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Tough Double-Network Gels and Elastomers from the Non-Pre-stretched First Network

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ABSTRACT: Double-network (DN) gels and elastomers, which consist of two (or more) rubbery polymer networks with contrasting physical properties, have received significant attention as they are extremely tough soft materials. The 1st network of tough DN materials should be more brittle and weaker than the 2nd network. In this paper, we reexamined the structural requirements of the covalently-cross-linked 1st network of tough DN materials and established a non-prestretching strategy. While prestretching of network strands has been considered necessary for preparation of the brittle and weak 1st network, we found that a non-prestretched network having a short strand length and low strand density can be used as the brittle and weak 1st network for preparation of both tough DN gels and elastomers. This work can further expand the chemical and mechanical diversity of DN materials.

Elastomers and gels, which are rubbery polymeric materials, have been widely used as industrial or medical materials owing to their unique softness. Examples include tires and stretchable electronics (elastomers) [1], contact lenses and cell cultivation scaffolds (gels) [2-3], and so on. Recently, various toughening methods for the rubbery materials have been introduced to improve their durability [4-5]. Specifically, the double network (DN) strategy has attracted much attention as an effective toughening method for both gels [6-11] and elastomers [11-15]. For example, the optimized DN gels show extremely high fracture energy of 4,000 J m⁻², whereas conventional gels show fracture energy of 1–100 J m⁻² [10].

Tough DN gels or elastomers are interpenetrating network materials, consisting of the contrasting two (or more) networks. Combinations of the two networks of DN materials that give high toughness are strongly limited [6, 11]. The following two conditions are considered important for the effective toughening:

1. The 1st network is more “brittle (low extensibility)” than the 2nd network [7]. Deformation ratio of a network at break, λ_f , can be used as an index of its brittleness.
2. The 1st network is “weaker” than the 2nd network [9]. Tensile nominal fracture stress, σ_f , can be an index of its weakness.

When a tough DN material having such contrasting two networks is deformed, as shown in Figure 1(a), the brittle strands of the 1st network firstly rupture, while the stretchable 2nd network keeps unity of the material. During the deformation process, massive 1st network strands get ruptured and dissipate large energy before fracture of the stretchable 2nd network, which leads extremely high toughness of a DN material [16-18]. Such 1st network fracture in wide range visually appears as yielding-like phenomenon and irreversible mechanical hystere-

sis during tensile test [7, 16-18]. Here we emphasize again importance of the above two conditions. If condition 1 is not satisfied, the two networks having similar extensibility fracture almost simultaneously like a single network gel. If condition 2 is not satisfied, after rupture of the 1st network strands, the 2nd network strands cannot sustain the transferred force, leading immediate macroscopic fracture of both the networks.

However, what are the structural requirements of the 1st network which satisfies these two conditions (small λ_f and σ_f)? Although the tough DN gels can be made from both chemically- and physically-cross-linked brittle 1st network [19-21], in this work we focus on the DN gels with the chemically-cross-linked 1st network. Let us assume a homogeneous chemically-cross-linked network with the Kuhn segment concentration, c , and the network strand density, n , as the 1st network of a DN material. Average number of Kuhn segments per a network strand, N , of this network is c/n without consideration of trapped entanglement. The average end-to-end distance of its network strands is expressed as bN^ν , where b is Kuhn length and ν is Flory exponent, which relates to the degree of expansion of the strands. For condition 1, λ_f of a gel is close to maximum deformation ratio of its network strands [22, 23]. As shown in Figure 1(b), maximum deformation ratio of a single strand is the ratio of its contour length, bN , to the end-to-end distance at its unperturbed state, bN^ν . Thus, λ_f of a gel is approximately described as

$$\lambda_f \approx \frac{bN}{bN^\nu} = N^{1-\nu} = \left(\frac{c}{n}\right)^{1-\nu} \quad (1).$$

For condition 2, σ_f should be approximately proportional to the area density of the 1st network strands at the relaxed state [8, 24]. In particular,

$$\sigma_f \propto n^{\frac{2}{3}} \quad (2).$$

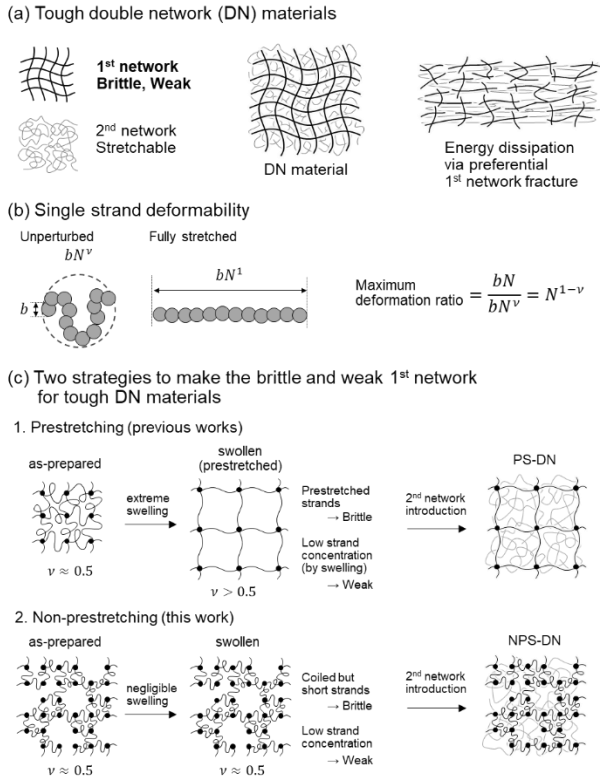


Figure 1. (a) Double-network materials consisting of the brittle and weak 1st network and stretchable 2nd network, and their energy dissipation mechanism. (b) Theoretical maximum deformation ratio of single network strand with Kuhn length b , Kuhn segment number N , and Flory exponent ν . (c) The two strategies to make the brittle and weak 1st network for tough DN materials.

Eq. (1) suggests that either large ν or small $N (=c/n)$ is necessary to make the network “brittle”. Eq. (2) implies lower strand density n is necessary to make the network “weak”. Therefore, there should be two possible strategies to make the brittle and weak 1st network, as shown in Figure 1(c). The first one, so-called prestretching strategy, is to use the highly swollen, prestretched 1st network to achieve large ν and small n . Most of the reported DN materials with the chemically-cross-linked 1st network have adopted this strategy. A polyelectrolyte (PE) network is typically used as the prestretchable 1st network [6,14]. A PE gel swells largely in polar solvents as dissociated counter-ions of the PE gel possess large osmotic pressure of the gel. As a result, a swollen PE gel has small c and n because the swelling induces dilution of the network. In addition, a swollen PE gel has large ν due to swelling-induced prestretching of their strands. Large ν leads small λ_f , which satisfies the condition 1, whereas small n leads small σ_i , which satisfies the condition 2. Thus, a PE network can be the 1st network of tough DN materials. This prestretching strategy has been also applied to the neutral polymer (NP)-based 1st network. Since an NP gel does not swell much in solvents due to lack of counter-ions, it exhibits a small ν of 0.5–0.6 even at its swollen state. To increase the swelling ratio of an NP gel, additional components can be introduced to the NP network to increase its entire osmotic pressure. For example, introduction of linear polyelectrolytes or ionic micelles (molecular stent method) effectively increases overall osmotic pressure and swelling ratio of a NP gel [8]. Such highly swollen NP gels having large ν and small n can be used as the 1st network of a tough DN materials. Additionally, triple

network method has been proposed based on the similar idea [12–13,25–26]. In this method, the neutral but concentrated 2nd network possesses large osmotic pressure to promote the 1st network swelling, and the stretchable 3rd network acts as the ductile network.

The other possible strategy to fabricate the brittle and weak 1st network is to synthesize networks having small segment number per a strand $N (=c/n)$ and small network strand density n without prestretching of the strands. N can be decreased by increasing n or decreasing c . Increase of n , however, causes increase of σ_i , which is incompatible with condition 2. Therefore, N should be decreased mainly by decreasing Kuhn segment concentration c while keeping strand density n low. The small $N = c/n$ (short strand length) makes the gels extremely brittle, which satisfies the condition 1. Its subdued strand density n makes the gels sufficiently weak, which satisfies the condition 2.

Although these two strategies can be theoretically used for fabrication of tough DN materials with the chemically-cross-linked 1st network, to the best of our knowledge, no study has adopted the latter strategy. Here, the purpose of this study is to experimentally confirm validity of the non-prestretching strategy for synthesis of the brittle and the weak 1st network for both tough DN gels and elastomers. First, we tried synthesis of tough DN gels with the non-prestretched 1st network synthesized by random copolymerization of monomer and cross-linker. To achieve low Kuhn segment concentration c of the network, we used low monomer concentration for the gel preparation. Also, to achieve short strand length c/n , molar ratio of the cross-linker to the monomer was kept sufficiently high. In particular, the 1st network was synthesized from the aqueous solutions containing 0.2–1 M of *N,N*-dimethylacrylamide (DMAAm) as a monomer and 3–21 mol% (to monomer) of *N,N'*-methylenebis(acrylamide) (MBAA) as a cross-linker. Note that the gelation reaction should not be ideal at such extreme low monomer concentration and high cross-linking ratio. The obtained networks may contain many defects, and some cross-linkers may not work as cross-linking points (connecting 3 or more strands) but substantially work as monomers (connecting 2 strands). In fact, the lowest monomer concentration of 0.2 M is near the critical concentration for gelation, below which bulk gels could not be synthesized. Subsequently, the ductile 2nd polyacrylamide (PAAm) network was synthesized in the presence of the 1st network. The obtained PDMAAm/PAAm DN gels with the non-prestretched 1st network are denoted as NPS-DN(x - y) gels, where x and y are feed monomer concentration (M) corresponding to c and ratio of the cross-linker to the monomer (mol%) corresponding to c/n , respectively. Thickness ratio of the 1st PDMAAm network in the NPS-DN gels to its as-prepared state, α , was around 1.1, suggesting the PDMAAm network is not prestretched in the NPS-DN gels (Supporting Information). As a control, the conventional DN gels with the prestretched poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), 1st network (PS-DN gels) were also prepared. α of the PAMPS network was 2.3, suggesting the network is highly prestretched. The obtained NPS-DN and PS-DN gels were tested without soaking in water unless specially mentioned.

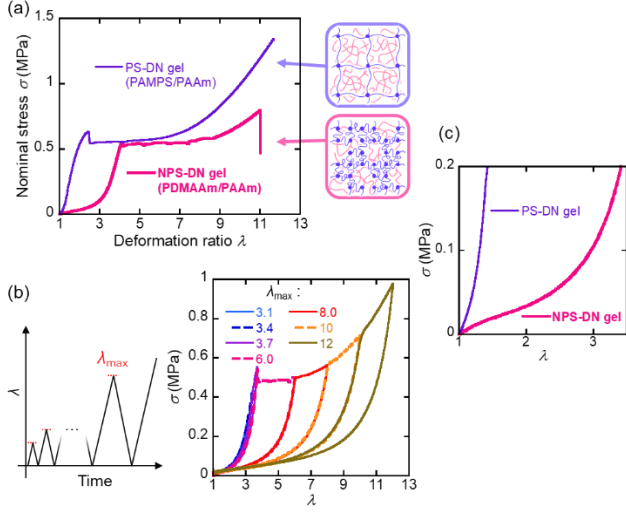


Figure 2. (a) Nominal tensile stress-deformation ratio (σ - λ) curves of the typical prestretched (PS)-DN gel and the non-prestretched (NPS)-DN(0.4-8) gel. (b) Cycle tensile test results of the NPS-DN(0.4-8) gel with the deformation ratio-time diagram. (c) Initial σ - λ curves of the PS-DN and NPS-DN gels.

Figure 2(a) shows nominal tensile stress-deformation ratio (σ - λ) curves of the typical NPS-DN and the PS-DN gels. The PS-DN gel showed high strength and stretchability as well as clear yielding. The NPS-DN(0.4-8) gel also displayed high mechanical performance like the PS-DN gel, such as high fracture stress of 0.8 MPa and high deformation ratio at break of 11 with clear yielding. Moreover, the NPS-DN gels possess high mechanical performance even after swollen in water (Supporting Information). As shown in Figure 2(b), the NPS-DN gel presented irreversible energy dissipation upon cycle tensile test, like PS-DN gels [16-18]. It suggests that the non-prestretched 1st network in the NPS-DN gels works as brittle sacrificial bonds to dissipate large energy during deformation, which contributes to high toughness of the DN gels. These results show validity of the non-prestretching strategy for preparation of tough DN gels. On the other hand, at small deformation, the mechanical response of the PS-DN and NPS-DN gels are quite different. As shown in Figure 2(c), the NPS-DN gel is initially soft and shows strain hardening at $\lambda > 3$, whereas the conventional PS-DN gel is stiff from the beginning of the stretch. Regarding this, the initial stiffness of the NPS-DN gels is much smaller than the PS-DN gel despite higher cross-linking ratio of the NPS 1st network. Moreover, the NPS-DN gel exhibits an S-shaped curve (softening-hardening) while the PS-DN gel shows a J-shaped curve (only hardening) at their low λ regime. σ - λ curves of DN materials, before yielding, are dominated by the 1st network [13,27-28]. Typical rubbery materials having coiled strands show S-shaped curves [29]. As the non-prestretched 1st network strands are in coiled state, an NPS-DN gel also exhibits a standard S-shaped curve with initial soft regime. However, the 1st network of a PS-DN gel is highly pre-stretched. Thus, initial softening regime in a S-shaped curve does not appear in the σ - λ curve of the PS-DN gel, resulting in the J-shaped curve. Furthermore, the prestretched strands have higher elastic energy than the non-prestretched strands, resulting in higher initial stiffness of the PS-DN gel than the NPS-DN gel.

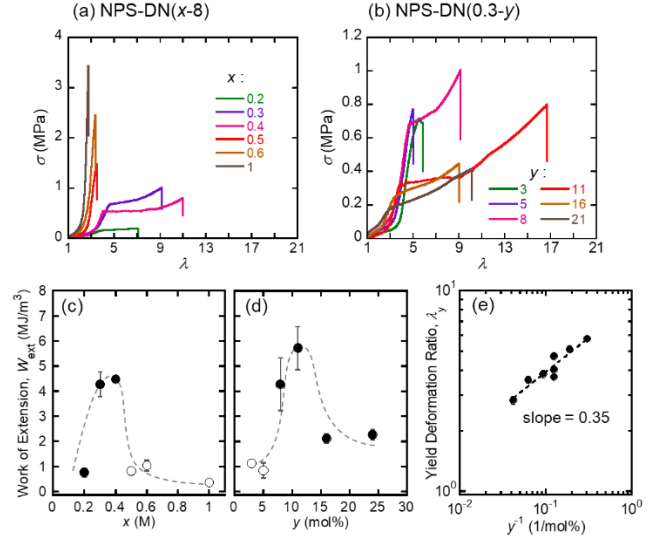


Figure 3. (a) σ - λ curves of the NPS-DN(x-8) gels. (b) σ - λ curves of the NPS-DN(0.3-y) gels. (c) Work of extension of the NPS-DN(x-8) and (d) work of extension of the NPS-DN(0.3-y) gels. The filled symbols denote the samples showing distinct yielding whereas the open symbols denote the samples without yielding. The dashed lines are guide for eyes. (e) Relationship between the yield deformation ratio and y^{-1} of the NPS-DN(x-y) gels. The small error bars are hidden by the symbols.

Effect of the 1st network composition to mechanical properties of NPS-DN gels was evaluated. Initially, feed monomer concentration x was varied but the ratio of cross-linker y was fixed to 8 mol%. As x and y correspond to c and c/n , respectively, varying x while keeping y same ideally corresponds to change of segment density c and strand concentration n , with constant strand length c/n . Figure 3(a) depicts tensile σ - λ curves of the NPS-DN(x-8) gels. When x is too large ($x > 0.4$ M), the NPS-DN gels are strong but brittle due to too large n (condition 2 is not satisfied). When $x \leq 0.4$ M, the obtained NPS-DN gels show yielding due to appropriate n . Secondly, x is fixed to 0.3 M and y is varied. It ideally corresponds to vary c/n and n while keeping c constant. Figure 3(b) shows tensile curves of NPS-DN(0.3-y) gels. When y is too small, the NPS-DN gels are brittle due to too large strand length c/n (condition 1 is not satisfied). The gels showed yielding and high toughness when $y \geq 6$ mol%. Note that, the NPS-DN gel with $y \geq 16$ mol% was turbid and showed unclear yielding because of inhomogeneous network structure induced by large cross-linking ratio. When the toughness of the DN gels are simply evaluated by the area under σ - λ curves (work of extension), it is clear that the NPS-DN gels which show yielding have significantly higher toughness than those without yielding, except the NPS-DN(0.2-8) gel (Figure 3(c, d)).

It would be interesting to explore the relationship between the mechanical properties of the NPS-DN gels and their 1st network structure. Our previous study implies that the yield deformation ratio λ_y of DN gels corresponds to the maximum stretching ratio of the 1st network strands, $(c/n)^{1-\nu}$, as,

$$\lambda_y \approx \left(\frac{c}{n}\right)^{1-\nu} \quad (3) [18].$$

Considering y is ideally inversely proportional to c/n , we plotted λ_y of the as-prepared NPS-DN(x-y) gels against y^{-1} as shown in Figure 3(e). A positive power-law relationship with the slope of

0.35 is found to exist between them. The slope ($\approx 1-\nu$) of 0.35 corresponds to ν of 0.65, which is close to theoretical ν of 0.5–0.6.

Subsequently, we applied this non-prestretching strategy to preparation of tough NPS-DN elastomers. Following the previous reports on DN elastomers, we adopt poly(ethyl acrylate) (PEA) network as the stretchable 2nd network [12–15]. Apart from the two requirements for the 1st network of DN materials, there are three additional requirements for the brittle, non-prestretched 1st network for DN elastomers: 1) Tg of the 1st network is lower than 0 °C, 2) bulk ethyl acrylate is a good solvent for the 1st network, 3) the monomeric units should be dissolvable in water (because water is the desired solvent for the network synthesis at such extremely-low monomer concentration owing to its negligible chain transfer reaction constant [30]). Polyethylene glycol diacrylate (PEGDA) was chosen as the monomeric units for the 1st network which conform to these additional requirements. We synthesized the poly(PEGDA) (PPEGDA) hydrogels from the PEGDA aqueous solutions with weight concentration of 10–30 wt%. Tg of the dried PPEGDA network was determined by the differential scanning calorimeter as -40°C (data not shown). The PPEGDA hydrogels were dehydrated and immersed in ethyl acrylate liquid containing cross-linker. Then, the PEA network was synthesized in the presence of the PPEGDA networks. The obtained PPEGDA/PEA NPS-DN elastomers are denoted as NPS-DN(*z*) elastomers, where *z* is feed PEGDA concentration (wt%).

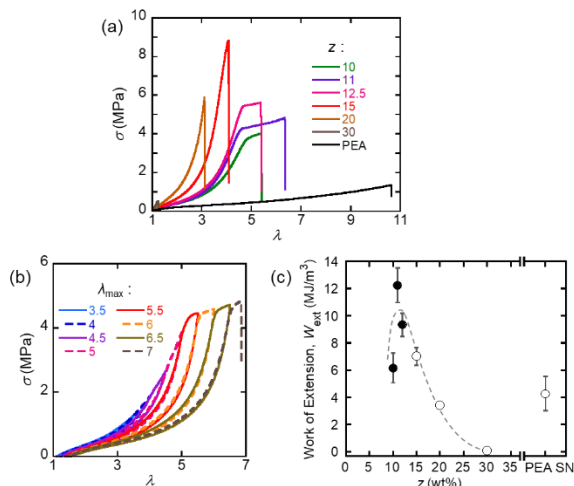


Figure 4. (a) σ - λ curves of the PPEGDA/PEA NPS-DN(*z*) elastomers and the PEA single network elastomer. (b) Cycle tensile test results of the NPS-DN(11) elastomer. (c) Work of extension of the NPS-DN(*z*) elastomers and the PEA elastomer. The filled and open symbols denote the samples with and without yielding, respectively. The dashed line is a guide for eyes.

Figure 4(a) shows effect of the PEGDA feed concentration *z* on the σ - λ curves of the PPEGDA/PEA NPS-DN(*z*) elastomers. When $z \geq 15$ wt%, the NPS-DN(*z*) elastomers were brittle without yielding. On the other hand, the NPS-DN elastomers show yielding when $z \leq 12$ wt%. At this condition, the NPS-DN elastomers show irreversible energy dissipation upon their cycle tensile test like DN gels (Figure 4(b)). Toughness (work of extension) of the NPS-DN elastomers with yielding was improved significantly in comparison with that of the PEA single network elastomer, as shown in Figure 4(c). These results clarify that the non-prestretching method can be principally applied

to fabricate tough DN elastomers. Optimization of preparation conditions for stronger and tougher DN elastomers is a future challenge.

In conclusion, we have established the novel non-prestretching strategy for preparation of tough DN gels and elastomers in addition to the conventional prestretching strategy, based on the theoretical investigation of structural requirements for tough DN materials. As PS-DN and NPS-DN materials commonly have high toughness but show different initial mechanical response, we can choose the appropriate one in accordance to the specific application. For example, NPS-DN materials with initial soft regime should be more suitable for sealing materials and stretchable electronics than rigid PS-DN materials. Moreover, this study can expand chemical diversity of DN materials. While conventional prestretching strategy basically requires the polyelectrolyte 1st network, this non-prestretching methodology enables to use more general neutral network as the 1st network. Since use of polyelectrolytes is harmful to biological tissues in some cases [31], the polyelectrolyte-free tough DN gels, realized by this study, can be desired medical materials.

Experimental Section.

For preparation of the non-prestretched 1st network, *x* M of DMAAm, *y* mol% of MBAA (to monomer), and 5 mM of potassium persulfate were dissolved in pure water. 5 mM of *N,N,N',N'*-tetramethylethylenediamine was then added to the solutions to initiate gelation. The solutions were immediately poured into the glass molds prepared with the two soda-lime glass plates (thickness: 3 mm) and the silicone rubber (thickness: 1 mm) as a spacer and kept for more than 24 h at 4 °C in air to synthesize the PDMAAm gels. For preparation of the pre-stretched network, 1 M of AMPS, 40 mM of MBAA, and 10 mM of 2-oxogutaric acid were dissolved in pure water. The solution was then poured into the glass mold. 365 nm UV (4 mW/cm²) polymerization was carried out for 7 h to synthesize the PAMPS gel in an argon blanket. The 1st network gels were immersed in the excess 2nd network precursor aqueous solutions containing 4 M of acrylamide (AAm), 0.4 mM of MBAA, and 0.4 mM of 2-oxogutaric acid for more than 24 h and then sandwiched with the two glass plates. After that, 365 nm UV (4 mW/cm²) polymerization was carried out for at least 7 h to synthesize the 2nd PAAm network within the 1st network gels in an argon blanket. Materials and sample preparation methods for the DN elastomers are described in the Supporting Information.

Mechanical measurements were performed on as-prepared samples unless specifically mentioned. Uniaxial tensile tests were performed on dumbbell-shaped specimens standardized as JIS K6251-7 (12 mm length and 2 mm width). Data shown in Figure 4 were measured with Tensilon RTC-1310A (Orientec Co.) while data shown in Figures 2 and 3 were measured with Instron 5965 (Instron Co.). Nominal stress, σ , and deformation ratio, λ , are defined as force divided by the initial cross-sectional area and sample gauge length divided by the initial length, respectively. Young's modulus is defined as the slope of σ - λ curves at $1 < \lambda < 1.1$. Work of extension, W_{ext} , is defined as the area under σ - λ curves. Tensile velocity was fixed at 100 mm/min, which corresponds to strain rate of 0.14 s⁻¹. Cyclic tensile tests were performed on the same specimens with the same tensile velocity. As shown in Figure 2(b), the specimen was stretched to the certain λ_{max} and then immediately unloaded. This process was repeated with increasing λ_{max} until sample rupture occurred without any waiting time between the cycles.

ASSOCIATED CONTENT

Supporting Information. Materials, elastomer preparation, swelling properties of the PDMAAm network, and mechanical properties of the NPS-DN gels at their swollen state. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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