Interpenetrating Inorganic–Organic Hybrid Gels: Preparation of Hybrid and Replica Gels

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An organic–inorganic hybrid gel was prepared by gelation of organic monomer or polymer solution in pores of a silica matrix. Furthermore, a replica organic gel was obtained from the organic–inorganic hybrid gel by treating the hybrid with aqueous hydrofluoric acid solution. The silica matrix of the hybrid gel was similarly dissolved using aqueous hydrofluoric acid solution, leaving the organic gel matrix.

Hybrid gels have been of great interest as a novel class of materials.[1–3] Especially organic–inorganic hybrid gels have been investigated extensively because of their unique properties.[4–14] Such gels would be expected to have high thermal, mechanical, and solvent-resistant properties. There are several ways to synthesize organic–inorganic hybrids, such as surface modification of silica with organic polymer[5–8], and molecular construction of organic polymer and silica via the sol–gel method.[9–11] In the system employed by Okano et al., the organic polymer domain and silica were linked through covalent bonding using silane coupling agents.[5] Mann et al. synthesized hybrid silica by the co-condensation of alkoxysilanes and organosiloxanes in the presence of surfactant templates.[12] The resulting materials had ordered organic–inorganic networks. These methods use covalent bonding to restrain the mobility of the organic matrix. Chujo et al. reported synthesis of hybrids that were interpenetrating polymer networks (IPNs) of organic gel and inorganic silica gel.[9] The hybrid gels were synthesized by radical copolymerization of organic monomers such as styrene in the presence of a cross-linker and the sol–gel reaction of alkoxysilanes. One of the advantages of this method is that there is no covalent bond between organic polymer gel and inorganic silica gel in the hybrid. It takes one week to form the hybrid gel sufficiently.

Recently, a novel process for preparing organic–inorganic hybrids has been developed by crystallizing inorganic hydroxyapatite within an organic gel.[13,14] This hybrid is a potentially valuable material, since porous inorganic material would be obtained after sintering the organic matrix of the hybrid. Furthermore, another organic matrix which has the same physical structure with the original sintered organic matrix could possibly be prepared just by gelation of the organic monomer or polymer solution in the pores of remaining inorganic matrix. In this study, we prepared a novel organic–inorganic hybrid material using porous silica that was used as a starting material and is relatively inexpensive. The hybrid gel was prepared by simple gelation of the organic monomer or polymer solution in the pores of the silica, which took less than 12 h. Moreover, a replica organic gel was obtained from the organic–inorganic hybrid gel by treating the hybrid gel with aqueous hydrofluoric acid solution. This procedure for preparing a replica organic gel by dissolving the inorganic matrix of the hybrid is quite unique and has never been achieved.

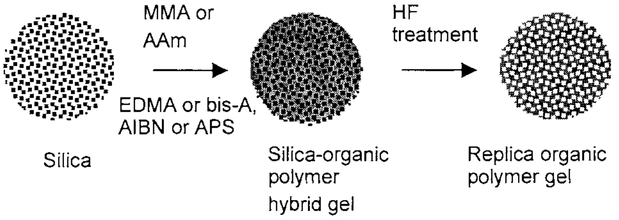

Figure 1. Preparations of silica-organic polymer hybrid gel and its replica organic polymer gel.

A typical inorganic–organic hybrid gel was prepared as follows (Figure 1). To make the silica-poly(methyl methacrylate) hybrid gel, methyl methacrylate (MMA) (2 mol), 2,2'-azobisisobutyronitrile (AIBN) (0.03 mol) and ethylene dimethacrylate (EDMA) (0.05 mol) were mixed and placed under a stream of nitrogen in a screw top bottle. One hundred g of silica (Suzuki Yushi Industrial Co., Ltd., particle diameter 2.0–4.0 mm, pore volume 0.78 mL/g) were immersed in the solution and placed under a stream of nitrogen for 2 h. After the removal of excess solution, the screw top bottles were sealed and heated at 80 °C for 12 h. After heating, the hybrid gel obtained was thoroughly washed using ethanol and then dried.

To make the silica–poly(AAm) hybrid gel, AAm (0.8 mol), ammonium peroxodisulfate (APS) (12 mmol) and *N*,*N*'-methylenebis(acrylamide) (bis-A) (19 mmol) were mixed with water (200 mL) and placed under a stream of nitrogen in a screw top bottle at 0 °C for 2 h. Silica particles (100 g) were immersed in the solution and placed under a stream of nitrogen for 2 h. Then 0.5 mL of *N*,*N*,*N*',*N*'-tetramethylethylenediamine was added to the mixture. The screw top bottles were sealed and kept at 0 °C for 12 h. The hybrid gel obtained was thoroughly washed with water and then dried. PMMA gel (840 mg) or PAAm gel (73 mg) was hybridized in one gram of silica, respectively.

The degree of swelling of each hybrid gel is shown in Table 1. A small amount of organic solvent was adsorbed in the silica–PMMA hybrid gel. Since a large amount of PMMA gel was hybridized in the silica, little pore volume existed to adsorb organic solvent in the silica–PMMA hybrid gel. On the other hand, a large amount of water was adsorbed in the silica–PAAm hybrid gel, since only a small amount of PAAm was hybridized in the silica. The silica–PAAm hybrid gel maintained its shape even after swelling, though PAAm gel prepared outside the silica was brittle when it was swollen.

The replica organic gel was prepared as follows (Figure 1). The inorganic–organic hybrid gels were immersed with 20% aqueous hydrofluoric acid solution and stirred slowly at room

Table 1. Swelling degree of silica, silica-organic polymer hybrid gel, and replica organic polymer gel[a]

Solvent	Silica	Silica-PMMA hybrid gel	Replica PMMA gel	Silica-PAAm hybrid gel	Replica PAAm gel
Water	1.17	-	-	1.00	6.92
Acetone	0.87	0.17	1.42	-	-
Toluene	0.95	0.15	0.66	-	-

[a] Swelling ratio was defined as swelling degree=$(W_{wet} - W_{dry})/W_{dry}$ where W_{wet} is the weight of swollen sample and W_{dry} is the weight of the dried sample.

temperature for 12 h. The hybrid gels were washed with distilled water several times and then freeze dried. By thermogravimetric analysis of the replica PMMA gel, all contents of the replica PMMA gel were completely burned out around 400 °C. This phenomenon clearly indicated that the silica matrix was completely dissolved by aqueous hydrofluoric acid solution and the PMMA gel matrix was remained as its replica gel. The dried replica gels appeared hard, whereas those were softened in good solvent in the same manner as usual gels. The replica PMMA gel and PAAm gel could adsorb large amount of organic solvent and water, respectively as shown in Table 1. The obtained replica gels swelled in the solvents but were not dissolved.

Figure 2 shows photographs of the silica, silica–PMMA hybrid gel and replica PMMA gel. The silica clearly became opaque after hybridization with PMMA gel. After dissolving the silica matrix in aqueous hydrofluoric acid solution, the remaining replica PMMA gel was still opaque. Scanning electron microscope study of the surface of silica–PMMA hybrid gel showed loading of PMMA gel into the pore of the silica which has rugged surface. The rugged surface could not be found in the replica PMMA gel. The surface of the replica PMMA gel found to be smooth, whereas the replica structure that correspond to the pore structure of silica could not be observed. The details of observations of fine surface character will be reported in the near future.

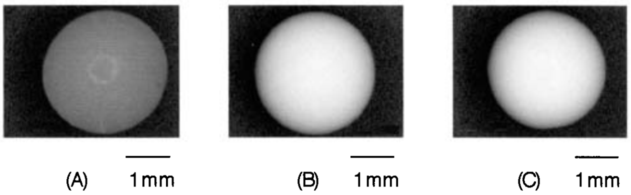

Figure 2. Photographs of (A) silica, (B) silica-PMMA hybrid gel, and (C) PMMA replica gel.

The pore volume and surface area of the silica, silica-PMMA hybrid gel and replica PMMA gel are shown in Table 2. These characteristics were measured by the Dollimore–Heal method[15] by calculating the amount of nitrogen adsorbed on the surface using a nitrogen gas adsorption apparatus (Bellsorp 28SA, Bell Japan, Inc.). After hybridization, the pore volume and surface area were drastically decreased. This indicates that the pores of the silica were completely filled with PMMA gel matrix. The pore volume and surface area of the replica PMMA gel were high in comparison with the values of PMMA gel prepared by suspension polymerization (pore volume 24.4 mm^3/g, surface area 5.8 m^2/g calculated by the Dollimore–Heal method[15]). This indicates the replica PMMA gel possessed a porous structure.

Table 2. Pore volume and surface area of silica, silica-PMMA hybrid gel and replica PMMA gel[a]

	Silica particle	Silica-PMMA hybrid gel	Replica PMMA gel
Pore volume / mm^{3}g^{-1}	778.3	9.1	467.9
Surface area / m^{2}g^{-1}	186.7	3.0	162.7

[a] Calculated by the Dollimore-Heal method.[15]

Other organic monomers such as styrene, methacrylic acid, etc. could be applied to prepare hybrid gels and replica gels. Furthermore, not only organic monomer but also organic polymer solutions such as agarose, gelatin, and chitosan could similarly be used for preparing hybrid gels and its replica gels. An organic polymer solution prepared at high temperature was poured into the silica pores. After removing the excess polymer solution, hybrid gel particles were obtained by simply cooling the silica.

In conclusion, organic–inorganic hybrid gel particles could be prepared simply by gelation of organic monomer or polymer solutions in the pores of a silica matrix. Furthermore, organic replica gels can be obtained from such organic–inorganic hybrid gels by treatment of the hybrid gel with an aqueous hydrofluoric acid solution. This method of preparing an organic–inorganic hybrid gel and its replica gel could be applied to a wide range of organic monomers and polymers. The resulting organic–inorganic hybrid gel has IPNs that are not covalently bonded. Further research on the preparation and properties of this hybrid gel and its replica gel are now under investigation. Applications of the hybrid gel include uses such as drug control release systems, support for enzymes, and affinity chromatography, etc. and will potentially be reported in the near future. Furthermore, inorganic materials such as hydroxyapatite, calcium carbonate, etc. can be crystallized and hybridized with such replica organic gels, and resulting inorganic materials may have the same structure as the silica used as the starting material.

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