materials, and the composite film-type high water-resistance aluminum-containing material film includes a passivated aluminum-containing core layer and an aluminum-containing The composite film layer on one or both sides of the core layer, the composite film layer is a weather-resistant fluoro resin film pasted on the film containing the aluminum core layer, or a weather-resistant coating coated on the film containing the aluminum core layer, Or UV and weather-resistant film; weather-resistant fluoro resin film is made of polyvinyl fluoride, polyvinylidene fluoride, ethylene-tetrafluoroethylene copolymer, polychlorotrifluoroethylene, polytetrafluoroethylene or ethylene-trifluorochloroethylene copolymer Any one or more of them; the weather-resistant coating is made of any one or more of fluorocarbon resins, acrylic resins, polyester resins, polyamide resins, polyurethane resins or epoxy resins, and is passed through a curing agent Curing or direct coating onto a weather-resistant surface; the UV-resistant and weather-resistant film is composed of any one

or more of polyester, polyolefin, polyimide or polyamide.

[0135]

756 The long-term weather-resistant adhesive is polyurethane pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from epoxy curing agent and isocyanate curing agent; the ultraviolet absorber in the long-term weather-resistant adhesive is selected from salicylic acid Esters UV absorbers.

[0136]

763 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0137]

768 S1: Take the raw material of polyurethane pressure-sensitive adhesive, mix and stir it evenly with an organic solvent, and obtain the master resin;

[0138]

773 S2: Take the master resin prepared in step S1, add a curing agent selected from epoxy curing agent and isocyanate curing agent, and add a salicylate UV absorber, mix and stir evenly to prepare an adhesive mixture liquid;

[0139]

779 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 50 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 60° C, and aged for 72 hours.

[0140]

785 Example 12

[0141]

789 A protective tape for a photovoltaic module panel of the present embodiment, as shown in Figure 1, comprises a base material layer 1, an adhesive layer 2 and a release layer 3 which are provided in sequence; The material film is formed, and the adhesive layer 2 is formed of long-term weather-resistant sticky glue.

[0142]

795 Among them, the high-water-resistance aluminum-containing material film is a co-extruded film-type high-water-resistance aluminum-containing material film composed of polyolefin materials directly coated on the aluminum-containing surface, and the co-extruded film-type high water-resistance aluminum-containing material film includes passivated The aluminum core layer and the weather-resistant fluororesin layer on one or both sides of the aluminum-containing core layer by coating, or the fluorine-free polymer resin layer; the weather-resistant fluororesin layer is made of polyvinyl fluoride, polyvinylidene fluoride, ethylene - any one or more of tetrafluoroethylene copolymer, polychlorotrifluoroethylene, polytetrafluoroethylene or ethylene-trifluorochloroethylene copolymer; the fluorine-free polymer resin layer is made of polyester, polyolefin, Any one or more of polyimide or polyamide.

[0143]

807 The long-term weather-resistant adhesive is polyurethane pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from epoxy curing agent and isocyanate curing agent; the ultraviolet absorber in the long-term weather-resistant adhesive is selected from salicylic acid Esters U V absorbers.

[0144]

814 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0145]

819 S1: Take the raw material of polyurethane pressure-sensitive adhesive, mix and stir it evenly with an organic solvent, and obtain the master resin;

[0146]

824 S2: Take the master resin prepared in step S1, add a curing agent selected from epoxy curing agent and isocyanate curing agent, and add a salicylate U V absorber, mix and stir evenly to prepare an adhesive mixture liquid;

[0147]

830 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 50 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 60° C, and aged for 72 hours.

[0148]

[0149]

840 A protective tape for a photovoltaic module panel of the present embodiment, as shown in Figure 1, comprises a base material layer 1, an adhesive layer 2 and a release layer 3 which are provided in sequence; The material film is formed, and the adhesive layer 2 is formed of long-term weather-resistant sticky glue.

[0150]

846 Among them, the high water-resistance aluminum-containing material film is a coating-type high water-resistance aluminum-containing material film composed of aluminum-containing materials directly coated with paint, and the coating-type high water-resistance aluminum-containing material film includes a passivated aluminum-containing core layer and a weather-resistant fluororesin layer coated on one or both sides of the aluminum-containing core layer, or a fluoropolymer resin layer; the weather-resistant fluororesin layer is made of fluorocarbon resin, and the fluoropolymer resin layer is composed of Any one or more of acrylic resin, polyester resin, polyamide resin, polyurethane resin or epoxy resin, and is cured by a curing agent or directly coated on the surface of the aluminum-containing core layer.

[0151]

857 The long-term weather-resistant adhesive is polyurethane pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from epoxy curing agent and isocyanate curing agent; the ultraviolet absorber in the long-term weather-resistant adhesive is selected from salicylic acid Esters UV absorbers.

[0152]

864 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0153]

869 S1: Take the raw material of polyurethane pressure-sensitive adhesive, mix and stir it evenly with an organic solvent, and obtain the master resin;

[0154]

874 S2: Take the master resin prepared in step S1, add a curing agent selected from epoxy curing agent and isocyanate curing agent, and add a salicylate UV absorber, mix and stir evenly to prepare an adhesive mixture liquid;

[0155]

880 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 50 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 60° C, and aged for 72 hours.

[0156]

886 Example 14

[0157]

890 A protective tape for a photovoltaic module panel of the present embodiment, as shown in Figure 1, comprises a base material layer 1, an adhesive layer 2 and a release layer 3 which are provided in sequence; The material film is formed, and the adhesive layer 2 is formed of long-term weather-resistant sticky glue.

[0158]

896 Among them, the high water-resistance aluminum-containing material film is composed of the composite film type high water-resistance aluminum-containing material film, the co-extruded film type high water-resistance aluminum-containing material film and the coated high water-resistance aluminum-containing material film in Examples 11-13. A cross-mixed high-resistance water-containing aluminum-containing material film composed of any two of the films.

[0159]

904 The long-term weather-resistant adhesive is polyurethane pressure-sensitive adhesive; the curing agent in the long-term weather-resistant adhesive is selected from epoxy curing agent and isocyanate curing agent; the ultraviolet absorber in the long-term weather-resistant adhesive is selected from salicylic acid Esters UV absorbers.

[0160]

911 A preparation method of a protective tape for a photovoltaic module panel of the present embodiment comprises the following steps:

[0161]

916 S1: Take the raw material of polyurethane pressure-sensitive adhesive, mix and stir it evenly with an organic solvent, and obtain the master resin;

[0162]

921 S2: Take the master resin prepared in step S1, add a curing agent selected from epoxy curing agent and isocyanate curing agent, and add a salicylate U V absorber, mix and stir evenly to prepare an adhesive mixture liquid;

[0163]

927 S3: Apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry adhesive thickness of 50 μ m, and combine the substrate layer coated with the adhesive mixture with the release type The layers are pasted together, placed at 60° C, and aged for 72 hours.

[0164]

933 The bonding process of a protective tape for photovoltaic module panels prepared in Examples 1-14 includes full bonding or segmental bonding of cleaned photovoltaic module panels.

[0165]

938 The bonding process of segmental bonding includes the following steps:

[0166]

942 Step 1) Place the photovoltaic module panel face up on the working platform, and use vacuum equipment to pre-vacuum the surface of the photovoltaic module panel;

[0167]

947 Step 2) Dedusting the surface of the photovoltaic module panel with a brush;

[0168]

951 Step 3) cleaning the surface of the photovoltaic module panel with an organic solvent;

[0169]

955 Step 4) vacuuming the surface of the photovoltaic module panel with a vacuuming device;

[0170]

959 Step 5) cutting the photovoltaic module panel into several sheets with protective tape;

[0171]

963 Step 6) Attach the first sheet to the lower end of the photovoltaic module panel. The short edge of the sheet is laid flat along the long side of the photovoltaic module panel, and the long edge of the sheet is laid flat along the short side of the photovoltaic module panel. Tear off the release layer in the middle, and at the same time stick it with a pressure roller or a scraper, so that the adhesive layer on the half side of the sheet is attached to the photovoltaic module panel, and remove the air bubbles between the adhesive layer and the photovoltaic module panel, repeat The above method completes the lamination of the other half of the sheet, thereby completing the lamination of the first sheet;

[0172]

973 Step 7) Repeat step 6) to attach the remaining sheets in turn until they are attached to the upper end of the photovoltaic module panel;

[0173]

978 Step 8) Seal the edge of the sheet and the edge of the parallel adjacent photovoltaic module panel with silica gel or insulating tape; the adjacent sheets are sequentially overlapped and bonded, and the width of the overlap and bonding is greater than or equal to 50 mm.

[0174]

984 The full lamination process includes the following steps:

[0175]

988 Step 1) Place the photovoltaic module panel face up on the working platform, and clean and remove the dust on the surface of the photovoltaic module panel with cleaning solution;

[0176]

993 Step 2) Spray an appropriate amount of water on the surface of the photovoltaic module panel;

[0177]

997 Step 3) Cutting the protective glue for the photovoltaic module panel into sheets consistent with the size of the photovoltaic module panel;

[0178]

1002 Step 4) After tearing off the release layer of the sheet, align the long side of the sheet with the long side of the photovoltaic module panel on which water is sprayed on the surface, and then spray an appropriate amount

of water on the tiled surface again, and use a water-squeezing scraper Drain the moisture from the sheet and photovoltaic module panel, and after the moisture is driven out, let it stand at room temperature for 24-72h;

[0179]

1009 Step 5) Sealing between the edges around the sheet and the edges of the photovoltaic module panel with silica gel or insulating tape.

[0180]

1014 Test case

[0181]

1018 Effect of the present invention can prove by following test:

[0182]

1022 Performance detection of protective tape for photovoltaic module panel of the present invention

[0183]

1026 1. Sample

[0184]

1030 Self-made according to Examples 1-14.

[0185]

1034 2. Test method

[0186]

1038 2.1 Peel force testing machine to test the 180° peel force of the sample

[0187]

1042 (1) Take a roll or sheet sample, first cut the product into 3-5 strips with a size of 25 mm × 300 mm.

[0188]

1046 (2) Mirror steel plate: length 150 ± 1 mm, width 50 ± 1 mm, thickness 1.5 mm-2 mm.

[0189]

1050 (3) Single-sided adhesive tape: tear off the release material on the adhesive tape, the adhesive surface cannot touch hands or other objects, connect the adhesive surface to one end of the mirror steel plate, and use a pressure roller (2Kg) without applying external pressure. The speed of 300 mm/min goes back and forth 3 times, so that the rubber surface is in full contact with the mirror steel plate, and no air bubbles are allowed at the joint between the sample and the mirror steel plate.

[0190]

1058 (4) After the sample is prepared, it is left to stand in the specified test environment for 20 minutes before testing.

[0191]

1063 (5) Fold the free end of the sample in half by 180° , peel off the bonding surface from the test plate by 25 mm, and clamp the free end of the sample and the sample plate on the upper and lower holders respectively, so that the peeled surface and the force line of the testing machine To keep consistent, the testing machine peels off continuously at a rising speed of $300 \text{ mm/min} \pm 10 \text{ mm/min}$, and an automatic recorder draws the peeling curve.

[0192]

1071 (6) Record the test data and the position of the failure interface, and take the average value.

[0193]

1075 2.2 The 180° peel force of the sample tested by the peel force tester after aging

[0194]

1079 (1) The sample preparation method is consistent with the above.

[0195]

1083 (2) After the sample is bonded to the mirror steel plate, they will be placed in high temperature and high humidity $85 \pm 2^\circ\text{C}$, $85 \pm 5\%$ R. H.

1085 Place it in the environment for 2000h, TC ($-40^\circ\text{C} \sim 85^\circ\text{C}$ 6H/cycle, 200cycle), then take it out and let it stand for 2h, and use the above peel force test method to test.

[0196]

1090 (3) Record the test data and the position of the failure interface, and take the average value.

[0197]

1094 2.3 Yellowing test method

[0198]

1098 (1) Cut the tape into 50 mm*150 mm samples (the fluorine coating surface is on top), test the b value with a colorimeter and record it as b1.

[0199]

1103 (2) Put the sample into the Q U V U V aging tester (the fluorine-coated surface is on top), irradiate with U V 100K W h, take out the sample and test the b value with the color difference meter again and record it as b2.

[0200]

1109 (3) Calculate $\Delta b = b2 - b1$.

[0201]

1113 3. Test results

[0202]

1117 The test results are shown in Table 1, and the results show that the protective tape for photovoltaic module panels of the present invention has good bonding performance, weather resistance, and yellowing resistance.

[0203]

1122 Table 1 Photovoltaic module of the present invention is used repair tape performance test result

[0205]

1126 The above is only a preferred embodiment of the present invention, but the scope of protection of the present invention is not limited thereto, any person familiar with the technical field within the technical scope disclosed in the present invention, according to the technical solution of the present invention Any equivalent replacement or change of the inventive concepts thereof shall fall within the protection scope of

the present invention.

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CLAIMS CN107987742A

1.

13 A protective tape for a photovoltaic module panel, characterized in that: it includes a substrate layer, an adhesive layer and a release layer arranged in sequence; It is composed of effective weather-resistant and anti-fouling film or modified PET film material, and the adhesive layer is composed of long-term weather-resistant sticky glue.

2.

20 A protective tape for a photovoltaic module panel according to claim 1, wherein the film of the high-resistance water-resistance aluminum-containing material is a composite film type high-resistance water-resistance aluminum-containing material film composed of aluminum-containing materials. Any of the co-extruded film-type high-resistance water-resistance aluminum-containing material films made of polyolefin materials directly coated on the surface, and any of the coating-type high-resistance water-resistance aluminum-containing material films composed of aluminum-containing materials directly coated with paint, Or a cross-mixed high water resistance film composed of any two of the composite film type high water resistance aluminum material film, co-extrusion film type high water resistance aluminum material film and coating type high water resistance aluminum material film Films of aluminum-containing materials;

29 The composite film-type high-resistance water-containing aluminum-containing material film includes a passivated aluminum-containing core layer and a composite film layer arranged on one or both sides of the aluminum-containing core layer, and the composite film layer is pasted on the aluminum-containing core layer. The weather-resistant fluoro resin film on the film of the aluminum core layer, or a weather-resistant coating coated on the film containing the aluminum core layer, or an ultraviolet-resistant weather-resistant film; the weather-resistant fluoro resin film is made of polyfluorine Any one or more of ethylene, polyvinylidene fluoride, ethylene-tetrafluoroethylene copolymer, polychlorotrifluoroethylene, polytetrafluoroethylene or ethylene-trifluorochloroethylene copolymer; the weather-resistant coating is composed of Any one or more of fluorocarbon resins, acrylic resins, polyester resins, polyamide resins,

polyurethane resins or epoxy resins, and are cured by a curing agent or directly coated on the weather-resistant surface; The UV-resistant and weather-resistant film is composed of any one or more of polyester, polyolefin, polyimide or polyamide;

41 The co-extruded film-type high water-resistance aluminum-containing material film includes a passivated aluminum-containing core layer and a weather-resistant fluororesin layer coated on one or both sides of the aluminum-containing core layer, or a fluorine-free polymer Resin layer; the weather-resistant fluororesin layer is made of polyvinyl fluoride, polyvinylidene fluoride, ethylene-tetrafluoroethylene copolymer, polytrifluorochloroethylene, polytetrafluoroethylene or ethylene-trifluorochloroethylene copolymer One or more components; the fluorine-free polymer resin layer is composed of any one or more of polyester, polyolefin, polyimide or polyamide;

48 The coating-type high water-resistance aluminum-containing material film includes a passivated aluminum-containing core layer and a weather-resistant fluororesin layer coated on one or both sides of the aluminum-containing core layer, or a fluorine-free polymer resin layer; the weather-resistant fluororesin layer is made of fluorocarbon resin, and the fluorine-free polymer resin layer is made of any one of acrylic resin, polyester resin, polyamide resin, polyurethane resin or epoxy resin or Various configurations, and are cured by a curing agent or directly coated on the surface of the aluminum-containing core layer.

3.

57 A protective tape for photovoltaic module panels according to claim 1, characterized in that: the long-term weather-resistant antifouling film is one or more selected from PVF, PVDF, ETFE, PCTFE, PTFE, ECTFE Highly transparent fluorine film.

4.

63 The protective tape for photovoltaic module panels according to claim 1, wherein the modified PET film is a PET film whose surface is hardened, AG-treated or AR-treated.

5.

68 A protective tape for photovoltaic module panels according to claim 1, wherein the long-term weather-resistant sticky adhesive is any one of silicone pressure-sensitive adhesive, acrylic pressure-sensitive adhesive or polyurethane pressure-sensitive adhesive; The curing agent in the long-term weather-resistant adhesive is selected from one or more of epoxy curing agents, platinum catalysts, and isocyanate curing agents; the ultraviolet absorber in the long-term weather-resistant adhesive is selected from salicylic acid Ester UV absorber.

6.

77 The preparation method of any kind of protective tape for photovoltaic module panel according to claim 1-5, is characterized in that comprising the steps:

79 S1: Take any one of the raw materials selected from silicone pressure-sensitive adhesive, acrylic pressure-

sensitive adhesive or polyurethane pressure-sensitive adhesive, and use organic solvent to mix and stir evenly to obtain the master resin;

82 S2: Take the master resin prepared in step S1, add one or more curing agents selected from epoxy curing agents, platinum catalysts, and isocyanate curing agents, and add UV absorbers selected from salicylate esters to carry out After mixing and stirring evenly, an adhesive mixture is obtained;

85 S3: apply the adhesive mixture prepared in step S2 on the substrate layer to obtain a dry glue thickness of the adhesive layer of 20 μ m-50 μ m, and combine the substrate layer on the side coated with the adhesive mixture with the substrate layer The release layer is attached, placed at 30° C-80° C, and aged for no less than 24 hours.

7.

92 A bonding process for a protective tape for a photovoltaic module panel is characterized in that it comprises the following steps:

94 Step 1: Clean the surface of the photovoltaic module to be bonded;

95 Step 2: Use the protective tape for photovoltaic module panels to fully or segmentally bond the cleaned photovoltaic module panels.

8.

100 A bonding process of protective tape for photovoltaic module panels according to claim 7, characterized in that: said step 1 specifically includes the following:

102 Step 1) Place the photovoltaic module panel face up on the working platform, and use vacuum equipment to pre-vacuum the surface of the photovoltaic module panel;

104 Step 2) Dedusting the surface of the photovoltaic module panel with a brush;

105 Step 3) cleaning the surface of the photovoltaic module panel with an organic solvent;

106 Step 4) vacuuming the surface of the photovoltaic module panel with a vacuuming device;

107 Described step 2 specifically includes as follows:

108 Step 1) cutting the photovoltaic module panel into several sheets with protective tape;

109 Step 2) Attach the first sheet to the lower end of the photovoltaic module panel. The short edge of the sheet is laid flat along the long side of the photovoltaic module panel, and the long edge of the sheet is laid flat along the short side of the photovoltaic module panel. Tear off the release layer in the middle, and at the same time stick it with a pressure roller or a scraper, so that the adhesive layer on the half side of the sheet is attached to the photovoltaic module panel, and remove the air bubbles between the adhesive layer and the photovoltaic module panel, repeat The above method completes the lamination of the other half of the sheet, thereby completing the lamination of the first sheet;

116 Step 3) Repeat step 2), and attach the remaining sheets in turn until they are attached to the upper end of the photovoltaic module panel;

118 Step 4) sealing by silica gel or insulating tape between the edge of the sheet and the edge of the parallel adjacent photovoltaic module panel;

120 Adjacent sheets are sequentially overlapped and laminated, and the overlapped width is greater than or equal to 50mm.

9.

125 A bonding process of protective tape for photovoltaic module panels according to claim 7, characterized in that: said step 1 specifically includes the following:

127 Step 1) Place the photovoltaic module panel face up on the working platform, and clean and remove the dust on the surface of the photovoltaic module panel with cleaning solution;

129 Step 2) Spray an appropriate amount of water on the surface of the photovoltaic module panel;

130 Described step 2 specifically includes as follows:

131 Step 1) Cut the protective glue on the photovoltaic module panel into sheets consistent with the size of the photovoltaic module panel;

133 Step 2) After tearing off the release layer of the sheet, align the long side of the sheet with the long side of the photovoltaic module panel on which water is sprayed on the surface, and then spray an appropriate amount of water on the tiled surface again, and use a squeeze scraper Drain the moisture from the sheet and photovoltaic module panel, and after the moisture is driven out, let it stand at room temperature for 24-72h;

137 Step 3) Sealing between the edges around the sheet and the edges of the photovoltaic module panel with silica gel or insulating tape.

10.

142 An application of any protective tape bonding process for photovoltaic module panels according to claims 7-9, characterized in that it is used for on-site bonding or replacement of the protective tape for photovoltaic module panels.



Espacenet

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Single-layer low-transmittance inorganic nano heat insulation film with high weather resistance and high definition and preparation method of single-layer low-transmittance inorganic nano heat insulation film

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Abstract of CN110760273 (A)

The invention discloses a single-layer low-transmittance inorganic nano heat insulation film with high weather resistance and high definition and a preparation method of the single-layer low-transmittance inorganic nano heat insulation film. The heat insulation film is of a layered structure formed by compounding an anti-scraping layer, a pretreated PET (polyethylene glycol terephthalate) base film, a mounting adhesive layer and a release film from top to bottom, wherein the anti-scraping layer is formed by smearing an ultraviolet curing coating; the mounting adhesive layer is formed by smearing a mounting adhesive coating; the ultraviolet curing coating comprises inorganic pigment slurry, ultraviolet curing resin, a photosensitizer, a solvent and the like; the inorganic pigment slurry further comprises at least one inorganic pigment with a low ultraviolet absorption rate in addition to a dispersing agent and a solvent; the mounting adhesive coating further comprises inorganic pigmentslurry in addition to an ultraviolet absorbent, a pressure-sensitive adhesive and a solvent; and the ultraviolet curing resin, the pressure-sensitive adhesive and the solvent must be matched with the dispersing agent on the aspect of compatibility. Through an inorganic pigment

combination with low ultraviolet absorption, a dispersing agent combination and a photosensitizer combination, the single-layer heat insulation film which achieves curing and film formation by ultraviolet light and has high weather resistance and high definition is realized, and the production of the heat insulation film is completed through two coating processes, so that the production cost is greatly reduced.

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DESCRIPTION CN110760273A

¹⁰ Single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition and preparation method thereof

[0001]

¹⁵ technical field

[0002]

¹⁹ The invention relates to a single-layer low-permeability inorganic nano heat insulation film with high weather resistance and high definition and a preparation method thereof, belonging to the technical field of heat insulation window films.

[0003]

²⁵ Background technique

[0004]

²⁹ The low-permeability thermal insulation film has the effect of blocking part of the visible light and infrared energy in sunlight at the same time, and can be used in automobile and building glass to improve comfort and reduce cooling energy consumption.

[0005]

³⁵ Generally speaking, there are two structures of low-permeability thermal insulation films: single-layer base film and double-layer base film, which are realized through two coating processes and three coating processes respectively.

38 In the existing market products, there are two kinds of single-layer base films, one is to form a dye primary color film by implanting dyes into the PET base film, and the other is to form a metal film by plating a metal layer on the PET base film. The single-layer film can be formed into a thermal insulation film through the two processes of coating the anti-scratch layer and installing the adhesive layer.

[0006]

45 Although the coating process is simple, the single-layer dye film has poor weather resistance, a lifespan of 1 to 2 years, and almost no infrared blocking effect.

47 Single-layer metal film also has the problem of high reflectivity of the disclosed single-layer metal film heat insulation film as Chinese patent document CN204296154U, that is, when the visible light transmittance is lower than 35%, its visible light reflectance is greater than 20%, which will cause serious problems. Light pollution and discomfort, and does not meet national standards.

[0007]

54 Nano pigments are divided into organic pigments and inorganic pigments, and their weather resistance is generally much better than dyes.

56 Compared with organic pigments, inorganic pigments also have a certain infrared blocking effect.

57 Chinese patent document CN106965518A discloses a thermal insulation film compounded with carbon black and organic pigments, which has the advantage of good weather resistance. This technology completes product production through the compounding of two transparent base films and three coating processes. Production The cost is high. In addition, because organic pigments are difficult to disperse and stabilize, it is difficult to maintain the clarity of the thermal insulation film continuously and stably in mass production.

62 Chinese patent document CN104789110A discloses a single-layer heat-insulating film prepared from a non-solvent-type UV-curable coating combined with carbon black and organic pigments. Although the problem of weather resistance is solved, the infrared rejection rate of the film is not high. The clarity is not high, that is, the haze is $\approx 2\%$, the UV curing energy demand is high, and it is difficult to ensure that the base film does not deform.

[0008]

70 Chinese patent document CN201210200691 discloses a method of coating a scratch-resistant layer containing inorganic nano-functional materials and an installation adhesive layer containing UV absorbers on both sides of a transparent base film, achieving a high visible light transmittance ($>70\%$) The single-layer inorganic nano heat insulation film with high infrared rejection rate is a production method involving only two coating steps.

74 However, using the same production method to complete the production of inorganic nano-insulation films with a visible light transmittance lower than 45%, it is necessary to solve the problem of dispersion of low-transmittance inorganic nano-pigments and the problem of ultraviolet curing of inorganic nano-pigments in the scratch-resistant layer, and then A single-layer low-transparency inorganic nano-heat insulation film with good weather resistance, high clarity, and moderate infrared blocking performance is obtained.

[0009]

82 Contents of the invention

[0010]

86 In order to solve the deficiencies of the prior art, the invention provides a single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition and a preparation method thereof.

89 In the present invention, through the combination of inorganic nano-pigments, dispersants and photosensitizers with low ultraviolet absorption rate, a single-layer heat-insulating film with high weather resistance and high definition is realized, which solves the problem better. The defective that existing technology exists.

[0011]

96 The purpose of the present invention is achieved through the following technical solutions:

[0012]

100 A single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition. The heat insulation film includes from top to bottom: a scratch-resistant layer formed by coating with UV-curable coatings, and pretreated on both sides. The layered structure formed by the PET base film, the installation adhesive layer formed by the installation adhesive coating and the release film; the haze value of the PET base film is <1%;

[0013]

108 The UV-curable coating includes inorganic nano-pigment slurry, UV-curable resin, photosensitizer, leveling agent and solvent;

[0014]

113 The inorganic nano-pigment slurry includes an inorganic nano-pigment, a dispersant and a solvent, the amount of the dispersant is 50-120% of the inorganic nano-pigment, and the inorganic nano-pigment includes at least one kind of Inorganic nano pigments, the inorganic nano pigments with low ultraviolet absorption rate are inorganic nano materials whose average transmittance is greater than 20% in the range of 280-380nm ultraviolet band when the visible light transmittance is 40%;

[0015]

121 Described installation glue coating comprises ultraviolet absorber, pressure-sensitive adhesive and solvent,

also optionally comprises inorganic nano-pigment slurry;

[0016]

¹²⁶ The solvent includes at least ethyl acetate.

[0017]

¹³⁰ Preferably, the pretreatment of the PET base film includes coating a precoat and corona treatment, and the precoat includes an acrylic layer or a polyurethane (PU) layer.

[0018]

¹³⁵ Preferably, the thickness of the PET base film is 30-100 μm , and the longitudinal heat shrinkage and transverse heat shrinkage of the PET base film are 1.0-1.5% and -0.1-0.5%, respectively.

[0019]

¹⁴⁰ Preferably, the inorganic nano-pigment with low ultraviolet absorption rate is silicon nitride titanium, wherein the silicon doping ratio in silicon nitride titanium is 0-20%.

[0020]

¹⁴⁵ Preferably, the inorganic nano-pigment also includes carbon black, and the weight ratio of the silicon nitride titanium to the carbon black in the scratch-resistant layer or in the UV-curable coating is 1:1 to 1:0.

[0021]

¹⁵⁰ Preferably, the inorganic nano-pigment slurry includes carbon black slurry and silicon nitride titanium slurry, wherein the carbon black slurry includes carbon black, dispersant and solvent, and the particle size of the carbon black is 10-20nm, the amount of dispersant is 50-80% of the weight of carbon black; the silicon nitride titanium slurry includes silicon nitride titanium, dispersant and solvent, the particle diameter of the silicon nitride titanium is 15-35nm, the amount of dispersant It is 60-100% of the weight of silicon nitride titanium.

¹⁵⁶ Described dispersant comprises small molecule dispersant and polymer dispersant, and the molecular weight of described small molecule dispersant <1000, and has acidic group, basic group or acid-basic group, and described polymer dispersant The molecular weight of the product is >3000, and the amine value or acid value is 10-100 mg KOH/g, wherein the proportion of small molecule dispersant is 0-30%, and the proportion of polymer dispersant is 70-100%.

[0022]

164 Preferably, the nano-inorganic pigment slurry also includes cesium-doped tungsten oxide thermal insulation material slurry, the cesium doping ratio in the cesium tungsten oxide is 3-6%, and the particle size of the cesium tungsten oxide is 20-80nm.

[0023]

170 Preferably, the UV-curable resin is an aliphatic urethane acrylate with a molecular weight >1000 and six functional groups or more, and the weight ratio of the UV-curable resin in the UV-curable coating is 20-50%, and the amount of UV-curable resin in the scratch-resistant layer is 1.8-4.5g/m²; the nano-inorganic pigment slurry includes a dispersant compatible with the UV-curable resin, and the dispersion agent is an acrylic ester copolymer dispersant; the leveling agent is a silicon modified copolymer, and the leveling agent is 0.5-2% of the weight of the ultraviolet curable resin.

[0024]

179 Preferably, the dosage of the photosensitizer is 4 to 10% of the UV-curable resin, and the photosensitizer includes photosensitizers that absorb long-wave, medium-wave, and short-wave ultraviolet light, wherein photosensitizers that absorb long-wave ultraviolet light account for 25% to 50% of the total amount of photosensitizers, photosensitizers that absorb mid-wave ultraviolet light account for 20% to 30% of the total amount of photosensitizers, and photosensitizers that absorb short-wave ultraviolet light account for 20% to 55% of the total amount of photosensitizers. %.

[0025]

188 Preferably, the photosensitizer that absorbs long-wave ultraviolet light is (2,4,6-trimethylbenzoyl) diphenylphosphine oxide or phenylbis(2,4,6-trimethylbenzoyl) Phosphine oxide; the photosensitizer that absorbs mid-wave ultraviolet light is 2-hydroxy-2-methyl-1-phenylacetone or 2-benzyl-2-dimethylamino-1-(4-morpholine phenyl) butanone or 2-hydroxy-2-methyl-1-phenylacetone, and the photosensitizer absorbing short-wave ultraviolet light is benzophenone or hydroxycyclohexyl benzophenone.

[0026]

196 Preferably, the weight ratio of the pressure-sensitive adhesive in the installation glue coating is 15-25%, and the pressure-sensitive adhesive is one-component acrylic or two-component acrylic, which is combined with the PET-based The peel strength of the film is 600-800 g/inch, the amount of the pressure-sensitive adhesive in the installation adhesive layer is 5.5-9.5 g/m², and the ultraviolet absorber includes but not limited to hydroxyphenyltriazines, which The dosage in the installation adhesive layer is 0.2-0.6g/m².

[0027]

204 Preferably, the installation glue coating can also include inorganic nano-slurry, the inorganic nano-slurry includes carbon black slurry, and the amount of carbon black in the installation adhesive layer in the carbon

black slurry is 0.0-0.06 g/m².

207 The nano-inorganic pigment slurry includes a dispersant compatible with the pressure-sensitive adhesive, and the dispersant is an acrylic copolymer dispersant.

[0028]

212 The conditions to be followed in the selection of the above polymer dispersant are that it must be compatible with aliphatic urethane acrylate, one-component acrylic compound glue, and solvent ethyl acetate. The polymer dispersant is acrylic acid Ester copolymer dispersant, so as to further ensure the high-definition performance of the heat insulation film, that is, low haze value.

216 When the dispersant layer wrapped on the surface of the nanomaterial is thin, the UV-curable resin or one-component acrylic composite adhesive needs to be compatible with the dispersion composed of the nanomaterial, small molecule dispersant and polymer dispersant in the slurry. Capacitive matching, so wrap a suitable thickness of dispersant layer according to different nanomaterials, that is, the proportion of dispersant is at least greater than 50%, so as to reduce the obstacles brought by the nanomaterial itself in the process of polarity matching.

[0029]

225 Preferably, the preparation method of a single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition may include the following steps:

[0030]

230 S1, selection of release film: select a piece of PET film, one side of which is coated with release silicone oil, and its peel strength is 15-30 g/inch;

[0031]

235 S2, base film selection: choose a transparent PET with a pre-coated pre-coating and a corona-treated corona surface on both sides of the front and back, and a haze of less than 1% as the base film, the pre-coating is PU pre-coating;

[0032]

241 S3, preparation of inorganic nano-pigment slurry: first mix and stir the dispersant and solvent in the pre-mixing tank, then pass it into the grinding chamber of the ball mill for grinding, and gradually add silicon nitride titanium or carbon black, and obtain nitrated pigments after grinding. Silicon titanium slurry or carbon black slurry;

[0033]

248 S4, preparation of U V-curable coating: first add the solvent into the mixing tank, then add the inorganic nano-pigment slurry prepared in S3 during the stirring, and finally add the U V-curable resin, photosensitizer and leveling agent gradually, and stir to prepare U V-curable coatings;

[0034]

254 S5, preparation of the installation glue coating: first add the solvent into the mixing tank, then add the U V absorber or the carbon black slurry prepared by S3 in the stirring, and finally gradually add the pressure sensitive adhesive and stir to make the installation glue coating;

[0035]

260 S6, preparation of the installation adhesive layer: apply the installation adhesive coating prepared in S5 on the corona surface of the PET base film selected in S2 by dimple coating, and compound the coating with the release film selected in S1 after drying in a 100° C oven ;

[0036]

266 S7, preparation of anti-scratch layer: apply the U V-curable coating prepared in S4 on the other side of the base film in the semi-finished product prepared in S6, that is, the PU pre-coating surface, by means of dimple coating, and dry the coating in an oven at 80° C Afterwards, the single-layer low-permeability inorganic nano heat-insulation film of the present invention is obtained through ultraviolet irradiation and curing under a nitrogen atmosphere.

[0037]

274 In the present invention, through the combination of inorganic nano-pigment, dispersant and photosensitizer with low ultraviolet absorption rate, a low-permeability single-layer inorganic nano-heat insulation film cured by ultraviolet light is realized on the transparent PET base film, which has high weather resistance , high definition, fewer coating processes (that is, two coating processes) and other advantages.

[0038]

281 The beneficial effects of the present invention are reflected in: the addition of inorganic nano-pigments in the anti-scratch layer realizes low visible light transmittance and ensures the weather resistance stability of the heat insulation film of the present invention, that is, the stability of ultraviolet resistance and high temperature resistance.

285 Under the condition of a temperature of 80° C, after 10 hours of irradiation with an ultraviolet intensity of 100m W /cm², the average visible light transmittance of the thermal insulation film of the present invention remains substantially unchanged.

[0039]

291 The ultraviolet light curing layer of the present invention adopts the combination of carbon black and silicon nitride titanium, especially silicon nitride titanium material, and its ultraviolet transmittance is higher than that of carbon black and organic pigment, which reduces the energy demand of ultraviolet light curing. Thereby overcoming the problem of deformation of the base film caused by the combination of carbon black and organic pigments in the patent application CN104789110A due to the high demand for ultraviolet energy. In addition, because the combination of small molecules and polymer dispersants is used in the solvent system, it is easy to match UV-curable resins. Therefore, the clarity is also greatly improved compared with the patent application CN104789110A, that is, the haze is increased from $\approx 2\%$ to $\approx 0.15\%$.

299 Compared with the disclosed single-layer metal heat-insulating film of patent application CN204296154U, the present invention has no reflective phenomenon of metal film, i.e. light pollution problem.

301 Compared with the heat-insulating film produced by three coating processes with two PET base films disclosed in the patent application CN106965518A, the present invention greatly reduces the production cost.

[0040]

307 Description of drawings

[0041]

311 Fig. 1: Schematic diagram of the layered structure of the nano heat insulation film of the present invention;

[0042]

315 Figure 2: Spectrogram of transmittance and UV aging of sample 1 in Example 1 of the present invention, wherein during the weather resistance test, the temperature of the test chamber was 80°C , and the intensity of ultraviolet irradiation was 100mW/cm^2 , which was 60 times the energy of ultraviolet rays in sunlight.

[0043]

321 Detailed ways

[0044]

325 The present invention discloses a single-layer low-permeability inorganic nano heat-insulating film with high weather resistance and high definition. As shown in Figure 1, the heat-insulating film is formed from top to bottom by UV-curable coatings. A layered structure formed by a scratch-resistant layer 301, a double-sided pretreated PET base film 302, an installation adhesive layer 303 coated with an installation adhesive paint, and a release film 304.

330 Wherein, the haze value of the PET base film is $<1\%$.

[0045]

- 334 The UV-curable coating includes inorganic nano-pigment paste, UV-curable resin, photosensitizer, leveling agent and solvent.
- 336 Wherein, the inorganic nano-pigment slurry at least includes an inorganic nano-pigment, a dispersant and a solvent.
- 338 Specifically, the amount of the dispersant is 50-120% of the inorganic nano-pigment, and the inorganic nano-pigment includes at least one inorganic nano-pigment with low ultraviolet absorption rate.
- 340 In the present invention, the inorganic nano-pigment with low ultraviolet absorption rate is silicon nitride titanium, wherein the silicon doping ratio in silicon nitride titanium is 0-20%, and the silicon doping in silicon nitride titanium can improve the Dispersing properties while also reducing blue absorption.
- 343 Of course, the inorganic nano-pigment with low ultraviolet absorption rate is not only silicon nitride titanium, as long as the visible light transmittance is 40%, its average transmittance in the range of 280-380nm ultraviolet band is greater than 20%. Inorganic nanomaterials all belong to the protection scope of the present invention.

[0046]

- 349 The inorganic nano-pigments also include carbon black, and the weight ratio of the silicon nitride titanium to the carbon black in the scratch-resistant layer or in the UV-curable coating is 1:1 to 1:0. The adjustment of the ratio of the two can adjust the color of the heat insulation film, such as yellow, yellow green, pure black and blue.
- 353 The inorganic nano-pigment also includes cesium-doped tungsten oxide with high visible light transmittance and high infrared rejection rate, the cesium doping ratio in the cesium tungsten oxide is 3-6%, and the particle size of the cesium tungsten oxide is 20~80nm.

[0047]

- 359 The inorganic nano-pigment slurry includes carbon black slurry and silicon nitride titanium slurry, the carbon black slurry includes carbon black, a dispersant and a solvent, the particle diameter of the carbon black is 10-20nm, and the dispersant The amount is 50-80% of the carbon black weight; the silicon nitride titanium slurry includes silicon nitride titanium, a dispersant and a solvent, wherein the particle size of the silicon nitride titanium is 15-35nm, and the amount of the dispersant is nitrogen 60-100% of the weight of titanium silicon oxide.
- 365 Described dispersant comprises small molecule dispersant and polymer dispersant, and the molecular weight of described small molecule dispersant<1000, and has acidic group, basic group or acid-basic group, and described polymer dispersant The molecular weight is >3000, and the amine value or acid value is 10-100 mg KOH/g, wherein the proportion of small molecule dispersant is 0-30%, and the proportion of polymer dispersant is 70-100%.

[0048]

- 373 The ultraviolet curable resin is an aliphatic urethane acrylate with a molecular weight > 1000 and more than six

functional groups, and its adhesion to the precoat of the base film after ultraviolet curing is better than grade 1.

376 The ultraviolet curable resin forms a good match with the polymer dispersant in the silicon nitride titanium and carbon black slurry, that is, the nano-inorganic pigment has no obvious agglomeration in the scratch-resistant layer, thereby ensuring high clarity. degree, that is, a low haze value <1%, and the dispersant is an acrylic copolymer dispersant.

380 The weight ratio of the UV-curable resin in the UV-curable coating is 20-50%, and the amount of the UV-curable resin in the anti-scratch layer is 1.8-4.5g/m².

[0049]

385 The dosage of the photosensitizer is 4-10% of the ultraviolet curable resin.

386 The photosensitizers include photosensitizers that absorb long-wave, medium-wave, and short-wave ultraviolet light, wherein photosensitizers that absorb long-wave ultraviolet light account for 25% to 50% of the total amount of photosensitizers, and photosensitizers that absorb medium-wave ultraviolet light account for 25% to 50% of the total amount of photosensitizers. 20-30% of the total amount of photosensitizers, and photosensitizers that absorb short-wave ultraviolet light account for 20-55% of the total amount of photosensitizers.

392 The photosensitizer that absorbs long-wave ultraviolet light in the present invention is (2,4,6-trimethylbenzoyl) diphenylphosphine oxide or phenylbis(2,4,6-trimethylbenzoyl) Phosphine oxide; The photosensitizer that absorbs mid-wave ultraviolet light is 2-hydroxyl-2-methyl-1-phenylacetone or 2-benzyl-2-dimethylamino-1-(4-morpholine phenyl) butanone, the photosensitizer absorbing short-wave ultraviolet light is benzophenone or hydroxycyclohexyl benzophenone.

397 The combination of multiple photosensitizers can fully match the absorption spectrum of carbon black and titanium silicon nitride, and then make better use of the remaining ultraviolet energy to achieve complete curing, reduce the energy demand for ultraviolet curing, and reduce the deformation of the base film caused by excessive temperature.

[0050]

404 The leveling agent is a silicon modified copolymer, and the leveling agent is 0.5-2% by weight of the ultraviolet curable resin.

[0051]

409 In addition to the UV absorber, pressure-sensitive adhesive and solvent, the installation glue coating can also include inorganic nano-slurry, and the inorganic nano-slurry includes carbon black slurry, and carbon black is present in the carbon black slurry. The dosage in the installation adhesive layer is 0.0~0.06g/m².

412 Wherein, the ultraviolet absorber includes but is not limited to hydroxyphenyltriazines, and its dosage in the installation adhesive layer is 0.2-0.6 g/m².

414 The weight ratio of the pressure-sensitive adhesive in the installation adhesive coating is 15-25%.

415 The pressure-sensitive adhesive is a one-component acrylic ester, and its peel strength with the PET base film

is 600–800 g/inch, and the amount of the pressure-sensitive adhesive in the installation adhesive layer is 5.5–9.5 g / m².

418 The polymer dispersant in the carbon black slurry forms a good match with the one-component acrylic composite adhesive to ensure that the heat insulation film has a suitable clarity, and the dispersant is an acrylic copolymer dispersed agent.

[0052]

424 The solvent includes at least ethyl acetate.

[0053]

428 The pretreatment of described PET base film comprises precoat precoat and corona treatment, and described precoat comprises acrylic layer or polyurethane layer.

430 In order to ensure that the adhesion between the ultraviolet curable resin, the inorganic nano-slurry and the PET base film is better than grade 1, the preferred PU pretreatment of the pre-coating layer.

432 At the same time, the ease of construction of the heat insulation film requires that the heat shrinkage rate of the PET base film is relatively large. Thermal shrinkage deformation, therefore, in order to meet the requirements of both, the longitudinal thermal shrinkage rate and transverse thermal shrinkage rate of the PET base film are respectively 1.0–1.5% and -0.1–0.5%.

436 The thickness of the PET base film is generally 30–100 μm, preferably 30–50 μm in order to further provide good workability.

[0054]

441 The preparation method of the above-mentioned single-layer low-permeability inorganic nano-heat insulation film specifically includes the following steps:

[0055]

446 S1, release film selection: select a 23 μm thick PET film, one side of which is coated with release silicone oil, and its peel strength is 15–30 g/inch;

[0056]

451 S2, base film selection: select a piece of transparent PET which has been precoated and corona treated on both sides, and the haze is less than 1% as the base film, and the precoated precoat is PU precoat;

[0057]

456 S3, preparation of inorganic nano-pigment slurry: first mix and stir the dispersant and solvent in the pre-mixing tank, then pass it into the grinding chamber of the ball mill for grinding, and gradually add silicon

nitride titanium or carbon black, and obtain nitrated pigments after grinding. Silicon titanium slurry or carbon black slurry;

[0058]

463 S4, preparation of UV-curable coating: first add the solvent into the mixing tank, then add the inorganic nano-pigment slurry prepared in S3 during the stirring, and finally add the UV-curable resin, photosensitizer and leveling agent gradually, and stir to prepare UV-curable coatings;

[0059]

469 S5, preparation of the installation glue coating: first add the solvent into the mixing tank, then add the UV absorber or the carbon black slurry prepared by S3 in the stirring, and finally gradually add the pressure sensitive adhesive and stir to make the installation glue coating;

[0060]

475 S6, preparation of the installation adhesive layer: apply the installation adhesive coating prepared in S5 on the corona surface of the PET base film selected in S2 by dimple coating method, and the coating is dried in a 100° C oven and then combined with the release film prepared in S1 complex;

[0061]

481 S7, preparation of anti-scratch layer: apply the UV-curable coating prepared in S4 on the other side of the base film in the semi-finished product prepared in S6, that is, the PU pre-coating surface, by means of dimple coating, and dry the coating in an oven at 80° C Afterwards, under a nitrogen atmosphere, it is irradiated and cured by ultraviolet rays to obtain the single-layer inorganic nano heat-insulating film with low light transmittance of the present invention.

[0062]

489 Example 1

[0063]

493 Release film selection: Select a silicone oil release film with a release force of 20 g/inch.

[0064]

497 Base film selection: select a 38 μ m thick PET base film with a haze of less than 1%, and its longitudinal and transverse thermal shrinkage rates are 1.2% and 0.2% respectively.

499 The base film is corona treated on one side and pre-coated with PU on the other side.

[0065]

503 Preparation of silicon nitride titanium slurry: Weigh 10 parts of silicon nitride titanium with a particle size of 20nm (the doping ratio of silicon is 5%), 2 parts of a small molecule dispersant with a molecular weight of 800, and a polymer dispersion with a molecular weight of 5000. 7 parts of dispersant and 81 parts of ethyl acetate, first mix the dispersant and solvent in the premix tank for 15 minutes, then gradually add silicon nitride titanium, stir at 500RPM for 30 minutes, and finally circulate into 8 Grinding in the grinding chamber of a ball mill, with a linear speed of 10 m/s, after 36 hours of grinding, 40 kg of silicon nitride titanium slurry was obtained.

[0066]

513 Preparation of carbon black slurry: Take 10 parts of carbon black with a particle diameter of 15nm, 1 part of a small molecule dispersant with a molecular weight of 800, 6.50 parts of a polymer dispersant with a molecular weight of 5000, and 82.50 parts of ethyl acetate. Mix and stir with the solvent in the pre-mixing tank for 15 minutes, then gradually add carbon black, stir at 500RPM for 45 minutes, and finally circulate through the pneumatic diaphragm pump into the grinding chamber of the 8-liter ball mill for grinding, at a line speed of 10m/s, After 24 hours of grinding, 35kg of carbon black slurry was obtained.

[0067]

522 Preparation of UV-curable coating: Weigh 6.30 parts of silicon nitride titanium slurry, 3.42 parts of carbon black slurry, 32.50 parts of hexafunctional aliphatic polyurethane acrylic resin with a molecular weight of 1000, silicon-modified copolymer leveling agent 0.42 parts, 0.81 parts of 2-hydroxy-2-methyl-1-phenylacetone, 0.49 parts of 2-hydroxy-2-methyl-1-phenylacetone, phenylbis(2,4,6-trimethyl Benzoyl) phosphine oxide 0.41 parts, ethyl acetate 55.65 parts.

527 First add the solvent into the mixing tank, then add the silicon nitride titanium slurry and the carbon black slurry respectively, stir at 300RPM for 5 minutes, then gradually add the rest of the materials, and stir at 500RPM for 30 minutes to obtain the required UV curable coatings.

[0068]

533 Preparation of mounting glue coating: Weigh 1.16 parts of hydroxyphenyltriazine UV absorber, 53.53 parts of one-component acrylic pressure-sensitive adhesive (34% solid content), 42.08 parts of ethyl acetate, and 3.23 parts of propylene glycol methyl ether acetate.

536 First add the solvent to the mixing tank, then add the carbon black slurry and UV absorber, stir at 300RPM for 10 minutes, then gradually add the pressure-sensitive adhesive, stir at 500RPM for 45 minutes to make the installation glue coating.

[0069]

542 Preparation of single-layer low light transmittance inorganic nano heat-insulating film: first, apply the above-mentioned installation glue coating on the corona surface of the above-mentioned selected PET base film by dimple coating method, and dry the coating in an oven at 100° C for 1 minute. Finally, a 6.3 μ m thick installation adhesive layer is formed, and then compounded with the release film.

546 On this semi-finished product, the above-mentioned UV-curable coating is coated on the PU pre-coating surface of the PET base film in the semi-finished product by dimple coating. The coating is dried in an oven at 80° C for 1 minute to form a 3.5 μ m thick anti-Scratch layer, under the conditions of nitrogen atmosphere and coating speed 23m/min, irradiated and cured by 110 W/cm high-pressure mercury lamp to prepare the low-permeability nano-metal thermal insulation film sample 1 of the present invention.

551 The color of sample 1 is black to bluish, and the UV transmittance of the anti-scratch layer at 280nm-380nm is 17.8% (see Table 1).

553 The adhesion of sample 1 on the PU precoated surface of PET base film is 0 level, and under the situation of load 500g, through 0000# steel wool reciprocating friction 60 times, its surface basically has no obvious scratches.

[0070]

559 For the convenience of optical and aging tests, the release film of sample 1 can be removed and attached to a glass slide with a thickness of 3mm.

561 After testing, the optical properties of the sample 1 are shown in Table 1 and Fig. 2, and its 400nm-700nm visible light transmittance is 41.1%, and its haze is 0.13%.

563 UV Aging Properties of Sample 1 As shown in Figure 2, after 10 hours of 100m W/cm² UV irradiation at a temperature of 80° C, its optical properties remain basically unchanged and it has good weather resistance.

[0071]

568 Example 2

[0072]

572 Preparation of UV-curable coating: Weigh 6.55 parts of silicon nitride titanium slurry, 6.55 parts of carbon black slurry, 32.32 parts of hexafunctional aliphatic polyurethane acrylic resin with a molecular weight of 1000, silicon-modified copolymer flow 0.42 parts of leveling agent, 0.75 parts of 2-hydroxy-2-methyl-1-phenylacetone, 0.49 parts of 2-hydroxy-2-methyl-1-phenylacetone, 0.49 parts of phenyl bis(2,4,6-tri 0.46 parts of methylbenzoyl) phosphine oxide and 52.46 parts of ethyl acetate.

577 First add the solvent to the mixing tank, then add silicon nitride titanium slurry and carbon black slurry respectively, stir at 300RPM for 5 minutes, then add the rest of the materials, stir at 500RPM for 30 minutes to obtain the required UV Light-curing coatings.

[0073]

583 In Example 2, except for the UV-curable coating, other coatings and materials are the same as in Example 1.

584 Sample 2 was prepared by the same method as described in Example 1.
585 The carbon black content of sample 2 is increased, and its color is yellowish.
586 After testing, the optical properties of sample 2 are shown in Table 1. The visible light transmittance of 400nm-700nm is 41.4%, the ultraviolet transmittance of 280nm-380nm is 16.4%, and the haze is 0.12%.
588 Although the UV light transmittance of the UV-cured coating of Sample 2 has declined somewhat, the adhesion and abrasion resistance of the scratch-resistant layer are basically consistent with Sample 1. The photosensitizer ratio and UV-cured strength in Example 1 are explained above. There is still some margin.

[0074]

594 Example 3

[0075]

598 Preparation of UV-curable coating: Weigh 10.35 parts of silicon nitride titanium slurry prepared in Example 1, 3.53 parts of carbon black slurry, 31.98 parts of hexafunctional aliphatic polyurethane acrylic resin with a molecular weight of 1000, silicon-modified copolymer 0.42 parts of logistics leveling agent, 0.73 parts of 2-hydroxy-2-methyl-1-phenylacetone, 0.50 parts of 2-hydroxy-2-methyl-1-phenylacetone, phenyl bis(2,4,6-Trimethylbenzoyl) phosphine oxide 0.61 parts, ethyl acetate 51.88 parts.
603 First add the solvent into the mixing tank, then add the silicon nitride titanium slurry and carbon black slurry respectively, stir at 300RPM for 5 minutes, and finally add the rest of the materials and stir at 500RPM for 30 minutes to obtain the required UV curing coating.

[0076]

609 Preparation of the mounting glue coating: take by weighing 0.56 parts of the carbon black slurry prepared in Example 1, take by weighing 1.16 parts of the hydroxyphenyltriazine class UV absorber, 53.53 parts of the one-component acrylic pressure-sensitive adhesive (34% solid content), 41.52 parts of ethyl acetate, 3.23 parts of propylene glycol methyl ether acetate.
613 First add the solvent to the mixing tank, then add the carbon black slurry and UV absorber and stir at 300RPM for 10 minutes, then gradually add the pressure-sensitive adhesive and stir at 500RPM for 45 minutes to make the installation glue coating.

[0077]

619 In embodiment 3, except that UV-curable coating and installation glue coating, all the other materials are identical with embodiment 1.
621 Sample 3 was prepared by the same method as described in Example 1, and its optical performance parameters are shown in Table 1.
623 In order to realize a product with a visible light transmittance of 25%, in Example 3, carbon black inorganic nano-pigments are added to the mounting adhesive layer, so that the UV transmittance of the scratch-resistant layer can also be maintained at about 13%, as shown in Table 1. Moderately adjust the ratio of

photosensitizer, under the same U V curing conditions, the adhesion and wear resistance of the scratch-resistant layer of sample 3 are basically the same as those of samples 1 and 2, and its color is also consistent with sample 1, that is, black to bluish.

[0078]

632 In the above-mentioned embodiments 1, 2 and 3, cesium tungsten oxide nano-slurry can be added to the U V-curable coating, which can further increase the infrared rejection rate to more than 90%, and the rest of the preparation process will not be repeated here.

[0079]

638 Comparative Example 1

[0080]

642 Preparation of U V-curable coating: Weigh 11.98 parts of carbon black slurry prepared in Example 1, 32.30 parts of hexafunctional aliphatic polyurethane acrylic resin, 0.42 parts of silicon-modified copolymer leveling agent, 2-hydroxy-2-methyl-0.73 parts of 1-phenylacetone, 0.50 parts of 2-hydroxy-2-methyl-1-phenylacetone, 0.61 parts of phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, ethyl acetate 53.43 parts of esters.

647 First add the solvent into the mixing tank, then add the carbon black slurry and stir at 300RPM for 5 minutes, and finally add the rest of the materials and stir at 500RPM for 30 minutes to obtain the desired U V-curable coating.

[0081]

653 In Comparative Example 1, except for the U V-curable coating, all the other coatings and substrates are the same as in Example 1.

655 Comparative Example Sample 1 was prepared in the same manner as described in Example 1.

656 The ultraviolet transmittance of the anti-scratch layer of comparative implementation sample 1 is 7.7%.

Although the ratio between the photosensitizers is optimized, it is difficult to fully ensure the surface and deep layers of the anti-scratch layer under the curing conditions of a high-pressure mercury lamp of 110 W/cm.

Curing, so the adhesion and wear resistance are not ideal.

660 If the curing ultraviolet energy is increased, the deformation problem of the PET base film needs to be solved.

661 Therefore, if carbon black is used to achieve about 30% of the product in the scratch-resistant layer, it is more feasible to adopt segmented curing, that is, to arrange two ultraviolet high-pressure mercury lamps when the distance between the cold drums is large enough.

[0082]

667 Comparative Example 2

[0083]

671 Preparation of UV-curable coating: Weigh 15.00 parts of the silicon nitride titanium slurry prepared above, 32.20 parts of hexafunctional aliphatic polyurethane acrylic resin, 0.42 parts of silicon-modified copolymer leveling agent, 2-hydroxy-2-methyl-0.74 parts of 1-phenylacetone, 0.51 parts of 2-hydroxy-2-methyl-1-phenylacetone, 0.61 parts of phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, ethyl acetate 50.54 parts of esters.

676 First add the solvent into the mixing tank, then add the silicon nitride titanium slurry and stir at 300RPM for 5 minutes, and finally add the rest of the materials and stir at 500RPM for 30 minutes to obtain the desired UV-curable coating.

[0084]

682 In Comparative Example 2, except for the UV-curable coating, all the other coatings and substrates are the same as in Example 1.

684 Comparative Example Sample 2 was prepared in the same manner as described in Example 1.

685 The visible light transmission of the anti-scratch layer of comparative example sample 2 is 31.6%, because it does not have carbon black, the ultraviolet transmittance of its anti-scratch layer is 16.8% (see table 1), like this, with the photosensitizer of embodiment sample 3 Formulated to produce products with transmittance as low as 30%, while increasing production speed by 25%.

[0085]

692 The present invention selects inorganic nano-pigments with low ultraviolet absorption, and realizes a single-layer low-transparency inorganic pigment with good weather resistance and high clarity through the combination of inorganic nano-pigments, dispersant combination and matching, and photosensitizer combination optimization. Nano insulation film.

696 Although only a product with a visible light transmittance as low as 25% has been realized in the embodiment, by optimizing the layout of the high-pressure mercury lamp, a single-layer low-transmittance inorganic nano-heat insulation film with a transmittance of about 15% can also be realized. forms are within the invention.

[0086]

703 Table 1: Comparison of optical properties between the samples of the examples of the present invention and the samples of comparative examples

[0088]

708 Finally, it should be noted that: the above embodiments are only used to illustrate the technical solutions of the present invention, rather than to limit them; although the present invention has been described in detail

with reference to the foregoing embodiments, those of ordinary skill in the art should understand that: it can still be Modifications are made to the technical solutions described in the foregoing embodiments, or equivalent replacements are made to some of the technical features; and these modifications or replacements do not make the essence of the corresponding technical solutions deviate from the spirit and scope of the technical solutions of the various embodiments of the present invention.

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CLAIMS CN110760273A

1.

- 13 A single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition is characterized in that: the heat insulation film includes from top to bottom: a scratch-resistant layer formed by coating UV-cured coatings, double-sided warp The pretreated PET base film, the layered structure formed by the installation adhesive layer formed by the installation glue coating and the release film; the haze value of the PET base film is <1%;
- 18 The UV-curable coating includes: inorganic nano-pigment slurry, UV-curable resin, photosensitizer, leveling agent and solvent;
- 20 The inorganic nano-pigment slurry includes an inorganic nano-pigment, a dispersant and a solvent, the amount of the dispersant is 50-120% of the inorganic nano-pigment, and the inorganic nano-pigment includes at least one Inorganic nano-pigments, the inorganic nano-pigments with low ultraviolet absorption rate are inorganic nano-materials whose average ultraviolet transmittance in the range of 280-380nm wave band is greater than 20% when the visible light transmittance is 40%;
- 25 The installation glue coating includes UV absorber, pressure sensitive adhesive and solvent, and also optionally includes inorganic nano-pigment slurry;
- 27 The solvent includes at least ethyl acetate, and the UV-curable resin, pressure-sensitive adhesive and solvent must match the compatibility of the dispersant.

2.

- 32 The single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition according to claim 1, characterized in that: the pretreatment of the PET base film includes coating precoating and corona treatment, and the pretreatment Coatings include acrylic or polyurethane layers.

3.

38 The single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition according to claim 2, characterized in that: the thickness of the PET base film is 30-100 μm , and the longitudinal thermal shrinkage rate of the PET base film and transverse thermal shrinkage are 1.0 to 1.5% and 0.1 to 0.5% respectively.

4.

45 The single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition according to claim 1, wherein the inorganic nano-pigment with low ultraviolet absorption rate is silicon nitride titanium, wherein silicon nitride titanium The silicon doping ratio is 0-20%.

5.

51 The single-layer low-permeability inorganic nano heat-insulating film with high weather resistance and high definition according to claim 1, characterized in that: the inorganic nano pigment also includes carbon black, and the silicon nitride titanium and the carbon black The weight ratio of the anti-scratch layer or in the UV-curable coating is 1:1 ~ 1:0.

6.

58 The single-layer low-permeability inorganic nano-insulation film with high weather resistance and high definition according to claim 1, wherein the inorganic nano-pigment slurry includes carbon black slurry and silicon nitride titanium slurry, wherein the The carbon black slurry includes carbon black, a dispersant and a solvent, the particle diameter of the carbon black is 10-20nm, and the amount of the dispersant is 50-80% of the weight of the carbon black; the silicon nitride titanium slurry includes Silicon titanium, dispersant and solvent, the particle size of the silicon nitride titanium is 15-35nm, the amount of dispersant is 60-100% of the weight of silicon nitride titanium, the dispersant includes small molecule dispersant and polymer dispersant agent, the molecular weight of the small molecule dispersant is <1000, and has an acidic group, a basic group, or an acid-base group, and the molecular weight of the polymeric dispersant is >3000, and has an amine value or an acid value of 10-100 mg KOH/g, the proportion of small molecule dispersant is 0-30%, and the proportion of polymer dispersant is 70-100%.

7.

72 The single-layer low-permeability inorganic nano heat insulation film with high weather resistance and high definition according to claim 6, wherein the inorganic nano pigment slurry also includes cesium tungsten oxide slurry, and the cesium tungsten oxide slurry The cesium doping ratio of cesium tungsten oxide is 3-6%, and the particle size of cesium tungsten oxide is 20-80nm.

8.

79 The single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high

definition according to claim 1, characterized in that: the ultraviolet curable resin is an aliphatic urethane acrylate with a molecular weight > 1000 and six functional groups or more. The weight ratio of the UV-curable resin in the UV-curable coating is 20-50%, and the amount of the UV-curable resin in the scratch-resistant layer is 1.8-4.5g/m²; the nano inorganic pigment slurry includes a dispersant compatible with the UV curable resin, the dispersant is an acrylic copolymer dispersant; the leveling agent is a silicon-modified copolymer, and the leveling agent is 0.5-2% of the weight of the ultraviolet curable resin.

9.

⁸⁹ The single-layer low-permeability inorganic nano heat insulation film with high weather resistance and high definition according to claim 1, wherein the dosage of the photosensitizer is 4-10% of the UV curable resin, and the photosensitizer The photosensitizers include photosensitizers that absorb long-wave, medium-wave, and short-wave ultraviolet light, wherein photosensitizers that absorb long-wave ultraviolet light account for 25 to 50% of the total amount of photosensitizers, and photosensitizers that absorb medium-wave ultraviolet light account for 25% to 50% of the total amount of photosensitizers. The photosensitizer absorbing short-wave ultraviolet light accounts for 20-55% of the total amount of the photosensitizer.

10.

⁹⁹ The single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition as claimed in claim 9, wherein the photosensitizer absorbing long-wave ultraviolet light is (2,4,6-trimethylbenzene Acyl) diphenyl phosphine oxide or phenyl bis (2,4,6-trimethylbenzoyl) phosphine oxide; the photosensitizer that absorbs mid-wave ultraviolet light is 2-hydroxyl-2-methyl-1-Phenylacetone or 2-benzyl-2-dimethylamino-1-(4-morpholine phenyl) butanone, the photosensitizer absorbing short-wave ultraviolet light is benzophenone or hydroxycyclohexylbenzene ketone.

11.

¹⁰⁸ The single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition according to claim 1, characterized in that: the weight ratio of the pressure-sensitive adhesive in the installation adhesive coating is 15-25%, so The pressure-sensitive adhesive is a one-component acrylic ester, and its peel strength with the PET base film is 600-800 g/inch, and the amount of the pressure-sensitive adhesive in the installation adhesive layer is 5.5-9.5 g/inch. m², the ultraviolet absorber includes but not limited to hydroxyphenyltriazines, and its dosage in the installation adhesive layer is 0.2-0.6 g/m².

12.

¹¹⁷ The single-layer low-permeability inorganic nano heat-insulating film with high weather resistance and high definition according to claim 11, characterized in that: the installation glue coating also includes inorganic nano pigment slurry, and the inorganic nano pigment slurry includes carbon Black slurry, the amount of carbon black in the installation adhesive layer in the carbon black slurry is 0.0-0.06g/m², and the nano-inorganic pigment slurry includes a material compatible with the pressure-sensitive adhesive A matching

dispersant, the dispersant is an acrylate copolymer dispersant.

13.

126 The preparation method of a single-layer low-permeability inorganic nano-heat insulation film with high weather resistance and high definition is characterized in that it includes the following steps:

128 S1, selection of release film: select a piece of PET film, one side of which is coated with release silicone oil, and its peel strength is 15-30 g/inch;

130 S2, base film selection: select a piece of transparent PET with pre-coating treatment and corona treatment on both sides and haze less than 1% as the base film, and the pre-coating layer is a PU pre-coating layer;

132 S3, preparation of inorganic nano-pigment slurry: first mix and stir the dispersant and solvent in the pre-mixing tank, then pass it into the grinding chamber of the ball mill for grinding, and gradually add silicon nitride titanium or carbon black, and obtain nitrated pigments after grinding. Silicon titanium slurry or carbon black slurry;

136 S4, preparation of UV-curable coating: first add the solvent into the mixing tank, then add the inorganic nano-pigment slurry prepared in S3 during the stirring, and finally add UV-curable resin, photosensitizer and leveling agent gradually, and make it after stirring UV-curable coatings;

139 S5, preparation of installation glue paint: firstly add solvent into the mixing tank, then add UV absorber or carbon black slurry prepared by S3 during stirring, finally add pressure sensitive adhesive gradually and stir to make installation glue paint;

142 S6, preparation of the installation adhesive layer: apply the installation adhesive coating prepared in S5 on the corona surface of the PET base film selected in S2 by dimple coating, and compound the coating with the release film selected in S1 after drying in a 100° C oven ;

145 S7, preparation of anti-scratch layer: apply the UV-curable coating prepared in S4 on the other side of the base film in the semi-finished product prepared in S6, that is, the PU pre-coating surface, by means of dimple coating, and dry the coating in an oven at 80° C Afterwards, under a nitrogen atmosphere, it is irradiated and cured by ultraviolet rays to obtain the single-layer inorganic nano heat-insulating film with low light transmittance of the present invention.

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Preparation method of room-temperature phosphorescent benzoate compound

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Abstract of CN109956869 (A)

The invention relates to a room-temperature phosphorescent benzoate compound. The benzoate compound is prepared by an efficient one-step method, and the prepared benzoate compound has obvious phosphorescence at room temperature, thereby broadening the application range of the benzoate compound. The product can be widely applied to phosphorescent materials.

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DESCRIPTION CN109956869A

10 A kind of preparation method of room temperature phosphorescent benzoate compound

[0001]

14 technical field

[0002]

18 The invention relates to a preparation method of a series of room-temperature phosphorescent benzoate compounds, belonging to the field of organic light-emitting materials.

[0003]

23 Background technique

[0004]

27 Phosphorescent materials and fluorescent materials are two common light-emitting materials.

28 From the point of view of the generation mechanism, the generation of fluorescence and phosphorescence is produced by the spontaneous emission of the material transition from the excited state.

[0005]

33 For some defective and complex inorganic crystal substances, light can be emitted within a certain period of time when the light is excited and after the light is stopped, and these crystals are called phosphorescent materials.

36 Compared with fluorescent materials, phosphorescent materials have the following advantages:

[0006]

40 First, it has a larger Stokes displacement, can effectively avoid the interference of excitation light, and has the advantage of strong anti-light interference ability;

[0007]

45 Second, through the intersystem crossing process, the phosphorescent material has a longer luminous lifetime;

[0008]

49 Third, because phosphorescence has a long luminescence lifetime, it can avoid the interference of short-lived fluorescence or scattered light, thereby obtaining a lower detection limit.

[0009]

54 At present, phosphorescent materials have been widely used in RGB anti-counterfeiting, biological imaging and other fields.

56 However, many materials can only exhibit phosphorescent properties at low temperature or doped with heavy metals such as iridium and platinum, which greatly limits the application of phosphorescent materials.

58 Organic room-temperature phosphorescent materials can just overcome these limitations.

59 Academician Tang Benzhong and others first used the confined environment of crystals to realize small molecule organic room temperature phosphorescence (Yuan W Z, Shen X Y, Zhao H, et al. J Phys Chem C, 2010, 114:6090 – 6099), and then Kim et al. used heavy atoms Effects and crystal design Emission of room-temperature phosphorescence with tunable orange, yellow, blue, green and other colors (Bolton O, Lee K, Kim H J, et al. Nat Chem, 2011, 3:201 – 210), 2015 An et al. used N, O, and P atoms to design phosphorescent materials with ultra-long phosphorescence lifetimes (An Z F, Zheng C, Tao Y, et al.

65 Nat Mater, 2015, 14:685 – 690).

66 The structure of the above phosphorescent material system is complex, the synthesis is difficult, and the cost is correspondingly high; therefore, in the prior art, it is an urgent technical problem to be solved in the field to find a room temperature phosphorescent material that is easy to prepare and low in cost.

[0010]

72 Contents of the invention

[0011]

76 The invention provides an easy-to-synthesize and low-cost room-temperature phosphorescent benzoate material and a preparation method thereof.

[0012]

81 In order to solve the problems of the technologies described above, the present invention is achieved through the following technical solutions:

[0013]

86 A room temperature benzoic acid ester compound has the following general formula:

[0015]

90 $X = H, CH_3, CH=CH_2, C \equiv CH, F, Cl, Br, I;$

[0016]

94 2, 5 substitutions, $R_2=R_3=H, R_1=R_4=COOC_nH_{2n+1}, n=1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18;$ or,

[0017]

98 3, 5 substitutions, $R_1=R_3=H, R_2=R_4=COOC_nH_{2n+1}, n=1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18;$ or,

[0018]

102 3, 4 substitutions, $R_1=R_4=H, R_2=R_3=COOC_nH_{2n+1}, n=1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18.$

[0019]

106 The present invention also discloses a preparation method of the above-mentioned compound, comprising the following steps:

[0021]

111 $n=1, 2;$

[0023]

115 $n=3, 4, 5, 6, 8, 10, 12, 14, 16, 18;$

[0024]

119 or

[0026]

¹²³ n=1,2;

[0027]

¹²⁷ or

[0029]

¹³¹ n=3, 4, 5, 6, 8, 10, 12, 14, 16, 18;

[0031]

¹³⁵ n=1,2;

[0033]

¹³⁹ n=3, 4, 5, 6, 8, 10, 12, 14, 16, 18.

[0034]

¹⁴³ The invention also discloses a room-temperature phosphorescent additive, which comprises the above-mentioned benzoic acid ester compound.

[0035]

¹⁴⁸ High molecular compounds are also included.

[0036]

¹⁵² Preferably, in parts by weight, the polymer compound is 100 parts, and the benzoic acid ester compound is 5-0.0001 parts.

[0037]

¹⁵⁷ Benzoic acid ester compound is 1-0.005 part, preferably 0.1-0.01 part.

[0038]

¹⁶¹ The polymer is one or more of polystyrene, polyethylene, polymethyl methacrylate, polyvinyl alcohol, polydimethylsiloxane, polyvinyl acetate, polyester and nylon.

[0039]

166 More preferably, the benzoate compound is didecyl 5-bromoisophthalate, and the polymer is nylon;

[0040]

170 The benzoate compound is 5-bromodidecyl isophthalate, and the polymer is polystyrene;

[0041]

174 The benzoic acid ester compound is 5-bromodidecyl isophthalate, and the polymer is polyvinyl alcohol.

[0042]

178 Described nylon is nylon 6, and the weight ratio of described nylon 6 and 5-bromodidecyl isophthalate is 99.9:0.1;

[0043]

183 The weight ratio of polystyrene and 5-bromodidecyl isophthalate is 100:1;

[0044]

187 The weight ratio of the polyvinyl alcohol to didecyl 5-bromoisophthalate is 100:1.

[0045]

191 The present invention further discloses a method for preparing the above-mentioned phosphorescent material, which includes the following steps:

[0046]

196 Dissolving the polymer with a solvent to obtain a first solution;

[0047]

200 Utilize the same solvent to dissolve the benzoic acid ester compound to obtain a second solution;

[0048]

204 Add the second solution to the first solution under stirring, and mix well;

[0049]

208 Dry the mixed solution and remove the solvent;

[0050]

212 The weight ratio of the solvent to the benzoate compound is (0.1-50):1.

[0051]

216 Wherein, the solvent is one or more of chloroform, tetrahydrofuran, dichloromethane, hexafluoroisopropanol, benzene, toluene, acetone, and dioxane.

[0052]

221 Another preparation method of the phosphorescent material comprises the following steps: at 70° C-300° C, mixing and melting the polymer and the benzoate compound, and stirring evenly.

[0053]

226 The present invention further discloses the use of the above-mentioned benzoic acid ester compound and the polymer compound as an additive for room-temperature phosphorescent materials.

[0054]

231 The above technical solution of the present invention has the following advantages compared with the prior art:

[0055]

236 The room-temperature benzoate compound of the present invention adopts an efficient one-step method to prepare benzoate compound, so that the prepared benzoate compound has obvious phosphorescence phenomenon at room temperature, thereby expanding the scope of benzoate compound. The range of applications can be widely used in phosphorescent materials.

[0056]

243 At the same time, by selecting a suitable polymer material, the benzoate compound and the polymer compound work together to form a better room temperature phosphorescent material, which further broadens the application of the benzoate compound.

[0057]

249 Description of drawings

[0058]

253 In order to make the content of the present invention more easily understood, the following will be further described in detail in conjunction with the accompanying drawings, wherein

[0059]

258 Fig. 1 is the phosphorescence test spectrogram of methyl bromoisophthalate series compound;

[0060]

262 Fig. 2 is the photoluminescence spectrum and the phosphorescence spectrum of 5-bromodidecyl isophthalate;

[0061]

267 Fig. 3 is the phosphorescent lifetime decay curve of 5-bromo-didecyl isophthalate;

[0062]

271 Fig. 4 is the long afterglow picture of 5-bromodidecyl isophthalate after removing the excitation light source;

[0063]

275 Fig. 5 is the photoluminescence spectrum and the phosphorescence spectrum of 5-methyldidecyl isophthalate;

[0064]

280 Fig. 6 is the phosphorescent lifetime decay curve of 5-methyldidecyl isophthalate;

[0065]

284 Fig. 7 is the photoluminescence spectrum and the phosphorescence spectrum of 2-bromodidecyl terephthalate;

[0066]

289 Fig. 8 is the phosphorescent lifetime decay curve of 2-bromodidecyl terephthalate;

[0067]

293 Fig. 9 is the photoluminescence and phosphorescence spectrum of 5-bromodidecyl isophthalate and polystyrene blend material;

[0068]

298 Figure 10 is the photoluminescence and phosphorescence spectra of 5-bromodidecyl isophthalate and polyvinyl alcohol blend material;

[0069]

303 Fig. 11 is the phosphorescence spectrum of decyl p-bromobenzoate and 5-bromodidecyl isophthalate;

[0070]

307 Figure 12 is the photoluminescence and phosphorescence spectra of polystyrene at room temperature;

[0071]

311 Figure 13 is the photoluminescence and phosphorescence spectra of polyvinyl alcohol at room temperature.

[0072]

315 Detailed ways

[0073]

319 In order to better understand the present invention, the present invention will be described in detail below in conjunction with examples.

[0074]

324 The present invention provides a kind of benzoic acid ester compound, and the general formula of this compound is shown in following formula (1):

[0076]

329 Wherein, X=H, CH₃, CH=CH₂, C≡CH, F, Cl, Br, I;

[0077]

333 For the substitution options of R1, R2, R3, R4, the present invention provides the structure shown in the following formula (2)-(4):

[0078]

338 2, 5 substitutions, the following formula (2), that is, select $R_2=R_3=H$ in formula (1), $R_1=R_4=COOC_nH_{2n+1}$, $n=1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18$;

[0081]

343 3, 5 substitutions, the following formula (3), that is, select $R_1=R_3=H$ in formula (1), $R_2=R_4=COOC_nH_{2n+1}$, $n=1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18$;

[0083]

348 3, 4 substitutions, as follows formula (4), select $R_1=R_4=H$ in formula (1), $R_2=R_3=COOC_nH_{2n+1}$, $n=1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18$;

[0085]

353 In the above structural formula, n is the carbon number corresponding to straight-chain alkanes.

[0086]

357 Example 1

[0087]

361 Synthesis of Dioctyl 5-Bromoisophthalate

[0089]

365 3 g of 5-bromoisophthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

367 5.79 g of n-bromooctane (0.03 mol) was added into the mixed solution, and the reaction was stirred at 90° C for 12 hours.

369 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

371 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (15/1) as the eluent for column chromatography to separate the crude product to obtain a white solid.

[0090]

376 Example 2

[0091]

380 Synthesis of Didecyl 5-Bromoisophthalate

[0093]

384 3 g of 5-bromoisophthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

386 6.64 g of n-bromodecane (0.03 mol) was added into the mixed solution, and the reaction was stirred at 90° C. for 12 hours.

388 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

390 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (15/1) as the eluent for column chromatography to separate the crude product to obtain a white solid.

[0094]

395 Example 3

[0095]

399 Synthesis of Dimethyl 5-Bromoisophthalate

[0097]

403 Add 6g of 5-bromoisophthalic acid (0.024 mol) to 80 mL of methanol, slowly add 6 mL of concentrated sulfuric acid dropwise under stirring, reflux at 70° C for 24 hours, cool to room temperature, and spin dry.

405 The resulting solid was dissolved in ethyl acetate, washed with aqueous sodium bicarbonate (5%) until neutral, dried over anhydrous sodium sulfate, filtered, and spin-dried to obtain a white solid.

[0098]

410 Example 4

[0099]

414 Synthesis of Dihexadecyl 5-Bromoisophthalate

[0101]

418 3 g of 5-bromoisophthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

420 9.16 g of n-bromohexadecane (0.03 mol) was added to the mixed solution, and stirred at 90° C. for 12 hours.

422 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

424 Dry over anhydrous sodium sulfate, filter and suspend to dry the solvent. The crude product is separated by column chromatography using petroleum ether/ethyl acetate (15/1) as the eluent to obtain a white solid.

[0102]

429 Example 5

[0103]

433 Synthesis of Diethyl 5-Bromoisophthalate

[0105]

437 Add 6g of 5-bromoisophthalic acid (0.024 mol) to 80 mL of ethanol, slowly add 6 mL of concentrated sulfuric acid dropwise under stirring, reflux at 90° C for 24 hours, cool to room temperature, and spin dry.

439 The resulting solid was dissolved in ethyl acetate, washed with aqueous sodium bicarbonate (5%) until neutral, dried over anhydrous sodium sulfate, filtered, and spin-dried to obtain a white solid.

[0106]

444 Example 6

[0107]

448 Synthesis of Didodecyl 5-Bromoisophthalate

[0109]

452 3 g of 5-bromoisophthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

454 7.48 g of n-bromododecane (0.03 mol) was added into the mixed solution, and stirred and reacted at 90° C. for 12 hours.

456 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

458 Dry over anhydrous sodium sulfate, filter and suspend to dry the solvent. The crude product is separated by column chromatography using petroleum ether/ethyl acetate (15/1) as the eluent to obtain a white solid.

[0110]

463 Example 7

[0111]

467 Synthesis of Ditetradecyl 5-Bromoisophthalate

[0113]

471 3 g of 5-bromoisophthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

473 8.32 g of n-bromotetradecane (0.03 mol) was added into the mixed solution, and stirred at 90° C. for 12 hours.

475 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

477 Dry over anhydrous sodium sulfate, filter and suspend to dry the solvent. The crude product is separated by column chromatography using petroleum ether/ethyl acetate (15/1) as the eluent to obtain a white solid.

[0114]

482 Example 8

[0115]

486 Synthesis of 5-Methyldidecyl Isophthalate

[0117]

490 1.8 g of 5-methylisophthalic acid (0.010 mol) and 4.0 g of potassium bicarbonate (0.040 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

492 5.53 g of n-bromodecane (0.025 mol) was added into the mixed solution, and the reaction was stirred at 90° C for 12 hours.

494 The reaction was stopped, and the solution was cooled to room temperature, poured into 250 mL of water, and extracted with ethyl acetate.

496 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (16/1) as the eluent for column chromatography to separate the crude product to obtain a white solid.

[0118]

501 Example 9

[0119]

505 Synthesis of Didecyl 5-Vinyl Isophthalate

[0121]

509 1.9 g of 5-vinylisophthalic acid (0.010 mol) and 4.0 g of potassium bicarbonate (0.040 mol) were added to 50 mL of D MF solvent, and stirred at room temperature to form a potassium salt.
511 5.53 g of n-bromodecane (0.025 mol) was added into the mixed solution, and the reaction was stirred at 90° C for 12 hours.
513 The reaction was stopped, and the solution was cooled to room temperature, poured into 250 mL of water, and extracted with ethyl acetate.
515 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (15/1) as the eluent for column chromatography to separate the crude product to obtain a white solid.

[0122]

520 Example 10

[0123]

524 Synthesis of Dioctyl Isophthalate

[0125]

528 Add 2.0 g of isophthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) to 50 mL of D MF solvent, and stir at room temperature to form a potassium salt.
530 5.79 g of n-bromooctane (0.03 mol) was added into the mixed solution, and the reaction was stirred at 90° C for 12 hours.
532 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.
534 Dry over anhydrous sodium sulfate, filter and suspend to dry the solvent. The crude product is separated by column chromatography using petroleum ether/ethyl acetate (20/1) as the eluent.

[0126]

539 Example 11

[0127]

543 Synthesis of Dioctyl 5-Fluoroisophthalate

[0129]

547 Add 2.2 g of 5-fluoroisophthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) to 50 mL of DMF solvent, and stir at room temperature to form a potassium salt.

549 5.79 g of n-bromooctane (0.03 mol) was added into the mixed solution, and the reaction was stirred at 90° C for 12 hours.

551 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

553 Dry over anhydrous sodium sulfate, filter and suspend to dry the solvent. The crude product is separated by column chromatography using petroleum ether/ethyl acetate (20/1) as the eluent.

[0130]

558 Example 12

[0131]

562 Synthesis of 5-Ethynyl Dihexyl Isophthalate

[0133]

566 Add 2.3 g of 5-ethynyl isophthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) to 50 mL of DMF solvent, and stir at room temperature to form a potassium salt.

568 4.80 g of n-bromohexane (0.03 mol) was added into the mixed solution, and the reaction was stirred at 90° C for 12 hours.

570 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

572 Dry over anhydrous sodium sulfate, filter and suspend to dry the solvent. The crude product is separated by column chromatography using petroleum ether/ethyl acetate (20/1) as the eluent to obtain a white solid.

[0134]

577 Example 13

[0135]

581 Synthesis of Didecyl Terephthalate

[0137]

585 2.0 g of terephthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

587 6.64 g of n-bromodecane (0.03 mol) was added into the mixed solution, and the reaction was stirred at 90° C. for 12 hours.

589 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

591 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (20/1) as the eluent for column chromatography to separate the crude product to obtain a white solid.

[0138]

596 Example 14

[0139]

600 Synthesis of Didodecyl 2-Methyl Terephthalate

[0141]

604 2.2 g of 2-methylterephthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

606 7.48 g of n-bromododecane (0.03 mol) was added into the mixed solution, and stirred and reacted at 90° C. for 12 hours.

608 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

610 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (20/1) as the eluent for column chromatography to separate the crude product to obtain a white solid.

[0142]

615 Example 15

[0143]

619 Synthesis of Didodecyl 2-Ethynyl Terephthalate

[0145]

623 2.3 g of 2-ethynyl terephthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

625 7.48 g of n-bromododecane (0.03 mol) was added into the mixed solution, and stirred and reacted at 90° C.

for 12 hours.

627 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

629 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (20/1) as the eluent for column chromatography to separate the crude product.

[0146]

634 Example 16

[0147]

638 Synthesis of Dipentyl 2-Fluoroterephthalate

[0149]

642 2.2 g of 2-fluoroterephthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

1

647 81 g of n-bromopentane (0.03 mol) was added into the mixed solution, and stirred at 90° C. for 12 hours.

648 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

650 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (20/1) as the eluent for column chromatography to separate the crude product.

[0150]

655 Example 17

[0151]

659 Synthesis of Dioctyl 2-bromoterephthalate

[0153]

663 3 g of 2-bromoterephthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

665 5.79 g of n-bromooctane (0.03 mol) was added into the mixed solution, and the reaction was stirred at 90° C for 12 hours.

667 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water,

and extracted with ethyl acetate.

669 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (20/1) as the eluent for column chromatography to separate the crude product to obtain a white solid.

[0154]

674 Example 18

[0155]

678 Synthesis of Didecyl 2-Bromoterephthalate

[0157]

682 3 g of 2-bromoterephthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

684 6.64 g of n-bromodecane (0.03 mol) was added into the mixed solution, and the reaction was stirred at 90° C. for 12 hours.

686 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

688 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (20/1) as the eluent for column chromatography to separate the crude product to obtain a white solid.

[0158]

693 Example 19

[0159]

697 Synthesis of Dipentyl 4-Fluorophthalate

[0161]

701 2.2 g of 4-fluorophthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

703 1.81 g of n-bromopentane (0.03 mol) was added into the mixed solution, and stirred at 90° C. for 12 hours.

704 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

706 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (25/1) as the eluent for column chromatography to separate the crude product.

[0162]

711 Example 20

[0163]

715 Synthesis of Didecyl Phthalate

[0165]

719 Add 2.0 g of phthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) into 50 mL of DMF solvent, and stir at room temperature to form potassium salt.

721 6.64 g of n-bromodecane (0.03 mol) was added into the mixed solution, and the reaction was stirred at 90° C. for 12 hours.

723 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

725 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (24/1) as the eluent for column chromatography to separate the crude product.

[0166]

730 Example 21

[0167]

734 Synthesis of Ditetradecyl 4-Methylphthalate

[0169]

738 2.2 g of 4-methylphthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

740 8.32 g of n-bromotetradecane (0.03 mol) was added into the mixed solution, and stirred at 90° C. for 12 hours.

742 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

744 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (25/1) as the eluent for column chromatography to separate the crude product.

[0170]

749 Example 22

[0171]

753 Synthesis of Didodecyl 4-Ethynylphthalate

[0173]

757 2.3 g of 4-ethynylphthalic acid (0.012 mol) and 4.8 g of potassium bicarbonate (0.048 mol) were added to 50 mL of DMF solvent, and stirred at room temperature to form a potassium salt.

759 7.48 g of n-bromododecane (0.03 mol) was added into the mixed solution, and stirred and reacted at 90° C. for 12 hours.

761 The reaction was stopped, and the solution was cooled to room temperature, poured into 300 mL of water, and extracted with ethyl acetate.

763 Dry over anhydrous sodium sulfate, spin to dry the solvent after filtration, and use petroleum ether/ethyl acetate (25/1) as the eluent for column chromatography to separate the crude product to obtain a milky white solid.

[0174]

769 Example 23

[0175]

773 Synthesis of Dimethyl 4-Bromophthalate

[0177]

777 Add 6g of 4-bromophthalic acid (0.024 mol) to 80 mL of methanol, slowly add 6 mL of concentrated sulfuric acid dropwise under stirring, reflux at 70° C for 24 hours, cool to room temperature, and spin dry.

779 The resulting solid was dissolved in ethyl acetate, washed with aqueous sodium bicarbonate (5%) until neutral, dried over anhydrous sodium sulfate, filtered, and spin-dried to obtain a white solid.

[0178]

784 The benzoate esters used in the following examples are all prepared in the above examples.

[0179]

788 Example 24

[0180]

792 The blending of 5-bromo-didecyl isophthalate and polystyrene was realized by using tetrahydrofuran as solvent.

[0181]

797 Dissolve 400 mg of polystyrene in 9 mL of tetrahydrofuran, add dropwise 4 mg of 5-bromoisophthalic acid didecyl ester that has been dissolved in 1 mL of tetrahydrofuran under stirring and mixing conditions, and then dry the solvent to obtain 5-bromoisophthalic acid didecyl Decyl ester and polystyrene blend material.

[0182]

803 Example 25

[0183]

807 The blending of 5-bromodidecyl isophthalate and polymethyl methacrylate was realized by using chloroform as solvent.

[0184]

812 Dissolve 200 mg of polymethyl methacrylate with 4 mL of chloroform, add dropwise 2 mg of 5-bromodidecyl isophthalate dissolved in 1 mL of chloroform, and then dry the solvent to obtain 5 - Blend material of didecyl bromoisophthalate and polymethyl methacrylate.

[0185]

818 Example 26

[0186]

822 Blending of didecyl-5-bromoisophthalate with polyvinyl alcohol was achieved by simple heating.

[0187]

826 At 70° C, 1 g of didecyl 5-bromoisophthalate and 100 g of polyvinyl alcohol were melted and mixed with stirring.

[0188]

831 Example 27

[0189]

835 The blending of 5-bromodidecyl isophthalate and polydimethylsiloxane was realized by using

dichloromethane as solvent.

[0190]

840 Dissolve 360 mg of polydimethylsiloxane A and 40 mg of polydimethylsiloxane B in 9 mL of dichloromethane, add dropwise 4 mg of 5-bromoisophthalic acid didecyl that has been dissolved in 1 mL of tetrahydrofuran under the condition of stirring and mixing ester, then dry the solvent, and keep the temperature at 35° C for 6 hours to obtain a blend material of didecyl 5-bromoisophthalate and polydimethylsiloxane.

[0191]

847 Example 28

[0192]

851 Blending of 5-bromodidecyl isophthalate and nylon 6 with hexafluoroisopropanol as solvent.

[0193]

855 Dissolve 200 mg of nylon 6 in 9 mL of hexafluoroisopropanol, add dropwise 2 mg of 5-bromodidecyl isophthalate dissolved in 1 mL of hexafluoroisopropanol under stirring and mixing conditions, and then dry the solvent to obtain 5-bromoisophthalate Didecyl isophthalate blended with Nylon 6.

[0194]

861 Example 29

[0195]

865 99.9kg of nylon 6 and 0.1kg of benzoate compound 5-dioctyl bromoisophthalate were mixed uniformly at 260° C, then extruded by a twin-screw extruder at a speed of 300rpm, and subjected to quenching grain.
867 The room temperature phosphorescent nylon composition can be obtained.

[0196]

871 Example 30

[0197]

875 Mix 99.9kg of nylon 6 and 0.1kg of benzoic acid ester compound 5-bromodidecyl isophthalate at 260° C, then extrude through a twin-screw extruder at a speed of 300rpm, and perform quenching grain.
877 The room temperature phosphorescent nylon composition can be obtained.

[0198]

881 Example 31

[0199]

885 Mix 99.9kg of nylon 6 and 0.1kg of benzoic acid ester compound: 5-dioctyl isophthalate at 260° C, and then extrude through a twin-screw extruder at a speed of 300rpm, and carry out the step Cold granulation.

887 The room temperature phosphorescent nylon composition can be obtained.

[0200]

891 Example 32

[0201]

895 Mix 99.9kg of nylon 6 and 0.1kg of benzoate compounds: 5-ethynyl dihexylphthalate at 260° C, and then extrude through a twin-screw extruder at a speed of 300rpm, and perform quenching Granulate.

897 The room temperature phosphorescent nylon composition can be obtained.

[0202]

901 Example 33

[0203]

905 99.9kg of nylon 6 and 0.1kg of benzoate compound: 5-bromodioctyl terephthalate were mixed uniformly at 260° C, then extruded through a twin-screw extruder at a speed of 300rpm, and subjected to quenching grain.

908 The room temperature phosphorescent nylon composition can be obtained.

[0204]

912 Example 34

[0205]

916 99.9kg of nylon 6 and 0.1kg of benzoate compound: 5-bromodidecyl terephthalate were mixed uniformly at 260° C, then extruded by a twin-screw extruder at a speed of 300rpm, and subjected to quenching grain.

918 The room temperature phosphorescent nylon composition can be obtained.

[0206]

922 test case 1

[0207]

926 The present invention carries out the detection of phosphorescence emission wavelength and phosphorescence lifetime for the brominated isophthalic acid ester compounds prepared in Examples 1-7, and the results are shown in Table 1 and Figure 1; state transient fluorescence spectrometer.

929 The steady-state transient spectrum tests of phosphorescence all use a microsecond lamp as the light source and cooperate with the gate operation.

931 Detectors are used P928P P M T detector.

932 It is found through testing that among the 3,5-substituted bromobenzoate, when n=8, it has the longest phosphorescence lifetime.

[0208]

937 Table 1 Room temperature phosphorescence emission wavelength and phosphorescence lifetime

[0209]

941 Example $\lambda_{\text{phos}}/\text{nm}$ $\tau_{\text{phos}}/\text{ms}$ C1-Br 492 161 C2-Br 518 8.1 C8-Br 550 798 C10-Br 520 236 C12-Br 483 5
C14-Br 486 5 C16-Br 523 210

[0210]

946 test case 2

[0211]

950 In this test example, the fluorescence/phosphorescence spectrum test is carried out on the didecyl bromoisophthalate prepared in Example 2. The test instrument is the FLS 980 steady-state transient fluorescence spectrometer from Edinburgh, U.K.

953 The excitation light source for the fluorescence steady-state spectrum test is a xenon lamp, the fluorescence lifetime test uses an LED laser or a supercontinuum laser as the light source, and the steady-state transient spectrum test for phosphorescence uses a microsecond lamp as the light source, with gate control operation.

956 Detectors are used P928P P M T detector.

957 The photoluminescence total quantum yield and phosphorescent quantum yield were measured with FLS 980 with integrating sphere attachment.

[0212]

962 The photoluminescence spectrum, phosphorescence spectrum, phosphorescence lifetime decay curve, long
afterglow photos and photophysical data of 5-bromodidecyl isophthalate at room temperature are shown in
Table 2 and Figures 2-4 below.

[0213]

968 Table 2 Photophysical data of didecyl 5-bromoisophthalate

[0216]

972 It can be seen from Figure 2 that at room temperature, the maximum fluorescence emission wavelength of
C10-Br in dichloromethane dilute solution is at 320nm, and the solution has no phosphorescence.

974 In the crystal state, the central wavelength of fluorescence emission is at 329nm, and the maximum emission
wavelength of phosphorescence is at 520nm.

976 Figure 3 shows that the C10-Br phosphorescence lifetime is as long as 236ms.

977 Figure 4 is the long afterglow photo of the crystal after being excited with a 365nm ultraviolet lamp and
removing the excitation light source. From left to right, the light source is removed for 0.1s, 0.2s, 0.5s, 1.0s,
1.5s, 2.0s, 2.5s, 3.0s and 4.0s optical photos, it can be seen that it has a bright green phosphorescence at the
beginning, and the brightness gradually weakens as time goes on, and its long afterglow lasts up to 4s.

[0217]

984 It can be seen from Table 2 that the fluorescence and phosphorescence maximum emission wavelengths of
C10-Br crystals at room temperature are located at 329nm and 520nm, respectively, and the total absolute
quantum yield and phosphorescence quantum yield are 11.4% and 8.2%, respectively.

[0218]

990 Test case 3

[0219]

994 This test example carries out optical test for the 5-methyl didecyl isophthalate prepared in Example 8, and the
specific optical measurement method and optical property data are as follows:

[0220]

999 Spectral test of 5-methyl didecyl isophthalate

[0221]

1003 The test instrument is the FLS 980 steady-state transient fluorescence spectrometer from Edinburgh, U.K.

[0222]

1007 The photoluminescence spectrum, phosphorescence spectrum, and phosphorescence lifetime decay curve of 5-methyl didecyl isophthalate at room temperature are shown in Figures 5 and 6.

[0223]

1012 It can be seen from Figure 5 and Figure 6 that at room temperature, the maximum fluorescence emission wavelength of C10-CH₃ in dichloromethane dilute solution is at 312nm, and the solution has no phosphorescence.

1015 In the crystal state, the central wavelength of its fluorescence emission is at 314nm, the maximum emission wavelength of phosphorescence is at 505nm, and its phosphorescence lifetime is as long as 651 ms.

[0224]

1020 Test case 4

[0225]

1024 Test Example An optical test was carried out on didecyl 2-bromoterephthalate prepared in Example 18. The specific optical measurement method and optical property data are as follows:

[0226]

1029 Spectral test of didecyl 2-bromoterephthalate

[0227]

1033 The test instrument is the FLS 980 steady-state transient fluorescence spectrometer from Edinburgh, U.K.

[0228]

1037 The photoluminescence spectrum, phosphorescence spectrum and phosphorescence lifetime decay curve of 2-bromo didecyl terephthalate at room temperature are shown in Figure 7 and Figure 8.

[0229]

1042 It can be seen from Fig. 7 and Fig. 8 that at room temperature, in the crystal state, the center wavelength of fluorescence emission is at 435nm, the maximum emission wavelength of phosphorescence is at 490nm, and the phosphorescence lifetime is 31 ms.

[0230]

1048 Test case 5

[0231]

1052 This test example carries out photoluminescence and phosphorescence spectrum detection for the mixture prepared in Example 24, and the detection results are shown in Figure 9, as can be seen from the figure, when C10-Br (5-bromodidecyl isophthalate) after blending with polystyrene, the maximum emission wavelength of its fluorescence is 328nm, and the maximum emission of phosphorescence is at 515nm., C10-Br can be used as an effective phosphorescent additive.

[0232]

1060 Test case 6

[0233]

1064 This test example carries out photoluminescence and phosphorescence spectrum detection for the mixture prepared in Example 26, and the detection results are shown in Figure 10, as can be seen from the figure, when C10-Br (5-bromodidecyl isophthalate) after blending with polyvinyl alcohol, the maximum emission wavelength of its fluorescence is 325nm, and the maximum emission of phosphorescence is at 517nm., C10-Br can be used as an effective phosphorescent additive.

[0234]

1072 Comparative example 1

[0235]

1076 A bromine monosubstituted ester, decyl p-bromobenzoate, was synthesized as a comparison with didecyl 5-bromoisophthalate. As shown in Figure 11, it can be found that its room temperature phosphorescence is close to none.

[0236]

1082 Comparative example 2

[0237]

1086 The fluorescence and phosphorescence spectra of polystyrene are shown in Figure 12. From the spectral data in the figure, it can be clearly seen that the polystyrene macromolecule itself does not have phosphorescence,

thus proving that the room temperature phosphorescent benzoic acid ester compound of the present invention is used as a macromolecule. The effect of the phosphorescent blending agent is also compared with its own strong phosphorescence from the side.

[0238]

1094 Comparative example 3

[0239]

1098 The fluorescent phosphorescence spectrum of polyvinyl alcohol is shown in Figure 13. From the spectral data in the figure, it can be clearly seen that the polyvinyl alcohol polymer itself has no phosphorescence, which proves that this series of halogen-containing room temperature phosphorescent benzoate materials are used as high. The role of the molecular phosphorescent blending agent is also compared with its own strong phosphorescence from the side.

[0240]

1106 The preferred embodiments of the present invention have been described in detail above, but the present invention is not limited to the specific details in the above embodiments. Within the scope of the technical concept of the present invention, various simple modifications can be made to the technical solutions of the present invention. These simple modifications All belong to the protection scope of the present invention.

[0241]

1113 In addition, it should be noted that the various specific technical features described in the above specific embodiments can be combined in any suitable way if there is no contradiction. The combination method will not be described separately.

[0242]

1119 In addition, various combinations of different embodiments of the present invention can also be combined arbitrarily, as long as they do not violate the idea of the present invention, they should also be regarded as the disclosed content of the present invention.

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CLAIMS CN109956869A

1.

¹³ A benzoic acid ester compound has the following general formula:

¹⁴ X=H, CH₃, CH=CH₂, C≡CH, F, Cl, Br, I;

2

¹⁸, 5 substitutions, R₂=R₃=H, R₁=R₄=C(O)OC_nH_{2n+1}, n=1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18; or,

3

²², 5 substitutions, R₁=R₃=H, R₂=R₄=C(O)OC_nH_{2n+1}, n=1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18; or,

²³ 3, 4 substitutions, R₁=R₄=H, R₂=R₃=C(O)OC_nH_{2n+1}, n=1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18.

2.

²⁷ The preparation method of the described compound of claim 1, comprises the steps:

²⁸ n=1,2; n=3, 4, 5, 6, 8, 10, 12, 14, 16, 18;

²⁹ or

³⁰ n=1,2;

³¹ or

³² n=3, 4, 5, 6, 8, 10, 12, 14, 16, 18;

³³ n=1,2;

³⁴ n=3, 4, 5, 6, 8, 10, 12, 14, 16, 18.

3.

38 A room temperature phosphorescent material, characterized in that it comprises the benzoic acid ester compound according to claim 1.

4.

43 The room temperature phosphorescent material according to claim 3, further comprising a polymer compound.

5.

48 The room temperature phosphorescent material according to claim 4, characterized in that, in parts by weight, the polymer compound is 100 parts, and the benzoic acid ester compound is 5-0.0001 parts.

6.

53 The room temperature phosphorescent material according to claim 5, characterized in that the benzoic acid ester compound is 1-0.005 parts, preferably 0.1-0.01 parts.

7.

58 The room temperature phosphorescent material according to any one of claims 4-6, wherein the polymer is polystyrene, polyethylene, polymethyl methacrylate, polyvinyl alcohol, polydimethylsiloxane, One or more of polyvinyl acetate, polyester and nylon.

8.

64 The room temperature phosphorescent material according to claim 7, wherein the benzoate compound is 5-bromodidecyl isophthalate, and the polymer is nylon;

66 The benzoate compound is 5-bromodidecyl isophthalate, and the polymer is polystyrene;

67 The benzoic acid ester compound is 5-bromodidecyl isophthalate, and the polymer is polyvinyl alcohol.

9.

71 The room temperature phosphorescent material according to claim 8, wherein the nylon is nylon 6, and the weight ratio of nylon 6 and 5-bromodidecyl isophthalate is 99.9:0.1;

73 The weight ratio of polystyrene and 5-bromodidecyl isophthalate is 100:1;

74 The ratio by weight of the polyvinyl alcohol to didecyl 5-bromoisophthalate is 100:1.

10.

78 The preparation method of the phosphorescent material described in any one of claims 3-9, comprising the steps of:

- 80 Dissolving the polymer with a solvent to obtain a first solution;
- 81 Utilize the same solvent to dissolve the benzoic acid ester compound to obtain a second solution;
- 82 Add the second solution to the first solution under stirring, and mix well;
- 83 Dry the mixed solution and remove the solvent;
- 84 The weight ratio of the solvent to the benzoate compound is (0.1-50):1.

11.

- 88 The method for preparing a phosphorescent material according to claim 10, wherein the solvent is one of chloroform, tetrahydrofuran, dichloromethane, hexafluoroisopropanol, benzene, toluene, acetone, and dioxane or more.

12.

- 94 The preparation method of the phosphorescent material according to any one of claims 3-9, comprising the following steps: at 70° C-300° C, mixing and melting the polymer and the benzoate compound, and stirring evenly.

13.

- 100 Use of the benzoic acid ester compound described in claim 1 and the material described in any one of claims 3-8 as a room temperature phosphorescent material or a phosphorescent material additive.



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MELT-FLOWABLE MATERIAL AND METHOD FOR SEALING SURFACE

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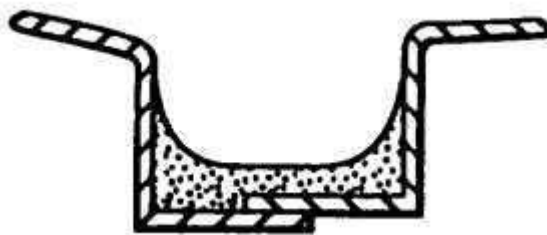
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Abstract of JP2007254752 (A)

PROBLEM TO BE SOLVED: To provide a meltable sealant material usable for visible and invisible uses, treatable as a strip or a tape, user friendly and paintable, which material is required in industrial world. ;SOLUTION: A method for imparting topographical or protective features to a substrate comprises

contacting a sheet material comprising a thermosettable layer with a substrate and heating the sheet material to an elevated temperature. ;COPYRIGHT:

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DESCRIPTION JP2007254752A

10 Melt flowable material and surface sealing method

[0001]

14 The present invention relates to methods for providing protective and aesthetic properties to surfaces using melt-flowable sheet materials.

[0002]

19 There are numerous applications in industry where it is desirable, and sometimes necessary, to provide protective and/or aesthetic properties to surfaces. Such uses include the use of paintable sealers on vehicle bodies. Historically, a wide variety of materials have been used as sealers to fill voids in structures and keep out dirt, moisture, and other substances.

[0003]

26 Sealers are provided as liquids or solids as required by the application.

27 As noted in US Pat. No. 4,900,771 (Gerace et al.), the automotive industry has used paste-like plastisols for decades to seal metal joints. These materials function by having PVC (polyvinyl chloride) particles that swell in a plasticizer when heated, fusing into a solid material. Due to the high level of plasticizers, paints generally exhibit poor adhesion to PVC-based sealers. Additionally, PVC sealers are not recyclable and release HCl when incinerated. For this reason they are not used in Europe.

[0004]

36 Hot melt sealants and adhesives are generally solid thermoplastic materials that melt rapidly on heating and then form a firm bond on cooling.

38 A typical type of hot melt adhesive composition employs polyolefins, which are known in the art to be difficult to paint and to have poor adhesion to non-porous metal surfaces such as steel and aluminum. ing.

[0005]

44 In use, the operator must apply a bead of liquid sealer to the splice seam as if applying caulk, and brush or even the material into a relatively uniform film.

46 Application of liquid sealers requires skill and often results in seams that fail to seal. Due to the non-uniform appearance of liquid sealers, they cannot be used in visible applications.

[0006]

51 Recently, there has been a trend towards more user-friendly sealer systems, such as ropes or tapes, whose handleability aids in quick installation and eliminates the need for tricky handling after material application.

54 Tapes and ropes of PVC-based sealant materials have begun to find use in the niche market. Other materials have also been provided as strips or tapes.

[0007]

59 US Pat. No. 3,659,896 (Smith et al.) describes a liquid polysulfide polymer-based semi-cured curable polymer sealing strip composition for bonding and sealing a windshield to a vehicle body.

62 Since the sealing strip is adhesive to both glass and metal, the windshield is instantly sealed at room temperature and exposure to moisture at ambient conditions accelerates the curing of the sealant material.

[0008]

68 U.S. Pat. No. 4,490,424 (Gerace) describes a hot melt adhesive and sealant tape in which the tape comprises a hot melt adhesive core encased in a plastic resin coating.

70 Plastic resins are compatible with hot melt adhesive cores in both liquid and solid states.

[0009]

74 There is a need in the industry for user-friendly, paintable meltable sealant materials that can be used in visible and invisible applications and that can be handled as strips or tapes.

[0010]

79 Thermoset pressure sensitive adhesives are known and have utility in many industries,

including automotive and home appliance assembly.

81 Such adhesives are described in US Pat. No. 5,086,088 (Kitano et al.).

82 These adhesives are pressure sensitive, ie tacky at the bonding temperature, and are generally used in the form of pressure sensitive adhesive transfer tapes in which the adhesive layer is provided on a release liner. The transfer tape can further include a nonwoven web for adhesive layer reinforcement. In use, the transfer tape bonds one surface to another at ambient temperature. The surface is then heated to a temperature sufficient to cure the adhesive to a thermoset state.

[0011]

91 In some applications, it may be desirable to have a thermosetting pressure sensitive adhesive tape that has a non-tacky surface and that can be activated into an adhesive state at the temperature of use.

[0012]

97 One such application is found on some automobile assembly lines where the door is temporarily attached to the body by bolting the hinges to the body prior to painting.

99 The door is placed on the vehicle by aligning the door hinges over the slots in the vehicle body and then securing the hinges to the vehicle body with one or more washers and corresponding bolts.

102 After the body is painted, the door is removed from the hinges so that the interior fittings can be installed. It is desirable to have the washer fixed in place on the hinge so that when the door is refitted, it will line up correctly without time consuming realignment.

[0013]

108 Japanese Patent Publication No. 64-67417 describes a washer that is secured to a door hinge by a sticky thermosetting adhesive film.

110 The washers act as alignment members for the bolts used to connect the hinge to the door. The film is sticky on both sides and is prone to contamination with dirt, oil, etc. found in assembly plants. Contaminated surfaces must be cleaned to ensure proper bonding. The films also tend to be very thin and difficult to handle, and stripping the liner so that the film can bond to the washer and bolting surfaces becomes a labor intensive operation that prevents assembly line automation.

[0014]

119 It is also known to impregnate the nonwoven fabric with a thermosetting adhesive as a backing material to increase the stiffness of the adhesive for easier handling, but this increases the cost and reduces the adhesive film. The other drawbacks mentioned above are

also unavoidable.

[0015]

- 126 Japanese Patent Publication No. 53-42280 describes a composite sheet having a sheet of thermoset material covered with a heat fusion material.
- 128 The heat fusible material is intended to cover the thermoset resin sheet so that the worker avoids direct skin contact with the thermoset adhesive.
- 130 The thermosetting material and the heat fusion material are mutually non-reactive and compatible, and are characterized by a maximum fusion temperature difference of 50 ° C. The heat fusion material melts and mixes with the thermosetting material before curing.

[0016]

- 136 Japanese Patent Publication JP H4-189885 describes thermosetting pressure sensitive adhesives made from acrylic acid copolymers and epoxy resins.
- 138 The adhesive composition can be coated on one or both sides of a nonwoven material that acts as a prepreg to increase the strength of the adhesive sheet.

[0017]

- 143 It is desirable to have a thermosetting pressure sensitive adhesive tape that is essentially tack-free at room temperature (approximately 21 ° C) on at least one major surface of the tape, although both major surfaces are compatible with other substrates. It can also be adapted for coupling.

[0018]

- 150 SUMMARY OF THE INVENTION The present invention provides an adhesive composite that includes a layer of thermoset pressure sensitive adhesive and a layer of hot melt adhesive that is essentially tack-free at room temperature.
- 153 The heat activation temperature for hot melt adhesives is preferably between about 50 ° C and the temperature used to cure thermosetting adhesives.

[0019]

- 158 The invention also provides an adhesive composite for bonding to the washer at ambient temperature, for bonding to the washer and for further bonding the washer to a surface after a heating cycle, and a washer bonded by the composite.

[0020]

164 The invention also provides a method for bonding the composite to the washer.

[0021]

168 Further, the present invention provides hot melt sealing tapes and uses of the tapes.

[0022]

172 Additional features and advantages of the invention will be set forth in the description that follows, and in part will be apparent from the description, or may be learned by practice of the invention.

175 The objectives and other advantages of the invention will be realized and attained by the method and provisions particularly pointed out in the written description and claims hereof.

[0023]

180 It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to further explain the scope of the invention.

[0024]

186 DETAILED DESCRIPTION OF THE INVENTION The present invention involves the use of melt-flowable sheet materials to provide substrates with protective and/or aesthetically pleasing properties.

189 Generally, the method of the invention involves placing a melt-flowable sheet material on a substrate and heating the sheet material to soften it sufficiently so that it bonds to the substrate.

192 The melt-flowable sheet is essentially tack-free when placed on a substrate at room temperature.

194 As it heats, the sheet first softens and conforms to the substrate surface, resulting in air entrapments being pushed out by the flowing material.

196 As the heating cycle progresses further and the sheet material gets hotter, it becomes tacky enough to wet and bond to the surface.

198 Also, in some applications, the sheet material melts and flows to hide defects, surface imperfections, and/or fill gaps.

[0025]

203 After bonding to the surface of the sheet, the sheet material remains melt-flowable, ie thermoplastic, and reheating may cause the material to reflow.

205 When heated, the sheet material may harden or crosslink, thermoset, and become non-

flowing when reheated.

207 Or, a portion of the sheet material may remain thermoplastic while a portion of the sheet material is cured or crosslinked, ie thermoset.

[0026]

212 The method of the invention has numerous applications in industry.

213 One utility of the method is in the automotive industry, where it can be used in automotive metal joint sealing methods.

215 In this method, first, a sheet material is prepared, such as by the method described above.

216 A sheet of material is then applied over the joint to be sealed.

217 A perfect seal and bond is obtained because the sheet material flows before curing.

218 The controlled flow of the sheet material edges results in an aesthetic appearance of the surface.

220 The exposed surface of the cured sheet material is then painted or otherwise decorated to match the vehicle body.

[0027]

225 An alternative application of the method of the invention is the application of emblems or plaques or design elements to surfaces such as vehicle bodies.

227 An example of a coat of arms or plaque is a car manufacturer's logo.

228 An example of a design element is a trim that complements and accentuates the curvature of the vehicle body and provides protection to the primed metal undercarriage without the need for complex metal stamping to obtain the shape.

231 In such a method, the sheet material is first formed, such as by stamping, into the shape of the desired coat of arms or plaque or design element.

233 Practice of the method of the present invention results in an aesthetically pleasing emblem or plaque having a smooth transition line to the mating surfaces.

[0028]

238 In yet another application of the method of the present invention, the substrate to which the sheet material initially adheres is a temporary substrate such as a disposable liner.

240 Since the cured sheet material may inherently lack pressure-sensitive adhesive properties, after curing the sheet material in such a way as to impart controlled flow to the edges, for example, the sheet material itself may A separate adhesive system may be used to secure (eg, adhere) the cured sheet material to a permanent substrate.

244 In this manner, the method of the present invention can be used to apply molded and cured sheet material or the like to surfaces such as wooden doors.

[0029]

249 The melt flowable sheet material can be placed in the roof grooves of the automobile prior to painting to hide unsightly blemishes in the metal, spot welds, and step joints where the roof sheet metal is welded to the body sheet metal. .

[0030]

255 In one particular example, the melt-flowable sheet material is cut into strips whose width is slightly greater than the width of the roof channel and whose length is equal to the length of the channel.

258 The roof groove may be unprimed, unprimed partially sealed with a conventional sealer, primed with a conventional primer, or primed and painted.

260 Typically, the automobile is primed with an electrocoat prior to strip application, as detailed below.

262 Heating the strip within the groove then causes the strip material to flow and level any imperfections and step joints within the roof groove to create a smooth and aesthetically pleasing appearance within the groove.

265 At the same time, the melt-flowable strip adheres to the inner surface of the roof channel and also provides a protective seal within the channel to prevent rainwater, dirt, snow, etc. from entering the roof channel and causing rust or corrosion.

268 In this application the width of the strip is slightly greater than the width of the roof channel, and the strip material also assumes a concave shape along the length of the roof channel to provide a channel for carrying water away from the vehicle roof.

[0031]

274 The strip material is preferably compatible with the paint and firmly bonds to both the paint and the roof channel surface while allowing the paint to dry and cure without wrinkling or cracking of the paint.

[0032]

280 The automobile can be painted with the strip in place and subjected to an oven cure cycle of about 170 ° C for about 20 minutes.

282 A protective clearcoat can also be applied and cured.

283 It is recognized that oven cure times and temperatures will vary depending on the type of coating and the curing requirements of the coating and clearcoat.

285 A typical cycle ranges from about 20-40 minutes at a temperature between about 120-200 ° C.

[0033]

290 In a preferred embodiment, the paint also chemically reacts with the melt-flowable strip material to improve adhesion between the paint and the melt-flowable strip.
292 The reaction of the strip material with the paint causes the strip material to thermoset at and around the paint-strip interface, while below the interface layer the strip material remains thermoplastic.

[0034]

298 In another preferred embodiment, the melt flowable strip itself is a thermoset material that reacts with the paint during the cure cycle and cures to provide a thermoset strip.
300 Curing can be accomplished by heating or irradiation methods, as described below.

[0035]

304 In an alternative embodiment, the strip may be placed in the roof groove after the vehicle has been painted.
306 The roof groove area is then heated with a conventional heater, such as an infrared heater or a quartz halogen lamp, to melt and bond the strip to the roof groove without further processing.
309 In this embodiment, the strips can also be mixed with pigments to provide opposite or complementary colors.
311 The molten sealing strip material may remain thermoplastic, may be heat set through the entire thickness of the strip, or may be heat set only on the surface of the strip.

[0036]

316 The melt-flowable sheet material is preferably solid and may be tacky or non-tacky at room temperature.
318 In some embodiments, the hot melt sealing sheet material also functions as a hot melt adhesive.
320 Hot melt adhesive materials preferably have melting points above about 50 ° C.
321 As used herein, "hot melt adhesive composition" refers to a composition that is solid and non-tacky at room temperature (approximately 21 ° C), but melts when heated to sufficiently wet and adhere surfaces. .
324 Adhesives with a melt temperature of less than 50 ° C may prematurely melt during storage in hot climates and may perform well in applications where parts need to be stamped or stamped on a stamping press as described below. may not work for

[0037]

330 Extrude the material through a heated die, heat the sheet material to the appropriate melt temperature and knife coat it onto a release liner, curtain coat the molten material, or diffuse

the material into a solvent and coat it onto the release liner and let the solvent out. The sheet material can be formed into sheets using conventional sheet forming techniques, including drying.

335 A preferred method for environmental reasons is a solvent-free system.

[0038]

339 The thickness of the melt-flowable sheet material will vary depending on its intended end use.

340 For sealing applications, a sheet that is thick enough to flow to level out pits, bumps, and other surface imperfections or to provide enough material to fill gaps between joints is desirable.

343 A useful thickness has been found to be in the range of about 0.05 to 25 mm.

344 For typical melt sealing applications where a protective seal is desired, the thickness ranges from 0.10-25 mm, preferably 0.20-10 mm, and more preferably 0.34-6 mm.

[0039]

349 The melt-flowable sheet material can be packaged in the form of roll-formed sheet material, roll-formed tape, i.e., narrow long strips of material, or stacks of sheets cut to the size or shape desired for the end use.

352 If the composition of the melt-flowable sheet material is tacky, a release liner may be interposed between adjacent sheets or between wound rolls.

354 In some two-ply sheet constructions in which one of the layers is tacky, the non-tacky layer may serve as the liner without requiring a separate liner.

356 If the sheet material contains a latent photoactive catalyst in the sheet, the sheet is preferably packaged and shipped in the absence of actinic radiation until immediately prior to use.

[0040]

361 Compositions for melt-flowable sheet materials can also be packaged for use in hot-melt applicator systems using pail unloaders, cartridge dispensers, and the like.

363 The composition can then be heated at the point of use and applied to the substrate in the molten state.

365 This method may require specialized equipment to apply the composition.

[0041]

369 The melt-flowable material can be applied and bonded to most substrates including plastics, metals, ceramics, glass, and cellulosic materials.

371 Metallic substrates such as primed, unprimed, or painted aluminum, cold rolled steel, galvanized steel, and magnetized steel are particularly preferred.

[0042]

376 The melt-flowable sheet can include one or more other layers for various purposes, as detailed below.

378 Such layers include a thermosetting melt sealing layer, a thermosetting pressure sensitive adhesive layer, a pressure sensitive adhesive layer, a second layer such as a layer having a different glass transition temperature than the first melt flowable layer. Melt-flowable layers, layers capable of cross-linking with the melt-flowable layer at the interface of the two layers, foamable layers, nonwoven layers, or polymeric films such as thermoplastic films, preferably dimensionally stable at application and use temperatures.

384 Various methods of bonding additional layers to the melt-flowable layer include thermal lamination, bonding with pressure sensitive adhesives, co-extrusion of the melt-flowable layer with the second layer, hot-melt coating, onto the first layer. techniques known in the industry such as direct coating of a second layer of

[0043]

391 Melt-flowable sheet materials useful in the practice of the present invention include thermoplastic polymeric materials having functional groups capable of reacting with typical paints used in the industry, such as melamine or epoxy-based paints.

[0044]

397 Preferred thermoplastic polymers are functionalized amorphous or semi-crystalline polymers with a glass transition temperature above -30°C and functionalized semi-crystalline polymers with a glass transition temperature below -30°C .

400 Useful polymers are those with functional groups such as $-\text{OH}$, $-\text{NH}$, $-\text{CONH}$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{SH}$, anhydrides, urethanes, and oxiranes.

402 Preferred functional groups are $-\text{OH}$, $-\text{COOH}$, and $-\text{NH}$.

403 Examples of useful polymers include polyesters, polyamides, functionalized ethylene (meth)acrylates such as those functionalized with $-\text{OH}$ groups, ethylene acrylic acid, polysulfides, and polyacetals such as polyvinyl butyral. and olefinic polymers with suitable functional groups such as ethylene-(meth)acrylic acid, propylene-(meth)acrylic acid, ethylene-(meth)acrylate, propylene-(meth)acrylate, and polycaprolactone, epoxy polycaprolactone compositions, and epoxy polyester hot melt compositions described in original US Ser. No. 08/047,862, filed Apr. 15, 1993, and compatible mixtures thereof.

[0045]

413 Preferred materials for the melt-flowable sheet materials include polycaprolactones and polyesters that are hydroxyl- and carboxyl-terminated and are amorphous or semi-crystalline at room temperature.

416 More preferred are hydroxyl-terminated polyesters that are semi-crystalline at room temperature.

[0046]

421 A material that is "amorphous" has a glass transition temperature but does not exhibit a crystalline melting point that can be measured by differential scanning calorimetry (DSC).
423 When used as described below, the glass transition temperature is preferably below the decomposition temperature of the photoinitiator and does not exceed about 120 ° C.
425 A "semi-crystalline" material exhibits a crystalline melting point as determined by DSC, preferably with a maximum melting point of about 200 ° C.

[0047]

430 Crystallinity in polymers is also observed as turbidity or opacification when a sheet heated to an amorphous state cools.
432 When the polyester polymer is heated to a molten state and knife-coated onto the liner to form a sheet, it is observed to be amorphous and the sheet is transparent with considerable light transmission.
435 Crystallization is characterized by turbidity of the sheet to a translucent or opaque state as crystalline regions form as the polymer in the sheet material cools.
437 The degree of crystallinity can be varied in the polymer by mixing compatible combinations of amorphous and semi-crystalline polymers with different degrees of crystallinity.
439 It is generally preferred to allow enough time before painting to allow the material heated to the amorphous state to return to the semi-crystalline state so that the paint is applied on a uniform and consistent surface.
442 The turbidity of the sheet provides a convenient non-destructive measurement of when some degree of crystallization has occurred in the polymer.

[0048]

447 The polymer may contain nucleating agents to increase the rate of crystallization at constant temperature.
449 Useful nucleating agents include microcrystalline waxes.
450 A suitable wax is available from Petrolite Corp.
451 C14 alcohol (CAS #71770-71-5) and ethylene homopolymer (CAS #9002-88-4), sold as Unilin 700 from Unilin Corporation.
453 A paint catalyst such as p-toluenesulfonic acid and melamine may be added to the polyester to improve adhesion of the melt-flowable layer to paints and coatings.

[0049]

458 Preferred polyesters are solid at room temperature.

459 Preferred polyester materials have a number average molecular weight of from about 7500 to 200,000, more preferably from about 10,000 to 50,000, and most preferably from about 15,000 to 30,000.

[0050]

465 Polyester components useful in the present invention include reaction products of dicarboxylic acids (or their diester equivalents) and diols.

467 Diacids (or diester equivalents) are saturated fatty acids containing 4 to 12 carbon atoms (including branched, unbranched, or cyclic materials containing 5 to 6 carbon atoms in the ring) and/or 8 carbon atoms. Aromatic acids containing 1 to 15 are also acceptable.

470 Examples of suitable fatty acids include succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,12-dodecanedioic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclopentanedicarboxylic acid, 2-methylsuccinic acid, 2-methylpentanedioic acid, 3-methylhexanedioic acid and the like.

474 Suitable aromatic acids include terephthalic acid, isophthalic acid, phthalic acid, 4,4'-benzophenonedicarboxylic acid, 4,4'-diphenylmethanedicarboxylic acid, 4,4'-diphenylthioetherdicarboxylic acid, and 4,4'-diphenylamine dicarboxylic acid and the like.

477 Preferably the structure between the two carboxy groups in the diacid contains only carbon and hydrogen, more preferably the structure is a phenylene group.

479 Mixtures of the aforementioned diacids may also be used.

[0051]

483 Diols include branched, unbranched and cycloaliphatic diols having 2 to 12 carbon atoms.

484 Examples of suitable diols include ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,3-butanediol, 1,5-pentanediol, 2-methyl-2,4-pentanediol, 1,6-hexanediol, cyclobutane-1,3-di(2'-ethanol), cyclohexane-1,4-dimethanol, 1,10-decanediol, 1,12-dodecanediol, and neopentyl glycol.

488 Long chain diols such as poly(oxyalkylene) glycols in which the alkylene group contains 2 to 9 carbon atoms, preferably 2 to 4 carbon atoms may also be used.

490 Mixtures of the aforementioned diols may also be used.

[0052]

494 Useful commercially available hydroxyl-terminated polyester materials include various saturated straighteners available from Huls America, Inc., such as Dynapol (S1401, Dynapol (S1402, Dynapol (S1358), Dynapol (S1359, Dynapol (S1227, and Dynapol (S1229). Chain semi-crystalline copolyesters may be mentioned.

498 Useful saturated linear amorphous copolyesters available from Huls America, Inc., include Dynapol (S1313 and Dynapol (S1430).

[0053]

- 503 A polyester resin can be melted at a temperature of about 100-150 ° C. to form a molten material and knife coated onto a liner such as a silicone release coated paper to cast the polyester into a sheet.
- 506 The polyester material may further include fillers, as epoxy polyester compositions, which are detailed below.

[0054]

- 511 Sheets formed from the polyesters described above are particularly useful for sealing and bonding to surfaces having gaps and imperfections such as in the automotive roof channel molding described above.
- 514 Additionally, these polyesters provide a paint-compatible surface for melamine and epoxy paints and are compatible with at least two typical paint cure cycles (e.g., 120 ° C for 20-30 minutes and 200 ° C for 20-30 minutes).) has been found to withstand
- 517 When coated with epoxy and melamine paints, these polyesters have been found to react with the paint at the interface between the melt-flowable sheet and the paint.

[0055]

- 522 Preferred melt-flowable sheet materials also include epoxy polycaprolactone compositions and epoxy polyester hot melt compositions.
- 524 Polycaprolactone is biodegradable in soil.
- 525 Particularly preferred are epoxy polyester hot melt compositions that cure upon exposure to radiation to provide high strength sealing materials with good adhesion to the substrates to which they are adhered.
- 528 The epoxy-containing material contributes to the final strength and heat resistance of the composition, while the polyester component conforms the sheet material to the substrate and provides initial adhesion to the substrate, and the photoinitiator is responsible for the composition upon exposure to radiation. The composition is cured (ie, covalently crosslinked).
- 533 The hot melt compositions of the present invention can also optionally contain hydroxyl-containing materials that provide flexibility and toughness to the hot melt composition.
- 535 Preferred polyesters for epoxy/polyester sheet materials are the hydroxyl- and carboxyl-terminated functional materials described above.
- 537 Particularly preferred are hydroxyl-terminated polyesters with some degree of crystallinity.

[0056]

- 541 Epoxy-containing materials useful in the compositions of the present invention are any

organic compound having at least one oxirane ring polymerizable by a ring-opening reaction,
.

545 Such materials, loosely referred to as epoxides, include both monomeric and polymeric epoxides and may be aliphatic, cycloaliphatic, or aromatic.

547 These materials generally have an average of at least two epoxy groups per molecule (preferably more than two epoxy groups per molecule).

549 The "average" number of epoxy groups per molecule is defined as the number of epoxy groups in the epoxy-containing material divided by the total number of epoxy molecules present.

552 Polymeric epoxides include linear polymers with terminal epoxy groups (e.g. diglycidyl ethers of polyoxyalkylene glycols), polymers with backbone oxirane units (e.g. polybutadiene polyepoxides), and pendent epoxy groups (e.g. glycidyl methacrylate polymers or copolymers).).

556 Molecular weights of epoxy-containing materials vary from 58 to over 100,000.

557 Mixtures of various epoxy-containing materials can also be used in the hot melt compositions of the present invention.

[0057]

562 Useful epoxy-containing materials include 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexanecarboxylate, and those containing a cyclohexane oxide group such as epoxycyclohexanecarboxylate typified by bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate.

566 See US Pat. No. 3,117,099 for a more detailed list of useful epoxides of the same class.

[0058]

570 Still other epoxy-containing materials that are particularly useful in the practice of the present invention include glycidyl ether monomers having the formula , where R' is alkyl or aryl and n is an integer value from 1 to 6. .

574 Examples include glycidyl ethers of polyhydric phenols obtained by reacting polyhydric phenols with excess chlorohydrin such as epichlorohydrin (e.g. diglycidyl ether of 2,2-bis-(2,3-epoxypropoxyphenol)propane).).

577 Further examples of this type of epoxide that can be used in the practice of this invention are set forth in US Pat. No. 3,018,262.

[0059]

582 There are many commercially available epoxy-containing materials that can be used in the present invention.

584 Particularly readily available epoxides include octadecylene oxide, epichlorohydrin, styrene oxide, vinylcyclohexane oxide, glycidol, glycidyl methacrylate (e.g., from Shell Chemical Co., under the tradenames EPON 828, EPON 1004, and EPON 1001F). , Dow Chemical Co.

587 Diglycidyl ether of bisphenol A (available under the tradenames DER-332 and DER-334 from Ciba-Geigy), diglycidyl ether of bisphenol F (such as ARALDITE GY281 from Ciba-Geigy), (eg Union Carbide Corp.).

590 vinyl cyclohexene dioxide (such as ERL 4206 from Union Carbide Corp.);

591 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexene carboxylate (such as ERL-4221 from Union Carbide Corp.);

593 2-(3,4-epoxysiloheptyl-5,5-spiro-3,4-epoxy)cyclohexane-methoxydioxane, such as ERL-4234 from Union Carbide Corp.

595 bis(3,4-epoxycyclohexyl)adipates (such as ERL-4299 from Union Carbide Corp.),

596 dipentene dioxide, such as ERL-4269 from FMC Corp.

597 epoxidized polybutadiene, silicone resins containing epoxy functionality, (-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and (-glycidoxypropyltrimethoxysilane, commercially available from Union Carbide, for example). epoxysilanes (such as methoxysilanes), (eg Dow Chemical Co.

601 flame retardant epoxy resins (such as DER-542, a brominated bisphenol type epoxy resin available from Ciba-Geigy), 1,4-butanediol diglycidyl ethers (such as ARALDITE RD-2 from Ciba-Geigy), Shell Chemical Co.

604 Hydrogenated bisphenol A-epichlorohydrin-based epoxy resins (such as EPONEX 1510 from Dow Chemical Co.) and (such as Dow Chemical Co.).



606 and polyglycidyl ethers of phenol-formaldehyde novolacs, such as DEN-431 and DEN-438 from Epsom.

[0060]

611 Photoinitiators useful in the compositions of the present invention are cationic and include three types: aromatic iodonium complex salts, aromatic sulfonium complex salts and metallocene salts.

614 Useful aromatic iodonium complex salts have the formula

615 wherein Ar1 and Ar2 are aromatic groups having 4 to 20 carbon atoms selected from the group consisting of phenyl, thienyl, furanyl, and pyrazolyl groups.

617 Z is oxygen, sulfur,  (wherein R is 6 to 20 carbons aryl such as phenyl or 2 to 20 carbons acyl such as acetyl, benzoyl), a carbon-carbon bond, or  (wherein R1 and R2 are selected from the group consisting of hydrogen, alkyl radicals of 1 to 4 carbons, and alkenyl radicals of 2 to 4 carbons.

623 The value of m is 0 or 1 and X is a halogen-containing complex anion selected from tetrafluoroborate, hexafluorophosphate, pentafluorohydroxyantimonate, hexafluoroarsenate, and hexafluoroantimonate is.

[0061]

629 Ar1 and Ar2 aromatic groups may optionally have one or more fused benzo rings (eg, naphthyl, benzothienyl, dibenzothienyl, benzofuranyl, dibenzofuranyl, etc.).

631 Also, if desired, the aromatic group may be substituted with one or more non-basic groups that are substantially non-reactive with the epoxide and hydroxyl functional groups.

[0062]

636 Useful aromatic iodonium complexes are more fully described in US Pat. No. 4,256,828.

637 Preferred aromatic iodonium complex salts are diaryliodonium hexafluorophosphate and diaryliodonium hexafluoroantimonate.

[0063]

642 Aromatic iodonium complexes useful in the compositions of the invention are photosensitive only in the ultraviolet region of the spectrum.

644 However, known sensitizers for photodegradable organohalogen compounds can sensitize them in the near UV and visible regions of the spectrum.

646 Examples of sensitizers include aromatic amines and colored aromatic polycyclic hydrocarbons.

[0064]

651 Aromatic sulfonium complex salt photoinitiators suitable for use in the compositions of the present invention have the formula

653 wherein R3, R4 and R5 may be the same or different and at least one group is aromatic.

654 These groups are selected from aromatic moieties having 4 to 20 carbon atoms (eg, substituted and unsubstituted phenyl, thienyl, and furanyl) and alkyl radicals having 1 to 20 carbon atoms.

657 The term "alkyl" includes substituted alkyl radicals (eg, halogen, hydroxy, alkoxy, aryl, etc. substituents).

659 Preferably R3, R4 and R5 are each aromatic.

660 Z, m and X are all as defined above for the iodonium complex.

[0065]

664 When R3, R4 or R5 is an aromatic group, it may optionally have one or more fused benzo rings (eg, naphthyl, benzothienyl, dibenzothienyl, benzofuranyl, dibenzofuranyl, etc.).

666 Also, if desired, such aromatic groups may be substituted with one or more non-basic groups that are substantially non-reactive with epoxide and hydroxyl functionalities.

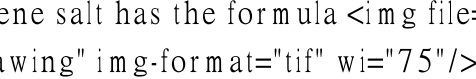
[0066]

671 Triaryl substituted salts such as triphenylsulfonium hexafluoroantimonate are preferred.
672 Useful sulfonium complex salts are described in greater detail in US Pat. No. 4,256,828.

[0067]

676 Aromatic sulfonium complexes useful in the present invention are photosensitive essentially only in the ultraviolet region of the spectrum.
678 However, it can be made sensitive in the near UV and visible regions of the spectrum by a selected group of sensitizers such as those described in US Pat. No. 4,256,828.

[0068]

683 A useful metallocene salt has the formula .
685 (Where Mp represents a metal selected from Cr, Mo, W, Mn, Re, Fe, and Co; L1 represents substituted and unsubstituted h3-allyl, h5-cyclopentadienyl, h7-cyclohepta h6-aromatics selected from trienyl, h6-benzene and substituted h6-benzene compounds, and compounds having 2 to 4 condensed rings each capable of contributing 3 to 8 p-electrons to the valence shell of Mp. L2 represents one or two ligands contributing p-electrons with the same or different ligands selected from the group compounds and L2 is the same or different ligands selected from carbon monoxide or nitrosonium; and represents an even number of (-no or 1-3 ligands contributing electrons, provided that L1 and L2 add the ionic charge of the metal Mp to the total electronic charge contributed to Mp, the complex has a net residual positive charge q, where q is an integer value with a value of 1 or 2 and is the residual charge of the complex cation, and Y is selected from AsF6-, SbF6- and SbF5OH- Halogen-containing complex anions, where r is an integer value with a value of 1 or 2, the number of complex anions required to neutralize the charge q of the complex cation.

698

[0069]

702 Useful metallocene salts are described in more detail in US Pat. No. 5,089,536 (Palazzotto et al.).
704 Examples of useful salts include ((5-cyclopentadienyl)((6-xylene)Fe+SbF6-, also denoted as Cp(xylene)Fe+SbF6-).
706 A useful amount range for the metallocene catalyst is about 0.05 to 20 parts by weight of the epoxy resin, preferably about 0.07 to about 10 parts, more preferably about 0.09 to about 3 parts.
709 The metallocene salts may also be used with accelerants such as oxalate esters of tertiary

alcohols.

[0070]

714 Useful commercial photoinitiators include aromatic sulfonium complex FX-512 (3M Company), aromatic sulfonium complex (Union Carbide Corp.), aromatic sulfonium complex UVI-6974 (Union Carbide Corp.), and the metallocene complex IRGACURE (261 (Ciba-Geigy)).

[0071]

721 The hot melt compositions of the present invention may optionally further contain hydroxyl-containing materials.

723 The hydroxyl-containing material may be any liquid or solid organic material having a hydroxyl functionality of at least 1, preferably at least 2, and most preferably about 3.

725 The hydroxyl-containing organic material should be free of other "active hydrogen" containing groups such as amino and mercapto moieties.

727 Also, the hydroxyl-containing organic material should be heat or light conditioned so that the material does not decompose or release volatile components at temperatures below about 100 ° C or upon exposure to actinic or electron beam radiation during curing. It is essentially free of decomposition-labile groups.

[0072]

734 Preferably, the organic material has two or more primary or secondary aliphatic hydroxyl groups (ie hydroxyl groups directly attached to non-aromatic carbon atoms).

736 The hydroxyl groups may be terminally located or may be pendent from the polymer or copolymer.

738 The number average equivalent weight of the hydroxyl-containing material is preferably about 31-2250, more preferably about 80-1000, and most preferably about 80-350.

[0073]

743 Representative examples of suitable organic materials having a hydroxyl functionality of 1 include alkanols, monoalkyl ethers of polyoxyalkylene glycols, and monoalkyl ethers of alkylene glycols.

[0074]

749 Representative examples of useful monomeric polyhydroxy organic materials include (e.g., 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 2-ethyl-1,6-hexanediol, bis(hydroxy alkylene glycols (such as methyl)cyclohexane, 1,18-dihydroxyoctadecane, and 3-chloro-1,2-

propanediol), polyhydroxyalkanes (such as glycerin, trimethylolethane, pentaerythritol, and sorbitol), and N,N-bis(hydroxyethyl)benzamide, 2-butane-1,4-diol and other polyhydroxy compounds such as castor oil.

[0075]

758 Representative examples of useful polymeric hydroxyl-containing materials include polyoxyalkylene poly(e.g., polyoxyethylene and polyoxypropylene glycols and triols having an equivalent weight to the diol of 31 to 2250 and an equivalent weight to the triol of 80 to 350). Hydric alcohols, polytetramethylene oxide glycols of different molecular weights, hydroxyl-terminated polyesters, and hydroxyl-terminated polylactones are included.

[0076]

766 Commercially useful hydroxyl-containing materials include the POLYMEG series of polytetramethylene oxide glycols, such as POLYMEG 650, 1000 and 2000 (QO Chemicals, Inc.

769) and the TERATHANE series of polytetramethylene oxide glycols such as TERATHANE 650, 1000 and 2000 (available from E.I. duPont de Nemours and Company) and BASF Corp.

771 and the BUTVAR series of polyvinyl acetal resins such as BUTVAR B-72A, B-73, B-76, B-90 and B-98 (available from Monsanto Chemical Company); TONE series of polycaprolactone polyhydric alcohols such as TONE 0200, 0210, 0230, 0240, and 0260 (available from Union Carbide) and DESMOPHEN 2000, 2500, 2501, 2001KS, 2502, 2505, 1700, 1800, and 2504, etc. DESMOPHEN series of saturated polyester polyhydric alcohols (Miles Inc.

776 available from Ruco Corp.) and the RUCOFLEX series of saturated polyester polyhydric alcohols such as S-107, S-109, S-1011 and S-1014 (Ruco Corp.

778 VORANOL 234-630 (trimethylolpropane) from Dow Chemical Company, VORANOL 230-238 (glycerol polypropylene oxide adduct) from Dow Chemical Company, and SYNFAC 8009, 773240, 8024, 8027, 8026, and SYNFAC series of polyoxyalkylated bisphenol A such as 8031 (available from Milliken Chemical) and the ARCOL series of polyoxypropylene polyhydric alcohols such as ARCOL 425, 1025, 2025, 42, 112, 168, and 240 (Arco Chemical Co.

784 available from).

[0077]

788 The amount of hydroxyl-containing organic material used in the composition of the present invention depends on the compatibility of the hydroxyl-containing material with both the epoxy-containing material and the polyester component, the equivalent weight and functionality of the hydroxyl-containing material, and the desired final cured composition. It varies widely depending on factors such as the physical properties used.

[0078]

- 796 Optional hydroxyl-containing materials are particularly useful in adjusting the flexibility of the hot melt compositions of the present invention.
- 798 As the equivalent weight of hydroxyl-containing material increases, the flexibility of the hot melt composition correspondingly increases, although there may be a consequent loss of cohesive strength.
- 801 Similarly, a decrease in equivalent weight may result in a loss of flexibility with the resulting increase in bond strength.
- 803 Thus, the equivalent weight of hydroxyl-containing material is selected to provide a balance between these two properties, with the proper balance depending on the particular application.

[0079]

- 809 Soft melt sealing compositions are useful in forming flexible sheets for sealing functions at lower temperatures, ie, below about 0 ° C.
- 811 Polyoxyethylene glycols and triols having an equivalent weight of about 31 to 2250 for glycols and about 80 to 350 for triols are particularly preferred when hydroxyl-containing materials are used to adjust the flexibility of the melt sealing composition.
- 814 More preferred are polyoxypropylene glycols and triols having an equivalent weight of about 31-2250 for the glycol and about 80-350 for the triol.

[0080]

- 819 The melt-flowable compositions of the present invention contain from 0.01 to 95 parts epoxy-containing material and correspondingly from 99.99 to 5 parts polyester component per 100 parts total.
- 822 More preferably, the melt-flowable composition of the present invention comprises 0.1 to 80 parts epoxy-containing material and correspondingly 99.9 to 20 parts polyester component.
- 824 Most preferably, the melt-flowable composition of the present invention comprises 0.5 to 60 parts epoxy-containing material and correspondingly 99.5 to 40 parts polyester component.
- 826 Increasing the amount of epoxy-containing material relative to the polyester component generally results in melt-flowable compositions with higher ultimate strength and heat resistance, but lower flexibility and viscosity.
- 829 Increasing the amount of polyester component generally results in a melt-flowable composition with lower ultimate strength and heat resistance, higher viscosity, but higher flexibility and green strength build-up.
- 832 In this way the relative amounts of these two components are balanced depending on the desired properties of the final composition.

[0081]

- 837 If a photoinitiator is used, it is present in an amount ranging from about 0.01 to 4% based on the combined weight of the epoxy-containing material and polyester component.
- 839 Increasing the amount of photoinitiator accelerates the cure rate.
- 840 Also, increasing the amount of photoinitiator reduces the energy exposure requirement.
- 841 The amount of photoinitiator depends on the speed at which the composition is to cure, the intensity of the radiation source, and the thickness of the composition.

[0082]

- 846 For some applications, it is useful to first radiation cure the melt flowable composition only on the surface of the sheet and then heat cure the entire sheet.
- 848 For example, an actinically curable epoxy polyester sheet material is exposed to actinic radiation to cure the surface of the sheet material, and then the aforementioned roof groove so that the sheet material forms a concave surface along the roof groove as shown in Figure 1b. put inside.
- 852 The strip is then heated within the grooves to a temperature sufficient to bond the strip to the surface to cure the entire thickness of the sheet.
- 854 As a result, a surface is obtained on the sheet material with a coating that helps provide a smooth surface for visual and functional reasons.

[0083]

- 859 Melt-flowable compositions containing polyether polyhydric alcohols may be useful for conforming melt-flowable sheets to replace air pockets prior to forming a permanent bond to a substrate.
- 862 In addition, if desired, (based on epoxy-containing material, polyester component, photoinitiator and optional hydroxyl-containing material) to reduce composition weight or cost, adjust viscosity and provide additional toughening up to 50% of the total volume of the composition, including various fillers, adjuvants, additives such as silica, glass, clay, talc, pigments, colorants, glass beads or foams, glass or ceramic fibers, antioxidants, etc. It can also be provided as a drug or the like.
- 868 Fillers capable of absorbing radiation used in the curing process should be used in amounts that do not adversely affect the curing process.

[0084]

- 873 Melt-flowable compositions comprising the aforementioned polyester and epoxy polyester materials are prepared by thoroughly melt-mixing the components in a suitable container that is preferably impermeable to actinic radiation when photoinitiators are used. It is prepared by mixing the various ingredients at an elevated temperature sufficient to liquefy the ingredients but not cause thermal decomposition of the materials so that they can be

efficiently mixed by agitation to a temperature.

- 879 Although the components can be added simultaneously or sequentially, it is preferred to mix the epoxy-containing material and polyester component first, followed by the addition of the hydroxyl-containing material and then the photoinitiator.
- 882 The melt-flowable composition should be compatible in the melt phase, ie, there should be no visually distinct phase separation between the components.

[0085]

- 887 Melt-flowable sheets made from epoxy polyester compositions may be tacky or non-tacky.
- 888 Mixtures of liquid and solid epoxy-containing materials are useful in providing adhesive sheets.

[0086]

- 893 In use, the melt-flowable sheet material containing the photoinitiator is exposed to a radiation source before, during, or after application of the sheet material to the substrate to activate the catalyst for curing the epoxy-containing material. can.
- 896 Upon exposure of the sheet material to any radiation source that emits actinic radiation (i.e., radiation having wavelengths in the ultraviolet or visible spectral region), activation of the catalyst occurs.
- 899 Suitable radiation sources include mercury, xenon, carbon arcs, tungsten filament lamps, quartz halogen lamps, fluorescent lamps, sunlight, and others.
- 901 The exposure time should be sufficient to activate the catalyst, approximately 1 second, depending on both the amount and type of reactants involved, the radiation source, the distance from the radiation source, and the thickness of the sheet. Varies from less than 20 minutes or more.

[0087]

- 908 The time required to achieve full cure can be shortened by curing the sheet material by heating, such as in an oven.
- 910 The curing time and temperature vary depending on the glass transition temperature of the polyester component, the concentration of the photopolymerization initiator, the radiation exposure conditions, and the like.
- 913 Typical cure cycle conditions range from 5 to 30 minutes at temperatures ranging from about 50 to 200 ° C.
- 915 One or more heating cycles can also be used to cure the sheet material.

[0088]

- 919 The composition can also be cured by exposure to electron beam radiation.

920 Dosages required are generally from less than 1 megarad to over 100 megarads.
921 As the amount of photoinitiator increases, the rate of cure for a given light exposure or radiation tends to increase.
923 Curing speed also increases with increasing irradiation intensity or electron dose.

[0089]

927 Other layers may also be included in the melt-flowable sheet for various purposes.
928 A second melt-flowable layer can also be adhered to one major surface of the first melt-flowable sheet to improve the morphological and aesthetic properties of the surface.

[0090]

933 A second layer may also be included in the melt-flowable sheet material to improve the outdoor weatherability of the tape.

[0091]

938 Thermal expansion agents such as expansion agents, foaming agents, expandable polymeric microspheres, etc. may also be included in the second layer of the melt-flowable tape to impart a convex shape to the surface.

[0092]

944 Woven or nonwoven webs or scrims can also be included in the melt flowable sheet material.
945 The web can be laminated to the melt-flowable layers with an adhesive or by thermal lamination techniques and can be interposed between two melt-flowable layers.
947 The addition of a nonwoven web has been found to be useful in controlling the flow of the melt-flowable layer.
949 Woven or nonwoven webs can also be used to provide strength to the sheet material for better handling properties.

[0093]

954 Another material that can be included as part of the melt-flowable sheet material is a thermoplastic film.
956 Preferably, the film is formed upon application of the melt-flowable sheet material to the substrate, e.g., upon heating the sheet material to a temperature necessary to cause flow and/or heat-setting of the sheet material, or after application, e.g. Dimensionally stable at temperatures that may occur with exposure to sunlight or otherwise.
960 Useful films include polyurethane films, oriented polyester films, polyimide films, polyolefin films, and the like.

962 The film can be used to provide a smooth surface for painting or as a finished surface after a melt-flowable sheet has been bonded to the surface.

[0094]

967 Thermoset films can also be used.

968 Examples of thermoset films include films made from the above-described crosslinked epoxy polyester materials, crosslinked epoxy films, and the like.

[0095]

973 Preferred films include films made from the epoxy polyester materials described above, polyester films including polyethylene terephthalate films, ultra high molecular weight polyethylene films, microporous ultra high molecular weight polyethylene films, ultra high molecular weight polypropylene films, ultra high molecular weight microporous polypropylene films, and polyimide films.

978 Ultra high molecular weight polyolefin films are preferred in some embodiments because the very long chains of ultra high molecular weight polyolefin soften upon heating without exhibiting the melt liquid flow typical of thermoplastic materials.

[0096]

984 Useful ultra-high molecular weight polyethylene films have an intrinsic viscosity of at least about 18 deciliters per gram (dL/g), with a typical range of intrinsic viscosity being about 18-39 dL/g, with a preferred range of 18-32. dL/g.

987 Useful ultra-high molecular weight polypropylene films have intrinsic viscosities of at least 6 dL/g.

989 A typical range for intrinsic viscosity is 6 to about 18 dL/g, with a preferred range of 6 to 16 dL/g.

[0097]

994 Both thermoset and thermoplastic films must be dimensionally stable at the temperatures to which they are exposed.

996 Dimensionally stable means that the film has sufficient integrity during the heat curing cycle of the melt sealing layer for 20 to 40 minutes at use temperatures, particularly about 120 to 200 ° C., and does not melt or flow. means that

999 Also, the film does not wrinkle when heated to the melt sealing temperature and subsequently cooled.

1001 The film also has sufficient integrity to prevent air entrapments in the fused sealing layer from expanding through the film and causing defects.

1003 After being laminated to the melt sealing layer and heated to the temperature required to

bond the melt sealing layer to the surface, the film preferably has a descending web and transverse web shrinkage of less than about 5%, more preferably about 3%, most preferably less than about 2%.

1007 In a highly preferred embodiment, the film has less than 1% shrinkage in the descending web direction and less than 0.5% shrinkage in the cross web direction.

[0098]

1012 In some applications, it may be desirable for the film to shrink a certain amount to help regulate the flow of the underlying molten sealing material.

[0099]

1017 Additives can also be included in the film to improve or impart various properties such as paint adhesion and thermal stability to the film.

1019 Materials useful for these purposes include silica-containing fillers such as silica, talc, zeolite, kaolinite, mica, alumina silica gel, glass; carbonaceous materials; inorganic metal oxides; Sulfates and carbonates are included.

1022 Examples include carbon black, iron oxide, titanium oxide, zirconia, zinc sulfide, barium sulfate, calcium carbonate, and magnesium carbonate.

1024 Preferred fillers are silica and clays, and preferred silica-containing fillers are precipitated silica, silica gel and fumed silica.

1026 Fillers can be used from about 5 to 90% by weight based on the total weight of the film.

[0100]

1030 In a preferred embodiment, the film is microporous ultra-high molecular weight micropores having silica-containing fillers in an amount of 50 to 90% by weight of the total film weight and an open pore network comprising 35 to 80% by volume of the film throughout the film. It is a flexible polyolefin film.

[0101]

1037 Useful commercially available films include microporous films sold under the trade name Teslin by PPG Industries and polyester films sold under the trade name Melinex by ICI Americas.

[0102]

1043 Suitable microporous films are also described in US Pat. Nos. 4,861,644 (Young et al.) and 4,439,256 (Shipman).

[0103]

1048 Dimensionally stable films can be used alone or in combination.

1049 For example, a suitable construction includes a 0.003 inch thick polyester film as the dimensionally stable film and has a 0.0005 inch thick film of thermoset epoxy polyester material laminated to the polyester film.

1052 A film that has good dimensional stability at higher temperatures, such as polyester, can also be laminated to a film that has less dimensional stability at the same temperature.

1054 An example of such a structure is a 0.001 inch thick ethylene vinyl alcohol film laminated to a 0.003 inch thick polyethylene terephthalate film.

1056 Combination films are produced by adhesively laminating the films together with an adhesive such as a hot melt adhesive or laminating adhesive, coextrusion of the films, extrusion coating of the film onto a more stable film, and curing of the coating if necessary. can be formed by conventional methods such as

[0104]

1063 The film can be modified and heat stabilized by conventional methods for improving the heat stability of films.

1065 Typically such treatment involves heating the film above the maximum use temperature without stress.

[0105]

1070 The dimensionally stable film can be processed to improve film adhesion to one or both of the fusible sealing layer and the paint or primer.

1072 Such treatments include corona treatment, flame treatment, chemical priming, chemical grafting, and the like.

1074 Processing is particularly useful for polyolefin films.

[0106]

1078 In a preferred embodiment, the dimensionally stable film is attached to a second film that provides a surface that readily accepts standard paints and primers such as those used in the automotive industry.

1081 Examples of such films include films made from ethylene vinyl alcohol and the epoxy polyesters described above.

[0107]

1086 Two or more melt-flowable layers with different melt-flow properties can also be laminated together to form a melt-flowable sheet material.

1088 For example, the upper layer should flow when heated to enclose the lower layer, so that the upper layer should have greater flow characteristics than the lower layer, while the lower layer should have higher strength to improve handling properties. can also

[0108]

1094 In other embodiments, a pressure sensitive adhesive (PSA) layer can be applied to the melt-flowable layer so that the melt-flowable sheet can be placed on the surface prior to heating the melt-flowable layer.

1097 The melt-fluidized bed either flows slightly to provide rounded ridges in the melt-flowable sheet without flowing around the PSA, or flows sufficiently to encapsulate the PSA with no exposed edges of the PSA. Either

[0109]

1103 Useful PSAs include block copolymer PSAs such as styrene-isoprene-styrene block copolymers that can be hot melt coated or solvent coated; acrylonitrile PSAs; acrylic acid PSAs, natural rubber PSAs, and silicone PSAs, such as copolymers of acrylic acid or methacrylic acid esters of non-tertiary alcohols having monomers and polymerized using known techniques such as solvent polymerization, emulsion polymerization, and irradiation polymerization; and vinyl acetate PSA.

1109 The PSA is melted by known techniques such as coating the PSA directly onto the sheet and curing the PSA, or allowing the solvent to evaporate, laminating a PSA transfer tape to the sheet, or coextrusion of the hot melt PSA with a melt-flowable layer. Can be bonded to fluid sheets.

[0110]

1116 In preferred embodiments, the PSA is an acrylic acid copolymer.

1117 Useful esters for use in copolymers include n-butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, isooctyl acrylate, decyl acrylate, dodecyl acrylate, and mixtures thereof. be done.

[0111]

1123 If a copolymerizable reinforcing monomer is used, it is a monomer that has a homopolymer glass transition temperature higher than that of homopolymers prepared from acrylic or methacrylic esters.

1126 Useful reinforcing monomers include acrylic acid, isobornyl acrylate, N-vinylpyrrolidone, acrylonitrile, N-vinylcaprolactam, N-vinylpiperidine, and N,N-dimethylacrylamide, and itaconic acid.

[0112]

1132 When reinforcing monomers are used, the acrylic or methacrylic ester is generally present from about 50 to 100 parts by weight and the reinforcing comonomer is correspondingly present from about 50 to 0 parts by weight.

[0113]

1138 The above-mentioned pressure-sensitive adhesive is prepared by mixing a polymerization initiator such as azobisisobutyronitrile in an organic solvent such as ethyl acetate, adding monomers at a desired ratio, and then polymerizing at a high temperature of about 80°C. It can be prepared by known methods with heating to completion.

1142 Adhesives can also be prepared by methods known in the art by UV polymerization and E-beam polymerization.

1144 Pressure sensitive adhesives are also commercially available as adhesive transfer tapes from numerous suppliers.

1146 Such tapes include Minnesota Mining and Manufacturing Co.

1147 and product numbers 465, 467, and 468, all commercially available from .

[0114]

1151 In another example, the melt-flowable sheet material can include a layer of a thermoset PSA that is tacky and pressure sensitive at room temperature and cures into a thermoset adhesive after heating.

1154 This type of melt-flowable sheet material involves bonding the two surfaces together at a lower temperature, i.e., around room temperature, to a sheet that bonds to the first surface on the thermoset PSA side, and then the second surface on the melt-flowable side. surface at higher temperatures, i.e., around the melting temperature of the melt-flowable layer.

1158 When the substrate is heated to higher temperatures, the PSA cures to form a thermoset adhesive with very high bond strength.

1160 In this application, a melt-flowable layer can be selected that has minimal flow at higher temperatures so that the melt-flowable material does not flow out of the bond.

[0115]

1165 Preferred melt-flowable layers for this embodiment include the polyesters and functionalized olefinic polymers previously described.

[0116]

1170 Suitable thermosetting PSAs include thermosetting components and pressure sensitive adhesive components.

1172 The thermosetting component is generally present from about 25 to 150 parts by weight based on 100 parts by weight of the PSA component.

1174 Coatable compositions for thermosetting PSAs can be formed in a variety of ways, as follows.

1175 A solvent-based PSA, a thermosetting resin, and a thermosetting curing agent are mixed together.

1177 A pressure sensitive elastomer such as nitrile-butadiene rubber is dissolved in a solvent and mixed with a thermosetting resin and curing agent.

1179 Monomers or prepolymers useful for making PSA, such as the monomers for making acrylic acid copolymers described above, are mixed with a thermosetting resin and a curing agent, and the mixture is photopolymerized.

[0117]

1185 Useful materials for the PSA component include those described above for PSA.

1186 Preferred materials include acrylonitrile and acrylates, with acrylates being particularly preferred.

[0118]

1191 Thermosetting components are thermosetting resins such as epoxy resins, urethane resins, and phenolic resins.

1193 Preferred thermoset resins are epoxies and urethanes, with epoxies being most preferred.

1194 Useful epoxy resins have been mentioned above.

1195 The epoxy resin may be solid, liquid or mixtures thereof, so long as the epoxy is miscible with the PSA component.

1197 Preferred epoxies include phenolic epoxies, bisphenol epoxies, hydrogenated epoxies, bisphenol epoxies, aliphatic epoxies, halogenated bisphenol epoxies, novalac epoxies, and mixtures thereof, with the most preferred epoxies being , diglycidyl ether of bisphenol A.

[0119]

1203 In a preferred embodiment, the thermosetting PSA is (i) an acrylic or methacrylic acid ester prepolymer syrup as described above (i.e., partially polymerized to a viscous syrup of typically about 100 to 10,000 centipoise). or a monomer syrup, (ii) optionally a reinforcing comonomer as described above, (iii) an epoxy resin, (iv) a photoinitiator, and (v) a heat-activated curing agent for the epoxy. It is a photopolymerization reaction product of a substance.

1209 The adhesive can be prepared according to the procedures found in US Pat. No. 5,086,088.

[0120]

1213 Photoinitiators useful for polymerizing the prepolymer syrup or monomer syrup can be any

conventional free-radical polymerization initiator activated by, for example, ultraviolet light.
1215 An example of a suitable photoinitiator is 2,2-dimethoxy-2-phenylacetophenone (Irgacure (651) available from Ciba-Geigy Corporation).
1217 The photoinitiator is used in an amount sufficient to polymerize the monomers, typically about 0.01 to 5 parts by weight per 100 parts of prepolymer syrup or monomer syrup.

[0121]

1222 A heat-activated curing agent is added to the composition to cure the epoxy resin upon heating.
1224 The curing agent can be of any type, but preferably is an amine-type curing agent such as dicyandiamide and polyamine salts.
1226 Suitable commercial hardeners are available from Omicron Chemical under the Omicure(tm) trademark and from Ajinomoto Chemical under the Ajicure(TM) trademark.
1228 The curing agent is used in an amount sufficient to cure the epoxy resin, typically 0.1 to 20 parts by weight, and preferably 0.5 to 10 parts by weight per 100 parts of epoxy resin.

[0122]

1233 Since the heat to which the composition is exposed may not be sufficient to fully activate the curing agent and cure the epoxy resin, it is useful to further add an accelerator to the adhesive composition.
1236 Accelerators allow the adhesive to cure at lower temperatures and/or shorter exposure times.
1238 Imidazole and urea derivatives are particularly preferred in embodiments of the present invention, and useful compounds include 2,4-diamino-6-(2'-methylimidazole)-ethyl-s-triazineisocyanurate, 2-phenyl-4-benzyl-5-hydroxymethylimidazole, hexakis(imidazole)nickel phthalate, and toluenebis-dimethylurea.
1242 Accelerators may be used up to 20 parts by weight per 100 parts by weight of epoxy resin.

[0123]

1246 In the manufacture of melt-flowable sheets with thermoset PSAs, the aforementioned solvent-based compositions are coated onto a flexible web, preferably a silicone-coated release liner, to the desired adhesive thickness, and the adhesive is heated. Heat below curing temperature to remove solvent.
1250 The adhesive is then laminated to the melt-flowable sheet for future use.
1251 Alternatively, the composition can be coated directly onto the melt-flowable sheet and dried at a temperature below the hot melt activation temperature.

[0124]

1256 In an alternative embodiment, the syrup composition is coated onto a silicone release liner, photopolymerized in an inert atmosphere, i.e., an essentially oxygen-free atmosphere such as a nitrogen atmosphere, and the composition is irradiated with ultraviolet light to A photopolymerized syrup composition is prepared having the thermosetting PSA component described above.

1261 A sufficiently inert atmosphere is achieved by covering the coating with a second polymeric film that is inherently transparent to UV radiation and irradiating through the film.

1263 The adhesive is then laminated to the melt-flowable layer.

1264 Alternatively, a sheet of melt-flowable layer can be used in place of either the top or bottom release liner.

[0125]

1269 For further handling purposes, a nonwoven or reinforcing scrim may be inserted between the layers or embedded within the thermoset PSA layer to provide additional strength.

[0126]

1274 The foregoing melt-flowable sheets with thermoset PSAs are particularly useful for washer bonding in automotive assembly.

1276 The washer is prepared by laminating the washer to a piece of thermosetting PSA that is cut to the size and shape of the washer, for example, by stamping or punching press.

1278 The cut thermosetting PSA is then laminated to the washer manually or by automated machinery, with the melt-flowable side exposed for bonding at higher temperatures.

1280 Alternatively, the thermosetting PSA is bonded to a metal sheet suitable for washer manufacture.

1282 The melt-flowable layer of the sheet is tack-free at room temperature.

1283 A washer of the desired size is then stamped out of the metal sheet.

[0127]

1287 In use, the washer is used to tighten the bolt to the door hinge when the door is aligned and attached to the vehicle frame.

1289 The automobile is then painted and put through an oven cure cycle to dry and cure the paint.

1290 The melt flowable side of the sheet also melts sufficiently in the oven to bond tightly to the metal surface of the frame.

1292 The door can then be removed for the installation of the trim and the door reinstalled in the aligned position indicated by the location of the washer.

1294 This washer-bonding method allows automatic dispensing of washers during assembly and eliminates liner and adhesive contamination problems associated with known washer-bonding methods.

[0128]

- 1300 For washer-bonding applications, the thickness of the melt-flowable sheet is preferably about 10-250 (μm), most preferably 25-100 (μm).
- 1302 If the thickness exceeds about 250 (μm), melt flowable material may leak out of the washer during the heat-setting operation, which may affect the bond strength between the washer and the vehicle frame.
- 1305 The thickness of the thermoset pressure sensitive adhesive layer should be in the range of about 10-300 (μm), preferably about 30-200 (μm).

[0129]

- 1310 Test Method Two 2.5 cm x 5 cm PPG ED-11 panels (electron available from Advance Coating Technologies, Inc., Primed steel (also referred to herein as ED-11 panels) were overlapped and bonded 2.54 cm x 1.27 cm.
- 1313 The sample was heated to bond the two panels together at the temperature indicated in the specific example, then cooled at room temperature for at least 16 hours.
- 1315 The panels were tested on an Instron(™) tensile tester using a crosshead speed of 5 cm per minute.
- 1317 The force at adhesive failure was recorded in megapascals (MPa).

[0130]

- 1321 Adhesive Shear Strength for Washer Bonding Adhesive shear strength was measured according to JISK6850.
- 1323 Two steel panels with a thickness of 1.6 mm were used as substrates.
- 1324 The adhesive was placed between the panels and then cured at a pressure of 500 g/cm² for 60 minutes at a temperature of 140 °C.
- 1326 The panels were then cooled to room temperature before testing.
- 1327 Adhesive shear strength was measured using a tensile tester at a jaw separation speed of 50 mm/min.
- 1329 Preferred adhesives have a shear strength greater than 50 kgf/cm².

[0131]

- 1333 Punching Performance Using a pressure-operated punching press, the bonding material was punched out in circles corresponding to the holes in the washer at a pressure of 30 kgf/cm².
- 1336 The number of samples per bonded material was 5.
- 1337 Samples were evaluated under the following criteria.
- 1338 Good: No punching failure.
- 1339 Pressure sensitive thermosetting adhesives do not leak from hot melt films.

1340 Cross section looks good.

1341 Relatively difficult punching: 1 or 2 samples punched incompletely.

1342 The thermoset adhesive leaked slightly from the hot melt film.

[0132]

1346 Adhesive Leakage Samples used for adhesive shear strength measurements were visually inspected for leakage of pressure sensitive thermoset adhesives or hot melt films from steel panels.

1349 Judgment criteria are shown below.

1350 No Leakage: Ok Slight Leakage: Good Large Leakage: Poor

[0133]

1354 Certain embodiments of the invention are illustrated in the following non-limiting examples.

1355 Parts are parts by weight unless otherwise specified.

[0134]

1359 Examples 1-2 In Example 1, 100 parts of a hydroxy-functional semi-crystalline polyester resin (Dynapol (1402) available from Huls America) was heated to about 110 ° C to form a melt mixture to form a melt flowable sheet. was prepared.

1362 The molten mixture was coated on a knife bar coater (heated to 127 ° C.) onto silicon coated kraft paper to form a 1.0 mm thick sheet.

1364 Sheets cooled to room temperature became opaque after about 2 hours, suggesting that crystallization had occurred.

[0135]

1369 Example 2 combines 10 parts diglycidyl ether of bisphenol A (EPON (828) available from Shell Chemical Company) with 89 parts DYNAPOL (S1402) and 1 part triphenylsulfonium hexafluoroantimonate (described in U.S. Patent No. No. 4,321,951 at column 5, line 48 to column 7, line 48) and mixed at about 110 ° C. for about 1 hour to prepare a melt flowable sheet.

1374 The resulting mixture was coated on a knife bar coater (heated to 127 ° C.) onto silicon coated kraft paper to form a 1.0 mm thick sheet.

1376 The sheet was cooled to room temperature.

[0136]

1380 A sample tape from Examples 1 and 2 measuring approximately 2.5 cm x 7.6 cm was crossed over a 2.5 cm wide anodized strip crossed over a larger anodized aluminum panel

(hereafter referred to as a step panel) than tested in Examples 1 and 2. It was left to cool and heated in an oven at 177 ° C for 30 minutes.

1384 Both tapes flowed and provided an aesthetically pleasing smooth surface between the aluminum strip and the panel with smooth transitions on the corners.

1386 The tape also flowed beyond the original dimensions of the strip on the panel and adhered tenaciously to the panel.

[0137]

1391 Each example was then cut into strips approximately 25.4 cm long by 1.9 cm wide and placed in a U-shaped groove having an inner width of 1.9 cm.

1393 Each U-shaped groove was formed by bending two pieces of cold rolled steel at a 90 ° angle and spot welding the pieces together to form a step-down joint within the U-shape.

1395 The U-shaped groove with the attached strip was tilted at an angle of about 15 ° and heated in an oven at 177 ° C for 30 minutes and cooled to room temperature.

1397 Both strips flowed and effectively sealed the joint, giving the groove a smooth surface without the appearance of a step joint on the surface.

[0138]

1402 The bottom edges of both strips were marked on the U-grooves, then both U-grooves were placed in an oven at 120 ° C at an angle of 15 ° for 30 minutes and then cooled.

1404 Flow upon subsequent heating was about 3.2 mm for Example 1 and about 25.4 mm for Example 2.

[0139]

1409 Additional samples of each Example 1 and Example 2 were tested on step panels as described above and heated at 177 ° C for 30 minutes.

1411 A total of four samples (two original samples that had been previously exposed to a heating cycle and two new samples that had not been exposed to subsequent heating cycles) were painted with a white water-based primer (H WB90934 available from PPG Industries) and subjected to 121 Heated at ° C for 5 minutes.

1415 Two-component clearcoats (CNCT2AH Part A and CNCT2BE Part B, both available from PPG Industries) were mixed according to the manufacturer's instructions and spray painted onto four panels.

1418 The panel was then heated at 140 ° C for 30 minutes and then cooled.

1419 The gloss, color and image clarity (indicative of its mirror-like quality) of the paint finish on the melt-flowable strip was identical to the surrounding metal surface.

1421 The paint transition between the melt-flowable strip and the metal surface was smooth with no evidence of parting lines or paint edge separation.

[0140]

- 1426 The samples, which had been heated once to melt-flow the tape prior to painting, were placed in an oven at 120 ° C for 30 minutes.
- 1428 After cooling, both the panel and the surface remained smooth and aesthetically pleasing with no additional flow observed.
- 1430 The panel with the melt-flowable strip of Example 2 had a slightly wrinkled surface at oven temperature, but the wrinkles disappeared when cooled to room temperature.

[0141]

- 1435 The foregoing examples and tests illustrate preferred embodiments of the present invention that provide a sealed, aesthetically pleasing and paintable surface on metal surfaces.

[0142]

- 1440 Example 3 The melt flowable layer of Example 1 was cut into strips measuring 2.5 cm x 7.6 cm and placed on ED-11 panels and heated in an oven at 177 ° C for 30 minutes.
- 1442 The panel was then cooled, painted with the white basecoat and clearcoat described above, and placed in an oven at 121 ° C for 30 minutes to cure the paint.
- 1444 The melt flowable tape created a ridge with rounded edges on the panel.
- 1445 The panel was subsequently placed horizontally in an oven at 177 ° C and heated for 30 minutes with no effect on distortion of the paint surface or buildup.
- 1447 The panels were then placed in an oven at 177 ° C for 30 minutes at an angle of 75 ° from horizontal.
- 1449 As the panel heated, the buildup became teardrop shaped and the rest of the paint surface remained intact.
- 1451 When the panel was cooled to room temperature at an angle of 75 °, the ridges returned to their original shape.

[0143]

- 1456 The same panel was reheated at a 75 ° angle, except that a pinhole was drilled through the paint layer to reach the melt-flowable layer.
- 1458 Upon heating, the underlying melt-flowable layer was still thermoplastic and oozed through the pinholes.

[0144]

- 1463 The preceding examples illustrate the formation of a reactive interface between the paint and the melt-flowable sheet material.

[0145]

1468 Example 4 A strip of the melt-flowable sheet of Example 1 measuring approximately 2.5 cm x 7.6 cm was placed on a silicone release coated polyester film, indicating that the tape had become clear and amorphous. Placed in the oven at 177 ° C until.

1471 The strips were removed from the oven and allowed to cool to room temperature (21-23 ° C).

1473 The still clear strip had sufficient tack to adhere to ED-11 at room temperature.

1474 The panel was then heated at 120 ° C for 10 minutes to adhere the strip to the panel and then reheated at 177 ° C for 30 minutes.

1476 The samples were then painted and cured in an oven at 140 ° C for 30 minutes.

[0146]

1480 This example illustrates how embodiments of the present invention can be temporarily placed on a substrate prior to being permanently bonded to the substrate.

[0147]

1485 Example 5 The melt-flowable sheet material of Example 1 was applied to an acrylic acid PSA transfer tape (Minnesota Mining & Manufacturing Co.

1487 467 Adhesive Transfer Tape available from Epson Co., Ltd.).

2

1491 .5 A strip measuring cm x 7.6 cm was laminated to the anodized aluminum panel and a strip measuring 2.54 cm x 1.27 cm was laminated to the ED-11 overlap shear panel described above.

1494 The sample was placed in an oven at 177 ° C for 15 minutes and allowed to cool at room temperature until opaque (approximately 90 minutes).

[0148]

1499 The sample on the anodized aluminum panel adhered well and the melt flowable sheet encapsulated the PSA.

1501 Lap shear samples were tested and had an average lap shear strength of 253.8 pounds per square inch.

1503 The fracture was observed to be intimate between the PSA and the melt flowable sheet.

[0149]

1507 The above example illustrates the usefulness of a PSA layer on a melt-flowable sheet to hold

the sheet in place until it is heated to seal the surface.

[0150]

1512 Examples 6-10 Two hydroxy functional polyesters of different degrees of crystallinity were mixed and coated as described in Example 1 to form sheets.

1514 As an indication of crystallization rate, the time taken for the sheet to return to opacity was measured.

1516 The polyester materials used were Dynapol (1402), a polyester resin with low crystallinity, and Dynapol (1359), a polyester resin with high crystallinity.

1518 The amount of each resin is shown in Table 1.

1519 The details given in Table 1 show that the crystallization rate varies.

[0152]

1523 Examples 11-18 and C1-C3 Various thermoplastic materials were evaluated for flow and paint adhesion.

1525 The material was provided in sheets of 1-3 mm thickness.

1526 Example 11 was prepared in the same manner as Example 1 except that a 1 mm thick sheet was prepared, and Example 12 was prepared in the same manner as Example 2 except that the thickness was 1 mm.

1529 The remaining sheets were prepared by placing pellets of material between release coated polyester liners and heating with an iron until the material was fused into a sheet approximately 0.08-0.15 mm thick.

1532 Multiple sheets were folded together to form a thicker sheet approximately 1-3 mm in size.

[0153]

1536 The flow properties were recorded by placing the samples on a 177 °C step panel (described above) for 20 minutes.

[0154]

1541 The samples were then painted with a white water-based primer (H WB90934 available from PPG Industries) and heated at 140 °C for 5 minutes.

1543 Two-component clearcoats (CNCT2AH Part A and CNCT2BE Part B, both available from PPG Industries) were mixed according to the manufacturer's instructions and spray painted onto four panels.

1546 The panels were then heated at 140 °C for 30 minutes and then cooled overnight.

1547 The panel was then reheated at 140 °C for 20 minutes.

[0155]

1551 The materials were tested as follows.

1552 (1) Flow before painting after heating (OK indicates that the material flows but remains sticky, and L indicates that the material has liquefied.

1554) (2) Paint quality after painting, after paint curing, and after reheating (OK indicates good surface appearance, Broken indicates paint cracks or does not cure.

1556) (3) After reheating (OK indicates no change in appearance, edge indicates the paint cracked at the outer edge of the sheet.

1558 Failure indicates that the paint has cracked and the polymer has flowed out of the cracks.

1559) (4) for cross-hatch adhesion expressed as the percentage of paint still adhering to the melt-flowable sheet tested according to ASTM D3359-90 (100% preferred.

1561 Broken indicates that the sample broke before the test was run).

1562 Detailed test results are shown in Table 2.

[0156]

1566 A - Sherex Co.

1567 TS-1502B - BUTVAR(B79 - Monsanto Co.

1568 Polyvinyl Butyral C - Surlyn (1605 - DuPont Co.

1569 Ethylene Acrylic Acid Film D - Primacor (3440 - Dow Chemical Co.

1570 Ethylene Acrylic Acid E - Elvax (260 - available from DuPont Co.

1571 Ethylene Vinyl Acetate F - SCX 8008 - available from J.C. Johnson Co.

1572 G - Carbowax available from Union Carbide (8000H - Carbowax available from Union Carbide (20 MI - TMP (trimethylolpropane) available from Aldrich Chemical) * Paint surface wrinkled when heated but cooled The surface became smooth**The paint film was brittle

[0157]

1578 Examples 19-21 Example 19 is a melt flowable sheet made in the same manner as Example 1 except that the thickness is about 2 mm.

1580 Example 20 was prepared using two sheets prepared as in Example 1 with a nylon nonwoven between the two sheets to a thickness of 1.27 mm.

1582 Non-woven fabric (Fiberweb N.A.

1583 CEREX (), available from Mercury Inc., is 0.3 ounces per square yard and was laminated with a heated iron to the first sheet between two silicone-coated polyester release liners.

1585 A second sheet was then laminated in the same manner.

1586 The sheet became transparent during lamination.

1587 Example 21 was prepared similarly to Example 20, except that a polyester nonwoven material (0.5 ounces per square yard of Reemay 2250 available from Reemay) was used.

[0158]

1592 Examples 19-21 were cut into 2.54 cm x 20.3 cm strips and tested placed vertically on curved metal surfaces formed by bending ED-11 primed metal panels at an angle starting at about 30 ° from horizontal. bottom.

1595 The bent panel was placed in an oven at 177 ° C for 10 minutes.

1596 After cooling, Example 19 was observed to have significant run-down on the sides of the panel.

1598 Example 20 had slight flow, but shrank about 8% due to nylon shrinkage.

1599 Example 21 also had slight flow but no shrinkage.

[0159]

1603 The foregoing examples illustrate the use of nonwoven scrims to flow control melt-flowable sheets.

[0160]

1608 Examples 22 and 23 Similar to Example 2, sheets with a thickness of 0.076 mm were prepared.

1610 The sheet of Example 22 was exposed to UV radiation (low dose black light) for 5 minutes.

1611 The sheets of each example were then cut and stacked to form a sheet with a thickness of 0.72 mm.

1613 The sheet was then cut into 2.54 cm x 7.62 cm strips, hung over two overlapping metal panels, and then heated at 177 ° C for 30 minutes.

1615 Figures 5a and 5b represent the panel and sheet before (Figure 5a) and after (Figure 5b) heating.

1617 When the panels were cooled, both examples showed sufficient fluidity to seal the seams.

1618 The non-irradiated sample, Example 23, had a smoother profile above the step in the overlapping panel, and the step in the panel was more pronounced in Example 22.

1620 The panels were then coated with a black primer from BASF, cured, and overcoated with a two-component clearcoat and cured.

1622 Both samples painted well with 100% crosshatch adhesion.

[0161]

1626 The above examples illustrate how the surface conformability changes with irradiation of the sheet material.

[0162]

1631 Example 24 10 parts cycloaliphatic epoxy (ERL-4221 available from Union Carbide), 89 parts low crystallinity saturated linear copolyester (DYNAPOL (S1402)) and 1 part triphenylsulfonium hexafluoroantimonate were mixed to prepare a composition, and a

crosslinkable melt-flowable sheet was prepared in the same manner as in Example 2, except that the composition was coated to a thickness of 2 mm.

1636 A second melt-flowable sheet was prepared in the same manner as in Example 1, except that the thickness was 2 mm.

1638 Two sheets were placed on top of each other between silicone release coated polyester liners and heated at 177 ° C for 10 minutes to form a 4 mm thick sheet.

1640 A strip about 2.54 cm wide was cut and placed crosslinkable sheet up in a 1.25 cm wide and about 1.9 cm deep roof channel mold.

1642 The master with strips was placed in an oven at 177 ° C for 20 minutes.

1643 After cooling, the strip retained an aesthetically pleasing concave surface along the longitudinal direction of the original.

1645 The underlayer melted and flowed into the joint of the master, and the sides of the tape tenaciously bonded to the sides of the groove, effectively sealing the groove.

1647 Some air entrapments were seen, but these may be related to the thickness of the tape.

[0163]

1651 Example 25 E.I.T.

1652 A 2 mm thick crosslinkable melt-flowable sheet of Example 24 was exposed to a UV black light for 20 seconds using a Uvirad radiometer (model number VR365CH3) from Electronics Instrumentation & Technology, Inc., Sterling, Va.) and photolyzed the surface with a total energy of 160 mJ/cm² (millijoules per square centimeter).

1656 The strips were cut as in Example 24, creased lengthwise with the photolysis side inward, and then placed photolysis side up in the prototype roof channel as described in Example 24.

1659 The master was then heated at 77 ° C for 20 minutes.

1660 The thinner strips provided a smoother transition line between the strips and the sides of the roof channel prototype while providing a stronger bond to the sides of the prototype.

1662 Some air entrapments were observed between the strip and the master, but the bubbles did not affect the aesthetically pleasing surface properties of the strip.

[0164]

1667 Examples 26-34 Melt-flowable sheets were prepared as described in Example 2, except that the composition and materials were varied as shown in Table 3.

1669 Examples 26-31 were 2 mm thick and Examples 32-34 were 1 mm thick.

1670 All examples showed good flow properties and paint adhesion was 100% for all samples.

[0165]

1674 PET - Dynapol (S1402) epoxy 1 - diglycidyl ether oligomer of bisphenol-A (Shell Chemical Co.

1675 Epon (1001) epoxy 2 - Epon (1002) epoxy 3 - diglycidyl ether of bisphenol-A available from

Shell Chemical Co.

1677 1 - Triphenylsulfonium hexafluoroantimonate catalyst 2 - (eta6-xylene (mixed isomers)) (eta5 cyclopentadienyl) iron (eta5 cyclopentadienyl) described in U.S. Pat. No. 5,089,536 1+)
Hexafluoroanimonate

[0166]

1683 Example 35 A melt flowable sheet having a thickness of 0.254 m m was prepared in the same manner as in Example 1.

1685 A second layer was prepared as follows.

[0167]

1689 A 50/50 mixture of butyl acrylate and N-vinylcaprolactam was combined to form a solution.

1690 75 parts butyl acrylate, 75 parts butyl acrylate/N-vinylcaprolactam solution, butyl methacrylate/methyl methacrylate copolymer (Rohm and Haas, Co.

1692 50 parts of Acryloid (B-60) available from Epoxy and 110 parts of a diglycidyl ether oligomer of bisphenol-A (Epon (1001)) were mixed in a jar on a roller mill until the epoxy and copolymer were in solution to achieve melt flow. A synthetic composition (57.7% acrylate and 42.3% epoxy) was prepared.

1696 To this solution was added 0.15 parts 2,2-dimethoxy-2-phenylacetophenone (Irgacure (651) available from Ciba-Geigy), 0.15 parts Irganox (1010) available from Ciba-Geigy, 1.0 parts carbon tetrabromide, dicyandiamide (DYHARD (100) available from SK W Chemical 3.86 parts, hexakis(imidazole) nickel phthalate 1.38 parts, glass foam (Minnesota Mining and Manufacturing Co.

1701 2 parts C15-250 glass foam available from Cabot Corp.) and silica (Cabot Corp.).

1702 Added 7 parts of Cab-o-sil (M-5) available from

1703 The composition was mixed with a high shear mixer and mixed on a roller mill for about 24 hours.

1705 The composition was then degassed and knife coated onto a silicone coated polyester liner to a thickness of about 2.0 to 0.05 m m.

1707 The coated composition was then exposed to an ultraviolet light source with 90% emission between 300 nm and 400 nm and a maximum emission at 351 nm.

1709 The light intensity on the web was 1.88 m W/cm² (milliwatts per square centimeter) and 1.29 m W/cm².

1711 The total energy used was 653.8 millijoules.

1712 The resulting melt-flowable tape was essentially tack-free at room temperature (approximately 21 ° C).

[0168]

1717 One of the polyester liners was removed from each sheet and the first and second melt-

flowable sheets were laminated together with an iron set at about 65.6 ° C to form a melt-flowable composite sheet.

[0169]

1723 A strip of the composite sheet was laid on a metal panel with shallow depressions in the surface, the first layer of the sheet facing the metal surface, heated at 177 ° C for 30 minutes and then cooled to room temperature.

1726 Example 38 showed no surface defects from pitting.

1727 As a comparison, a sheet having only the second layer described above was tested in the same way.

1729 The surface of the second sheet had a visible depression in the center of the sheet overlying the depression.

[0170]

1734 Example 36 Ethylene acrylic acid with an acrylic acid content of 9% (Dow Chemical Co.

1735 A melt-flowable sheet was prepared by extruding a 0.076 mm thick layer of PRIMACOR 3440, available from Epson.

[0171]

1740 A 50/50 mixture of butyl acrylate and N-vinylcaprolactam was heated to about 50 ° C to form a solution.

1742 120 parts of butyl acrylate, 80 parts of butyl acrylate/N-vinylcaprolactam solution, butyl methacrylate/methyl methacrylate copolymer (Rohm and Haas, Co.

1744 50 parts of Acryloid (B-60), available from Chemical Co., and a diglycidyl ether oligomer of bisphenol-A (Shell Chemical Co.).

1746 A melt-flowable composition (50% acrylate and 50% epoxy) was prepared by mixing 200 parts of Epon (1001) available from Microsoft in a jar on a roller mill until the epoxy and copolymer went into solution.

1749 To this solution were added 0.2 parts 2,2-dimethoxy-2-phenylacetophenone (KB-1 available from Sartomer), 0.2 parts antioxidant (Irganox (1010) available from Ciba-Geigy), 0.8 parts carbon tetrabromide, dicyandiamide, (7.0 parts DYHARD (100) available from SK W Chemical, 3.0 parts hexakis(imidazole)nickel phthalate, glass bubbles (Minnesota Mining and Manufacturing Co.

1754 4 parts C15-250 glass foam available from Cabot Corp.) and silica (Cabot Corp.).

1755 14 parts of Cab-o-sil (M-5) available from Sigma Chemical Co. was added to form a mixture.

1756 The mixture was compounded, coated and cured according to the procedure of Example 38 to form a melt-flowable tape.

[0172]

1761 An adhesive composite was prepared by laminating the hot melt adhesive layer to the thermosetting melt flowable tape with an iron as described above.

[0173]

1766 Example 37 76 parts butyl acrylate, 24 parts N-vinylpyrrolidone, and 0.04 parts Irgacure (651 photoinitiator (2,2-dimethoxy-2-phenylacetophenone available from Ciba Geigy) are mixed and swept under constant nitrogen. A pressure sensitive adhesive composition was prepared by photopolymerizing with an ultraviolet (UV) source under a purge to form a syrup with a viscosity of about 2000 cps.

1771 With constant mixing, the following ingredients were added to 100 parts of acrylate syrup and mixed for about 2 hours.

1773 0.1 part of Irgacure™ 651, diglycidyl ether oligomer of bisphenol-A (Shell Chemical Co.

1774 40 parts of Epikote TM 1001, available from Epikote TM 1001, available from Shell Chemical Co.;

1776 50 parts of ELA 128 (available from Omicron Chemical Co.), dicyandiamide (Omicron Chemical Co.

1778 3.5 parts of CG1200 available from Shikoku Chemical Co., Ltd., 2,4-diamino-6-[2'-methylimidazolyl-(1')]-ethyl-S-triazine isocyanurate adduct (Shikoku Chemical Co., Ltd.

1780 6.0 parts fumed silica (Aerosil TM 972 available from DeGussa), and 0.03 parts hexanediol diacrylate.

1782 The mixture was then degassed and knife coated to a thickness of 0.3 ounces per square yard onto a polyamide non-woven fabric (N.A. CEREX from Fiberweb) over a clear silicone coated polyester release liner approximately 0.05 mm thick.

1785 A similar release liner was placed over the coated composite and the coated mixture was photopolymerized above and below the web with a UV lamp with an average intensity of about 1.1 mW/cm² for a total energy usage of 500 mJ/cm². bottom.

1788 The lamp used had 90% emission between 300 and 400 nm, with a maximum emission at 351 nm.

1790 The resulting thermoset pressure sensitive adhesive tape (TPSA) layer thickness was about 0.3 mm.

[0174]

1795 Ethylene acrylic acid with an acrylic acid content of 6.5% (Dow Chemical Co.

1796 A hot-melt adhesive layer (HMA) was prepared by extruding a 0.076 mm thick layer of PRIMACOR 3440 available from Mercury.

1798 The layer thickness was 50 (m.

[0175]

1802 An adhesive tape composite was prepared by removing one of the liners from the pressure sensitive adhesive tape and laminating the hot melt adhesive layer.
1804 The composites were tested for adhesive shear strength, punch performance and leakage.
1805 The test results are shown in Table 4.

[0176]

1809 Example 38 Acrylonitrile rubber (Nippon Zeon Co., Ltd.
1810 A thermoset pressure sensitive adhesive was prepared by dissolving 150 g of Nippol 1001) available from Epson in 400 g of methyl ethyl ketone.
1812 The following materials were then added to the solution and mixed for 24 hours to obtain a homogeneous mixture.
1814 100 g of Epikote(tm) 828, 100 g of Epikote(1001), 20 g of dicyandiamide, Amicure PN (Ajinomoto Co., Inc.
1816 235 g of epoxy hardener available from Nippon Aerosil Co., Ltd.) and silica powder (Nippon Aerosil Co., Ltd.
1818 20 g of Aerosil (A-200) available from
1819 The mixture was then knife coated onto a silicone coated polyester liner and dried at 70 ° C for 15 minutes.
1821 The thickness of the resulting thermosetting pressure sensitive adhesive layer was 100 (m).

[0177]

1825 An adhesive composite was prepared by laminating a thermosetting pressure sensitive adhesive layer to a 50 μ m hot melt adhesive layer prepared as described in Example 37.
1827 The test results are shown in Table 4.

[0178]

1831 Examples 39-42 Adhesive composites were prepared as described in Example 38 with different thicknesses for each layer as shown in Table 4.
1833 Test results are also shown.

[0180]

1837 Examples 43-46 As shown in Table 5, the heat cured pressure sensitive adhesive of Example 37 was laminated to various hot melt adhesive layers.
1839 The thickness of the thermosetting pressure sensitive adhesive layer was 100 (m).
1840 Hot melt adhesive resins shown in Table 5 were extruded to prepare hot melt adhesive layers.
1842 Test results are shown in Table 6.

[0183]

- 1846 Example 47 Hydroxy-functional semi-crystalline polyester resin (Dynapol (S1359) available from Huls America, 88.9 parts by weight and microcrystalline wax (Petrolite Corp.).
- 1848 A first radiation curable epoxy polyester composition was prepared by mixing with 1 part of Unilin (700) available from Unilin.
- 1850 A liquid mixture containing 10 parts epoxy resin (Epon (828)) and 1 part triphenylsulfonium hexafluoroantimonate was pumped into the extruder approximately in the middle of the barrel and mixed with the polyester resin mixture.
- 1853 A vacuum of less than 25 inches Hg was applied to the same area of the extruder barrel to remove air from the mixture.
- 1855 The extruder temperature ranged from 65 to 110 ° C and the feed throat temperature was about 25 ° C.
- 1857 The temperature of the flat die was kept at 82 ° C.
- 1858 The extrudate was coated onto a 0.00291 inch thick raw polyester film and the coated film was cooled and wound into rolls.
- 1860 The thickness of the extrudates ranged from 0.0005 to 0.0007 inches.

[0184]

- 1864 Then into an ultraviolet (UV) treatment unit (model QC250244ANIR supplied by Aetek International, Plainfield, Ill.) with one medium pressure UV lamp having an energy output of 0.201 J/cm² at a line speed of 30 feet per minute. , exposed the coating on the polyester film.
- 1868 The resulting coating on polyester film was heat cured and had excellent adhesion to the polyester film.

[0185]

- 1873 The dry composition was then 77.9 parts Dynapol (S1359, and 1 part microcrystalline wax (Unilin (700)) and the liquid mixture was 20 parts epoxy resin (Epon (828), polyhydric alcohol (Dow Chemical Co.
- 1876 A second epoxy polyester prepared in the same manner as the first epoxy polyester composition except that it contained 1 part Voranol (230-238 polyhydric alcohol) available from Epoxy Inc., and 0.1 part Cp(xylene)Fe+SbF₆-0.1 part The composition was coated on the other surface of the polyester film.
- 1880 A second epoxy polyester composition was coated onto a polyester film to a thickness of 0.040 inch to form a sheet material.

[0186]

- 1885 Example 48 The second epoxy polyester composition of Example 47 was applied to a 0.007

inch thick filled ultra high molecular weight polyolefin film (PPG Industries, Inc.).
1887 A sheet material was formed by coating to a thickness of 0.040 inch on Teslin (sp 700)
available from Epson.

[0187]

1892 A 2.5 inch wide by 10 inch long strip of sheet material was applied to the anodized
aluminum panel and heated to 177 ° C for 15 minutes.
1894 A transverse web shrinkage after cooling of 0% and a descending web shrinkage of about
1.5% was measured.

[0188]

1899 Example 49 A polyester/isocyanate laminate adhesive (Adcote 76T3A/catalyst F available
from Morton) diluted to 30% solids with ethyl acetate was used to laminate a 0.00265 inch
thick polyester film (ICI, Westchester, Pa.). A film layer was prepared by laminating Melinex
054 primed polyester film 2.65 mil available from Films) to a 0.025 m m thick ethylene
vinyl alcohol film (E-25 from EVAL) having 44 mole percent ethylene.
1904 The adhesive was applied to the ethylene vinyl alcohol film using a gravure coater at a dry
coating weight of approximately 32 grams per square meter.
1906 The adhesive was dried at about 63 ° C to evaporate the solvent.
1907 The polyester film was then corona treated and heat laminated at about 93 ° C. to the
adhesive-coated side of the ethylene vinyl alcohol film using a nip roller.

[0189]

1912 The polyester side of the film laminate was then coated with a 0.040 inch thick layer of a
second epoxy polyester composition as described in Example 47.

[0190]

1917 It will be apparent to those skilled in the art that various modifications and variations can be
made in the methods and products of the present invention without departing from the
spirit or scope of the invention.
1920 Thus, it is intended that the present invention cover modifications and variations of this
invention provided they come within the scope of the appended claims and their
equivalents.

[0191]

1926 FIG. 3 is a cross-sectional view of a sheet material according to the present invention located
in a motor vehicle roof groove prior to heating;

1928 1b is a cross-sectional view of the sheet material shown in FIG. 1a after heating; FIG.
1929 1 is a cross-sectional view of a two-layer sheet material according to the invention; FIG.
1930 Figure 3 is a cross-sectional view of yet another two-ply sheet material according to the
present invention;
1932 FIG. 3b is a cross-sectional view of the sheet material of FIG. 3a positioned in a vehicle roof
groove prior to heating;
1934 Fig. 3b is a cross-sectional view of the sheet material of Fig. 3a positioned in a vehicle roof
groove after heating;
1936 Figure 2 is a top view of a washer with adhered sheet material of the present invention;
1937 Figure 4b is a cross-sectional view along line 4b of Figure 4a;
1938 Figure 4b is a sectional view showing the embodiment of Figure 4a with bolts inserted to
connect the door hinge to the door frame;
1940 See Examples 22 and 23.
1941 See Examples 22 and 23.

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CLAIMS JP2007254752A

1.

13 (a) a sheet material having a dimensionally stable film having an upper surface and a lower melt-flowable layer having a lower surface and comprising a melt-flowable composition, wherein the sheet material seals joints of a vehicle body; wherein the melt-flowable layer is formed to have a thickness of 0.05 mm to 25 mm, the dimensionally stable film is heated to the melt-sealing temperature of the melt-flowable composition, followed by providing a sheet material which, when cooled, has sufficient dimensional stability so that it does not melt and flow or wrinkle; (c) applying the sheet material to the step joint by flowing the melt-flowable composition to smooth out or fill in surface imperfections in the step joint, and to bond the sheet material to the step joint; and (d) allowing the sheet material and the step joint to cool, the melt flowable layer flowing to seal the step joint. The sheet material remains adhered to the step joint and the sheet material imparts a structural or protective feature to the step joint. A method of imparting a morphological or protective feature to a stepped junction.

2.

28 The melt-flowable composition comprises (i) an epoxy, and (ii) a polyester, a polyamide, a functionalized ethylene (meth)acrylate copolymer having —OH groups, a polysulfide, a polyacetal, an ethylene (meth)acrylic acid copolymer, propylene (2. The method of claim 1, comprising at least one thermoplastic polymer selected from the group consisting of meth)acrylic acid copolymers, ethylene (meth)acrylic acid ester copolymers, and polycaprolactone.

3.

37 2. The method of claim 1, wherein said melt-flowable layer has a thickness of 0.10 mm to 25

m m.

4.

42 The dimensionally stable film is polyurethane film, oriented polyester film, polyimide film, polyolefin film, crosslinked epoxy film, crosslinked epoxy polyester film, polyethylene terephthalate film, ultra high molecular weight polyethylene film, microporous ultra high molecular weight polyethylene film, ultra high molecular weight polypropylene. A method according to claim 1, which is a film, or an ultra-high molecular weight microporous polypropylene film.

5.

51 2. The method of claim 1, wherein said melt-flowable layer has a thickness of 0.20 m m to 10 m m.

6.

56 The provided sheet material is in the form of a strip, the contacting step comprises contacting a lower surface of the melt-flowable composition to an inner surface of an automotive roof groove having a stepped joint, and the heating heating the strip within the roof groove so that the melt-flowable composition flows over imperfections and joints within the roof groove to create an aesthetically pleasing appearance within the groove and the strip is 2. The step of adhering to the inner surface of the roof groove to provide a protective seal within the roof groove to prevent rainwater, dirt, snow, etc. from entering the roof groove and causing rust or corrosion. 6. The method according to any one of -5.

7.

67 The method of claim 6, further comprising painting the sheet material after cooling the sheet material.

8.

72 (a) a dimensionally stable film having an upper surface; and (b) a sheet material having a lower melt-flowable layer having a lower surface and containing a melt-flowable composition and having a thickness of 0.05 m m to 25 m m. An article adapted for placement on a joint of a vehicle to impart a structural or protective feature to the joint of the vehicle, the sheet material being shaped to seal the joint within the vehicle, so that the film does not melt and flow when the sheet material is heated to a melt sealing temperature sufficient to cause the melt flowable composition to flow and adhere to the joints of the vehicle body and is subsequently cooled, or is dimensionally stable enough not to wrinkle, the melt-flowable layer

is thick enough to flow to provide sufficient material to seal the step joint, and the sheet material is and wherein the sheet material imparts a structural or protective feature to the joint.

9.

86 The melt-flowable composition comprises (i) an epoxy, and (ii) a polyester, a polyamide, a functionalized ethylene (meth)acrylate copolymer having —OH groups, a polysulfide, a polyacetal, an ethylene (meth)acrylic acid copolymer, propylene (9. The article of claim 8, comprising at least one thermoplastic polymer selected from the group consisting of meth)acrylic acid copolymers, ethylene (meth)acrylate copolymers, and polycaprolactone.

10.

94 9. The article of claim 8, wherein said melt-flowable layer has a thickness of 0.10 mm to 25 mm.

11.

99 The dimensionally stable film is polyurethane film, oriented polyester film, polyimide film, polyolefin film, crosslinked epoxy film, crosslinked epoxy polyester film, polyethylene terephthalate film, ultra high molecular weight polyethylene film, microporous ultra high molecular weight polyethylene film, ultra high molecular weight polypropylene. 9. The article of claim 8, which is a film, or an ultra-high molecular weight microporous polypropylene film.

12.

107 9. The article of claim 8, wherein said melt-flowable layer has a thickness of 0.20 mm to 10 mm.

13.

112 The sheet material is in the form of a strip sized to bring the lower surface of the melt-flowable composition into contact with the inner surface of an automobile roof groove having a step joint, and When the lower surface is in contact with the inner surface of the automotive roof groove and the sheet material is heated to a melt sealing temperature, the melt flowable composition flows over the imperfections in the joint in the roof groove to form the strip into the roof. Adhesive to the inner surface of the groove to provide a protective seal within the roof groove to prevent rainwater, dirt, snow, etc. from entering the roof groove and causing rust or corrosion, providing an aesthetically pleasing appearance within the groove. 13. The article of any one of claims 8-12, wherein the article is produced in

14.

125 13. The article of any of claims 8-12, wherein the melt-flowable layer has a thickness of 0.34
mm to 6 mm.

15.

130 13. The article of any of claims 8-12, wherein the dimensionally stable film has a descending
web shrinkage and a transverse web shrinkage of less than 5% during the heating step.

Pr Nons

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ABSTRACT: The methods and mechanisms of nonsolvent induced phase separation have been studied for more than fifty years. Today, phase inversion membranes are widely used in numerous chemical industries, biotechnology, and environmental separation processes. The body of knowledge has grown exponentially in the past fifty years, which suggests the need for a critical review of the literature. Here we present a review of nonsolvent induced phase separation membrane preparation and characterization for many commonly used membrane polymers. The key factors in membrane preparation discussed include the solvent type, polymer type and concentration, nonsolvent system type and composition, additives to the polymer solution, and film casting conditions. A brief introduction to membrane characterization is also given, which includes membrane porosity and pore size distribution characterization, membrane physical and chemical properties characterization, and thermodynamic and kinetic evaluation of the phase inversion process. One aim of this review is to lay out the basics for selecting polymer–solvent–nonsolvent systems with appropriate film casting conditions to produce membranes with the desired performance, morphology, and stability, and to choose the proper way to characterize these properties of nonsolvent induced phase inversion membranes.

1.

Filtration is the process through which a solid component is separated from a fluid stream primarily based on differences in size between particles and fluid. Usually filtration refers to the separation of particulate matter from a liquid or gaseous stream.¹ Membrane filtration extends the range of solid–liquid separations to colloidal particles, macromolecules, and dissolved solutes for selective separation of gas mixtures and multicomponent solutions.² For molecular separations, membranes offer numerous advantages such as (1) not requiring a phase change for solute or the carrier solvent; (2) excellent combination of selectivity and productivity; and (3) no need for regeneration of solid or liquid sorbents. As such, membranes are widely used in many important chemical, biological, and environmental applications.

Many kinds of synthetic materials can be used for preparing membranes such as ceramics, glasses, metals, or polymers. The aim is to prepare the material to obtain a membrane structure with morphology tailored for a specific separation. A number of preparation techniques exist such as sintering, stretching, track-etching, template-leaching, and dip-coating, which enable a membrane to be constructed from a given material and with the desired membrane morphology.³ Phase inversion techniques are among the most important and commonly used processes for preparing membranes from a large number of polymeric building blocks. Publications on phase inversion increased exponentially in the past fifty years (Figure 1).

An asymmetric membrane with a very thin, dense skin layer can be prepared by either dry or wet phase inversion processes, such as solvent evaporation, precipitation from the vapor phase, precipitation by controlled evaporation, thermal precipitation, and immersion precipitation.³ Of all these techniques, immersion precipitation is among the first to be commercially explored and is one of the most popular membrane formation methods because it allows for the preparation of many membrane morphologies.

Development of integrally skinned asymmetric membranes by Loeb and Sourirajan in the 1960s is a major breakthrough in membrane technology.⁴ In their research, the phase inversion method was employed to transform a polymer in a controlled manner from a liquid dispersion to a solid film. Over the past half century, a plethora of knowledge has been generated about phase inversion membranes formed by immersion precipitation, also known as nonsolvent induced phase inversion.

Generally, flat sheet membranes are formed by coating a porous mechanical support with a thin film of polymer solution. The polymer solution, or dope, is composed of at least one polymer, at least one good solvent, and may contain additives. The thin film and support are immersed into a coagulation bath, which consists of a poor solvent, i.e., the nonsolvent, and may contain additives. The polymer film solidifies through exchange of the solvent and nonsolvent; hence, the solvent–nonsolvent system must be miscible.^{5,6} The tubular form is the alternative geometry for a membrane, including hollow fiber membranes (diameter <0.5 mm), capillary membranes (0.5 mm < diameter <5 mm), and tubular membranes (diameter >5 mm).³ Tubular membranes usually have large dimensions and must be supported, whereas hollow fibers and capillaries are self-supported. Hollow fibers and capillaries can be prepared via three different methods: wet spinning, melt spinning, and dry spinning. Spinning parameters and fiber dimensions are very important with respect to membrane performance.^{7–10}

Different separation processes require membranes with specific physical and chemical properties as described in Table 1. To produce a membrane with suitable chemical stability and permeation properties, some key factors for the casting solution system

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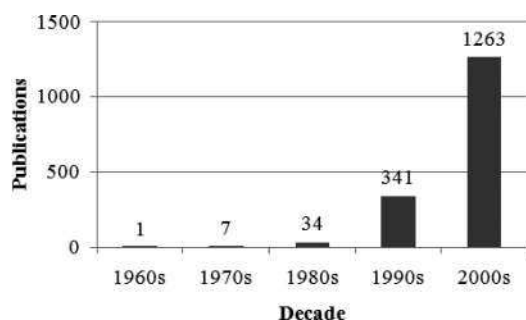


Figure 1. Publications on phase inversion membranes in *Web of Knowledge*.

should be considered. The key factors that influence phase inversion membrane formation include the choice of solvent–nonsolvent system, the composition of the polymer solution, the composition of the coagulation bath, and film casting conditions.¹¹ In this paper, we review these factors for nonsolvent induced phase separation membrane preparation and characterization for the most common membrane polymers.

2.

In early research, Strathmann et al. used the ternary phase diagram to discuss the thermodynamic aspects of instantaneous demixing and delayed demixing processes, which lead to different types of membrane structures.¹² This phase diagram can conveniently be used to analyze the thermodynamics of the membrane precipitation process. Typical phase diagrams are shown schematically in Figure 2. The corners of the triangle represent the three components (polymer, solvent, and nonsolvent), while any point within the triangle represents a mixture of three components. The system consists of two regions: a one-phase region where all components are miscible and a two-phase region where the system separates into polymer-rich and polymer-poor phases. The line which connects a pair of equilibrium compositions in the phase diagram is called a tie line. The liquid–liquid phase boundary is the so-called binodal. Every composition inside the binodal curve will demix into two liquid phases which differ in composition but which are in thermodynamic equilibrium with each other. Wijmans et al. elaborated two ways, including a rapid titration method and a turbidity measurement method, to measure the cloud point in order to determine the binodal.¹³

Using this ternary phase diagram, the composition path of a polymer film can be expressed schematically at a certain time of immersion in a nonsolvent bath.³ From Figure 2a it can be seen that at $t < 1$ s, the composition path crosses the binodal line, which means liquid–liquid demixing starts immediately after immersion. Figure 2b shows that all compositions directly beneath the top layer remain in the one-phase region and are still miscible, which means no demixing occurs immediately after immersion. After a longer time interval, compositions beneath the top layer will cross the binodal and demixing will also start in this case. Thus two distinctly different demixing processes can be distinguished and the resulting membrane morphologies are also completely different.^{3,14} Strathmann et al. also observed these two fundamentally different structures depending on the rate of polymer precipitation by nonsolvent induced phase separation.¹⁵ Precipitation rate is measured as the time between immersing the casting solution in a precipitation bath and the time when that solution turns opaque or when the membrane separates from the glass plate. Their research showed that slow precipitation

rates produced membranes with “sponge-like” morphologies. These membranes usually had high salt rejections and low water fluxes when tested as reverse osmosis membranes. Fast precipitation rates produced membranes with large “finger-like” macrovoids in the substructure. These membranes had low salt rejections and high water fluxes. In general, changes in membrane formation chemistry or casting conditions that slow down the rate of precipitation tend to produce a membrane with sponge-like morphology, low flux, and high solute rejection.

A mass transfer model for the early stages of the phase inversion process was developed by Cohen et al.¹⁶ They created a model for the diffusion-controlled formation of porous membranes obtained by nonsolvent induced phase separation. It was assumed that when phase separation occurs, a three-dimensional structure consisting of two interspersed equilibrium phases will form. This two-phase structure will then spread to all compositions below the binodal. It was also assumed that solvent and nonsolvent diffusion coefficients are equal, so the flow of solvent and nonsolvent in the film can be treated as a one-dimensional diffusion process as shown in Figure 3. At time t a propagating diffusion layer bounded on one side by the nonsolvent bath and on the other by casting solution has developed. With their diffusion model they also confirmed the exchange of solvent and nonsolvent could lead to unstable compositions in the polymer solution.

Following Cohen’s work, Reuvers et al.,¹⁷ Tsay et al.,¹⁸ and Radovanovic et al.^{19,20} predicted precipitation paths. The model built by Radovanovic et al.¹⁹ was frequently used to describe mass transfer phenomena occurring during the immersion step. Using the continuity equation (eq 1) a set of general diffusion equations and boundary conditions have been derived for the mass transport in a ternary polymer solution after immersion into a coagulation bath and prior to demixing process

$$\frac{\partial(\phi_i/\phi_3)}{\partial t} = \frac{\partial J_i^p}{\partial m}, \quad i = 1, 2 \quad (1)$$

where m is the position coordinate in the polymer-fixed frame of reference and is defined as

$$m(z, t) = \int_0^z \phi_3(x, t) dx \quad (2)$$

Here J_i^p is the volume flux of component i , ϕ_i is the volume fraction of component i , t is time, $i = 1, 2, 3$ represents the nonsolvent, solvent, and polymer, respectively. Initial concentrations are assumed constant

$$\phi_i(m, 0) = \phi_i^0, \quad i = 1, 2 \quad (3)$$

After immersion, the following boundary conditions exist:

$$\phi_i(0, t) = \phi_i^s, \quad i = 1, 2 \quad (4)$$

$$\phi_i(\infty, t) = \phi_i^0, \quad i = 1, 2 \quad (5)$$

where ϕ_i^s is the volume fraction of component i that is in equilibrium with the coagulation bath at the film–bath interface. Fluxes in the polymer-fixed reference frame are related to component velocities, v_i , by

$$J_i^p = \frac{1 - \phi_j}{\phi_3} \phi_i v_i + \frac{\phi_i}{\phi_3} \phi_j v_j, \quad i, j = 1, 2, \quad i \neq j \quad (6)$$

Table 1. Desirable Phase-Inversion Membrane Material Properties by Application^{2,3,116,199–214}

membrane type		desirable properties	applications	ref
MF	physical morphology	thin, porous skin layer with narrow pore size distribution (0.05–10 μm)	sterile filtration of pharmaceuticals, cell harvesting, clarification of fruit juice/wine/beer, ultrapure water,	3,116,199–203
	chemical properties	chemical stability over a wide pH range; mechanically and thermally stable	metal recovery as colloidal orhydroxides, water-wastewater treatment, fermentation, separation of oil–water emulsions	
UF	physical morphology	porous skin layer; asymmetric structure; much denser top layer than MF membranes; pore size (0.5 μm –1 nm) (lower limit a few thousand Dalton); macro void morphology: finger-like, sponge-like	food and dairy industry, pharmaceutical industry, textile industry, chemical industry, metallurgy, paper industry, water treatment	2,3,116,201
	chemical properties	good chemical, mechanical, and thermal stability; low fouling tendency		
NF & RO	physical morphology	thin dense top layer and porous sublayer; pore size <2 nm; good thermal and mechanical stability; higher membrane resistance for higher pressure, tensile strength	desalination, removal of micropollutants, water softening, wastewater treatment, retention of dyes (textile industry), ultrapure water (electronic industry), concentration of food, juice, and sugars (food industry), concentration of milk (dairy industry)	3,116,204–207
	chemical properties	good chemical and thermal stability; hydrophilic; antifouling		
gas separation	physical morphology	porous/nonporous, asymmetric/composite membrane; elastometric/glassy polymeric top layer; selectivity as important as permeability; permeable top layer, defect-free; thin (0.1 to few μm); open porous support layer for mechanical support for top layer (minimize resistance); no macro voids	removal of H_2O , organic vapors from air, dehydration (compressed air, natural gas, air conditioning), acid gases from flue gas	3,116,208,209
	chemical properties	chemically stable in separation gas (such as Cl_2)		
pervaporation and vapor permeation	physical morphology	nonporous membrane; thickness should be 0.1 to few μm for top layer; anisotropic morphology: dense top layer, open porous sublayer; narrow pore size distribution, no macrovoids	dehydration of organic solvent, removal of organic components from water (alcohols, aromatics, chlorinated hydrocarbons), separation of polar/nonpolar (e.g., alcohols/aliphatics), separation of saturated/unsaturated (e.g., cyclohexane/benzene), separation of isomers	3,116,206,210,211
	chemical properties	stable in vapor and solvent		
dialysis	physical morphology	minimize thickness (10–100 μm)	hemodialysis (removal of toxic substance from blood),	3,116,200,212
	chemical properties	hydrophilic polymers for aqueous application, blood compatibility for hemo dialysis	alcohol reduction in beer, desalination of enzymes and coenzymes, alkali recovery in pulp and paper industry	
membrane distillation	physical morphology	symmetric or asymmetric; porous, thickness should be 0.2–1.0 μm ; high porosity with pore size in the range of 0.2–0.3 μm ; no macrovoids	pure water production, laboratories, semiconductors industry, desalination, production of boiler feedwater, concentration of aqueous solution, removal of VOCs, contaminated surface water (benzene, TCE), fermentation products (ethanol, butanol), aroma compounds	3,116,213
	chemical properties	very hydrophobic materials, liquid must not wet membrane		
forward osmosis and pressure retarded osmosis	physical morphology	dense active layer for high solute rejection; porous support for higher water flux; high mechanical strength, highly ordered, open, interconnected finger-like voids to promote internal mass transfer	wastewater treatment and water purification, desalination, food processing, pharmaceutical industry, osmotic pumps, osmotic power, pressure-retarded osmosis	3,116,214
	chemical properties	very hydrophilic to enhance flux and reduce membrane fouling		

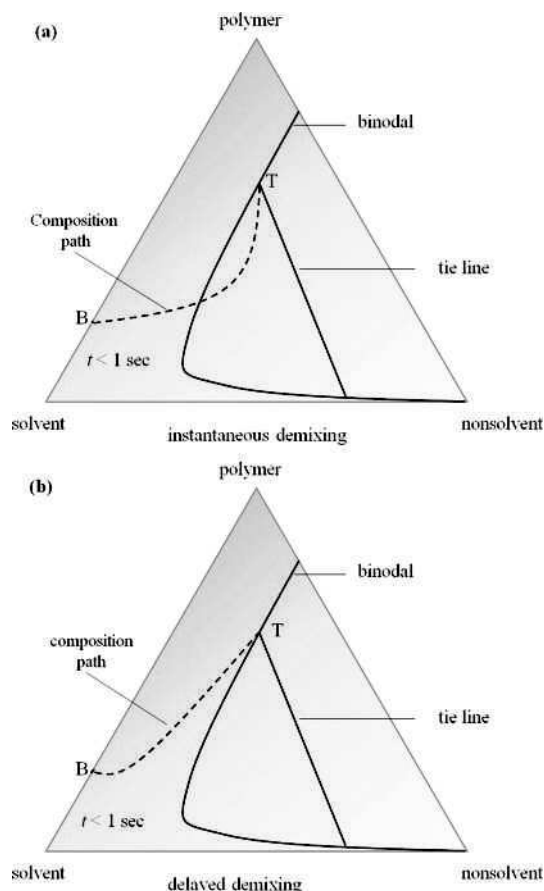


Figure 2. Composition paths of a cast film immediately after immersion ($t < 1$ s) demonstrating (a) instantaneous demixing and (b) delayed demixing; T and B represent top and bottom of the film, respectively.³

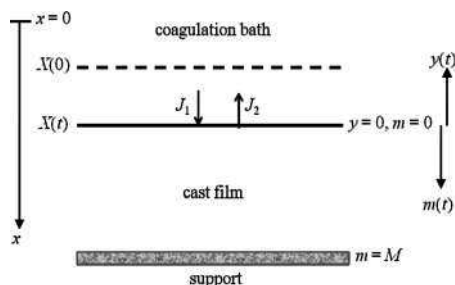


Figure 3. Flow of solvent and nonsolvent treated as a one-dimensional diffusion process and coordinate systems for membrane formation model.^{17,19}

Component fluxes are related to chemical potentials, μ_i , by

$$\frac{1}{RT} \frac{\partial \mu_i}{\partial z} = \sum_{j=1}^3 \phi_j \xi_{ij} (v_j - v_i), \quad i = 1, 3 \quad (7)$$

where ξ_{ij} is a frictional coefficient between components i and j . A modified flux is defined as

$$N_i = J_i^p t^{1/2}, \quad i = 1, 2 \quad (8)$$

along with a new variable

$$\eta = m t^{-1/2} \quad (9)$$

Equation 1 simplifies to the ordinary differential equation

$$\eta \frac{d(\phi_i/\phi_3)}{d\eta} + 2 \frac{dN_i}{d\eta} = 0 \quad (10)$$

with new boundary conditions of

$$\phi_i(0) = \phi_i^s, \quad i = 1, 2 \quad (11)$$

$$\phi_i(\infty) = \phi_i^o, \quad i = 1, 2 \quad (12)$$

Equation 7 transforms to

$$N_i = - \sum_{j,k} F_{ij} T_{jk} \frac{d\phi_k}{d\eta}, \quad i = 1, 2 \quad (13)$$

where F_{ij} and T_{jk} are frictional and thermodynamic contributions which are defined by Radovanovic et al.¹⁹

Diffusion in the coagulation bath is described by

$$\frac{\partial v_i}{\partial t} = \frac{\partial}{\partial y} \left(D \frac{\partial v_i}{\partial y} \right) - \frac{\partial v_i}{\partial y} \frac{dX}{dt} \quad (14)$$

$$\frac{dX}{dt} = -J_1^p(0, t) - J_2^p(0, t) \quad (15)$$

where v_i is the volume fraction of component i in the coagulation bath, X is the position of the interface between the film and the coagulation bath, x is the spatial position coordinate normal to the membrane surface, $y = -x + X(t)$ is the position coordinate that moves with the interface. Initial and boundary conditions for the nonsolvent are

$$v_1(y, 0) = v_1^o \quad (16)$$

$$v_1(0, t) = v_1^s \quad (17)$$

$$v_1(\infty, t) = v_1^o \quad (18)$$

By defining a new variable

$$\theta = y t^{-1/2} \quad (19)$$

equation 14 transforms to

$$\frac{\partial v_1}{\partial \theta} = -\frac{2}{\theta} \left\{ [N_1(0) + N_2(0)] \frac{dv_1}{d\theta} + \frac{d}{d\theta} \left(D \frac{dv_1}{d\theta} \right) \right\} \quad (20)$$

with boundary conditions

$$v_1(0) = v_1^s \quad (21)$$

$$v_1(\infty) = v_1^o \quad (22)$$

The mutual diffusion coefficient, D , is concentration dependent and defined by Radovanovic et al.¹⁹

The diffusion model explained the two types of demixing taking place during the phase inversion process and was used to predict the range of the initial composition of the casting film. To calculate the critical initial compositions at which the demixing changes from instantaneous to delayed, the diffusion equation for the film (eq 10) and for the bath (eq 20) must be solved simultaneously.¹⁹ When from solving eq 10, the composition profile touches or crosses the binodal line (Figure 2a), instantaneous demixing will happen which means the polymer precipitates and a solid film is formed very rapidly after immersion in the nonsolvent bath. This type of

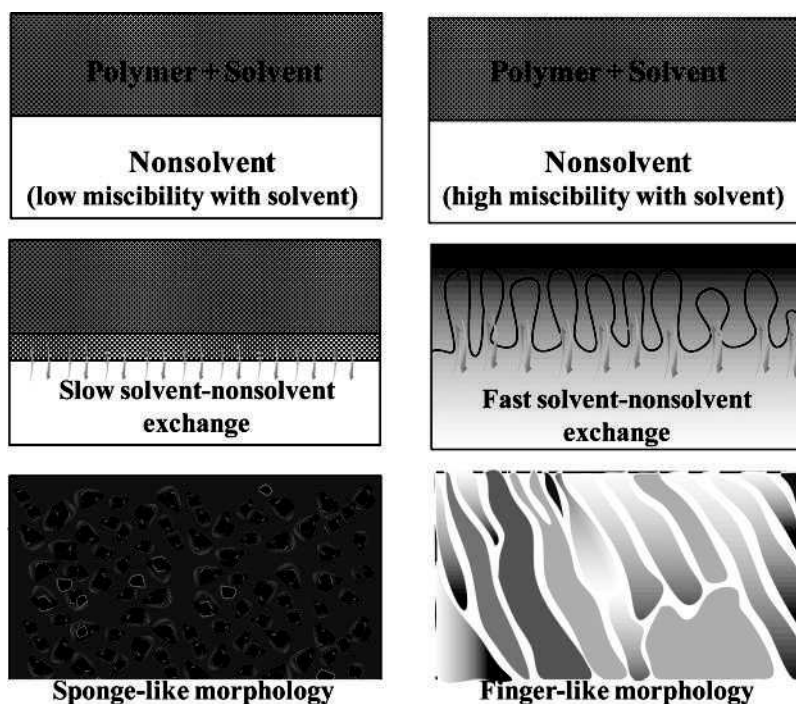


Figure 4. Different membrane morphologies caused of different types of demixing.

demixing generally shows a highly porous substructure (with finger-like macrovoids) and finely porous, thin skin layers. If the composition profile does not touch the binodal line (Figure 2b), demixing is delayed, precipitation is slow, and it takes much longer for the membrane to form. Membranes with a relatively dense top layer and sponge-like substructure are obtained. The structures of these two types of membrane are shown in Figure 4.

Asymmetric membranes consist of a thin top layer supported by a porous sublayer that often contain large void spaces, or macrovoids. These macrovoids may exhibit different morphologies (i.e., finger-like or sponge-like) depending on phase inversion kinetics and thermodynamics. See discussion below for more detail about macrovoid formation and morphology. The presence of macrovoids in membranes has both advantages and disadvantages. Macrovoids could result in compaction or collapse of membranes and therefore limit the application in high pressure processes such as reverse osmosis. On the other hand, the macrovoid structure is suitable for ultrafiltration processes and can be employed as support layers for composite membranes.¹⁴

Several mechanisms have been proposed to describe the formation of macrovoids. Matz²¹ and Frommer and Lancet²² suggested that the interfacial hydrodynamic instability driven by a surface tension gradient is responsible for the initiation of macrovoids. Strathman et al. proposed that precipitation rate determines macrovoid structure.¹⁵ Ray et al. proposed that the formation of macrovoids is associated with the excess intermolecular potential gradients induced by the steep concentration gradient near the interface.²³ The study from Boom et al.²⁴ and Smolders et al.¹⁴ also showed that macrovoid formation in phase separation occurs from freshly formed nuclei of the diluted phase when the composition in front of the nuclei remains stable for a relatively long period of time. Diffusion of solvent expelled from the surrounding polymer solution causes macrovoid growth. Macrovoids are generally formed in systems where instantaneous demixing takes place, except when the polymer additive concentration and the nonsolvent concentration in the polymer solution exceed

a certain minimum value.^{14,24–26} Therefore, the polymer solution composition close to the binodal composition favors the formation of spongy structures.

Cohen et al.¹⁶ first calculated the diffusion path using the ternary phase diagram, which was later improved by many research groups to study membrane formation mechanisms.^{17,18,27,28} According to the calculated diffusion path, instantaneous liquid–liquid demixing can account for the initiation of macrovoids quite well. It was also found that the miscibility between the solvent and the coagulant plays an important role in determining whether the membrane formation system demixes instantaneously.¹⁷ The importance of the miscibility between the solvent and the coagulant was also noticed by Termonia²⁹ and Cheng et al.³⁰ For a more complete review of the formation mechanisms of macrovoids, one can refer to the works of Smolders et al.¹⁴ and Paulsen et al.³¹

The slower nonsolvent uptake which occurs in vapor-induced phase separation (VIPS) favors solid–liquid demixing (polymer crystallization) over liquid–liquid demixing when this process is used to prepare membranes from a semicrystalline polymer like poly(vinylidene fluoride) (PVDF).³² Li et al. have shown that PVDF membrane morphology can be controlled by adjusting polymer dissolution temperature.³³ Two gelling processes are occurring: crystallization-initiation and noncrystallization-initiation. Above a critical dissolution temperature, crystallization-initiation gelation outcompetes noncrystallization-initiation and forms nodular structures. Below this critical temperature, noncrystallization-initiation is the dominant gelling process and fibrillar structures are formed. The competition between the two gelling processes is vital in determining PVDF membrane morphology.

In summary, factors that affect the rate of liquid–liquid and solid–liquid demixing or polymer precipitation ultimately determine the physical morphology of membranes formed by nonsolvent induced phase separation. Membranes with these different physical morphologies finally have different separation properties and can be applied in various types of separation processes.

Table 2. Solvents for Cellulose Acetate and Polysulfone³

cellulose acetate	polysulfone
dimethylformamide (DMF)	dimethylformamide (DMF)
dimethylacetamide (DMAc)	dimethylacetamide (DMAc)
acetone	dimethylsulfoxide (DMSO)
dioxan	formylpiperidine (FP)
tetrahydrofuran (THF)	morpholine (MP)
acetic acid (HAc)	N-methylpyrrolidone (NMP)
dimethylsulfoxide (DMSO)	

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3. The choice of solvent–nonsolvent system in phase inversion membrane formation has a dramatic influence on membrane morphology, mechanical properties, interfacial characteristics, and separation performance. The polymer must be soluble or easily dispersible in the chosen solvent, and the solvent and nonsolvent must be miscible. There are usually several solvents that are compatible with a given polymer. For example, Table 2 lists several solvents that are compatible with cellulose acetate and polysulfone.³

There are a very large number of compatible solvent–nonsolvent pairs, each with their own specific thermodynamic behavior and miscibility. Frequently, the higher the mutual affinity (or miscibility) between the solvent and nonsolvent is, the more likely instantaneous demixing will occur and more porous membrane will be obtained.³ In the case of low mutual affinity, an asymmetric membrane with a dense nonporous top layer is likely obtained. Although other parameters influence membrane structure, the choice of solvent–nonsolvent is crucial.³

Several approaches to determining polymer solubility have been developed. Flory and Huggins developed a two-dimensional lattice-based model to describe polymer solutions.^{34–36} In this model, polymer segments and solvent molecules are assumed to be the same size, and only one molecule or polymer segment can occupy a single lattice site.³⁷ The Gibbs free energy of mixing, ΔG_m , is calculated as

$$\Delta G_m = kT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} n_1 \phi_2) \quad (23)$$

where k is Boltzmann's constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is absolute temperature, n_1 and n_2 are the number of solvent (component 1) and polymer (component 2) molecules, ϕ is the volume fraction, and χ_{12} is the Flory interaction parameter. The dimensionless Flory interaction parameter is a characterization of polymer–solvent interaction energy. Inverse gas chromatography is the most common method used to experimentally determine χ_{12} .^{37,38} Modifications to the Flory–Huggins model have been made to describe dilute polymer solutions³⁹ and to account for the concentration dependence of χ_{12} .⁴⁰

Solubility parameters, δ , may be used to estimate χ_{12} and help choose appropriate solvent–polymer matches. Solubility parameters of solvents are related to the molar energy of vaporization, ΔE^v , and molar volume, V , of a pure liquid by the following

$$\delta = \sqrt{\frac{\Delta E^v}{V}} \quad (24)$$

where ΔE^v represents the energy change after the isothermal vaporization of the saturated liquid to the ideal gas state at infinite dilution. The energy of vaporization is related to the enthalpy of vaporization by $\Delta E^v \approx \Delta H^v - RT$.³⁷

The solubility parameters of polymers can be approximated from group contribution methods.^{41–43} Polymer solubility parameters can also be determined experimentally by immersing polymer in different solvents whereby the polymer solubility parameter value is taken as that of the solvent which causes maximum polymer swelling.³⁷

The Flory interaction parameter can be approximated from solvent (δ_1) and polymer (δ_2) solubility parameters using the following relation:

$$\chi_{12} = \frac{v_1}{RT} (\delta_1 - \delta_2)^2 \quad (25)$$

where v_1 is the molar volume of the solvent and R is the ideal gas constant.³⁷ Scatchard and Hildebrand estimated the heat of mixing, ΔH_m , using polymer and solvent solubility parameters by the following relation:

$$\Delta H_m = V_m (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (26)$$

where V_m is the molar volume of the mixture.^{44,45} Solvents can be matched to polymers by using the Scatchard–Hildebrand equation to minimize the heat of mixing. However, this equation is only applicable for $\Delta H_m > 0$ and does not account for specific interactions such as hydrogen bonding.

Hansen proposed that the total energy of vaporization of a liquid was due to dispersion forces, permanent dipole–permanent dipole forces, and hydrogen bonding.^{46–51} Therefore, the solubility parameter, which is related to the total cohesive energy, should be broken into three components: dispersive (δ_d), polar (δ_p), and hydrogen bonding (δ_h). The total, or Hildebrand, solubility parameter is equal to

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (27)$$

Calculation of solvent δ_d and δ_p is described by Blanks and Prausnitz.⁵² Hansen and Beerbower found that solvent δ_p could be calculated as

$$\delta_p = 37.4 \frac{\mu}{V^{0.5}} \quad (28)$$

where μ is the solvent dipole moment and V is the solvent molar volume.⁴⁸ Solvent hydrogen bonding solubility parameter has typically been calculated by subtracting δ_d and δ_p from δ . The group contribution method is also a viable approach to calculating δ_h . Hansen believes the group contribution approach is best for determining solubility parameters for polymers.⁵³ A solubility parameter distance, R_a , was developed by Skaarup.⁵¹ This “distance” between polymer (1) and solvent (2) is a measure of their affinities based on their individual Hansen solubility parameters, which is calculated below as

$$R_a = \sqrt{4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2} \quad (29)$$

The relative energy difference, RED, is equal to R_a/R_o , where R_o is the radius of interaction of a Hansen solubility parameter sphere. The RED should not exceed a value of 1 if solubility is to be maintained. Solubility increases as RED approaches 0. The radii of interaction (R_o) for several common polymers are tabulated by Hansen.⁵⁴ Sample RED values are tabulated below for cellulose acetate and polysulfone (Table 3a and 3b).⁵⁴ Several potentially compatible solvents ($\text{RED} < 1$) can be quickly and easily selected using this model and published solubility parameters.

Table 3a. Relative Energy Density Calculation for Several Common Solvents and Cellulose Acetate⁵³

	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Ro (MPa ^{1/2})	
cellulose acetate	16.9	16.3	3.7	13.7	
	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Ra (MPa ^{1/2})	RED
acetic acid	14.5	8	13.5	13.7	1.0
acetone	15.5	10.4	6.9	7.3	0.5
acetonitrile	15.3	17.9	6.1	4.3	0.3
benzene	18.4	1	2.9	15.6	1.1
<i>n</i> -butanol	15.9	5.7	15.7	16.1	1.2
butyl acetate	15.8	3.7	6.3	13.1	1.0
carbon tetrachloride	17.6	0	0	16.8	1.2
chloroform	17.6	3	4.2	13.4	1.0
cyclohexane	16.7	0	0	16.7	1.2
1,2-dichloroethane	19	7.4	4.1	9.8	0.7
dichloromethane	18.2	6.3	7.8	11.1	0.8
<i>N,N</i> -dimethylacetamide	16.8	11.5	10.2	8.1	0.6
dimethylformamide	17.4	13.7	11.2	8.0	0.6
dimethyl sulfoxide	18.4	16.3	10.2	7.2	0.5
dioxane	16.8	5.7	8	11.4	0.8
ethanol	15.8	8.8	19.4	17.5	1.3
ethyl acetate	15.8	5.3	7.2	11.8	0.9
diethyl ether	19	1.8	7.4	15.5	1.1
heptane	15.1	0	0	17.1	1.2
hexane	14.8	0	0	17.2	1.3
methanol	15.1	12.2	22.2	19.3	1.4
methyl- <i>t</i> -butyl-ether	15.5	3.6	5.2	13.1	1.0
methyl ethyl ketone	15.9	9	5.1	7.7	0.6
<i>N</i> -methyl-2- pyrrolidone	18	12.3	7.2	5.8	0.4
pentane	14.3	0	0	17.5	1.3
<i>n</i> -propanol	15.8	6.7	17.3	16.8	1.2
isopropanol	15.8	6.1	16.4	16.4	1.2
di-isopropyl ether	14.4	2.9	5.1	14.4	1.0
tetrahydrofuran	19	10.2	3.7	7.4	0.5
toluene	18	1.4	2	15.2	1.1
trichloroethylene	18	3.1	5.3	13.5	1.0
water	15.5	16	42.3	38.7	2.8
xylene	17.6	1	3.1	15.4	1.1

3. For porous membranes, the type of polymer will affect solute adsorption, membrane hydrophilicity, and the thermal and chemical stability of the membrane. For nonporous membranes, the choice of polymer directly affects membrane performance because intrinsic membrane separation properties (solubility and diffusivity) depend on polymer chemical structure, and, hence, on the choice of polymer. In nonsolvent induced phase separation, the choice of polymer is an important factor because it limits the solvents and nonsolvents that can be used in the phase inversion process. In addition, the solvent also plays an important role along with polymer concentration during membrane formation.

Many different polymers are used in the synthesis of micro-filtration, ultrafiltration, nanofiltration, and reverse osmosis membranes. Polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile (PAN), cellulotics, poly(vinylidene fluoride) (PVDF),

poly(tetrafluoroethylene) (PTFE), polyimides (PI), and polyamides (PA) are among the most common polymeric membrane materials in use today. Each of these polymers is briefly discussed in the following.

3.2.1. *Polysulfone*. Polysulfone (PSf) is one of the most common polymers used to make membranes by phase inversion process. Polysulfone is often selected because of its commercial availability, ease of processing, favorable selectivity-permeability characteristics, and glass transition temperature (T_g) value of 190 °C. It possesses good mechanical, thermal, and chemical properties. Moreover, it is generally easy to prepare asymmetric membranes by the phase inversion method, in which a thin layer of PSf solution in an appropriate solvent is immersed into the nonsolvent coagulation bath, such as water. The solvents most frequently used for PSf are *N*-methylpyrrolidone (NMP),^{55–63} *N,N*-dimethylacetamide (DMAc),^{58,59,61,64,65} and *N,N*-dimethylformamide (DMF).^{66,67}

3.2.2. *Polyethersulfone*. Polyethersulfone (PES) possesses very good chemical and thermal stability as indicated by its glass transition temperature (T_g) value of 230 °C. This polymer is also widely used as support material for composite membranes. Like polysulfone, it is generally easy to prepare asymmetric membranes with water as a coagulant by the phase inversion method. The solvents usually used for PES are *N*-methylpyrrolidone (NMP),^{68–73} *N,N*-dimethylformamide (DMF),^{67,69,74} and *N,N*-dimethylacetamide (DMAc).^{73,75–77}

3.2.3. *Polyacrylonitrile*. Polyacrylonitrile (PAN) is also a popular membrane material because it is a resinous, fibrous, or rubbery organic polymer with sufficient chemical stability and hydrophilicity. Other common membrane materials such as PSf and PES are relatively hydrophobic and prone to fouling whereas PAN membranes are relatively hydrophilic, low fouling in aqueous filtration applications, and are already commercialized.⁷⁸ Polyacrylonitrile has good resistance to solvents and cleaning agents such as chlorine and sodium hypochlorite. Polyacrylonitrile has been used as a substrate for MF, UF, NF, RO, and pervaporation membranes.^{79–85} It is very difficult to reduce the pore size of PAN membranes due to its poor solubility in various solvents except polar solvents such as NMP,^{81,86} DMF,^{87–89} and DMAc.^{89–91}

3.2.4. *Cellulotics*. Cellulotics generally include cellulose acetate, cellulose acetate butyrate, and cellulose propionate, all of which are cellulose esters. Cellulose acetate was the first cellulosic polymer used to form phase inversion membranes^{21,92} and is the most frequently employed to prepare membranes.^{93–96} Cellulose acetate has low chemical, mechanical, and thermal resistance. Cellulotics can be used in ultrafiltration applications or be made into RO membranes by nonsolvent induced phase separation. Cellulose acetate can be made into a film or into a fiber, but it must be chemically modified to produce a thermoplastic material. It is mainly used as a material for dialysis membranes. Cellulose acetate is frequently blended with other polymers such as PSf or additives such as polyethylene glycol (PEG) to improve the membrane properties.^{93,96–99} Cellulose triacetate can be used to form chlorine tolerant hollow fiber RO membranes.^{100,101}

3.2.5. *Polyimides (PI)/Polyamides (PA)*. Polyimides are a group of polymers with good gas selectivity and chemical stability, and excellent thermal stability. Therefore, in recent years studies have been performed for their application as membrane materials.^{102–105} Polyamide membranes are mechanically very strong and exhibit excellent wet and dry strength.¹⁰⁶ Their hydrophilicity makes them suitable for aqueous and organic solutions.^{107,108} *N*-methylpyrrolidone (NMP) is most widely used as a solvent for these two polymers.^{102,103,105}

Table 3b. Relative Energy Density Calculation for Several Common Solvents and Polysulfone⁵³

	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Ro (MPa ^{1/2})	
polysulfone	19.7	8.3	8.3	8.0	
	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Ra (MPa ^{1/2})	RED
acetic acid	14.5	8	13.5	11.6	1.5
acetone	15.5	10.4	6.9	8.8	1.1
acetonitrile	15.3	17.9	6.1	13.2	1.7
benzene	18.4	1	2.9	9.4	1.2
<i>n</i> -butanol	15.9	5.7	15.7	10.9	1.4
butyl acetate	15.8	3.7	6.3	9.3	1.2
carbon tetrachloride	17.6	0	0	12.5	1.6
chloroform	17.6	3	4.2	7.9	1.0
cyclohexane	16.7	0	0	13.2	1.6
1,2-dichloroethane	19	7.4	4.1	4.5	0.6
dichloromethane	18.2	6.3	7.8	3.6	0.5
<i>N,N</i> -dimethylacetamide	16.8	11.5	10.2	6.9	0.9
dimethylformamide	17.4	13.7	11.2	7.7	1.0
dimethyl sulfoxide	18.4	16.3	10.2	8.6	1.1
dioxane	16.8	5.7	8	6.4	0.8
ethanol	15.8	8.8	19.4	13.6	1.7
ethyl acetate	15.8	5.3	7.2	8.4	1.1
diethyl ether	19	1.8	7.4	6.7	0.8
heptane	15.1	0	0	14.9	1.9
hexane	14.8	0	0	15.3	1.9
methanol	15.1	12.2	22.2	17.1	2.1
methyl- <i>t</i> -butyl-ether	15.5	3.6	5.2	10.1	1.3
methyl ethyl ketone	15.9	9	5.1	8.3	1.0
<i>N</i> -methyl- 2- pyrrolidone	18	12.3	7.2	5.4	0.7
pentane	14.3	0	0	16.0	2.0
<i>n</i> -propanol	15.8	6.7	17.3	12.0	1.5
isopropanol	15.8	6.1	16.4	11.5	1.4
di-isopropyl ether	14.4	2.9	5.1	12.3	1.5
tetrahydrofuran	19	10.2	3.7	5.2	0.6
toluene	18	1.4	2	9.9	1.2
trichloroethylene	18	3.1	5.3	6.9	0.9
water	15.5	16	42.3	35.9	4.5
xylene	17.6	1	3.1	9.9	1.2

3.2.6. Fluoropolymers. Fluoropolymers frequently used to prepare membranes include polytetrafluoroethylene (PTFE) and poly(vinylidene fluoride) (PVDF). Both polymers are hydrophobic and exhibit good chemical and thermal stability due to their chemical structure. Their hydrophobic nature makes them useful materials in membrane distillation.³ Microfiltration membranes formed from PTFE may be prepared by sintering and stretching whereas PVDF membranes are made by phase inversion.^{3,109–115} Poly(vinylidene fluoride) shows good thermal and chemical resistance, although not quite as good as PTFE. Poly(vinylidene fluoride) is soluble in aprotic solvents such as DMF, DMAc, NMP, and triethylphosphate (TEP).

3. Polymer concentration in the dope solution is yet another parameter affecting membrane morphology. Typical polymer concentration ranges from 15 to 25 wt %.¹¹⁶ Increased polymer concentration in the casting

solution results in higher polymer concentration at the nonsolvent interface.⁷¹ This implies that the volume fraction of polymer increases and consequently a lower porosity is obtained. When polymer concentration is increased beyond a certain value, the resulting membrane has lower porosity and the pure water flux can be reduced to zero despite the occurrence of instantaneous demixing. Strathmann et al.^{12,15} focused on the effect of polymer concentration on membrane morphology. Their research demonstrated that varying initial polymer solution concentration changes the path to precipitation, which can be shown from the ternary phase diagram. Two different structures were obtained depending on the different ways of precipitation.

3. The choice of nonsolvent will influence the precipitation. When a polymer solution is cast as a thin film upon a support and then immersed in the nonsolvent, the miscibility of solvent and nonsolvent and the affinity between polymer and nonsolvent will affect the demixing rate and finally influence the final membrane structure.³ Water is frequently used as a nonsolvent, but other nonsolvents such as acetone and lower aliphatic alcohols are also used.^{117–120} The addition of solvent to the coagulation bath is another parameter that influences the membrane structure. However, the maximum amount of solvent that can be added is determined by the position of the binodal of the phase diagram. By adding solvent to the coagulation bath, instantaneous demixing can be stopped. A delay in demixing occurs, which leads to the formation of a nonporous membrane. This effect is unusual because there appears to be two competing processes. The addition of solvent to the coagulation bath lowers the polymer concentration at the film interface. This would lead to a more open membrane.^{3,121} Addition of solvent to the coagulation bath lowers the nonsolvent activity and diffusion rate into the polymer film, which further delays demixing. Ghosh et al. found that by adding a small percentage of solvent to the coagulation bath (3% NMP in water) membrane permeability could be increased by more than 25%.¹¹ Others believe that the delay in liquid–liquid demixing is the dominant effect as this method is typically used to produce dense films.³ In addition, other additives to the coagulation bath such as methanol, isopropanol, and salt were found to affect the demixing process.^{9,89,117,122}

3. A number of researchers have studied the role of additives on membrane structure. Most casting solutions contain high or low molecular weight additives for improving the morphology and function of phase inversion membranes, which makes analysis of solvent–nonsolvent system properties more complex. The addition of organic or inorganic components as a third component to a casting solution has been one of the important techniques used in membrane preparation. The addition of these additives can create a spongy membrane structure by preventing finger-like macrovoid formation, enhance pore formation, improve pore interconnectivity, and increase hydrophilicity. For example, finger-like macrovoid formation can be suppressed by the addition of polyvinylpyrrolidone (PVP). Other frequently used additives include polyethylene glycol (PEG), propionic acid (PA), surfactants such as sorbitan monoleate (Span-80), alcohols, dialcohols, water, polyethylene oxide (PEO), LiCl, and ZnCl₂. Here, the general results of adding PVP, PA, PEG, and surfactant will be discussed.

3.5.1. Polyvinylpyrrolidone. Boom et al.^{24,123} studied the role of polyvinylpyrrolidone (PVP) as a polymeric additive in the

formation of polyethersulfone (PES)/NMP membranes. They found the addition of PVP suppresses the formation of macrovoids. Polyvinylpyrrolidone can become entrapped in polymeric films and impart some hydrophilic character.¹²⁴ This hydrophilic additive may also leach out of membranes after many hours of operation.¹²⁵ Several studies have since been reported on PVP additives of varying molecular weight^{58,103,111,126,127} and concentration^{57,71,76,96,98,128–130} in an attempt to improve membrane morphology and function.

Yeo et al. concluded that PVP addition to the casting solution of PSf and DMF contributed to the enlargement of the macrovoid structure in the prepared membranes rather than the suppression of that structure.¹³¹ This was confirmed by Jimenez et al. through molecular weight cut off (MWCO) and pure water permeation tests.⁷¹

The study of Yoo et al. explained that adding PVP of different molecular weights into casting solutions produced membranes with significantly different morphologies.¹⁰³ Addition of 40 kDa PVP increased macrovoid formation. However, addition of 360 kDa PVP suppressed the formation of finger-like macrovoids. The authors suggest that changes in solution viscosity brought on by addition of PVP alter the rate of phase separation, which ultimately causes the differences in membrane morphology. Chakrabarty et al. also studied an increase from 24 to 360 kDa PVP added to the casting solution.⁵⁸ As PVP molecular weight increased, membrane sublayers had dense structures with fewer macrovoids, and the pore number and porosity of the prepared membrane was found to increase. Membrane skin layers were found to be thicker as more PVP was added, and the number of finger-like macrovoids gradually disappeared. Jung et al. concluded that the top layers became thicker as more PVP was added, and the number of finger-like macrovoids gradually disappeared in the membrane. Hypochlorite was successfully used to wash out residual PVP.¹²⁷

3.5.2. Polyethylene Glycol. Polyethylene glycol (PEG) is also frequently added to the casting solution as a third component in membrane preparation. Studies have investigated the effect of PEG additives with different molecular weights.^{59–61,70,74,97,98,109,132,133} Polyethylene glycol acts as a pore-forming agent and also affects the thermodynamics and kinetics of the phase inversion process. Kim et al. systematically studied the effect of PEG on membrane formation by phase inversion.⁶⁰ The study showed that by increasing the ratio of PEG additive to solvent NMP, the casting solution becomes thermodynamically less stable. Membrane surface pore size becomes larger, and the top layer becomes more porous. Shieh et al. extended that PEG, being hydrophilic in nature, can be used to improve membrane selectivity and as a pore-forming agent.¹³⁴ Kim and Lee investigated the effect of various PEG molecular weights on the formation of polyetherimide (PEI) asymmetric membranes.¹³³ They reported that small molecular weights of PEG, such as PEG 200, work as a pore-reducing agent for PEI membranes. Zheng et al. found that PEG addition could thermodynamically enhance and rheologically hinder PSf solution demixing.⁶¹ Also, their research compared the cross-sectional morphologies of membranes prepared at different coagulation bath temperatures.⁶⁴ When PSf concentration is 18 wt % and the coagulation bath temperature is 20 °C, the size of finger-like macrovoids increases and then decreases rapidly with increasing PEG concentration.

The effects of PEG concentration have also been studied in other solvent systems. The research of Liu et al. showed that PEG

can be used to enhance polymer (PES) solution viscosity and to enhance pore interconnectivity when added in appropriate amounts.⁷⁰ The effects of PEG on the porosity of polycarbonate (PC) membranes prepared via dry-/wet-phase inversion methods was studied by Deniz.¹³⁵ It was observed that membrane porosity increased with an increase in the initial PEG concentration ranging from 5 to 20 wt %. Idris et al.⁷⁴ and Chakrabarty et al.⁵⁹ reported the effect of PEG with different molecular weights from 400 to 20 000 Da on morphology and performance of PSf membranes. They showed that PEG 6000 can be a suitable additive for making asymmetric membranes having a dense skin layer and a relatively macrovoid-free sponge-type support layer. By increasing the molecular weight of PEG, the pore number and porosity of the prepared membrane was increased, so PEG can be regarded as a pore-forming agent rather than a pore-reducing agent in this case.

3.5.3. Propionic Acid. Propionic acid has been studied as an additive by many research groups. Fritzsche et al. reported that when a PSf solution film is rapidly formed by immersion precipitation, the propionic acid added in the casting solution increased the gas permeability by nearly 10-fold.¹³⁶ Han showed that by adding propionic acid to the coagulation bath, polymer packing density significantly decreased in membranes made by phase inversion.⁶³ The decrease is due to both the significant increase of nodule structures and the pore formation between polymer aggregates. Laninovic showed that the addition of propionic acid in a polymer solution inhibited the growth of macrovoids, which resulted in improved mechanical characteristics of the formed membranes.¹³⁷ Water fluxes through the membranes prepared from a polymer solution with propionic acid had a lower value in relation to a membrane prepared from a polymer solution without an additive.

3.5.4. Surfactants. The addition of surfactants can affect the membrane structure because it can dramatically affect the interfacial properties between the coagulant and the polymer solution. The study by Lin et al. proposed that the addition of appropriate surfactants can enhance the affinity between solvent and coagulant, resulting in a shift from delayed demixing to instantaneous demixing, and macrovoids can then be induced.¹³⁸ Later they extended the study to a dual-bath system, in which casting solution was immersed in one coagulant for a very short time (<2 s) and then moved to a second bath containing different coagulants. They found that the difference in the void structure can be explained by the difference in the growth mechanism of macrovoids. For the system polymethylmethacrylate (PMMA)/NMP/water, the growth of macrovoids is by convection. For the system PMMA/acetone/Tween80/water, the growth of macrovoids is by diffusion.^{139,140} Tsai et al. systematically studied the effect of sorbitan monooleate series surfactant as an additive on the structure of polysulfone membranes.^{55,56,141,142} From their research, addition of surfactant (Span-80) in the casting solution can suppress macrovoids in asymmetric PSf membranes. Also, they studied the effects on membrane structure using Span-20 and Span-80 at different concentrations.⁵⁶ The results showed that the addition of Span-80 could effectively inhibit the formation of vast macrovoids, and penetration experiments offered a reasonable explanation for this observation, suggesting that macrovoid formation was inhibited by the reduction of the water penetration rate.

3.5.5. Other Chemicals. Besides PVP, PA, PEG, and surfactants, some other small molecules can be used as additives. Kim et al. tried acetic acid (AA) as an additive to the system of

polyetherimide/NMP/water.¹⁴³ They showed that increasing the content of AA makes the membrane cross-section a closely connected, cellular sponge-type structure. Acetone has been used as an additive in PSf/DMF/water, PES/DMF/water, and PSf/NMP/water systems to compare the finger-like pores formed by PES and PSf.^{67,144} Butanol, propanol, and chloroform have also been applied as polar and nonpolar additives to show that the polar additive caused rapid demixing and formed porous asymmetric membranes with defective skin layers. The nonpolar additive decreases the demixing rate of the casting solution in this ternary system.¹⁴⁴

3.5.6. Nanoparticles as Additives. Inorganic particles have been used as fillers in various applications ranging from clothing to tennis racquets and computer circuits to improve properties such as stiffness, toughness, chemical stability, electrical conductivity, and resistance.¹⁴⁵ Typically used fillers are on the order of nanometers and because of their size are needed at concentrations as high as 20% by volume, which limits their application.¹⁴⁶ Therefore, a composite with improved properties and lower particle concentration is sought after. Nanocomposites are one possible solution.

When all three dimensions of a particle are on the order of nanometers, such as a spherical particle, it is referred to as an isodimensional nanoparticle.^{147–149} If only two dimensions are in the nanometer range, an elongated structure is formed and the structure formed is referred to as a nanotube, nanofiber, or whisker.^{150–152} Particles with only one nanoscale dimension form flat sheets. These three categories are used in different applications.

The use of nanoparticles as a filler in polymeric membranes, creating polymer nanocomposites, has begun to attract wide interest due to the improved electrical and mechanical properties, such as increased strength and modulus.³⁷ The improved properties result from a microstructure with a large fraction of filler atoms at the surface of the nanoparticles and the strong interfacial interactions the nanoparticles have with the surrounding polymer.¹⁴⁶ Isodimensional nanoparticles are typically used because they provide the best surface area to volume ratio. Nanoparticles based on materials such as clays, zeolites, carbon nanotubes, metals, and oxides have been explored in polymeric membranes, but the use of nanoparticles in formation of thin film composite membranes for desalination is an emerging area of research.^{153,154}

3. Temperature is a parameter that affects the viscosity of the casting solution. Casting solution viscosity can affect the exchange rate of solvent and nonsolvent during phase inversion. Therefore, temperature can be considered an influential parameter on membrane formation kinetics and surface and internal membrane morphology.^{55,60,89,129,155,156} Because a cloud-point curve represents an approximate boundary when liquid–liquid demixing occurs, it should be a good method to depict the thermodynamic process of phase inversion.

The research of Tsai et al. showed that coagulation bath temperature had tremendous influence after adding surfactants to polysulfone casting solution.⁵⁵ They found that temperature affects the viscosity of the coagulation bath and finally the size of the formed macrovoids. Zheng et al. studied the influence of temperature on the viscosity of the casting solution.⁶¹ They showed that increasing casting solution temperature decreased polysulfone casting solution viscosity and increased solvent–nonsolvent miscibility. They also

showed that with the increase of temperature, the kinetic parameter of membrane formation, D_a , ($= d^2/t$, where d is membrane thickness and t is coagulation time) increased. Zheng et al. also measured the cross-sectional morphologies of membranes prepared at different coagulation bath temperatures.⁶⁴ The size of finger-like macrovoids increased with increased coagulation bath temperature.

4. MEMBRANES

The performance, stability, and durability of a membrane are determined largely by their chemical composition and physical morphology. These properties can be characterized by a wide range of analytical methods. Understanding the fundamental characteristics of the membrane not only help to select a proper membrane for specific applications, but also guide the design of membranes with desired properties.¹⁵⁷ This section is by no means an exhaustive effort in accounting for all characterization methods; rather, it provides general fundamental principles and knowledge of membrane characterization techniques to obtain the essential information correlating membrane properties with their performance.

4.

t 4.1.1. Process Kinetics. The solvent–nonsolvent exchange rate is one of the kinetic factors attracting the most attention. It determines the path on the phase diagram during membrane formation. The method used for kinetic characterization is to observe the penetration of nonsolvent into the casting solution. This technique was described in the research of Frommer and Lancet,²² Strathmann et al.,¹⁵ and Wang et al.¹⁵⁸ In their methods, they placed a drop of the casting solution between two microscope slides and a drop of the coagulant (distilled water), added with phenolphthalein or rhodamine B in order to better observe the movement in precipitation. The coagulant penetrated into the casting solution when they were brought into contact. The penetration fronts of water and rhodamine B into the casting solutions were observed and videoed with an optical microscope. The video then was analyzed by image processing software to determine the time dependence of the water penetration, from which the demixing rate of the chosen solvent–nonsolvent system can be measured. This demixing rate finally determines the structure of the membrane as mentioned in a previous section.

4.1.2. System Thermodynamics. System thermodynamics are generally demonstrated by a ternary phase diagram. The binodal curve of liquid–liquid phase separation was considered an important factor affecting the membrane structure. Cloud points are defined as the moment when the solution changes from clear to turbid. The cloud point curve was usually measured to represent the binodal curve. To determine the composition or temperature at which the solution is no longer thermodynamically stable, turbidity or cloud points must be determined.³

For the construction of binodal curves, the titration method is described¹⁵⁹ and widely used.^{15,56,160} In this case, the nonsolvent or a mixture of the solvent and nonsolvent is added slowly to a solution of the polymer and solvent. During titration, the polymer solution is well stirred and kept at a constant temperature. The composition at which permanent turbidity occurs is the cloud point, which represents the composition where phase transition occurs. This technique can be operated visually. When the mixing solution changes from clear to turbid, the volume of

the solvent solution and the volume of the nonsolvent solution are recorded, and the exact cloud point is determined.

Another technique is cooling. With this technique, a tube is filled with either a binary mixture of polymer/solvent or a ternary mixture of polymer/solvent/nonsolvent and then sealed. The solution is homogenized at elevated temperature and the temperature of the thermostat bath is then decreased slowly at a constant cooling rate. At a certain temperature the solution is no longer thermodynamically stable and demixing occurs, which causes the solution to become turbid. This technique can be operated visually or by light transmission. The cloud point is observed when the reading of the light transmission instrument increases sharply.³

4. 4.2.1.

Membrane Thickness. For membranes prepared by the way of nonsolvent induced phase inversion, the thickness of the sublayer is usually between 50 and 200 μm , while the skin layer is a few micrometers or less. A micrometer is widely used to measure the total thickness of a porous filtration membrane. For approximation of skin layer thickness, generally scanning electron microscopy (SEM) is used, which can provide a clear view of the overall structure of the membrane, the skin layer, and the cross-section.^{69,161}

4.2.2. Membrane Porosity and Pore Size Distribution. Much effort has been made to characterize the pore size, pore size distribution, and solute or particle rejection for filtration membranes. Methods to characterize membranes can be classified into (1) physical methods to determine pore size and pore size distribution of a membrane and (2) methods based on permeation and rejection performance using reference molecules and particles.¹⁶²

4.2.2.1. Physical Methods. For characterizing the pore size and pore size distribution from rejection data, quantitative transport models, such as the Hagen–Poiseuille equation, were used. Nakao¹⁶² and Zhao et al.¹⁶³ have given reviews for determination of membrane pore size and pore size distribution. The following physical methods for pore size and pore size distribution determination are well-known: (1) microscopic, (2) bubble pressure and gas transport, (3) mercury porosimetry, (4) liquid–vapor equilibrium, (5) liquid–solid equilibrium (thermoporometry), and (6) gas–liquid equilibrium (permporometry).

Electron microscopy (EM) is one of the most powerful tools that can provide detailed information about the pore size, pore shape, morphology, and structure of membranes. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the two most commonly used EM methods. The operational principle of SEM relies on the detection of different scattered electrons by scanning the sample surface with a high energy electron beam. To observe cross sections by SEM the dried membrane is first fractured at liquid nitrogen temperature, and then fixed perpendicularly to the sample holder. Pores larger than 1 nm can be imaged by SEM.^{58,59,89} In contrast, TEM measurement analyzes the transmitted or forward-scattered electrons through the specimen.¹⁶⁴ The dried sample is first embedded and then sliced by a microtome. An embedding media with no influence on the membrane must be chosen. Both SEM and TEM are more widely used in recent years because of their convenient operation.^{162,165–167}

The bubble point method was used in the early years of the last century. This method essentially measures the pressure needed to blow air through a liquid-filled membrane. As the air pressure

is gradually increased, bubbles of air penetrate through the membranes at a certain pressure. It is a simple technique for characterization of the largest pores in microfiltration membranes. However, different results will be obtained when different liquids are chosen, and the rate of pressure increase and the pore length may influence the result.¹⁶² If water is used as the wetting medium, then this method can measure pores down to a few nanometers.³

The mercury intrusion technique is a variation of the bubble-point method. In this technique, mercury wets the membrane and is forced into a dry membrane with the volume of the mercury being determined at each pressure. The relationship between pressure and pore size is given by the Laplace equation. All microfiltration membranes, as well as a substantial proportion of ultrafiltration membranes, can be characterized using this method (pore size from 5 nm to 10 μm). The disadvantage is that the apparatus is rather expensive and some small pore sizes require high pressure, which may damage membrane structure.^{3,168}

The liquid–vapor equilibrium method was employed in the past.¹⁶⁹ This method for calculating pore size distributions is based on a model of the adsorbent as a collection of cylindrical pores. The theory accounts for capillary condensation in the pores using the classical Kelvin equation, which in turn assumes a hemispherical liquid–vapor meniscus and a well-defined surface tension. This theory also incorporates thinning of the adsorbed layer through the use of a reference isotherm.

Introduced by Brun et al., thermoporometry is based on the calorimetry of a solid–liquid transition in a porous material.¹⁷⁰ The principle is that the temperature at which the water in the pores freezes depends on the pore size. As the pore size decreases the freezing point of water decreases. So through the measurement of the freezing point, the pore size can be obtained. It is a simple method but all pores are measured with this technique, including dead-end pores, which make no contribution toward transport.^{170–172}

Permporometry is based on the blockage of pores with a condensable gas while simultaneously measuring gas flux through the membrane. This technique can only characterize the active pores which contribute to the transport. However, this technique is difficult to employ especially for hollow fiber membranes due to the difficulty of maintaining the same pressure on both sides of the membrane.^{167,173}

4.2.2.2. Permeability and Rejection Test. Methods based on permeation and rejection performance can also be employed to determine the pore size and pore size distribution of membranes.³ The pore size can be obtained by measuring the flux through a membrane at a constant pressure using the Hagen–Poiseuille equation,

$$J_v = \frac{\varepsilon r_p^2}{8\mu\tau} \frac{\Delta p}{\Delta x} \quad (30)$$

Here J_v is the water flux through the membrane at a driving force of $\Delta p/\Delta x$, with Δp being the pressure difference across the membrane of thickness Δx . The proportionality factor contains the pore radius r_p , liquid dynamic viscosity μ , surface porosity of the membrane ε , and the tortuosity factor τ . The pore size distribution can be obtained by varying the pressure, i.e., by a combination of the bubble-point method and permeability methods. It is not essential that the liquid should wet the membrane. The permeability method is widely employed both

for microfiltration and ultrafiltration membranes because it has the distinct advantage of experimental simplicity, especially when liquids are used. However, the Hagen–Poiseuille equation assumes that pores are cylindrical, so the geometry is very important and will affect the result. For asymmetric membranes, Δx is the skin layer thickness and must be known to determine pore size.

The pore size of a filtration membrane can be described by the membrane's ability to retain solutes or particles of a given size or molecular weight. The term *molecular weight cutoff* is used to relate the size of a solute that would be retained, or almost completely retained, by a given membrane to that membrane's pore size.⁷ Molecular weight cutoff is determined by performing rejection tests using solutes or globular proteins of known sizes with the membrane of interest. Figure 5 shows the comparison between a membrane with a so-called "sharp cutoff" and a membrane with a "diffuse cutoff". Solute used in molecular weight cutoff tests should ideally be soluble in water or in a mildly buffered solution, cover a wide range of sizes, and should not adsorb to the membrane surface. Average pore size and pore size distribution can be determined from solute rejection data.¹⁶²

Solute rejection measurements provide a very simple technique for determining membrane performance. However, some other factors such as adsorption, concentration polarization, and membrane fouling can have a drastic effect on the result, so it is difficult to obtain quantitative results by such a method.

4.2.3. Membrane Interfacial Properties. Composite membrane properties are determined largely by the extremely thin skin layer, so surface characterization is necessary. A wide range of physical and chemical surface analysis techniques are available. Here, some popular analytical methods are briefly summarized in Table 4.¹⁷⁴ In many situations, several connected processes may be going on more or less simultaneously, with a particular analytical technique picking out only one aspect (e.g., the extent of incident light absorption or the kinetic energy distribution of ejected electrons).

4.2.3.1. Surface Morphology. The surface morphology of membranes can also be examined by atomic force microscopy (AFM). The working principle of AFM is to use a sharp tip to scan the sample surface. When the tip is close to the surface, van der Waals forces will change the vibrating frequency of the tip or cause deflections. By detecting the vibrating frequency or deflections of the tip, a three-dimensional map of membrane surface topography can be obtained. Atomic force microscopy is widely used to characterize membrane surfaces and has the advantage of providing quantitative nanoscale measurements of both lateral and vertical morphology. In addition to morphology mapping, AFM can quantify the interaction force between the membrane surface and the probe used. Thus, much information besides the surface morphology, such as the fouling propensity and electrical properties, can be revealed.^{175,176}

4.2.3.2. Membrane Chemical Structure. Many methods used to analyze chemical compounds can also be used to obtain the same information for membranes. The analytical methods generally used to examine the chemical composition of membranes include Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, energy-dispersive X-ray spectroscopy (EDX), electron spectroscopy for chemical analysis (X-ray photoelectron spectroscopy) (ESCA, XPS), auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), atomic force microscopy (AFM), and secondary ion mass spectrometry (SIMS). It should be noted that each analytical method has its

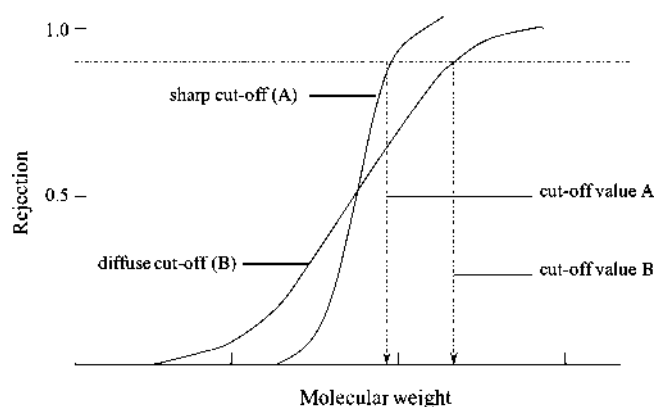


Figure 5. Rejection characteristics for a membrane with (A) a "sharp cut-off" compared with that of a membrane with (B) a "diffuse cut off".³

unique operation principles, and the information obtained differs. Thus, combining several methods is generally required to infer the correct chemical composition of an unknown or novel membrane. The operation principles and applicability of some popular analytical methods will be discussed in the following section. Table 4 briefly summarizes the general information of applicability of some popular analytical methods.¹⁷⁴

In general, XPS, AES, SIMS, EELS, and EDX are most suitable to obtain chemical information for membrane skin layers due to their low penetration capability. In contrast, Raman and FTIR reveal the chemical composition of both surface layer and the bulk materials. Another great advantage of Raman, FTIR, and AFM is the possibility of analyzing samples in their wet state, which is more relevant to membrane applications. If considering the lateral resolution in mapping the chemical composition of membranes, EDX, XPS, and AFM give more detailed information on the surface composition than other methods.¹⁵⁷

Fourier transform infrared spectroscopy and Raman are two nondestructive methods commonly used to probe the lateral and vertical chemical composition of membranes. Both methods allow identification of the molecular bonds existing in the membrane and subsequently determination of the chemical structure. Besides providing the overall chemical composition, recent development in FTIR and Raman spectrometry has enabled depth profiling of the membrane surface.^{177,178} By tuning the incident angle, the refractive indices of crystals, and the wavelength, the penetration of the IR signal into the membrane sample can be controlled. Thus, FTIR is suitable to reveal vertical chemical information of membrane samples with a spatial resolution of 0.5 to 1 μm .¹⁵⁷

The surface chemical composition of membranes can also be revealed by EDX/EDS, XPS, and SIMS qualitatively and quantitatively. The operational principle of EDX/EDS relies on the detection of characteristic X-ray emitted from the specimen surface induced by incident of high energy beam. As each element has a unique energy of X-ray emission, the elemental composition and abundance of the materials can be measured.¹⁴⁹ The detection limit of EDX/EDS is about 0.1 atom-% and the spatial resolution is generally below 1 μm . However, the vertical penetration of the electron beams is generally less than 0.5 μm , which limits the vertical information that can be revealed.¹⁷⁹ X-ray photoelectron spectroscopy works on a similar principle but relies on the detection of the excited electrons from the materials. By measuring the number and the energy of electrons

Table 4. Popular Analytical Techniques for Membrane Physical–Chemical Characterization^{58,59,74,86,89,104,196,215–228}

technique	main information	vertical resolution (depth probed, typical)	lateral resolution (typical)	types of solid specimen (typical)	application examples
atomic force microscopy (AFM); scanning force microscopy (SFM)	topographic imaging, friction force, mapping, morphology, profilometry, film thickness, wear volume, structure, surface roughness	<0.03 to 0.05 nm	atomic to 1 nm	all kinds of solids	75, 217, 218
auger electron spectroscopy (AES)	elemental composition, chemical state, depth profiling, imaging and mapping	0.5 to 10 nm	a few tens of nm or less	ultrahigh vacuum compatible solids	219, 220
energy-disperse X-ray spectroscopy (EDS); wavelength dispersive X-ray spectroscopy (WDS)	elemental composition ($Z \geq 5$; boron to uranium), spectroscopy, imaging and mapping	0.02 to 1 μm	0.5 to 1 μm for bulk specimens; as small as 1 nm for thin specimens	ultrahigh vacuum compatible solids	221,222
Fourier transform infrared spectroscopy (FTIR)	chemical species' binding, structural inhomogeneity, defects, depth profile	10 nm to μm	20 μm to 5 mm	all kinds of solids	87, 198
Raman spectroscopy	identification of unknown compounds, chemical state, bonding state, structural order, phase transitions, depth profiling	few μm to mm	1 μm	all kinds of solids	223–225
scanning electron microscopy (SEM)	imaging and mapping, morphology, defects	variable from a few nm to a few μm	1 to 50 nm in secondary electron mode	ultrahigh vacuum compatible solids	59, 60, 90
secondary ion mass spectroscopy (SIMS)	chemical structure/binding, imaging, elemental composition, depth profile	0.3 to 2 nm	10 nm to 2 mm	ultrahigh vacuum compatible solids	226, 227
transmission electron microscopy (TEM)	atomic structure, microstructure, crystallography, structure, defect imaging, morphology, chemical bonding	none	≤ 0.2 nm	ultrahigh vacuum compatible solids	105, 228
X-ray photoelectron spectroscopy (XPS)	elemental composition, chemical state, depth profiling, imaging and mapping	a few to several nm	5 μm to 5 mm	ultrahigh vacuum compatible solids	226, 229
X-ray diffraction (XRD)	crystalline phases, orientation and size, atomic arrangements, defect imaging, film thickness	a few μm	none; ~ 10 μm with microfocus	dry solid	220, 230

that escaped from the surface with X-ray irradiation, the elemental composition, empirical formula, chemical state, and electronic state of the elements can be revealed.¹⁴⁹ One advantage of XPS analysis is the low energy incident X-rays, which enables nondestructive examination of the surface.^{149,180} The typical analysis depth is 1–3 nm, making XPS a valuable tool to reveal skin layer information. However, both EDX and XPS require the samples to be conductive. Thus, most polymeric membranes have to be coated with conductive material before analysis. Secondary ion mass spectrometry collects and analyzes the ejected secondary ions from the sample surface sputtered by primary ion beams. The secondary ions measured by mass spectrometer can be used to determine the elemental, isotopic, and molecular composition of the membrane. In modern SIMS equipment, the charging of sample can be avoided with electron flood sources. As the primary ion beam can rapidly sputter the surface, SIMS technique is applicable to reveal the depth profile of chemical composition.^{157,181}

4.2.3.3. Surface Hydrophilicity and Surface Energy. Membrane hydrophilicity is a very important interfacial property that can be modified by changing phase inversion process conditions or polymer chemistry. The most common method to determine the hydrophilicity of a membrane is the measurement of contact angle. Among the various ways to measure the contact angle, the sessile drop method is the most widely used.¹⁸² Because of surface tension, the surface of any liquid is an interface between that liquid and another medium. Interfacial tension is a property of the liquid's interaction with another medium, e.g., the membrane. Where the two materials meet, the geometry of the interface is determined from the balance of interfacial forces.¹⁸³ So, a wealth of information can be obtained through the measurement of the contact angle between the liquid and membrane surface.

One piece of important information that can be obtained by contact angle measurement is the surface free energy of the membrane. Analysis of contact angles of liquid droplets on a solid substrate provide parameters describing Lifshitz–van der Waals, electron-donor, and electron-acceptor components of the solid surface tension.^{184,185} The surface tension parameters collectively describe the Lifshitz–van der Waals and Lewis acid–base interfacial free energy (per unit area) of any material immersed in water. Although simple water contact angles suggest a material's "hydrophilicity", the interfacial free energy of cohesion (per unit area) of a given material immersed in water gives an indication of inherent (thermodynamic) stability or aggregation propensity. The more positive the overall free energy of *cohesion*, the more hydrophilic, stable, and resistant to *aggregation* is the material. Alternatively, the free energy of *adhesion* (per unit area) of two different materials (e.g., a colloidal particle and a sand grain) immersed in water gives an indication of inherent (thermodynamic) stability or deposition propensity. The more positive the overall free energy of *adhesion*, the more hydrophilic, stable, and resistant to *deposition* is the material.

Probe liquids with known surface tensions (such as diiodomethane, glycerol, and water) enable determination of the three surface tension parameters by solving the extended Young equation simultaneously for each liquid.^{185,186} The polar (electron-donor/acceptor) components of surface tension both change with subtle variations in aqueous solution chemistry (ionic strength, pH, plurivalent ions, and buffer capacity); hence, one can also record contact angles of various aqueous electrolytes to determine the variation in polar surface tension compo-

nents.^{184,186,187} In addition, contact angles measured for buffered and unbuffered water drops adjusted to different pH values can be used to quantify solid substrate surface charge density and ionization fraction as a function pH.^{185,188,189}

4.2.3.4. Surface Roughness. The interaction potentials between membrane surface and particulate matter are also influenced by membrane surface roughness.^{190,191} Recent studies indicate that the roughness/morphology of membrane surfaces impacts the magnitudes of interaction potentials to the same extent as similar changes in the magnitudes of chemical free energy and electrostatic interaction.^{192,193} Although EM provides fine resolutions of surface topography, the quantitative and statistical analysis of surface roughness features is obtained through AFM measurements.¹⁹⁴ Key parameters describing membrane surface morphology (e.g., mean roughness, average roughness, root-mean-square roughness, surface area difference, peak count per unit area, and the ratio of asperity separation to asperity size) can be obtained through AFM examination.¹⁹⁴

4.2.3.5. Surface Charge. Most polymers acquire an electric surface charge when brought into contact with an aqueous solution. Once the membrane is brought into contact with an aqueous electrolyte solution, the dissociation of functional groups and adsorption of ions/molecules causes most of the membrane surface to become charged. It has been well recognized that charge or electrical properties of polymeric membranes have a substantial influence on their filtration performances.¹⁹⁵ The surface charge properties of membranes are often characterized by zeta potential, which is the electric potential in the interfacial double layer at the location of the slipping plane versus a point in the bulk fluid away from the interface. Generally, the fundamental equation relating the measured streaming potential to the zeta potential (ζ) is given by the classical Helmholtz–Smoluchowski formula¹⁹⁶

$$\zeta = \frac{\Delta V}{\Delta P} \frac{\mu \kappa_b}{\varepsilon_r \varepsilon_0} \quad (31)$$

where $\Delta V/\Delta P$ is the streaming potential, ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant of the liquid, μ is the liquid viscosity, and κ_b is the conductivity of the bulk electrolyte. This equation was later modified by Yaroshchuk et al.¹⁹⁷ and experimentally verified by Fievet et al.¹⁹⁸ as

$$\zeta = \frac{\Delta V}{\Delta P} \kappa_t \frac{\mu}{\varepsilon_r \varepsilon_0} \frac{L}{hD} \quad (32)$$

where κ_t is the total conductance of the membrane/channel/membrane system, L is the length of the slit channel, h is the height of the slit channel, and D is the width of the slit channel.

Many methods have been developed to qualitatively and quantitatively characterize membrane surface charge, including streaming potential measurement, impedance spectroscopy, membrane potential measurements, and titration. The obtained zeta potential is a function of material intrinsic properties, such as membrane backbone materials, surface functional groups, and internal structure. Solution chemistries are also proven to have pronounced influence on the zeta potential measurements, such as solution pH, ionic strength, and even ionic composition.

5.

In this Review, a basic description about the preparation and characterization was given for nonsolvent induced phase inversion membranes. Basic formation mechanisms for different

membrane morphologies were introduced. Key factors of the membrane preparation process including the choice of solvent—nonsolvent system, the composition of the polymer solution, the composition of the coagulation bath, the choice of additives in the system, and film casting conditions were discussed. Mechanisms of the system thermodynamics and process kinetics were also discussed. We can predict that membranes with suitable morphology, stability, and permeation properties can be obtained from judging such key factors.

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REFERENCES

- (1) Crittenden, J. C.; Trussel, R. R.; Hand, D. W.; Howe, K. J.; Tchobanoglous, G. *Water Treatment: Principles and Design*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2005.
- (2) Cheryan, M. *Ultrafiltration and Microfiltration Handbook*; Technomic: Lancaster, PA, 1998.
- (3) Mulder, M. *Basic Principles of Membrane Technology*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003.
- (4) Loeb, G. S.; Sourirajan, S. Sea water demineralization by means of an osmotic membrane. *Adv. Chem. Ser.* **1968**, 38, 117.
- (5) Guillotin, M.; Lemoyne, C.; Noel, C.; Monnerie, L. Physico-chemical processes occurring during formation of cellulose diacetate membranes - research of criteria for optimizing membrane performance - 4. Cellulose diacetate-acetone-organic additive casting solutions. *Desalination* **1977**, 21, 165.
- (6) Koenhen, D. M.; Mulder, M. H. V.; Smolders, C. A. Phase separation phenomena during formation of asymmetric membranes. *J. Appl. Polym. Sci.* **1977**, 21, 199.
- (7) Cabasso, I.; Klein, E.; Smith, J. K. Polysulfone hollow fibers. 1. Spinning and properties. *J. Appl. Polym. Sci.* **1976**, 20, 2377.
- (8) Cabasso, I.; Klein, E.; Smith, J. K. Polysulfone hollow fibers. 2. Morphology. *J. Appl. Polym. Sci.* **1977**, 21, 165.
- (9) Sukitpaneevit, P.; Chung, T. S. Molecular elucidation of morphology and mechanical properties of PVDF hollow fiber membranes from aspects of phase inversion, crystallization and rheology. *J. Membr. Sci.* **2009**, 340, 192.
- (10) Koops, G. H.; Nolten, J. A. M.; Mulder, M. H. V.; Smolders, C. A. Integrally skinned polysulfone hollow-fiber membranes for pervaporation. *J. Appl. Polym. Sci.* **1994**, 54, 385.
- (11) Ghosh, A. K.; Jeong, B. H.; Huang, X. F.; Hoek, E. M. V. Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties. *J. Membr. Sci.* **2008**, 311, 34.
- (12) Strathmann, H.; Kock, K. Formation mechanism of phase inversion membranes. *Desalination* **1977**, 21, 241.
- (13) Wijmans, J. G.; Kant, J.; Mulder, M. H. V.; Smolders, C. A. Phase-separation phenomena in solutions of polysulfone in mixtures of a solvent and a nonsolvent - relationship with membrane formation. *Polymer* **1985**, 26, 1539.
- (14) Smolders, C. A.; Reuvers, A. J.; Boom, R. M.; Wienk, I. M. Microstructures in phase-inversion membranes. 1. Formation of macrovoids. *J. Membr. Sci.* **1992**, 73, 259.
- (15) Strathmann, H.; Kock, K.; Amar, P.; Baker, R. W. Formation mechanism of asymmetric membranes. *Desalination* **1975**, 16, 179.
- (16) Cohen, C.; Tanny, G. B.; Prager, S. Diffusion-controlled formation of porous structures in ternary polymer systems. *J. Polym. Sci., Part B: Polym. Phys.* **1979**, 17, 477.
- (17) Reuvers, A. J.; Vandenberg, J. W. A.; Smolders, C. A. Formation of membranes by means of immersion precipitation. 1. A model to describe mass-transfer during immersion precipitation. *J. Membr. Sci.* **1987**, 34, 45.
- (18) Tsay, C. S.; McHugh, A. J. Mass-transfer modeling of asymmetric membrane formation by phase inversion. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, 28, 1327.
- (19) Radovanovic, P.; Thiel, S. W.; Hwang, S. T. Formation of asymmetric polysulfone membranes by immersion precipitation. 1. Modeling mass-transport during gelation. *J. Membr. Sci.* **1992**, 65, 213.
- (20) Radovanovic, P.; Thiel, S. W.; Hwang, S. T. Formation of asymmetric polysulfone membranes by immersion precipitation. 2. The effects of casting solution and gelation bath compositions on membrane-structure and skin formation. *J. Membr. Sci.* **1992**, 65, 231.
- (21) Matz, R. Structure of cellulose-acetate membranes. 1. Development of porous structures in anisotropic membranes. *Desalination* **1972**, 10, 1.
- (22) Frommer, M. A.; Lancet, D. The mechanism of membrane formation: Membrane structures and their relation to preparation conditions. In *Reverse Osmosis Membrane Research*; Lonsdale, H. K., Podall, H. E., Eds.; Plenum Press: New York, 1972.
- (23) Ray, R. J.; Krantz, W. B.; Sani, R. L. Linear-stability theory model for finger formation in asymmetric membranes. *J. Membr. Sci.* **1985**, 23, 155.
- (24) Boom, R. M.; Wienk, I. M.; Vandenboomgaard, T.; Smolders, C. A. Microstructures in phase inversion membranes. 2. The role of a polymeric additive. *J. Membr. Sci.* **1992**, 73, 277.
- (25) Kimmerle, K.; Strathmann, H. Analysis of the structure-determining process of phase inversion membranes. *Desalination* **1990**, 79, 283.
- (26) Lai, J. Y.; Lin, F. C.; Wang, C. C.; Wang, D. M. Effect of nonsolvent additives on the porosity and morphology of asymmetric TPX membranes. *J. Membr. Sci.* **1996**, 118, 49.
- (27) Yilmaz, L.; McHugh, A. J. Analysis of nonsolvent solvent polymer phase-diagrams and their relevance to membrane formation modeling. *J. Appl. Polym. Sci.* **1986**, 31, 997.
- (28) Cheng, L. P.; Dwan, A. H.; Gryte, C. C. Membrane formation by isothermal precipitation in polyamide formic-acid water-systems. 1. Description of membrane morphology. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, 33, 211.
- (29) Termonia, Y. Fundamentals of polymer coagulation. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, 33, 279.
- (30) Cheng, J. M.; Wang, D. M.; Lin, F. C.; Lai, J. Y. Formation and gas flux of asymmetric pmma membranes. *J. Membr. Sci.* **1996**, 109, 93.
- (31) Paulsen, F. G.; Shojaie, S. S.; Krantz, W. B. Effect of evaporation step on macrovoid formation in wet-cast polymeric membranes. *J. Membr. Sci.* **1994**, 91, 265.
- (32) Young, T. H.; Cheng, L. P.; Lin, D. J.; Fane, L.; Chuang, W. Y. Mechanisms of PVDF membrane formation by immersion-precipitation in soft (1-octanol) and harsh (water) nonsolvents. *Polymer* **1999**, 40, 5315.
- (33) Li, C. L.; Wang, D. M.; Deratani, A.; Quemener, D.; Bouyer, D.; Lai, J. Y. Insight into the preparation of poly(vinylidene fluoride) membranes by vapor-induced phase separation. *J. Membr. Sci.* **2010**, 361, 154.
- (34) Flory, P. J. Thermodynamics of high polymer solutions. *J. Chem. Phys.* **1941**, 9, 660.
- (35) Huggins, M. L. Solutions of long chain compounds. *J. Chem. Phys.* **1941**, 9, 440.
- (36) Huggins, M. L. Theory of solutions of high polymers. *J. Am. Chem. Soc.* **1942**, 64, 1712.
- (37) Fried, J. *Polymer Science and Technology*; Prentice Hall: Upper Saddle River, NJ, 2003.

- (38) Lipson, J. E. G.; Guillet, J. E. In *Developments in Polymer Characterisation*; Dawkins, J. V., Ed.; Applied Science Publishers: London, 1982.
- (39) Flory, P. J.; Krigbaum, W. R. Statistical mechanics of dilute polymer solutions. II. *J. Chem. Phys.* **1950**, *18*, 1086.
- (40) Koningsveld, R.; Kleintjens, L. A.; Schoffeleers, H. M. Thermodynamic aspects of polymer compatibility. *Pure Appl. Chem.* **1974**, *39*, 1.
- (41) Hoy, K. L. New values of solubility parameters from vapor pressure data. *J. Paint Technol.* **1970**, *42*, 76.
- (42) Small, P. A. Some factors affecting the solubility of polymers. *J. Appl. Chem.* **1953**, *3*, 71.
- (43) van Krevelen, D. W. *Properties of Polymers*; Elsevier: Amsterdam, 1990.
- (44) Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolytes*; Reinhold: New York, 1959.
- (45) Scatchard, G. Equilibria in non-electrolyte solutions in relation to the vapor pressures and densities of the components. *Chem. Rev.* **1931**, *8*, 321.
- (46) Hansen, C. M. The three dimensional solubility parameter and solvent diffusion coefficient. Ph.D. Thesis, University of Copenhagen, 1967.
- (47) Hansen, C. M. Solubility Parameters - An Introduction. In *Hansen Solubility Parameters - A User's Handbook*; CRC Press: Boca Raton, FL, 2000; Chapter 1.
- (48) Hansen, C. M.; Beerbower, A., Solubility parameters. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Standen, A., Ed.; Interscience: New York, 1971.
- (49) Hansen, C. M. The three dimensional solubility parameter - key to paint component affinities I. *J. Paint Technol.* **1967**, *39*, 104.
- (50) Hansen, C. M. The three dimensional solubility parameter - key to paint component affinities II. *J. Paint Technol.* **1967**, *39*, 505.
- (51) Hansen, C. M.; Skarup, K. The three dimensional solubility parameter - key to paint component affinities III. *J. Paint Technol.* **1967**, *39*, 511.
- (52) Blanks, R. F.; Prausnitz, J. M. Thermodynamics of polymer solubility in polar + nonpolar systems. *Ind. Eng. Chem. Fundam.* **1964**, *3*, 1.
- (53) Hansen, C. M. Methods of Characterization - Polymers. In *Hansen Solubility Parameters - A User's Handbook*; CRC Press: Boca Raton, FL, 2000; Chapter 3.
- (54) Hansen, C. M. Appendix. In *Hansen Solubility Parameters - A User's Handbook*; CRC Press: Boca Raton, FL, 2000.
- (55) Tsai, H. A.; Li, L. D.; Lee, K. R.; Wang, Y. C.; Li, C. L.; Huang, J.; Lai, J. Y. Effect of surfactant addition on the morphology and pervaporation performance of asymmetric polysulfone membranes. *J. Membr. Sci.* **2000**, *176*, 97.
- (56) Tsai, H. A.; Ruaan, R. C.; Wang, D. M.; Lai, J. Y. Effect of temperature and Span series surfactant on the structure of polysulfone membranes. *J. Appl. Polym. Sci.* **2002**, *86*, 166.
- (57) Han, M. J.; Nam, S. T. Thermodynamic and rheological variation in polysulfone solution by PVP and its effect in the preparation of phase inversion membrane. *J. Membr. Sci.* **2002**, *202*, 55.
- (58) Chakrabarty, B.; Ghoshal, A. K.; Purkait, A. K. Preparation, characterization and performance studies of polysulfone membranes using PVP as an additive. *J. Membr. Sci.* **2008**, *315*, 36.
- (59) Chakrabarty, B.; Ghoshal, A. K.; Purkait, M. K. Effect of molecular weight of PEG on membrane morphology and transport properties. *J. Membr. Sci.* **2008**, *309*, 209.
- (60) Kim, J. H.; Lee, K. H. Effect of PEG additive on membrane formation by phase inversion. *J. Membr. Sci.* **1998**, *138*, 153.
- (61) Zheng, Q. Z.; Wang, P.; Yang, Y. N. Rheological and thermodynamic variation in polysulfone solution by PEG introduction and its effect on kinetics of membrane formation via phase-inversion process. *J. Membr. Sci.* **2006**, *279*, 230.
- (62) Ahmad, A. L.; Sarif, M.; Ismail, S. Development of an integrally skinned ultrafiltration membrane for wastewater treatment: Effect of different formulations of PSf/NMP/PVP on flux and rejection. *Desalination* **2005**, *179*, 257.
- (63) Han, M. J. Effect of propionic acid in the casting solution on the characteristics of phase inversion polysulfone membranes. *Desalination* **1999**, *121*, 31.
- (64) Zheng, Q. Z.; Wang, P.; Yang, Y. N.; Cui, D. J. The relationship between porosity and kinetics parameter of membrane formation in PSF ultrafiltration membrane. *J. Membr. Sci.* **2006**, *286*, 7.
- (65) Hou, T. P.; Dong, S. H.; Zheng, L. Y. The study of mechanism of organic additives action in the polysulfone membrane casting solution. *Desalination* **1991**, *83*, 343.
- (66) Fontyn, M.; Vantriet, K.; Bijsterbosch, B. H. Surface spectroscopic studies of pristine and fouled membranes. 1. Method development and pristine membrane characterization. *Colloids Surf.* **1991**, *54*, 331.
- (67) Barth, C.; Goncalves, M. C.; Pires, A. T. N.; Roeder, J.; Wolf, B. A. Asymmetric polysulfone and polyethersulfone membranes: Effects of thermodynamic conditions during formation on their performance. *J. Membr. Sci.* **2000**, *169*, 287.
- (68) Baik, K. J.; Kim, J. Y.; Lee, H. K.; Kim, S. C. Liquid-liquid phase separation in polysulfone/polyethersulfone/N-methyl-2-pyrrolidone/water quaternary system. *J. Appl. Polym. Sci.* **1999**, *74*, 2113.
- (69) Chaturvedi, B. K.; Ghosh, A. K.; Ramachandran, V.; Trivedi, M. K.; Hanra, M. S.; Misra, B. M. Preparation, characterization and performance of polyethersulfone ultrafiltration membranes. *Desalination* **2001**, *133*, 31.
- (70) Liu, Y.; Koops, G. H.; Strathmann, H. Characterization of morphology controlled polyethersulfone hollow fiber membranes by the addition of polyethylene glycol to the dope and bore liquid solution. *J. Membr. Sci.* **2003**, *223*, 187.
- (71) Mosqueda-Jimenez, D. B.; Narbaitz, R. M.; Matsuura, T.; Chowdhury, G.; Pleizier, G.; Santerre, J. P. Influence of processing conditions on the properties of ultrafiltration membranes. *J. Membr. Sci.* **2004**, *231*, 209.
- (72) Hwang, J. R.; Koo, S. H.; Kim, J. H.; Higuchi, A.; Tak, T. M. Effects of casting solution composition on performance of poly(ether sulfone) membrane. *J. Appl. Polym. Sci.* **1996**, *60*, 1343.
- (73) Barzin, J.; Sadatnia, B. Theoretical phase diagram calculation and membrane morphology evaluation for water/solvent/polyethersulfone systems. *Polymer* **2007**, *48*, 1620.
- (74) Idris, A.; Zain, N. M.; Noordin, M. Y. Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives. *Desalination* **2007**, *207*, 324.
- (75) Li, J. F.; Xu, Z. L.; Yang, H. Microporous polyethersulfone membranes prepared under the combined precipitation conditions with non-solvent additives. *Polym. Adv. Technol.* **2008**, *19*, 251.
- (76) Rahimpour, A.; Madaeni, S. S. Polyethersulfone (PES)/cellulose acetate phthalate (CAP) blend ultrafiltration membranes: Preparation, morphology, performance and antifouling properties. *J. Membr. Sci.* **2007**, *305*, 299.
- (77) Rahimpour, A.; Madaeni, S. S.; Mansourpanah, Y. High performance polyethersulfone UF membrane for manufacturing spiral wound module: Preparation, morphology, performance, and chemical cleaning. *Polym. Adv. Technol.* **2007**, *18*, 403.
- (78) Cornelissen, E. R.; Boomgaard, T.; Strathmann, H. Physicochemical aspects of polymer selection for ultrafiltration and microfiltration membranes. *Colloids Surf., A* **1998**, *138*, 283.
- (79) Chandorikar, M. V.; Bhavsar, P. C. Evaluation of polyacrylonitrile and poly(methyl methacrylate) as membrane materials for reverse-osmosis. *Indian J. Technol.* **1983**, *21*, 124.
- (80) Belfer, S. Modification of ultrafiltration polyacrylonitrile membranes by sequential grafting of oppositely charged monomers: pH-dependent behavior of the modified membranes. *React. Funct. Polym.* **2003**, *54*, 155.
- (81) Kim, I. C.; Yun, H. G.; Lee, K. H. Preparation of asymmetric polyacrylonitrile membrane with small pore size by phase inversion and post-treatment process. *J. Membr. Sci.* **2002**, *199*, 75.
- (82) Scharnagl, N.; Buschatz, H. Polyacrylonitrile (PAN) membranes for ultra- and microfiltration. *Desalination* **2001**, *139*, 191.
- (83) Musale, D. A.; Kumari, A.; Pleizier, G. Formation and characterization of poly(acrylonitrile)/chitosan composite ultrafiltration membranes. *J. Membr. Sci.* **1999**, *154*, 163.

- (84) Zhu, T. R.; Luo, Y. B.; Lin, Y. W.; Li, Q.; Yu, P.; Zeng, M. Study of pervaporation for dehydration of caprolactam through blend NaAlg-poly(vinyl pyrrolidone) membranes on PAN supports. *Sep. Purif. Technol.* **2010**, *74*, 242.
- (85) Zhang, G. J.; Meng, H.; Ji, S. L. Hydrolysis differences of polyacrylonitrile support membrane and its influences on polyacrylonitrile-based membrane performance. *Desalination* **2009**, *242*, 313.
- (86) Oh, N. W.; Jegal, J.; Lee, K. H. Preparation and characterization of nanofiltration composite membranes using polyacrylonitrile (PAN). I. Preparation and modification of PAN supports. *J. Appl. Polym. Sci.* **2001**, *80*, 1854.
- (87) Reddy, A. V. R.; Patel, H. R. Chemically treated polyethersulfone/polyacrylonitrile blend ultrafiltration membranes for better fouling resistance. *Desalination* **2008**, *221*, 318.
- (88) Qin, J. J.; Cao, Y. M.; Li, Y. Q.; Li, Y.; Oo, M. H.; Lee, H. W. Hollow fiber ultrafiltration membranes made from blends of PAN and PVP. *Sep. Purif. Technol.* **2004**, *36*, 149.
- (89) Yang, S.; Liu, Z. Z. Preparation and characterization of polyacrylonitrile ultrafiltration membranes. *J. Membr. Sci.* **2003**, *222*, 87.
- (90) Nouzaki, K.; Nagata, M.; Arai, J.; Idemoto, Y.; Koura, N.; Yanagishita, H.; Negishi, H.; Kitamoto, D.; Ikegami, T.; Haraya, K. Preparation of polyacrylonitrile ultrafiltration membranes for wastewater treatment. *Desalination* **2002**, *144*, 53.
- (91) Yang, S.; Liu, Z. Z.; Chen, H. Z. A gas-liquid chemical reaction treatment and phase inversion technique for formation of high permeability pan of membranes. *J. Membr. Sci.* **2005**, *246*, 7.
- (92) Matz, R. Structure of cellulose-acetate membranes. 2. Physical and transport characteristics of porous layer of anisotropic membranes. *Desalination* **1972**, *11*, 207.
- (93) Arockiasamy, D. L.; Nagendran, A.; Shobana, K. H.; Mohan, D. Preparation and characterization of cellulose acetate/aminated polysulfone blend ultrafiltration membranes and their application studies. *Sep. Sci. Technol.* **2009**, *44*, 398.
- (94) Arthanareeswaran, G.; Devi, T. K. S.; Raajenthiren, M. Effect of silica particles on cellulose acetate blend ultrafiltration membranes: Part I. *Sep. Purif. Technol.* **2008**, *64*, 38.
- (95) Nagendran, A.; Vidya, S.; Mohan, D. Preparation and characterization of cellulose acetate-sulfonated poly (ether imide) blend ultrafiltration membranes and their applications. *Soft Mater.* **2008**, *6*, 45.
- (96) Raguime, J. A.; Arthanareeswaran, G.; Thanikaivelan, P.; Mohan, D.; Raajenthiren, M. Performance characterization of cellulose acetate and poly(vinylpyrrolidone) blend membranes. *J. Appl. Polym. Sci.* **2007**, *104*, 3042.
- (97) Arthanareeswaran, G.; Thanikaivelan, P.; Srinivasn, K.; Mohan, D.; Rajendran, M. Synthesis, characterization and thermal studies on cellulose acetate membranes with additive. *Eur. Polym. J.* **2004**, *40*, 2153.
- (98) Vidya, S.; Vijayalakshmi, A.; Nagendran, A.; Mohan, D. Effect of additive concentration on cellulose acetate blend membranes-preparation, characterization and application studies. *Sep. Sci. Technol.* **2008**, *43*, 1933.
- (99) Malaisamy, R.; Mahendran, R.; Mohan, D.; Rajendran, M.; Mohan, V. Cellulose acetate and sulfonated polysulfone blend ultrafiltration membranes. I. Preparation and characterization. *J. Appl. Polym. Sci.* **2002**, *86*, 1749.
- (100) Fujiwara, N.; Fukuda, T.; Yanaga, Y.; Sekino, M.; Goto, T. The reference and analysis of a double-element type hollow-fiber RO module in seawater desalination. *Desalination* **1994**, *96*, 441.
- (101) Elguera, A. M.; Nunez, A.; Nishida, M. Experimental test of TOYOBO membranes for seawater desalination at Las Palmas, Spain. *Desalination* **1999**, *125*, 55.
- (102) Yoo, S. H.; Jho, J. Y.; Won, J.; Park, H. C.; Kang, Y. S. Effect of solvent and cosolvent on the morphology and permeance of asymmetric polyimide membrane. *J. Ind. Eng. Chem.* **2000**, *6*, 129.
- (103) Yoo, S. H.; Kim, J. H.; Jho, J. Y.; Won, J.; Kang, Y. S. Influence of the addition of PVP on the morphology of asymmetric polyimide phase inversion membranes: Effect of PVP molecular weight. *J. Membr. Sci.* **2004**, *236*, 203.
- (104) Perez, S.; Merlen, E.; Robert, E.; Addad, J. P. C.; Viallat, A. Characterization of the surface-layer of integrally skinned polyimide membranes - relationship with their mechanism of formation. *J. Appl. Polym. Sci.* **1993**, *47*, 1621.
- (105) Jeon, J. Y.; Tak, T. M. Preparation of newly asymmetric polyimide membranes by phase inversion. *J. Appl. Polym. Sci.* **1996**, *61*, 2345.
- (106) Blais, P.; Polyamide membranes. In *Reverse osmosis and synthetic membranes: Theory-technology-engineering*; Sourirajan, S., Ed.; National Research Council of Canada: Ottawa, 1977.
- (107) Zeni, M.; Riveros, R.; de Souza, J. F.; Mello, K.; Meireles, C.; Rodrigues, G. Morphologic analysis of porous polyamide 6,6 membranes prepared by phase inversion. *Desalination* **2008**, *221*, 294.
- (108) Dey, T. K.; Misra, B. M. Characteristic properties of a few selected polymers for reverse osmosis applications. *J. Polym. Mater.* **1999**, *16*, 13.
- (109) Zuo, D. Y.; Xu, Y. Y.; Xu, W. L.; Zou, H. T. The influence of PEG molecular weight on morphologies and properties of pvdf asymmetric membranes. *Chin. J. Polym. Sci.* **2008**, *26*, 405.
- (110) Wu, B.; Li, K.; Te, W. K. Preparation and characterization of poly(vinylidene fluoride) hollow fiber membranes for vacuum membrane distillation. *J. Appl. Polym. Sci.* **2007**, *106*, 1482.
- (111) Wang, D. L.; Li, K.; Teo, W. K. Preparation and characterization of polyvinylidene fluoride (PVDF) hollow fiber membranes. *J. Membr. Sci.* **1999**, *163*, 211.
- (112) Hou, D. Y.; Wang, J.; Qu, D.; Luan, Z. K.; Zhao, C. W.; Ren, X. J. Preparation of hydrophobic PVDF hollow fiber membranes for desalination through membrane distillation. *Water Sci. Technol.* **2009**, *59*, 1219.
- (113) Zhang, Z. L.; Chen, S. M. SEM study on the morphological structure of PTFE stretching porous membranes - SEM identification for PTFE stretching porous membranes in preparation. *Chin. J. Chem. Phys.* **2003**, *16*, 151.
- (114) Kang, K.; Kang, P. H.; Nho, Y. C. Preparation and characterization of a proton-exchange membrane by the radiation grafting of styrene onto polytetrafluoroethylene films. *J. Appl. Polym. Sci.* **2006**, *99*, 1415.
- (115) Choi, S. H.; Tasselli, F.; Jansen, J. C.; Barbieri, G.; Drioli, E. Effect of the preparation conditions on the formation of asymmetric poly(vinylidene fluoride) hollow fibre membranes with a dense skin. *Eur. Polym. J.* **2010**, *46*, 1713.
- (116) Baker, R. W. *Membrane Technology and Applications*; John Wiley & Sons, Ltd.: New York, 2004.
- (117) Han, M. J.; Bhattacharyya, D. Morphology and transport study of phase inversion polysulfone membranes. *Chem. Eng. Commun.* **1994**, *128*, 197.
- (118) Kang, Y. S.; Kim, H. J.; Kim, U. Y. Asymmetric membrane formation via immersion precipitation method. I. Kinetic effect. *J. Membr. Sci.* **1991**, *60*, 219.
- (119) Chen, L. W.; Young, T. H. Effect of nonsolvents on the mechanism of wet-casting membrane formation from EVAL copolymers. *J. Membr. Sci.* **1991**, *59*, 15.
- (120) Nechifor, G.; Popescu, G. Asymmetric membranes prepared by immersion-precipitation technique. *Rev. Roum. Chim.* **1990**, *35*, 899.
- (121) Chun, K. Y.; Jang, S. H.; Kim, H. S.; Kim, Y. W.; Han, H. S.; Joe, Y. I. Effects of solvent on the pore formation in asymmetric 6FDA-4,4' ODA polyimide membrane: Terms of thermodynamics, precipitation kinetics, and physical factors. *J. Membr. Sci.* **2000**, *169*, 197.
- (122) Oh, S. J.; Kim, N.; Lee, Y. T. Preparation and characterization of PVDF/TiO₂ organic-inorganic composite membranes for fouling resistance improvement. *J. Membr. Sci.* **2009**, *345*, 13.
- (123) Boom, R. M.; Vandenboomgaard, T.; Smolders, C. A. Mass-transfer and thermodynamics during immersion precipitation for a 2-polymer system - evaluation with the system PES-PVP-NMP-water. *J. Membr. Sci.* **1994**, *90*, 231.
- (124) Wienk, I. M.; Boom, R. M.; Beerlage, M. A. M.; Bulte, A. M. W.; Smolders, C. A.; Strathmann, H. Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers. *J. Membr. Sci.* **1996**, *113*, 361.

- (125) Wan, L. S.; Xu, Z. K.; Wang, Z. G. Leaching of PVP from polyacrylonitrile/PVP blending membranes: A comparative study of asymmetric and dense membranes. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 1490.
- (126) Matsuyama, H.; Maki, T.; Teramoto, M.; Kobayashi, K. Effect of PVP additive on porous polysulfone membrane formation by immersion precipitation method. *Sep. Sci. Technol.* **2003**, *38*, 3449.
- (127) Jung, B.; Yoon, J. K.; Kim, B.; Rhee, H. W. Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes. *J. Membr. Sci.* **2004**, *243*, 45.
- (128) Yuan, Z.; Xi, D. L. Effect of PVP additive on PVDF/TPU blend hollow fibre membranes by phase inversion. *Iran. Polym. J.* **2007**, *16*, 241.
- (129) Saljoughi, E.; Amirilargani, M.; Mohammadi, T. Effect of poly(vinyl pyrrolidone) concentration and coagulation bath temperature on the morphology, permeability, and thermal stability of asymmetric cellulose acetate membranes. *J. Appl. Polym. Sci.* **2009**, *111*, 2537.
- (130) Miyano, T.; Matsuura, T.; Sourirajan, S. Effect of polyvinylpyrrolidone additive on the pore-size and the pore-size distribution of polyethersulfone (Victrex) membranes. *Chem. Eng. Commun.* **1993**, *119*, 23.
- (131) Yeo, H. T.; Lee, S. T.; Han, M. J. Role of a polymer additive in casting solution in preparation of phase inversion polysulfone membranes. *J. Chem. Eng. Jpn.* **2000**, *33*, 180.
- (132) Torrestiana-Sanchez, B.; Ortiz-Basurto, R. I.; Brito-De La Fuente, E. Effect of nonsolvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes. *J. Membr. Sci.* **1999**, *152*, 19.
- (133) Kim, I. C.; Lee, K. H. Effect of poly(ethylene glycol) 200 on the formation of a polyetherimide asymmetric membrane and its performance in aqueous solvent mixture permeation. *J. Membr. Sci.* **2004**, *230*, 183.
- (134) Shieh, J. J.; Chung, T. S.; Wang, R.; Srinivasan, M. P.; Paul, D. R. Gas separation performance of poly(4-vinylpyridine)/polyetherimide composite hollow fibers. *J. Membr. Sci.* **2001**, *182*, 111.
- (135) Deniz, S. Characteristics of polycarbonate membranes with polyethylene glycol prepared via dry/wet-phase inversion methods. *Desalination* **2006**, *200*, 42.
- (136) Fritzsche, A. K.; Cruse, C. A.; Kesting, R. E.; Murphy, M. K. Polysulfone hollow fiber membranes spun from lewis acid - base complexes. 2. The effect of lewis acid to base ratio on membrane-structure. *J. Appl. Polym. Sci.* **1990**, *39*, 1949.
- (137) Laninovic, V. Structure of flat sheet membranes obtained from the system polyethersulfone-dimethylacetamide-nonsolvent additive-water. *Polym. Sci., Ser. A* **2005**, *47*, 744.
- (138) Lin, F. C.; Wang, D. M.; Lai, C. L.; Lai, J. Y. Effect of surfactants on the structure of PMMA membranes. *J. Membr. Sci.* **1997**, *123*, 281.
- (139) Lai, J. Y.; Lin, F. C.; Wu, T. T.; Wang, D. M. On the formation of macrovoids in PMMA membranes. *J. Membr. Sci.* **1999**, *155*, 31.
- (140) Wang, D. M.; Lin, F. C.; Wu, T. T.; Lai, J. Y. Formation mechanism of the macrovoids induced by surfactant additives. *J. Membr. Sci.* **1998**, *142*, 191.
- (141) Tsai, H. A.; Huang, D. H.; Fan, S. C.; Wang, Y. C.; Li, C. L.; Lee, K. R.; Lai, J. Y. Investigation of surfactant addition effect on the vapor permeation of aqueous ethanol mixtures through polysulfone hollow fiber membranes. *J. Membr. Sci.* **2002**, *198*, 245.
- (142) Tsai, H. A.; Huang, D. H.; Ruaan, R. C.; Lai, J. Y. Mechanical properties of asymmetric polysulfone membranes containing surfactant as additives. *J. Ind. Eng. Chem. Res.* **2001**, *40*, 5917.
- (143) Kim, I. C.; Lee, K. H.; Tak, T. M. Preparation and characterization of integrally skinned uncharged polyetherimide asymmetric nanofiltration membrane. *J. Membr. Sci.* **2001**, *183*, 235.
- (144) Chen, S. H.; Liou, R. M.; Lai, J. Y.; Lai, C. L. Effect of the polarity of additional solvent on membrane formation in polysulfone/N-methyl-2-pyrrolidone/water ternary system. *Eur. Polym. J.* **2007**, *43*, 3997.
- (145) Alexandre, M.; Dubois, P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater. Sci. Eng., R.* **2000**, *28*, 1.
- (146) Rong, M. Z.; Zhang, M. Q.; Zheng, Y. X.; Zeng, H. M.; Walter, R.; Friedrich, K. Structure-property relationships of irradiation grafted nano-inorganic particle filled polypropylene composites. *Polymer* **2001**, *42*, 167.
- (147) von Werne, T.; Patten, T. E. Preparation of structurally well-defined polymer-nanoparticle hybrids with controlled/living radical polymerizations. *J. Am. Chem. Soc.* **1999**, *121*, 7409.
- (148) Reynaud, E.; Gauthier, C.; Perez, J. Nanophases in polymers. *Rev. Metall. (Paris)* **1999**, *96*, 169.
- (149) Wiesner, M.; Bottero, J.-Y. *Environmental Nanotechnology: Applications and Impacts of Nanomaterials*; McGraw-Hill Professional: New York, 2007.
- (150) Calvert, P. Potential applications of nanotubes. In *Carbon Nanotubes - Preparation and Properties*; Ebbesen, T. W., Ed.; CRC Press: Boca Raton, FL, 1997.
- (151) Favier, V.; Canova, G. R.; Shrivastava, S. C.; Cavaillie, J. Y. Mechanical percolation in cellulose whisker nanocomposites. *Polym. Eng. Sci.* **1997**, *37*, 1732.
- (152) Chazeau, L.; Cavaillie, J. Y.; Canova, G.; Dendievel, R.; Bouterin, B. Viscoelastic properties of plasticized pvc reinforced with cellulose whiskers. *J. Appl. Polym. Sci.* **1999**, *71*, 1797.
- (153) Kulprathipanja, S.; Neuzil, R. W.; Li, N. *Separation of gases by means of mixed matrix membranes*. US Patent 4740219, 26 April, 1988.
- (154) Jia, M. D.; Peinemann, K. V.; Behling, R. D. Molecular-sieving effect of the zeolite-filled silicone-rubber membranes in gas permeation. *J. Membr. Sci.* **1991**, *57*, 289.
- (155) Wang, X. Y.; Zhang, L.; Sun, D. H.; An, Q. F.; Chen, H. L. Effect of coagulation bath temperature on formation mechanism of poly(vinylidene fluoride) membrane. *J. Appl. Polym. Sci.* **2008**, *110*, 1656.
- (156) Yang, Y. N.; Zhang, H. X.; Wang, P.; Zhang, M. Y.; Yang, H. D.; Hu, M. Z.; Jin, J. Kinetic and thermodynamic research of polysulfone/TiO₂ hybrid ultrafiltration membrane. *Acta. Chim. Sin.* **2007**, *65*, 1258.
- (157) Li, N. N.; Fane, A. G.; Ho, W. S. W.; Matsuura, T. *Advanced Membrane Technology and Applications*; John Wiley & Sons, Inc.: Hoboken, NJ, 2008.
- (158) Wang, D. M.; Lin, F. C.; Chiang, J. C.; Lai, J. Y. Control of the porosity of asymmetric TPX membranes. *J. Membr. Sci.* **1998**, *141*, 1.
- (159) Strathmann, H.; Scheible, P. Formation mechanism of asymmetrical cellulose acetate membranes. *Kolloid Z. Z. Polym.* **1971**, *246*, 669.
- (160) Lau, W. W. Y.; Guiver, M. D.; Matsuura, T. Phase-separation in polysulfone solvent water and polyethersulfone solvent water-systems. *J. Membr. Sci.* **1991**, *59*, 219.
- (161) Wyart, Y.; Georges, G.; Demie, C.; Amra, C.; Moulin, P. Membrane characterization by microscopic methods: Multiscale structure. *J. Membr. Sci.* **2008**, *315*, 82.
- (162) Nakao, S. Determination of pore-size and pore-size distribution. 3. Filtration membranes. *J. Membr. Sci.* **1994**, *96*, 131.
- (163) Zhao, C. S.; Zhou, X. S.; Yue, Y. L. Determination of pore size and pore size distribution on the surface of hollow-fiber filtration membranes: A review of methods. *Desalination* **2000**, *129*, 107.
- (164) Powers, K. W.; Brown, S. C.; Krishna, V. B.; Wasdo, S. C.; Moudgil, B. M.; Roberts, S. M. Research strategies for safety evaluation of nanomaterials. Part VI. Characterization of nanoscale particles for toxicological evaluation. *Toxicol. Sci.* **2006**, *90*, 296.
- (165) Abaticchio, P.; Bottino, A.; Roda, G. C.; Capannelli, G.; Munari, S. Characterization of ultrafiltration polymeric membranes. *Desalination* **1990**, *78*, 235.
- (166) Cao, G. Z.; Meijerink, J.; Brinkman, H. W.; Burggraaf, A. J. Permporometry study on the size distribution of active pores in porous ceramic membranes. *J. Membr. Sci.* **1993**, *83*, 221.
- (167) Cuperus, F. P.; Bargeman, D.; Smolders, C. A. Permporometry - the determination of the size distribution of active pores in UF membranes. *J. Membr. Sci.* **1992**, *71*, 57.
- (168) Calvo, J. I.; Hernandez, A.; Pradanos, P.; Martinez, L.; Bowen, W. R. Pore size distributions in microporous membranes. 2. Bulk characterization of track-etched filters by air porometry and mercury porosimetry. *J. Colloid Interface Sci.* **1995**, *176*, 467.

- (169) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. The determination of pore volume and area distributions in porous substances. 1. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373.
- (170) Brun, M.; Lallemand, A.; Quinson, J. F.; Eyraud, C. New method for simultaneous determination of size and shape of pores - thermoporometry. *Thermochim. Acta* **1977**, *21*, 59.
- (171) Quinson, J. F.; Mameri, N.; Guihard, L.; Bariou, B. The study of the swelling of an ultrafiltration membrane under the influence of solvents by thermoporometry and measurement of permeability. *J. Membr. Sci.* **1991**, *58*, 191.
- (172) Cuperus, F. P.; Bargeman, D.; Smolders, C. A. Critical-points in the analysis of membrane pore structures by thermoporometry. *J. Membr. Sci.* **1992**, *66*, 45.
- (173) Meymarom, A.; Katz, M. G. Measurement of active pore-size distribution of microporous membranes - a new approach. *J. Membr. Sci.* **1986**, *27*, 119.
- (174) Miyoshi, K. *Surface Characterization Techniques: An Overview*; Glenn Research Center: Cleveland, 2002.
- (175) Kang, S.; Elimelech, M. Bioinspired single bacterial cell force spectroscopy. *Langmuir* **2009**, *25*, 9656.
- (176) Bowen, W. R.; Doneva, T. A. Artefacts in AFM studies of membranes: Correcting pore images using fast fourier transform filtering. *J. Membr. Sci.* **2000**, *171*, 141.
- (177) Boccaccio, T.; Bottino, A.; Capannelli, G.; Piaggio, P. Characterization of PVDF membranes by vibrational spectroscopy. *J. Membr. Sci.* **2002**, *210*, 315.
- (178) Kim, K. J.; Fane, A. G.; Nystrom, M.; Pihlajamaki, A. Chemical and electrical characterization of virgin and protein-fouled polycarbonate track-etched membranes by FTIR and streaming-potential measurements. *J. Membr. Sci.* **1997**, *134*, 199.
- (179) Holmbom, B.; Stenius, P. Analytical methods. In *Forest Products Chemistry*; Stenius, P., Ed.; Fapet Oy: Jyväskylä, 2000.
- (180) Fulghum, J. E. Recent developments in high energy and spatial resolution analysis of polymers by XPS. *J. Electron.* **1999**, *100*, 331.
- (181) Garbassi, F.; Morra, M.; Occhiello, E. *Polymer Surfaces: From Physics to Technology*; Rev Upd Su ed.; Wiley: New York, 1998.
- (182) Adamson, A. W. *Physical Chemistry of Surfaces*; John Wiley & Sons, Inc: New York, 2007.
- (183) de Gennes, P.-G.; Brochard-Wyart, F.; Quéré, D. *Capillary and Wetting Phenomena—Drops, Bubbles, Pearls, Waves*; Springer: New York, 2002.
- (184) Mirza, M.; Guo, Y.; Arnold, K.; van Oss, C. J.; Ohki, S. Hydrophobizing effect of cations on acidic phospholipid membranes. *J. Dispersion Sci. Technol.* **1998**, *19*, 951.
- (185) Hurwitz, G.; Guillen, G. R.; Hoek, E. M. V. Probing polyamide membrane surface charge, zeta potential, wettability, and hydrophilicity with contact angle measurements. *J. Membr. Sci.* **2010**, *349*, 349.
- (186) Butkus, M. A.; Grasso, D. Impact of aqueous electrolytes on interfacial energy. *J. Colloid Interface Sci.* **1998**, *200*, 172.
- (187) van Oss, C. J.; Giese, R. F.; Docoslis, A. Hyperhydrophobicity of the water-air interface. *J. Dispersion Sci. Technol.* **2005**, *26*, 585.
- (188) Whitesides, G. M.; Biebuyck, H. A.; Folkers, J. P.; Prime, K. L. Acid-base interactions in wetting. *J. Adhes. Sci. Technol.* **1991**, *5*, 57.
- (189) Wamser, C. C.; Gilbert, M. I. Detection of surface functional-group asymmetry in interfacially-polymerized films by contact-angle titrations. *Langmuir* **1992**, *8*, 1608.
- (190) Bhattacharjee, S.; Ko, C. H.; Elimelech, M. DLVO interaction between rough surfaces. *Langmuir* **1998**, *14*, 3365.
- (191) Wolansky, G.; Marmur, A. The actual contact angle on a heterogeneous rough surface in three dimensions. *Langmuir* **1998**, *14*, 5292.
- (192) Huang, X. F.; Bhattacharjee, S.; Hoek, E. M. V. Is surface roughness a "scapegoat" or a primary factor when defining particle-substrate interactions?. *Langmuir* **2010**, *26*, 2528.
- (193) Hoek, E. M. V.; Agarwal, G. K. Extended DLVO interactions between spherical particles and rough surfaces. *J. Colloid Interface Sci.* **2006**, *298*, 50.
- (194) Hoek, E. M. V.; Bhattacharjee, S.; Elimelech, M. Effect of membrane surface roughness on colloid-membrane DLVO interactions. *Langmuir* **2003**, *19*, 4836.
- (195) Fievet, P.; Sbai, M.; Szymczyk, A.; Vidonne, A. Determining the zeta-potential of plane membranes from tangential streaming potential measurements: Effect of the membrane body conductance. *J. Membr. Sci.* **2006**, *281*, 757.
- (196) Wang, M.; Wu, L. G.; Zheng, X. C.; Mo, J. X.; Gao, C. J. Surface modification of phenolphthalein poly(ether sulfone) ultrafiltration membranes by blending with acrylonitrile-based copolymer containing ionic groups for imparting surface electrical properties. *J. Colloid Interface Sci.* **2006**, *300*, 286.
- (197) Yaroshchuk, A.; Ribitsch, V. Role of channel wall conductance in the determination of zeta-potential from electrokinetic measurements. *Langmuir* **2002**, *18*, 2036.
- (198) Fievet, P.; Sbai, M.; Szymczyk, A.; Vidonne, A. Determining the zeta-potential of plane membranes from tangential streaming potential measurements: Effect of the membrane body conductance. *J. Membr. Sci.* **2003**, *226*, 227.
- (199) Belfort, G.; Davis, R. H.; Zydney, A. L. The behavior of suspensions and macromolecular solutions in cross-flow microfiltration. *J. Membr. Sci.* **1994**, *96*, 1.
- (200) Mir, L.; Michaels, S. L.; Goel, V.; Kaiser, R. Crossflow microfiltration: Applications, design and cost. In *Membrane Handbook*; Ho, W. S. W., Sirkar, K. K., Eds.; Van Nostrand Reinhold: New York, 1992.
- (201) Zeman, L. J.; Zydney, A. L. *Microfiltration and Ultrafiltration—Principles and Applications*; Marcel Dekker, Inc.: New York, 1996.
- (202) Porter, M. C. Microfiltration. In *Synthetic Membrane: Science, Engineering and Applications*; Bungay, P. M., Lonsdale, H. K., de Pinho, M. N., Eds.; Reidel Publishing Company: Boston, 1986.
- (203) Eykamp, W. Microfiltration and ultrafiltration. In *Membrane Separation Technology—Principles and Applications*; Nobel, R. D., Stern, S. A., Eds.; Elsevier: Amsterdam, 1995.
- (204) Lonsdale, H. K. Reverse osmosis. In *Synthetic Membrane: Science, Engineering and Applications*; Bungay, P. M., Lonsdale, H. K., Pinho, M. N., Eds.; Reidel Publishing Company: Boston, 1986.
- (205) Fell, C. J. D. Reverse osmosis. In *Membrane Separation Technology—Principles and Applications*; Noble, R. D., Stern, S. A., Eds.; Elsevier: Amsterdam, 1995.
- (206) Wijmans, J. G.; Baker, R. W.; Athayde, A. L. Pervaporation: Removal of organics from water and organic/organic separations. In *Membrane Processes in Separation and Purification*; Crespo, J. G., Boddeker, K. W., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.
- (207) Amjad, Z. *Reverse Osmosis: Membrane Technology, Water Chemistry, and Industrial Applications*; Van Nostrand Reinhold: New York, 1993.
- (208) Paul, D. R.; Yampolskii, Y. *Polymeric Gas Separation Membranes*; CRC Press: London, 1994.
- (209) Toshima, N. *Polymer for Gas Separation*; VCH: Weinheim, Germany, 1991.
- (210) Huang, R. Y. M. *Pervaporation Membrane Separation Processes*; Elsevier: Amsterdam, 1991.
- (211) Eustache, H.; Histi, G. Separation of aqueous organic mixtures by pervaporation and analysis by mass-spectrometry or a coupled gas chromatograph-mass spectrometer. *J. Membr. Sci.* **1981**, *8*, 105.
- (212) Moonen, H.; Niefind, H. J. Alcohol reduction in beer by means of dialysis. *Desalination* **1982**, *41*, 327.
- (213) Schneider, K.; Vangassel, T. J. Membrane distillation. *Chem. Ing. Tech.* **1984**, *56*, 514.
- (214) Cath, T. Y.; Childress, A. E.; Elimelech, M. Forward osmosis: Principles, applications, and recent developments. *J. Membr. Sci.* **2006**, *281*, 70.
- (215) Ochoa, N. A.; Pradanos, P.; Palacio, L.; Pagliero, C.; Marchese, J.; Hernandez, A. Pore size distributions based on AFM imaging and retention of multidisperse polymer solutes - characterisation of polyethersulfone UF membranes with dopes containing different PVP. *J. Membr. Sci.* **2001**, *187*, 227.
- (216) Fan, Z. F.; Wang, Z.; Sun, N.; Wang, J. X.; Wang, S. C. Performance improvement of polysulfone ultrafiltration membrane by blending with polyaniline nanofibers. *J. Membr. Sci.* **2008**, *320*, 363.

- (217) Chen, Y. L.; Zhu, G. S.; Peng, Y.; Yao, X. D.; Qiu, S. L. Synthesis and characterization of (*h0l*) oriented high-silica zeolite beta membrane. *Microporous Mesoporous Mater.* **2009**, *124*, 8.
- (218) Yang, J. Y.; Nishimura, C.; Komaki, M. Preparation and characterization of Pd-Cu/V-15Ni composite membrane for hydrogen permeation. *J. Alloys Compd.* **2007**, *431*, 180.
- (219) Benavente, J.; Oleinikova, M.; Munoz, M.; Valiente, M. Characterization of novel activated composite membranes by impedance spectroscopy. *J. Electroanal. Chem.* **1998**, *451*, 173.
- (220) Campos, E. A.; Gushikem, Y. Composite membrane of niobium(V) oxide and cellulose acetate: Preparation and characterization. *J. Colloid Interface Sci.* **1997**, *193*, 121.
- (221) Kim, H. J.; Tabe-Mohammadi, A.; Kumar, A.; Fouda, A. E. Asymmetric membranes by a two-stage gelation technique for gas separation: Formation and characterization. *J. Membr. Sci.* **1999**, *161*, 229.
- (222) Bottino, A.; Capannelli, G.; D'Asti, V.; Piaggio, P. Preparation and properties of novel organic-inorganic porous membranes. *Sep. Purif. Technol.* **2001**, *22–23*, 269.
- (223) Khulbe, K. C.; Matsuura, T. Characterization of synthetic membranes by Raman spectroscopy, electron spin resonance, and atomic force microscopy; a review. *Polymer* **2000**, *41*, 1917.
- (224) Wei, J.; Helm, G. S.; Corner-Walker, N.; Hou, X. L. Characterization of a non-fouling ultrafiltration membrane. *Desalination* **2006**, *192*, 252.
- (225) Saito, N.; Yamashita, S. Characterization of surface-charge-mosaic-modified ultrafiltration membranes prepared by laser-induced surface graft polymerization. *J. Appl. Polym. Sci.* **1998**, *67*, 1141.
- (226) Kazama, S.; Sakashita, M. Gas separation properties and morphology of asymmetric hollow fiber membranes made from cardo polyamide. *J. Membr. Sci.* **2004**, *243*, S9.
- (227) Ferjani, E.; Mejdoub, M.; Roudesli, M. S.; Chehimi, M. M.; Picard, D.; Delamar, M. XPS characterization of poly(methylhydro-siloxane)-modified cellulose diacetate membranes. *J. Membr. Sci.* **2000**, *165*, 125.
- (228) Yang, Y. N.; Zhang, H. X.; Wang, P.; Zheng, Q. Z.; Li, J. The influence of nano-sized TiO₂ fillers on the morphologies and properties of PSF UF membrane. *J. Membr. Sci.* **2007**, *288*, 231.



A novel green solvent alternative for polymeric membrane preparation via nonsolvent-induced phase separation (NIPS)

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ABSTRACT

The membrane market has grown rapidly over the past several decades, supported by continuous improvements in membrane performance, module and process design, and fouling control. However, such growth will be unsustainable with current membrane fabrication methods that employ significant amounts of toxic solvents (e.g., N-methylpyrrolidone, dimethylacetamide, and dimethylformamide), thereby producing billions of liters of contaminated wastewater each year. A possible solution is to identify greener alternatives with appropriate properties that are compatible with conventional polymers. In this work, we employed a novel green solvent, Rhodiasolv PolarClean[®], that is less toxic than current solvents and eco-friendly, while exhibiting the necessary properties to be employed as a solvent for membrane preparation via the nonsolvent-induced phase separation (NIPS) method. Rhodiasolv PolarClean[®] has been successfully applied to membrane preparation for water desalination and reclamation by ultrafiltration (UF) and nanofiltration (NF) with conventional polymers, including polysulfone (PSF), polyethersulfone (PES), and cellulose acetate (CA). The UF membranes prepared from PES/Pluronic F127 and PSF/polyvinylpyrrolidone exhibited pure water permeabilities greater than $314.5 \pm 57.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and tensile strength $3.78 \pm 0.12 \text{ MPa}$ with BSA rejection of $98.1 \pm 0.4\%$. Cellulose acetate membrane used for NF applications demonstrated pure water permeability of $1.5 \pm 0.25 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with NaCl and MgCl_2 rejection of $85.1 \pm 5.7\%$ and $93.2 \pm 4.7\%$, respectively. The performance of the prepared membranes was competitive with current state-of-the-art membranes across all applications, indicating immediate applicability to improving the sustainability of membrane fabrication processes.

1. Introduction

Since the invention of immersion precipitation for high-performance membranes in the 1960s [1], the range of applications for membrane technology has expanded from desalination of seawater and wastewater [2,3] and water reclamation by ultrafiltration (UF) and nanofiltration (NF) to gas fractionation [4–6], food processing [7,8], energy-related applications [2,9,10], and solvent processing [11,12]. Although membrane processes have become a key platform for process intensification and “green” technology, it is not well-known that membrane fabrication itself is hardly “green,” producing more than 50 billion liters of contaminated wastewater every year [13]. A great deal of research has therefore been conducted to develop green solvents.

Figoli et al. [14] emphasized that toxicity and membrane preparation factors such as solvent power and morphology were important considerations for green solvent selection. Clarke et al. [15] suggested that technical, economic, and environmental factors should be included in green, sustainable solvent development. Pereira and Tobiszewski [16] mainly focused on environmental impact and safety issues to guide green solvent selection. Kim et al. [17] explored the availability of green solvents and discussed their effects on membrane morphology. However, identifying environmental-friendly solvents in membrane manufacturing remains elusive. In this paper, we focus on the application of a novel green solvent for fabrication of polymeric membranes.

Several techniques are used to fabricate polymeric membranes, including nonsolvent-induced phase separation (NIPS), thermally-

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induced phase separation (TIPS), melt-extrusion, and track-etching. The NIPS method (also referred to as the immersion precipitation or Loeb-Sourirajan method) is by far the most versatile and widely employed to fabricate asymmetric structures in industrial standard flat-sheet and hollow fiber membranes. NIPS is considered advantageous and widely applicable due to simplicity of processing and high performance of the resulting membranes. The NIPS method requires at least three components: polymer to determine membrane properties, solvent to dissolve the polymer, and nonsolvent to control phase inversion phenomena. In a typical NIPS process, a homogeneous dope solution, which contains a polymer, a solvent, and a small portion of nonsolvent, is first prepared. Then, the solution is cast into a thin film or spun into a hollow fiber and subsequently immersed in a nonsolvent bath (e.g., water). Due to chemical affinities with polymer, polar aprotic solvents such as N-methyl-pyrrolidone (NMP), dimethylacetamide (DMAc), and dimethylformamide (DMF) are widely used as doping solution. The nonsolvent should have high affinity toward the solvent but not toward the polymer to induce phase inversion and to remove residual solvent. Upon immersion of the cast film into a nonsolvent bath, the solvent and nonsolvent mix spontaneously, which lowers the free energy of the polymer, leading to solidification (e.g., precipitation or crystallization). By controlling the rates of mutual diffusion and polymer solidification, membrane morphology can be precisely tuned for desired membrane applications. Additives are frequently employed either in the dope solution or nonsolvent bath to control solution thermodynamics and phase inversion kinetics [18,19]. Consequently, the NIPS method requires strong organic solvents, which tend to be highly toxic to human health and to ecosystems. NIPS also inevitably generates a large amount of wastewater contaminated by solvents [14].

It has been estimated that 20–100 billion liters of solvent-contaminated wastewater are generated each year by membrane manufacturing facilities [13]. As environmental regulations become more stringent worldwide, the use of less toxic solvents is a requirement for sustainable membrane technology. The use of DMF and DMAc for large-scale production will soon be banned in Europe, and NMP is on a watch list [20]. A survey of the relevant literature over the past five years indicates that toxic solvents such as NMP, DMAc, and DMF remain the most commonly used solvents for membrane preparation by NIPS (Fig. 1(a)). Although green alternatives have been introduced, such as ionic liquids [21,22], supercritical CO₂ (scCO₂) [23,24], and environmental-friendly solvents [25–28], the use of ionic liquids and scCO₂ for practical applications is limited by low polymer solubility and complicated scCO₂ generation conditions [29]. As shown in Fig. 1(b), the polymers used in membrane preparation are poly(vinylidene fluoride) (PVDF), polyethersulfone (PES), polysulfone (PSF), and cellulose acetate (CA), all of which require solvents with strong polarity for membrane processing. Most of the solvents used for membrane

preparation are water-miscible. Compared to solvents that cannot mix with water (the most widely used nonsolvent), water-soluble solvents can be employed for immersion precipitation to induce a variety of membrane morphologies. For instance, membranes prepared using water-soluble solvents such as PolarClean®, glyceryl triacetate (GTA), and dimethyl sulfoxide (DMSO) can achieve wider ranges of mean pore sizes and membrane morphologies [18,30–33]. Therefore, to enhance the growth of the membrane technology market, it is imperative to identify a suitable “green” solvent that is water-soluble and can dissolve conventional polymers.

Although many potential green alternatives have been introduced, most are intended for use in TIPS membrane preparation, which occurs at high temperatures [27,28,31,34]. It has been comparatively difficult to identify solvents that dissolve polymer at ambient temperature for use in NIPS processes. Since polymers used in membrane fabrication typically exhibit high chemical resistance, solvents with high solvent power are required to dissolve them. Such solvents are usually classified as toxic chemicals. PolarClean® is one of the exceptions, as it exhibits high solubility for conventional polymers but low toxicity and good biodegradability. For these reasons, PolarClean® has been used for membrane preparation with PES, PSF, and PVDF [18,27,30,35,36]. Despite its promising properties, the feasibility of PolarClean® compared to other conventional polymers has been investigated in relatively few studies.

In this work, we investigate the feasibility of PolarClean® for use in NIPS membrane fabrication for applications such as UF and NF. The top three most frequently used polymers other than PVDF, *i.e.*, PES, PSF, and CA, were fabricated into asymmetric membranes via NIPS. We characterized the performances of the resulting membranes in terms of water flux, salt rejection, and mechanical properties and compared them to other UF and NF membranes described in the literature.

2. Experimental

2.1. Materials

PSU (P3500, Mw = 66.1 kDa) and Rhodiasolv PolarClean® (Methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate) were provided by Solvay Specialty Polymers (Bollate, Italy) and Solvay Novacare, respectively. PES (Mw = 75 kDa) was purchased from BASF (Ludwigshafen, Germany). CA (39.7% acetyl content, Mn = 50 kDa), Pluronic F-127 (Mw = 12.5 kDa), polyvinylpyrrolidone (PVP, Mw = 55 kDa), and bovine serum albumin (BSA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Analytical grade ethanol (EtOH), sodium chloride (NaCl), magnesium sulfoxide (MgSO₄), and hexane were purchased from Daejung Chemicals (Siheung, South Korea). All materials were used without further purification.

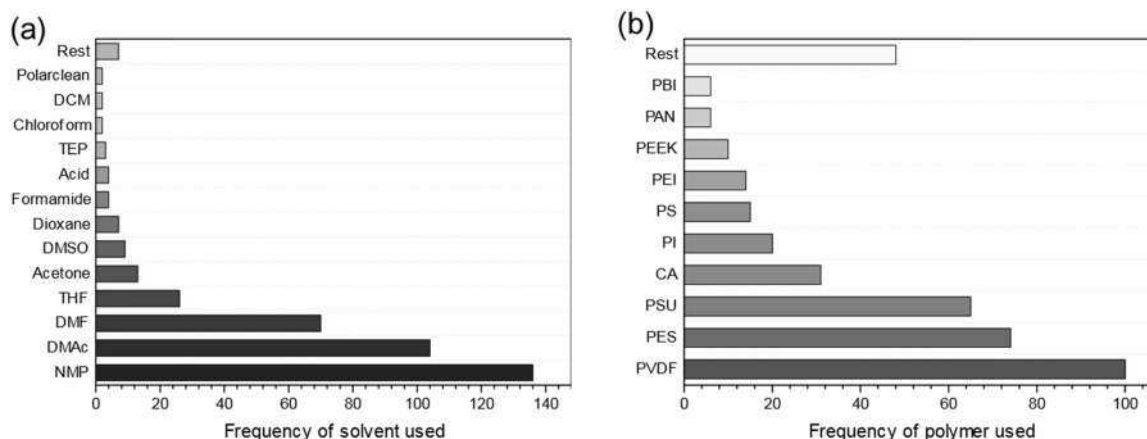


Fig. 1. Results of a literature survey documenting frequency of use: (a) solvents and (b) polymers used for NIPS membrane preparation over the past five years.

2.2. Characterization of phase separation behavior

The binodal curves in ternary phases of polymer, solvent, and nonsolvent system were experimentally obtained for determining the onset of phase separation behavior in the NIPS process. Binodal curves were measured by the cloud point method [19,37]. In the first step, 20 g of clear and homogeneous polymer solutions with different polymer concentrations of 10, 15, and 20 wt% were prepared. At coagulation temperature (30 °C), a known quantity of deionized (DI) water was added as a non-solvent until the polymer solution was no longer homogeneous and became turbid. If regional precipitation was observed, the point was recorded as a coagulation value involving only separation of liquids. Finally, each coagulation value in the phase diagram was marked with the amount of nonsolvent in the polymer-solvent solution.

2.3. Preparation of asymmetric flat sheet membranes

Homogenous polymer dope solutions were prepared (15–25 wt% polymer in Polarclean®) at elevated temperatures between 30 °C and 60 °C. For membranes prepared with additives, 5 wt% of either Pluronic F-127 or polyvinylpyrrolidone (PVP, Mw = 55 kDa) was added to the dope solution based on the total mass of the dope solution [additive / (additive + polymer + solvent)]. Detailed solution compositions are summarized in Table 1. The dope solution was cooled to ambient temperature (25 °C) and stored overnight for degassing. For membranes used for UF applications, the solution was cast on a glass plate. PET nonwoven sheets were used as supports for NF membranes to withstand the high pressures applied during the operation. A casting knife was purchased from Elcometer Ltd. (Manchester, UK), and the thickness of the cast membranes was fixed at 200 µm. After casting, the membranes were immediately immersed in a coagulation bath (30 °C tap water) for 6 h for complete removal of residual solvents. Solidified membranes were stored in DI water at ambient temperature (25 °C) until used.

2.4. Characterization

2.4.1. Membrane morphology

The microscopic morphologies of membranes were observed using a scanning electron microscope (FE-SEM S-4800, Hitachi, Tokyo, Japan) at 10 kV. The membranes were sampled in liquid nitrogen and then sputtered with platinum for 90 s at 15 mA using a platinum sputterer (E-1045, Hitachi) prior to analysis.

2.4.2. Pure water permeability

The pure water permeability of the membranes was measured by a multi-cell crossflow system with a surface area of 6.23 cm² (Sepratek Ltd., Daejeon, South Korea). The water permeation process comprised the following steps: 1) membranes were wetted with EtOH for over 30 min to facilitate penetration by water; 2) wetted membranes were placed in a water permeation apparatus and pressurized to 1.0 bar for UF applications or 16.0 bar for NF applications; 3) the membranes were pre-compacted until the flux reached a plateau (approximately 5 h) to exclude the effects of compaction.

2.4.3. Rejection rate

BSA solution was introduced to measure rejection properties. First,

0.1 M sodium monobasic phosphate (PBS) solution was prepared to provide BSA solution in a stable environment, and then NaOH solution was added to adjust the pH to 7.0. The BSA solution was poured into the tank at a concentration of 1.0 g/L (BSA/PBS) after pre-compaction. Rejection experiments were performed using an in-house multi-cell cross-flow apparatus. Cross-flow velocity was set at 1000 ml min⁻¹, and the rejection rate was measured after circulating 1 L of BSA solution at 1 bar for 20 min. The flux and UV signal (calculated using UV spectra (SPECORD 200, Analytik Jena, Jena, Germany) of the permeate and retentate) were recorded and measured at the same time. The rejection rate was calculated using Eq. (1).

$$\text{Rejection(\%)} = \frac{C_o - C}{C_o} \times 100 \quad (1)$$

where c_o and c refer to the concentrations of retentate and permeate, respectively.

2.4.4. Overall porosity

The overall porosity of the membrane was calculated using the following equation (Eq. (2)).

$$\varepsilon = 1 - \frac{\frac{M_p}{\rho_p}}{w \times l \times t} \quad (2)$$

where M_p and ρ_p where and represent the polymer mass and density, respectively. w , l , and t are the width, length, and thickness of the prepared membranes, respectively.

2.4.5. Mechanical properties

Tensile strength was measured with a Universal Testing Machine (UTM, AGS-J 500N, Shimadzu, Kyoto, Japan) at room temperature and a constant elongation rate of 10 mm min⁻¹. The sample gauge length was 20 mm, and the elongation rate was 10 mm min⁻¹.

2.4.6. Thickness and contact angle

The thickness of each membrane was measured with a thickness gauge (ID-C112XBS, Mitutoyo Corp, Kawasaki, Japan). The contact angle was determined using an optical contact angle apparatus (Phoenix-300 Touch, SEO, Korea). Both thickness and contact angle were measured more than seven times at different locations for data reliability.

2.4.7. Dope solution viscosity

The viscosity of the dope solution was measured by a viscometer (SV-100, A&D Company, Japan) to analyze the effects of additives in the polymer/PolarClean® system. The coagulation bath temperature was set to 30 °C for measurement and purged by dry air.

2.4.8. Pore size distribution

The mean pore size and pore size distribution were investigated using a capillary flow porometer (CFP-1500-AE, Porous Materials Inc., Ithaca, NY, USA). Tests were carried out by a wet-up/calculated dry Darcy method using Galwick as wetting fluid and nitrogen as the flowing gas.

2.4.9. Surface porosity measurement

To evaluate the surface porosity, SEM images were analyzed using open source ImageJ software, which can calculate multidimensional

Table 1

Dope compositions and target applications.

Application	Polymer	Coagulation temperature	Additive	Membrane type	Rejection
UF	PES, 15–20 wt%	30 °C	Pluronic	Asymmetric (skin layer on porous sub-layer)	BSA
UF	PSF, 15–20 wt%	30 °C	PVP		BSA
NF	CA, 20–25 wt%	30 °C	None		NaCl, MgSO ₄

images. Through ImageJ, the black parts of the SEM image were perceived as surface pores, and automatic thresholding was used to convert the image to binary format. Surface porosity was calculated by averaging the results of measurements at different locations in the same membrane.

3. Results and discussion

3.1. Phase separation behavior of the polymer and PolarClean® solvent system

In membrane preparation via the NIPS process, the cast polymer solution is immersed in a coagulation bath filled with nonsolvent to induce phase separation and phase inversion. The composition of the dope solution is a significant factor determining membrane morphology and performance by controlling phase separation behavior [19]. Ternary phase diagrams show how the state of the polymer solution changes according to the composition of the three components – polymer, solvent, and nonsolvent – revealing the thermodynamic stability of the polymer solution. This stability is often expressed as a coagulation value [38–40] that indicates the amount of nonsolvent that must be added to the polymer solution to cause phase inversion at specific polymer concentrations. Larger coagulation values indicate greater stability of the polymer and solvent system, and vice versa. Depending on the thermodynamic stability, the immersed solution undergoes either liquid-liquid separation (L-L separation) of solvent and nonsolvent followed by gelation and vitrification or gelation and vitrification without L-L separation [41]. The former is suitable to prepare porous membranes and the latter for nonporous membrane preparation [19,41]. Therefore, depending on the desired applications, it is necessary to select appropriate polymer and solvent systems while considering the thermodynamic factors of PolarClean® and polymer, as described in the ternary phase diagram.

According to the phase diagrams shown in Fig. 2, binodal curves with L-L separation instead of gelation or crystallization were clearly seen in the polymer (PES, PSF, and CA), solvent (PolarClean®), and nonsolvent (water) system, indicating that dope solution including PolarClean® and polymer tends to create pores on the membrane surface. However, the surface pore size of the membrane can vary depending on thermodynamic stability as represented by coagulation value. For instance, membranes produced using PES or PSF with PolarClean® that have relatively low coagulation values will have observable pores on the membrane surface and are therefore suitable for

applications requiring more porous membranes such as UF. On the other hand, membranes produced using CA in PolarClean® that have high coagulation values have non-porous surfaces that are more appropriate for applications such as NF, RO, and gas separation.

3.2. Preparation of porous membranes from PES and PSF

When preparing membranes through the NIPS process, the diffusion rates of the solvent and the nonsolvent are also crucial for determining membrane morphology. When the diffusion is intense only at the interface between the coagulant (nonsolvent) and the membrane surface, the resulting membrane has small pores on the surface and a porous sub-layer composed of finger-like macrovoids [41,42]. Thus, porous membranes can be prepared by controlling factors such as coagulant composition, coagulation temperature, polymer concentration, or by the addition of additives that control the NIPS process. We investigated the effects of additives and polymer concentration and characterized the resulting membranes in terms of pure water permeability (PWP), BSA rejection, and mechanical properties.

3.2.1. Effects of initial polymer concentration in membrane preparation

Fig. 3 shows the morphologies of PES and PSF membranes prepared with different polymer concentrations (15–20 wt%). All PES membranes, regardless of polymer concentration, exhibited typical asymmetric NIPS morphology composed of a top layer with small pores and a porous macrovoid sub-layer (Fig. 3(a)), indicating that vigorous solvent-nonsolvent exchange occurred at the interface due to the high water affinity of PolarClean®. PSF membranes displayed similar pore sizes as PES membranes, but the cross-sectional morphology was significantly different. As discussed in the context of the ternary phase diagram shown in Fig. 2, the PSF dope stability is lower than that of the PES dope solution, which enables PSF solution to achieve phase separation more readily. As shown in Fig. 3, PSF membranes from 15 and 20 wt% solutions had coagulation values below 1.1 and produced sponge-like structures (Fig. 3(b)), while PES membranes with coagulation values greater than 1.5 (Table S1) exhibited macrovoid structures (Fig. 3(a)).

Polymer concentration also affected membrane mechanical strength, as shown in Fig. 4. The tensile strength of PES membrane was enhanced linearly from 2.83 ± 0.34 to 4.44 ± 0.12 MPa when polymer concentration increased (15–20 wt%). This increase in tensile strength is consistent with a general trade-off between tensile strength and overall porosity. In particular, the mechanical strength of the PSF membranes increased dramatically with increasing polymer concentration. These differences are due not only to the relatively low overall porosity of membranes, but also to the cross-sectional morphologies of membranes, as shown in Fig. 3. In fact, PES membranes exhibit macrovoids, whereas PSF membranes show bicontinuous morphology. As reported in previous studies [18,43,44], bi-continuous morphology is associated with greater mechanical strength compared to macrovoidic morphology, which agrees with our findings that the mechanical strength of PSF membrane with bi-continuous morphology was greater than that of the macroporous PES membrane.

Filtration performance also varied depending on initial polymer concentration. As predicted and described in Fig. 4(c), PWP of both PES and PSF membranes decreased as polymer concentration increased. PES membranes showed BSA rejection close to 100% regardless of polymer concentration, whereas PSF membranes exhibited rejection greater than 95% as polymer concentration increased from 15 wt to 20 wt%. This indicates that the mean membrane pore size of PES is smaller than that of PSF, and that pore size becomes smaller as polymer concentration increases.

3.2.2. Effects of additives in membrane preparation

Since varying the polymer concentration did not create enough pores on membrane surfaces, pore-forming agents were employed in

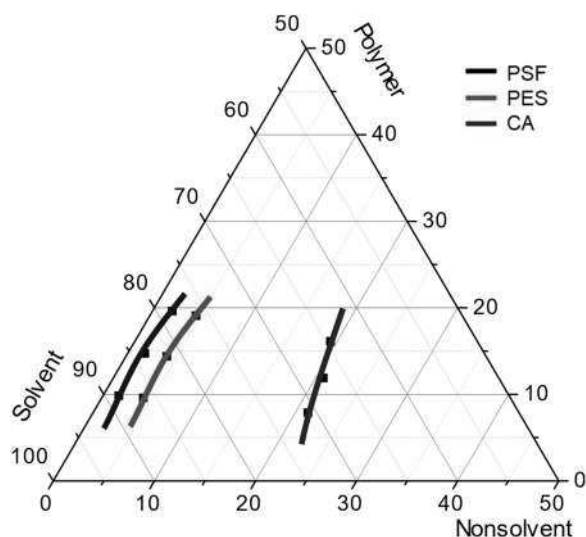


Fig. 2. Ternary phase diagram of PES, PSF, and CA, with PolarClean® used as solvent and water as nonsolvent.

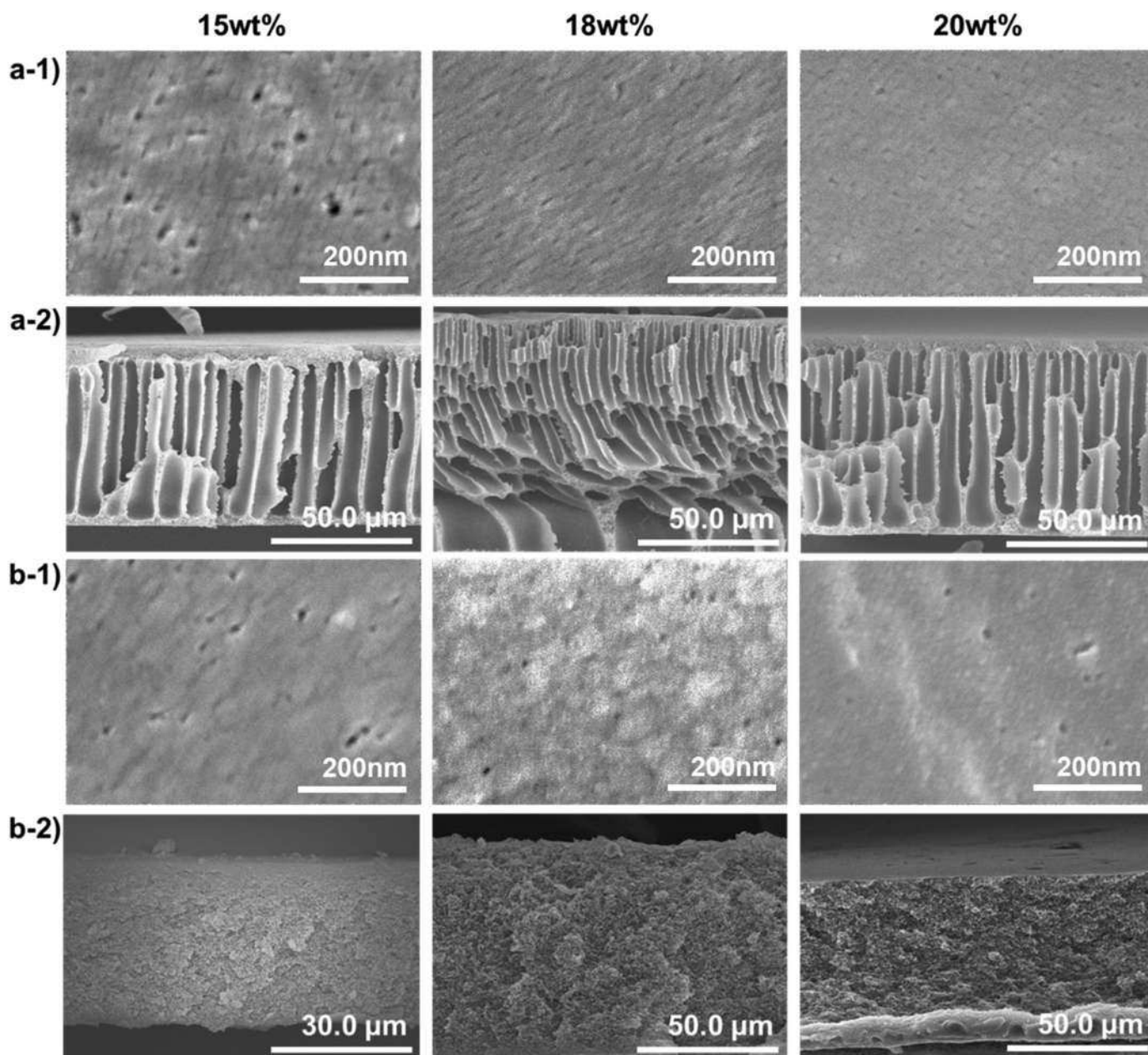


Fig. 3. SEM images showing the effects of polymer concentration on PES (a-1 and a-2) and PSF (b-1 and b-2) in PolarClean®: (1) top surface, (2) cross-section. The top surface refers to the membrane surface in contact with the coagulant.

the dope solution. This is an effective method of generating membrane surface pores to improve water flux [32,45,46]. However, depending on the interactions between polymer, additive, and solvent, the additive may not act as a pore-forming agent. In some cases, use of an additive facilitates gelation of the polymer solution rather than inducing L-L separation, resulting in a denser membrane structure [33,47]. For this reason, we introduced two effective and widely-studied pore-forming agents: Pluronic F-127 for PES membranes [48] and PVP for PSF membranes [46]. These agents tend to increase dope instability and induce instantaneous demixing during the NIPS process. Since Pluronic F-127 and PVP have high water affinity, they remain well-mixed with water during phase separation, forming pores on the surface when immersed for membrane formation. In these experiments, PES and PSF membranes were prepared with additives at 5 wt% concentration and polymers at 15, 18, and 20 wt%.

The viscosities of dope solutions prepared with and without additives are summarized in Fig. S1(b). As predicted, viscosity increased

with inclusion of additives. Among the two additives, PVP (MW = 55 kDa) induced higher dope viscosity than Pluronic F-127 (MW = 12.5 kDa), likely due to its higher molecular weight. In addition to viscosity, membrane morphology varied depending on addition of additives, as shown in Fig. 5. According to cross-sectional SEM images, the prepared PES membranes exhibited similar membrane morphology with macrovoids, regardless of the addition of Pluronic F-127. On the other hand, when PVP was added to the PSF dope solution, it induced macrovoidic structures, indicating fast intrusion of water into the polymer matrix upon phase inversion. In addition, surface porosity increased in the presence of additives. The surface and cross-sectional SEM images shown in Fig. 5 clearly indicate pore formation by instantaneous demixing, preventing gelation in the dope solution when the instability of the solution was increased by additives in the PES and PSF solution in PolarClean®.

Structural variance caused by additives also affects membrane properties such as overall porosity, tensile strength, surface porosity,

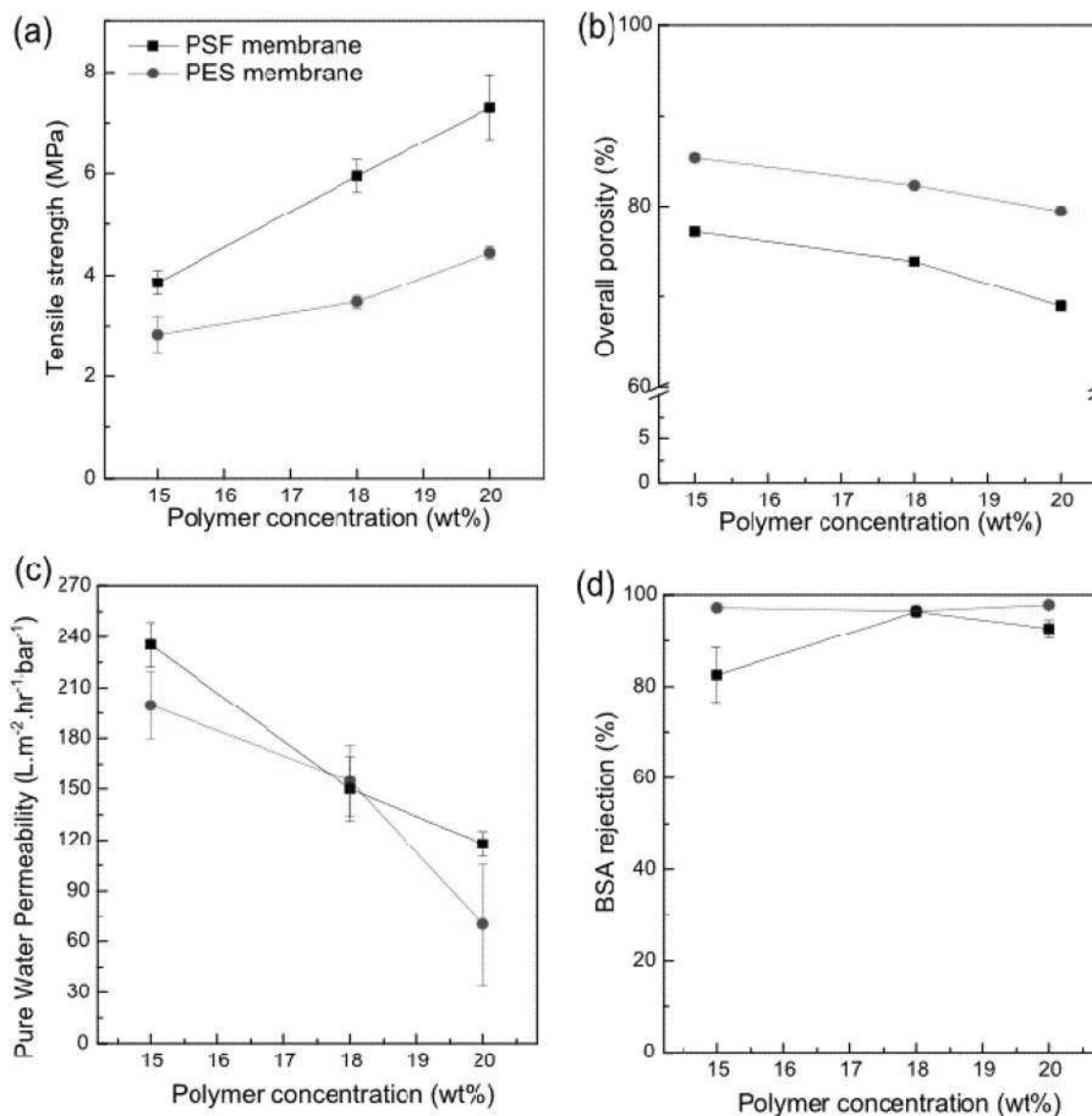


Fig. 4. Effects of PolarClean® polymer concentration on PES and PSF membranes: (a) tensile strength, (b) overall porosity, (c) pure water permeability, and (d) BSA rejection (all data include an error bar).

and water permeability. As summarized in Fig. 6(a) and (b), introducing additives as pore-forming agents influenced the overall porosity of the membrane, which is related to mechanical strength. PES membranes exhibited similar macrovoid structures even after Pluronic additive, resulting in similar tensile strength and overall porosity. However, PSF membrane morphology changed from sponge-like to finger-like structures with macrovoids after introduction of the PVP additive. This trend is illustrated in Fig. 6(b), which clearly indicates that the addition of pore-forming agents caused variation in morphology inside the membrane, which resulted in variation of both overall porosity and tensile strength.

In addition, membrane water transport property, pore size, overall porosity, hydrophilicity, and surface porosity changed due to addition of additives. The effect of each additive was different, as summarized in Fig. 6. As described in Fig. 6(a, c, d), Pluronic F-127 increased the surface porosity and mean pore size of PES membranes while inducing a small increase in overall porosity. On the other hand, PVP 55 K increased the mean pore size, surface porosity, and overall porosity of PSF membranes.

As shown in Fig. 6(e), the water contact angles were similar

regardless of polymer concentration and inclusion of additive, indicating that increases in PWP are due to higher surface porosity, overall porosity, and mean pore size rather than membrane hydrophilicity. Interestingly, Fig. 6(f) suggests that the increase in PWP was more distinct in PSF membranes than in PES. Changes in the cross-sectional morphology of PSF membranes from bicontinuous to macrovoidic may have improved PWP at the cost of decreased mechanical properties. Macrovoidic structures typically exhibit low mechanical strength but superior permeability due to lower tortuosity and lower flow resistance [49,50]. Such structural transformations increase the overall porosity of membranes.

Finally, the PES and PSF membranes showed similar rejection properties when produced with or without additives regardless of polymer concentration, indicating that additives did not change membrane pore size significantly.

3.3. Preparation of nonporous membranes using CA

Unlike the preparation of porous membranes, fabrication of nonporous membranes requires a skin layer with smaller pores a few

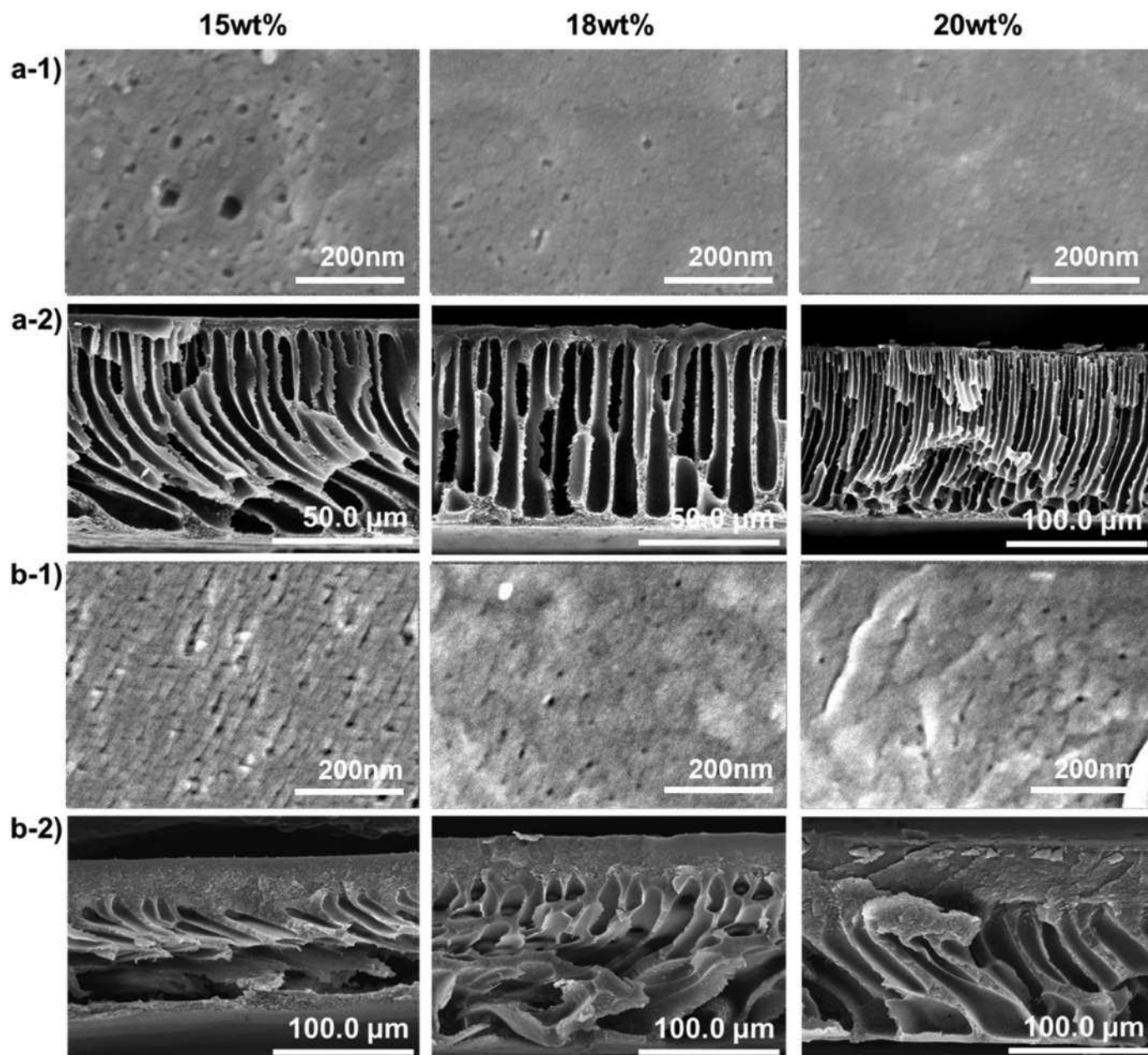


Fig. 5. SEM images showing the effects of additives on PES/Pluronic F127 (a-1 and a-2) and PSF/PVP (b-1 and b-2) membranes prepared using PolarClean®: (1) top surface, (2) cross-section. The top surface refers to the membrane surface in contact with the coagulant.

nanometers in size and a porous sub-layer for mechanical support. Therefore, intense diffusion at the interface of the coagulant and the membrane surface is essential. That is, gelation or vitrification should be favored over L-L separation and it advantageous for increasing the concentration of the polymer. For this reason, we applied high polymer concentrations of 20, 22.5, and 25 wt% without using additives.

3.3.1. Effects of polymer concentration on the preparation of CA membrane

Fig. 7 illustrates the morphologies of CA membranes prepared using different polymer concentrations. Prepared membranes exhibit a dense skin layer on the surface with a porous, macrovoid-filled layer beneath the surface. The dense skin layer was formed due to the large polymer phase in the high-concentration solution, resulting in instant phase separation of the polymer at the interface of coagulant and polymer solution. After forming the dense skin layer, the exchange of solvent and nonsolvent at the interface becomes limited because the dense layer acts as a barrier. However, the high coagulation value of CA in

PolarClean® delayed the instant demixing of the polymer phase, favoring gelation over L-L separation. The thickness of the skin observed in the SEM image in Fig. 7 was less than 1 μm and was constant regardless of polymer concentration. However, as the polymer concentration increased, the PWP decreased and the rejection of mono/divalent ions increased, indicating that this formulation is applicable for NF applications (Fig. 8).

3.4. Performance comparison

Some membrane properties are known to be involved in trade-offs such as tensile strength versus PWP or PWP versus salt rejection [70]. In UF applications, it is crucial to achieve both high water flux and rejection properties due to the relatively large sizes of contaminants (> 10 nm), but high tensile membrane strength is required without decreasing water flux. Separating target molecules, i.e., mono or divalent ions, in NF applications requires dense, tight surface structures,

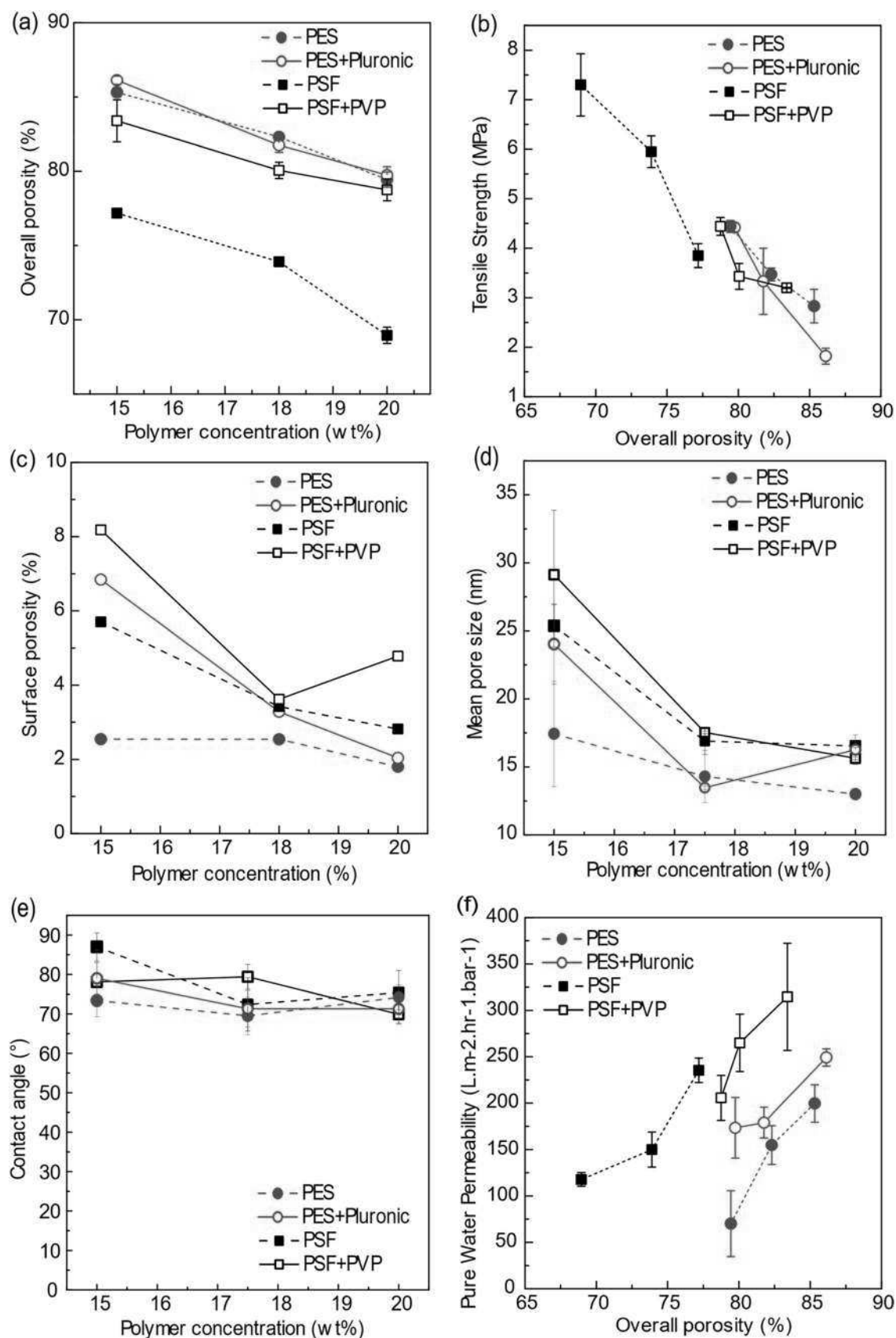


Fig. 6. Effects of polymer concentration on PES/Pluronic and PSF/PVP membranes: (a) overall porosity, (c) surface porosity, (d) mean pore size, (e) contact angle. The effects of overall porosity on membranes: (b) tensile strength, (f) pure water permeability (all data include an error bar). (PES: dotted red line, PES/Pluronic: solid red line, PSF: dotted black line, PSF/PVP: solid black line) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

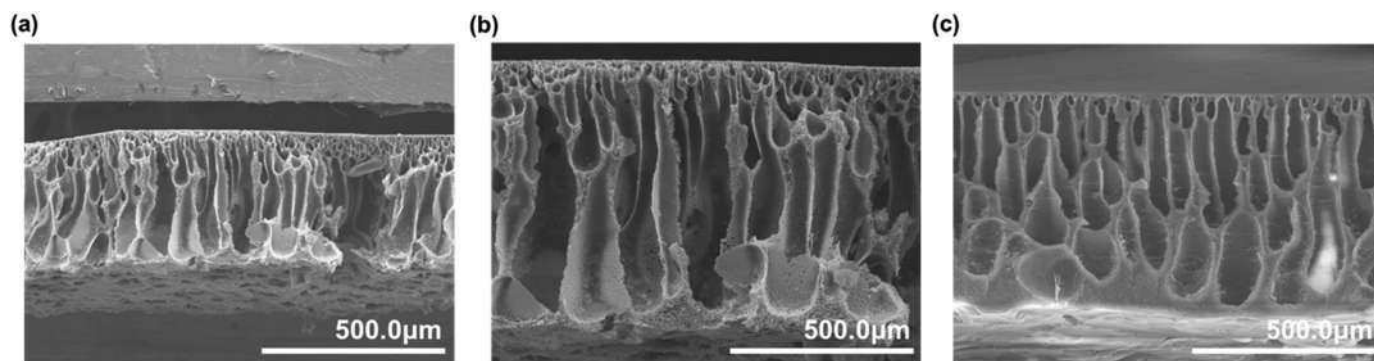


Fig. 7. Cross-sectional SEM images showing the effects of polymer concentration on CA/PolarClean[®] membranes: (a) 20 wt%, (b) 22.5 wt%, (c) 25 wt% CA solution.

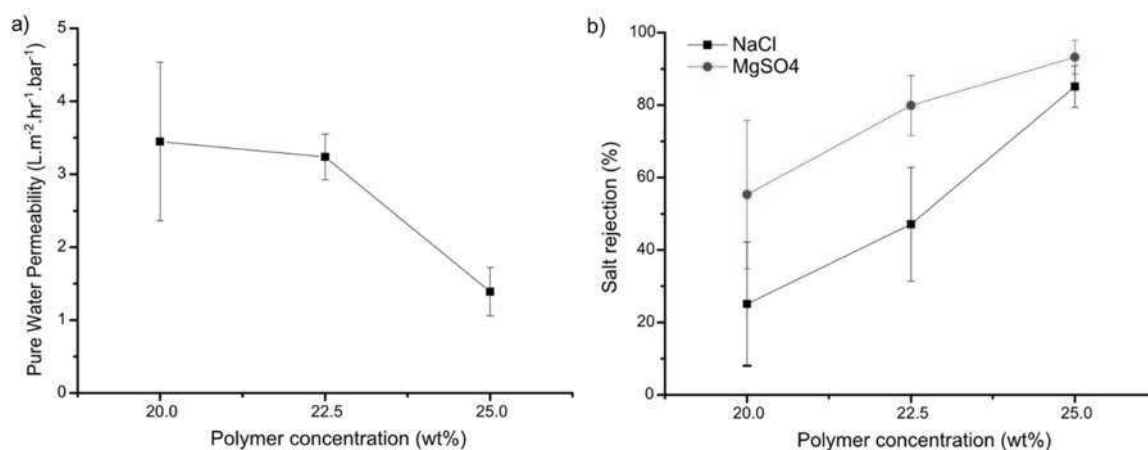


Fig. 8. Effects of polymer concentration on CA/PolarClean[®] membranes: (a) pure water permeability, (b) salt rejection.

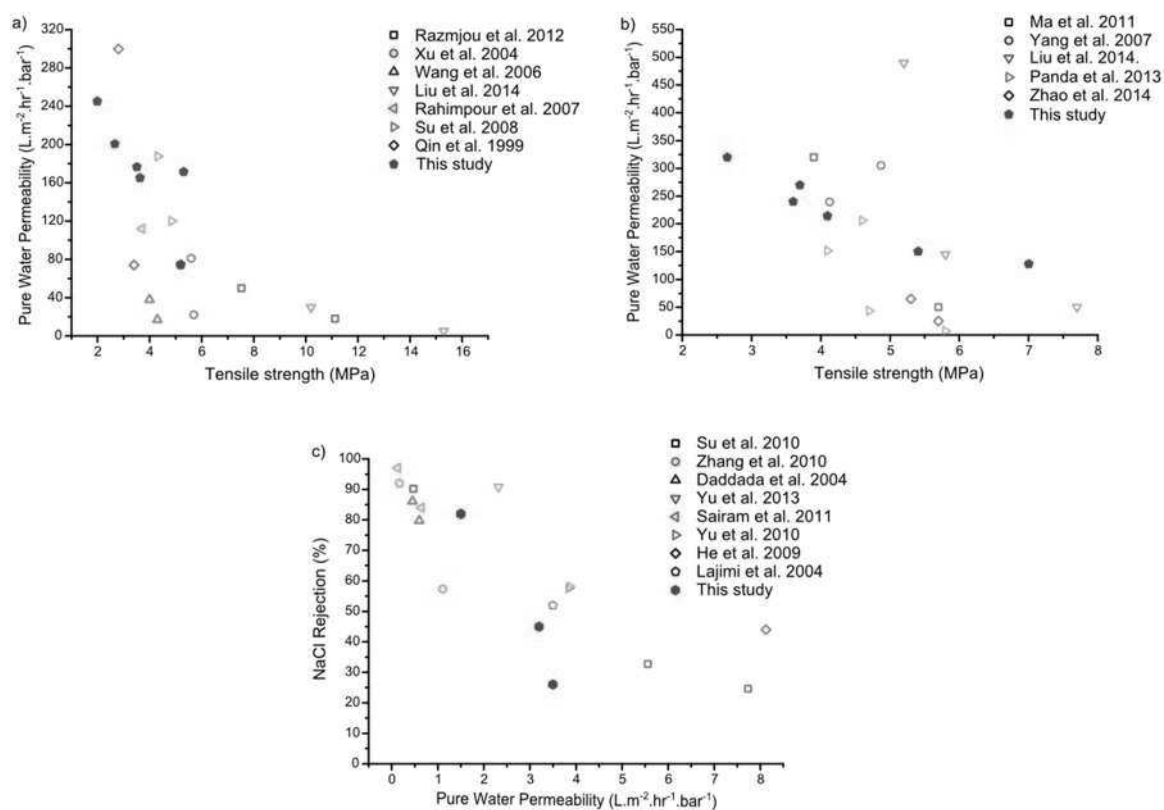


Fig. 9. Performance comparison between membranes prepared in this study and those previously reported: (a) PES, (b) PSF, and (c) CA membranes [36,48,51–69].

producing a trade-off between permeability and selectivity. Fig. 9 outlines the performances of the PES, PSF, and CA membranes produced in this study in comparison to previously-described membranes prepared using conventional solvents such as NMP and DMAc [70]. All three membranes examined in this study, PES, PSF, and CA, demonstrated competitive or superior performance compared to other membranes, near the upper bound in Fig. 9, indicating that high-performance UF and NF membranes can be prepared using environmentally friendly PolarClean® solvent. In addition, better performance may be achieved by further optimizing the preparation conditions. Changes in membrane preparation parameters including additives, surface modification, and thermal annealing will help improve membrane properties such as tensile strength, PWP, and salt rejection for use in UF and NF applications.

4. Conclusion

In this study, UF and NF membranes were fabricated using an environmentally-friendly solvent, PolarClean®, to investigate its feasibility in membrane preparation. PES, PSF, and CA were selected because they were the most commonly used polymers for membrane preparation during the past five years and are used in widespread industrial applications. A full characterization of their phase separation behaviors was first carried out to determine which polymers were suitable for applications such as UF or NF. Due to the different intrinsic affinities of different polymers with PolarClean®, the resulting phase separation behaviors and membrane morphologies varied significantly. PES and PSF exhibited low solution thermodynamic stability in PolarClean® and produced a porous surface that was more suitable for UF applications, whereas CA produced a dense surface with smaller pores, suitable for NF applications because the phase separation of CA from PolarClean® was delayed due to high solution thermodynamic stability. The PES and PSF UF membranes and CA NF membranes exhibited competitive permselectivity. Our results indicate that PolarClean® is a promising alternative to conventional organic solvents such as DMAc, DMF, and NMP.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2018.12.051.

References

- [1] S. Loeb, S. Sourirajan, Sea Water Demineralization by Means of an Osmotic Membrane, University of California, Department of Engineering, 1960.
- [2] J.H. Kim, S.J. Moon, S.H. Park, M. Cook, A.G. Livingston, Y.M. Lee, A robust thin film composite membrane incorporating thermally rearranged polymer support for organic solvent nanofiltration and pressure retarded osmosis, *J. Membr. Sci.* 550 (2018) 322–331.
- [3] J.H. Kim, S.H. Park, M.J. Lee, S.M. Lee, W.H. Lee, K.H. Lee, N.R. Kang, H.J. Jo, J.F. Kim, E. Drioli, Y.M. Lee, Thermally rearranged polymer membranes for desalination, *Energy Environ. Sci.* 9 (2016) 878–884.
- [4] G. Dong, Y.M. Lee, Microporous polymeric membranes inspired by adsorbent for gas separation, *J. Mater. Chem. A* 5 (2017) 13294–13319.
- [5] S. Kim, Y.M. Lee, Rigid and microporous polymers for gas separation membranes, *Prog. Polym. Sci.* 43 (2015) 1–32.
- [6] J.G. Seong, Y. Zhuang, S. Kim, Y.S. Do, W.H. Lee, M.D. Guiver, Y.M. Lee, Effect of methanol treatment on gas sorption and transport behavior of intrinsically microporous polyimide membranes incorporating Tröger's base, *J. Membr. Sci.* 480 (2015) 104–114.
- [7] B. Jiao, A. Cassano, E. Drioli, Recent advances on membrane processes for the concentration of fruit juices: a review, *J. Food Eng.* 63 (2004) 303–324.
- [8] A. Cassano, E. Drioli, G. Galaverna, R. Marchelli, G. Di Silvestro, P. Cagnasso, Clarification and concentration of citrus and carrot juices by integrated membrane processes, *J. Food Eng.* 57 (2003) 153–163.
- [9] C.H. Park, S.Y. Lee, D.S. Hwang, D.W. Shin, D.H. Cho, K.H. Lee, T.-W. Kim, T.-W. Kim, M. Lee, D.-S. Kim, C.M. Doherty, A.W. Thornton, A.J. Hill, M.D. Guiver, Y.M. Lee, Nanocrack-regulated self-humidifying membranes, *Nature* 532 (2016) 480.
- [10] D.W. Shin, M.D. Guiver, Y.M. Lee, Hydrocarbon-based polymer electrolyte membranes: importance of morphology on ion transport and membrane stability, *Chem. Rev.* 117 (2017) 4759–4805.
- [11] P. Silva, L. Peeva, A. Livingston, Nanofiltration in organic solvents, *Adv. Membr. Technol. Appl.* (2008) 451–467.
- [12] I.B. Valtcheva, S.C. Kumbharkar, J.F. Kim, Y. Bhole, A.G. Livingston, Beyond polyimide: crosslinked polybenzimidazole membranes for organic solvent nanofiltration (OSN) in harsh environments, *J. Membr. Sci.* 457 (2014) 62–72.
- [13] M. Razali, J.F. Kim, M. Attfield, P.M. Budd, E. Drioli, Y.M. Lee, G. Szekely, Sustainable wastewater treatment and recycling in membrane manufacturing, *Green Chem.* 17 (2015) 5196–5205.
- [14] A. Figoli, T. Marino, S. Simone, E. Di Nicolò, X.-M. Li, T. He, S. Tornaghi, E. Drioli, Towards non-toxic solvents for membrane preparation: a review, *Green Chem.* 16 (2014) 4034–4059.
- [15] C.J. Clarke, W.-C. Tu, O. Levers, A. Bröhl, J.P. Hallett, Green and Sustainable Solvents in Chemical Processes, *Chem. Rev.* 118 (2018) 747–800.
- [16] F. Pena-Pereira, M. Tobiszewski, The Application of Green Solvents in Separation Processes, Elsevier, 2017.
- [17] J. Kim, J. Jung, H. Wang, E. Drioli, Y.M. Lee, 1.15 effect of solvents on membrane fabrication via thermally induced phase separation (TIPS): thermodynamic and kinetic perspectives, *Comprehensive Membrane Science and Engineering*, Elsevier, Oxford, 2017.
- [18] J.T. Jung, J.F. Kim, H.H. Wang, E. di Nicolò, E. Drioli, Y.M. Lee, Understanding the non-solvent induced phase separation (NIPS) effect during the fabrication of microporous PVDF membranes via thermally induced phase separation (TIPS), *J. Membr. Sci.* 514 (2016) 250–263.
- [19] G.R. Guillen, Y. Pan, M. Li, E.M. Hoek, Preparation and characterization of membranes formed by nonsolvent induced phase separation: a review, *Ind. Eng. Chem. Res.* 50 (2011) 3798–3817.
- [20] D. Kim, O.R. Salazar, S.P. Nunes, Membrane manufacture for peptide separation, *Green Chem.* 18 (2016) 5151–5159.
- [21] P. Kubisa, Application of ionic liquids as solvents for polymerization processes, *Prog. Polym. Sci.* 29 (2004) 3–12.
- [22] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, Dissolution of cellulose with ionic liquids, *J. Am. Chem. Soc.* 124 (2002) 4974–4975.
- [23] H. Matsuyama, H. Yano, T. Maki, M. Teramoto, K. Mishima, K. Matsuyama, Formation of porous flat membrane by phase separation with supercritical CO₂, *J. Membr. Sci.* 194 (2001) 157–163.
- [24] H. Matsuyama, A. Yamamoto, H. Yano, T. Maki, M. Teramoto, K. Mishima, K. Matsuyama, Effect of organic solvents on membrane formation by phase separation with supercritical CO₂, *J. Membr. Sci.* 204 (2002) 81–87.
- [25] T. Marino, F. Russo, A. Criscuolo, A. Figoli, TamiSolve® NxG as novel solvent for polymeric membrane preparation, *J. Membr. Sci.* 542 (2017) 418–429.
- [26] J.F. Kim, J.T. Jung, H.H. Wang, S.Y. Lee, T. Moore, A. Sanguineti, E. Drioli, Y.M. Lee, Microporous PVDF membranes via thermally induced phase separation (TIPS) and stretching methods, *J. Membr. Sci.* 509 (2016) 94–104.
- [27] Z. Cui, N.T. Hassankiadeh, S.Y. Lee, J.M. Lee, K.T. Woo, A. Sanguineti, V. Arcella, Y.M. Lee, E. Drioli, Poly(vinylidene fluoride) membrane preparation with an environmental diluent via thermally induced phase separation, *J. Membr. Sci.* 444 (2013) 223–236.
- [28] Z. Cui, N.T. Hassankiadeh, S.Y. Lee, K.T. Woo, J.M. Lee, A. Sanguineti, V. Arcella, Y.M. Lee, E. Drioli, Tailoring novel fibrillar morphologies in poly(vinylidene fluoride) membranes using a low toxic triethylene glycol diacetate (TEGDA) diluent, *J. Membr. Sci.* 473 (2015) 128–136.
- [29] F. Rindfleisch, T.P. DiNoia, M.A. McHugh, Solubility of polymers and copolymers in supercritical CO₂, *J. Phys. Chem.* 100 (1996) 15581–15587.
- [30] J.T. Jung, H.H. Wang, J.F. Kim, J. Lee, J.S. Kim, E. Drioli, Y.M. Lee, Tailoring nonsolvent-thermally induced phase separation (N-TIPS) effect using triple spinneret to fabricate high performance PVDF hollow fiber membranes, *J. Membr. Sci.* 559 (2018) 117–126.
- [31] S. Rajabzadeh, T. Maruyama, T. Sotani, H. Matsuyama, Preparation of PVDF hollow fiber membrane from a ternary polymer/solvent/nonsolvent system via thermally induced phase separation (TIPS) method, *Sep. Purif. Technol.* 63 (2008) 415–423.
- [32] J. Lee, B. Park, J. Kim, S.B. Park, Effect of PVP, lithium chloride, and glycerol additives on PVDF dual-layer hollow fiber membranes fabricated using simultaneous spinning of TIPS and NIPS, *Macromol. Res.* 23 (2015) 291–299.
- [33] K.-Y. Lin, D.-M. Wang, J.-Y. Lai, Nonsolvent-induced gelation and its effect on membrane morphology, *Macromolecules* 35 (2002) 6697–6706.
- [34] B.J. Cha, J.M. Yang, Preparation of poly(vinylidene fluoride) hollow fiber membranes for microfiltration using modified TIPS process, *J. Membr. Sci.* 291 (2007) 191–198.
- [35] X. Dong, A. Al-Jumaily, I.C. Escobar, Investigation of the use of a bio-derived solvent for non-solvent-induced phase separation (NIPS) fabrication of polysulfone membranes, *Membranes* 8 (2018) 23.
- [36] T. Marino, E. Blasi, S. Tornaghi, E. Di Nicolò, A. Figoli, Polyethersulfone membranes prepared with Rhodiasolv® PolarClean as water soluble green solvent, *J. Membr. Sci.* 549 (2018) 192–204.
- [37] S. Kim, S.H. Han, Y.M. Lee, Thermally rearranged (TR) polybenzoxazole hollow fiber membranes for CO₂ capture, *J. Membr. Sci.* 403 (2012) 169–178.
- [38] D. Wang, K. Li, W. Teo, Relationship between mass ratio of nonsolvent-additive to

- solvent in membrane casting solution and its coagulation value, *J. Membr. Sci.* 98 (1995) 233–240.
- [39] C. Yao, R. Burford, A. Fane, C. Fell, Effect of coagulation conditions on structure and properties of membranes from aliphatic polyamides, *J. Membr. Sci.* 38 (1988) 113–125.
- [40] J.-H. Kim, K.-H. Lee, Effect of PEG additive on membrane formation by phase inversion, *J. Membr. Sci.* 138 (1998) 153–163.
- [41] J. Mulder, *Basic Principles of Membrane Technology*, Springer Science & Business Media, 2012.
- [42] P. Van de Witte, P.J. Dijkstra, J. Van den Berg, J. Feijen, Phase separation processes in polymer solutions in relation to membrane formation, *J. Membr. Sci.* 117 (1996) 1–31.
- [43] N. Peng, T.-S. Chung, K.Y. Wang, Macrovoid evolution and critical factors to form macrovoid-free hollow fiber membranes, *J. Membr. Sci.* 318 (2008) 363–372.
- [44] P. Sukitpaneevit, T.-S. Chung, High performance thin-film composite forward osmosis hollow fiber membranes with macrovoid-free and highly porous structure for sustainable water production, *Environ. Sci. Technol.* 46 (2012) 7358–7365.
- [45] C.H. Loh, R. Wang, L. Shi, A.G. Fane, Fabrication of high performance polyethersulfone UF hollow fiber membranes using amphiphilic Pluronic block copolymers as pore-forming additives, *J. Membr. Sci.* 380 (2011) 114–123.
- [46] S. Simone, A. Figoli, A. Criscuolo, M. Carnevale, A. Rosselli, E. Drioli, Preparation of hollow fibre membranes from PVDF/PVP blends and their application in VMD, *J. Membr. Sci.* 364 (2010) 219–232.
- [47] M. Yeow, Y. Liu, K. Li, Morphological study of poly (vinylidene fluoride) asymmetric membranes: effects of the solvent, additive, and dope temperature, *J. Appl. Polym. Sci.* 92 (2004) 1782–1789.
- [48] Y. Wang, Y. Su, Q. Sun, X. Ma, X. Ma, Z. Jiang, Improved permeation performance of Pluronic F127–polyethersulfone blend ultrafiltration membranes, *J. Membr. Sci.* 282 (2006) 44–51.
- [49] N.Y. Yip, A. Tiraferri, W.A. Phillip, J.D. Schiffman, M. Elimelech, High performance thin-film composite forward osmosis membrane, *Environ. Sci. Technol.* 44 (2010) 3812–3818.
- [50] A. Tiraferri, N.Y. Yip, W.A. Phillip, J.D. Schiffman, M. Elimelech, Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure, *J. Membr. Sci.* 367 (2011) 340–352.
- [51] A. Razmjou, A. Resosudarmo, R.L. Holmes, H. Li, J. Mansouri, V. Chen, The effect of modified TiO₂ nanoparticles on the polyethersulfone ultrafiltration hollow fiber membranes, *Desalination* 287 (2012) 271–280.
- [52] Z.L. Xu, F.A. Qusay, Effect of polyethylene glycol molecular weights and concentrations on polyethersulfone hollow fiber ultrafiltration membranes, *J. Appl. Polym. Sci.* 91 (2004) 3398–3407.
- [53] T.-Y. Liu, R.-X. Zhang, Q. Li, B. Van der Bruggen, X.-L. Wang, Fabrication of a novel dual-layer (PES/PVDF) hollow fiber ultrafiltration membrane for wastewater treatment, *J. Membr. Sci.* 472 (2014) 119–132.
- [54] A. Rahimpour, S. Madaeni, Polyethersulfone (PES)/cellulose acetate phthalate (CAP) blend ultrafiltration membranes: preparation, morphology, performance and antifouling properties, *J. Membr. Sci.* 305 (2007) 299–312.
- [55] Y. Su, C. Li, W. Zhao, Q. Shi, H. Wang, Z. Jiang, S. Zhu, Modification of polyethersulfone ultrafiltration membranes with phosphorylcholine copolymer can remarkably improve the antifouling and permeation properties, *J. Membr. Sci.* 322 (2008) 171–177.
- [56] J. Qin, T.-S. Chung, Effect of dope flow rate on the morphology, separation performance, thermal and mechanical properties of ultrafiltration hollow fibre membranes, *J. Membr. Sci.* 157 (1999) 35–51.
- [57] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li, The influence of nano-sized TiO₂ fillers on the morphologies and properties of PSF UF membrane, *J. Membr. Sci.* 288 (2007) 231–238.
- [58] F. Liu, B.-R. Ma, D. Zhou, Y.-h. Xiang, L.-x. Xue, Breaking through tradeoff of polysulfone ultrafiltration membranes by zeolite 4A, *Microporous Mesoporous Mater.* 186 (2014) 113–120.
- [59] S.R. Panda, S. De, Role of polyethylene glycol with different solvents for tailor-made polysulfone membranes, *J. Polym. Res.* 20 (2013) 179.
- [60] L.-B. Zhao, Z.-L. Xu, M. Liu, Y.-M. Wei, Preparation and characterization of PSf hollow fiber membrane from PSf–HBPE–PEG400–NMP dope solution, *J. Membr. Sci.* 454 (2014) 184–192.
- [61] J. Su, Q. Yang, J.F. Teo, T.-S. Chung, Cellulose acetate nanofiltration hollow fiber membranes for forward osmosis processes, *J. Membr. Sci.* 355 (2010) 36–44.
- [62] S. Zhang, K.Y. Wang, T.-S. Chung, H. Chen, Y. Jean, G. Amy, Well-constructed cellulose acetate membranes for forward osmosis: minimized internal concentration polarization with an ultra-thin selective layer, *J. Membr. Sci.* 360 (2010) 522–535.
- [63] R. Haddada, E. Ferjani, M.S. Roudesli, A. Deratani, Properties of cellulose acetate nanofiltration membranes. Application to brackish water desalination, *Desalination* 167 (2004) 403–409.
- [64] S. Yu, Q. Cheng, C. Huang, J. Liu, X. Peng, M. Liu, C. Gao, Cellulose acetate hollow fiber nanofiltration membrane with improved permselectivity prepared through hydrolysis followed by carboxymethylation, *J. Membr. Sci.* 434 (2013) 44–54.
- [65] S. Yu, M. Liu, M. Ma, M. Qi, Z. Lü, C. Gao, Impacts of membrane properties on reactive dye removal from dye/salt mixtures by asymmetric cellulose acetate and composite polyamide nanofiltration membranes, *J. Membr. Sci.* 350 (2010) 83–91.
- [66] M. Sairam, E. Sereewatthanawut, K. Li, A. Bismarck, A. Livingston, Method for the preparation of cellulose acetate flat sheet composite membranes for forward osmosis—desalination using MgSO₄ draw solution, *Desalination* 273 (2011) 299–307.
- [67] Y. He, G.-M. Li, H. Wang, Z.-W. Jiang, J.-F. Zhao, H.-X. Su, Q.-Y. Huang, Experimental study on the rejection of salt and dye with cellulose acetate nanofiltration membrane, *J. Taiwan Inst. Chem. Eng.* 40 (2009) 289–295.
- [68] R.H. Lajimi, A.B. Abdallah, E. Ferjani, M.S. Roudesli, A. Deratani, Change of the performance properties of nanofiltration cellulose acetate membranes by surface adsorption of polyelectrolyte multilayers, *Desalination* 163 (2004) 193–202.
- [69] Y. Ma, F. Shi, Z. Wang, M. Wu, J. Ma, C. Gao, Preparation and characterization of PSf/clay nanocomposite membranes with PEG 400 as a pore forming additive, *Desalination* 286 (2012) 131–137.
- [70] J.F. Kim, J.H. Kim, Y.M. Lee, E. Drioli, Thermally induced phase separation and electrospinning methods for emerging membrane applications: a review, *AIChE J.* 62 (2016) 461–490.