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Necking Phenomenon of Double-Network Gels

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Most of animal and plant tissues can be regarded as natural composites made of rigid and soft components. Some of them, such as nacre, bone, or enamel, correspond to mineral−polymer composites, and others, such as the plant cell wall or tendon, correspond to polymer−polymer composites. It has been believed for a long time that the outstanding mechanical properties of these natural composites are due to well-organized geometric and chemical interactions between the rigid and soft components. Recent studies[1−11] have reported that many natural composites with high mechanical strength can be characterized by the following structural features: (i) consisting of an alignment of elongated stiff particles or stiff fibers (often on the scale of micrometers to nanometers), embodied in a flexible matrix of soft component, and (ii) existence of the tight interface between the stiff element and the soft matrix; these features conform with the design principle of industrial composites, such as fiberglass reinforced plastics. In addition, some researchers[9,10] propose that high viscoelasticity and well-developed hierarchy of structure, which are inherent in the animal and plant tissues, also enhance their bulk and adhesive strength.

Recently, novel hydrogels, which seem to be analogous to the cartilage and other natural composites, have been developed.[12] The gels were named as "double-network (DN) gel" because they consist of two rigid and soft interpenetrating polymer networks synthesized by a two-step polymerization: in the first step, a rigid polyelectrolyte gel (first network) is prepared, and then mutually entangled flexible polymers (second network) are synthesized in the preexisting rigid gel. Such DN gel, containing about 90 wt % water, possesses both hardness (elastic modulus of 0.3 MPa) and toughness (fracture stress of ∼10 MPa) comparable to cartilage and tendon. The invention of DN gels is quite significant in both fundamental studies and practical applications of polymer gels.

Now we report new DN gels that show necking phenomenon; i.e., during elongation of the gels, constricted zones appear in the sample and grow up with further elongation. The necking phenomenon is first observed in gel systems to the best of our knowledge. After the necking, the gels become very flexible: they sustain an elastic elongation as large as several tens of the original length. The necking DN gels, possessing both toughness and ductility, propose a challenging problem in the study for mechanical properties of polymer networks.

The necking DN gels can be obtained by modification of the first network structure: either by reducing the cross-linker concentration or by adopting γ-ray radiation as cross-linking method. For example, a former tough DN gel, not exhibiting necking, consists of the first network of poly(2-acrylamido-2-methylpropanesulfonic acid), abbreviated as PAMPS, radically polymerized from the solution of 1 M AMPS monomer and 4 mol % cross-linker (*N*,*N*-methylenebisacylamide; MBAA) with respect to the monomer, and of the second network of poly(acrylamide) (PAAm) polymerized from the solution of 2 M AAm monomer and 0.02 mol % MBAA with respect to the AAm monomer (see Experimental Section for details). Hereafter, we abbreviate this DN gel as PAMPS-1-4/PAAm-2-0.02 and use such kinds of abbreviations. On the other hand, PAMPS-1-2/PAAm-2-0.02 gel (i.e., the DN gel with a half amount of the cross-linker for the first network) exhibits the necking phenomenon. The necking is also observed for a DN gel PAMPS-1-γ/PAAm-2-0.02, of which the first network is formed by γ-ray radiation to a 1 M PAMPS (polymer) solution ("γ" in the abbreviation stands for the cross-linking by γ-ray irradiation). In addition, slight but nonzero cross-linking of the second PAAm

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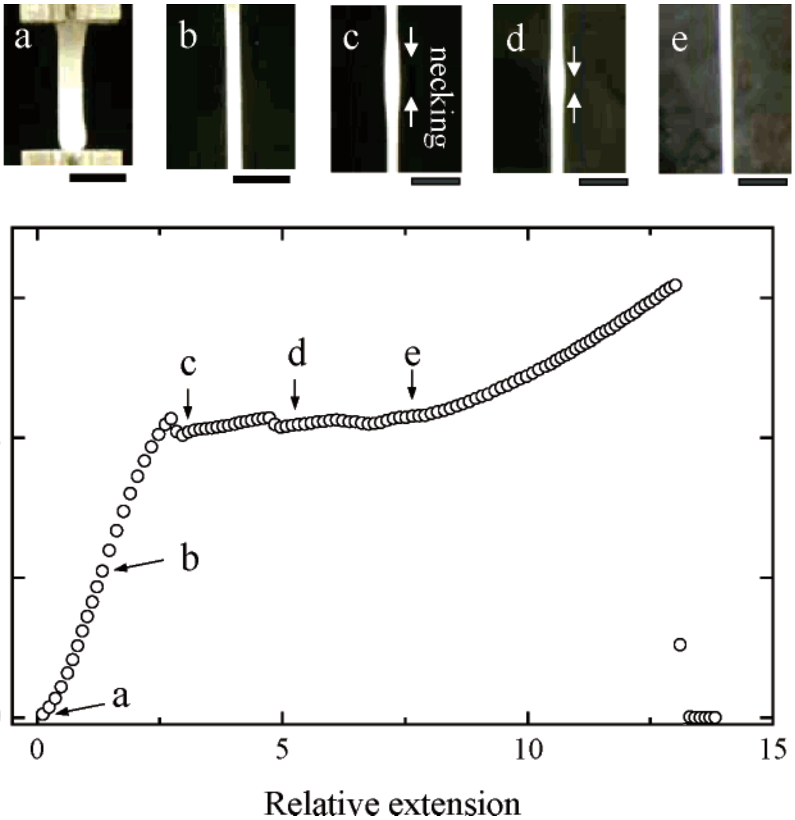

Figure 1. Loading curve of PAMPS-1-2/PAAm-2-0.02 DN gel under uniaxial elongation at an elongation velocity of 500 mm/min and pictures demonstrating how the necking process makes progress. The insert letters represent the correspondence between the pictures and the arrowed data points. Scale bars show 10 mm, and the width of the undeformed gel in picture a corresponds to the thickness of the sample (~4 mm). In pictures c and d, the upper and lower parts (necked regions) of the gel are slightly narrowing compared with the middle part (un-necked region). The necked regions grow up with the extension of the sample (the opposite arrows in the pictures).

network is also indispensable to obtain the necking gel; for example, PAMPS-1-γ/PAAm-2-0 gel is fairly fragile and does not show the necking.

Figure 1 shows a typical loading curve of PAMPS-1-2/PAAm-2-0.02 DN gel at an elongation velocity of 500 mm/min. The vertical axis shows the nominal elongation stress, i.e., the elongation force divided by the *initial* cross section of the sample, and the horizontal axis is the relative extension, i.e., the change of the sample length divided by the initial length, which is identical to the usual strain as long as the deformation of the sample is uniform. Inserted pictures show the deformation process of the sample (the sample was coated with alumina (aluminum oxide) powder to be taken clear photographs). The letters a−e represent the correspondence between the pictures and the data points. At the early stage of the elongation, the stress monotonically increases with the extension; at this stage, the sample was uniformly elongated as shown in pictures a and b. When the stress reaches the critical value σ_c (σ_c is about 0.21 MPa, hardly depending on the elongation velocity), the necked regions appear around the upper and lower clamps (the clamps are not shown in pictures c−e). Upon further elongation, the necked regions grow up, eating the un-necked region located in the middle part of the sample, while the elongation stress hardly increases (pictures c and d). After the un-necked region disappears, the sample is uniformly stretched again (picture e), which corresponds to the reincrease of the stress in the loading curve. The necking propagation starts at the extension of 2−3 and finishes at that of 7−8 usually. The gel remarkably softens after the necking: the Young's modulus of the softened gel, E_s, is ca. 0.015 MPa, which is much smaller than that before necking $E_h \approx 0.1$ MPa. (We determined the values of E_s and E_h by a compression test on plate-shaped samples, rather than the slope in Figure 1, to avoid a large error due to the clumping in the tensile test.) The softened gel can sustain an extraordinarily large extension (more than 10 times the initial length) before breaking.

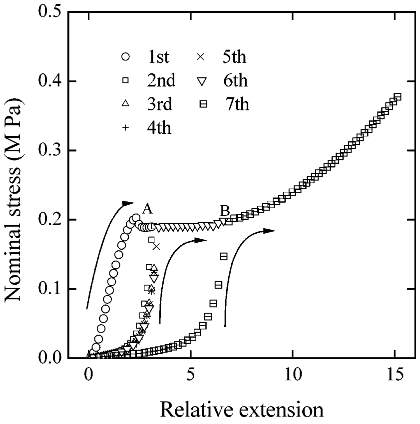

Figure 2. Loading curves of PAMPS-1-2/PAAm-2-0.02 DN gel for repeated elongation at an elongation velocity of 250 mm/min.

The large deformation of the softened DN gels produced by necking was almost reversible. Figure 2 shows loading curves of repeated elongation tests for PAMPS-1-2/PAAm-2-0.02 DN gel at a elongation velocity of 250 mm/min. (For clarity, curves for the unloading processes are not presented.) On the first loading, the sample is stretched up to a length at which the necked region appears (the point A) and retracted to the tension-free state. On the second loading, where the sample is stretched up to the same length as the first loading, the deformation preferentially occurs in the soften necked region, and the loading curve follows a different path from the first one, but the final

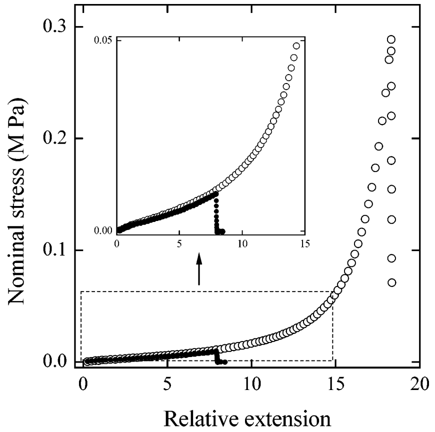

Figure 3. Comparison of the loading curves for PAMPS-1-2/PAAm-2-0.02 DN gel after necking (open circles) and a PAAm single network gel with the same acrylamide concentration and initial Young's modulus (filled circles).

state, point A, is identical. On the third to fifth loadings, the same stretching is imposed; the loading curves of them completely overlap with each other, indicating that the deformation is rubber-elastic. On the sixth loading, the sample is stretched up to state B, beyond state A. In the deformation process from A to B, where the stress is almost constant, the necked region extends. On the seventh loading, the sample is stretched beyond B and up to the breaking point. It should be noticed that the first curve, the plateau of the sixth curve (from A to B), and the latter part of the seventh curve (beyond B) are smoothly connected, composing a curve seems to be obtained by a single loading.

Softened DN gels, produced by the necking, exhibit an excellent extensibility compared with the usual PAAm single network (SN) gels. Figure 3 represents a comparison between loading curves of a softened DN gel and that of the "corresponding" PAAm SN gel; this SN gel is prepared to have the same Young's modulus and monomer (AAm) concentration as the softened DN gel by adjusting the concentration of the cross-linker (MBAA). The softened DN gel can withstand high levels of deformation; in contrast, the PAAm SN gel breaks at a low fracture stress.

The following observations on the softened gels after the tensile test demonstrate that irreversible structural change takes place inside the gels, although their appearance is almost unchanged: (E1) Few percent of permanent strain remains in the softened DN gels, and (E2) the gels swell up in water, although they reached swelling equilibrium before the necking. (The shape of the swollen gels is almost similar to that before swelling; i.e., there is no wavy or other irregular deformations, indicating that the softened gels have uniform structures on the macroscopic scale.) (E3) During the necking propagation of the gels (without the alumina coating), the boundary zone between the necked and un-necked regions becomes remarkably opaque (the completely necked region regains the transparency), indicating that inhomogeneity with a characteristic size comparable with the wavelengths of visible light arises in the boundary zone and that the size finally decreases below the wavelengths in the completely necked region.

From the above experimental findings and the fact that the PAMPS SN gels are quite brittle and break into small pieces at small deformations, it is probable that in the course of necking deformation the first PAMPS network fragments into small clusters, and it is also probable that the clusters play a role of cross-linker of long PAAm chains (see Figure 4) because the cross-linker concentration of the second network (0.02 mol % with respect to the AAm monomer) is so slight that the "bare" PAAm-2-0.02 SN gel behaves as a sticky sol rather than a gel.

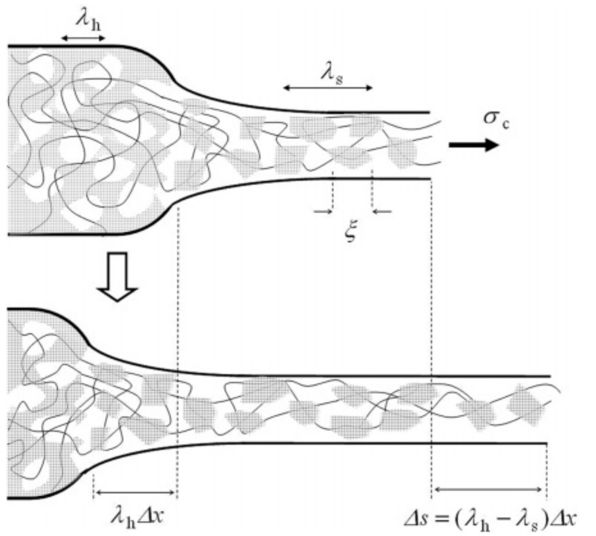

Figure 4. Illustrations of the necking propagation and a model of the network structure of the softened DN gel after the necking. The mesh and the curves represent the first (PAMPS) and the second (PAAm) networks, respectively.

The fragmentation should involve dissipation, which is reflected in the hysteresis of the loading curves in Figure 2, i.e., the closed region bounded by the first, the (plateau of) sixth, and the (latter part of) seventh curves. Assuming that the concept of fracture energy applies to the microscopic fragmentation of the first PAMPS network in the DN gel and that the fracture energy for the fragmentation can be substituted by the fracture energy G for the bare PAMPS SN gel *in water*, we can estimate the typical size ξ of the PAMPS clusters in terms of macroscopic observables, i.e., the critical stress σ_c (= 0.21 MPa for PAMPS-1-2/PAAm-2-0.02 gel) and the fracture energy G ($\approx$ 0.8 J/m^2 for PAMPS-1-2 SN gel in water; this value was evaluated by the three-point bending test on the square bar-shaped gel with a notch according to the normal procedure of linear fracture mechanics[13]). We consider the coexistence of necked and un-necked regions in a sample gel, of which initial cross section (i.e., the cross section at stress-free state) is A. When it is further stretched at a distance Δs, the portion of length Δx (Δx is the length of the portion at the reference (stress-free) state) is converted from the un-necked to the necked regions; Δs and Δx are related as $\Delta s = \lambda_s \Delta x - \lambda_h \Delta x \approx \lambda_s \Delta x$, where λ_s and λ_h ($\ll \lambda_s$) are elongation ratios for the necked (softened) and un-necked (hard) regions, respectively, and λ_s is about 7 as shown by the extension of the point B in Figure 2. (This point corresponds to the state where the necking propagation completes.) Macroscopically, the work $\Delta w = A\sigma_c \Delta s \approx A\sigma_c \lambda_s \Delta x$ is done to the sample. Microscopically, the PAMPS clusters are newly created by the necking propagation; the number of the clusters is given by $A\Delta x/\xi^3$, and the newly created surface is totally $\xi^2 A\Delta x/\xi^3 = A\Delta x/\xi$. Since the work done to the system is consumed to create the cluster, $\Delta w = A\sigma_c \lambda_s \Delta x \cong (G/\xi)A\Delta x$, we obtain $\xi \cong G/\lambda_s \sigma_c$. (Strictly speaking, a portion of Δw is stored as elastic energy in the necked region; however, this factor can be ignored in this *order estimation*.) For the above values of σ_c, λ_s, and G, the size ξ falls onto the order of hundreds of nanometers. Since the above-mentioned finding (E3) indicates that the characteristic size of the inhomogeneity in the necked region is below the wavelengths of visible light, the reasonable value of ξ is a few hundred nanometers. The value of ξ may reflect quenched inhomogeneity of the first network of DN gels found in our study;[14] that is, DLS measurement on DN gels revealed the existence of Rouse-like relaxation modes of PAAm chains, suggesting that the DN gels contain "void regions" where PAAm chains behave like in solution.[22]

From the viewpoint of polymer physics, the softened gel is a fascinating system. First, the PAMPS clusters, playing a role of cross-linker, are not chemically bonded to the PAAm chains; thus, the "molecular weight between cross-linking" can be adjusted by chain sliding in response to deformation. The capability of chain sliding is in common with the so-called topological gel[15] well-known as ductile and tough hydrogel, which was developed around the same time as the former rigid and tough DN gel. Furthermore, the PAMPS cluster can be redivided; when a cluster in a deformed sample suffers a larger stress than other ones, the inequality of stress can be corrected by the redivision. Owing to these effects, the resultant network structure has less mechanical defects. The excellent mechanical property of the softened gel can be attributed to the above structural features. Additionally, the PAMPS clusters are much larger compared with the molecular scale and thus to be penetrated by many long PAAm chains. The ultra-multifunctionality of cross-linkers, which is an essential feature of the nanocomposite (NC) gel[15] well-known as another ductile and tough hydrogel, also may affect the toughness of the soften gel.

The finding of the necking phenomena has significance in discussions of the high toughness of the original (former) DN gels that do not exhibit the necking *on the macroscopic scale*. As reported in our previous papers,[16−18] it is suggested from some experimental and theoretical observations that the inhomogeneity of the first network plays a role for the high toughness. However, the detail mechanism has been an open question until now. The necking phenomena give an idea for explaining the phenomenon: if the necking deformation occurs in a mesoscale region around the crack tip of the DN gels, the stress concentration is remarkably reduced, resulting in the large toughness.

In summary, we discovered the necking phenomenon in double-network hydrogels. The necking gels can be produced by merely adjusting the cross-linker density of the first network or by adopting γ-irradiation as cross-linking method. The necking deformation can be attributed to the fragmentation of the first PAMPS network. In contrast to the former DN gels that possess both hardness and toughness, the new necking DN gels show superior extensibility with nearly complete recovery. This is meaningful both for practical applications such as biomedical engineering and for the fundamental study in physics of polymer networks.[19−21]

Experimental Section. In our experiment, DN gels were prepared by a two-step sequential network formation technique. For example, in the preparation of PAMPS-1-2/PAAm-2-0.02 gel, of which the first network is formed by radical polymerization of monomer and cross-linker, the PAMPS-1-2 SN gel was first synthesized from an aqueous solution of 1 M 2-acrylamido-2-methylpropanesulfonic acid (AMPS) containing 2 mol % cross-linking agent, *N*,*N*-methylenebisacylamide (MBAA), and 0.1 mol % radical initiator, 2-oxoglutaric acid (the mole percentages are with respect to AMPS monomer). After being bubbled with nitrogen gas for 30 min, the solution was poured into molds with two parallel glass plates and silicone spacers. Radical polymerization was carried out under a nitrogen atmosphere with ultraviolet lamp for 10 h. This first network gel was then immersed in an aqueous solution containing 2 M AAm, 0.02 mol % MBAA, and 0.1 mol % 2-oxoglutaric acid for 1 day until equilibrium was reached. (During the swelling, the volume of the gel increased up to more than 10 times; accordingly, the concentration of AMPS reduced below 0.1 M.) The second network was subsequently synthesized in the same manner as the first network. The gel thus prepared consists of two independent polymer networks entangled with each other. In the case that the first network is formed by γ-irradiation to polymer solution, the aqueous solution of 1 M AMPS containing 0.1 mol % initiator without cross-inking agent was made, and the polymerization was carried out in the same manner as the above case. The prepared polymer solution was exposed to a γ-ray source (^{60}Co) with a dose rate of 4.37 kGy/h for 30 h at room temperature for cross-linking. The procedure for the second network formation is identical to the above case. These DN gels were immersed in water to reach the swelling equilibrium. The swelling ratios, defined as the weight ratio to the dried state, are 7.1 (the former DN gel) and 6.5 (the latter one).

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: 3−4 mm; gauge length: 12 mm; inner width: 2 mm) with a gel cutting machine. Fracture energy of PAMPS-1-2 (single network) gel in water was measured by the three-point bending test on square bar-shaped samples (length: 40 mm; width: 10 mm; thickness: 6 mm) with a notch. The critical stress intensity factor and the fracture energy were evaluated from the sample dimension, experimental geometry, the Young's modulus of the gel, and the critical loading force for fracture, based on a procedure given by Brown and Srawley.[13]

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(22) In fact, the reasonability of the proposed fragmentation mechanism depends on the inhomogeneous structural model of DN gels, as described below. It is certain that (i) DN gels are incompressible and that (ii) the soften DN gels contain “PAMPS-free” regions where the PAAm chains behave as in solution because the gels are flexible like normal PAAm gels. In addition, we can expect that (iii) in a DN gel the volume occupied by the PAMPS network is almost constant before and after necking due to the rigidity of PAMPS being much higher than that of PAAm. To match the fragmentation mechanism to the above restrictive conditions, we must assume the PAMPS-free regions exist in the DN gel before necking.

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