

Development of Organic-inorganic Hybrid Materials Using Photo-crosslinking Reactions

Introduction

Polymeric materials such as inks, coatings and adhesives are now used for a wide range of applications. Molecular design that gives these materials the desired physical properties can be achieved by using polymerization of the reactive monomers that serve as raw materials (crosslinking reactions) to create three-dimensional crosslinking structures. Furthermore, there are many cases in which complex compositions are created by adding fillers or functional compounds to suit the characteristics required for practical application. Two main methods are used to create crosslinked materials: thermal curing and photo curing. However, many types of work require rapid processing and simple processes, and photo-crosslinking reactions are an effective solution in such cases. Organic-inorganic hybrid materials are also gaining prominence as functional materials that possess the characteristics of both organic polymers and inorganic nanomaterials. By using photo-crosslinking reactions, the hybridization of polymers and inorganic components mainly composed of silica can be achieved extremely easily. This article provides an overview of photo-crosslinking reactions and describes photo-crosslinked organic-inorganic hybrid materials developed by the authors.

Table of Contents

Introduction.....	1	3. Development of Hybrid Materials Using Thiol-ene Reactions.....	6
1. Types and Characteristics of Photo-crosslinking Reactions.....	2	Conclusion.....	8
2. Development of Hybrid Materials Using Photo-radical Polymerization/ Photo-sol-gel Reactions.....	3		

1. Types and Characteristics of Photo-crosslinking Reactions

Photo curing requires less energy than thermal curing, making it more environmentally friendly, and is used to manufacture various industrial products. Photo-crosslinking reactions that lead to photo curing consist of photoinitiators, which produce active species through exposure to light, and reactive monomers/oligomers. These reactions are an indispensable part of modern industry. These reactions can be subdivided into radical polymerization, cationic polymerization, anionic polymerization and thiol-ene reactions. The respective advantages and disadvantages of each type are summarized in Table 1. The next section provides an overview of each type of reaction.

In terms of practical application, radical polymerization is currently the most-used type of photo curing. It is the result of polymerization reactions between photo-radical initiators, which create radicals with photo-irradiation, and acrylic monomers. Example reaction mechanisms are shown in Fig. 1.¹⁾ The reaction speed is high, and rapid curing occurs through photo-irradiation. However, polymerization is easily inhibited by oxygen in the air, and surface curing may fail in some cases. There are many

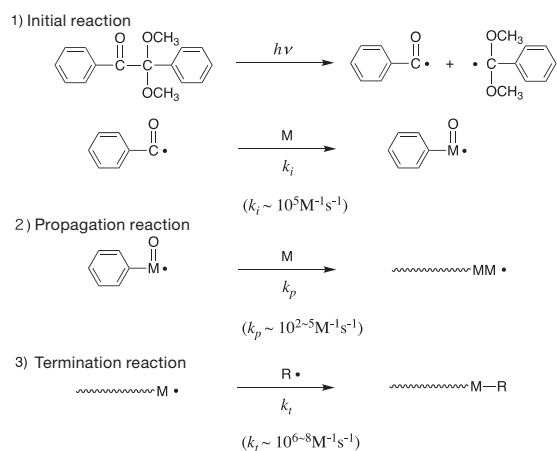


Fig. 1 Photo-radical Polymerization Reaction Mechanism

types of commercially-available acrylic monomers and oligomers, and various formulations can be implemented to achieve the desired physical properties. Consequently, these materials are used in numerous fields for applications ranging from adhesives to hard coatings. Hard coatings with high crosslinking density often experience issues as a result of curling and cracking due to curing shrinkage. In order to resolve these issues, a flexible coating is required.

Cationic polymerization comprises reactions between photo-acid generators, which create acid under photo-irradiation, and reactive resins such as epoxides. Example reaction mechanisms are shown in Fig. 2. Termination reactions occur less easily than with radical polymerization. As a result, polymerization continues even after photoirradiation has stopped. In the case of ring-opening polymerization of epoxy resin, there is low

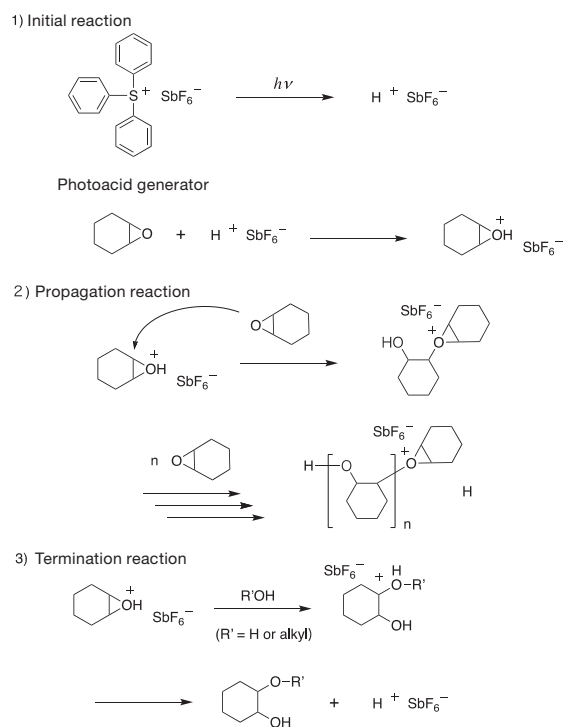


Fig. 2 Photo-cationic Polymerization Reaction Mechanism

Table 1 Characteristics of Photo-assisted Polymerization and Reaction

	Polymerization speed	Inhibition by oxygen	Volumetric shrinkage	Adhesion	Other
Radical polymerization	Very high	Occurs	High	Poor	Wide variety of monomers, low material cost, inhibited by oxygen
Cationic polymerization	Average	None	Low	Good	Corrosion of metal substrates, significantly affected by humidity
Anionic polymerization	High	None	Low	Good	Low sensitivity
Thiol-ene reaction	Very high	None	Low	Good	Odor occurs, dark reaction control is required

volumetric shrinkage due to polymerization and adhesion to the substrate is good. However, polymerization is stopped by the influence of water during the reaction. This means that cationic polymerization has the disadvantages of being easily affected by atmospheric humidity and having unstable reactions. In addition, the use of strong acids generated by the photo-acid generators means that corrosion of metals is also a concern.

Anionic polymerization comprises photo-base generators, which create base catalysts under photo-irradiation, and base-reactive resins. Reaction mechanisms are shown in Fig. 3. Photo-base generators are less sensitive than photo-radical initiators and photo-acid generators, and research and development of high-efficiency photo-base generators had been comparatively slow. However, the existence of outstanding photo-base generators has been reported in recent years, and the field is gaining prominence once more.²⁾ As shown in Table 1, anionic polymerization may be able to overcome some disadvantages of radical polymerization and cationic polymerization. As a result, further development can be expected.

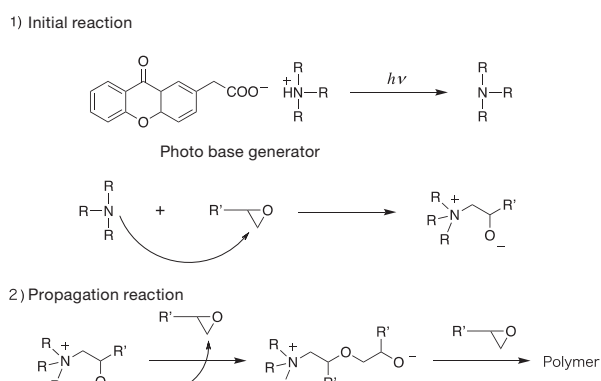


Fig. 3 Photo-anionic Polymerization Reaction Mechanism

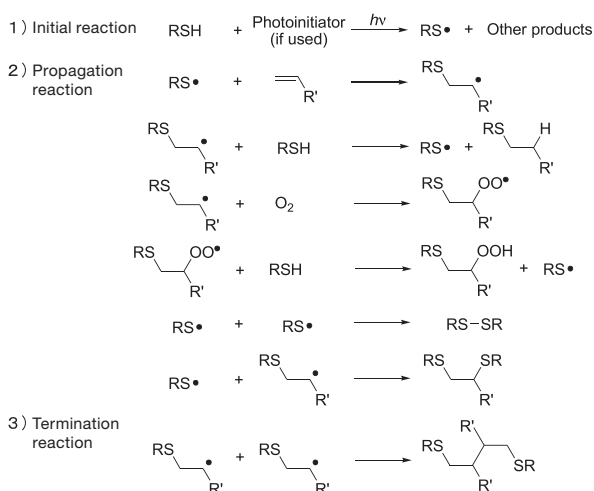


Fig. 4 Photo-thiol-ene Reaction Mechanism

Thiol-ene reactions are addition reactions between thiol groups and carbon-carbon double bonds (ene) under photo-irradiation. They are regarded as click chemistry reactions because they have high chemoselectivity, high functional group tolerance and low tendency to produce side reactions. The assumed reaction mechanism is as shown in Fig. 4. Even if carbon radicals generated by the addition of thiyl radicals to double bonds (the propagation reaction in Fig. 4) are denatured to peroxy radicals due to the effects of oxygen, thiyl radicals are generated through hydrogen abstraction from thiols and the addition reaction proceeds again without stopping. In other words, unlike photo-radical polymerization, thiol-ene reactions are not inhibited by oxygen, and this capacity to resolve a major problem seen with photoradical curing reactions is their most notable feature. Furthermore, because thiol-ene reactions are addition reactions, the curing shrinkage is low and the resulting thioether compounds are highly flexible. These characteristics reduce the risk of curling. Crosslinked materials created through reactions between polyfunctional thiol compounds and olefin compounds are flexible and can also provide toughness.

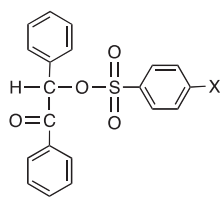
In terms of light sources, there has been a recent shift away from conventional high-pressure mercury lamps and metal halogen lamps towards the use of LEDs. At present, 365 nm is the most widely-used wavelength for LEDs, and monochromatic light is emitted at wavelengths such as 375 nm, 385 nm, 395 nm and 405 nm. With high-pressure mercury lamps and metal halogen lamps, multiple line spectra that emit in the ultraviolet region are used for photoinitiator decomposition. By comparison, LEDs use monochromatic light, resulting in slower photoinitiator decomposition and lower sensitivity in the photocrosslinking reaction. It is therefore necessary to either select monochromatic LEDs that can be easily absorbed by photoinitiators or to develop photoinitiators that are well-suited to LED light.

2. Development of Hybrid Materials Using Photo-radical Polymerization/Photo-sol-gel Reactions

Light-cured organic hard coatings generally comprise structures formed by three-dimensional crosslinking of multifunctional acrylates that are given surface hardness. multifunctional acrylates with a high number of functional groups and finer crosslinked structures tend to have higher hardness. However, this also increases the curing contraction rate, which leads to drawbacks such as increased warping and the occurrence of cracks. In contrast, inorganic hard coatings are based on sol-gel reactions of inorganic compounds such as silica and are characterized by forming hard coatings with excellent chemical

resistance and heat resistance. Issues with these substances include liquid storage stability and process complexity. In order to overcome these drawbacks, organic-inorganic hybrid hard coatings that combine the advantages of light-cured organic hard coatings and inorganic hard coatings are garnering attention. Carbon-functional alkoxy silanes used as silane coupling agents in these compounds are extremely useful as raw materials for organic-inorganic hybrids. By inciting polymerization reactions and sol-gel reactions simultaneously with carbon-functional alkoxy silanes, organic-inorganic hybrid products can be given high crosslinking density. Through sol-gel reactions using photopolymerization and hydrolysis/condensation of carbon-functional alkoxy silanes containing groups such as vinyl groups, acryl groups, and epoxy groups, photo-irradiation processes can be used in the rapid preparation of organic-inorganic hybrids. Here, the preparation of acryl/silica organic-inorganic hybrids through photo-binary-crosslinking reactions is described.

The chemical structure of a benzoin sulfonate compound is shown in Fig. 5. It is a photoacid/radical generator (PARG) that simultaneously generates sulfonic acid (cationic species) and radical species through photolysis. It is well suited to the creation of organic-inorganic hybrids through photo-radical polymerization and alkoxy silane hydrolysis/condensation.³⁾ Acryl/silica organic-inorganic hybrids with high silica content were prepared by adding benzoin tosylate (BT) to the multifunctional acrylate monomers pentaerythritol triacrylate (PETA) and trimethylolpropane triacrylate (TMPTA) and tetraethoxysilane (TEOS), then performing photo curing.⁴⁾ For example, when 1 to 3 mol% of BT was added to PETA/TEOS (50/50), the crosslinking reaction was complete in about two minutes. For organic-inorganic hybrids in which the composition ratio of TEOS was changed to 0, 20, 40 and 50 mol%, the gel contents were 99%, 91%, 72% and 60% respectively. The fact that gel content decreased as the amount of TEOS was increased could be attributed to a weight reduction caused by hydrolysis of ethoxysilane groups to silanol groups (ethanol elimination) and



BT : X = CH₃
 B4CBS : X = Cl

Fig. 5 Chemical Structure of Benzoin Sulfonate

condensation to siloxane bonds. A radical photoinitiator (benzoin ethyl ether) and photoacid generator (diaryliodonium tetrakis(pentafluorophenyl)borate) were added separately to PETA/TEOS (50/50), photo-crosslinking was performed, and the gel content was measured (Fig. 6). Radical polymerization was found to be fast and hydrolysis/condensation reactions of TEOS were found to be comparatively slow. Meanwhile, Fig. 7 shows the results of real-time infrared spectroscopy of changes in C=C bonds of acryl groups and Si-O-Si bonds in photo-crosslinking using BT. It was confirmed that radical polymerization of acryl groups and hydrolysis/condensation reactions of alkoxy silane groups proceed almost simultaneously. It is conceivable that improving the dispersibility of each acrylic/silica formation can lead to improved performance.

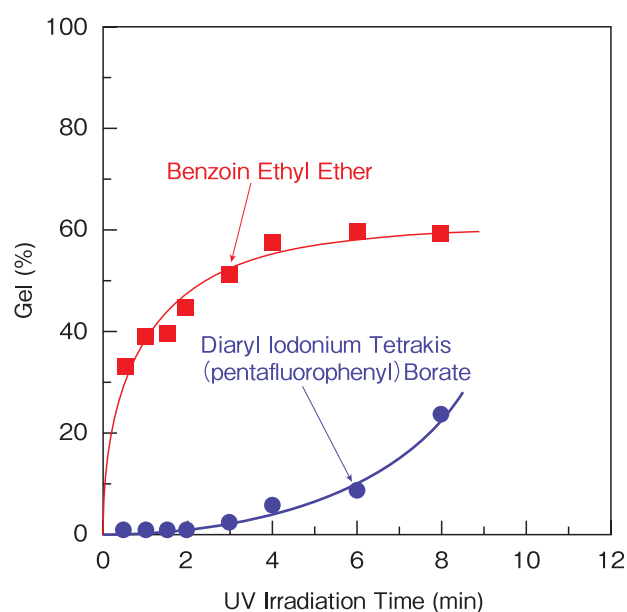


Fig. 6 Photo-curing of PETA/TEOS (50/50) with Radical Photoinitiators and Photo-acid Generators

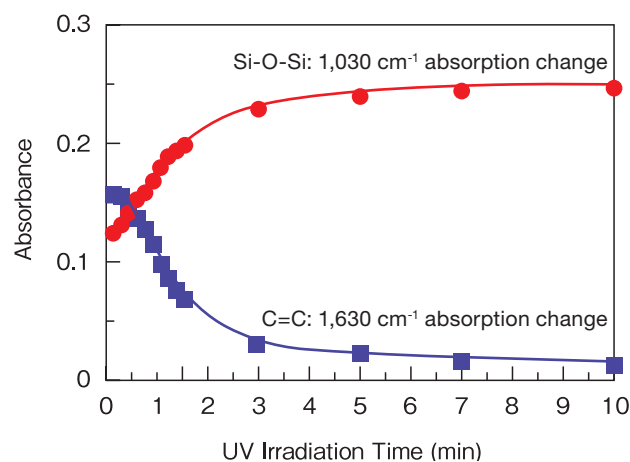


Fig. 7 Changes in Infrared Absorption (C=C: 1,630 cm⁻¹ and Si-O-Si: 1,030 cm⁻¹) of Photo-curing PETA/TEOS/BT (50/50/1)

Accordingly, it was observed that, if a small amount (5 to 10 mol%) of 3-acryloxypropyltrimethoxysilane (APTMS) is added to a PETA/TEOS composition, the effects of the acryl groups and methoxysilane groups present in the APTMS improve dispersion of PETA and TEOS, resulting in improvements to both surface hardness and adhesion to substrates.⁵⁾ It was also found that a uniform photo-crosslinked coating can be obtained regardless of the TEOS content. Furthermore, when considering the preparation of hybrid films using dipentaerythritol penta-/hexa-acrylate (DPHA) as a multifunctional acrylic monomer, DPHA/TEOS/APTMS photo-cured coatings using BT as a photo-radical/acid generator can be expected to have extremely high transparency, excellent adhesion and surface hardness, providing significant practical value as transparent negative resists.

Organic-inorganic hybrids in which organic and inorganic formations are dispersed on a nanometer scale are transparent, making them useful as optical materials. Bisphenoxyethanolfluorene diglycidyl ether (BPEFG) containing a bisphenylfluorene skeleton with two phenyl groups bonded to the 9-position carbon, an epoxy monomer with a high refractive index and low birefringence, is expected to support the development of such applications as an optical material with a high refractive index of 1.62 or higher (Fig. 8). Based on well-known results regarding the preparation of organic-inorganic hybrids through hydrolysis/condensation of silane coupling agents containing epoxy groups with photocationic polymerization⁶⁾, the synthesis of epoxyfluorene organic-

inorganic hybrids was examined. However, when the alkoxysilane hydrolysis/condensation reactions are performed under UV irradiation, one problem is that cracks tend to occur due to shrinkage as a result of the generation of alcohol and water. Consequently, a method was adopted whereby random-type polysilsesquioxane obtained through hydrolysis/condensation of silane coupling agents containing epoxy groups was mixed with BPEFG, and photo-cationic polymerization was performed.⁷⁾ Glycidoxypropyltriethoxysilane (GPTES) and epoxycyclohexylethyltrimethoxysilane (ECHETMS) were used as silane coupling agent containing epoxy groups for condensation with phenyltrimethoxysilane (PTMS) to prepare two co-condensation products (copolysilsesquioxane GPTES/PTMS and ECHETMS/PTMS). 1 to 2 wt% of photoacid generator was added to the mixture of BPEFG and copolysilsesquioxanes. The solution was spin-coated onto a substrate and irradiated with UV light (using a high-pressure mercury vapor lamp) at 1,300 mJ/cm² and post-exposure baking was performed at 150°C to form a thin, cured film. Cationic polymerization with BPEFG was performed on epoxy groups in these copolysilsesquioxanes to form stable organic-inorganic hybrids. Although BPEFG has a refractive index of 1.625, the creation of a hybrid with a silica component resulted in a slight decrease in refractive index. However, the hybrid showed excellent adhesion and heat resistance properties while retaining a high refractive index of about 1.6. Furthermore, UV-visible light spectra recorded the hybrid thin film (thickness 5 μm) showed light transmittance of 95% or more in the visible spectrum, indicating that the thin film had extremely high transparency. Table 2 shows the results of ellipsometry measurements of the refractive index of hybrid thin films generated on silicon wafers. The refractive index can be controlled by adjusting the ratio of BPEFG and copolysilsesquioxane, and these materials are extremely attractive as optical materials.

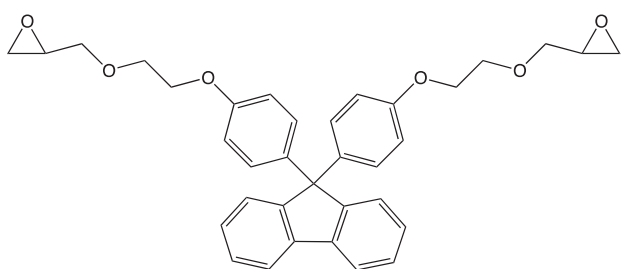


Fig. 8 Structure of Bisphenoxyethanolfluorene Diglycidylether (BPEFG)

Table 2 Refractive Index of Epoxyfluorene-based Organic-inorganic Hybrids

BPEFG	Hybrid formation		Refractive index
	GPTES/PTES	ECHETMS/PTMS	
1	1	-	1.591
1	-	1	1.596
2	1	-	1.612
2	-	1	1.615

3. Development of Hybrid Materials Using Thiol-ene Reactions

The creation of organic-inorganic hybrids through the simultaneous use of photo-thiol-ene reactions between multifunctional thiol compounds and vinylsilane coupling agents and sol-gel reactions using alkoxy-silyl groups was examined.⁸⁻¹⁰ Vinyltrimethoxysilane was used as a vinylsilane coupling agent and was mixed with trimethylolpropane tris(3-mercaptopropionate) (TMMP) as a multifunctional thiol compound. The solution was irradiated with light, and the thiol-ene reactions proceeded efficiently. However, the difference in reaction rate compared to the sol-gel reactions (alkoxysilyl group hydrolysis/condensation) meant that it was difficult to obtain a uniform, stable crosslinked film. Consequently, vinyltriacetoxysilane (VTAS) was used as a vinylsilane coupling agent with greater hydrolyzability. A small amount of photo-acid generator was added, and the

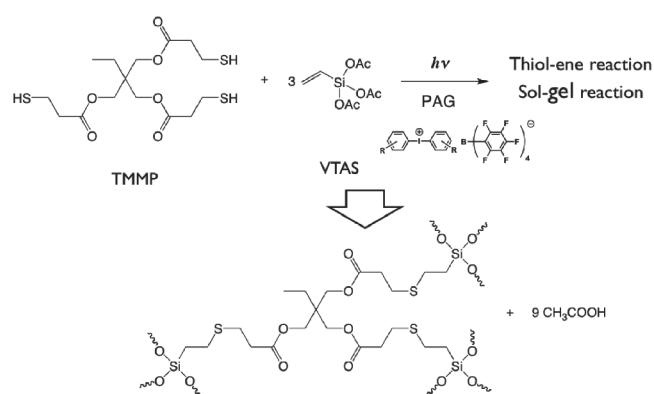


Fig. 9 Photo-crosslinking Through Thiol-ene Reaction/Simultaneous Sol-gel Reaction

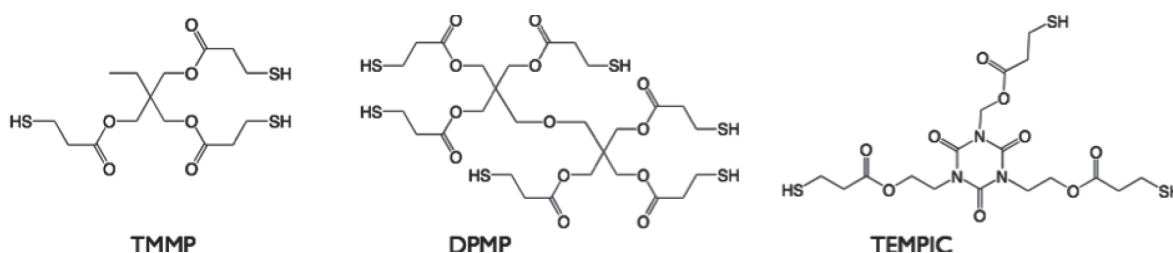
generated acid caused the VTAS to smoothly hydrolyze with moisture in the air. Efficient sol-gel reactions were then observed (Fig. 9). Thiol-ene reactions using TMMP, a trifunctional thiol, require three times the molar amount of VTAS, and this hydrolysis produces 9 times molar amount of acetic acid. It is suggested that these features promote sol-gel reactions. Organic-inorganic hybrids created through two-dimensional photo-crosslinking reactions comprising these photo-thiol-ene reactions and sol-gel reactions are made up of covalent bonds. Acetic acid was removed by post heating, and transparent, odorless thin films were produced.

As shown in Table 3, these organic-inorganic hybrids were made into hard coatings with a pencil hardness of about 2H on a PET film and 4H to 5H on a glass substrate. These thin films had a refractive index of about 1.55. This relatively high refractive index is due to sulfur element. As thiol-ene organic-inorganic hybrid films with TMMP do not contain any aromatic rings, resulting in a high Abbe number of 59.9, and it was also found that the creation of a coating with low chromatic dispersion is possible. Furthermore, mandrel bending test results showed excellent bending properties. At the same time, it was also confirmed that the material exhibits high durability even against repeated bending.

As described above, random-type polysilsesquioxane is effective as an inorganic component for use in organic-inorganic hybrids. Consequently, the preparation of hybrids using thiol-containing polysilsesquioxane was examined. Thiol-containing polysilsesquioxane was obtained by performing hydrolysis and condensation from mercaptopropyltrimethoxysilane (MPTMS). By controlling the reaction conditions, random-type polysilsesquioxane with a molecular weight of about 950

Table 3 Characteristics of Organic-inorganic Hybrids from Thiol-ene Reaction/So-gel Reaction

Polyfunctional thiol	TEOS (wt%)	Pencil hardness on PET	Pencil hardness on glass	Refractive index	Mandrel bend test (mm)
TMMP	0	2H	5H	1.540	2
TMMP	17	3H	6H	1.539	2
DPMP	0	2H	5H	1.553	2
TEMPIC	0	2H	4H	1.558	2



to 1,000 was synthesized without gelation. Mixtures of this thiol-containing polysilsesquioxane and polyfunctional olefins such as triallyl isocyanurate (TAIC) were irradiated with light, and photo-crosslinked organic-inorganic hybrids with high transparency, high refractive indices, high heat resistance, and low shrinkage were produced through photo-thiol-ene reactions. (Fig. 10).^{11, 12} The progression of thiol-ene reactions was confirmed by the decrease of S-H and allyl C=C peaks in the Raman spectroscopy. Based on the UV-visible absorption spectrum shown in Fig. 11, the photo-crosslinked organic-inorganic hybrid films (thickness 30 μm) were found to have high transparency of 95% or more in the visible light region. The solvent-free viscous liquids of these compositions were dripped onto glass plates and cured with UV-light, a process which enabled lens shapes to be formed with ease. The refractive index and Abbe number of these hybrid films were 1.56 and 46 respectively. These relatively high values indicate that these materials can be expected to contribute to the development of materials for optical applications. In addition, curing shrinkage was evaluated through comparison with a DPHA photo-radical polymer coated on a PET film. While warping occurred due to large curing shrinkage with the photo-cured DPHA film, the hybrid films made from thiol-containing silsesquioxane and TAIC demonstrated low curing shrinkage and exhibited

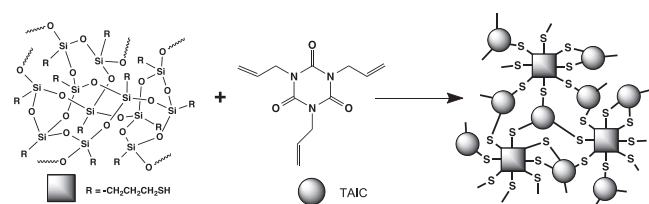


Fig. 10 Organic-inorganic Hybrids Prepared via Thiol-containing Polysilsesquioxane/TAIC Thiol-ene Reactions

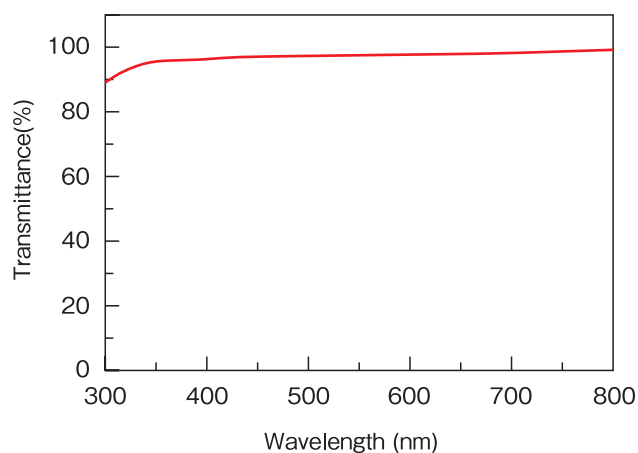


Fig. 11 UV-visible Spectra of Thiol-containing Polysilsesquioxane/TAIC Hybrid Film

almost no warping. It was also confirmed that the coating film had excellent flexibility and high durability against bending. These characteristics due to crosslinking through thiol-ene reactions and are of significant interest. With a pyrolysis temperature of over 300°C, the excellent heat resistance is another important characteristic. The organic-inorganic hybrid materials developed in this case have high flexibility and are useful as a flexible coating materials. Imparting more flexibility can be expected to result in demonstration of self-healing properties. It was subsequently confirmed that adding more polyfunctional thiol results in high elasticity and self-repair of dents.¹³ As is shown in the estimated structure of the three-dimensional crosslinked hybrid shown in Fig. 12, it is believed that hard silsesquioxane is bound by soft sulfide. A metal needle was used to scratch the surface of organic-inorganic hybrid thin films. Observation with a laser microscope showed that these scratches were repaired naturally in about 10 minutes. An example is shown in Fig. 13. With these hybrid thin films, polysilsesquioxane surface segregation has also been confirmed, which has also been found to lead to the development of self-healing films with low-friction surfaces.

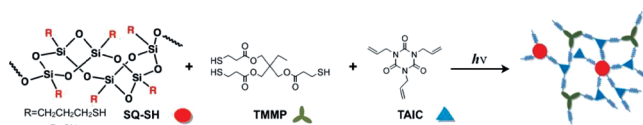


Fig. 12 Estimated Structure of Ternary Crosslinked Hybrid Created from Thiol-containing Polysilsesquioxane

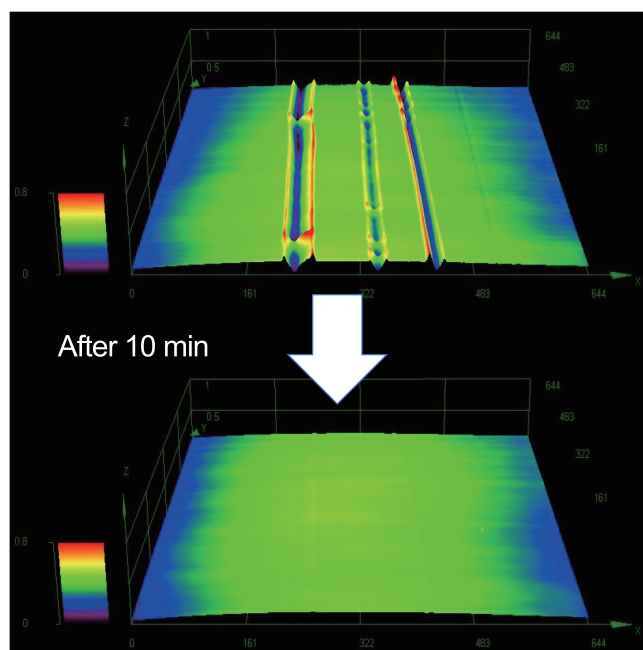


Fig. 13 Self-healing Behavior of Hybrid Thin Films Created from Thiol-containing Polysilsesquioxane

Conclusion

Photo-crosslinking is a useful method in the design and manufacture of various materials, including coatings and adhesives. This article outlined four types of photo-crosslinking reaction and described the preparation and properties of organic-inorganic hybrids made using each reaction. By binding inorganic nanomaterials to crosslinked polymers, organic-inorganic hybrids are attractive as materials that exhibit complementary properties and new functions. The organic-inorganic hybrids generated through photo-crosslinking reactions described in this article facilitate the production of functional materials.

The process of simultaneously photo-curing acryl groups, epoxy groups and alkoxy silane groups contained in a silane coupling agent to produce organic-inorganic hybrids is also beneficial in terms of practical considerations such as energy saving and environmental concerns. Organic-inorganic hybrids obtained by photo-cationic polymerization of bisphenyl fluorene glycidyl ether, a monomer with a high-refractive index, and epoxy-containing polysilsesquioxane are expected to provide hard coatings with high refractive indices. In addition, organic-inorganic hybrids that can be generated by simultaneous thiol-ene/sol-gel binary reactions demonstrated a high refractive index as a result of the effects of sulfur while also exhibiting the contradictory properties of hard coating and flexibility. Thiol-ene reaction crosslinking with thiol-containing silsesquioxane was shown to produce organic-inorganic hybrids with high refractive indices and toughness. Thin films with a controlled refractive index are used for applications such as anti-reflection films and ITO refractive index matching layers. They make a significant contribution to improving the visibility of devices, making them an indispensable component in information terminals. These flexible organic-inorganic hybrid materials with high refractive indices can be expected to contribute to the development of new optical materials.

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