APPLICATIONS

CONTRIBUTORS

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DISPERSION OF FINE SILICA PARTICLES USING ALKOXYSILANE AND INDUSTRIALIZATION

1. Sol–gel hybrid

Development of composite materials that have the properties of rigid light plastics and hard heat-resistant ceramics is a key objective of R&D in nanotechnology together with the preparation of nanocomposites by the layer intercalation method and nanofiller dispersion method [1–3].

A recent technology called the sol–gel hybrid method enables the mixing of plastics and ceramics in the nanosized range. The sol–gel method is used to produce a metal oxide thin layer by hardening metal alkoxide represented by alkoxysilane [TMOS (tetramethoxysilane) or TEOS (tetraethoxysilane)] as shown in Fig. 1.1. When this sol–gel hardening reaction takes place in a selected melted polymer or polymer solution, the growth of the siloxane bond by the sol–gel hardening is hindered by the polymer and consequently the hardened composite material with the nanosized silica particles dispersed in the polymer is obtained, which is called a sol–gel hybrid. Principally, it utilizes the interaction between the silanol group (Si-OH) generated in the process of sol–gel hardening and the hydrogen bond in the polymer [1, 2]. The composite material made by the sol–gel method is completely transparent and does not look like a mixture of different kinds of materials. Therefore the terminology "hybrid" is applied for this material rather than "composite".

2. Molecular design

The finer the ceramic particles dispersed in the matrix polymer in the composite materials, the greater the interface between both the materials inversely proportional to the particle size and the more significant its effects on the properties of the composite materials. For this reason, we examined the hybrid by sol–gel

method for developing a molecular hybrid dispersed with silica particles smaller than polymer chain length.

For the sol–gel hybrid, the kinds of applicable polymers are restricted to those soluble to alcohol or water having strong interaction with the generated silica. In the forming process of the sol–gel hybrid, the sol–gel hardening reaction takes place at competitive speed considering the evaporation of the solvent and the hardening of the polymer, the relative speed of which is affected by environmental changes in the kind of solvent. The hardening conditions and thickness of hybrid material etc. determines the quality of the hybrid materials, namely the dispersion state of silica. For this reason, it is difficult to utilize the sol–gel hybrid for various industrial applications with constant quality [1, 4]. Therefore we aimed at developing a hybrid method by which anyone can easily obtain good dispersion of silica for diverse sorts of polymers.

Plastic materials become harder and were brittle but gain in heat resistance when ceramic materials like glass are mixed into them. By mixing these different kinds of materials, the advantages and disadvantages of each material can be reflected in the properties of the composite material. Our research target was not the preparation of composite material of polymer and silica having arithmetically averaged properties but the creation of new material with the advantages of both the materials in consideration of individual applications.

The site selective molecular hybrid method developed was a hybrid method, which overcomes each of the above-mentioned problems of conventional composite materials. As shown in Fig. 1.2, by a site selective molecular hybrid method, an alkoxysilane compound is polymerized to produce polyalkoxysiloxane with a functional group like a glycidyl group. Using this functional group, polyalkoxysiloxane is introduced to a certain position of a polymer, producing an alkoxysilane-denatured polymer [5].

At the site of polyalkoxysiloxane, a sol–gel hardening reaction takes place like the monomer to generate silica. By covalent bonding of the alkoxysiloxane with the polymer by their prior reaction, the hybrid technology can be applied to various kinds of polymers and realize good stable dispersion of silica, which is barely affected by environmental parameters such as the film thickness and the hardening conditions.

The most important advantage of the site selective molecular hybrid method developed here, is that the structure can be designed to suit the applications (Fig. 1.3). In a similar manner used by polymer
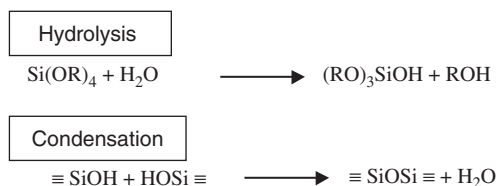

Hydrolysis

$$Si(OR)_4 + H_2O \longrightarrow (RO)_3SiOH + ROH$$

Condensation

$$\equiv SiOH + HOSi \equiv \longrightarrow \equiv SiOSi \equiv + H_2O$$

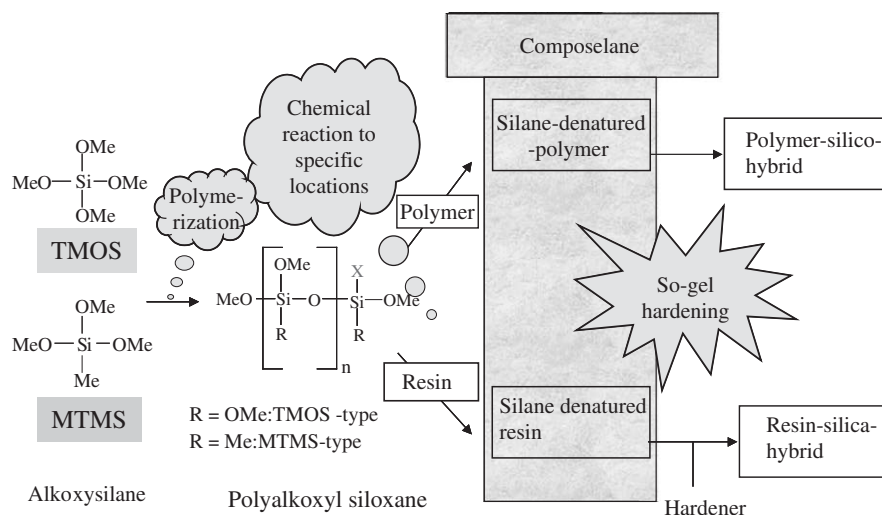**Figure 1.1**
Sol–gel curing reaction.

Figure 1.2
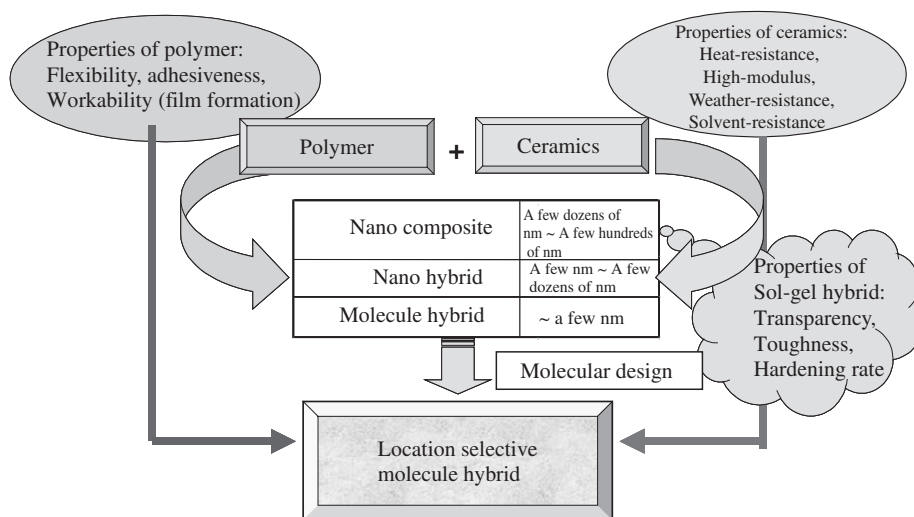Process of location selective molecular hybrid method.

Figure 1.3
Advantages of location selective molecular hybrid.

scientists to control the bulk properties by designing the kind and arrangement of monomers, the position of silica is designed by the hybrid method regarding the generated silica as a kind of monomer that has bulk properties meeting the customers' requirements for each application.

Silica, sufficiently smaller than the polymer chain length can produce hybrid materials having the advantages of both materials by modifying the specified site of the polymer effectively and minimizing the influence on the other sites.

The polymer–silica hybrid material commercialized by Arakawa Chemical Industries, Ltd. for industrial use called "Compoceran" is a product developed using this site selective molecular hybrid method [5].

3. Unmeltable plastics: epoxy resin hybrid

The properties of polymer materials are heavily deteriorated when the temperature exceeds *T*g (glass transition temperature) and is softened. In addition, there is increasing need for heat-resistant and flame-retarded epoxy resins in advanced fields such as the electronic device industry as halogenated epoxy resin may become unusable because of environmental issues.

To improve the heat resistance of an epoxy resin hybrid, silica was introduced at the heat-sensitive site of epoxy resin by hardening the alkoxysilane oligomer as shown in Fig. 1.4. This process realized the disappearance of *T*g of the hardened material (Fig. 1.5), increase in the decomposition temperature and reduction of the rate of thermal expansion [6].

Additionally, owing to the advantages of the low dielectric constant and good adhesiveness with inorganic substrates of silica, this hybrid material is utilized as a base material for various industrial applications. As for the electrical insulation material related with the printed board, its high heat-resistance and good electrical insulating property are highly evaluated and used for resist ink, electric resistant resin between the build-up board layers and reinforcing materials.

For semiconductors, this hybrid material is being used as a heat-resisting component for anisotropic electroconductive film (ACF). Concerning the coating material for non-adhesive materials, the hybrid material is utilized as undercoating paint for repairing Japanese roof tiles and as a hard coating material for the polycarbonate used for car ports because of its high adhesiveness and anti-yellowing performance.

Application of the hybrid material to the anchoring agent for hot-dip galvanization has the great environmental benefit of avoiding the waste fluid produced in
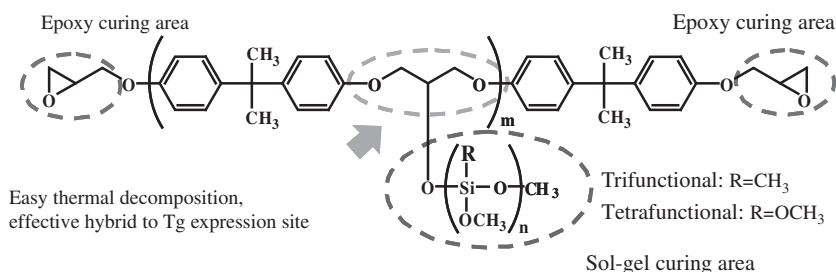

Figure 1.4
Chemical structure of silane-modified epoxy resin (Composelane E).

Hardener: DICY Curing condition: $100°C \times 30$ min $+ 170°C \times 2$ hours
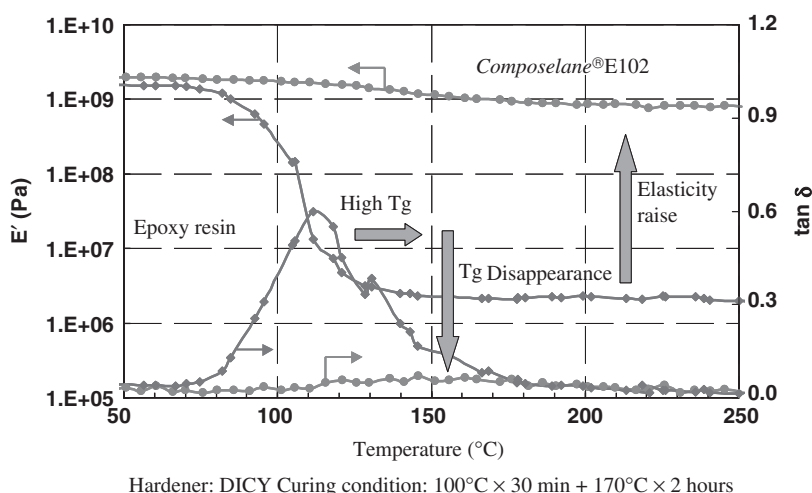
Figure 1.5
Heat-resistance of epoxy resin–silica hybrid (DMA).

chromate treatment. In the field of liquid crystal display, consumption of the hybrid material has increased as the sealing material due to its high heat-resistance and adhesiveness onto glass substrate and is being investigated for use as the protection coating for color filters.

Furthermore, three-phase hybrid consisting of epoxy resin, silica hybrid and liquid polymer phases has also been developed by this method and commercialized as adhesives for flexible printed boards with high heat-resistance, adhesiveness and flexibility.

The water absorption, electric property and mechanical strength are controlled by adjusting tetramethoxysilane and alkyltrimethoxysilane as raw silane compound. In addition, bisphenol and novolac for epoxy resin are also in the product line to meet diverse customer requirements.

4. Tough resin: hybrid of the phenol resin system

When the novolac phenol resin used as a hardening agent for epoxy resin is combined with silica, it develops mechanical toughness as well as disappearance of *T*g as the epoxy system by the introduction of silica, although it is not superior to the epoxy system in terms of the low rate of thermal expansion and the decomposition temperature [7].

These phenol-system hybrids are commercialized as the material for loudspeakers, taking advantage of its heat-resistance, flame retardancy and mechanical strength.

5. Soft silica hybrid: hybrid of the urethane system

The specified orientation of the silica site is essential for making a hybrid of silica making use of the rubber elasticity of urethane. Urethane is a typical rubber material having a structure with solid hard segment domains (HS) dispersed in the liquid phase of soft segment domains (SS).

As shown in Fig. 1.6, it was contrived to form the hybrid domain with silica generated only in the HS phase in the urethane-silica hybrid. The silica contributes to give the heat-resistance to the HS domain and does not affect its flexibility by the existence of the SS phase.

We previously demonstrated the structure of the molecular hybrid from the photoluminescence spectrum of colorimetric substrate on the silica surface and reported the interaction between the domains using SALS [8, 9]. This material has an expanded range of uses as a coating material for flexible boards, fiberscopes, elastic paints and sealants.

6. Cheap engineering plastics in place for imide: hybrid of the amideimide system

Amideimide is hardly used in the advanced electronic industries because of its low flexibility, high dielectric constant and high water absorption, in spite of its low monomer cost of less than a fifth compared with imide. Although the ductility of the material cannot be increased by the addition of silica, water absorption and dielectric constant similar to those of polyimide were obtained whilst maintaining the original flexibility of polyamideimide limiting the influence of silica to the bridge of molecules by introducing polymethoxysiloxane at only the edge of the molecules as shown in Fig. 1.7 [10]. A hybrid of the amideimide system is being commercialized as a material for super heat-resistant enamel wire, sliding parts and belts for printers.
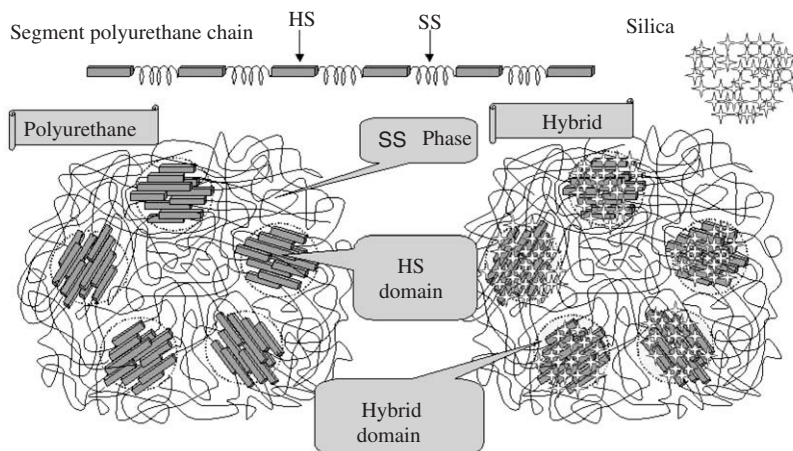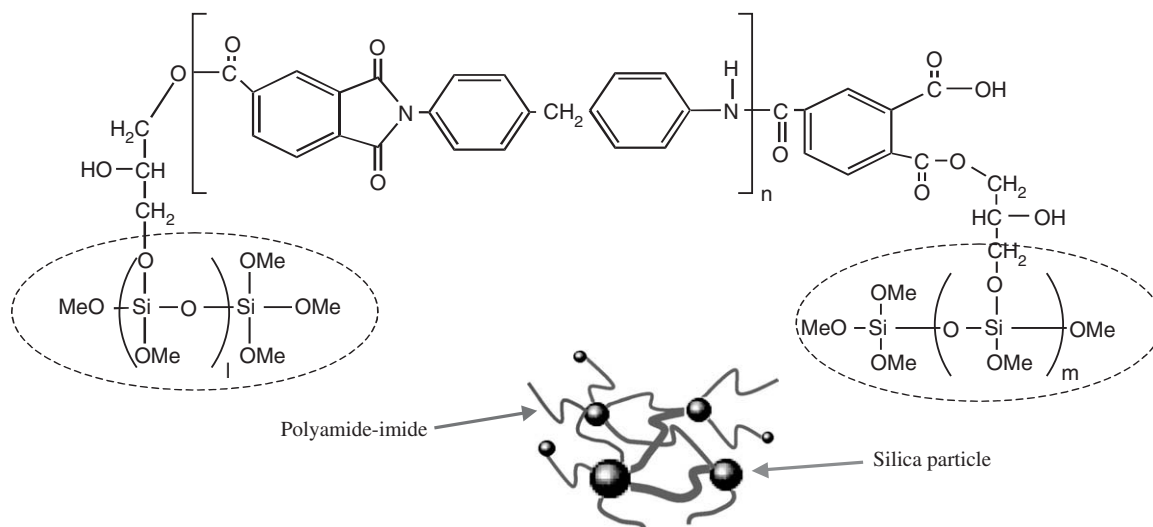

Figure 1.6
Model of urethane–silica hybrid.

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Figure 1.7
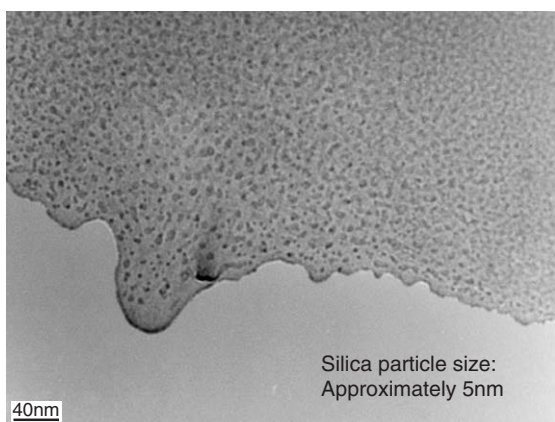Chemical structure of silane-denatured amideimide.

Figure 1.8
TEM picture of imide–silica hybrid.

7. Imide useful for electroless plating: hybrid of the imide system

The imide film is used as a heat-resistant and insulation material in various fields but is insufficiently adhesive onto electroconductive materials such as metal. However, when amic acid with alkoxysilane-oligomer is hardened to imide on metal film, a printed board with dispersed nanosized silica as seen in Figs. 1–8 can be obtained. It has recently been applied for industrial use as a double-layer flexible circuit board with high adhesiveness.

In imide–silica hybrid film, the silica is located as a crosslinker between imide chains and realizes wet plating with simple preprocessing without the roughening procedure (Fig. 1.9) [11]. By this wet plating method, layered products with a flat interface between the plastic film and the metal can be obtained, which is a useful technology for meeting the requirements
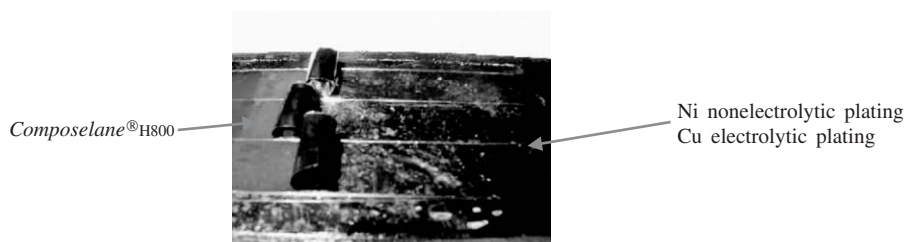

Figure 1.9
Imide–silica hybrid film after plating.

for advanced printed boards with thin conductive layers and flat interfaces.

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APPLICATION 2

2 GENERATION OF METAL NANOPARTICLES USING REACTIVE PLASMA ARC EVAPORATION

1. Summary of the reactive plasma arc evaporation method

(1) Features of the reactive plasma arc evaporation method

The reactive plasma arc evaporation method has been developed by M. Uda et al., of the National Research Institute for Metals, in the late of 1970's, and which is classified as one of plasma heating methods. The plasma heating methods are technique to obtain nanoparticles by metal plasma evaporation.

A gas evaporation method which has been developed previously must be conducted under several hundreds to thousands Pa of argon (Ar) or helium (He) atmosphere for nanoparticle synthesis [1].

On the other hand, the reactive plasma arc evaporation method can be under atmospheric pressure of diatomic molecular gas such as nitrogen (N_2) and hydrogen (H_2). These gases greatly influenced on the nanoparticle generation mechanism.

(2) Nanoparticle generation mechanism

Fig. 2.1 shows a schematic diagram of the nanoparticle generation mechanism under H_2 gas atmosphere [2]. According to M. Uda et al., the mechanism is as follows: diatomic molecular gases dissociate to single atoms in the arc plasma, and then these atoms dissolve in the molten metal.

The transfer of these atoms to supersaturated area in the molten metal caused by convection flow. The atoms rebond and be discharged. At the same time, lots of excited metals evaporate from the surface of
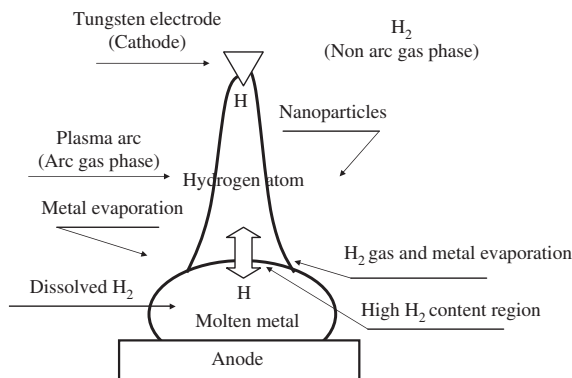

Figure 2.1
Schematic diagram of the nanoparticles generation mechanism under H_2 gas atmosphere.

the molten metal. The metal evaporation condenses and nanoparticles are obtained [3].

H_2 gas can catalyze during metal nanoparticles generation from molten metal under H_2 arc plasma.

(3) Outline of the metal nanoparticle generation device

Fig. 2.2 shows the outline drawing of the metal nanoparticle generation device with the reactive plasma arc evaporation method.

Bulk as a starting material is placed on the water-cooled copper hearth, the bulk is irradiated with the