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Water-Induced Brittle-Ductile Transition of Double Network Hydrogels

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ABSTRACT: In the previous studies, we have developed double network hydrogels (DN gels) with extraordinarily high mechanical strength and toughness although the gels contain 90 wt % of water. In this study, we investigated the effect of water content on the mechanical behavior of the DN gel consists of poly(2-acrylamido-2-methylpropanesulfonic acid) gels (PAMPS gels) as the first network and polyacrylamide gels (PAAm gels) as the second network. When the DN gel was dried gradually from its equilibrium swelling state (90 wt % water content), it exhibited a ductile behavior with a very high fracture stress and strain at an intermediate water content c (65 wt % $< c <$ 75%), and then became brittle upon further decreasing in water content ($c <$ 60 wt %). The behavior of the DN gel was compared with the corresponding single network gels, PAMPS and PAAm. It is found that at the intermediate water content, the fracture stress and strain of PAAm gel reached maximum, and the brittle−ductile change of DN gel upon with the change in water content was the results of the change in the mechanical properties of PAAm network.

Introduction

Biological tissues, both of hard tissue like bone and tooth and soft tissues like cartilage and muscle, contain 50−80 wt % of water.[1] A dehydration substantially changes mechanical function of the tissues. The tissues usually become more rigid and brittle in relative to their water containing state upon drying.[2,3] For example, the articular cartilage is a soft connective tissue bearing a major load in the body. By drying, cartilages become rigid, losing these functions.[4] The strong hydration ability, and therefore the softness of the cartilages, is due to proteoglycan in extracellular matrix(ECM). Proteoglycan contains large amount of negatively charged sulfate and uronic acid groups, which exerts a high ionic osmotic pressure on the ECM even in a medium with a high ionic strength.[4−6]

Hydrogels are a typical soft and wet material, similar to living soft tissues. It is an interesting question: How does the mechanical behavior of hydrogels change with the amount of water in hydrogel? In this study, we investigate the mechanical behavior of three kinds of chemically cross-linked hydrogels upon drying. They are poly(2-acrylamido-2-methylpropanesulfonic acid) hydrogel (PAMPS gel), which is a rigid and brittle polyelectrolyte gel, polyacrylamide hydrogel (PAAm gel), which is a soft and ductile neutral gel, and PAMS/PAAm double-network hydrogel (DN gel), which is a tough composite gel. Our previous studies have shown that PAMPS/PAAm DN gels exhibit anomalous high-strength and toughness.[7−9] Although the fracture energy G of the PAMPS gels is about 1 J/m^2 and G of the PAAm gels is about 10 J/m^2, G of the DN gels becomes anomalously high about 1000 J/m^2 at its maximum, 100−1000 times higher than the primary gels, and it is comparable to natural articular cartilage.[4−6]

We found that the initial elastic modulus, the fracture stress, and fracture strain of these gels dramatically changed with the water content. A ductile−brittle transition is observed for the DN gels accompanied by the decrease of water content from its equilibrium swelling state. The results will merit the understanding of the role of water in the soft tissue in terms of mechanical performance.

Experimental Section

Materials. 2-Acrylamido-2-methylpropansulfonic acid (AMPS) (Toagosei Co., Ltd.) and acrylamide (AAm) (Junsei Chemical Co., Ltd.) were used as received. *N*,*N*′-Methylenebis (acrylamide) (MBAA) (Tokyo Kasei Kogyo Co., Ltd.) used as a cross-linking agent, was recrystallized from ethanol. 2-Oxoglutaric acid (Wako Pure Chemical Industries, Ltd.) as an initiator was used as received.

Synthesis of the PAMPS Gels. PAMPS gels were synthesized by free-radical polymerization. Four mol % cross-linking agent of MBAA and 0.1 mol % initiator of 2-oxoglutaric acid, in respective to AMPS, were added to 1 M AMPS solution. Under an argon gas atmosphere, the solution was poured into the space between two glass plates separated by a 1−2 mm silicone rubber spacer with the suitable thickness in 1−2 mm. Photopolymerization was carried out with an UV lamp for 7 h.

Synthesis of the PAAm Gels. PAAm gels were synthesized by free-radical polymerization. 0.05 mol % cross-linking agent of MBAA and 0.02 mol % initiator of 2-Oxoglutaric acid, in respective to AAm, were added to 2 M AAm solution. Under an argon gas atmosphere, the solution was poured into the space between two glass plates separated by a 1−2 mm silicone rubber spacer. Photopolymerization was carried out with an UV lamp for 7 h.

Synthesis of the Double Network Gels. DN gels were synthesized by a two-step sequential free-radical polymerization. In the first step, 4 mol % cross-linking agent of MBAA and 0.1 mol % initiator of 2-oxoglutaric acid, in respective to AMPS, were added to 1 M AMPS solution. Under an argon gas atmosphere, the solution was poured into the space between two glass plates

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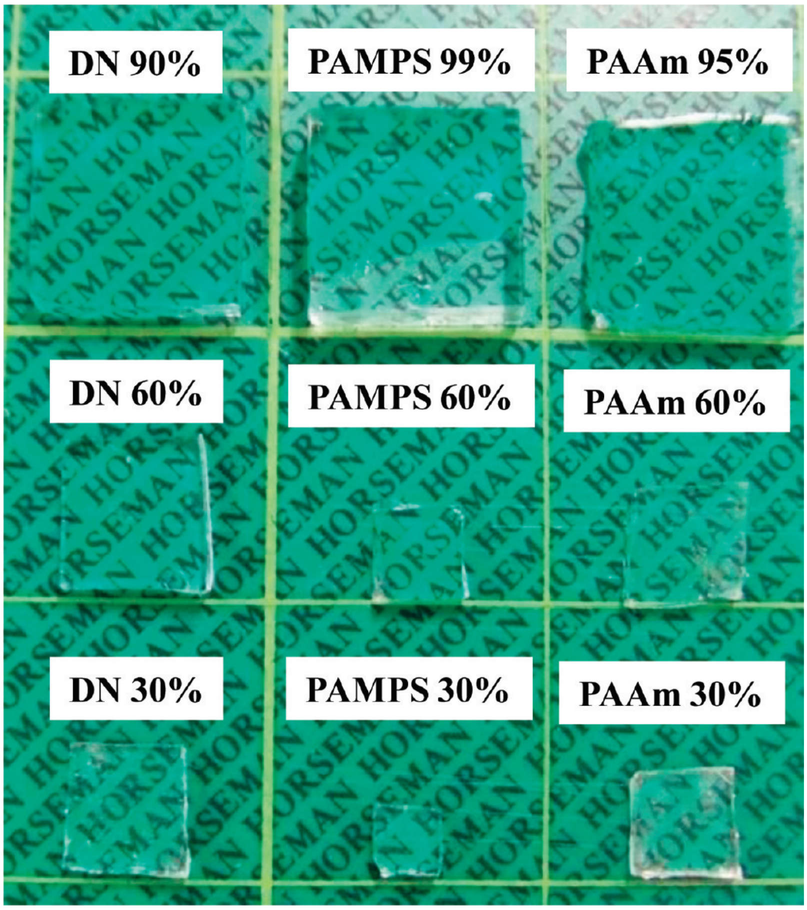

Figure 1. Photos of hydrogels with different water contents.

separated by a 1 mm silicone rubber spacer. Photopolymerization was carried out with an UV lamp for 7 h. In the second step, after the gelation of the first PAMPS gel was completed, the gel was immersed into a large amount of aqueous solution containing 2 M AAm, 0.02 mol % MBAA, and 0.005 mol % 2-oxoglutaric acid. The PAMPS gel swelled about 10 times in volume of the as-prepared state in the aqueous solution due to its polyelectrolyte nature. By the irradiation with the UV lamp for 7 h, the second network was subsequently synthesized in the presence of the first PAMPS network.[7−9]

Preparation of a Gel with a Different Water Content. The water content of the gel was controlled by drying the as-prepared gels (PAMPS, 80 wt %; PAAm, 90 wt %; DN, 85 wt %) to a prescribed weight at room temperature. After the sample reaching the prescribed weight, they were wrapped in plastic wrap for a week to let the water be uniformly diffuse in the samples. The gel at equilibrium swelling state was obtained by immersing the sample in pure water. The water content of the samples was measured by the weight change upon drying using the Electronic moisture balance (Shimazu Co., Kyoto, Japan) that evaporates the water in the gel at 150 °C.

The water content c (wt %) is defined as the ratio percentage between the weight of water in gel to the total weight of the gel.

$$c(wt\%) = \frac{\text{weight of water}}{\text{total weight of gel}} \times 100\%$$

So the water content c is related to the volume fraction ϕ as

$$\phi^{-1} = 1 + \left(\frac{c}{1-c}\right)\frac{\rho_p}{\rho_w}$$

Here, ρ_p, ρ_w are densities of polymer and water, respectively. Since the molar ratio of PAMPS to PAAm in the DN gel used in this work was 1:20,[7−9] which corresponding to a weight ratio of 1:7, so

$$\rho_p^{DN} = \frac{\rho_{PAMPS} + 7\rho_{PAAm}}{8}$$

for DN gel. Using $\rho_w = 1$ g/cm^3, $\rho_{PAMPS} = 1.739 \pm 0.3$ g/cm^3, and $\rho_{PAAm} = 1.437 \pm 0.2$ g/cm^3,[10] we have $\rho_P^{DN}/\rho_w = 1.475$.

Tensile Test. Tensile experiments were performed using a tensile test machine. Samples were cut to the standardized JIS K6251−7 ISO 37−4 size shape (w = 1.3−2.3 mm, d = 2 mm, L = 12 mm), with a cutting machine specially designed for soft materials (SDAP-100N, Dumbbell Co., Ltd.). Both ends of a test piece were cramped and pulled apart at a constant velocity, V = 100 mm/min, with a commercial test machine (Tensilon RTC-1150A, Orientec Co.). Cyclic tests were performed by performing subsequent tests immediately following the initial loading.

DSC Measurement. A differential scanning calorimeter (Model DSC22, SII Nano Technology Inc.) connected to a thermal analysis system (model, SSC 5100) was used. The sealed samples were cooled from 30 to −100 °C at a rate of 2 °C/min. The sample weight was 7−8 mg. The sample was sealed in a DSC aluminum sample pan.

IR Measurement. IR spectra were measured with a resolution of 2 cm^{-1} using a Nicolet 6700 FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. An attenuated total reflection (ATR) technique was employed for the IR measurements. A total of 512 scans were coadded for each spectrum. The ATR cell used was made of a horizontal Ge crystal (the refractive index is 4.0026). The temperature of the ATR cell was kept at 299 K (26 °C) by a temperature controller (KOMATSU DR-610B) within ±2 °C.

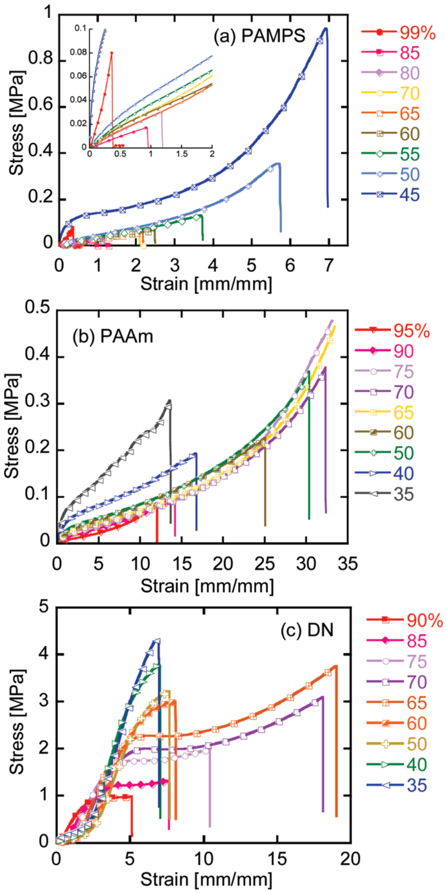

Figure 2. Loading curves in the tensile test of (a) PAMPS gels, (b) PAAm gels, (c) DN gels with different water contents. Please notice the difference in the scale of axes. The inset in part a is the result over an initial narrow strain range.

Results and Discussion

Figure 1 shows the appearance of PAMPS, PAAm, and DN gels with different water contents. The figures on the top line are gels in their equilibrium swelling state. The gels were cut into pieces of the same size after being swelling in water to the equilibrium state. Then the water content of the gels was controlled by drying with a proper time. Since the gels had different water contents in the initial equilibrium swelling state, their sizes became different after drying even to the same water content, for example 60 wt % (Figure 1, middle) and 30 wt % (Figure 1, bottom). All the samples kept their transparency after drying.

Figure 2 shows the loading curves in the tensile test of the gels with different water contents. As shown in Figure 2a, the single PAMPS gels showed a relatively high nominal fracture stress when they are in equilibrium swelling state (having 99 wt % water). However, they showed low fracture strains (below 1 mm/mm), indicating its rigid and brittle nature. As the water content decreased, the fracture strain increased rapidly. In particular, the fracture stress and strain dramatically increased when the water content of the PAMPS gels was 45 wt %.

As shown in Figure 2b, the mechanical performance of PAAm gel dramatically changed with the water content, and in the intermediate range of 50−75 wt %, it showed an excellent extensibility with a fracture strain higher than 20 mm/mm.

As shown in Figure 2c, the mechanical behavior dramatically changed from ductile-like to brittle-like when the water content of DN gels was decreased. In the case of the high water contents above 80 wt %, the gel showed a yielding behavior but with a relatively low nominal fracture stress and strain. For the intermediate water contents in the range of 65−75 wt %, the DN gels was ductile-like with a distinct yielding and a hardening region before fracture, and the nominal fracture stress and strain became high. However, when the water content was below 60 wt %, the sample became brittle-like, with a high fracture stress but a low fracture strain.

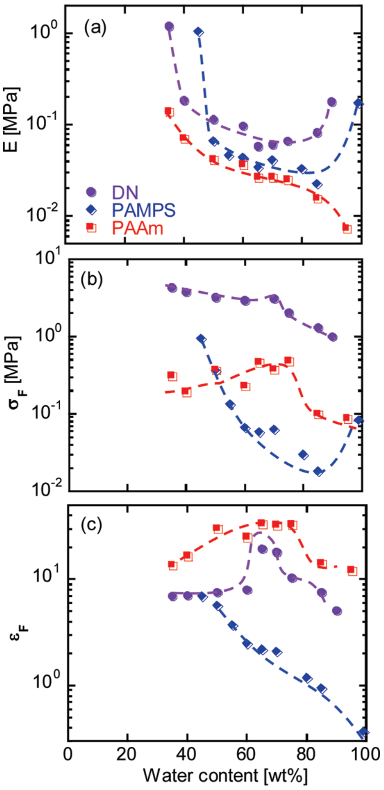

Figure 3. Water content dependencies of the nominal Young's modulus E (a), the nominal fracture stress σ_F (b), and the nominal fracture strain ε_F (c) for PAMPS gel, PAAm gel, and DN gel.

Thus, the fracture stress and strain of the PAMPS gels was much lower than that of the DN gels. However, PAAm gels could reach the highest fracture strain at proper water content.

Figure 3a shows the dependencies of the Young's modulus E on the water content for these three kinds of gels. E was obtained from the initial slope (less than 10% strain) of the stress−strain curves of Figure 2. The PAMPS and DN gels showed the similar concave curves of E with water content. On the other hand, E of the PAAm gels monotonously decreased with the increase in the water content, and it was less than one-tenth of those of the DN and PAMPS gels in the high water content range. It implies that the Young's modulus of the DN gels is dominated by that of the PAMPS gels.

Young's modulus of a polymer gel is proportional to the number of effective chains that sustain the force. With the decrease in the water content of the gel, the number of elastic chains per unit volume of the gel increases. To remove the effect caused by the change in the polymer density, the normalized Young's modulus, $E^N = E/\phi$, equivalent to the Young's modulus of an elastic network in dry state (that is, at c (wt %) $= 0$, or $\phi = 1$), was calculated and the results are shown in Figure 4a. After the normalization, all the data showed a concave shape with a flat region that E^N showed a very weak dependence on the water content ($50\text{ wt }\% < c < 80\text{ wt }\%$). We consider that this region is related to the state that the polymer chains of the network are in Gaussian distribution. So the shear modulus G in this region can be expressed by the rubber elasticity theory,

$$G^N = \frac{E^N}{3} = \nu_e RT = \frac{\rho}{M_c}RT$$

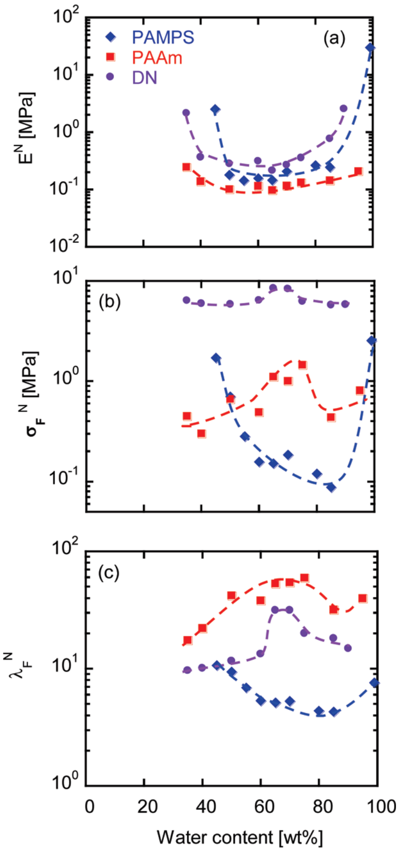

Figure 4. Water content dependencies of the normalized Young's modulus E^N (a), the normalized fracture stress $\sigma_F{}^N$ (b), and the normalized fracture strain $\varepsilon_F{}^N$ (c) for PAMPS gel, PAAm gel, and DN gel.

Here, ν_e is the number of elastic chains per unit volume of the network, ρ the polymer density at dry state, M_c the molecular weight between two cross-linking points, and R and T have their usual meanings.[11] The above relation permitted us to estimate the theoretical value of M_c from Figure 4a as 8.2×10^4, 9.2×10^4, and 3.5×10^4 g/mol, respectively, for PAMPS, PAAm, and DN gels. Here the M_c value for DN was the average over two networks. The estimated value of M_c for PAAm network was one order lower than expected from the amount of chemical cross-linker used in preparing the PAAm gel. This discrepancy may be originated from the physical association of PAAm chains, as indicated by the strong heterogeneity of PAAm solution and gel in water.[10]

A higher E^N at the regions of $c < 40$ wt % is assumed to be owing to the interaction between the polymer chains via hydrated water molecules. On the other hand, a higher E^N at the regions of $c > 80$ wt % is owing to the stretching of the polymer chain due to extensive swelling, which makes the chain conformation deviate from Gaussian distribution. Especially, for PAMPS and DN gels, the normalized E^N increased dramatically with the increase in the water content in the high water content region (>80 wt %), indicating the characteristic behavior of a polyelectrolyte network. That is, in pure water, the counterions of the polyelectrolyte network are dissociated and generate a large osmotic pressure $\pi_{ion}=fc_{ion}k_BT$ on the network.[12,13] Here, c_{ion} is the number concentration (m^{-3}) of counterions in the gel, f is the fraction of the counterions that contribute to the osmotic pressure. By this ionic osmotic pressure π_{ion}, the PAMPS subchains between the cross-linking points are in highly stretched state to give a high swelling of the gel. Since the contribution of each subchain to the elasticity increases with the extent of stretching and becomes much larger than k_BT when the subchains are at the extended state, the overall elastic modulus increases with the water content for the PAMPS gel and DN gel.

Figure 3b shows the dependencies of the nominal fracture stress σ_F on the water content for the three gels. The corresponding results for the normalized fracture stress, $\sigma_F^N = \sigma_F/\phi^{2/3}$, is shown in Figure 4b. Both σ_F and σ_F^N of DN was much higher than those of PAMPS and PAAm over the whole water content range, indicating the synergetic effect of the DN structure. Maximum values of σ_F and σ_F^N were observed for DN and PAAm gels around the water content of 70 wt %. On the other hand, PAMPS gel showed a concave shape with a very low σ_F^N at the intermediate water content region, while it reached the highest σ_F^N at the fully equilibrium swelling state. These results indicate that the final fracture process of DN gel is related to the fracture of PAAm network.

Figure 3c shows the dependencies of the fracture strain ε_F on the water content of the gels. In the intermediate region of the water contents (65−75 wt %), the fracture strain of the PAAm and the DN gels showed the maximum with the highest values, which corresponding to the ductile behavior. However, the fracture strain of the PAMPS gels monotonically increased as the water content decreased. These results imply that the fracture strain of the DN gels essentially depends on the behavior of the PAAm gels.

Comparing the behavior of the DN gels with both the PAMPS and the PAAm gels, we know that the brittle-ductile behavior of the DN gels depends on the balance of the strength of the PAMPS gels and the PAAm gels. When σ_F of the PAMPS gels was higher than that of PAAm, which occurred at the low water content region ($c < 60$ wt %), the DN gel was brittle. When σ_F of the PAMPS gels was much lower than that of PAAm gels, the DN gels became ductile, which occurred at the intermediate water content region (65 wt % $< c <$ 75 wt %).

Since the change in the water content cause a change in the initial length of the sample, we use the parameter of the extension ratio at fracture, λ_F, which is related to the fracture strain ε_F as $\lambda_F = \varepsilon_F + 1$ for the following discussion. The normalized extension ratio at fracture, λ_F^N, defined as the ratio of the sample length at fracture in swollen state ($\phi < 1$) to that at nondeformed dry state, is related to λ_F as, $\lambda_F^N = \lambda_F/\phi^{1/3}$.

The water content dependence of λ_F^N is shown in Figure 4(c). PAAm gel showed the highest fracture strain λ_F^N among the 3 kinds of gels, with a local maximum around 70 wt %. DN gel also showed a local maximum of λ_F^N at 65 wt % of water content, which was very close to that of PAAm. On the other hand, λ_F^N of the PAMPS gel showed an upward concave shape with water content. These results again demonstrate that the fracture strain of DN gel is related to that of PAAm.

Previous studies on the fracture of DN gels have shown that, the yielding phenomenon of the DN gels is due to the breaking of the first brittle PAMPS gels during the highly stretching.[14−18] The breaking process of the PAMPS gels in the DN gels occurs owing to the brittle nature of the PAMPS gels, as clearly shown by the present work. So the balance of the two components is crucial to determine the overall mechanical behavior of the DN gels. This can be clearly seen in Figure 5 that shows the water content dependencies of $\sigma_F\varepsilon_F/\phi$. The parameter $\sigma_F\varepsilon_F/\phi$ can be related, roughly, to the energy density needed to fracture the gel (in its dry state) by extension. PAMPS gel has a minimum around a water content of 60−90 wt % while PAAm showed a maximum around 70 wt %. As a result, DN gel also showed a maximum around 70 wt %.

It is well-studied that water molecules in the vicinity of the polymer strongly bound with its hydrophilic groups and therefore failed to freeze even well below the melting temperature of the water.[19,20] To elucidate the relationship between the state of

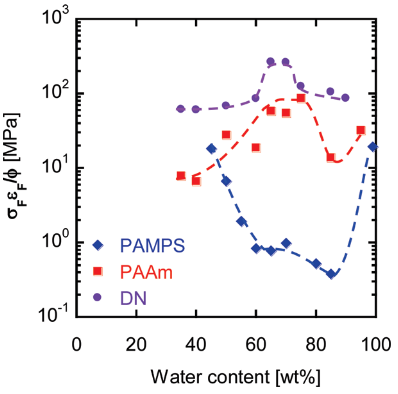

Figure 5. Water content dependencies of the normalized fracture energy for PAMPS gel, PAAm gel, and DN gel.

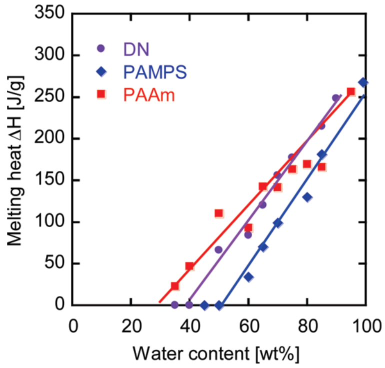

Figure 6. Water content dependencies of the melting heat of water in PAMPS gel, PAAm gel, and DN gel.

water and the mechanical properties, the melting heat of water in gels have been investigated by using DSC, as shown in Figure 6. The melting heat decreased with the decrease of water content. No melting heat was observed when the water content decreased to 40 and 50 wt %, for DN gels and PAMPS gels, respectively. That is, DN and PAMPS gels contain 40 and 50 wt % nonfreezing water, respectively. As shown in Figure 6, for the PAMPS gels, the melting heat was smaller than that of the DN gels and PAAm gels. It implies that the PAMPS gels have more nonfreezing water than that of the DN and the PAAm gels, indicating a stronger interaction between the polymer and the water for PAMPS gels. This strong interaction may explain the result of Figure 4a where the Young's modulus E of the PAMPS gel and DN gel was much higher than that of PAAm in the water contents around 35 wt %. Accordingly, the dramatic increase in E of the PAMPS gel and DN gels at the low concentration region is due to the association of polymer chains via strongly hydrated water molecules that are nonfreezable. It implies that the polymer chain of the DN gels becomes less mobile without the free water.

As shown in Figure 2−4, PAAm gel showed highest fracture strain and stress at the intermediate water content, which results in the ductile behavior of DN gel. According to previous studies, the Flory−Huggins interaction parameter χ for PAAm in water is 0.45, indicating that water is a marginal solvent for PAAm.[10] In order to investigate the molecular interaction between the polar moiety of PAAm and water, we further performed IR measurement for PAAm and DN gels with different water contents. Figure 7 shows the plot of weighted-average peak wavenumber of the amide II band ($\nu_{\text{am II}}$) against water content, where $\nu_{\text{am II}}$ is estimated by Savitzky−Golay method.[21] It is of note that the accuracy of $\nu_{\text{am II}}$ is ±0.2 cm^{-1}. The amide II mode contains contribution from N−H bending (~60%) and C−N stretching (~40%) vibration mode. Since the molar concentration of PAAm in DN gel is 20 times higher than that of PAMPS, the amide II band of DN gel may reflect the molecular environment around the NH_2 group of PAAm. The water-content dependence of $\nu_{\text{am II}}$ showed a concave shape. A higher wavenumber shift of the amide II band is generally caused by forming a hydrogen-bond, either between the amide group of PAAm and water or between the amide groups of PAAm.[22−24] Therefore, the displacement of the amide II band is proportional to the strength of interaction. The higher wavenumber shift observed in Figure 7 for both PAAm gel and DN gel in the low and high water content region might be associated with the strong interaction between amide groups and between amide group and water, respectively. The concave shape of the $\nu_{\text{am II}}$ plot was resemble to the convex shape of Figure 3c that showed very high fracture stress and strain in the intermediate water content region for these two gels. Therefore, high fracture strength of the PAAm gel and DN gel might be related to less interaction between amide groups at the intermediate water content region. Further study on this interesting behavior of PAAm gel is under progressing.

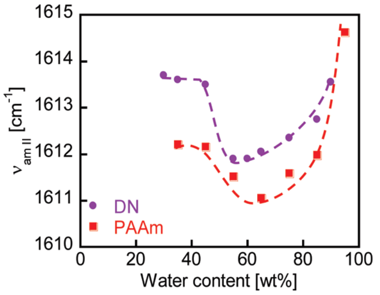

Figure 7. Weighted-average IR spectra peak wavenumber of the amide II band ($\nu_{\text{am II}}$) against water content of DN gel and PAAm gel.

Conclusions

Depending on the mechanical behaviors of the DN gel, the water content in gels can be divided into three regions: (1) high water content region (80 wt % $< c <$ 90 wt %) where the gel showed a distinct yielding with a moderate fracture stress and stain; (2) intermediate water content region (65 wt % $< c <$ 75 wt %) where the gel showed a ductile behavior with yielding and hardening; (3) low water content region ($c <$ 60 wt %) where the gel became brittle with a high fracture stress but a small fracture strain. Accordingly, at the intermediate water content (65 wt % $< c <$ 75 wt %), the DN gel possessed the highest toughness, showing both a high fracture stress and fracture strain. The brittle-ductile change of DN gel upon with the change in water content was the results of the change in the mechanical properties of individual components consisting of the DN gels. At the intermediate water content, the fracture stress and strain of PAAm network reached maximum, and were much larger than that of PAMPS network. As a result, the PAMPS network broke into fragments (softened) above a critical stress (yielding stress). After yielding, the stress was sustained by the PAAm chains. Further extension of the DN gel stretched the PAAm chains to a level of hardening. At the low water content region, interactions between polymer chains, mediated by the strongly hydrated water molecules, increased and the polymer chain of the DN gels became less mobile. As a result, the DN gel became brittle.

The observed optimized water content (65 wt % $< c <$ 75 wt %) for a tough DN gel is quite close to the water content of soft tissues. This coincidence suggests that a similar effect of water might exist in biotissues for their good mechanical performance.

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