ORIGINAL ARTICLE

Membranes for hydrogen separation: a significant review

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Abstract

Hydrogen (H_2)-selective membranes involve significantly less energy and generally a better way to manage them. Partial inlet/outlet pressure of H_2, as well as temperature, are the best parameters for membrane processes. Membrane processes are appropriate for portable applications and small scale as opposed to other separation techniques. The membrane can also be performed at different pressure and temperature ranges. The critical purpose of the separation membrane is the suitable usage in membrane reactors that permit the purification and production of synchronous H_2. Observations of alterations in the structural and chemical properties have been commonly performed to understand the process by which polymers degrade. The validity of each observational procedure depends primarily on the test material and type of degradation. An appropriate method for the characterization of polymers can often be utilized to examine the properties of degradation. The service life of a polymer depends strongly on the conditions to which the material is subjected. On the other hand, the stability of the material, including nanocomposite polymer blends, often dictates its usefulness. Thus, this review was aimed to evaluate the degradation of nanocomposite polymer blends, with specific focus on the role of the fillers and the composition of the blends. The factors that could significantly affect the degradation of the same were the presence of a filler, as well as the morphology and composition of the blends.

Keywords Hydrogen separation · Polymer degradation · Photodegradation · Durability · Energy

1 Introduction

The use of polymeric membranes in gas separation based on the combination of carbon dioxide (CO_2) and H_2 was first reported by Mitchell more than 180 years ago [1]. The first efficient application of membrane gas separation technologies in the 1970s was revealed to focus on removing H_2 from ammonia purge gas streams through polymeric membranes as well as adjusting the H_2/CO ratio in gas synthesis [2]. They found, as studied by Wisniak et al. [1], that Graham and his colleagues found the successful essential phase of understanding the process of permeation in 1866 by suggesting the participation of a solution-diffusion system in permeation in which permeate molecules are placed in the upstream part of the membrane before being transferred across the membrane through analogous processes as in liquid diffusion. There are a few main historic studies over the ancient growth for gas separation expertise grounded on the earlier discovery in water desalination membrane as illustrated in Fig. 1. Different from water desalination, the difficulties in the progress of membrane in gas separation is more noticeable and tough owing to the tiny sub-Ångstrom-level dissimilarities in terms of size among the gas molecules. By way of illustration, in the separation process of O_2 and N_2, both of them displayed the variance of only 0.18 Å hinge on their kinetic diameters of 3.46 and 3.64 Å, individually [3].

Being a relatively new and rapidly expanding field, membrane innovations offer numerous benefits (e.g., energy productivity, cost-effectiveness, and environmental friendliness) over the conventional partitioned procedures. In addition, layer innovations can easily be combined with other partitioning

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Fig. 1 a The progress in the fabrication of membrane throughout the years, **b** present membrane-based gas separation for different types of applications [4]
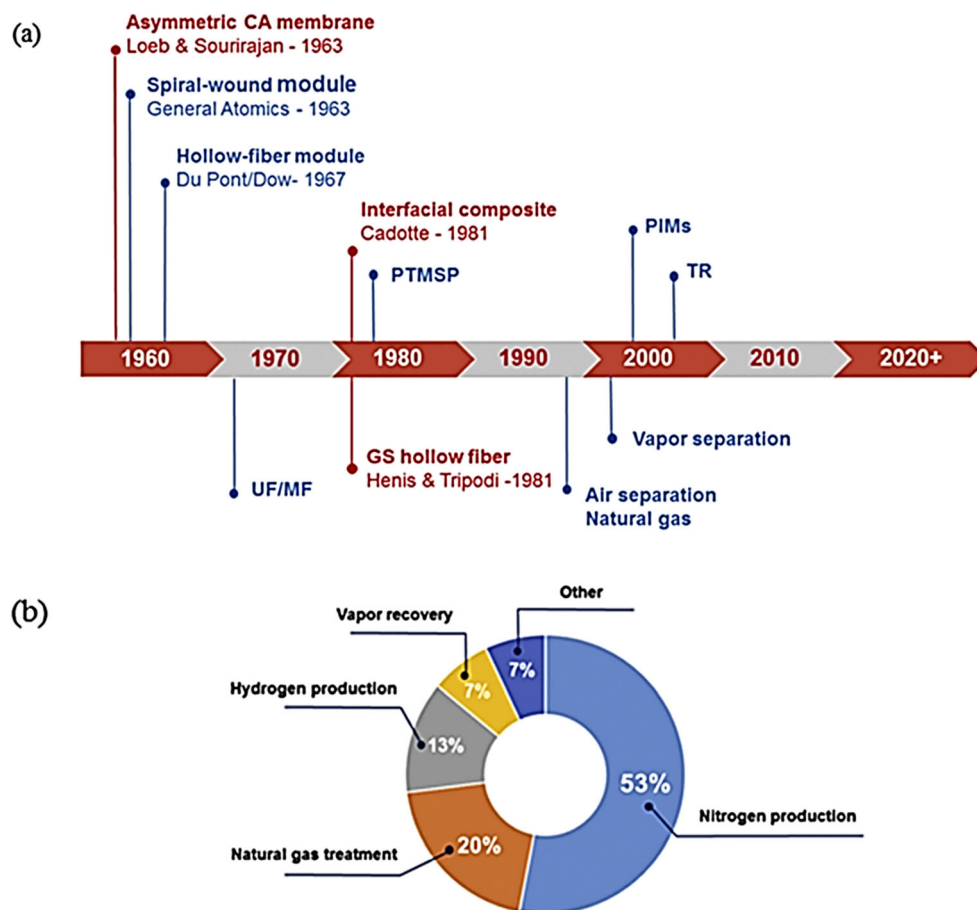
strategies to improve the efficiency of the overall process as well as cut down the cost of experimental. However, its relatively lower thermal resistance restricts its utilization in certain industries. While some polymeric membranes can be run in extreme conditions, the need to cool down hot streams for example, will cancel off the energy and cost efficiencies of the technology, thereby rendering it impractical [5–7]. In view of that, polymer modification efforts have been made to come up with synthetic polymeric membranes which can withstand high temperatures.

Thermally stable polymers—especially carbocyclic and heterocyclic ones—have been introduced by scientists [6]. Yet, these polymers are poorly soluble in common organic solvents and have high phase-transition temperatures. Despite their low processability, some studies have reported the successful utilization of thermally stable polymers to produce membranes with satisfactory separation characteristics and performances [6, 8, 9]. The future trajectory of the gas separation field entails full exploitation of the advantages of thermally stable polymeric membranes for market-worthy performances. The said polymers can be made up of a single repeat monomer (homopolymers) or two or more monomers (copolymers), apart from being either amorphous or crystalline [10]. Generally, most polymers have both amorphous and crystalline regions, the latter of which gives rise to a stronger polymer since the tendency of slippage between the chains is lower [11–13]. Figure 2 shows the schematic diagrams of (a) H_2-selective membranes and (b) CO_2-selective membranes.

Below glass-transition temperatures [Tg], polymers form a hard structure, and vice versa. Subsequent to their discovery, synthetic polymers have been employed in various applications. Tailoring of the polymers' properties will produce polymeric devices of different strengths for use in biomedical (e.g., pharmaceutical, medical, dental, food, and cosmetic) industries [15–17]. The way by which a polymer degrades following its implantation in a biological system can determine whether it is biodegradable or non-biodegradable. Usually, polymers with C–C backbones are highly resistant to degradation while those with heteroatoms (i.e., esters and anhydrides) are susceptible to degradation. Furthermore, polymeric H_2 membranes are useful for the application at moderate temperatures of 350 up to 450 °C. Thus, in the steam regeneration of natural gas, also the main H_2 manufacturing technique, the range suits the high-temperature for the reaction of water-gas shift. As a matter of reality, in accordance with the type of separation membrane, H_2 separation membranes can produce multi-level purity. Membranes are divided into two main groups: dense and porous [18, 19]. Depending on carbon,
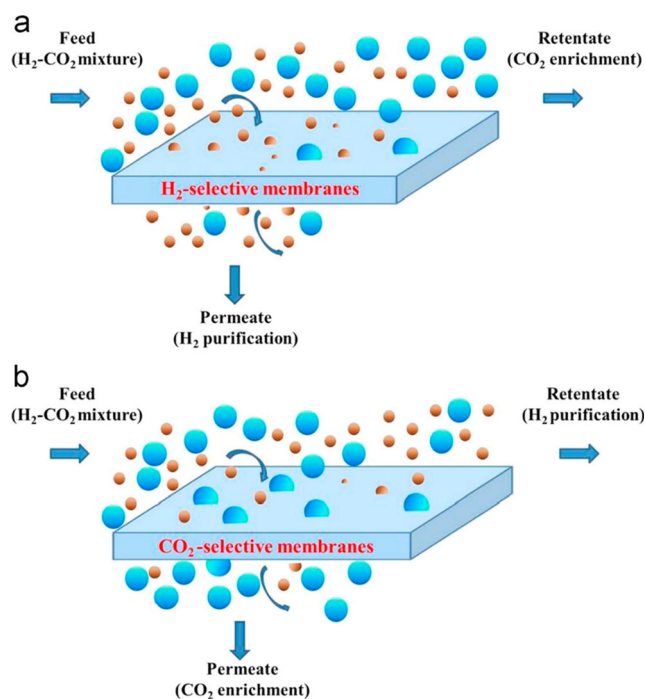
Fig. 2 Schematic diagrams of (**a**) H_2-selective membranes and (**b**) CO_2-selective membranes [14]

ceramic, and metal-polymer, the porous membrane can be created. Polymer membranes, dense metallic membranes, and ion-conductive ceramics were considered as the latter. Figure 3 summarizes the stages involved in the degradation of biodegradable polymers, where the primary mode of
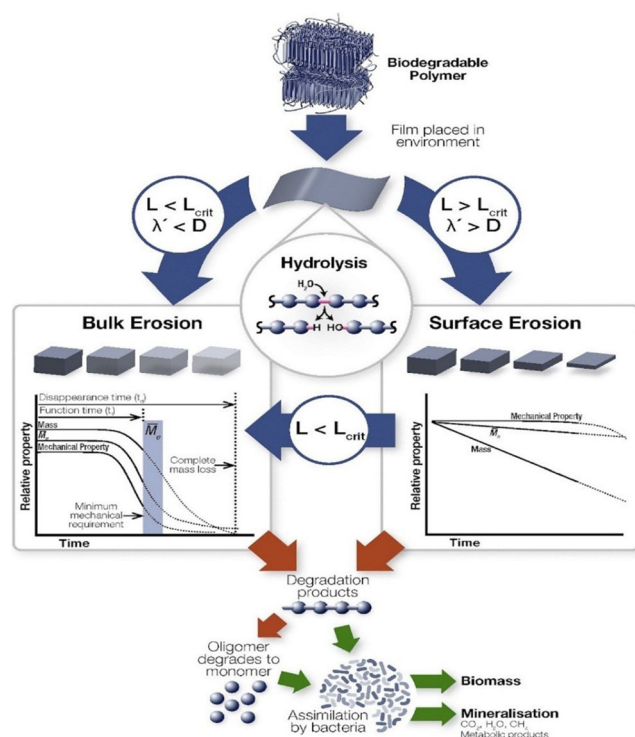

Fig. 3 Steps involved in polymer biodegradation by hydrolysis [20]

degradation is chain-cleavage via hydrolysis (either through abiotic/ non-enzymatic hydrolysis or enzyme-promoted hydrolysis). On the other hand, polymers which are very resistant to hydrolysis are characterized as oxo-degradable systems [20].

Numerous hard work is now focused on improving the technology needed to build supporting infrastructure on "H_2 economy" with enormous stress on energy costs, environmental sustainability and security (for both transportation and stationary separations) [21, 22]. Over the previous several years, a dramatic increase in H_2's worldwide investment can be noted and is presently estimated at several billion USD. Previously, Bush Administration has declared a 1.7 billion USD program specifically for the advancement of H_2 technologies, particularly the fuel cell vehicles [23]. Japan plans to deploy 4000 H_2 filling stations by 2020 [24]. Iceland seeks a thorough transition to H_2 by 2030 to be one of the best-known examples of "H_2 economy" [24]. Iceland plans to generate H_2 for transport adaptation (busses, vehicles, fishing vessels) and stationary applications (companies, homes) through its own geothermal and hydropower resources. A feasibility study is currently being coordinated by Hawaii to evaluate the prospects for large-scale H_2 use, renewable energy and fuel cells. It is necessary to solve various technological problems linked to H_2 distribution and storage. Also, the path to H_2 remains unsure. Globally, there are various countries with lavish gas and coal resources, which play an important role in the mentioned transition [25]. Substantial investment in new infrastructure, for example, storage facilities, fueling stations, and pipelines are required by any main initiative of H_2. H_2 comes with encouraging diversity potential in the energy mix of a nation while offering a cleaner environment [26, 27].

2 H_2 as demand for energy

The growth of world population and economy together with the speedy urbanization has increased the usage of energy demand. Previously, the sources of the energy highly depends on the hydrocarbon sources, such as fossil fuels that have become more reduced due to topographical scattering and thus, are easily obtained. The use of fossil fuel has increased the chances for the discharge of CO_2 and greenhouse gases (GHG) into the atmosphere that directly causes global warming effect [28, 29]. Alternatively, due to this situation, there is an approach for new and clean energy technologies that are able to minimize the effect of climate change and shelter a worldwide energy sanctuary that is depending on dependable and renewable energy (RE). RE will become the main source to a clean and sustainable system. Instead, "hydrogen economy" has been proposed as a probable way to solve the growing energy calamity. To be specific, hydrogen economy speaks of the full utilization of RE via the

implementation of Hydrogen-based energy storage systems (HydESS). This system is the process to collect and store RE in an energy carrier such as hydrogen that is storable, easy to be transported and simple to utilize. By 2050, the energy consumption is predicted to be doubled due to the extreme use of fossil fuels as a result of increase in power growth rate up to 2.6% per year [30].

Recently, the increase in popularity of the H_2 economy is one of the primary causes of H_2 recovery's growing attention as the top candidate in providing for the growing demand of energy needed by the industrialized countries [31]. Another attractive replacement for fossil fuel combustion to generate power is the proton-exchange membrane (PEM) fuel cell that utilizes H_2 as a fuel to generate electrical energy from chemical energy [32]. These fuel cells have several benefits such as having higher fuel efficiency compared to internal combustion engines, generate almost no HC, NO_x or CO and have low CO_2 level. However, a proper distribution regarding H_2 supply is required in order for these fuel cells to be widely used. The solution-diffusion mechanism cannot completely omit the trace contaminants that restrict the financial capacity of polymeric materials for ultra-high purity products [33]. H_2 is the most abundant element on Earth that can be extracted from, for instance, natural gas or coal (hydrocarbons) biomass or water. Production of H_2 can either be done via nuclear energy or electricity produced from sustainable resources, for example, solar, biomass, or wind [34].

Due to the outstanding potential of H_2 as a clean energy carrier, the H_2 energy system was globally mentioned and known as the eternal solution to the petroleum-based fuel diminution and environmental crisis catastrophe. In H_2 energy system, the sources of the energy can be sourced from solar, biomass, etc. that will firstly be transferred into H_2 carrier via many types of reaction including gasification, water splitting, reforming, and many others. The transformed energy can be finally utilized by the users. The summary of the process in H_2 energy system is illustrated in Fig. 4. Through this system, the H_2 functioned as intermediary to relocate the energy between energy resource to the phase of utilization to the consumers [35].

H_2 combustion generates only water that is referred to as "clean energy", yet H_2 production from hydrocarbons generates a greenhouse gas that is CO_2 [36]. H_2 production has already reached substantial quantities worldwide (about 5 billion m^3 each year) and is primarily used in the production of ammonia for use in the metallurgical and chemical sectors (4%), methanol production (8%), petroleum processing (37%), and fertilizer manufacturing (about 50%) [37, 38]. It is commonly accepted that the degradation is an irreversible process for H_2. Chemical degradation of polymers for instance, significantly affects their performance including the daily used plastic materials. Commonly, the change of polymer properties from its initial state, either desirable or not is

called "degradation" [39]. Thus, degradation can be considered as a generic term for all kinds of reaction in a polymer [33, 40], usually involving a number of physical and/or chemical processes with small morphological changes. These processes can lead to significant decline of the polymeric material quality, i.e., poor mechanical or electrical properties, before finally losing its functionality [17, 41].

In biological tissues, polymers undergo degradation by means of hydrolytic or enzymatic lysis of their polymeric bonds, thereby forming waste metabolites. Evidently, hydrolytic degradation of polymers is preferred over its enzymatic counterpart since the polymers undergo a more consistent degradation rate at different sites of the body [17, 40, 42]. As a side note, biodegradable polymers include natural polymers (i.e., cellulose), modified natural polymers (i.e., cellulose acetate), or chemically synthesized polymers. After the growth and use of synthetic polymeric membranes in the 1980s, membrane technology has shown notable advancement. This polymeric artificial membrane functions as a physical obstacle between two stages while allowing for differential transport through it. Manufacturing of various composite membranes is to be used in several applications, mostly for hydrogen purification gas separation. Choi et al. manufactured polyethersulfone (PES)-based composite membranes using the method of interfacial polymerization [43]. It has been used to explore the H_2/CO gas mixture separation. In their research, the aqueous phase monomer is 1,3-cyclohexanebis methylamine (CHMA), while the organic phase monomer is trimesoyl chloride (TMC). Circulating air has been inserted into the oven to ensure steady operating temperature. Bubble flow meter functions to calculate the gas' retentate flow rate and permeance. Synthetic biodegradable polymers are largely favored since they can be modified to improve the consistency of their degradation behaviors and properties [42].

Chemical degradation significantly affects the performance of the polymers, including plastic materials of daily use. Throughout degradation, polymer oxidation (mechano-oxidation) produces hydroperoxide, which affects the thermo-/photo-oxidation rate during the subsequent aging and weathering. Information of the mechanism of polymer degradation has facilitated the development of efficient stabilizers and sensitizers to enhance the performance of the product [41, 44], and produce environment-friendly (biodegradable) plastics, respectively [45]. Biodegradation can be achieved by any one of the ways as shown in Fig. 5 [46]. Evidently, polymer degradation has both harmful and beneficial aspects. In terms of the former, reduction in polymeric performance and manifestation of safety hazards can occur if the process is left unchecked. Otherwise, with proper management, it can be utilized to create new and promising materials [17, 47, 48].

Numerous feed streams must be handled by the H_2 separation industry according to the manufacturing technique. An important advantage of membrane separation is its versatility
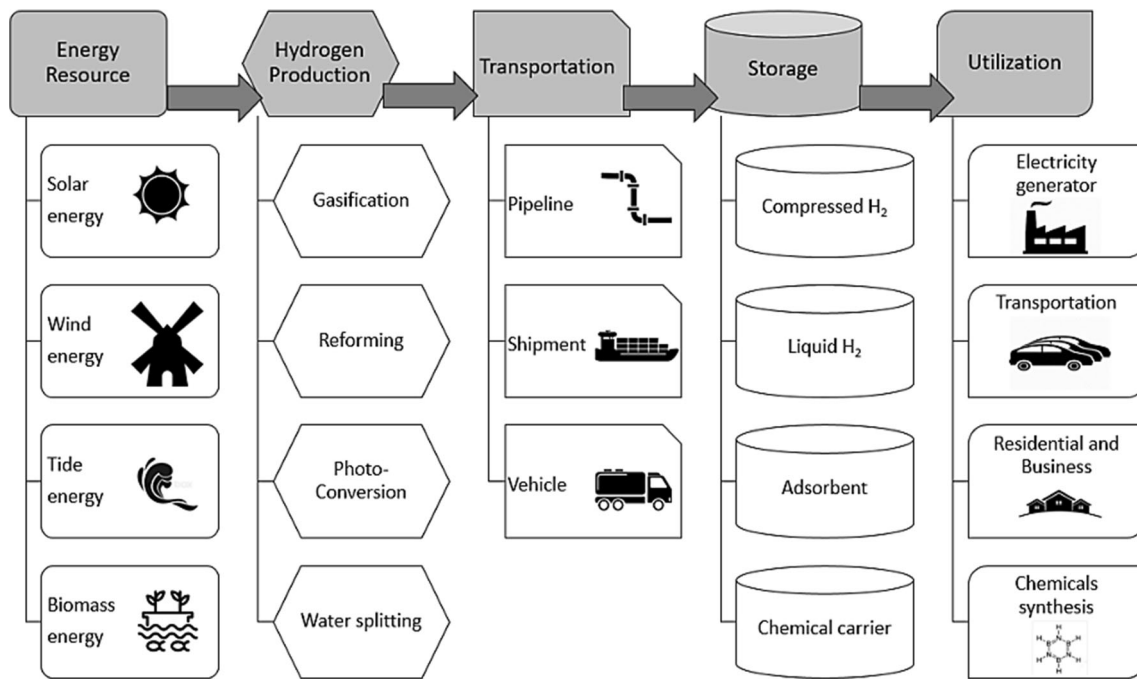
Fig. 4 The summarized of the process in H₂ energy system [35]

that is uncommon in other H_2 separation techniques. In order to achieve ideal separation and design, numerous variables need to be manipulated. However, versatility also may display the difficulty of offering the membrane system's in-depth design database. Three supporting areas need to be integrated in order to design an effective H_2 separation scheme which includes membrane formation, modules, and system configurations as well as material selection. Selectivity and permeability are the key elements in assessing the ability of membrane material to separate gas. Measuring time lag during the barometric establishment of gas permeability provides an estimation of gas diffusion coefficients, while indirectly providing an estimation on coefficients of solubility. Meanwhile, measurements of gravimetric sorption give direct coefficients of solubility in a membrane material. In gas transport, the characteristics of polymeric membranes correlate with their

Fig. 5 Biodegradation pathway to treat plastics [46]

morphological and structural characteristics. Using multiple techniques such as differential scanning calorimetry, Fourier-transform infrared spectroscopy, and scanning electron microscopy properties, as well as the composition of polymer materials such as elastic modulus and glass transition, can be evaluated [49]. These characteristics, together with the parameters of gas transport, have a relation with the nature of the free volume element within the polymer matrix. 129Xe nuclear magnetic resonance and positron annihilation lifetime spectroscopy are used to test cavity space in dense polymer films and microporous solids. Positron annihilation lifetime spectroscopy associates the probability and lifetime of ortho-positronium with the dimension and concentration of free volume, respectively. Numerous testing methods can generate distinct quantitative outcomes; however, the findings may be fundamental in understanding dense polymers' transport characteristics.

Implementation of membrane technologies for upgrading H_2 refineries is hastily developing at commercial-grade, leading in benefits such as low capital expenses, low energy needed as well as modularity. Reliability, process flexibility, effortless response to differences, versatility, and expansion capacity are the primary parameters in selecting the best technology. Implementation of membrane technologies for H_2 regeneration provides advantageous on the environment, for example, waste reduction, as well as restoration of precious raw materials, lost to flares or fuel. Most of the membranes used today are susceptible to impurities that are generally discovered in coal-derived syngas, for example, trace metals, mercury, ammonia, and sulfur. Thus, immense gas clean-up is crucial, also taking into account appropriate technologies as membrane
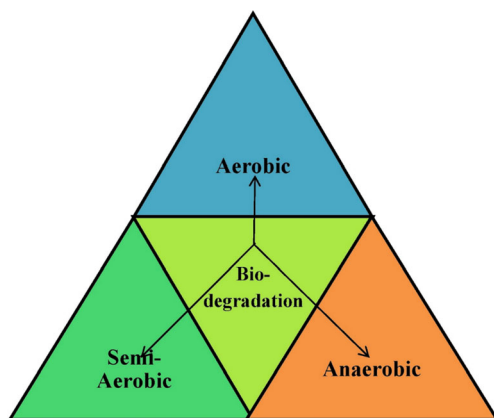
pretreatment is required. Besides, polymeric membranes also have a restriction that is modest thermal stability; only some groups have the capability to operate for long periods at high temperatures. Extensive studies are needed to optimize the accessible membrane materials.

Artificial weathering gadgets are instruments for acquiring data with respect to the potential debasement behaviors of polymeric materials. In spite of the fact that these gadgets have certain inadequacies, they still provide valuable data on the behaviors of the said materials. The most preferred feature of research gadgets is that they accelerate the debasement of the test materials. This can be achieved either by extending the time of exposure to the environmental factors (e.g., persistent exposure to artificial light, heat, and wet/dry cycles) or increasing the intensity of the variables. Specific stabilizers can be incorporated into a polymer framework to protect the latter from the ecological variables. Hence, information of the debasement of the polymer is highly essential for enhancing the strength and security of the material. By and large, debasements can be evaluated by observing the progressive changes in the structures and properties of the polymers. One benefit of a touchy procedure is that it enables the time of initiation of debasement to be identified, thereby reducing the amount of time required for assessments. Despite the legitimacy of the aforementioned method, the relationships between the outcomes to the commonsense material execution (e.g., carbonyl compound development versus embrittlement) need to be determined.

2.1 Polymer additives

In most cases, the introduction of additives may alter the service lives of polymers. For instance, sensitizers can be introduced to promote the oxidation of polymers via the production of singlet oxygen ($1 O_2$) molecules which results in energy transfer to the polymer or its self-decomposition [50, 51]. In addition, stabilizers can be added to the polymers to improve the latter's durability by minimizing the rate of degradation or by protecting them from environmental factors [52]. The disadvantages of the utilization of the single-additive system include compatibility issues, migration of low molecular weight stabilizers, immobility of high molecular weight stabilizers, and inadequately efficient organophosphites. Excellent protection against degradation can arise from the synergistic effects of screeners, quenchers, ultraviolet absorbers, and antioxidants [53]. To overcome the evaporation and migration problems, higher molecular weight stabilizers—which are usually polymers—can be added. These stabilizers can be produced via three methods:

i.   Stabilizer-polymer grafting;
ii. Homo-/ co-polymerization of monomers anchored with stabilizers;
iii. Incorporation of photo-rearranging polymers as additives

Sensitizers or stabilizers are commonly employed to enhance the properties of polymeric materials, especially during the preparation of nanocomposites [13]. Generally, an equilibrium between execution and operation times is required for all materials, including polymers [54]. Unlike polymers which originate from renewable resources, petroleum-based ones are cheaper to produce and frequently perform better in any application. Thus, the idea is to utilize polymers with long lives to enhance the performance of their short-lived counterparts (such as biological polymers). Ultimately, to achieve this goal, the study approach should entail the management of the production-service-waste process with respect to the three pillars of sustainability, namely Planet (environmental pillar), People (social pillar), and Profit (economic pillar).

In particular, the sustainability of bio-based polymers is a theme which has been put forward because of its significance with regard to the environment, technological development, and economic growth [55, 56]. In view of the decent potencies and capabilities of the most commonly used petroleum-based polymers, bio-based ones need to be meticulously modified in terms of properties like modulations, applications, and disposal methods so that the valorization, service conditions, and/ or discarding of the said polymers fulfill the expectations. Moreover, the aforementioned processes have to be financially and economically efficient, and environmentally friendly. The selection of suitable materials and synthesis methods is paramount in order to ensure that the applications of bio-based polymers perform well with respect to their long-term properties [57]. There needs to be a balance between the performance and processing of these polymers. Thus, the end-of-life fates of bio-based products should not only be determined with respect to the carbon life cycle, but also from the perspectives of their valorization in feedstock, conversion into distinctive materials, as well as vitality [58, 59]. In this case, the long-term properties of polymers are reflected by the durability of the materials in the presence of degrading factors such as humidity, temperature, or sunlight. The next three sections concern the energetic, biological, and material valorizations, all of which are essential to enhance the values of the polymers with respect to their expected end-of-life and performance prospects. To sum up, the current research has proposed various methods to improve the end-of-life and long-term properties. The specific purpose of this exercise was to expand the literature on the maintainable and sustainable designs of bio-based polymers [60].

Dense polymer membranes are suitable to isolate H_2 from gas mixtures at moderately lower temperature around 110 °C. The polymeric membranes are categorized into two primary groups; rubbery and glassy polymeric membranes, in which generally, glassy membranes have relatively greater selectivity with reduced H_2 flux and, standard H_2 permeability of

fundamental polymeric membranes. Polymer membranes are favorable due to their low cost [61]. Nevertheless, the polymeric membranes for H_2 selectivity and permeability compared with thick metallic membranes is much lower. In the existence of H_2S, HCl, and CO_2, they are equally essential against impurities [62]. The polymer membranes are subsequently less interesting than other dense membranes.

Low selectivity material like cellulose acetate has been used in the separation of H_2 gas for polymer-based membrane. Breakthrough in gas separation membrane material launched fresh commercial membranes based on brominated polysulfone and polyimides, with both selectivity and permeability enhancement. Polyimides, known to have small free-volume glass polymer, are currently the most commonly used material for membrane in separating hydrogen [63]. Because of high glass transition temperature characteristic, aromatic polyimides are more appropriate to be used at elevated temperatures compared to cellulose acetate and polysulfone [64].

The effective implementation of polyimide membranes in refineries for hydrogen regeneration, according to Takht Ravanchi et al. [65], is due to their characteristics of excellent stability with attractive separation variables, for example, H_2/N_2 of ca 100–200. Matrimid 5218, which is based on polyimide material, demonstrates a decent selectivity of 100 for H_2/CH_4. On the other side, as opposed to non-fluorinated polyimides, fluorinated polyimides display good H_2 permeability with low selectivity. Fluorinated polyimide, 6FDA-DDBT demonstrates 156 Barrer hydrogen permeability with the selectivity of only 80 for H_2/CH_4 while BPDA-ODA, non-fluorinated polyimide, demonstrates 1.33 Barrer H_2 permeability with the selectivity of 370 for H_2/N_2 [66]. Among the existing polyimide-based materials, diamino-modified polyimides are the most superior with an ideal H_2/CO_2 selectivity of 100 that exceeds the upper-bound line of the Robeson [7].

Due to the intrinsic physicochemical properties such as proton conductivity above a temperature of 100 °C without humidification and heat resistance, polybenzimidazole (PBI) has appeared as a prime candidate for low-cost PEMs. Due to superior thermal stability and excellent inherent selectivity of H_2/CO_2 under high-temperature settings, polybenzimidazole has been recognized to be a distinctive polymeric material in separating H_2 [67]. Although membrane use was previously regarded, DuPont developed small-diameter hollow-fiber membranes until the later seventies. Nevertheless, the output of hollow fibers of the first generation was very low to meet the economic prevalent gas separations [68]. Monsanto Co. overcomes this problem by developing multi-component hollow-fiber polysulfone membranes to recover H_2 [69]. Limiting dense and discerning fiber areas to a very tiny region significantly enhanced fiber transport. It has been effective to implement these asymmetric membranes to recover industrial-scale H_2 from ammonia purge gases.

Next, the Separex® spiral-wound cellulose acetate membranes were established by Separex Corp. with the aim of the identical type of segregation using the previous technology and the dehydration of natural gas as well as purification [13]. Cellulose acetate membranes showed better efficiency primarily due to their high resistance to impurities of hydrocarbons [70, 71]. Approaching in the mid-1980s, membrane application is frequently used to further other applications such as recovering H_2 from refinery gas recycling. Ube introduced a polyimide membrane with the finest solvent- and heat-resistance features of his moment in Japan. These membranes were first applied by Seibu Oil's Onoba City refinery.
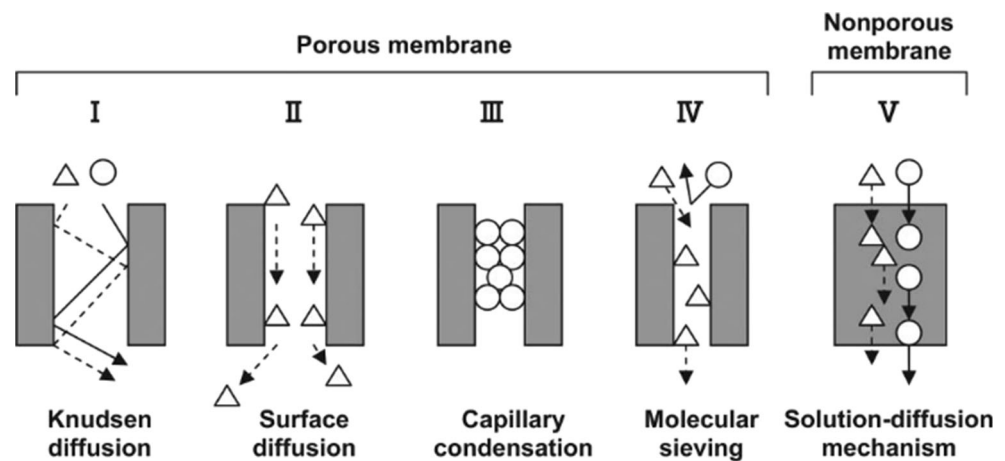
2.2 Mechanism of gas transport in polymeric membrane

Polymeric membrane can be classified into two main groups which are porous and nonporous. The mechanism for the transportation of gases via the polymeric membranes can be varied based on the difference in terms of the types of classified groups. As presented in Fig. 6, the way for the gas transportation in a porous membrane is highly affected by the morphology of the membrane which is the pore size and the size of the gas molecules. The diffusion methods in the porous membrane can be divided into main mechanisms which are Knudsen diffusion, surface diffusion, capillary condensation, and molecular sieving. In Knudsen diffusion, the pore size of the diffusing molecules collides more repeatedly with the pore wall compared to the collision with the same diffusing molecules. Different from Knudsen diffusion, surface diffusion involved the adsorption of the molecules onto the pores' surfaces and then passage from one site to another having lower concentration.

Meanwhile, in capillary condensation, the transfers of the gas molecules will occur in the presence of different rate diffusions between the pore size of the gas molecules and the pore at the wall of the membrane. Molecular sieving happened when the pore size come within the diffusing molecules, hence needing the activation energy that is strongly coordinated by the size of the molecule that has to be faced before diffusion occurs. In the nonporous membrane, the transportation of the gas molecules is arising via solution-diffusion mechanism. This mechanism involved the presence of chemical potential gradient that will initiate the diffusion process of the penetrant molecules into the membrane [72].

Henis and Tripodi constructed a resistance model (RM) in order to detail on the gas transport process that occurred in composite membrane. The porous substrate that is used are polysulfone (PSF), polyacrylonitrile (PAN), and a silicone rubber coating layer. The gas permeate passes through the membrane, corresponding to the electric current running via a resistor in series and parallel circuits [73]. By the utilization of the RM, the gas permeation pattern such as selectivity can

Fig. 6 The different types of mechanism: porous and nonporous mechanism [72]

Porous membrane — Nonporous membrane

I II III IV V

Knudsen diffusion — Surface diffusion — Capillary condensation — Molecular sieving — Solution-diffusion mechanism

be predicted. As presented in Fig. 7, the composite membrane that comprises a single dense-selective layer usually intrudes into the pores of the substrate [74].
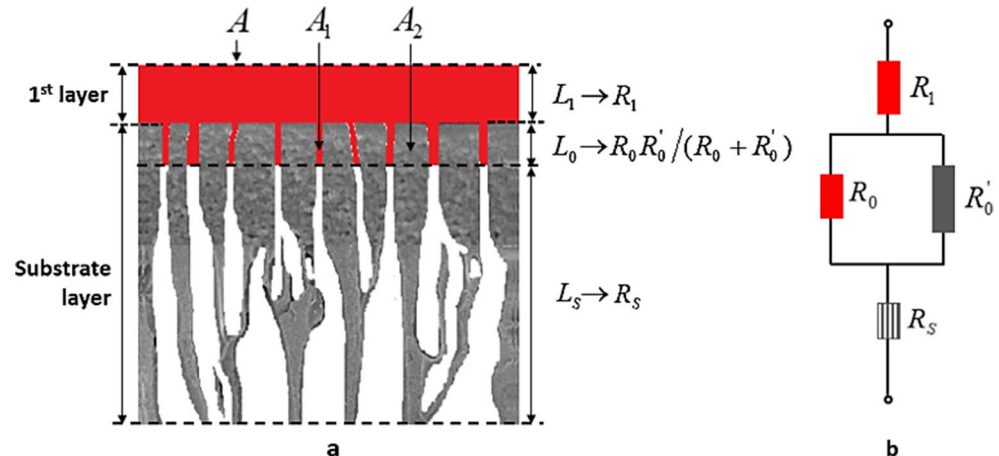
3 Polymer degradation

As part from authors knowledge, natural degradation for H_2 refers to the changes in the properties of a material following exposure to natural outdoor conditions, namely sunlight (directly or indirectly), heat, oxygen, moisture, and other factors. The types of polymer degradation are shown in Fig. 8. Microorganisms, ozone, airborne chemical pollutants (e.g., sulfur oxides and nitrogen oxides), and salt are some of the external factors that can exert a significant impact on the process of degradation. Furthermore, these environmental agents will also act on other components—such as dyes, pigments, processing additives, absorbers, and stabilizers—that reside within the polymer matrices.

Each aforementioned component is subject to environmental effects individually or in combination. Accordingly, various factors in a typical habitat—sun-based radiation, temperature, moisture, oxidative conditions, and mechanical
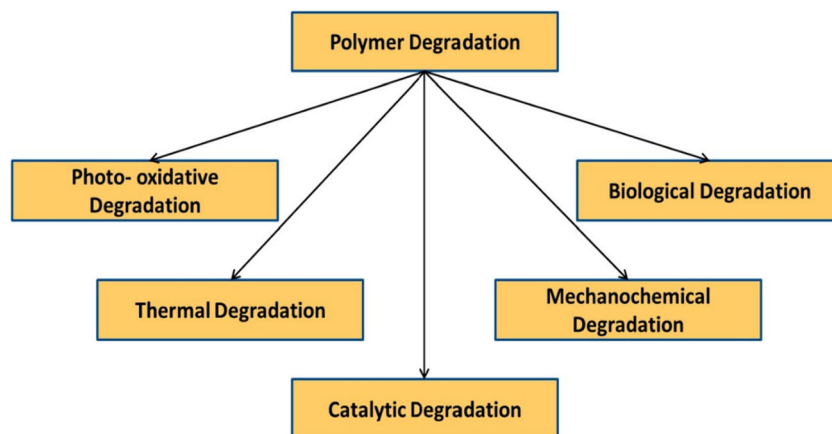
toxins—can act intelligently via a debasement procedure. Therefore, the general impact of degradation can be greatly complex. With reference to the basis above, polymer degradation is categorized into thermal debasement (heat), thermo-oxidative debasement (heat and oxygen), thermomechanical debasement (heat and stress), photo degradation (light), photo-oxidative corruption (light and oxygen), biodegradation (natural operators), mechanical debasement (mechanical stress), and so on. A polymeric material will typically experience warm, thermo-oxidative, and photograph oxidative debasements throughout its preparation and utilization. Figure 9 shows the types of degradation and stabilization pathways of polymer.

The terms "durability" and "degradation", as well as "long-term properties" and "end-of-life" of polymers, are related to one another. Degradation refers to a process which results in the deterioration of any physical property of a polymer. In general, the said process starts at the amorphous/crystalline interface, and affects the mechanical properties, thermal stability, distribution of lamellar thickness, as well as crystallinity. The distinct aspects of each term will be demonstrated with respect to the scope of the analysis in question. Although bio-based polymers are expected to perform well,

Fig. 7 **a** The cross-section of composite membranes encompassing a single dense-selective layer with intrusion and **b** the analog of an electrical circuit [74]

A A_1 A_2

1st layer — $L_1 \rightarrow R_1$

$L_0 \rightarrow R_0 R_0^{'} / (R_0 + R_0^{'})$

Substrate layer — $L_s \rightarrow R_s$

R_1 R_0 $R_0^{'}$ R_s

a b

Fig. 8 Types of polymer degradation

the improvement of their long-term properties is determined by the extent to which their strengths are conserved. It is essential to monitor and select the most effective degradation pathways to eliminate plastic waste [76]. Evidently, these two aspects should be taken into consideration during the selection of appropriate materials for particular applications. In addition, a balance between the simple end-of-life pathway and durability of a plastic product needs to be struck in order to minimize the negative impact on the environment. Instead of the end-of-life of a material, the end-of-life of a polymer should be considered instead so as to provide such products with second-life uses. This in turn will enhance the service-life and value of the polymer. A simple method to realize the above idea is by sending discarded polymers to downgraded applications, for which they will be incorporated into other materials to improve their applicability, generate energy or feedstock, or recoup carbon sources [77, 78]. The physico-chemical properties of bio-based polymers are subjected to different operations or evaluations of the applied valorization conditions. Specifically, the maintenance of the performances of the polymers, or the monitoring of the extent of degradation, will guarantee the appropriate valorization of the materials. In this case, the evaluations of the properties began with a miniaturized approach (i.e., structure-morphology), culminating in macro-response assessments (i.e., thermal or rheological properties, mechanical characteristics, interfacing with the application at the durability stage and with the environment, effects on the environmental and human well-being, release of low-molecular weight compounds during degradation, durability, as well as reenactment of service conditions).

Fig. 9 Different pathways of degradation and stabilization [75]
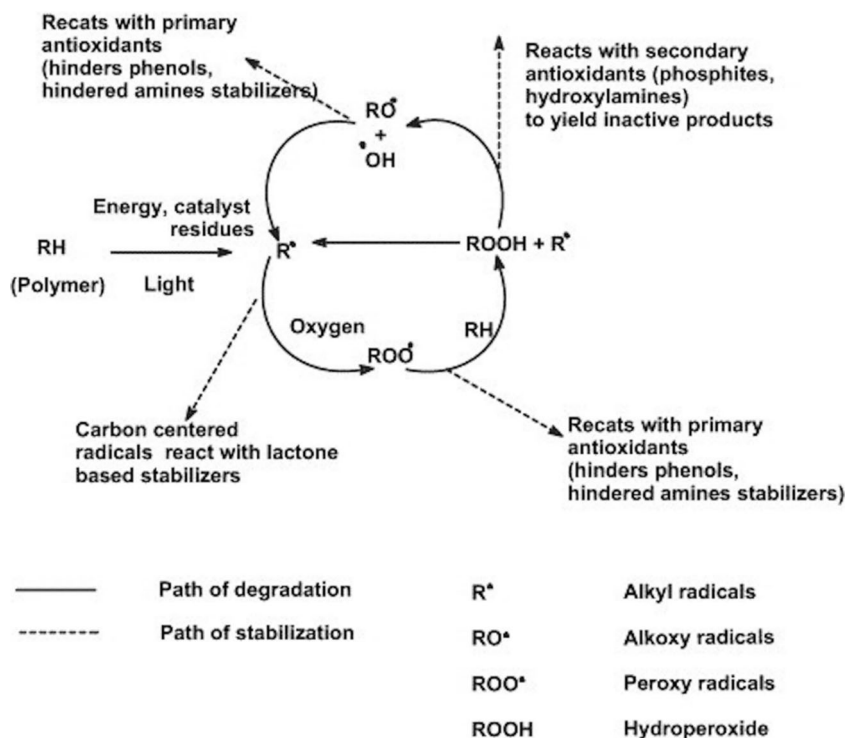
Separation capability is determined by the interactions of membrane and gas molecules which penetrate the membrane. The mechanism for these interactions is dominated by the solution diffusion and Kundsen diffusion. Polymer membrane can be classified into polymeric rubber (elastic) as well as polymeric glass (rigid). The dissimilarity is according to the temperature of the H_2 separation test relative to the polymers' temperature of glass transition (Tg). Generally, polymer membranes have operating temperatures of almost 100 °C (373 K). The membranes are rubbery as the operating temperature is above Tg, while the membrane is glassy as the operating temperature is smaller than Tg [79]. Glassy and dense membranes are rigid with low flux and greater selectivity, whereas rubber-like elastic-dense membranes have greater flux with low selectivity [80]. The smaller free volume also reduced rigid polymer chain flexibility relative to rubber polymer chain which gives outcomes of high selectivity rigid polymer. Molecules are segregated by size while favoring the passage of smaller molecules. However, with huge free volume, the rubbery polymer is extremely flexible. This means that due to the distinct condensability characteristic of gas molecules, high permeability and selectivity were influenced. Generally speaking, it favors the rejection of small permeable molecule across large hydrocarbons. Meanwhile, achieving the required capability to separate is essential in developing the polymeric material's molecular structure. Normally, highly permeable polymers are rigid with twisted molecular backbones that provide several free volume microvoids [67]. The material needs to be processed with great ease and robustness. Polymers of ester (PE), sulfone (PSF), cellulose acetate (CA), benzimideazole (PBI), imide (PI), etherimide (PEI), and other arrangements have recently been used as the basis for the primary polymers used in H_2 separation [62, 66, 81]. Based on the concept of polyimide material, the design of the structure and alteration of the chemical are taken into account in the tuning of the gas separation behavior as well as relative robustness to carry out the desired research.

3.1 Thermal degradation

In order to fully understand the concept of membrane thermal stability, there are a few main key theories that need to be fully understood. As visualized in Fig. 10, the demanding factors which establish their decisive utility are stability, durability, and processability. The continuing membrane performance endorses the reliability of operation and the sustainable of the gas performance process. Failure analysis can be practically applied as a tool to recognize the failure and can act as the prevention step to prevent any unpredictable failure [6].

Specifically, thermal degradation in membrane refers to the heat-induced deterioration of chemical compounds into smaller components which do not recombine after cooling. In the case of polymers, this process is divided into four categories:
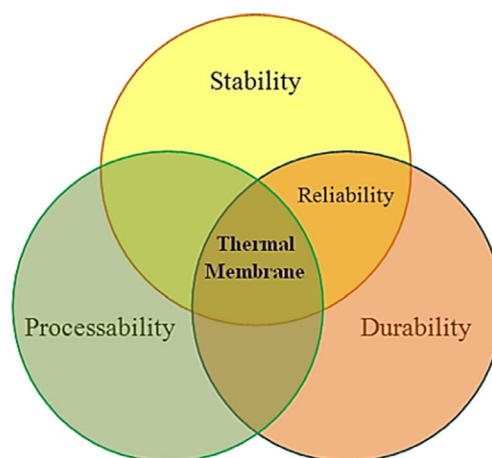
Fig. 10 The key categories that need to be taken into account to reach the thermal stability of the membrane [6]

i. Degradation occurring below glass transition temperature, which can initiate basic alterations known as physical aging;

ii. Degradation occurring between glass transition and melting temperatures, which results in the loss of dimensions owing to the transformation of the material into a more crystalline structure or the decomposition of the low molecular weight additives;

iii. Degradation occurring between melting and decomposition temperatures, which is an extremely important piece of information in ensuring the processability of second-life bio-based goods; and

iv. Degradation above decomposition temperature, which is also referred to as energetic valorization

The growing interest and utilization of polymeric materials over the last couple of decades contributed to their commercial success, apart from giving rise to creative researches on the same. Even though this scenario is encouraging for the polymer-related organizations, the immense rate of utilization of these materials worldwide poses dangers to the nature in view of the accumulation of difficult-to-dispose waste materials [82]. As indicated by a study by Achilias et al. [83], 78 wt% of all plastic wastes are accounted for by polymers like polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), as well as those which contain epoxy resins and polyurethanes. Thermal degradation is not preferred in manufacturing and application. However, polymers with high thermal sensitivity can be degraded faster. This property is highly valuable for polymer squander administration and furthermore to recoup vitality.

In view of the current challenges in landfilling and reusing polymer wastes, pyrolysis is a promising technique to overcome the issues [82]. In this study, polymeric materials were heated in the presence of oxygen under controlled conditions, thereby resulting in the breaking of the macromolecular

structure. From here, oligomeric items and even monomers of interest can be created. For instance, the monomers, dimers, and trimers of styrene can be recouped into essential items via the warm corruption of PS. The degradation pathway of polymers can be controlled by modifying the reactant decomposition processes to yield profitable substances [84]. With the existing researches on waste-to-energy innovations, it has been discovered that catalytic fast pyrolysis (CFP) was an appropriate method to specifically convert biomass into high-quality biofuel. The processing of waste plastics via CFP can enhance the aromatic yield and reduce the coke arrangement [85].

Numerous reports on the thermal degradation of different polymers (i.e., polymers which have been used commercially and the progressing ones with their diverse blends and composite configurations) have surfaced in the past few years. The type of degradation is heavily dependent on the type of polymer and many other factors. Distinctive modern analytical instruments have been utilized to decide the key factors that trigger and sustain degradation following prolonged contact to heat in a latent environment [86]. Experiments have also been conducted in air to comprehend the role of oxygen in degradation. These analyses are especially helpful in the predictions of the administration lives and highest temperatures for the safe utilization of the material. Information on the same will be important in the determination of the capacities and applications of the end products, thereby promoting a more effective utilization of the existing materials. Awareness of the unpredictability of the outcomes of decomposition and the persistence of the chemical nature of the materials post-degradation can facilitate the development of appropriate safety protocols to minimize the associated hazards.

In light of these blending investigations, the corruption pathway systems and the response energies were created [87]. Nevertheless, exact predictions of the polymeric material reactions in thermal environments are still difficult to achieve. This is because the test results remain uncertain, and that the exact mechanisms of the procedure are, as yet, obscure. Hence, a more inclusive methodology needs to be devised to describe the degradation energies of polymers. Thermal degradation of polymer composites is a much more complicated issue because the fillers frequently influence the rearrangement of the polymers [88]. With the exception of the relatively new field of nanocomposites, there is surprisingly little information on the commercial viability of the composite frameworks; the overall strengths of unfilled polymers have not been taken into consideration. With reference to waste-to-vitality innovations, additional research is needed to come up with pyrolytic fluids with higher octane values which reduce the build-up of substances. This in turn gives rise to superb materials for the delivery of gas without much need for refining. An increase in the amount of rubber in

dumps and landfills (the majority of which is accounted for by old tires) constitutes a nidus for ecological and fire hazards.

Pyrolysis of waste rubber is regarded as one of the most encouraging methods for the recoupment of significant items. The present routine with regard to the landfilling of waste polymers does not permit the recovery of the materials' esteem, apart from having natural outcomes, while modern mechanical reusing misfortune [89–91]. Hence, a more sustainable method is needed to better understand the recyclability and end-of-life issues of polymers, which would likewise build up a circular materials economy [92]. Yao and Wilkie [93] have examined the heat degradation of PS, poly (sodium 4-styrenesulfonate), PSSNa, and poly(styrene-co-sodium 4-styrenesulfonate) copolymer blends. Accordingly, they have demonstrated that the warm degradation of the blends occurs in two autonomous steps: when low amounts of PSSNa are present, there is direct inhibition hindrance of the corruption of PS. Conversely, when larger amounts of the former are utilized, there is an expanded arrangement of char which provides thermal protection. All in all, the phenomenon likely to occur when the temperature of corruption of the synthesized polymer is close to the moderately high temperature of degradation of PSSNa. Naffakh et al. [94] who examined the thermal decompositions of blends of poly(aryl ether ketone), PEEK, and a thermotropic fluid crystalline polymer (LCP), have found that the mechanisms of degradation were essentially expedited by mixing. In further detail, they have demonstrated that the mechanisms of corruption of the pure polymers were the same as those of the components of the blend. Hence, the abovementioned thermal degradation behavior was, for the most part, related to a higher corruption rate rather than an altered system.

Meanwhile, the thermoplastic polymer will become soft and formable when being exposed to a certain temperature, while heating of a thermoset destroys it outwardly going through the fluid state. In addition, thermoplastic polymers do not required any extra chemical processing before molding. It can be shaped into any form or figure to its softening point, but the shape become rigid below this point. Besides, the thermoplastic polymer can be re-shaping when they are being reheated. The main category of the thermoplastic polymer can be grouped into amorphous, semi-crystalline, and crystalline. Different types of polymers having different types of performance are shown in Fig. 11. The classification of the thermoplastic membrane is allocated based on thermal, chemical, and mechanical stability [6].

3.2 Hydrolytic and hydrothermal degradation

In the case of bio-polymer, the most established type of bio-based polymer degradation is the hydrolysis of ester linkages. Therefore, polyesters account for the majority of such
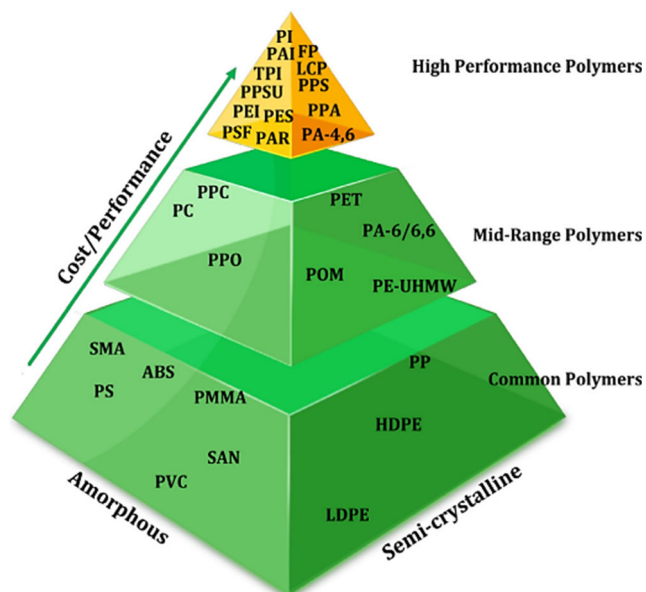
Fig. 11 The classification of thermoplastic membrane [6]

polymers in biomedical applications. There are two main ways by which biopolymers are hydrolyzed, namely passive and active methods which employ chemical hydrolysis and enzymatic reactions, respectively. Evidently, the latter is more useful in natural polymers like polyhydroxyalkanoates (PHAs) and polysaccharides. Polylactic acid or polylactide (PLA) and polyglycolide (PGA) degrade via simple hydrolysis of their ester bonds—a process which does not require the catalysis by enzymes [84, 95]. During hydrolysis, a series of overlapping stages progressively reduces the molar mass and thus, alters the macroscopic physicochemical properties. The ISO10993-13:2010 protocol is usually employed to simulate the service-life conditions of biomedical materials. In short, this method involves the exposure of materials to an analytic medium (e.g., water, human fluid simulants, or phosphate buffer solution) for different durations at 37 °C to mimic in vivo conditions. Degradation can be monitored in both liquid and solid fractions. On the other hand, for non-biomedical purposes, the ISO62:2008 (a modified water absorption protocol) can be used to accelerate the hydrothermal degradation of polymers. In this case, both water and temperature resembled the actual service conditions.

4 Polymer characteristic for ideal H$_2$ separation

Polymeric materials function as membrane materials for separating H$_2$ from other gas molecules, for example, CO$_2$, CH$_4$, or N$_2$ [96]. The yields of the membranes are determined by permeability, while selectivity contributes to the efficiency of separation. Overall, the permeability of high-selectivity membrane tends to be very low. The thickness of the membrane

with either heterogeneous or homogeneous structures as well as porous or dense structures also affects these gas separation characteristics. The membrane, meanwhile, can be either porous or dense films, consisting of mesoporous (size of pore from 2 nm up to 50 nm), macroporous (size of pore larger than 50 nm), also microporous (size of the pore is less than 2 nm). Additionally, charged or neutral membranes can be used for active or passive transport of H$_2$ molecules. In addition, for example, chemical potential, concentration stress, magnetic or electrical fields, multiple gradients of driving force can be used in conducting separation. With the exception of outstanding gas separation performance, the membrane producer must meet the requirement as follows [97].

Firstly, the process should be cost-effective and simple. Secondly, material stability in terms of chemical and physical properties required, for example, excellent mechanical properties, chemical and thermal resistance, plasticization tolerance, and physical aging resistance to ensure adequate durability and membrane robustness. Meanwhile, cost-effective manufacturing processes need to be considered for industrial execution. Among these characteristics, the chemistry of the membrane as well as structures are the key elements. H$_2$ separation membranes are expected to break free of defects within the enormous scales with outstanding mechanical, chemical, thermal robustness and high selectivity at high permeability. Only a few systems were marketed, although hundreds of membrane and polymer compositions were tested as contenders for the H$_2$ separation membrane. Improvement of the upper bound was performed between 1991 and 2008, but research on high permeability and high selectivity is still a long way to go [7, 98].

The chemical composition of a polymer determines the important robustness aspects and the quality of H$_2$ separation performance. The membrane was provided with crosslinking as well as chemical adjustment for free volume tuning, which affect the efficiency of H$_2$ separation for the dense glassy polymer. Furthermore, the microstructure and composition of membrane are essential in modulating the separation capability. Besides free volume in membrane with dense, rigid polymer characteristics, pore size tuning can be done through various approaches such as gradient porosity, fibrous structure, intrinsic polymer microporosity based on molecular free volume design as well as hybrid mixed matrix membrane with porous filler.

The mixing of at least two polymers is a typical practice in the synthesis of materials with upgraded attributes relative to their parent components. These enhanced polymers are finished by basic preparation procedures rather than costly or high-natural effect synthetic blends [99, 100]. Another approach entails the improvement of a polymeric material via the inclusion of fillers that have a fortifying impact, thereby conferring new properties to the resulting material or reducing its production cost [101]. The less component of the filler (i.e.,

large surface area) guarantees critical enhancements of a few physical properties (e.g., mechanical and thermomechanical) following the inclusion of small amounts of the filler into the material.

This method also preserves other essential properties like thickness, and processability. Obviously, it is important to attain immense scattering and attachment. For this reason, the nanofillers can be treated or adjusted; in some cases, a third additional substance is also used. A few researchers have attempted incorporate nanocomposites in polymer networks to generate materials with further enhanced properties [54, 102–105]. For the most part, these attempts revolved around investigations into the morphological similarities between the substances. Specifically, it has been reported that the uneven circulation of nanoparticles in the polymers may result in unexpected enhancements of the resulting mechanical and transport properties. This occurrence has been ascribed to the strengthening activity of the filler and the benefits of adjustments in the microstructure of the mixture. Examples of the said benefits included the refinement of the morphology, upgrading of the interfacial attachments, and development of growth morphologies. Be that as it may, the convenience of any material depends upon its degradability and sturdiness [106].

The ways by which polymeric blends degrade are difficult to anticipate based on the debasements of their individual segments. Another reason of the above issue is that both synergistic and inhibitory effects may be observed. A moderate behavior that complies with the blend rule is normal only for mixes with connections between the two stages, and macromolecules in particular. Evidently, the results of the approaching debasement are unimportant. The same was true for the miscibility of the segments. In fact, miscibility appears to assume a crucial role in the corruption of polymer mixes only on occasion.

Having said that, the debasements of both perfect and inconsistent mixes are completely different from the corruption behaviors of the individual segments. For the most part, the resulting properties of the corrupted mixes are especially difficult to predict on the grounds that they were dependent not just on the degree of debasement of the two homopolymers. Rather, the nearness of new species created from the aforementioned collaborations are crucial. Additionally, the said procedures are complicated by the reactivities of compatibilizers.

The debasement courses of single polymers should be fundamentally attributed to (1) the propagation of macromolecular radicals subsequent to the changes in certain external factors (temperature, radiation, etc.) as well as (2) the resulting reactions of such radicals with both the polymer macromolecules and oxygen. The formation of reactive oxygenated species facilitates the generation of stable macromolecules with oxygenated social affairs with extra in purposes of

enthusiasm, diminishing of the atomic weight, possible proximity of stretching and, in a few cases, improvement of the cross-connected structures [51].

Figure 12 shows the categorization of different cross-linked polymers with respect to the quality of the cross-links. The last case happens mostly in the debasement of polyethylenes. Meanwhile, most polymers generally experience a decrease in their nuclear weights. The presence of two polymeric stages in a blend results in a change in the otherwise unpredictable arrangement. Overall, the macroradicals of the two sections (in two fragments of the blend) formed during the beginning of the debasement process may react between themselves or between the macromolecules of subsequent stages.

The history of polymer blends is associated with the polymers themselves. The mixing of two or more polymers is a cost- and time-saving process that produces new polymeric systems with unique properties unlike those of their individual components [12, 108–110]. However, the polymers always formed immiscible and incompatible blends with unstable morphologies as well as poorly distributed and poorly adherent particles in the matrices. Thus, the immiscible polymer mix needs to have its interfacial properties modified via compatibilization to reduce the interfacial tension coefficients [102, 111, 112]. Recently, nanoparticles have been used as compatibilizers to modify the morphologies of the polymer blends [113, 114]. Despite the growing industrial and academic interest, there are very few studies on the degradations of these polymeric systems. La Mantia [115] has reviewed polymeric blends in terms of thermal, thermomechanical, and photo-oxidative degradations of the same. Subsequent reviews on the thermomechanical degradations of these systems have been published by La Mantia and Valenza [116], followed by Matusinovic and Wilkie [117].

5 Characterization technique for polymer degradation

The thermolysis of the covalent bond in the molten polymer that created macroradicals initiated the thermal degradation reaction of the polymer. This distinctive reaction of the polymer will change the volume and the molecular weight of the
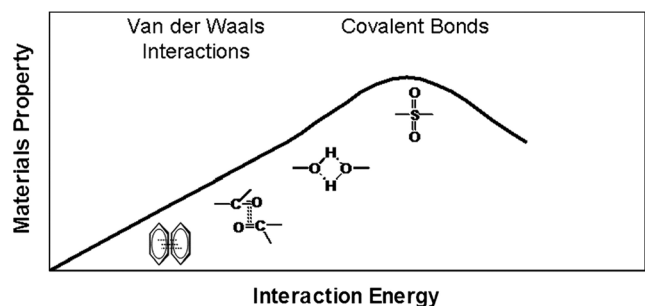
**Fig. 12** Strength of crosslinking interactions [107]

membrane. The changes that occur during the degradation process via thermal reaction in the polymer membrane can be analyzed via mathematical calculation that combines elementary reaction and related elements that can be examined in the rate of volatile products and residual weight of the molten of nonvolatile components. Nonvolatile and volatile products are derived from the intermolecular and intramolecular hydrogen abstraction (back-biting) of terminal macroradicals trailed by β-scission.

There are numerous methods for the evaluation of thermal degradation of polymers. The simplest one entails the use of ovens to detect the presence of impurities (e.g., moisture) without resulting in the decomposition of the main polymers [11, 18, 19, 118]. From there, thermal degradation is assessed in terms of molar masses and physicochemical properties. To evaluate thermal degradation (at temperatures up to the melting point or glass transition temperature), crystallinity, crystallization, as well as cold crystallization temperatures or the crystallinity degree, differential scanning calorimetry (DSC) is a feasible method. However, DSC is not suitable for the induction of thermal degradation at sub-glass transition temperatures since it consumes a lot of time. Rather, dynamic mechanical thermal analysis (DMTA) is a more appropriate method to test the impact of temperature on polymers [19]. Specifically, it can be used to evaluate the mechanical properties of polymers far below the melting temperatures by means of creep experiments. Finally, thermogravimetric analysis (TGA) is a very useful method to analyze the thermal decomposition of polymer-based materials in either inactive or oxidative conditions [63, 119, 120].

The mixed matrix membranes (MMMs) that is reinforced with zeolitic imidazolate framework-8 (ZIF-8) has been successfully fabricated displayed an outstanding H_2 separation performance. The H_2 permeability reached 1206 Barrer, H_2/N_2 selectivity of 22.3, and H_2/CH_4 selectivity of 25.7 [121]. Thermal treatment is one of the methods that can be used in order to eradicate the interfacial voids that is present amid the polymer phase and inorganic fillers in MMMs. The thermal stability of the fabricated ZIF-8 was analyzed by TGA is illustrated in Fig. 13. From the findings, it was found that the ZIF-8 is stable up to 500 °C with only small of 5% weight loss.

In other approaches, Strugova and groups fabricated novel metal-based polymer composite materials for H_2 separation that contain $LaNi_5$ and polyethylene (PE) [122]. The preparation of the membrane was prepared by varying the filler concentration that containing 0, 10, 50, and 70 weight percent (% wt.) of $LaNi_5$. The fine powder form of $LaNi_5$ was prepared via hydrogenation-dehydrogenation cycles is illustrated in Fig. 14.

In terms of thermal stability of the fabricated $LaNi_5$-PE membrane, the method of DSC was employed. The obtained result that is presented in Fig. 15 discovered that the PE/$LaNi_5$
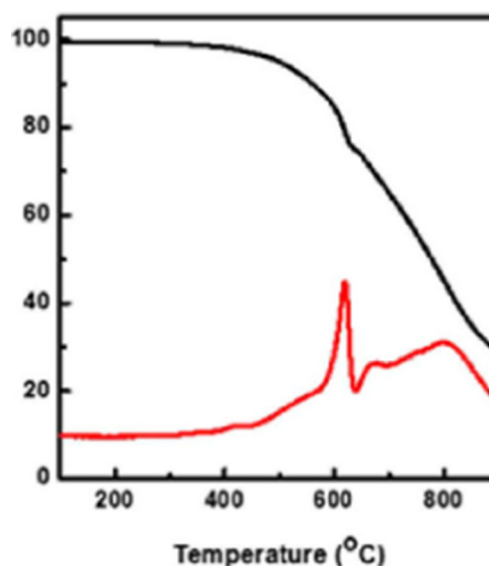
Fig. 13 TGA curve of ZIF-8 crystal under N_2 (weight percent (black) and first derivative thermograms (red)) [121]

stable up to 120 °C. In addition, no observable thermal effect can be seen related with the chemical reaction within the temperature range. Meanwhile, for composite membrane, there is a noticeable peak due to the PE melting that is swung to lower temperature. This alteration occurred owing to the thermal pressing accompanied by the rolling process that directly alters the degree of crystallinity of the PE.

6 Membranes for H_2 separations

Due to cheap and uncomplicated manufacturing as well as processability, polymeric membranes are more desirable [123]. Although there are other inorganic membranes with the superior performance, polymer membranes are the present predominant commercial membranes. In gas separation, conventional polymeric membranes are mainly consisting of the dense membrane with the permeation of gas molecules across these membranes as per the solution-diffusion mechanism. H_2 is kinetically preferable owing to the small kinetic diameter, whereas CO_2 is thermodynamically preferable in favor of its high ability to condensate. This contention is resulting in unparalleled complications in the process of creating dense polymeric membranes that are extremely selective according to the H_2–CO_2 separation solution-diffusion mechanism, regardless of either CO_2-selective or H_2-selective membranes [96]. The combination of diffusion selectivity enhancement and decreasing selectivity solubility is efficient in attaining elevated selectivity of H_2/CO_2 for H_2-selective polymer membranes. Glassy polymers, which are mainly affected by their rigid framework as well as narrow free volume dissemination, are an illustration of outstanding material for membranes. Polymer membranes with such structural characteristics are slightly comparable to molecular sieving
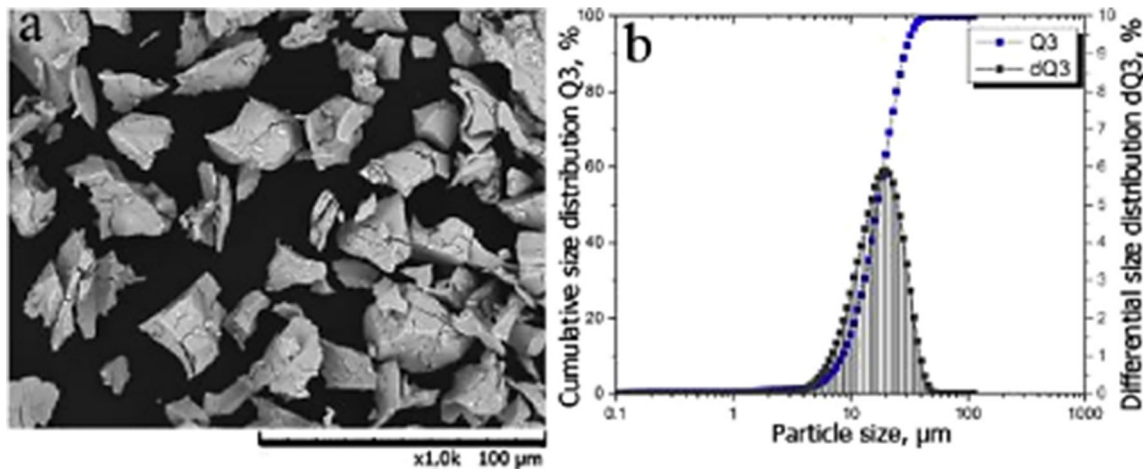
Fig. 14 SEM images of LaNi$_5$ which undergo hydrogenation-dehydrogenation [122]

inorganic membranes [7]. The present emblematic membrane materials in H$_2$/CO$_2$ separation are polybenzimidazole (PBI), polyimide (PI), and their derivatives. In addition, textile rubber (TR) polymers obtain increased interest for H$_2$ purification despite being a comparatively fresh material for membrane application [124].

The membrane is engineered in H$_2$-selective membranes with H$_2$ as the main component in the permeate while other components in the mixture of gas remain in the retentate. As described in the previous section, solution-diffusion is the primary transportation mechanism in polymer membranes, so membranes are developed to make the best use of these
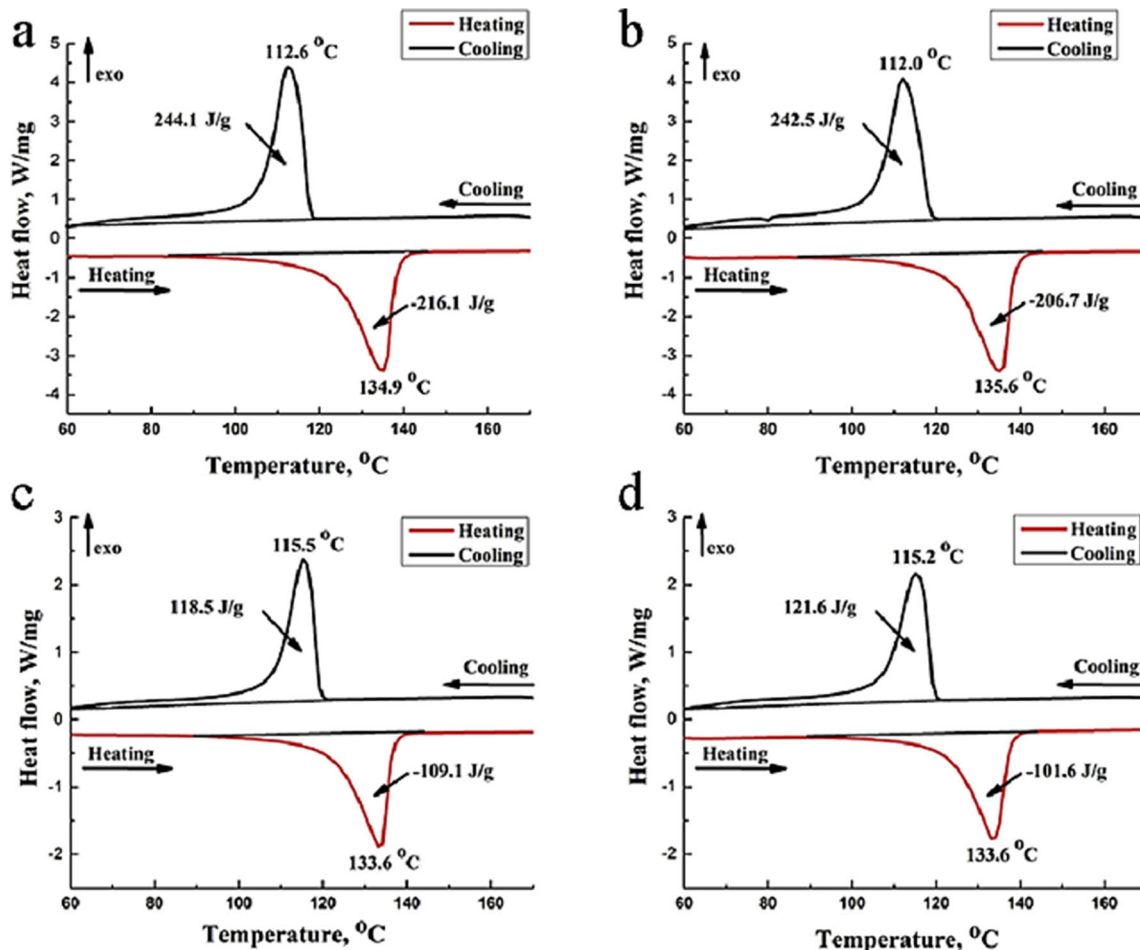

Fig. 15 DSC of the PE powder (**a**), the plain PE membrane (**b**), the PE/50% LaNi5 composite (**c**), and the PE/50% LaNi5 membrane (**d**) [122]

two primary parts. Although H_2 has almost the smallest gas molecule size, its tiny size adds to its high diffusivity feature while also reduces critical temperature compared to most gases [11]. Its low critical temperature shows its condensability, and it tends to be much lower in solubility. The objective of an H_2-selective membrane is to manipulate the high diffusivity features of H_2 and to restrict the outcome of reduced solubility. The membrane may be designed with its solubility selectivity, which is prone to more condensable compounds to be reduced, according to the intended separation.

Furthermore, the material can be chosen to complement H_2's generally high diffusivity. There have been numerous quantities of permeation research involving H_2, but the separation that can be accomplished through solution-processed capable polymer membranes is restricted even with the present advancement of polymer science. Robeson suggested in 1991, the concept of an "upper bound" trade-off between selectivity and permeability [98]. This "upper bound" offers a notion of selectivity that can be achieved for the presumed permeability as the polymeric membranes were used for the separation of gas selected. Upper bound for H_2/N_2 separation is recognized through numerous poly(methyl methacrylate)s at low permeability end of H_2 as well as by poly(1-trimethylsilyl-1-propyne) (PTMSP) for the high permeability of H_2. A large quantity of research is designed to be extremely efficient in the growth of gas separation membranes; however, the "upper bound" developed over 15 years ago is still being used.

Currently, membranes can presently be developed from polymers with a range of permeabilities as broad as several levels of magnitude, but distinct technology is needed when characteristics exceeding the upper bound are used. The use of cross-linkable polymers is tailored to improve the efficiency of polymer membranes [66]. In some conditions, cross-link inclusion in polymers shows exceptional selectivity development. However, in adapting such method using old-fashioned solution handling methods, complex issues would be counted. Construction would include post-formation cross-linking with the capability to increase processing expenses for large-scale execution considerably. To validate the practicality of its extensive use, it is necessary to concentrate the study on overcoming these issues. While the recent development of accessible membrane materials mentioned in the patent literature, progress in advancing membrane separation shifts to building highly efficient membrane processing as well as membrane systems. The goal of these works centered on H_2-selective membranes is to use the available engineering technology to find economically efficient membranes for gas separation.

Due to the extremely high diffusion coefficient of H_2 compared to other molecules with the exception of He gas, the separation of H_2 from highly supercritical gases, for example, CO, N_2, and CH_4 could be efficiently accomplished by polymeric membranes. Although the aspect of solubility is

unfavorable for H_2, the impact of diffusion dictates generally providing high selectivity. For instance, some new rigid polyaramide and polyimide membranes have a selectivity of H_2/CH_4 around 200. The most complex but also a significant task for scientists is to scale-up H_2 membrane technologies. Developing small-scale membranes with high research quality is cost-effective as it is easy to ignore failed units. Rejecting failed large membranes is therefore costly, the vital challenge to overcome this situation is to use large surface areas to prepare high-quality fused membranes into high-temperature sealing process components. Nevertheless, even with outstanding separation performance, the industrial application was discovered to be very scarce. Extremely high fabrication costs make dense metallic membranes suitable for only small-scale applications, for example, the electronics industry, which requires a tiny quantity of ultra-high-purity H_2.

Of late, polymers have garnered a lot of attention owing to certain reasons. One simple example is the development of inflatable rubber tires. This would have been unlikely to happen without the use of natural or later, synthetic rubber as an energy-absorbing component. Moreover, materials like plastics have replaced some traditional materials as packaging in view of their superior physical properties (toughness and strength), lightness and barrier properties. Additionally, plastics have the ability to protect consumables against degeneration at low cost, thereby leading to improved distribution of foodstuff to the extent that plastics are now indispensable in modern retailing [36, 125]. Plastics are also more energy-efficient as compared with traditional materials [83, 126]. Relative to paper, the efficacy of plastics like polyethylene in protecting goods is around 1 to 2 by weight, which greatly reduces the consumption of paper and hence, deforestation rate [83].

However, the volumes of waste plastics, synthetic fibers, and rubber pose an increasingly serious problem to the disposal authorities. It used to be relatively inexpensive to dispose of domestic and industrial wastes in holes in the ground at the peripheries of towns and cities. Unfortunately, reductions in the number of such sites, coupled with the increasing bulk of the wastes, have led to an unacceptable increase in the cost of transporting packaging wastes to landfill sites. There is also increasing awareness that societies should treat wastes as a resource by recycling the same into useful products rather than by burying them. Accordingly, in developed countries, it has become a responsibility for the producers of packaging to recover and recycle such materials that would otherwise have ended up in landfills [127].

It is now accepted, for reasons that will become apparent in the following discussion, that the term "recycling" needs to be broadened to not only include reprocessing or mechanical recycling, but also other methods for the conservation of the materials' intrinsic values (e.g., energy- and biological-recycling). It is likely that hitherto the end of the second

decade of this century, domestic and industrial wastes will be reused by means of a combination of these methods, and that only wastes with little or no potential value will be disposed of at sanitary landfills [83, 127, 128].

7 Photodegradation and stabilization

The functions of materials depend on their durability in the operating environment and the extent to which they interact with the environmental elements [129]. Therefore, information of the degradation and stabilization of polymer-nanocomposites are very crucial from the scientific and industrial perspectives. However, there are limited studies on these aspects. Only with an understanding of the mechanisms of degradation of the materials can the products' service lives be prolonged. Nowadays, polymer-clay hybrids, which are being used in outdoor applications, are exposed to UV rays and other undesirable environmental aspects. With reference to outdoor applications, it is especially imperative to take into account the resistances of the materials to photo-oxidation. Evidently, even when polymers are subjected to ordinary utilization conditions, photo-oxidative degradation will still occur, which in turn leads to the general deterioration of their macroscopic properties because of the variety in molecular weights, compound structures, and morphologies [130].

The concentrations of the blends have an influence on the photodegradative behavior of a polymer mix. Evidently, these behaviors may not resemble those of the pure parts, connections among the distinctive species in the blends amid degradation and among the degradation items can happen. These chemical responses can either speed up the rate of degradation of the pure components or stabilize the impact [125]. The additional substances are not regularly connected in the event of the photostability of polymer blends and as such, it is hard to estimate the photostability of the polymer blends with reference to the photoresistance of the unmodified parts. The photostability of PVC has been enhanced by its mixing with excess poly(vinyl alcohol) (PVA) [115]. Also, it has been demonstrated that the photostability of PVC/PVA blends was greater than that of unmodified PVC, even though both materials were less photostable than PVA. Specifically, in PVC/PVA blends, the number of carbonyl compounds was lower than the estimation derived from the additivity rule. Hence, this suggested that photo-oxidation prevented the formation of C=O to some degree in the blends. As a matter of fact, the photodecomposition of PVC/PVA blends relies on their connections between the segments.

The abovementioned negative impact was attributable to the way by which Cl radicals formed during the photodehydrochlorination of PVC react with the tertiary H molecules in the polystyrene of the MBS (one of the modifying agents used to improve the plastic properties) copolymer.

The molecules then enter the poly(methyl methacrylate) (PMMA) chains of the MBS copolymer to initiate the depolymerization of MBS. It has been reported that MBS hastened the photo-oxidation of PVC [131]. Apparently, peroxides break down into carbonyl and hydroxyl groups since the polybutadiene of MBS effortlessly forms peroxides in the presence of O_2. The accumulation of carbonyl groups in MBS can lead to the photoinitiation of PVC, thereby speeding up photo-oxidation. It is extremely cumbersome to predict the degradation behavior of a polymer blend with respect to the properties of its pure components. The concentrations of the blends, in addition to the presence of a compatibilizer, can influence the degradation behavior of a polymer mix. As such, the behavior can have variable courses of corruption of the unadulterated segments since communications between the distinctive species in the blends and degrading substances take place during corruption. In this way, regular connections between the added substances are unlikely to occur during the degradation of polymer blends. This is in view of the fact that the rate of corruption of a polymer blend can be higher, equal to, or lower than that of the unadulterated parts.

8 Importance of durability/degradability of polymers

According to some researches, the main outcomes of nanoscience and nanotechnology did not live up to their potential in terms of economic returns. While nanotechnology is an interesting field, a lot of claims about its business potential are worryingly important [129]. However, there will be expectations when the advantages and limitations of new nanomaterials surface. The usage of nanomaterials in commercial products raises the argument as to whether the environmental and social effects of nanotechnology outweigh its benefits [132]. Even though studies have been conducted on the toxicological and environmental impact of nanomaterials, there are no guidelines to quantify these effects. As such, researches on the durability/degradability of the polymers with nanoparticulate systems may provide an insight on their benefits and limitations. The aim of nanotechnological advancement is to develop new polymeric materials; for example, the utilization of clay minerals and carbon nanotubes to enhance their physical, mechanical, as well as thermal properties. In a few cases, nanoparticulates are embedded in polymers as "nano-additives" to enhance the polymers' degradation and stabilization. This exercise may increase or decrease the polymers' stability and interactions with respect to their chemical nature. Hence, future studies should focus on the degradation of nanoparticles like clay, carbon nanotubes, metal oxides, and metal salts in their respective environments.

Since nanoparticles have large surface areas, they can interact with polymers efficiently. Accordingly, new

nanocomposites will possess enhanced physical, mechanical, and thermal properties, in addition to better durability. To realize the potential applications of nanoparticles in different polymers, the degradation, durability, and toxicity of the polymer-nanoparticulate systems have to be assessed under various environmental conditions. The degradability and durability of polymer blends will usually determine their feasible application [133]. Also, the degradation behavior of each polymer blend differs with respect to their blend compositions. Likewise, the degradation pathways of polymer blends differ from those of pure components owing to the interactions between different species in the blends and between the degradation products. These interactions may induce either more rapid or more stabilized degradation rates as compared to those of the pure components. Hence, the properties of individual compounds cannot justify or predict the degradation behaviors of polymer blends.

Environmentally, biodegradable polymers have very important roles in environmental protection as well as waste management in the polymer industry. Evidently, these aspects have often been overlooked or neglected when environmental issues pertaining to the disposal of polymers and plastics were evaluated in general. In order to become a biodegradable polymer, clear definitions and test protocols are paramount. The applications of these polymers are becoming more diverse owing to an improved understanding of their degradation behaviors and morphological properties (i.e., pore size and volume). Despite the sufficiency of information in these aspects, further researches into these materials are needed to tackle the issues that are related to their degradation rates, mechanical characteristics, biocompatibility, and tissue regeneration capability. Novel and innovative methods for the fabrication of the polymers have generated promising results in terms of their mechanical resistance. On the other hand, the incorporation of bio-ceramic additives in polymers helps researchers predict the degradation rates and bioactivities of the composites. Many biomolecules for encapsulation into biodegradable polymers have been identified through tissue repair and regeneration researches. These findings will help determine the potential outcomes for the usage of the materials in biomedical and pharmaceutical applications, as depicted in Fig. 16 [134].

The fields of nanoscience and nanotechnology constantly expand the applications of science and technology [135, 136]. Similarly, the polymer-nanoparticle/-nanocomposite field is generating more interest as researchers begin to focus on the enhancement of the materials' structures. Since polymer nanocomposites are becoming a growing trend in the field, studies on their degradation rates and durability under various environmental conditions are highly crucial. Nanoscience and nanotechnology comprise materials whose dimensions are in nanometers. The combination of physics and chemistry give rise to novel nanomaterial properties [137]. In terms of chemistry, nanomaterials can be associated with colloids, micelles,

and polymeric molecules [138]. Apparently, buckytubes, silicon nanorods, and semiconductor quantum dots have become the highly interesting classes of nanostructures. As for physics, nanoscience can be associated with quantum behaviors such as electronic and photonic behaviors. Meanwhile, biology and biochemistry are also related to nanostructures. In fact, the most important structures in biology are nanostructures [139]. Legit reasons for the development of multidisciplinary research have been reported by Whitesides and co-workers [140]. In addition, nanomaterials have exerted an impact on the industries, as reflected by the increase in production of ceramics, chemical polishing agents, cosmetics, and many more. The manufacturing of many types of nanoparticles has resulted in the development of new nanomaterials and devices [141]. For instance, clusters, nanoparticles, nanowires, nanotubes, polynucleotides, and functional supramolecular nanostructures are now being used as building blocks of nanoelectronic devices as well as circuits [142].

Synthetic polymers are currently replacing inorganic materials (i.e., metals) and natural polymers (i.e., fibers) [6, 54, 143]. Flame-retardants are added to these synthetic polymers to counter their high flammability. Owing to restrictions in the use of halogenated flame-retardants, alternatives such as inorganic nanoparticles have been used since they can enhance the physical and mechanical properties of the polymers as well. Nanocomposites have been incorporated into polymer matrices to produce polymeric materials with the desired properties. Most researches have focused on the development of materials development and their relationship of structural properties. Yet, the functions of the materials are dependent on their durability and interactions with environmental parameters [144]. Hence, knowledge of their degradation rates and durability under different environmental factors is important. Polymer-nanocomposites that are embedded with clay minerals (layered silicates) are of great interest. Accordingly, there
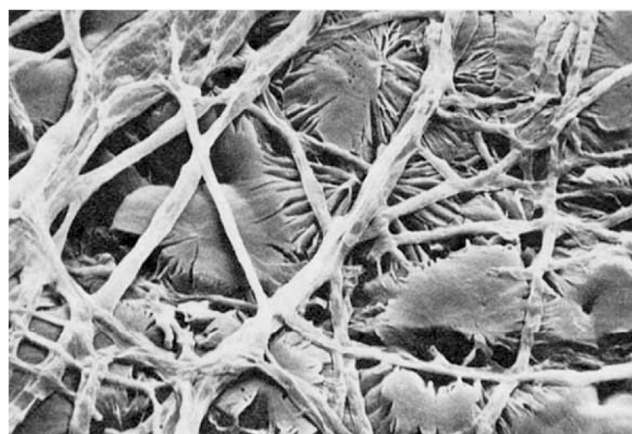
Fig. 16 Biodegradation of PCL by *Penicillium funiculosum* showing areas of severe biodegradation near mycelium. Complete degradation of amorphous and crystalline regions seen; magnification 1080 × [134]

Fig. 17 Schematic representation of the postulated cross-linked polymer structure [151]
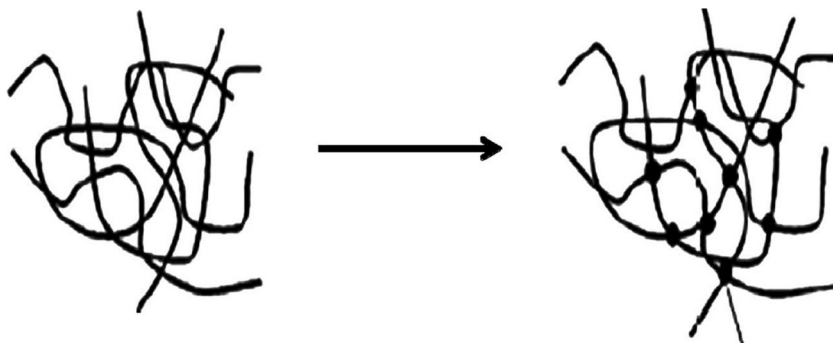
exist reports of their durability under various environmental conditions (thermal and photo-aging) [145, 146].

Numerous materials have been used to treat diseases, thereby leading to the emergence of biomaterials which are utilized in biological systems to repair, enhance, or replace any tissue or organ. Biomaterials can take the form of metals, polymers, ceramics, and composites [147, 148]. Nevertheless, the usage of metals as biomedical implants has raised concerns on stress-shielding and biological complications in view of corrosion [149]. Ceramic-based materials such as calcium phosphates are used in musculoskeletal, oral, and maxillofacial applications. However, their brittle and difficult-to-fabricate natures have limited their usage [150]. Meanwhile, polymers are macromolecules which contain monomers of linear, branched, or cross-linked structures. Figure 17 shows the schematic representation of the postulated cross-linked structure of a polymer.

9 Conclusions

In summary, the information of degradation and stability of polymer are crucial in order to ensure its practicability to be applied in various applications can be enhanced. Therefore, the in-depth understanding of degradation mechanism of the polymer under specific condition is beneficial by gaining information for further modification of physical and chemical properties. While the use of polymeric membranes has been effective in large-scale H_2 regeneration, rooms for enhancement for these systems are still available. Membranes are particularly desirable and useful with enhanced productivity, and selectivity also enhanced resistance to hydrocarbons or other compounds as well as aggressive streams of feed. Cross-linkable polymers show huge potentials in solving certain problems. The efficacy of polymeric membranes under certain conditions can be enhanced by further improvement in the region of membrane processing and implementation. Directing this study to highly specific applications allows the membranes to participate actively in the H_2 separation development industry. The use of membranes in the recovery of H_2 comes with another huge obstacle which increases the cost of recompression owing to the manufacturing of purified H_2 by traditional membranes in low pressure permeate. Some major technical problems need to be resolved before implementing some of the new materials developed; however, the polymer membranes for H_2 separations have a promising future with outstanding growth prospects. However, obtaining data from experimental analysis in the effort to understand the fundamental understanding on degradation, durability and stability is still insufficient for H_2 separation. Therefore, the requirement on theoretical study based on modeling and simulation would give the researcher a clear picture on the fundamentals behind those arising issues. The exploration on the research regarding the improvement, durability, and stability properties of the polymers can be realized by adopting the nanotechnology aspect especially in self-healing polymer structures and integrity. This self-healing properties of polymer can open up a new versatility of the polymer material to be applied in various application where the half-life of the polymer, either synthetic or bio-based, are becoming a critical factor for its commercialization.

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