Toughening of Hydrogels with Double Network Structure

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Hydrogels are made of swollen polymer networks containing more than 90% water. If modified with free chains on their surface, gels exhibit low surface friction and thus have been attractive candidates as artificial cartilage and low frictional materials. However, most hydrogels are mechanically too weak to be used as any load bearing devices. We have overcome this problem by synthesizing hydrogels with a double network (DN) structure. Despite of 90% water, these tough gels exhibit a fracture stress of 170 kg/cm², similar to that of cartilage. Extremely high mechanical property is due to peculiarly inhomogeneous structure of DN gels. The inhomogeneous structure is thought that large ‘voids’ of the first network may exist, and the second polymers exist in ‘voids’ of first network act as ‘molecular crack-stopper’ in DN gels, keeping the crack from growing to a macroscopic level. [DOI: 10.1380/ejssnt.2005.8]

Keywords: Hydrogel; Network; Fracture strength; Inhomogeneous structure; Dynamic light scattering (DLS)

I. INTRODUCTION

Hydrogels consist of swollen, cross-linked polymer networks and contain in excess of 90% water by volume. If hydrogels are functionalized with free dangling polymer chains on their surfaces [1], these gels exhibit low surface friction and thus serve as attractive candidates as artificial replacements for damaged cartilage. Unfortunately, most of hydrogels made from either natural or synthetic sources suffer from lack of mechanical strength, which prevents the gels to be used as substitutes of natural tissues.

Recently, we have overcome this problem by inducing a double network (DN) structure for various combinations of hydrophilic polymers. These DN hydrogels, containing about 60 - 90% water, exhibit fracture strength as high as a few to several tens of megapascals [2–5] and show high wear resistance due to their extremely low coefficient of friction. The DN gels are comprised of two independently cross-linked networks, and an optimal combination is found when the first network is a rigid polyelectrolyte and the second one is a flexible neutral polymer. We also found that the cross-linking density of the two networks and the molar ratio of the two polymers are two crucial parameters in improving the resistance against stress. A gel with highest strength is obtained when the first network is highly cross-linked, and the second is slightly cross-linked or even without cross-linking.

As the highly cross-linked first network has a high Youngs modulus but is quite brittle on its own, we have assumed that the dramatically enhanced mechanical strength is due to an effective relaxation of stress by loosely cross-linked second networks which dissipates the fracture energy and prevents crack development. In this work, we concentrated our attention on the molecular dynamics of the second network by changing the cross-linking density of the second network while fixing the molar ratio between the two networks using dynamic light scattering (DLS) technique. Through these results, the structure of DN gels and enhancing mechanism of strength has been discussed.

II. EXPERIMENTAL

DN hydrogels were synthesized by a two-step sequential network formation technique. The gels are referred to as P1-x1-y1/P2-x2-y2, where P, i, x, and y (i =1, 2) are the abbreviated polymer name, the molar monomer concentration, and the cross-linker concentration in mol-% with respect to the monomer, for the ith network, respectively. For example, the first network of the PAMPS-1-4/PAAm-2-0.1 DN gel was synthesized from an aqueous solution of 1M 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) containing 4 mol-% cross-linking agent, N,N-methylenbis(acrylamide) (MBAA), and 0.1 mol-% initiator, 2-oxoglutaric acid, in a reaction cell containing a pair of glass plate with 2 mm spacing. This first network gel was then immersed in an aqueous solution of 2M Acrylamide (AAn), containing 0.1 mol-% MBAA and 0.1 mol-% 2-oxoglutaric acid, for one day until equilibrium was reached. The second network was subsequently synthesized in the presence of the first network. The gel thus prepared consists of two independent polymer networks entangled with each other.

The compressive stress-strain measurements were performed on water-swollen gels using a tensile-compressive tester (Tensilon RTC-1310A, Orientec Co.). A cylindrical gel sample of 9 mm diameter and 4 mm thickness was set on the lower plate and compressed by the upper plate, which was connected to a load cell, at a strain rate...
of 10%/min. A tensile tester (Tensilon RTC-1150A, Orientec Co.) was used to carry out uniaxial stretching on specimens at a strain rate of 10%/min. The strain under compression (or stretching) is defined as the change in the thickness (or length) relative to the freestanding thickness (or length) of the specimen. DLS experiments were carried out on a static/dynamic compact goniometer (SLS/DLS-5000, ALV, Langen, Germany) at a fixed angle of 90° [6]. A He-Ne laser with 22 mW (the wavelength in a vacuum; $\lambda = 632.8$ nm) was used as the incident beam. A typical measuring time was 30 s. The temperature of the sample was regulated at 25.0°C within an error of $\pm 0.1$°C. Molecular weights of PAAm samples were measured by a high performance liquid chromatography (HPLC) system (LaChrom, HITACHI Co.), equipped with L-7490 RI-detector and KB-806M column (Shodex Co.). The commercial PAAms having regulated molecular weight were used as standard (PolyScience Co.).

III. RESULTS AND DISCUSSIONS

The DN hydrogels with an optimized network structure can sustain a mechanical stress as high as several tens of megapascals. This is in stark contrast to most common hydrogels with a single network, which are easily broken either by pressing with a finger or pulling with the hands. As shown in Fig. 1, for example, the PAMPS-1-4/PAAm-2-0 DN gel is so tough that it is resistant to tearing of 800~1000 J/m² of fracture energy, despite containing 90% water. The fracture energy of DN gel is comparable to that of general rubber. The high-strength DN gel showed a good reproducibility.

The DN gel sustains a high compression while the PAMPS single-network (SN) gel breaks down easily. The fracture stress of PAMPS-1-4 SN gel is 0.4 MPa while that of PAMPS-1-4/PAAm-2-0 DN gel 17.2 MPa. The stretching efficiency of the DN gel is also much greater than that of the component SN gels: the DN sample can sustain up to 75% stretching and breaks at a stress of 0.68 MPa, while the PAMPS SN gel breaks at only 6% and a stress of 0.05 MPa.

We should emphasize that two structural parameters, that is, the molar ratio and the cross-linking density of the two polymers are crucial for obtaining these strong gels. It is seen that a dramatic enhancement in the mechanical strength of the gel is obtained only when the molar ratio of the second network to the first network is in the range of several to a few tens. This is in strong contrast with conventional interpenetrated network (IPN) hydrogels, which do not exhibit any substantial improvement in mechanical strength [7]. The cross-linking density for the second network is critical for a dramatic increase in the mechanical strength of DN gels. When the cross-linking density of the first network is kept at 4 mol-% and only that of the second network is changed systematically from 0 to 3.0 mol-%, all the PAMPS/PAAm DN gels show a similar elastic modulus of 0.3 MPa, a water content of 90 wt%, and a molar ratio of the second network to the first network of 20, regardless of the change in the cross-linking density of the second network. However, a dramatic change in the mechanical strength of DN gels is found as shown in Fig. 2 (For Fig. 2, the area ratio will be discussed later in conjunction with Fig. 3.)

![Figure 1: Picture demonstrating how a DN gel sustains a high tearing. Sample: PAMPS-1-4/PAAm-2-0 DN gel. Fracture energy: 800~1000 J/m².](http://www.sssj.org/ejssnt)

![Figure 2: Effects of the cross-linking density of the second network ($y_2$) on fracture stress and on the area ratios of the slow mode to the 'gel mode' obtained from Fig. 3. Sample: PAMPS-1-4/PAAm-2-$y_2$ DN gels (swelling degree:10).](http://www.sssj.org/ejssnt)
corporation of a second polymer with higher cross-linking density results in substantial lowering of the mechanical strength of the DN gel. Over the cross-linking density of 0.5 mol%, the fracture strength becomes a constant minimum. These results indicate that DN gels with a loosely cross-linked second network exhibit a higher mechanical strength.

Figure 3 shows the effect of cross-linking density of second network (y2) on the characteristic decay time distribution function (DF) of light scattering in the PAMPS/PAAm DN gels. As the first network PAMPS behaves as a background material in the time range of the DLS measurements, the DF of PAMPS/PAAm DN gels represents that of the second network PAAm. Similar to the DF behavior of PAAm SN gels, a slow relaxation has been observed besides the ‘gel mode’ for 0 ≤ y2 ≤ 0.25 mol%, but the slow relaxation almost disappears for y2 ≥ 0.5 mol%. Compared with that of PAAm SN gels, the slow mode in PAMPS/PAAm DN gels has a much wider relaxation distribution and a much large characteristic decay time distribution function value, G(Γ). The area ratio of the slow mode to the ‘gel mode’ has been calculated and its relationship with the cross-linking density of PAAm (second network) is shown in Fig. 2. The result shows that the cross-linking density dependence of the area ratio is very similar to that of mechanical strength. This suggests that the increased mechanical strength of DN gels correlates to the slow modes of Γ−1 = 10−4 ~ 1 second in DN gels.

If we assume the slow mode of DN gel is diffusive to discuss the structural dynamics of DN gels, the diffusion coefficient of the slow mode in DN gels with low y2, \( D_{\text{slow}} \), can be obtained from the result of DLS measurement as follows:

\[
D_{\text{slow}} = \frac{\Gamma}{q^2},
\]

where \( \Gamma \) is the characteristic decay rate and \( q = 0.0187 \text{ nm}^{-1} \) is the scattering vector at 90°. From Fig. 3, \( D_{\text{slow}} \) is obtained as 2.9 × 10^{-11} ~ 2.9 × 10^{-15} m^2/s for Γ−1 = 10^{-4} ~ 1 second. What is the origin of the slow mode in DN gel? If it is due to the reptation of PAAm (second component) in PAMPS network (first component), \( D_{\text{rep}} \) can be estimated from the reptation model [8],

\[
D_{\text{rep}} = \frac{R_0^2}{\tau_{\text{rep}}},
\]

\[
\tau_{\text{rep}} = N^3 \tau_{\text{blob}},
\]

\[
\tau_{\text{blob}} = \frac{n \xi^3}{k_B T},
\]

where \( R_0 \) is the radius of PAAm polymer (cluster) with a Kuhn number \( N \) performing reptation in a swollen gel with a mesh size \( \xi \). \( \tau_{\text{rep}} \) is the relaxation time for a blob with the correlation length, \( \xi \). \( n \) is the solvent viscosity at temperature \( T \) and \( k_B \) is the Boltzmann constant. According to the result of HPLC measurement, the number-average molecular weight (\( M_w \)) and polydispersity index (\( M_w/M_M \)) of the linear PAAm polymer are 2.0 × 10^6 and 2.7, respectively. Approximately, the Kuhn number, \( N \), is equal to the degree of polymerization in this work, so \( N \) is c.a. 2.8 × 10^4 and \( R_0 = a N^{3/5} \) (\( a = 2.5 \) Å) is c.a. 120 nm. Supposing that the first network PAMPS is in a fully extended conformation, \( \xi \) is estimated to be 13 nm using swelling degree, \( Q_{\text{swell}} = 45 \) [9]. From above results, \( D_{\text{rep}} \approx 10^{-21} \text{ m}^2/\text{s} \) is found. This estimation shows that \( D_{\text{rep}} \) is much smaller than \( D_{\text{slow}} \) from that of DLS measurement, indicating that the slow mode of DN gel is not due to the reptation of PAAm in PAMPS network.

How can the PAAm polymer with \( R_0 = 120 \) nm possibly exhibit a motion with a characteristic diffusion constant as high as a polymer cluster in free solution in PAMPS network with small mesh size of 13 nm? A possible answer is due to the inhomogeneity of PAMPS network. As studied by many gel scientists [10–20], the inhomogeneity is an intrinsic property of polymer gel obtained from radical polymerization. Wu et al. pointed out that large ‘voids’ are formed if the growing rate of polymer ‘clusters’ is much higher than their relaxation rates (diffusion), and the voids between polymer ‘clusters’ (microgels) are much larger than the mesh size between cross-linked chains inside the microgels [16–18]. Consequently, the dynamics of slow mode in DN gels might result from a free motion of PAAm clusters in ‘voids’ of PAMPS networks. The wide distribution of the slow mode in the DN gels with low y2 is probably due to the partial entanglement of PAAm to PAMPS networks.

In the end, we propose a structural model for PAMPS/PAAm DN gels showing a high mechanical strength. PAMPS networks (first component) are rigid and inhomogeneous, and large ‘voids’ exist due to the specific radical polymerization mechanism. When PAAm are polymerized in the PAMPS network, some of them are interpenetrated in the PAMPS network, and others are filled in the large ‘voids’ of PAMPS gel, partially entangled with the PAMPS network. The linear or loosely
cross-linked PAAm in the ‘voids’ effectively absorbs the crack energy either by viscous dissipation, or by large deformation of the PAAm chains, preventing the crack growth to a macroscopic level. In other words, one possibility is that the increased mechanical strength of DN gels results from the effective relaxation of locally applied stress and dissipation of the crack energy through diffusive fluctuation of PAAm polymer (cluster). The other is that the part of PAAm polymer entangled with PAMPS network can be as ‘anchor’ and PAAm polymers with high molecular weight may be stretched very largely and ruptured during fracture process, consuming the crack energy [21].

IV. CONCLUSION

Despite containing 90% water, DN gels exhibit a fracture stress of several tens of megapascals. High strength gel is obtained by optimizing two key parameters, that is, the molar ratio and the cross-linking density of the two polymers.

Enhancement of the fracture energy of soft polymeric gels is due to an inhomogeneous structure which consists of PAMPS network with large ‘voids’ and flexible and soft PAAm polymers. The proposed structural model of DN gel shows that the ‘crack-stop’ occurs not in the polymer mesh size level (∼nm) but in larger spatial scale (size of voids), probably several hundred nanometers. The DN gel should be a good model system to investigate the viscoelastic effect on the fracture of biomaterials such as articular cartilage, tendon, etc.

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