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Effect of Constituent Networks of Double-Network Gels on their Mechanical Properties and Energy Dissipation Process

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Double-network (DN) gels, consisting of brittle first and ductile second networks, possess extraordinary strength, extensibility, and fracture toughness while maintaining high solvent content. Herein, we prepared DN gels consisting of various concentrations of the first and second networks to investigate the effect of each network structure on the tensile and fracture properties of DN gels. The results showed that the tensile properties of DN gels before yielding are mainly dominated by the first network, serving as a skeleton, whereas the properties after necking are determined by both networks. Moreover, we found that the DN gels with significant energy dissipation capacities exhibit high fracture resistance. Thus, this study not only confirms the factors determining the mechanical characteristics of DN gels but also explains how the two networks concordantly improve the toughness of DN gels.

Introduction

Double-network (DN) gels are interpenetrating network gels with extremely high strength and toughness. They are mechanically so robust that they can withstand a strike by a golf club. Tough DN gels are comprised of two contrasting networks: the first weak and brittle network and the second stretchy and relatively strong network. This DN concept for toughening of soft materials is universal and principally applicable to rubbery polymeric materials comprising various chemical species, including synthetic and natural polymers.

The initial reports on DN gels confirmed the presence of a chemically (covalently) cross-linked polyelectrolyte network because their extreme swelling in water results in a brittle and weak network. It was also reported that chemically cross-linked non-ionic polymer networks, whose network strands are sparse and close to their stretching limit, can also be used as a brittle and weak first network. Moreover, physically (non-covalently) cross-linked brittle gels have been widely used as the first network for tough DN gels.

DN gels possess superior mechanical properties to single-network gels. The elastic single-network gels made from flexible polymer strands typically show low tensile fracture stresses of approximately 0.1 MPa or less. The DN gels with the chemically cross-linked first network exhibit a high tensile fracture stress of 0.1–2 MPa while maintaining a significant tensile fracture strain of 100–1,500%, which are strongly affected by the two network compositions. The DN gels with the physically cross-linked first networks sometimes possess significantly enhanced properties such as Young’s modulus of 30 MPa and fracture stress of 13 MPa shown by the DN gels with the calcium alginate first network. Such high toughness of DN gels also contributes to their good fatigue resistance and the large adhesion energy of DN gel-solid interfaces.

The excellent fracture resistance of DN gels is explained based on the internal fracture mechanism, that is, catastrophic fracture of the brittle first network prior to macroscopic failure of gels. Because a tough DN gel is comprised of a brittle first network and a stretchy second network, under large deformation, strands or bonds in the brittle first network undergoes partial scission and fragmentation before the stretchy second network reaches the breaking point. In the case of the DN hydrogels with the chemical first network, the internal rupture of the first network strands was confirmed by the large and irreversible mechanical hysteresis, decreasing modulus (Mullins effect) after deformation, and the chemical detection of the covalent bond rupture of the network. Regarding the internal fracture, some DN gels exhibit yielding upon uniaxial deformation. In yielding of the DN gels, the first network loses its integrity due to fragmentation and the mechanical properties of the DN gels change from the first network-based stiffness to the second

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network-based stretchability. Such a yielding phenomenon also occurs at the crack tip of the DN gels. When a DN gel with an initial crack is deformed, stress concentrates near the crack tip, leading to local deformation and yielding of the DN gels. Consequently, a wide yielding zone formed around the crack tip of the DN gel prior to crack leading to local deformation and yielding of the DN gels. Because the formation of the damage zone dissipates a significant amount of energy, the energy required to fracture the DN gel is significantly high. This explains the extraordinarily high fracture energies of the DN gels.23,24

Recently, this internal fracture of DN gels has been applied chemically to create muscle-like self-growing materials.21 As the internal fracture of the chemical DN gels is covalent bond rupture, active chemical species such as radicals are formed at the end of the ruptured strands,26 which can initiate chemical reactions inside the DN gels. Thus, when the DN gels containing monomers and cross-linkers are deformed, the generated radical induces radical polymerisation of the monomers and cross-linkers to synthesise a new polymer network inside the DN gels. As a result, the mechanical properties of the DN gels are significantly improved after such chemical stimuli like muscle training. Since the radical generation in the deformed DN gels is originated from the internal fracture, concentration of the generated radical has been found to be almost proportional to irreversible hysteresis loss (energy dissipation density) of the DN gels.21

As mentioned earlier, DN gels show high mechanical robustness and unique internal fracture mechanisms in addition to the intrinsic properties of gels such as high water content. These properties make DN gels useful as tough medical and industrial materials, including tough and biocompatible artificial cartilage and soft conductive materials for electronics.27,28 In addition, owing to their internal fracture-based self-growing ability, DN gels are considered self-adaptive materials capable of transforming their properties in response to their mechanical environment.21,29 Each of these various possible applications requires tailor-made DN gels with adjustable mechanical and internal fracture properties for unique functions. In principle, the mechanical properties of DN gels can be controlled by tuning the composition of the two networks that comprise DN gels. Several researchers have synthesised a series of chemical DN gels with a variety of compositions to clarify the composition–mechanical properties relationship of the DN gels. For example, Na et al. varied the composition of the second network to optimise the DN gels.30 Matsuda et al. controlled the swelling ratio of the first network to obtain the yielding criterion of the DN gels.31 These studies have partly clarified the relationships between the structural parameters and mechanical properties of DN gels. However, these studies only changed the composition of one network, not both networks. Because the mechanical behaviours of DN gels can be controlled by the synergistic effect of the first and second networks, comprehensive studies on the effects of the structures of the two networks on the mechanical properties of the DN gels are needed. Some of the authors have varied the two network compositions of the DN gels and measured their mechanical properties.19 However, they only aimed to clarify the toughening criterion of the DN gels. Therefore, the role of the compositions of the two networks must be studied further.

Herein, we intend to elucidate the effect of the two network compositions on the tensile properties, energy dissipation process, and fracture properties of the chemical DN gels. We use the typical chemically cross-linked DN gels, namely, poly(2-acrylamido-2-methylpropanesulfonic acid)/poly(acrylamide) double-network gels (PAMPS/PAAm DN gels), as a model system, which are original DN hydrogels and have been widely used in the previous studies.1,3,12 We tuned mechanical properties of the DN gels by controlling the cross-linker concentration in feed for the first network preparation, c1st_MBAA, and the monomer concentration in feed for the second network preparation, cAm. The structure and mechanical properties of each network are remarkably changed by c1st_MBAA and cAm, and thus the properties of the DN gel can be effectively tuned by these factors. Tensile and tearing tests were performed on these gels to clarify how the compositions of the two networks determine the mechanical properties and energy dissipation process of the DN gels. Moreover, origins of the obtained composition–properties relationships are discussed by using the theoretical models.

Experiment

Materials.

We recrystallised 2-acrylamido-2-methylpropanesulfonic acid (AMPS, Toa Gosei Co., Ltd.) from methanol, acrylamide (AAm, Junsei Chemical Co., Ltd.) from chloroform and N,N'-methylenebis(acrylamide) (MBAA, Wako Pure Chemical Industries, Ltd.) from ethanol. 2-Oxoglutaric acid (Wako Pure Chemical Industries, Ltd.) was used as received.

t-DN gel preparation.

As has been clarified in previous studies, conventional DN gels prepared by two-step polymerisation contain internetwork bonds between the first and second networks. These bonds are formed due to copolymerisation of the second network with the unreacted cross-linker of the first network.14,32 Truly independent DN gels, or simply t-DN gels, are a special type of DN gels that contains a negligible amount of covalent bonds between the two networks.14 Because t-DN gels have simpler structures than the conventional DN gels, we prepared t-DN gels for the analysis of the properties of the DN gels. First, the first network precursor solutions were prepared from 1 M of AMPS, 1–16 mol% of MBAA as the cross-linker, and 0.1 mol% of 2-oxoglutaric acid as the photo-initiator (the molar percentages are respect to the monomer). The solutions were then moved to an argon blanket and poured into glass moulds consisting of two soda-lime flat glass plates separated by silicone rubber as a spacer (the thicknesses of the glass plates and silicone rubber were 3 mm and 1 mm, respectively.). Photopolymerisation of PAMPS gels was performed by irradiation with 365 nm UV light (4 mW cm⁻²) from both sides of the mould for 10 h. The PAMPS gels were then immersed in a 0.1 M 2-oxoglutaric acid (photo-initiator) aqueous solution for 1 day. The samples were
irradiated with 365 nm UV light for 10 h to generate excess radicals in the gels. These radicals acted on the unreacted vinyl groups of the cross-linkers in the gels and rendered the vinyl groups inert. The PAMPS gels containing less unreacted vinyl groups in the cross-linker were immersed in pure water for 5 days to remove any excess photo-initiator. Pure water was replaced every day during immersion. These PAMPS gels were then immersed in the second network precursor aqueous solutions consisting of 1–8 M of AAm, 0.02 mol% of MBAA, and 0.01 mol% of 2-oxoglutaric acid for at least 2 days. The solutions were replaced once during immersion. After immersion, the gels were sandwiched between two flat glass plates and wrapped with a plastic film in an argon blanket. Photo-polymerisation of the PAAm network was performed in the presence of PAMPS gels by irradiation with the 365 nm UV for 9 h. In this study, the term “t-DN(x-y)” is used to describe the compositions of the t-DN gels, where x is the cross-linker concentration of the first network precursor solutions in feed, $c_{\text{1st, MBAA}}$ (mol%), and y is the monomer concentration of the second network precursor solutions in feed, $c_{\text{AMN}}$ (M). The following mechanical tests were performed on these t-DN gels in the as-prepared state without immersion in any solvents.

Concentration of each component in the t-DN gels.

The volume swelling ratio of the PAMPS network in the t-DN gels, $Q$, is defined as $V/V_0$, where $V$ and $V_0$ are the volumes of the as-prepared t-DN gel and the corresponding as-prepared PAMPS gel, respectively. $V/V_0$ is determined by $V/V_0 = (t/t_0)^3$, where t and $t_0$ are the thicknesses of the as-prepared t-DN gel and the corresponding as-prepared PAMPS gel, respectively, measured with a calliper. True monomer unit concentration of the first network in the t-DN gels, $c_{\text{1st}}$, is estimated as

$$c_{\text{1st}} = \frac{c_{\text{AMPS}}R}{Q}$$

(1)

where $c_{\text{AMPS}}$ is the AMPS molar concentration in the first network precursor solutions in feed and $R$ is the conversion ratio of the AMPS monomer to the PAMPS network. In this study, the former was 1 M and the latter was almost 100% after 8 h of polymerisation.

Uniaxial tensile test.

A commercial tensile-compressive tester (Tensilon RTC-1310A, Orientic, Co.) was used for the uniaxial tensile test. The test was performed on dumbbell-shaped specimens standardised to the JIS-K6252 1/2 size (50 mm in length (with 20 mm long initial legs) and 7.5 mm in width) using a Tensilon RTC-1310A. The tensile test was performed in mode III loading mode by pulling one leg of the specimen by a rate of 500 mm/min while the other leg was fixed. The tearing velocity at a crack tip is about 250 mm/min at the steady state crack growth. The energy required to fracture a unit area of a sample was estimated as $T = 2F_{\text{ave}}/t$ without consideration of stretch of the legs, where $F_{\text{ave}}$ is the average tearing resistance force and t is the thickness of the gel.23 Since the leg stretch is neglected, the obtained tearing energy by the above equation is underestimated a little but not far from the actual value considering the leg stretch. In fact, tearing energy of the typical DN gel with and without considering leg stretch have been reported as 991 and 935 J m$^{-2}$, respectively.33 All the values shown are averages of at least three measurements.

Mechanical hysteresis measurement.

Cycle tensile tests were performed with a commercial tensile tester Instron 5965 (Instron Co.) and a noncontact video extensometer (AVE, Instron Co.). The gels were cut into dumbbell-shaped pieces and standardised to the JIS-K6252-1/2 size. The samples were first uniaxially stretched to the desired strain, $\varepsilon_{\text{max}}$, and then immediately unloaded (the unloading process was not recorded) with a fixed tensile velocity at 100 mm/min. After reaching their original length, the samples were immediately elongated beyond $\varepsilon_{\text{max}}$. In general, mechanical hysteresis measurements were performed by measuring the cycle of the loading and unloading curves. For DN gels, it is known that the second loading curve completely overlaps with the first unloading curve. Thus, we measured the second loading curves instead of the unloading curves in this study. The dissipated energy density, $U_{\text{hys}}(\varepsilon_{\text{max}})$ (J m$^{-3}$), which is defined as the area between the first and second loading curves at the maximum strain $\varepsilon_{\text{max}}$ of the first loading, was calculated as

$$U_{\text{hys}}(\varepsilon_{\text{max}}) = \int_0^{\varepsilon_{\text{max}}} (\sigma_1 - \sigma_2) \, d\varepsilon$$

(2)

where $\sigma_1$ and $\sigma_2$ are the nominal stresses of the first and second loading curves, respectively. Note that these notations are not the same as $\sigma_{\text{1st}}$ and $\sigma_{\text{2nd}}$ which are defined later as the stresses of the first and second networks, respectively.

Results and discussion

Swelling of the first network.

We synthesised 35 types of t-DN gels with different compositions of the two networks by varying the cross-linker concentration of the first network precursor solutions, $c_{\text{1st, MBAA}}$.
(mol%), and the monomer concentration of the second network precursor solutions, $c_{AAm}$ (M). These t-DN gels are called t-DN($x$-$y$) gels, where $x$ is $C_{1st, MBAA}$ and $y$ is $c_{AAm}$. They showed a wide variety of mechanical properties, all of which were transparent and uniform to the eye, regardless of the change in composition. First, we characterised swelling properties of the first network in the t-DN gels. The first PAMPS network largely swelled in the second network precursor aqueous solution due to polyelectrolyte nature of PAMPS. Note that swelling ratio of the PAMPS gels in the second precursor solutions is independent of their AAm concentration $c_{AAm}$. Large swelling of a polyelectrolyte gel in polar solvent is due to contribution of movable dissociated counterions to total osmotic pressure of a gel. According to the Manning’s condensation theory, ratio of the movable counterions among total ones of a polyelectrolyte chain is dominated by dielectric constant of the solution. Thus, independency of $Q$ of the PAMPS gels from the AAm concentration means that effect of AAm concentration on dielectric constant of the second precursor solution is negligible.

Figure 1(a) depicts the volume swelling ratio, $Q$, of the PAMPS network in the as-prepared t-DN gels synthesised using various cross-linker concentrations, $C_{1st, MBAA}$. As cross-linking suppresses the swelling of networks, a higher cross-linker concentration in the PAMPS network leads to less swelling of the network in the AAm aqueous solution, and therefore to a small $Q$. Figure 1(b) depicts the dependence of the first network concentration of the t-DN gel, $C_{1st}$, on $C_{1st, MBAA}$, indicating that an increase in the cross-linker concentration leads to an increase in the $C_{1st}$. Here, we obtained power-law relationships between $Q$ of $C_{1st}$ and $C_{1st, MBAA}$ as

$$Q \propto C_{1st, MBAA}^{-1.14} \quad (3a)$$

$$C_{1st} \propto C_{1st, MBAA}^{1.14} \quad (3b)$$

Ideally, segment number of a network strand of the first network $N$ is inversely proportional to the ratio of cross-linker concentration $C_{1st, MBAA}$ to monomer concentration $c_{AMPS}$ used for the first network synthesis;

$$N \propto \frac{c_{AMPS}}{C_{1st, MBAA}} \quad (4)$$

Considering constant $c_{AMPS}$, we rewrite eqn (3) by using $N$ as;

$$Q \propto N^{-1.14} \quad (5a)$$

$$C_{1st} \propto N^{1.14} \quad (5a)$$

This relationship is consistent to the theoretical prediction. To derive this relationship theoretically, we adopt the tension blob (Pincus blob) model to the network strands of the swollen first network. According to this model, the network strand with $N$ segments under tension is represented by a series of tension blobs with $g$ segments lined up along the tension direction. Number of tension blobs per a strand is thus $Ng$. Segments in each tension blob are unperturbed, thus average size and thermal energy of each tension blob are $g = b倪ν$ and of the order of $kT$, respectively, where $b$ is segment length and $ν$ is Flory exponent. Considering the balance of osmotic pressure due to movable (uncondensed) counterions and elastic pressure of an equilibrium swollen polyelectrolyte gel, one can obtain $g = α^{-1}$ for a polyelectrolyte gel, where $α$ is a ratio of movable counterions among total counterions in the gel and should be constant in this case. Considering the average end-to-end distance of a network strand at as-prepared state is $bN^{-1}$, one can describe equilibrium swelling ratio of the first network gel in a salt-free medium as;

$$Q = \left( \frac{(Ng)^{-1}}{(bN)^{-1}} \right)^{3} = \left( \frac{bN^{-1}^{-1}}{bN^{-1}} \right)^{3} = \left( \frac{N}{N} \right)^{3(1-ν)} \propto N^{3(1-ν)} \quad (6a)$$

By using $Q \propto C_{1st}^{-1}$,

$$C_{1st} \propto N^{3(ν-1)} \quad (6b)$$

can be also derived. Substitution of $ν=0.6$ for a real chain to eqn (6) leads $Q \propto N^{-1.2}$ and $C_{1st} \propto N^{-1.2}$, which are enough close to the experimental eqn (5). Slight deviation of the experimental results from the theory implies that the ideal eqn (6a) does not perfectly explain the results. Possible reasons of the deviation include the effect of osmotic pressure due to the mixing of the polymer and the solvent and the electrostatic repulsion between the charges fixed on polymers, which were ignored during the derivation of eqn (6) for simplicity.

![Figure 1](image1.png)

**Figure 1.** Effect of cross-linker concentration of the first network precursor solution, $C_{1st, MBAA}$ (mol%), on (a) the swelling ratio $Q$ and (b) true first network concentration, $C_{1st}$ (M), of the as-prepared t-DN gels. $Q$ was independent of the AAm concentration $c_{AAm}$ and the error bars are hidden by the symbols.

![Figure 2](image2.png)

**Figure 2.** (a) The tensile behaviour diagram of the t-DN($x$-$y$) gels with various $x$-$y$ combinations. Circle symbols denote the stretchy DN gels, cross symbol denotes the brittle DN gels and triangle symbols denote the DN gels broken just after yield point. All the experimental data were observed on as-prepared DN gels. (b) Typical examples of stress-strain curves of the stretchy DN gel (t-DN(4-2) gel) and the brittle DN gel (t-DN(4-1) gel).
**Tensile behaviour of t-DN gels.**

The synthesised t-DN gels can be classified into brittle and stretchy groups based on their tensile mechanical behaviours. Figure 2(a) depicts the tensile behaviour diagram of the t-DN(x-y) gels in the x-y space, and typical tensile stress–strain curves for the brittle and stretchy groups are shown in Figure 2(b). The stretchy DN gels (circle in Figure 2(a)) were mechanically robust and showed yielding and significantly high fracture strain, which are the features of tough DN gels.7 In contrast, the brittle DN gels (cross) could be easily broken. They do not have any characteristics of tough DN gels, such as yielding, high fracture stress, and high fracture strain. As exceptions, some DN gels with high C_{1st_MBAA} break just after reaching the yield point; thus, they are classified into the intermediate group (triangle). As quantitatively discussed in a previous experimental and theoretical papers, altering the balance of the strengths of the two networks leads to this transition.13,38 In order for DN gels to be tough, the relative strength of the second network to the first network must be enough large. When the AAm concentration, C_{AAm}, was below a critical value, the DN gels showed a brittle behaviour due to insufficient strength of the second network. In contrast, when the AAm concentration was higher than the critical value, the DN gels became stretchy. This critical concentration of C_{AAm} depended on C_{1st_MBAA} as strength of the first network increases with C_{1st_MBAA}.

From this section, we focus on the mechanical properties of the stretchy t-DN gels marked as circles in Figure 2(b). Figure 3 depicts the tensile stress–strain curves for the t-DN(x-4) and t-DN(4-y) gels, where x and y were 2–8 (mol%) and 2–8 (M), respectively. The different contributions of each network to the stress–strain curves of the DN gels were determined. As depicted in Figure 3(a), x (C_{1st_MBAA}) strongly affects the stress–strain curves of the DN gels. With an increase in C_{1st_MBAA}, the tensile stress of the DN gels significantly increases from the origin to the fracture point. In contrast, the effect of the second network is found mainly after reaching the yield point (Figure 3(b)). Before reaching the yield point, even though C_{AAm} was varied from 2 to 8 M, the tensile curves of the DN(4-y) gels were nearly coincident. In contrast, after reaching the yield point, the higher the second network concentration, the higher the tensile stress. Next, we discuss the reason for the different contributions of the two networks. The yield point of DN gels has been considered as the point where the brittle first network reaches its stretching limit.31 Thus, before the yield point, the first network is in a highly stretched state and shows obvious strain hardening, whereas the second network remains in a coiled state. Thus, the mechanical properties of DN gels in this regime are dominated by the stiff first network. The dominance of the first network on the mechanical properties of pre-necked DN gels has already been pointed out by Ducrot et al. and by some of authors.31,39 In contrast, after reaching the yield point, the first network is considered to be ruptured into discontinuous pieces, which are topologically connected by the second network through entanglement.40 In such cases, the second network contribution to the mechanical behaviour of DN gels can no longer be ignored, whereas the remaining first network serving as macroscopic cross-linking points continues to contribute to the mechanical behaviour. Thus, after reaching the yield point, the mechanical properties of the DN gels are determined by both networks.

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Figure 3. The tensile stress-strain curves of (a) the t-DN(x-4) gels and (b) the t-DN(4-y) gels where x/C_{1st_MBAA} and y/C_{2nd} are 2–8 (mol%) and 2–8 (M), respectively. The tensile velocity was fixed at 100 mm/min. The insert figure in (b) shows the enlarged small strain region.

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Figure 4. Composition dependencies of (a-b) the Young’s modulus, E, (c-d) the yield stress, \(\sigma_y\), (e-f) the yield strain, \(\varepsilon_y\), and (g-h) the fracture strain, \(\varepsilon_f\), of the t-DN gels measured by the tensile test.
Figure 4 exhibits the dependence of various mechanical properties on the t-DN gel compositions. Figure 4(a,b) shows the elastic modulus, $E$, and Figure 4(c,d) shows the yield stress, $\sigma_y$, of the t-DN gels with different compositions. The $E$ and $\sigma_y$ of the t-DN gels significantly increase with $c_{1st\_MBAA}$, but are less dependent on $c_{AAm}$. The optimised DN gel with the dense first network (t-DN(8-8)) showed the elastic modulus of 0.7 MPa and the yield stress of 3.7 MPa. Furthermore, among the non-stretchy DN gels, t-DN(16-8) showed the highest elastic modulus of 1.3 MPa and the highest yield stress of 8.4 MPa. Figure 4(e,f) shows the yield strain of the t-DN gels. The yield strain is weakly dependent on both $c_{1st\_MBAA}$ and $c_{AAm}$. Figure 4(g,h) shows the fracture strain, $\varepsilon_f$, of the t-DN gels of various compositions. Note that the values of $\varepsilon_f$ should contains some systematic errors such as overestimation due to not using extensometer and possible effect of sample geometry on fracture points of the DN gels. Nevertheless, these figures show the trend between $\varepsilon_f$ and compositions. One can see that $\varepsilon_f$ tends to decrease with an increase in both $c_{1st\_MBAA}$ and $c_{AAm}$ and the t-DN gels with low $c_{1st\_MBAA}$ and $c_{AAm}$ show high extensibility.

Herein, the dependences of the above mechanical properties of the t-DN gels on both $c_{1st\_MBAA}$ and $c_{AAm}$ are analysed. For the elastic modulus, let DN gels be assumed to be a simple bi-continuous composite material, wherein their elasticity is simply the sum of the two components. Under this assumption, the $E$ of the DN gels at small strain can be assumed to be

$$E \approx E_{1st} + E_{2nd}$$

(7)

where $E_{1st}$ and $E_{2nd}$ are the elastic parts of the first and second networks, respectively. For the as-prepared DN gels, $E_{1st}$ which is elastic modulus of the polyelectrolyte first network gel at swelling equilibrium in a salt-free medium, should be nearly proportional to its true polymer concentration $C_{1st}$, and thus;

$$E_{1st} \approx E - E_{2nd} \propto C_{1st}$$

(8)

We plot $E$ of the t-DN gels against $C_{1st}$ as shown in Figure 5(a). For the t-DN gels with the same $c_{AAm}$, the obtained $E - C_{1st}$ curves are almost linear regardless to $c_{AAm}$, and the slope of the linear regression curves are almost constant, suggesting validity of the eqn (8). On the other hand, the curves are slightly convex downward especially for $c_{AAm}=8$ M, implying contribution of inter-network entanglements to Young’s modulus of the DN gels. The larger first and second network concentrations give the denser inter-network entanglements, which may lead nonlinear increase of the modulus at larger $C_{1st}$. Importance of the inter-network entanglement will be also mentioned in the discussion of the fracture strain.

According to our previous study, yield point of DN gels is where the first network reaches its maximum allowable strain ($\approx$ yield strain), $\varepsilon_y$, thus $\varepsilon_y$ has been known to be almost independent of the second network composition. Under the assumption of affine deformation in which macroscopic deformation corresponds to microscopic deformation, the yield point of DN gel is considered to be the point at which the first network strands reach their contour length. Thus, the following equation can be derived;

$$\frac{dN}{d\varepsilon} \approx N^{1-v} \approx Q^{\frac{1}{2}}(\varepsilon_y + 1)$$

(9)

This equation expresses that the network strand of the first network reaches its contour length $dN$ by the swelling $Q^{1/2}$ times from the as-prepared state and the stretching $\varepsilon_y + 1$ times. Here, by using eqn (6a), one can derive $Q^{1/3} \propto N^{-1-v}$. Combination of this relationship and eqn (9) leads the prediction that the yield strain does not depend on the first network composition. Since $\varepsilon_y + 1$ of DN gels is almost equal to the average end-to-end distance of the first network strands with respect to their contour length, this theoretical prediction (independency of $\varepsilon_y$) means that the size of the first network strands relative to their contour length should be constant regardless of $c_{1st\_MBAA}$. In the actual experiments, slight negative correlation between $\varepsilon_y$ and $c_{1st\_MBAA}$ was observed, probably because of the non-ideal swelling of the first network discussed in the analysis of swelling behaviour.

For the nominal yield stress $\sigma_y$, the previous study shows that the yield stress of DN gels is proportional to their area density of the first network strands at the unstretched state, $d$, as $\sigma_y \propto d$. The area density is given by;

$$d \approx v_c \frac{2}{3} \left( \frac{C_{1st}}{N} \right)^{\frac{2}{3}}$$

(10)

where $v_c$ is density of the elastically effective first network strands. Substitution of eqn (6b) to eqn (10) leads

$$\sigma_y \propto d \propto C_{1st}^{\frac{2(2-v)}{3(2-v-1)}}$$

(11)

Substitution of $v = 0.6$ to eqn (11) leads the theoretical relationship $\sigma_y \propto C_{1st}^{1.22}$. To confirm this prediction, the experimental dependence of $\sigma_y$ on $C_{1st}$ was plotted (Figure 5(b)). We observed a power-law relationship $\sigma_y \propto C_{1st}^{1.13}$, which is enough close to the theoretical estimation.

The dependence of $\varepsilon_f$ on $c_{1st\_MBAA}$ and $c_{AAm}$ can be understood as follows. After the first network ruptures into discontinuous fragments, the mechanical properties of the DN gels changed to the second network-based stretchy ones. Thus, the extensibility of DN gels after yielding should be mainly determined by the second network cross-linking density. Since the second network is sufficiently dense and interpenetrates with the first network, three types of cross-linking of the second

![Figure 5. The relationships between (a) $E$ and $C_{1st}$ and (b) $\sigma_y$ and $C_{1st}$ of the t-DN gels.](image-url)
network are possible: covalent cross-linking, intra-network entanglement,\(^4\,^4\) and inter-network entanglement between the second and first networks.\(^10\,^4\) Covalent cross-linking is formed by co-polymerisation of the divinyl cross-linker MBAA with the monomer AAm. Because the feed ratio of MBAA to AAm was fixed at 1/5000 regardless of \(c_{\text{AAm}}\), if the chemical cross-linking determines the fracture strain, it should depend on neither \(c_{\text{AAm}}\) nor \(c_{\text{1st MBAA}}\). In addition, if the intra-network entanglement in the second network determines the fracture strain, it should only depend on \(c_{\text{AAm}}\). However, the actual \(\varepsilon_f\) strongly depends on both \(c_{\text{AAm}}\) and \(c_{\text{1st MBAA}}\), suggesting the inter-network entanglement between the first and second networks should dominate the fracture strain \(\varepsilon_f\). As the entanglement density increases with the concentration of both components, \(\varepsilon_f\) of the DN gels qualitatively decreases when both \(c_{\text{AAm}}\) and \(c_{\text{1st MBAA}}\) increase.

**Mechanical hysteresis loss.**

The mechanical hysteresis in the cycle tensile tests was characterised to clarify the energy dissipation process of the various t-DN gels upon uniaxial deformation. Note that strain is correctly measured in this experiment by using an extensometer. Figure 6 depicts the cyclic tensile test results of the t-DN(4-2) gels, which show extremely large and irreversible mechanical hysteresis in agreement with other DN gels reported in previous studies.\(^12\,^16\,^19\) The area between the first and the second loading curves at the desired strain \(\varepsilon_{\text{max}}\), defined as the dissipated energy density, \(U_{\text{hys}}(\varepsilon_{\text{max}})\), is a parameter used to characterise the amount of energy consumed during the tensile deformation due to internal fracture of the first network. \(U_{\text{hys}}\) increases with an increase in \(\varepsilon_{\text{max}}\), even in the hardening region, which is in agreement with our previous report.\(^12\) Figure 7(a) depicts the dependence of \(U_{\text{hys}}\) on \(\varepsilon_{\text{max}}\) of the DN gels consisting of the same first network but different second network concentrations, t-DN(4-y) gels \((y = 2–8 \text{ M})\). The graphs almost overlap regardless of the second network concentration, with a linear relationship between \(U_{\text{hys}}\) and \(\varepsilon_{\text{max}}\). Figure 7(b) depicts the dependence of \(U_{\text{hys}}\) on \(\varepsilon_{\text{max}}\) for the DN gels consisting of the same second network but different first network, t-DN(x-4) gels \((x = 2–8 \text{ mol%)}\). The results strongly depend on \(c_{\text{1st MBAA}}\). All samples show a linear relationship between \(U_{\text{hys}}\) and \(\varepsilon_{\text{max}}\), similar to the t-DN(4-y) gels, whereas the slope significantly increases with an increase in \(c_{\text{1st MBAA}}\). As the high \(c_{\text{1st MBAA}}\) leads to a high first network concentration \(c_{\text{1st}}\), the result in Figure 7(b) indicates that the energy required for fracturing the first network increases with an increase in its concentration \(c_{\text{1st}}\). As the linear relation between \(U_{\text{hys}}\) and \(\varepsilon_{\text{max}}\) roughly goes through the coordinate origin, we obtain \(dU_{\text{hys}}/d\varepsilon_{\text{max}} = U_{\text{hys}}(\varepsilon_{\text{max}})/\varepsilon_{\text{max}}\). In Figure 7(c), we plotted \(U_{\text{hys}}\) against \(\varepsilon_{\text{max}}c_{\text{1st}}\) and found the empirical relationship;

\[
U_{\text{hys}} \propto \varepsilon_{\text{max}}c_{\text{1st}} \tag{12}
\]

Eqn (12) is the general relationship applicable for both t-DN(4-y) and (x-4) gels. This equation does not include a term related to the second network, suggesting that the energy dissipation (internal fracture process of the first network) of the DN gels upon stretching is independent of the second network. In other words, the existence of the second network does not affect the internal fracture of the first network in the DN gels. This discussion may seem to be in conflict with the previous discussion about fracture strain, which concludes that the fracture strain of DN gels is determined partly by the entanglement between the first and second networks. This conflict may be due to the different nature of the two networks. The strands of the brittle first network are almost fully stretched, whereas the strands of the stretchy second network are soft and flexible. Thus, the existence of inter-network entanglement may not affect the deformation and fracture behaviours of the first network but may strongly affect the behaviour of the soft second network.

The structural origin of eqn (12) can be discussed as follows. According to the discussion in ref. 12 based on the Lake-Thomas theory, total energy required for the internal fracture of the first network in DN gels is given by

$$U_{\text{hys}} \propto \varepsilon_{\text{max}}c_{\text{1st}} \tag{12}$$

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J. Name., 2013, 00, 1-3 | 7

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Crack propagation is initiated when the characteristic significant energy dissipation due to the internal fracture in this local region ahead of a crack tip is damage zone around a fracture surface. Prior to the crack fracture energy of a DN gel is the formation of a strip‐like zone, the real damage zone structure around a crack tip of the DN gels although not only $U_{\text{dis}}$ but also $h$ must affect the fracture energy of the DN gels according to eqn (15). To this end, we note that while the model by Brown and Tanaka simply assumes a homogeneous damage zone, the real damage zone should have a damage gradient from a crack surface to the edge. Thus, future investigations on the damage gradient are necessary to completely understand the relationship between toughness and composition of the DN gels. Such damage gradient has been observed in the multiple network elastomers having similar toughening mechanism. }
distribution near the fracture surface of DN gels. The results of that investigation will be published in future papers.

Conclusions
First, we highlighted the contributions of the two networks to the tensile stress–strain curves of the DN gels. Initial mechanical response and yield stress of the DN gels are mainly dominated by the stiff and brittle first network but weakly depend on the stretchy second network. After reaching the yield point where the first network breaks into fragments, mechanical response and fracture strain of the DN gels are determined by both network structures, where the second component serves as network strands and the fragmented first network may work as macroscopic cross-linking points through the inter-network entanglements. These knowledges contribute to synthesis of DN gels showing desired mechanical responses at various strains. Second, the internal fracture process of various DN gels showing desired mechanical responses at various network structures, where the second component serves as the first network breaks into fragments, mechanical response and toughness of DN gels.

Conflicts of interest
There are no conflicts of interest to declare.

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Notes and references