Tear Velocity Dependence of High-Strength Double Network Gels in Comparison with Fast and Slow Relaxation Modes Observed by Scanning Microscopic Light Scattering

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ABSTRACT: To investigate the mechanical strength of double network (DN) gels in a wide dynamical range, the gel solvent was replaced with viscous solvents—ethylene glycol and glycerol—and with their mixtures with water. The viscosity dependence of fracture energy in a tearing test was weak but demonstrated the existence of characteristic tear velocity for maximum fracture energy as a function of solvent viscosity. Fast and slow relaxation modes in the gels' dynamics were simultaneously observed by scanning microscopic light scattering, which reveals that the DN-gel structure stays unperturbed by the solvent change. These results implied that the solvent viscosity weakly affect the toughness and structure of the DN gels. Further, we demonstrated that the effect of solvent viscosity on the fracture energy can be incorporated into a scaled tear velocity that distributes over 6 orders of magnitude. We concluded that the viscous friction between polymer and solvent is not particularly significant for the energy dissipation of DN-gel fracture.

Introduction

Since 2001, three novel hydrogels having excellent mechanical properties have been developed independently. Okumura and Ito[1] synthesized slide-ring gels (SR gels) with figure-eight cross-links, which are able to slide along polymer chains and effectively relax their tension. Haraguchi and Takeshita[2] synthesized nanocomposite gels (NC gels) containing homogeneously dispersed sheet-shape clay as a multifunctional cross-linker, which shows a resistance to extension as large as 1000%. Gong et al.,[3] some of the present authors, synthesized double network gels (DN gels), containing 90% water, which exhibit large fracture strengths of more than 20 MPa and a high Young's modulus (0.1−0.3 MPa). For each of these gels, the mechanisms for the excellent mechanical properties have been studied intensely.

The DN gels are composed of two independently cross-linked networks, synthesized via a two-step network formation procedure. An optimal combination has been found to be a first network of a rigid polyelectrolyte and a second network of a flexible neutral polymer. When the DN gels consist of highly cross-linked poly(2-acrylamido-2-methylpropane-sulfonic acid) (PAMPS) as the first component and linear polyacrylamide (PAAm) as the second component, containing about 90% water, the DN gels exhibit large fracture strength, which is comparable to that of natural cartilage (3−18 MPa). The mechanical strength of the DN gels is so high that compression tests cannot determine their fracture strength. Thus, we applied a tearing test to determine the fracture energy G of the DN gels.[4] Then, we found that the G of the DN gels reaches an anomalous value as high as 10^3 J/m^2, which is much higher than that of normal PAAm gels (10 J/m^2) and PAMPS gels (1 J/m^2).[5]

When compared to SR gels and NC gels, it seems quite difficult to explain the large fracture strength of the DN gels, even if we look at the credible theories that have been proposed for the different mechanisms enhancing the fracture energy G of soft polymeric systems, such as the Lake−Thomas theory[6] and de Gennes theory.[7] For example, the fracture energy G estimated by the Lake−Thomas theory is around 10 J/ m^2, which is 100 times less than the experimental value of the DN gels.[8]

In order to clarify the large fracture strength of the DN gels, we have studied them extensively and obtained the following information:
(i) The DN gels become strong in mechanical properties when the molar ratio of the second network PAAm to the first network PAMPS is in the range of several to a few tens.[3]
(ii) The cross-linking degrees for each network are crucial parameters. The first network should be highly cross-linked, and the second network should be cross-linked very little or not cross-linked. Surprisingly, the fracture energy G increases as the cross-linking density of the second network decreases.[4,8]
(iii) For an un-cross-linked second network, the molecular weight M_w of the linear chain of the second network's PAAm should be higher than a critical value of $M_w \sim 10^6$ for the large enhancement in G.[5]
(iv) The G of the DN gels does weakly depend on the tearing rate[4] (velocity) V_t.
(v) The DN gels show a kind of necking phenomenon in tensile tests.[9]
(vi) The DN gels become strong in mechanical properties when both the first and second networks strongly entangle each other.[10]
(vii) The first and second networks prefer each other rather than the common solvent of water.[11,12]

Based on the remarkable finding of (v), Brown and Tanaka (one of the authors) proposed, independently, similar local necking models to explain the fracture process of the DN gels[13,14] during the deformation process, the first brittle PAMPS network breaks into small clusters, yielding large fracture energy, and the clusters play the role of multifunctional cross-linkers of the second ductile PAAm chains. It was also observed that, after the deformation, the elastic modulus of the DN gels

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is relatively reduced due to the breaking process of the first network.[9,15]

Although these phenomenological models could explain the anomalous high strength of the DN gels, other unsolved problems still exist. The results (ii, iii) imply that the chain sliding of the second ductile PAAm chains is important for the large *G*. Thus, we tend to consider that the viscoelastic energy dissipation mechanism comes from the friction of the chain sliding as well as the breaking process of the first brittle PAMPS network. However, this consideration is contrary to result (iv), because the friction usually depends on the velocity. Thus, we may consider that the sliding friction of the second chain is not the main reason for the energy dissipation. On further consideration of the previous experiment for result (iv), the velocity range was somewhat limited due to the apparatus of the tearing test. If we expanded the velocity range, we could observe the velocity dependence of *G*, due to the chain sliding or the first network breaking. Thus, we should advance our studies of the DN gels to a much wider velocity range.

Here, we focus on the velocity dependence of the fracture energy of the DN gels in a wide velocity range and compare it with the dynamics of the DN gels, for the purpose of obtaining the unknown information about the relation between the fracture process and the dynamic process in the DN gels. The solvent of the DN gels is replaced with viscous, barely volatile solvents—ethylene glycol (Eg) and glycerol—and with their mixtures with water, instead of pure water, to control both the dynamics of the second network and the attractive interaction between the first and second networks in the DN gels. Then, we apply both the tearing experiment and dynamic light scattering simultaneously, to study the strength and the dynamics, respectively, and to discuss the relation between them. In the case of the rheological study of a polymer, to change the time scale, we usually change the temperature in the experiment. However, in the case of gels swollen in water, the temperature cannot be changed widely. On the other hand, the exchange of the gels' solvent can increase the viscosity, making it about 1000 times larger than that of water. Also, it is easy to exchange the solvent in gels, and thus it provides a quite wide range of velocities in the experiments. Moreover, if we can achieve the excellent mechanical properties of DN gels even in a hardly volatile solvent, it will show the potential to apply the strong DN gels to industrial environments, such as in the open air, with wider temperature windows than in a water medium.

Experimental Section

Materials. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) (Tokyo Kasei Co., Ltd.) and acrylamide (AAm) (Junsei Chemical Co. Ltd.) were used as received. *N*,*N*′-methylenebis(acrylamide) (MBAA) (Tokyo Kasei 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 Double-Network Gels. DN gels are 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, with respective to AMPS, were added to 1 M AMPS solution. After being bubbled by argon gas for 30 min, the solution was poured into the space between two glass plates separated by a 2 mm silicone rubber spacer. Photopolymerization was carried out under an argon gas atmosphere with an UV lamp (double 15 W black lights with 365 nm peak) for 10 h. The distance between the lamp and the sample chamber was 20 cm. In the second step, after the gelation of the PAMPS was completed, the gel was immersed into a large amount of 2 M AAm solution in the presence of 0.1 mol % 2-oxoglutaric acid and 0−0.25 mol % MBAA for at least 2 days until equilibrium was reached. Through irradiation with the UV lamp for 10 h, the second network was subsequently synthesized in the presence of the first network. Then, the prepared DN gel, consisting of the two independent polymer networks entangled with each other, where the cross-link density of the first network was fixed at 4 mol % and only that of the second network was changed systematically. Hereafter, DN-*x* represents the PAMPS/PAAm DN gel with *x* mol % cross-linker concentration to the monomer concentration of the second network. As reported in the previous paper,[3] every PAMPS/PAAm DN gel shows almost the same elastic modulus (0.1 MPa), under the same water content (90 wt %) and the same molar ratio of the second network to the first network of 20, despite the change in the cross-link density of the second network. The DN gel samples were washed with deionized water to remove the residual chemicals, and then immersed in water, Eg, and water−ethylene glycol (Eg) mixtures (1:2 and 1:4 in weight). The relative viscosities to water of these solvents are shown in Table 1.

Table 1. The Relative Viscosities Compared to Water and the Dielectric Constants of Water−Ethylene Glycol (Eg) Mixtures and Glycerol at a Temperature of 25.0 °C

	water	$\mathrm{Eg}_{67\mathrm{wt}\%}$	$\mathrm{Eg}_{80\mathrm{wt}\%}$	Eg	glycerol
η/η_0	1	5.6	8.7	16.9	945
ε	78	59	53	42	

Mechanical Strength Measurement. For the measurement of fracture energy, the DN gel samples were cut to the standardized JIS-K6252 1/2 size shape ($w = 5-5.5$ mm, $d = 7.5$ mm, $L = 30$ mm, initial notch = 20 mm), with a gel cutting machine (Dumb Bell Co., Ltd.). The two arms of a test piece were cramped and pulled apart at a constant velocity V_t, and the tearing force was recorded with a commercial test machine (Tensilon RTC-1150A, Orientec Co.). Fracture energy *G*, defined as the energy required to create a unit area of fracture surface in a gel sample, is calculated by the following equation,

$$G = \frac{F_{\mathrm{ave}}\Delta L_z}{w\Delta L_y} \tag{1}$$

where F_{ave} is the average tearing resistance force, ΔL_z is the distance of crosshead movement, ΔL_y is the distance of crack front propagation in the steady state of the fracture, and *w* is the width of the gel. Thus, $F_{\mathrm{ave}}\Delta L_z$ is the work done on the gel to create the fracture surface of $w\Delta L_y$. In the present study, the value of ΔL_z was regarded as the same as that of ΔL_y without particular consideration for fracture roughness. Therefore, *G* can be written as the next equation,[16]

$$G \cong \frac{F_{\mathrm{ave}}}{w} \tag{2}$$

Thus, the *G* of the samples was measured, changing the tearing rate (velocity) from 10^{-5} to 10^{-2} m/s.

Scanning Microscopic Light Scattering (SMILS). Dynamic light scattering measurements were performed with a scanning microscopic light scattering system.[17] Dynamic light scattering experiments were carried out on a compact goniometer at respective angles of 40, 60, 90, 125°. A 22 mW He−Ne laser (the wavelength in a vacuum: $\lambda = 632.8$ nm) was used as the beam through a cylindrical sample tube with a 10 mm outer diameter. A typical measuring time at a position was 100 s. The temperature of the sample was kept at 30.0 °C. 100 points per sample were measured with the stepping motor moving the sample holder vertically in 10 μm steps. The dynamic component of the ensemble-averaged correlation function was rigorously determined from the 100 data points and was numerically transformed into a relaxation−time distribution composed of two logarithmic Gaussian distributions (LGD).[10] Then the two relaxation modes were quantitatively characterized. Based on the results of previous studies about the two modes,[8,10] the faster mode can be assigned to the cooperative diffusion mode of the second network in the DN gels, which is related to the dynamically fluctuating motion of the second network. In the present study, we discuss especially the behavior of this fast mode of the second network because we focus on its sliding motion.

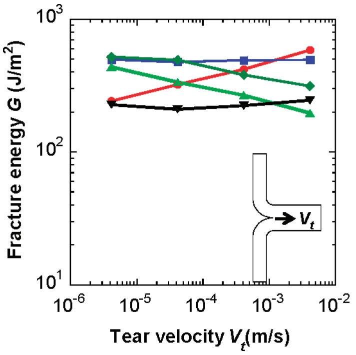

Figure 1. Dependence of fracture energy on tearing velocity for DN-0 gels swollen in different solvents ((●) water, (■) $\mathrm{Eg}_{67\mathrm{wt}\%}$, (◆) $\mathrm{Eg}_{80\mathrm{wt}\%}$, (▲) Eg, (▼) glycerol) with no cross-linking of second network.

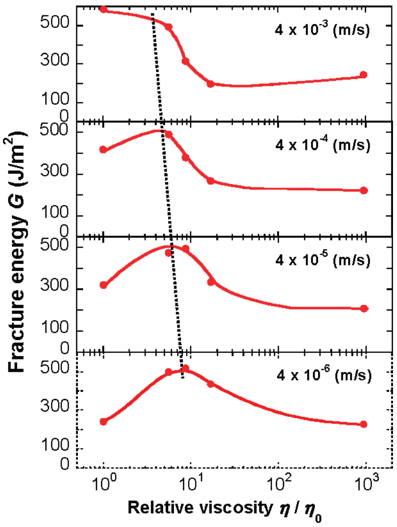

Figure 2. Dependence of fracture energy of DN-0 gels on the relative viscosity of different solvents for different tear velocities. Broken line is a guide to the eye.

Results and Discussion

Figure 1 shows the fracture energy G of the DN gels with the non-cross-linked second network, DN-0, swollen in the differently mixed solvents as a function of the tear velocity V_t. The dependency of G on V_t weakly depends on the composition of the mixed solvents. It implies that the solvent viscosity weakly affect the toughness of the DN gels; the viscous between polymer and solvent is not particularly significant for the energy dissipation of DN-gel fracture. On the other hand, in water, G increases with V_t. In a water–Eg mixture of $\mathrm{Eg}_{67\mathrm{wt}\%}$, G becomes a maximum, and it is almost constant to V_t. In a water–Eg mixture of $\mathrm{Eg}_{80\mathrm{wt}\%}$ and in pure Eg, G decreases with V_t. Further, in pure glycerol, G is reduced to a third of the maximum value of G for $\mathrm{Eg}_{67\mathrm{wt}\%}$. It was found that G depends on the composition of the viscous solvents, though the V_t-dependence is weak with $G \sim V_t^{\alpha}$ where α lies in a range of $-0.11 \lesssim \alpha \lesssim 0.13$.

Figure 2 shows the relative viscosity dependence of G at different tear velocities. For each tear velocity, G has a maximum, the position of which depends on the tear velocity. The viscosity at the maximum of G can be called the "characteristic viscosity", which shifts to the low viscosity side with an increase in tear velocity. In Figure 2, the interpolating curves indicate the positions of the peaks. To determine them numerically, the plotted data is fitted by using the symmetric experimental equation

$$G = G_0 + \Delta G \frac{\left(\frac{\eta/\eta_0}{\eta^*}\right)^{\alpha}}{1 + \left(\frac{\eta/\eta_0}{\eta^*}\right)^{2\alpha}} \tag{3}$$

where G_0, ΔG, and η^* are fitting parameters and we simply set $\alpha = 1.3$ to make the data fit well in all four graphs, since the value of α is not a critical parameter for the fitting. Then, the position of the peak η^* can be determined. (The fitted results are not shown here, because the height of the peak becomes too large and ranges out of the graph.) At $V_t = 4 \times 10^{-6}$ m/s, the determined characteristic viscosity is about $\eta^* = 8.4$, which corresponds to approximately $\mathrm{Eg}_{80\mathrm{wt}\%}$. The broken line drawn in Figure 2 for the guide to the eye indicates that there exists a power-law-type relationship between the characteristic tear velocity and the relative velocity at the maximum G. This means that the fracture process of the DN gels strongly depends on the viscosity of the solvent inside the DN gels with a kind of power law function.

Figure 3 shows the characteristic tear velocity for the fracture process V_G*, as power-law functions of the relative viscosity η/η_0. The slope of V_G* indicates a very large exponent of −4.4, which varies around −4.4 to −5.5, depending on the analysis condition. Although the exact exponent could not be determined in the present study, this large exponent means that a little difference in viscosity caused a quite large shift in the characteristic tear velocity of maximum G.

On the other hand, the change in the solvent viscosity also possibly affects the dynamics in the DN gels. This effect was studied with scanning microscopic light scattering.[17] By observing the characteristic behavior of the dynamics, it became possible to understand why the characteristic viscosity exists. Figure 4 shows examples of the dynamic component of the ensemble-averaged correlation function, $\Delta g_{\mathrm{en}}^{(1)}(\tau)$, for the DN-0 and PAAm-0.02, which were determined from 100 measurements at different points for a sample. In addition, the same profiles were also observed at other angles and q^2 dependence was confirmed, where q is the absolute value of scattering vector. Then, we know that all the relaxation modes observed here are assigned to translational diffusion dynamics, regardless of the composition of the solvent.

Figure 5 shows the effect of the solvent composition on the relaxation–time distribution function, $P_{\mathrm{en}}(\tau_R)$, for the samples mentioned above. Here, $P_{\mathrm{en}}(\tau_R)$ were numerically calculated from $\Delta g_{\mathrm{en}}^{(1)}(\tau)$ by using the established method.[17] For quantitative

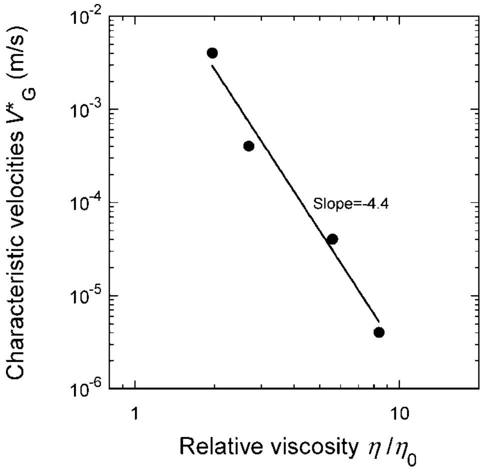

Figure 3. Dependence of three characteristic velocities on relative viscosity for DN-0 gels. One was determined by a tear test. The other two were determined from the gel and slow modes observed by SMILS.

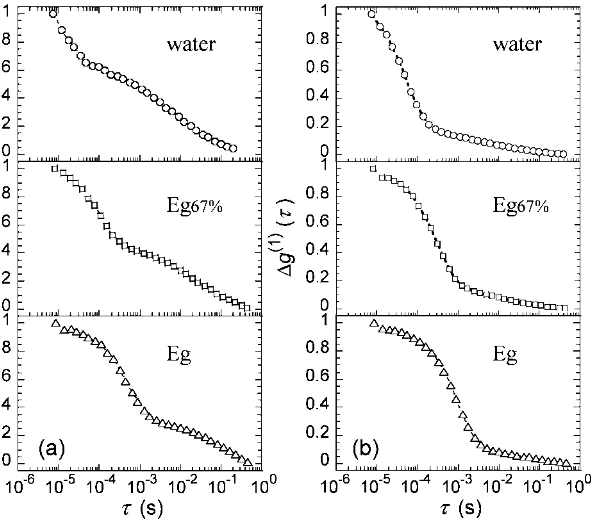

Figure 4. The dynamic component of the ensemble-averaged correlation function for (a) DN-0 gels and (b) PAAm-0.02 gels swollen in solvents of different viscosities ((○) water, (□) Eg$_{67wt\%}$, (△) Eg). The measurements were performed at a 90° scattering angle at 30 °C.

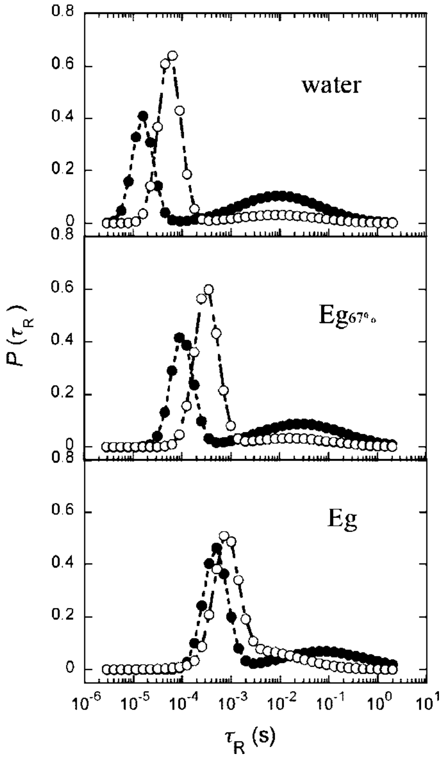

Figure 5. The ensemble-averaged relaxation−time distribution for (●) DN-0 gels and (○) PAAm-0.02 gels swollen in several solvents (water, Eg$_{67wt\%}$, and Eg, respectively).

analysis, we used the distribution function for a two-peak model, composed of a couple of logarithmic Gaussian distributions on the "LGD scheme".[10] Details were explained in the previous paper. It should be noted that the contribution of the first PAMPS network to DLS signals was negligible, compared to that of the second PAAm network. In actuality, the molar ratio is PAMPS: PAAm = 1:20 in the DN gels. Thus, both functions $\Delta g_{en}^{(1)}(\tau)$ and$P_{en}(\tau_R)$ almost represent the dynamics of the second PAAm network.

For both samples, the fast relaxation mode of the cooperative diffusion, which is often called the "gel mode", was simply observed in the relaxation−time range of 10^{-5}−10^{-3} s, as shown in Figure 5. At the same time, the "slow relaxation mode" was observed in the range of 10^{-3}−10^{0} s. It was found that (1) the fast mode of both samples became slower as the solvent viscosity increased. This means that the dynamics of the DN and the PAAm gels obviously depends on the solvent viscosity. Further, (2) the fast mode of the DN gels is always faster than that of PAAm gel. It is noted that the quantitative evaluation for both fast mode and slow mode in the DN gels has been carried out in another experiment.[10] Based on the previous results, the fast mode in DN gels is always faster than that in a PAAm semidilute solution, whose PAAm concentration is controlled to be the same as the PAAm concentration in the corresponding DN gels. Thus, we proposed that the fast mode of the DN gels originated from the PAAm entangled with the highly stretched rigid PAMPS network. That is, the entanglement has a role of attractive interaction between the first and second networks in water. Also, the SANS experiment on the DN gels found that the χ-parameter between the first PAMPS and the second PAAm is much lower than that between an individual polymer and water, which means that there is an attractive interaction between the polymers in water.[11,12]

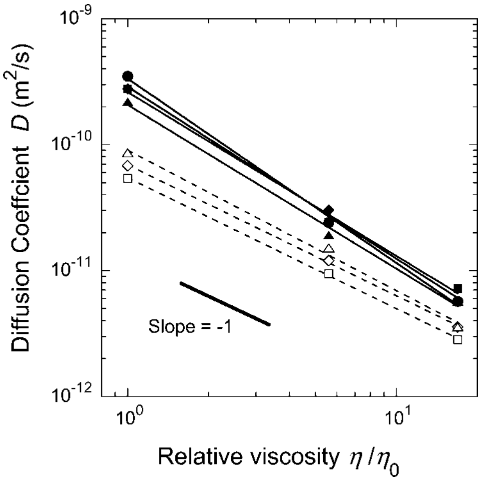

Figure 6. Dependence of the diffusion coefficient on relative viscosity for DN gels and PAAm gels with various cross-link densities for PAAm network: DN-0 (●), DN-0.02 (■), DN-0.1 (◆), DN-0.25 (▲), PAAm-0.02 (□), PAAm-0.1 (◇), PAAm-0.25 (△). Solid and dashed lines are the power-law functions fitted to the data.

Figure 6 shows the cooperative diffusion coefficient D of the fast mode as a function of the relative viscosity, η/η_0, for both the DN gels and the PAAm gels with various cross-linker concentrations for the PAAm network. This result means that the D of the DN gels was higher than that of the PAAm gels, where the slope of D for PAAm was very close to −1, and it was usually based on the Stokes law as $D \sim \eta/\eta_0$. Hence, the behavior of D implies that the network structure of the DN gels, which was characterized by the fast mode, stays unperturbed by the solvent change, for the various cross-link densities.

However, the slope of D for the DN gels was steeper than −1, which means the dynamics of the fast mode in the DN gels was little different from the usual gel mode. As shown in Figure 6, the difference of D between the DN gels and the PAAm gels became smaller with an increase in η/η_0. In the case of Eg, the diffusion coefficient of the DN gels was close to that of the PAAm gels. This means that the effect of the first PAMPS network on the dynamics of the second PAAm network decreased with the solvent composition. That is, the attractive interaction between the first PAMPS and the second PAAm became minor in the case of Eg, which was consistent with the decrease of G in Eg and glycerol (shown in Figure 1). This was probably related to the lower solubility of PAMPS in Eg than in water, which results from the change in dielectric

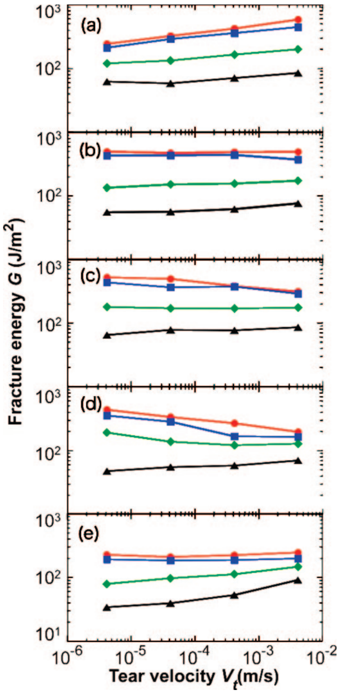

Figure 7. Dependence of fracture energy on tearing velocity for DN gels swollen in several solvents ((a) water, (b) Eg$_{67wt\%}$, (c) Eg$_{80wt\%}$, (d) Eg, and (e) glycerol) with various cross-link densities for the second network: DN-0 (●), DN-0.02 (■), DN-0.1 (◆), DN-0.25 (▲).

constant, ε, of Eg compared to water (shown in Table 1, which was measured by using a network analyzer[18]). It should be noted that the DN samples were highly transparent in all of the solvents, indicating that no phase separation occurred.

Thus the scattering experiment revealed that the network structure of the DN gels, characterized by the fast mode, stays unperturbed during the solvent change, for the various cross-link densities. Is this tendency also observed by the tearing test? Figure 7 shows the effect of the cross-link density in the second network on G and the dependence of G on V_t for the DN gels, swollen in the different solvents. By the introduction of chemically cross-linking points between the second polymer chains, G decreases largely. While this behavior is different from the above-mentioned tendency, it is similar to the tendency of the slow mode, as follows. In our previous study,[10] we found that the amount of the slow mode decreases as the cross-link density increases. These findings imply that the existence of the slow mode is due to the mobility of the second PAAm, and the mobility is important to the toughness of the DN gels. As mentioned in the Introduction, Brown and Tanaka proposed, independently, similar local necking models[13,14] during the deformation process, the first brittle PAMPS network breaks into small clusters, yielding large fracture energy. Thus, the increase of cross-link density causes a restriction of the sliding motion of the second PAAm due to the cross-linking points, and it prevents the breaking of the first PAMPS gels during the deformation process. Thus, the amount of slow-mode fluctuation decreases as the cross-linker density increases and it is closely related to a decrease in the fracture energy of the DN gels.

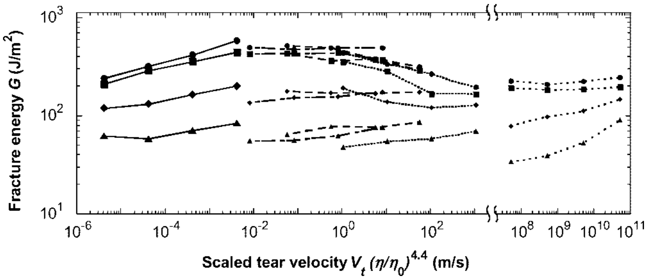

Figure 8. Dependence of fracture energy of DN gels on scaled tear velocity with various cross-link densities for the second network: DN-0 (●), DN-0.02 (■), DN-0.1 (◆)), DN-0.25 (▲).

We found that the viscosity effect on the fracture energy can be incorporated into the tear velocity by a scaled tear velocity. Figure 8 shows the dependence of the fracture energy of the DN gels on the scaled tear velocity. This figure was derived from the data shown in Figure 3 by using the relation $V_t/V_G{}^* \sim V_t(\eta/\eta_0)^{4.4}$. The scaled tear velocity dependence of G has a very large broad peak, which ranges over 6 orders of magnitude from 10^{-4} to 10^2. Why does the fracture energy of the DN gel have such a broad dependence on the scaled tear velocity? We consider that it is because the DN-gel structure stays unperturbed by the solvent change and also the viscous friction between polymer and solvent is not particularly significant for the energy dissipation of DN-gel fracture. Therefore, the DN gels keep high strength over a wide dynamical range.

Before concluding the present work, we should address the relation between the present results and our recent studies. As mentioned in the Introduction, we recently found that slightly modified DN gels show a necking phenomenon.[9] Based on this finding, Brown and Tanaka (one of the authors) proposed, independently, similar phenomenological models to explain the fracture process of the DN gels.[13,14] During the fracture process, the first brittle PAMPS network breaks into small clusters, yielding a large fracture energy, and the clusters play the role of multifunctional cross-linkers for the second ductile PAAm chains.

We tried to understand the present results based on these Brown and Tanaka models. Here, we introduce the new concepts of "sacrificial bonds" and "hidden length", which have been proposed recently.[19] We consider that if we embrace these concepts based on the Brown and Tanaka models, we can explain the present results as follows. The sacrificial bonds are named for the bonds that easily break before the main structure is broken. The hidden length is defined as the part of the molecules that was constrained from stretching by the sacrificial bonds. Thus, in this concept, the first brittle PAMPS behaves as the sacrificial bonds. Also, the sliding and disentanglement of the second PAAm network, which was loosely cross-linked by the small broken clusters of the first network, behave as the hidden length. When the tearing test is performed in the appropriate intermediate velocity region, the second PAAm can behave as the hidden length. However, if the tearing velocity is much faster than the fast relaxation process of the DN gels, the second PAAm chains cannot follow the deformation, and then the sliding and disentanglement of the second PAAm do not occur; that is, the second PAAm cannot behave as the hidden length. On the other hand, if the tear velocity is much slower than the slow relaxation process of the DN gels, the second PAAm chains relax completely and then the stretching and hardening of the second PAAm do not occur; that is, the second PAAm cannot behave as the hidden length, either. Thus, for the fracture experiment of DN gels, the concepts of sacrificial bonds and hidden length are suitable for the existence of the appropriate tear velocity range. In the future, we will focus on this new concept and try to confirm whether or not it is valid for DN gels, by the further experiments in much wider velocity range.

Finally, Figure 9 shows the apparent comparison of a couple of DN gels swollen in water and glycerol. The common solvent of the DN gels was water. Thus, these DN gels were easily affected by drying. If the DN gels were left in air at room temperature, they would have dried up. On the other hand, other DN gels were swollen in glycerol, which is a well-known hardly

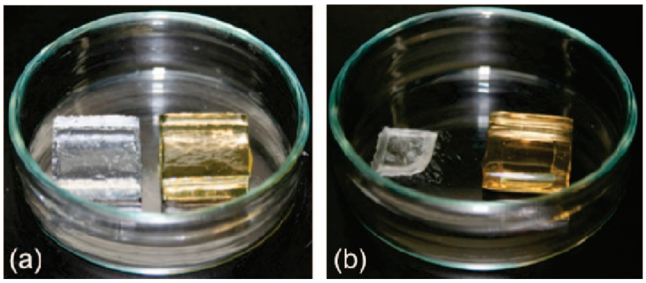

Figure 9. Visual comparison of two DN-0 gels swollen in water and glycerol. (a) Equilibrium swollen state of both gels. (b) Change in volume after 9 h drying in a vacuum oven at 50 °C well below 10 Pa.

volatile solvent, to prepare fixed DN gels. As shown in Figure 9(b), after 9 h drying in a vacuum oven at 50 °C, the fixed DN gels containing glycerol (with only a small amount of water) shrank only by 7.5% in thickness, while the usual DN gels containing water shrank by 57% in thickness. This stable property of the fixed DN gels free from drying is very useful in engineering applications.

Conclusion

By varying the viscosity of the solvent, the fracture energy behavior of high-strength DN gels was studied by tearing tests. It revealed that the solvent viscosity weakly affects the toughness of the DN gels. It implied that the viscous friction between polymer and solvent is not particularly significant for the energy dissipation of DN-gel fracture. On the other hand, at a constant tear velocity, the fracture energy as a function of the relative viscosity had a broad peak. It was possible to determine the characteristic viscosity, at which the fracture energy reached a maximum. There was a power-law relation between the tear velocity at the maximum fracture energy $V_G{}^*$ and the characteristic viscosity η^* as $V_G{}^* \sim \eta^{*-4.4}$, which is apparently not at all proportional to the inverse of the viscosity.

Simultaneously, the dynamics of the DN gels was studied with SMILS. Two different modes (fast and slow) for the dynamic fluctuation of the second network were found to exist. The relaxation time of the fast mode in the DN gels was relatively faster than that in polymer solution at similar conditions. This implied that the existence of the first rigid polyelectrolyte had the effect of making the fast mode faster due to the coupling of the dynamic fluctuations between the first and second networks. The strength of the coupling effect depended on the kind of solvent. For water, a typical polar solvent, the effect was significant, but for ethylene glycol, a relatively nonpolar solvent, the effect looked diminishing. Thus, a change in solvent was very effective for the dynamics of the DN gels, due, not to the viscosity, but to the solvent-induced interaction. However, roughly, the network structure of the DN gels, which was characterized by the fast mode, stays unperturbed during the solvent change, for the various cross-link densities of the second network.

Finally, the tear-velocity dependence of the fracture energy was scaled by using the power-law relation. We then obtained a unified distribution of the fracture energy as a function of the scaled tear velocity. This unified distribution of the fracture energy ranges over 6 orders of magnitude of the scaled tear velocity. With the knowledge of such a broad distribution, we should be able to claim that the DN gels keep the high strength over a wide velocity range during the change in the solvent viscosity. On the other hand, by introducing the chemical cross-link to the second network, the fracture energy decreased steeply and the amount of the slow mode decreased simultaneously. Thus, we concluded that the change in the interaction between the first and second networks was much more important than the change in the solvent viscosity for both the toughness and structure of the DN gels.

Also, it was shown that the excellent mechanical properties of the strongest DN gels, even in Eg, a hardly volatile solvent, were promising in relation to the application of such strong DN gels in industrial environments, such as open air, with wider temperature windows than in a water medium.

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