Preparation of Organic/Inorganic Hybrid Gel after γ-Ray Radiation

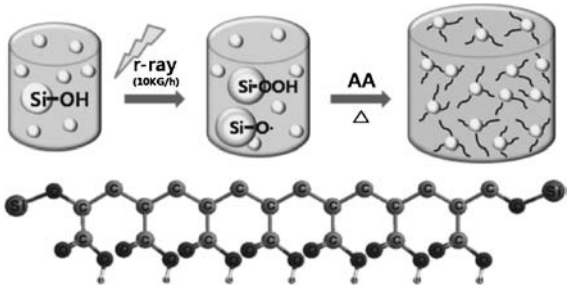
Jinwoo Kim,[1] Junmo Koo,[1] Tomoko Shirahase,[2] Atsushi Takahara,[2] and Daewon Sohn*[1]
[1]*Department of Chemistry and Research Institute for Natural Sciences, Hanyang University, Seoul 133-791, Korea*
[2]*Institute for Material Chemistry & Engineering, Kyushu University, Fukuoka 819-0395*

(Received August 21, 2009; CL-090773; E-mail: dsohn@hanyang.ac.kr)

This paper focuses on increasing the mechanical strength of hydrogels that connect silica particles via acrylic acid polymer chains. This is done by directly polymerizing the silica particle surface with γ-ray radiation in water.

A hydrogel is a material that has a 3D network structure which may be obtained using radiation, ion beam, chemical crosslinker, or physical interactions. Industrial and biomedical applications of hydrogels made from either natural or synthetic sources are limited by their poor mechanical properties. Many efforts have been focused on increasing the mechanical strength of hydrogels, but the robustness still remains unsatisfactory. Many novel hydrogels with unique structures and high mechanical strength have been developed in recent years, such as topological gels, double-network hydrogels, and nanocomposite (NC) hydrogels.[1,2] Also, synthetic hydrogel has many injurious components like initiator, crosslikers, and monomers which are residual reactants. As conventional hydrogels are very fragile, the characteristics of NC gels especially have great advantages for material use. NC gels are made of hybrid materials consisting of organic polymers and inorganic clay nanoparticles, which are synthesized by free radical polymerization in the presence of clay nanoparticles without any organic crosslinkers. Especially, Wang's group made hydrogel with organic (macromolecular microspheres)/organic by γ-ray radiation.[3] We tried to increase the mechanical strength of hydrogel by an organic/inorganic hybrid system.

We report a new way of synthesizing hydrogels with a nontoxic, well-defined network structure and higher mechanical strength than previous work. To synthesize hydrogels by free radical polymerization, γ-ray radiation was used to control the polymer chemical reaction at low temperatures. Furthermore, preparation of hydrogels by γ-ray radiation does not require the use of crosslinkers, unlike chemical methods.[4] In this method, a peroxidized silica particle acts as initiator as well as crosslinker. The mechanism for the formation of the peroxide and the initiation of polymerization, and for the formation of a hydrogel, is depicted in Scheme 1. During synthesis, the distance between two silica particles varies with their concentration and size. It is possible for two silica particles to be joined by a grafted chain, either by the mutual termination of two growing grafted chains that initiate at different silica particles or by the termination of a grafted chain from one silica particle by a radical on the surface of a second silica particle. In general, entanglement coupling is not likely to cause significant strength or toughness enhancement within a highly swollen gel because the chains are highly mobile and can slip past the entanglements. However, poly(acrylic acid) (pAA) chains are known to form inter- and intramolecular hydrogen bonds and act as stickers that enhance the dissipation involved in pulling out the entanglements.[5]



Scheme 1. Formation and molecular structure of the hydrogel.

Silica particles are synthesized by the well-known Stober method,[6] in which the particle size can easily be controlled. The volume ratio of tetraethyl orthosilicate (TEOS) and ammonium hydroxide (NH_4OH) was controlled to change the size of silica particles. Three samples of silica particles, with an average radii of 70, 120, and 260 nm, were prepared. Their sizes were determined by dynamic light scattering (DLS), and the uniform shape was confirmed by scanning electron microscopy (SEM). We prepared a 2 wt % silica particle solution that was diluted with deionized water to use for the gelation. This solution was irradiated with ^{60}Co γ rays (dose rate: 10 kGy h^{-1}) at KAERI, Jeongeup (KOREA), under ambient conditions for 2 h to create peroxides on the surface of the silica particles. The formation of peroxides on the particles was proven with iodometry, a common method used to verify peroxide formation. Potassium iodide and isopropyl alcohol were added to the irradiated silica particle solution during which the solution was heated and refluxed for 30 min. The solution gradually became yellow, which indicated the formation of I_2 and further establishes the presence of peroxides. SEM images were obtained to confirm that the silica particles were not changed or broken by high-resolution γ rays.

A cylindrical ampoule was manufactured to synthesize the hydrogel. In the ampoule, 2.5 mL of peroxide silica particle solution and 2 mL of acrylic acid (monomer, AA) were mixed. A freeze–thaw method composed of freezing, vacuuming, and melting was repeated three times in order to remove the other active materials like oxygen. When the temperature of the ampoule reached 40 °C in an oil bath, the peroxide on the silica particle changed to an oxide radical, which acted as both initiator and crosslinker. The reaction time was 24 h. The polymerization of hydrogel was confirmed by FT-IR, taking advantage of the easily followed C=C unsaturation AA conversion into a saturated C–C linkage. To purify the synthesized hydrogel, freeze-drying for 48 h was used to remove unreacted monomer and remaining water. The dried hydrogel was used for further characterization and had the same volume as the "wet" hydrogel. The peroxides on the silica particles decomposed under heat to form free radicals and initiate the grafting of monomers onto the surface of silica particles.

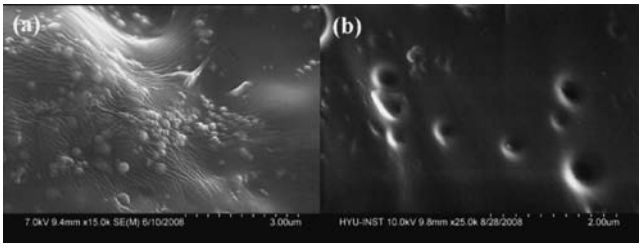


Figure 1. SEM images of (a) the particle imbedded hydrogel (contained particle radius is 120 nm) and (b) the hydrogel surface after HF treatment (contained particle radius is 260 nm).

Figure 1 shows an SEM image of the surface of a dry silica particle/polymer hybrid gel. Empty holes were observed when the gel was placed in HF solution for 30 min, which indicated the dissolved silica particles.

The T_g of the hydrogel was 3 °C, which was verified by dynamic mechanical analysis (DMA). The low T_g of the hydrogel is due to the Si–O–C bond of the silica particle surface. In quantitative calculation, the 2 wt % silica solution had a volume of 2.5 mL, silica particles (240-nm diameter) numbered 3.14×10^{12} and took up 1/87 volume in which one particle was in cubic interparticular distance (859 nm). The oxide radicals per particle were 2.5×10^7 per cubic interparticular distance.

The synthesized hydrogel contained only irradiated silica particles, acrylic acid monomers, and water. The relatively low T_g (near 3 °C) of the hydrogel was not due to the pAA chains because the T_g of pAA is 106 °C. The water content in the hydrogel influences the hydrogen bonding between pAA chains and can increase the mobility of pAA chains. This hydrogen-bonding effect of the hydrogel was proven by the fact that the strength decreased significantly after swelling in a high pH solution.

To confirm the mechanical properties of hydrogels, compressive and tensile tests were performed. The instrument used to measure the strength and ductility of the hydrogel was a universal testing machine (UTM), Instron 4465. For the compressive test, the scan rate was 1 mm min^{-1} and the load cell was 500 kgf. The shape of the hydrogel was a 13-mm diameter cylinder with a height of 15 mm.

In the tensile test, the scan rate was 5 mm min^{-1} and the load cell was 50 kgf. The used shape of the hydrogel was a rod, 15 mm long, 3.5 mm wide, and 1 mm thick. In the compressive test, not surprisingly, the NS (normal structure) hydrogel fractured under low deformation.[3] The NS hydrogel broke at a stress of 0.08 MPa and a strain of 45.5%. The synthesized hydrogel did not break, even under extremely high strain (most of the hydrogel was squeezed out of the plates), and it quickly recovered its original shape after the release of its load. Figure 2a shows the corresponding stress–strain curves of the synthesized hydrogels. The synthesized gel (70-nm silica particle hydrogel) did not break, even at a stress of 30.8 MPa and a strain of 98.2%. Specifically, when the strain reached 80%, there was a rapid increase in stress. All the synthesized hydrogels could sustain a much higher stress and strain than the NS hydrogels. Using 70-nm particles, the hydrogel has 30.8-MPa strength with 98.2% strain. For the 120-nm particles, the strength was 30.8 MPa with 96.1% strain. For the 260 nm, the strength was 22.7 MPa with 92.4% strain.

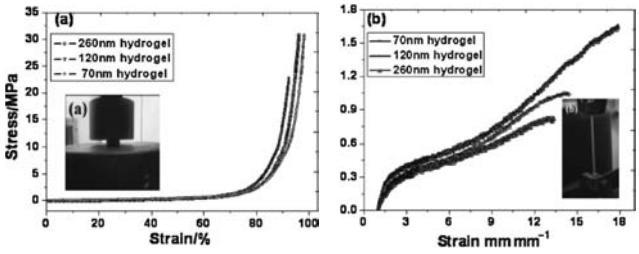


Figure 2. The compressive and tensile tests for the hydrogel by the universal testing machine (UTM), (a) demonstrates the hydrogel comprised of large particles is stronger than that of small particles because of the Si–O–C bonds, (b) shows the hydrogel of small particles has higher deformation than that of large particles.

In conclusion, the mechanical strength of the synthesized hydrogel has been dramatically improved in the silica particle/pAA hybrid gel. The chemical bonding between particles and acrylic acid by γ-ray radiation increases the connectivity of the hybrid gel, which also makes the intermolecular hydrogen bonding beween the acrylic acid chains. The synthesized hydrogel also has different mechanical properties depending on the size of the silica particle. Both the number of particles and total surface area are greater for a suspension of small particles than for a suspension of large particles given the same solid to liquid composition. This results in a greater number of surface Si–O–C bonds and more compact bonding by small particles. The hydrogel of small particles has more compact bonding than that of large particles. Figure 2b also shows that the hydrogel of small particles is more elastic than that of large particles. Furthermore, the hydrogel of large particles breaks at lower strain value than that of small particles. In 70-nm particles, the hydrogel showed 1.65-MPa strength at 1800% strain. In 120-nm particles, the strength was 1.08 MPa at 1500% strain. In 260 nm, the strength was 0.78 MPa at 1370% strain.

This work has been supported by the Nano Core Project in Korea (KOSEF). DS would like to acknowledge the JSPS fellowship (No. S08716) for the support during his stay at Kyushu University and Hanyang University (HYU-2008-T).

References

1 K. Haraguchi, T. Takehisa, *Adv. Mater.* **2002**, *14*, 1120.
2 Y. Tanaka, J. P. Gong, Y. Osada, *Prog. Polym. Sci.* **2005**, *30*, 1.
3 T. Huang, H. Xu, K. Jiao, L. Zhu, H. Brown, H. Wang, *Adv. Mater.* **2007**, *19*, 1622.
4 J. M. Rosiak, P. Ulanski, *Radiat. Phys. Chem.* **1999**, *55*, 139.
5 N. Tanaka, H. Kitano, N. Ise, *Macromolecules* **1991**, *24*, 3017.
6 W. Stober, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62.

Published on the web (Advance View) October 24, 2009; doi:10.1246/cl.2009.1112