New Preparation Methods for Organic–Inorganic Polymer Hybrids

Yoshiki Chujo and Ryo Tamaki

Introduction

Nano-ordered composite materials consisting of organic polymers and inorganic compounds have been attracting attention for their use in creating high-performance or high-functionality polymeric materials. The term "polymer hybrid" describes blends of organic and inorganic components with molecular-level dispersions.[1] By combining these two components, it is possible to enhance the mechanical strength of organic polymers with silica particles.[2–6] The high transparency of these materials is another important property, which makes them indispensable in the development of optical waveguides,[7–11] optical biosensors,[12] nonlinear optical materials,[13,14] and contact lenses.[15] Hybrid materials are also potential candidates for catalysts[16–18] and gas-separation membranes.[19–23]

It is generally impossible to disperse silica gel at the molecular level. However, tetra-alkoxysilane, a precursor of silica gel in the so-called sol-gel reaction, can be dissolved in organic solvents such as alcohol. Thus, the sol-gel reaction makes it possible to incorporate the organic polymer segments in the network matrix of inorganic materials.[24–37] The elementary reactions of the sol-gel procedure are shown in Scheme I, in which Si-OH species acting as a Brønsted acid are the key intermediates.[38–42] The polymer hybrids were prepared by means of the sol-gel reaction of tetra-alkoxysilane in the presence of organic polymers. Typical examples of organic polymers incorporated are poly(2-methyl-2-oxazoline) (POZO) (Structure **1**), poly(*N*-vinylpyrrolidone) (PVP) (Structure **2**), and poly(*N*,*N*-dimethylacrylamide) (PDMAAm) (Structure **3**).[43–48] One of these organic polymers was dissolved in ethanol with tetraethoxysilane, and the resulting mixture was subjected to an acid- or base-catalyzed sol-gel reaction. After drying for several days, a homogeneous and transparent glass material was produced. These colorless, transparent, and homogeneous hybrids were obtained in a wide range of compositions that demonstrate the characteristic properties of these organic polymers.

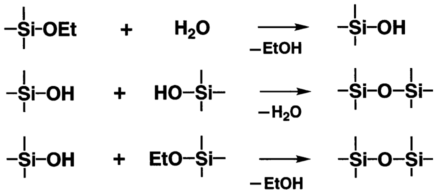
The high homogeneity of the present hybrid strongly suggests that the organic polymer segments and inorganic segment were blended at the molecular level. This may be due to the strong hydrogen bonds between amide carbonyl groups and silanol groups. As a representative example, Figure 1 illustrates the interaction between POZO (**1**) and silica gel through hydrogen bonds. The hydrogen bonds in these hybrids were confirmed by Fourier transform infrared (FTIR) spectra, in which the stretching bands due to amide carbonyl groups were shifted to the lower wavenumber region after the formation of hybrids. The molecular dispersion of organic polymers in a silica matrix has been confirmed by the pore size of porous silica prepared by the pyrolysis of hybrids[49] and also by atomic force microscopy.[50]

In the hybrid matrix, the organic polymer segments are dispersed without aggregation, as described before. Accordingly, the characteristics of organic polymers as a group, such as their thermal stability or glass-transition temperature, can be expected to differ from those of organic polymers. In fact, thermally stable hybrid membranes were prepared without decomposition of organic parts, even at high temperature (e.g., 200°C).[21] In addition, the mechanical properties of the polymer hybrids were highly improved compared with those of the corresponding organic polymers. In this sense, molecular hybrids can be considered not only as the combination of organic polymer and inorganic materials, but as new materials in their own right.

In Situ Polymerization Method

Previously, Novak[51–53] and Schmidt[15] proposed interesting methods for preparing organic–inorganic polymer hybrids. They utilized silane coupling agents in the reactions to introduce organic parts into the silica matrix. Modification would attach these organic polymers covalently to the silica network and disperse the polymers in the silica gel homogeneously.

The inorganic matrix is formed by the sol-gel reaction, which consists of the hydrolysis of the alkyl silicate and the ensuing condensation reaction, as described before. This means that the inorganic matrix is constructed by a polycondensation reaction. Here, as the starting material, an organic monomer was used instead of the polymer. In other words, the polymerization of the organic monomer was carried

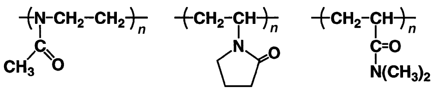


$$\equiv\mathrm{Si{-}OEt} + \mathrm{H_2O} \xrightarrow[-\mathrm{EtOH}]{} \equiv\mathrm{Si{-}OH}$$

$$\equiv\mathrm{Si{-}OH} + \mathrm{HO{-}Si}\equiv \xrightarrow[-\mathrm{H_2O}]{} \equiv\mathrm{Si{-}O{-}Si}\equiv$$

$$\equiv\mathrm{Si{-}OH} + \mathrm{EtO{-}Si}\equiv \xrightarrow[-\mathrm{EtOH}]{} \equiv\mathrm{Si{-}O{-}Si}\equiv$$

Scheme I.



(**1**) (**2**) (**3**)

*Structures **1**, **2**, and **3**.*

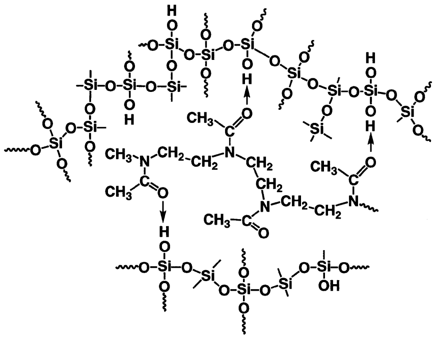


Figure 1. Schematic representation of hydrogen bonds in polymer hybrids.

out simultaneously with the sol-gel reaction. Generally, radical polymerization was used for the formation of the organic component. The advantage of this method might be in the dispersion of the organic components, that is, the monomer should be dispersed more easily than the polymer. Here, *N,N*-dimethylacrylamide (DMAAm) was used as a typical example of organic monomers.[54]

DMAAm was added as a starting material to a sol-gel reaction mixture of tetramethoxysilane (TMOS) with azobisisobutyronitrile (AIBN) as the radical initiator. The sol-gel reaction was catalyzed by an acid catalyst to produce a silica gel matrix. Therefore, it was expected that organic and inorganic polymerizations would proceed simultaneously when the mixture was heated to 60°C. The polymer hybrids were found to be homogeneous and transparent. The homogeneity of the hybrids was assumed to be due to the strong interaction between the polymer and silica gel.

It was confirmed that the simultaneous radical polymerization of DMAAm with hydrolysis and condensation of TMOS produced highly homogeneous PDMAAm and silica gel hybrids. *In situ* polymerization of DMAAm proceeded effectively to produce PDMAAm with a high molecular weight. The homogeneity of the hybrids depended on the amount of the acid catalyst and gelation degree of the silica gel, indicating the critical role of physical entrapment of the polymer in forming silica gels, as well as the hydrogen bonding interaction for uniform dispersion of the polymer. This method seems to offer greater versatility than prepolymer incorporation methods. At the same time, it does not require modification of organic monomers to obtain homogeneous polymer hybrids. Thus, the number of processes required for preparation is reduced.

This method should prove useful for the synthesis of polymer hybrids starting from organic polymers without high affinity to silica gel, since the aggregation may be suppressed if the monomer polymerizes in the "cage" of the silica matrix. Based on this idea, homogeneous polystyrene and silica gel polymer hybrids were also prepared.[55] A styrene monomer was introduced into a sol-gel reaction mixture of TMOS, and the polymerization was initiated by AIBN, while the sol-gel reaction of TMOS proceeded to form a silica gel. The homogeneity was confirmed quantitatively by measuring the porosity of charred hybrids using nitrogen porosimetry. It was found that polystyrene was dispersed at the nanometer scale in the silica matrix.

Interpenetrating Polymer Network (IPN) Hybrids

In *in situ* polymerization, when a bifunctional organic monomer is used together with a monofunctional monomer, the organic component should be a three-dimensional cross-linked structure. The inorganic matrix is a silica gel, which is of course a cross-linked structure. This material is, in fact, an interpenetrating polymer network (IPN).

Homogeneous IPN polymer hybrids of PDMAAm gel and silica gel were synthesized by the *in situ* polymerization method.[56] DMAAm and methylenebisacrylamide (MBAAm), as a cross-linking agent, were added into a methanol solution of TMOS. Radical polymerization of DMAAm and sol-gel reaction of TMOS were carried out simultaneously, resulting in homogeneous glassy materials. The formation of an IPN structure was confirmed by solvent extraction. As demonstrated in Figure 2, while 60% of PDMAAm was extracted with MeOH from the polymer hybrid prepared without MBAAm, the content of organic segment hardly changed before and after the extraction when 0.1 equivalent of MBAAm was introduced. These results indicate that the PDMAAm gel and silica gel formed an IPN structure with the addition of MBAAm. The homogeneity of these IPN polymer hybrids was supported by nitrogen porosimetry measurements. It was found that the porous silica obtained from the polymer hybrids had high surface areas and large pore volumes and exhibited a sharp peak in pore-size distribution at 1.8 nm. The results indicate a molecular-level dispersion of the polymer gels in the IPN polymer hybrids.

Homogeneous IPN polymer hybrids of polystyrene gel and silica gel were also prepared by applying an *in situ* polymerization method to a styrene monomer and divinylbenzene.[57] The monomers were mixed in the sol-gel reaction mixture of TMOS and subjected to radical polymerization, resulting in transparent glassy materials. The homogeneity was again confirmed by nitrogen porosimetry methods. The organic group was found to be dispersed at the nanometer scale. The IPN polymer hybrids obtained were found to be highly solvent-resistant.

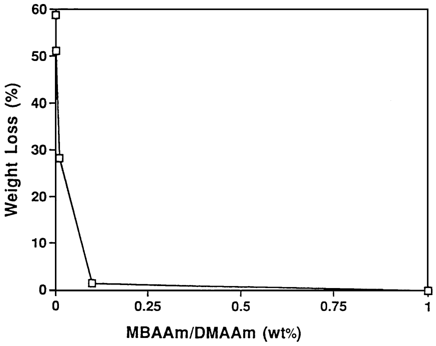


Figure 2. Loss of organic-component PDMAAm-silica interpenetrating polymer network (IPN) hybrids by MeOH extraction. PDMAAm (Structure ***3****) is poly(*N,N*-dimethylacrylamide), MBAAm is methylenebisacrylamide, and DMAAm is* N,N*-dimethylacrylamide.*

In Situ Hydrolysis Method

When poly(vinyl alcohol) (PVA) was used as an organic polymer in the sol-gel reaction, the aggregation of the polymer took place due to the interaction among hydroxyl groups in the organic component, which caused phase separation. As a result, heterogeneous and milky materials were obtained. Generally, PVA can be prepared by hydrolysis of poly(vinyl acetate). Here, acid-catalyzed *in situ* hydrolysis of poly(vinyl acetate) was performed simultaneously with the acid-catalyzed sol-gel reaction.[58] It should be noted that ester groups of poly(vinyl acetate) can act as hydrogen bond acceptors to interact with silanol groups.

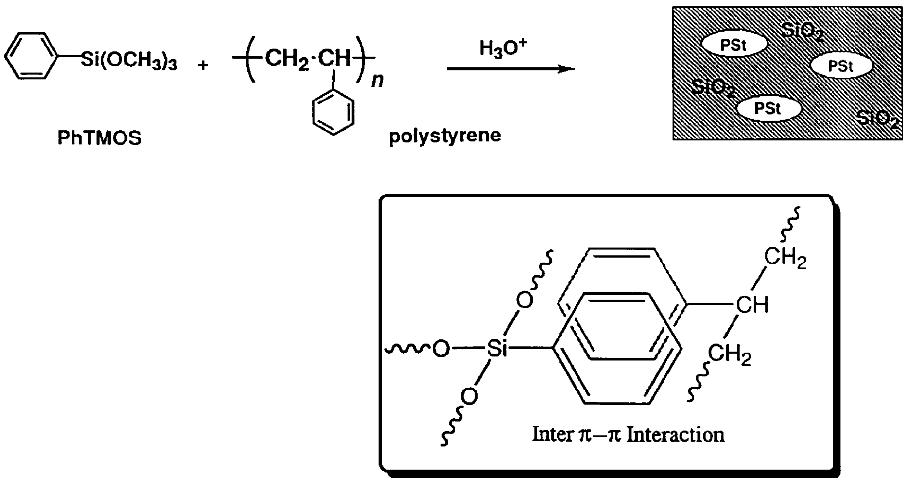
In the presence of poly(vinyl acetate), the acid-catalyzed sol-gel reaction of TMOS was carried out. The degree of hydrolysis of poly(vinyl acetate) was estimated by FTIR or ^{13}C CP/MAS (coupled plasma/magic angle spinning) nuclear magnetic resonance (NMR) and was found to be controlled (0–85%) by the amount of acid catalyst. As a result, a homogeneous and transparent polymer hybrid of PVA and silica gel was effectively obtained by this procedure.

π–π Interaction

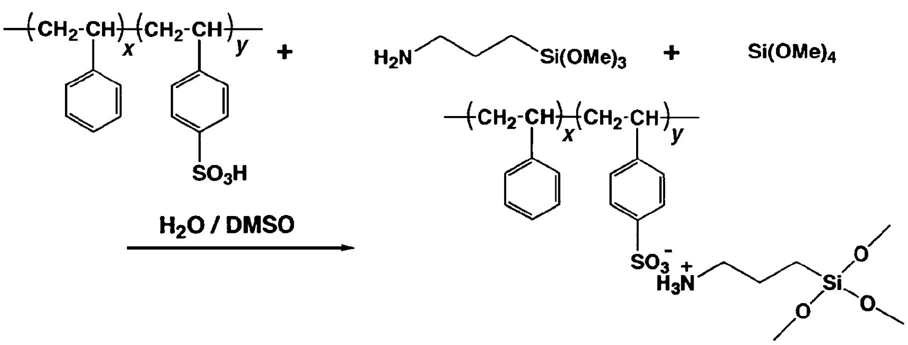
The interactions utilized to integrate organic and inorganic phases are generally classified into two groups: covalent bonding and hydrogen bonding interactions. On the other hand, π–π interaction is known as one of the types of attractive non-covalent bonding interactions that play a critical role in, for example, the stabilization of the double-helical structure of DNA and complexation in host–guest systems.[59] This π–π interaction can be used in the preparation of homogeneous polymer hybrids. The principle of this method is an interaction between the organic and inorganic components by π–π interaction. For this interaction, phenyltrimethoxysilane (PhTMOS) was used as a starting material for the sol-gel reaction, by which phenyl groups can be incorporated into the inorganic matrix. As an organic component, polystyrene was used. Thus, polystyrene and silica gel polymer hybrids were prepared utilizing a sol-gel reaction of PhTMOS.[60] When an alkyl- (or aryl-) substituted alkoxysilane is used as a starting material, the alkyl group is introduced into the silica gel, since the Si–C bond does not undergo hydrolysis. Phenyl groups would be introduced into the silica gel by the sol-gel reaction of PhTMOS. As shown in Scheme II, the alkoxysilane was added to a tetrahydrofuran (THF) solution of polystyrene, followed by the addition of an acid catalyst. For comparison, other alkoxysilanes such as TMOS, methyltrimethoxysilane (MTMOS), and isobutyltrimethoxysilane (iBuTMOS) were also used as starting materials. The mass ratio of alkoxysilane to polystyrene was 0.1 or 1.0. The homogeneity of the obtained polymer hybrids was evaluated optically. Transparency of the polymer hybrids was attained only when silica gel particles embedded within polystyrene were smaller than the wavelength of light. Transparent polymer hybrids were obtained for both mass ratios when PhTMOS was used as a starting material for the sol-gel reaction. In contrast, polymer hybrids became translucent or turbid when TMOS, MTMOS, or iBuTMOS was used. Mesityltrimethoxysilane (MesTMOS) gave homogeneous polymer hybrids when the mass ratio was 0.1. However, the homogeneity deteriorated as the mass ratio was increased to 1.0. The result might be attributed to methyl groups on the phenyl ring of MesTMOS, which are suspected to interrupt the π–π interaction. When phenethyltrimethoxysilane (phenethylTMOS) was used as the starting material, homogeneous polymer hybrids were obtained for both mass contents. These results demonstrate that a phenyl ring is necessary for the homogeneous dispersion of polystyrene and silica gel.

By using this idea, poly(diallyl phthalate) or polycarbonate prepared from bisphenol-A could be utilized as an organic component.[61] In all cases, very transparent and homogeneous polymer hybrid materials were obtained by the sol-gel reaction of PhTMOS or phenethylTMOS. As observed in the case of polystyrene, TMOS, MTMOS, and iBuTMOS gave only inhomogeneous polymer hybrids. These results indicate that π–π interaction is quite effective for the synthesis of homogeneous polymer hybrids of silica gel and organic polymers having aromatic groups.

Cubic phenylsilsesquioxane also produced a homogeneous hybrid material with polystyrene through π–π interaction.[62] The polymer hybrid obtained showed high solubility in common organic solvents and good processability.



Scheme II.



Scheme III.

Ionic Interaction

Ionic interaction between anion and cation is one of the simplest interactions. For example, polystyrene sulfonic acid was used as an organic component. As an inorganic component, 3-aminopropyltriethoxysilane, a popular silane coupling agent, was used in order to produce an ionic interaction with the sulfonic acid groups in the organic component. Thus, in the presence of polystyrene sulfonic acid, the sol-gel reaction of a mixture of TMOS and 3-aminopropyltriethoxysilane was carried out, as illustrated in Scheme III.[63] The resulting hybrid materials were found to be very homogeneous and transparent. This method via ionic interaction might be applied to other organic polymers having sulfonic acid or carboxylic acid groups. Poly(acrylic acid) is one such example.

Conclusions

The molecular hybrids of organic polymers and silica gel are expected to show many possibilities as new composite materials. These hybrids may show intermediate properties between plastics and glasses (ceramics). In addition, the composition of the hybrids can be widely varied. In other words, the hybrids can be used to modify the organic polymer materials or to modify the inorganic glassy materials. Thus, the exploration of new preparative methods for organic–inorganic polymer hybrids should be one of the most important technologies for the creation of high-performance or high-functionality polymeric materials.

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