Brittle, ductile, paste-like behaviors and distinct necking of double network gels with enhanced heterogeneity

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Abstract. We propose a simple method to obtain double network (DN) hydrogels containing 85-90wt% water with various kinds of mechanical performance by taking advantage of the heterogeneity of the first network: By synthesizing the first network in a poor solvent that enhancing the heterogeneity of the network, the DN gel exhibits rich mechanical behavior: from brittle, ductile (necking), to paste-like. For a proper heterogeneity, a distinct necking deformation with extensibility of about 20 times is observed for post-necking gels. The necking gels have a high initial modulus (0.1-0.5 MPa) and high mechanical toughness (nominal fracture stress: 1 MPa), both values are similar to that of living tissues.

1. Introduction

Living tissues, containing 50-80 wt% water, are soft and wet materials with an excellent mechanical property: They have the elasticity in a range of several 100 kPa to MPa, and sustain deformations as large as 100% and failure stresses of 1-10MPa [1]. Material scientists are facing challenges in providing synthetic soft tissues using hydrogels, the same soft and wet materials. Common hydrogels are usually mechanically weak due to 1) high water contents; and 2) heterogeneity in the cross-link structure either formed by covalent cross-links (chemical gel) or attractive interactions (physical gel). High water content leads to low elasticity and heterogeneity concentrates the tension, bringing about failure of the hydrogels at small stresses.

To reduce the high water content (usually higher than 95 wt% for a common hydrophilic gel), a common method is to increase the cross-linking density, this in turn, enhances the heterogeneity and the gel becomes brittle.

One method to avoid the concentrated stress caused by heterogeneity is with a sliding cross-linking structure (sliding ring gel): polymer chains with bulky end groups are interlocked by figure-of-either cross-links. Hence, these cross-links can pass along the polymer chains freely to equalize the tension of the threading polymer chains and sustain large deformation [2].

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Here, we propose an alternative method to obtain a tough gel containing 85-90wt% water by taking advantage of the heterogeneity of double network (DN) gels: We demonstrate how the mechanical toughness be improved by enhancing the heterogeneity in the double network (DN) gels. By synthesizing the first network in a poor solvent that enhancing the heterogeneity of the network, the DN gel exhibits rich mechanical behavior: from brittle, ductile (necking), to paste-like. For a proper heterogeneity, a distinct necking deformation with extensibility of about 20 times is observed for post necking gels. The necking gels have a high initial modulus (0.1-0.5 MPa) and high mechanical toughness (nominal fracture stress: 1 MPa), both values are similar to that of living tissues [1].

2. Experiment

The synthesis procedure of the DN gel, consists of densely cross-linked polyelectrolyte, poly(2-acrylamido-2-methylpropanesulfonic acid)( PAMPS), as the first network and loosely cross-linked neutral polymer, polyacrylamide(PAAm), as the second network, is identical to previous studies [3-6], except that the polymerization (gelation) reaction of the first network (PAMPS) is carried out in special reaction solvent, mixtures of water and 1,4-dioxane (details for sample preparation are given in the next paragraph). Below the volume fraction of 1,4-dioxane in the reaction solvents is denoted by \( \phi \). The solvents can dissolve AMPS monomer (and cross-linker) but the existence of 1,4-dioxane induces weak segregation of the PAMPS during the polymerization, leaving enhanced heterogeneity in the first network.

2-Acrylamido-2-methylpropanesulfonic acid (AMPS; Tokyo Kasei Co., Ltd.) was used as received. Acrylamide (AAm; Junsei Chemical Co. Ltd) was recrystallized from chloroform. N,N'-Methylenebis-(acrylamide) (MBAA; Tokyo Kasei Co., Ltd.), a cross-linking agent for both AMPS and AAm gels, was recrystallized from ethanol. 2-oxoglutaric acid (Wako Pure Chemical Industries, Ltd.), a radical initiator for the gelation reactions, was used as received. The PAMPS gels are synthesized by free-radical polymerization. 1 M AMPS, 4 mol % of MBAA, 0.1 mol % of 2-oxoglutaric acid (the molar percentages, 4 and 0.1 mol %, are determined with respective to the AMPS monomer) were dissolved into the mixture solvents. Photo-initiated polymerization was carried out under argon atmosphere with an ultraviolet (UV) lamp for 9 h (The distance between the lamp and the sample mold was about 200 mm.). The DN gels are synthesized through a two-step sequential free-radical polymerization. The first step is described above. In the second step, after the gelation was completed, the platy PAMPS gel was immersed into 2 M AAm solution containing 0.1 mol % of 2-oxoglutaric acid and prescribed amount of MBAA (0 ~ 1mol %) for at least 2 days until the equilibrium was reached. By irradiation with the UV lamp for 8 h, the second network was subsequently synthesized in the presence of the first network. Samples were swollen in water for 1 week. The main material parameter in this study is the volume fraction \( \phi \) of the dioxane. In addition, we changed the cross-linker (MBAA) density in the second PAAm network to obtain data in Fig. 4. The final water content of the DN gel is 85-90wt%.

The internal structure of the PAMPS gels in water was observed by confocal laser scanning microscope (BX 50, Olympus Co. The laser wavelength was 568nm) with 60x objective lens (N.A. = 1.4) in refractive mode without any fluorescent dye, where the special resolution was estimated about 200nm in an ideal condition.

Dynamic light scattering measurements of the PAMPS gels were performed with a scanning microscopic light scattering system [7]. 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: \( \lambda = 632.8\text{nm} \)) was used as the beam through a cylindrical sample tube with a 10 mm outer diameter. Before the measurement, the PAMPS gels were immersed in 1mM NaCl aqueous solutions for two days, in order to modify the A typical measuring time at a position was 90 s. The temperature of the sample was kept at 30.0 °C. 31 points per sample were measured with the stepping motor moving the sample holder vertically in 30\( \mu \text{m} \) steps. The dynamic component of the ensemble-averaged correlation function was rigorously determined from the 31 data points and was transformed
into a relaxation-time distribution function $P(\tau_R)$ by using numerical inversed Laplace transformation method [7], where $\tau_R$ is the relaxation time. Then the two relaxation modes were quantitatively characterized. It is very similar to the results of previous studies about the two modes in the DN gels [8-10]. In the present study, we simply estimate the size of characteristic fluctuation from the behavior of both the faster and slower modes $\xi$, based on the Stokes-Einstein equation $\xi = k_B T |q|^2 \tau_R / 6\pi \eta$, where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $|q|$ is the amplitude of scattering vector, and $\eta$ is the viscosity of solvent.

The tensile mechanical properties were measured with a commercial test machine (Tensilon RTC-1150A, Orientec Co.). The gels were cut into a dumbbell shape standardized as the JIS-K6251-7 sizes (length: 35 mm; width: 6 mm; thickness: 2-3 mm; gauge length: 12 mm; inner width: 2 mm). The nominal stress was used in the tensile curves. The tensile strain rate was $1.3 \times 10^{-3}$ s$^{-1}$.

3. Result and discussions

Fig. 1a shows appearance of PAMPS gels synthesized at different $\phi$. For $\phi \geq 0.6$, the gels were turbid and the turbidity increased with $\phi$; the increase in turbidity indicates the existence and growth of heterogeneity on the scale of visible light wavelength. This also suggests that even for $\phi < 0.6$ where the gels were transparent, the heterogeneity gradually increased with $\phi$.

The internal structure in gels were observed by a confocal scanning microscope (CLSM) as seen in Figs. 1b and 1c. The inner structure in the PAMPS gels at $\phi = 0.8$ looks more inhomogeneous than that at $\phi = 0$.

Figure 1. (a): The first PAMPS gels synthesized in water and 1,4-dioxane mixed reaction solvents with different volume fraction of poor solvent, 1,4-dioxane $\phi$. (b, c): Confocal laser scanning microscope images of the PAMPS gel at $\phi = 0$ (a) and $\phi = 0.8$ (b).
In order to characterize the heterogeneous structure in the PAMPS gels more precisely, the dynamic light scattering was performed. Fig. 2a shows the relaxation-time distribution of the DN gels prepared at different fraction of poor solvent $\phi$. For all the gels, the fast mode with a sharp peak profile and the slow mode with uni- or bimodal peak profile were observed. Here we consider that the bimodal peak profile we observed is not correct. The true profile of the slow mode is probably made from an unimodal peak with wide distribution. Thus, we estimated the two kinds of characteristic length $\xi$ from the fast and slow modes, as shown in Fig. 2b. We consider that the short length is related to the mesh size in the DN structure and the long length is related to the large-scale inhomogeneity induced by the addition of the poor solvent. For $\phi < 0.6$, both the sizes of the network structure and the large-scale inhomogeneity increase as $\phi$ increases. On the other hand, for $\phi \geq 0.6$, the size of the network structure decreases but the size of the inhomogeneous structure increases as $\phi$ increase. The behavior of the inhomogeneous structure is consistent with the behavior of the turbidity, as above mentioned. Also, the behavior of the mesh size is also consistent with the behavior of the swelling weight ratio, as will be described below.

Fig. 3a shows the behavior of the equilibrium weight ratio $q$ of the PAMPS gels used as the first network and the initial Young’s modulus $E$ as functions of $\phi$. Here, $q$ is the weight ratio of PAMPS gel at swelling equilibrium in water to that after drying. Since the weight of the swollen gel is dominated by water, $1/q$ is approximately proportional to the concentration (g/l or mol/l) of PAMPS in gel, and also to that in the resultant DN gels [11]. As shown in Fig. 3a, for $\phi < 0.6$, $q$ increases as $\phi$ increases, and for $\phi \geq 0.6$, $q$ decreases as $\phi$ increases. This behavior is the similar to the behavior of the mesh size. It implies that the change in the swelling weight ratio comes from the change in the mesh size.

To elucidate the relationship between the $q$ and $E$, we plot of the same data as the relation of $E$ versus $q$, in Fig. 3b ($\phi$ is indicated in the plot.) For $\phi \leq 0.65$, $E$ decreased with $q$; this behavior is
quite usual for polyelectrolyte gel, because $E$ is roughly proportional to osmotic pressure of counter ions from PAMPS. On the other hand, $E$ is almost independent of $q$ for $q \geq 0.7$. This indicates that for the turbid gels, the counter ions are confined in PAMPS rich domains, which reduces the activity of the counter-ions and the apparent (whole) swelling volume of the gels is not simply determined by the counter-ion concentration.

Fig. 4a gives a comparison of loading curves of the DN gels with different $\phi$ (and uncross-linked second network, tensile strain rate is $1.3 \times 10^{-3}$ s$^{-1}$), and the stretching process of the sample DN gel with $\phi = 0.2$ (photos A-G). The initial (low strain) behaviors of the loading curves are similar with each other. On the other hand, the yielding and the fracture behaviors strongly depend on $\phi$. For $0.2 \leq \phi \leq 0.4$, the DN gels showed lower yielding stresses (around 0.5 MPa) and fairly higher fracture strain (larger than 15), compared with the gels with $\phi = 0$ [12]. At $\phi = 0.5$, the gel underwent necking, however it broke during necking. Above $\phi = 0.5$, the gels got pasty and sticky, and broke quite easily without necking. As seen in photographs (and data points) C, D, and E, a plateau region was created in the loading curve during the necking propagation (the arrows in the photos shows a boundary of the necking zone). After the boundary of the neck reached around the clamped parts (F), the stress re-increased with further stretching and the necked gel was uniformly stretched withstanding high extensions (G). The post-necking gels almost returned to the original lengths when the tensile force was removed (although a few percent of permanent strains remained). Figs. 4b and 4c show the yielding stress (and strain) and the fracture stress (and strain) as a function of $\phi$, respectively. The yielding stress monotonously decreased with $\phi$. The yielding strain showed similar behavior, but the dependence was weaker. On the other hand, the fracture stress (strain) had a peak around $\phi = 2.0$ ($\phi = 3.0$). The peak corresponds to the result that only the DN gels with intermediate $\phi$ can withstand the large extensions in Fig. 4a.

In our previous work, some DN gels with modified first network structure show necking phenomena during tensile tests [6]. We proposed a structural model of the necked gel that the first network breaks into small fragments and they are interconnected by the second PAAm chains. The monotonously decrease of the yielding stress (in Fig. 4b) can be directly understood based on the structural mode: the heterogeneity works as mechanical defects and expedites the onset of catastrophic breakdown of the
Figure 4. (a): A comparison of tensile curves of the DN gels with different $\phi$, and photographs of the necking process for the DN gel with $\phi = 0.2$. The tensile strain rate is $1.3 \times 10^{-1} \text{ s}^{-1}$. The photos of C-E correspond to the neck propagation. During this period, a plateau was produced in the loading curve. (b): The dependence of the yielding strain (and stress) on $\phi$ determined from the curves; (c): The dependence of the fracture strain (and stress) on $\phi$ determined from the curves.

First network. If post-necking gel with high extensibility is free from large scale heterogeneities that causes strong stress concentration, its maximum breaking strain $\lambda_b$ could be related to the ratio of the average contour length $L_c$ to the average radius $R$ of the partial PAAm chains between two cross-linked points: $\lambda_b \approx L_c / R$. Employing $L_c = aN$ and $R \approx aN^{3/5}$ [13], $\lambda_b \approx N^{2/5}$, here $N$ is the Kuhn number, which is approximately equal to the repeated units of PAAm, between the effective cross-linkages of PAAm. With the observed value of breaking strain, $\gamma_b \approx 17$, and the relation $\lambda_b = \gamma_b + 1$, we have $N \approx 10^6$. This order estimation for $N$ is consistent with an estimation based on our very recent experiments [14]. On the other hand, it is impossible at present to explain why the DN gels with intermediate heterogeneity show the highly extensibility because of lack in detailed information about the structure of the post-necking gels and their fracture mechanism. At least, however, we can interpret the deterioration in the mechanical properties for larger $\phi$ as follows: when the spatial scale of the heterogeneity is larger than average radius $R$ of PAAm random coils (around a few hundreds nm [5]), the PAAm chains filling void (or PAMPS poor) region behave like in the bulk state, that is, a flowable sol; thus they are incapable of connecting with PAMPS rich domains after onset of breaking-up of the first network.
The above argument can be verified by increase the cross-linker, N,N’-Methylenebis-(acrylamide) (MBAA), in the formation of the second network, PAAm. In Fig. 5, we give a phase diagram-like representation of the tensile behavior of the DN gels. To construct the diagram, we varied the cross-linker concentration \( y \) of the second network, MBAA (the concentration is represented in the unit of mol\% with respect to AAm monomer), in addition to \( \phi \). As mentioned above, the tensile behavior of DN gels with \( y = 0 \) (second network is polymerized without adding cross-linker) changed with \( \phi \) in the following manner: (i) at \( \phi = 0 \), the gel underwent ‘moderate’ necking, i.e., the gel showed relatively low extensibility and sometimes broke during neck propagation; (ii) for \( 0.2 \leq \phi \leq 0.4 \), the gels showed pronounced necking with high extensibility; (iii) for larger \( \phi \), the gels broke quite easily without necking.

The necking behavior (dependence on \( \phi \)) at \( y = 0.02 \) shifts to the larger \( \phi \) side compared with the behavior at \( y = 0 \); for \( 0.2 \leq \phi \leq 0.4 \) the gels showed the moderate necking, and for \( \phi > 0.5 \), the pronounced necking occurred. These results show that the necking behavior of the DN gels is determined by a balance between the fragility of the first network and the ductility of the second network.

On the other hand, for the highest value of \( y = 0.1 \), the necking never occurs for all \( \phi \); the gels behave like usual chemical gels and suddenly broke during stretching. This behavior is reasonable because at this cross-linker density, the bare second PAAm network itself behaves as a densely chemically cross-linked gel that is brittle-like and that never show necking.

In summary, we have studies the tensile behavior of the DN gels containing the first network synthesized in the mixed solvent of water and 1,4-dioxane. Our results clearly show that using the mixed solvent is a good way to systematically enhance the heterogeneity of the first network, and to control the mechanical properties of the resultant DN gels from brittle, ductile, necking, to pasty. The condition to realize the pronounced necking deformation and to obtain highly extensible DN gels are: (1) the second network should be synthesized with a little amount of cross-linker (or even without cross-linker), and (2) it is preferable to introduce a certain degree of heterogeneity in the fist network; with increasing the heterogeneity, the DN gels show lower yielding stress and higher extensibility. (Too strong heterogeneity, however, results in drastic deterioration in mechanical properties for the uncross-linked second network.) The present study proposes a new method to realize flexible and tough hydrogels with an elasticity of several hundred kPa and breaking stress in MPa order, which are comparable to those of living tissues [1].

**Figure 5.** A phase diagram-like representation of tensile behavior of PAMPS/PAAm DN gels with different volume fraction of 1,4-dioxane \( \phi \) for synthesizing the first network, and different cross-linker MBAA density \( y \) of the second network.
Acknowledgments
The present work was supported by the Grants-in-Aid for Specially Promoted Research (No. 18002002) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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[11] This statement is based on the following experimental facts: (i) the equilibrium volume of the PAMPS gels in AAm monomer solutions for the second network, say $V_{AAm}$, is very close to that in pure water, $V_{wat}$; (ii) after the formation of the second network, the volume of the resultant DN gels, $V_{DN}$, is hardly changed from $V_{AAm}$ even after swelling equilibrium in water is accomplished. That is, $V_{DN} \approx V_{mon} \approx V_{wat}$.
[12] It should be commented here that even the original tough DN gel, the one with $\phi = 0$, shows the necking phenomena (although the extension is not so high). The authors had not realized this point when they wrote [1] and [7], because they mainly employed the compression test to characterize the mechanical strength then and the necking did not occur in the compression test.
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