Polymer Journal (2019) 51:851–859
https://doi.org/10.1038/s41428-019-0203-6

ORIGINAL ARTICLE

Mechanical properties of doubly crosslinked gels

Takuya Katashima[1] · **Ung-il Chung**[2] · **Takamasa Sakai**[2]

Received: 17 February 2019 / Revised: 4 April 2019 / Accepted: 6 April 2019 / Published online: 22 May 2019

Abstract

We fabricated the doubly crosslinked gel, with internal stress by stretching the gel during the gelation reaction using tetra-PEG gels, which are formed by the AB type crosslink-coupling of two mutually reactive tetra-arm polyethylene glycol (PEG). In a doubly crosslinked gel, two networks having different reference states coexist with and balance each other, resulting in enhanced Young's modulus and residual strain. We investigated these properties by tuning the time for the imposition of the stretching of the gels and the stretching ratio. The residual strain increased with increase in the time for the imposition of stretching and the stretching ratio. On the other hand, the Young's modulus had a maximum value at a certain time for the imposition of the stretching of the gels and increased with increasing stretching ratio. These results were well explained by the balance between the strain energies of the first and second networks under the framework of the classical two-network theory, where the total strain energy is described as a simple sum of the energies of the first and second networks.

Introduction

Anisotropic mechanical materials exist widely in nature. For example, skeletal muscles have fibrous structures and exhibit contraction-elongation motion along the fiber axis. Elastomeric materials, including muscles, exhibit reversibly large deformability and markedly nonlinear stress-elongation relationships with small stress stemming from the entropic elasticity. Anisotropic responses become significant when the anisotropic moieties are trapped in these soft elastomeric matrices. There have been many attempts to introduce anisotropic structures in the elastomeric matrices. Such structures are installed by introducing anisotropically aligned moieties, including the liquid crystal mesogen [1–4] and carbon nanomaterials [5, 6], with external mechanical, magnetic, and electric fields. In addition to introducing moieties with a high aspect ratio, one can introduce anisotropy by chemical crosslinking under an external mechanical field such as uniaxial extensional flow. Materials formed by this type of method have been referred to as "double-network rubbers" for more than half a decade. The double-network rubbers are crosslinked twice: crosslinking in an initial nondeformed state first and subsequently crosslinking in a deformed state. The initial stretched network is pinned by the second network, resulting in the mechanical and optical anisotropies. Notably, these materials are different from the "double-network gels" developed by Gong et al., which are formed by two different monomeric networks, a rigid and brittle one and a soft and ductile one. Here, we use the term "doubly crosslinked gels" to avoid confusion.

Until now, many studies have been carried out on the doubly crosslinked gels. Tobolsky et al. first introduced the double crosslinking concept to explain the physical aging of rubbers, which involved free-radical scission and crosslinking under deformation [7, 8]. After that, many researchers studied the physical properties, such as mechanical properties, of the doubly crosslinked gels [9–14]. The mechanical properties and permanent set of doubly crosslinked gels were discussed based on the "two-network theory" proposed and developed by Berry et al. [9], Flory [15], and Fricker [16]. In the two-network theory, the elastic free energy (W) for the doubly crosslinked gel is

---

✉ Takuya Katashima
takuya.katashima@riken.jp

✉ Takamasa Sakai
sakai@tetrapod.t.u-tokyo.ac.jp

[1] Biomacromolecules Research Team, RIKEN Center for Sustainable Resource Science, 2-1 Hirosawa, 351-0198 Wako-shi, Saitama, Japan

[2] Department of Bioengineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, 113-8656 Tokyo, Japan

expressed merely as the sum of the first (W_1) and second (W_2) networks.

$$W = W_1 + W_2 \quad (1)$$

W is determined by the deformation ratio relative to the state of "reference", which generally corresponds to the state where the crosslinking is introduced. In the two-network theory, the reference state is different from either the first or second network. The residual strain and Young's modulus are determined by the balance between the first and second networks.

However, the quantitative understanding of these properties remains incomplete mainly due to three reasons. The first problem is the viscoelastic property, which is a feature of general rubbers. After the imposition of stretching with high strain rate, the stress and the orientation of the first networks reduces with time. The stretching rate and the second crosslinking reaction rate strongly influence the orientation of the first networks. Thus, the balance between the viscoelastic relaxation and the crosslinking reaction rate determines the orientation of the first network strands in the resultant networks, which deviates the situation from the simple concept represented by Eq. 1.

The second problem is the difficulty of independently controlling the network structures, such as the network strand length and the functionality of the crosslinking point. Conventional elastomers have many inhomogeneities, including spatial and connectivity heterogeneities and trapped entanglements [17]. These inhomogeneities are uncontrollable and preclude the systematical understanding of the relationships between the network structures and the strain energy density (W) function. In addition, general rubbers exhibit the significant strain-softening effect under uniaxial stretching, which cannot be explained by the classical rubbery theory [18–21]. Although this softening behavior is phenomenologically described by the complex W function with higher-order terms of the first and second invariants of the Green's deformation tensor [22–28], this deviation hinders the correct estimation of the first and second network components of W.

The third problem is the coupling of the W function and connectivity. Pioneering works assumed that the W function of the first and second networks is identical to the network formed without any deformation. However, in a conventional crosslinking process, the formation of crosslinks decreases the network strand length, resulting in a decrease in the maximum stretching ratio. Furthermore, crosslinking freezes the topological constraints by entanglements, which contributes to elasticity [29, 30]. Although there have recently been some attempts to assess the effects of these topological effects on the doubly crosslinked networks by molecular dynamic simulation [31, 32], separating these effects experimentally is still difficult.

Because of these difficulties, the experimental examination of the two-network theory is limited. To overcome these problems, a system with little viscoelastic effect and good controllability over network structures is necessary. Gels are promising for avoiding the viscoelastic effect because dilution generally reduces the entanglements and enhances the molecular motion. Even for gels, however, the uncontrollability of the network structures remains a long-standing problem.

Recently, we have successfully designed and fabricated a "tetra-PEG gel", which forms nearly ideal networks [33–35]. Tetra-PEG gels are formed by the AB type crosslink-coupling of two mutually reactive tetra-arm polyethylene glycol (PEG). In the small angle neutron scattering (SANS) measurement, we observed no appreciable degree of excess scattering relative to that of the uncrosslinked PEG solutions with the same concentration, suggesting that practically no spatial inhomogeneity exists in regions up to 200 nm in size [36]. Investigation of infrared spectroscopy (IR) showed that the reaction conversion is up to 0.9 [37–39]. Nuclear magnetic resonance (NMR), investigation of small deformation and fracture testing showed that the elastically active junctions are merely governed by chemical crosslinks, whereas the contribution of entanglements between the network strands and elastically ineffective loops are small [37, 38, 40]. A tetra-PEG gel has high reaction conversion, few elastically ineffective loops, and trapped entanglements and thus is a promising system for evaluating the physical properties of polymer gels. The W function of the tetra-PEG gels can be ideally approximated in the small-deformation region by the classical rubber elasticity theory [38, 41]. In addition, above a certain degree of connectivity, the stress-strain curves of the tetra-PEG gel normalized by the shear modulus are independent of connectivity [42]. These previous works suggest that the tetra-PEG gel is a promising material for the examination of the two-network theory.

In the present study, we fabricated doubly crosslinked gels using the tetra-PEG gels. We measured the residual strain and the mechanical properties of the samples with various time for the imposition of the stretching of the gels during gelation (t_i) and the imposed elongation ratios (λ_i). Based on the obtained data, we experimentally examined the validity of the two-network theory.

Materials and methods

Materials

Tetra-amine-terminated PEG (Tetra-PEG-NH$_2$) and tetra-succinimidyl ester (OSu)-terminated PEG (Tetra-PEG-OSu) were purchased from NOF Co. (Tokyo, Japan). Details of Tetra-PEG-NH$_2$ and Tetra-PEG-OSu preparation have been previously reported [33]. The molecular weights of the prepolymers (M_{pre}), Tetra-PEG-NH$_2$ and Tetra-PEG-OSu, were equal to each other ($M_{\mathrm{pre}} = 20$ kg/mol). Equal amounts of Tetra-PEG-NH_2 and Tetra-PEG-OSu (100 g/L) were dissolved in phosphate buffer (pH 7.4) and phosphate-citric acid buffer (pH 5.8), respectively. The corresponding initial polymer volume fractions (φ_0) were approximately 0.081 (mass density of the dry polymer = 1.129 g/cm^3). We preliminary checked the validity of the calculation method for the polymer volume fraction. The corresponding volume fraction was above the overlapping polymer volume fraction (=0.035). To control the reaction rate, the ionic strength of the buffers was 100 mM.

Fabrication of doubly crosslinked gel

The two solutions were mixed, and the resulting solution was poured into a silicon tube with $d_0 = 1$ mm. (i) When a certain time ($t_i = 720$, 1000, 1200, 1370, 1800, 1980, 3180, 5490, and 7830 s) passed after the gelation reaction was started, the tube was stretched with an elongation ratio $\lambda_i = 2.6$. (ii) When a certain time ($t_i = 1800$ s) passed after the mixing was started, the tube was stretched with elongation ratios $\lambda_i = 1.5$, 1.9, and 2.6. At least 12 h were allowed to pass for the reaction to complete in the stretched state.

Fabrication of p-tuned tetra-PEG gels

Equal amounts of Tetra-PEG-NH_2 (20k) and Tetra-PEG-OSu (20k) ($\varphi_0 = 0.081$) were dissolved in phosphate buffer (pH 7.4) and phosphate-citric acid buffer (pH 5.8), respectively. The Tetra-PEG-OSu solution was incubated at 25 °C for 0, 20, 80, and 240 min. After the incubation time, the Tetra-PEG-NH_2 and Tetra-PEG-OSu solutions were mixed, and the resulting solution was poured into the mold. At least 12 h were allowed for the completion of the reaction before the following experiment was performed. The corresponding reaction conversions, which were measured by infrared spectroscopy, ranged from 0.68 to 0.92.

Uniaxial stretching and compression

A uniaxial stretching measurement was carried out in air using a mechanical testing apparatus (Autograph AG-X plus; Shimadzu, Kyoto, Japan) at a crosshead speed of 60 mm/min. The lengths of the tensile samples ranged from 12 mm to 139 mm. The corresponding strain rates ranged from 0.083 to 0.0072 s^{-1}. The stretching measurements of the doubly crosslinked networks with various t_i values and of the p-tuned tetra-PEG gels were performed. In addition, for the tetra-PEG gel with $p = 0.92$, a uniaxial compression test was carried out using a mechanical testing apparatus (Instron 3365, Instron Corp.) at a velocity of 0.50 mm/min. The initial height of the compression samples was 7.5 mm. The corresponding strain rate was 0.00011 s^{-1}. The obtained stress-elongation relationships corresponded to the equilibrium relationships without time effects, because no appreciable relaxation in stress was observed after imposing constant strain at this crosshead speed.

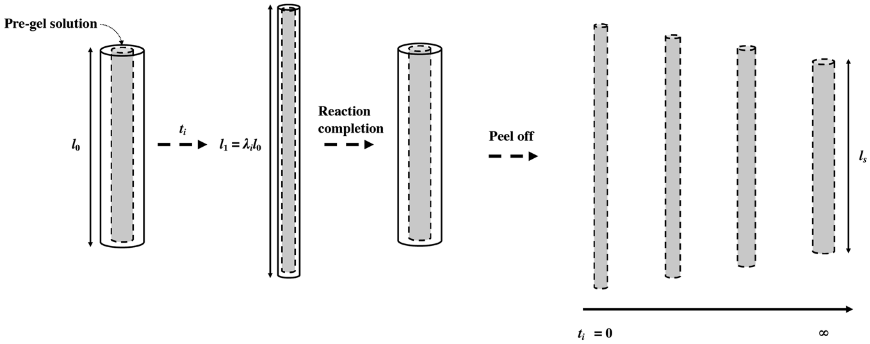
Results and discussion

Doubly crosslinked gel and two-network theory

We first explain the overview of the fabrication method of doubly crosslinked gel and the prediction of the two-network theory. A schematic illustration of the experimental procedure is shown in Fig. 1. The pregel solution was poured into soft silicone tubes with length (l_0). When a particular time (t_i) passed after the initiation of the gelation reaction, the silicone tube and gelling solution inside were stretched to $l_1 = \lambda_i l_0$. The gelling solution adhered to the surface of the silicone tube and deformed in the same manner as the silicone tube. According to the two-network theory, the network structure formed before $t = t_\mathrm{i}$ is called "the first network". The silicone tube was kept stretched until the completion of the reaction. For time $t > t_\mathrm{i}$, an additional network was formed at the deformed state ($\lambda = \lambda_i$), which is called "the second network". Notably, the first and second networks coexist in a polymer network and are covalently bonded with each other, which is different from double-network gels. The difference between the first and second networks is the state of preparation; the first network is formed at $\lambda = 1$; on the other hand, the second network is formed at $\lambda = \lambda_i$. When the samples were peeled off from the tube, the first network shrinks, and the second network competes against the shrinkage of the first network. As a result of the balance of internal tensions, the length of the gel becomes $l_\mathrm{s} = \lambda_s l_0$ ($l_0 < l_\mathrm{s} < l_\mathrm{i}$). Here, there are two extreme cases where we do not need to consider the balance of internal stresses: $t_i = 0$ or ∞. At $t_i = 0$, the gelation reaction naturally occurs in a stretched silicone tube. Thus, only the second network exists, and $l_\mathrm{s} = l_i$. On the other hand, at $t_i = \infty$, the gelation reaction is completed before the stretching, and the reacted gel inside the silicone tube is merely stretched. In this case, only the first network exists, and $l_\mathrm{s} = l_0$. In the intermediate time scale, the length of the obtained samples decreases with increasing t_i, because the internal tension originating from the first networks increases with increasing t_i. As a result, when the entire polymer network is relaxed, the first network is stretched to λ_s, and the second network is compressed to $\lambda_\mathrm{s}/\lambda_i$.

According to the two-network theory developed by Berry et al. and Flory [9, 15], the elastic free energy (W), which is the energy stored when the system is deformed, for the doubly crosslinked gel is merely expressed as the sum of

Fig. 1 Schematic illustration of the doubly crosslinked gel formation



the individual contributions of the first and second networks (Eq. 1). Here, we assume that the W for each network is expressed according to the classical rubbery theory following previous works [18–21, 43],

$$W = \frac{G}{2}\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right), \tag{2}$$

where G is the shear modulus and λ_j ($j = x, y, z$) is the stretching ratio of the polymer network relative to a network at ease. Under uniaxial stretching ($\lambda_x = \lambda$, $\lambda_y = \lambda_z = \lambda^{-1/2}$), Eq. 2 can be rewritten as

$$W = \frac{G}{2}\left(\lambda^2 + 2\lambda^{-1} - 3\right) \tag{3}$$

We note that λ in Eq. 3 is defined as the deformation referenced to the condition of ease of the entire polymer network; the effective deformation ratios of the first and second networks are different from λ. Instead, the net elongation ratios of the first and second networks are described as $\lambda_s\lambda$ and $(\lambda_s/\lambda_i)\lambda$, respectively. As a result, W_1 and W_2 are expressed as

$$W_1 = \frac{g_1}{2}\left\{(\lambda_s\lambda)^2 + 2(\lambda_s\lambda)^{-1} - 3\right\} \tag{4a}$$

$$W_2 = \frac{g_2}{2}\left(\left(\frac{\lambda_s}{\lambda_i}\lambda\right)^2 + 2\left(\frac{\lambda_s}{\lambda_i}\lambda\right)^{-1} - 3\right) \tag{4b}$$

Here, g_1 and g_2 represent the virtual shear moduli of the first and second networks, respectively, when they were formed independently in the undeformed states. The stress-elongation relationships are expressed as the first derivation of W with respect to λ:

$$\sigma = \frac{\partial W}{\partial \lambda} = \frac{\partial W_1}{\partial \lambda} + \frac{\partial W_2}{\partial \lambda} \tag{5}$$

Here, the stresses attributed to the first and second components are expressed as

$$\sigma_1 = \frac{\partial W_1}{\partial \lambda} = g_1\lambda_s\left\{(\lambda_s\lambda) - (\lambda_s\lambda)^{-2}\right\} \tag{6a}$$

$$\sigma_2 = \frac{\partial W_2}{\partial \lambda} = g_2\lambda_s\left\{\left(\frac{\lambda_s}{\lambda_i}\lambda\right) - \left(\frac{\lambda_s}{\lambda_i}\lambda\right)^{-2}\right\} \tag{6b}$$

In a network at ease, the contributions from the first and second networks are just balanced ($\sigma_1 + \sigma_2 = 0$), and λ_s is expressed as

$$\lambda_s = \left\{\frac{\lambda_i^3 - 1}{(g_1/g_2)\lambda_i^2 + 1} + 1\right\}^{1/3} \tag{7}$$

On the other hand, the Young's modulus of the doubly crosslinked gels, which corresponds to the slope of the stress-elongation curve when the sample is stretched from the state at ease, is expressed as the second derivation of W with respect to λ as

$$E = \left[g_1\lambda_s^2\left(1 + 2\lambda_s^{-3}\right) + g_2\left(\frac{\lambda_s}{\lambda_i}\right)^2\left\{1 + 2\left(\frac{\lambda_s}{\lambda_i}\right)^{-3}\right\}\right] \tag{8}$$

In this study, g_1 was estimated as the shear modulus at t_i, and g_∞ was estimated as the shear modulus of the gel formed in the undeformed state. The values of g_1 and g_∞ are proportional to the numbers of active chains in the first network and the whole network, respectively. Thus, the virtual modulus of the second network (g_2) was determined according to the equation, $g_\infty = g_1 + g_2$. Figure 2 shows the theoretical predictions of λ_s and E as a function of g_1/g_∞ based on Eqs. 7 and 8, respectively. Here, we set $\lambda_i = 2.6$ as a fixed parameter fit to our experimental condition. The Young's modulus was normalized by that of the whole undeformed network (E_0). λ_s monotonically decreased from 2.6 to unity with increasing g_1/g_∞, qualitatively agreeing to the above discussion.

Additionally, E/E_0 shows a maximum value at $g_1/g_\infty \approx 0.43$. Evidently, we can predict that $E/E_0 = 1$ at $t_i = 0$ or ∞ because only the second or first network exists, and no internal tension is induced. For intermediate t_i, a certain extent of crosslinking was formed in the nondeformed state, and further crosslinking was formed in the stretched state, resulting in enhanced elastic modulus ($E/E_0 > 1$). This

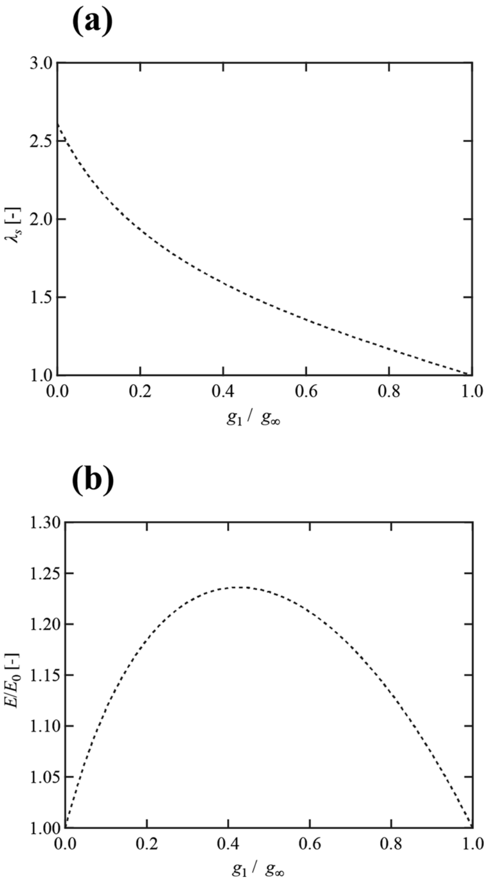


Fig. 2 Theoretical prediction of **a** the residual strain (λ_s) and **b** Young's modulus (E) of the doubly crosslinked networks. The Young's modulus is normalized by that of the pure network

enhancement is caused by the decreased entropy of doubly crosslinked gels. The anisotropy of the first network remains frozen by the second network, because the latter, which is isotropic in the deformed state, precludes the relaxation of the former.

Effect of reaction conversion on mechanical properties of the tetra-PEG gel

To experimentally examine the two-network theory, the W function of the model network should be well known and robust against gelation reaction conversion (p). Figure 3 shows the stress-elongation curve for the tetra-PEG gel with $p = 0.92$. The data with $\lambda < 1$ and $\lambda > 1$ correspond to those for compression and elongation, respectively. The red line represents the prediction of the classical rubber theory (Eq. 3) [18–21]. The experimental results well agree with the theoretical prediction within a moderate strain region. We should note that the upward deviation for a large deformation region is attributed to the finite extensibility of the network strands, as discussed previously [42]. In this paper, the maximum λ_i was set to 2.6 to minimize the effect of the finite extensibility.

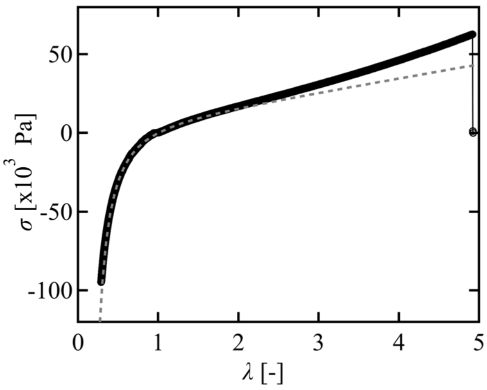


Fig. 3 Stress-elongation curve for the tetra-PEG gel. The red line represents the prediction of the classical rubber theory (color figure online)

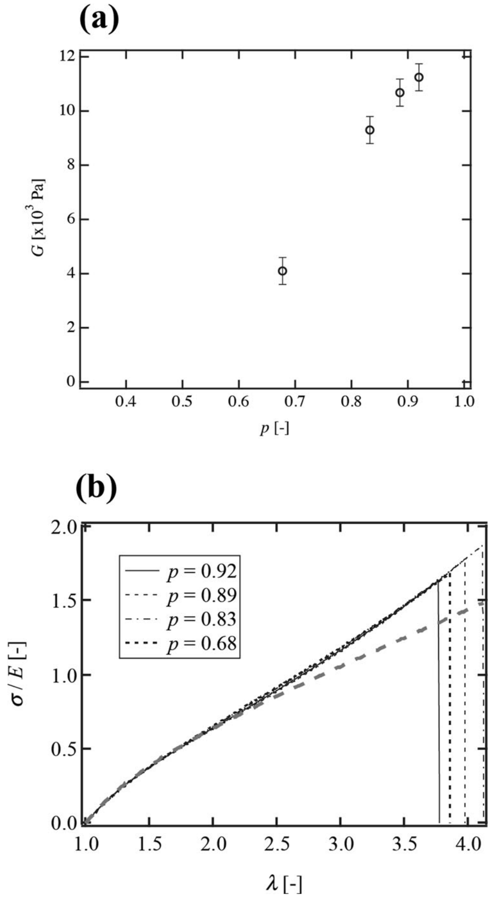


Fig. 4 **a** Stress-elongation curves of the p-tuned tetra-PEG gels. **b** shear modulus against p. **c** Stress-elongation curves normalized by the Young's modulus. The dashed line represents the prediction of the classical rubber theory

Figure 4a shows the Young's modulus of the tetra-PEG gels with $p = 0.68$–0.92. The variation in p from 0.92 to 0.68 resulted in tuning g_1/g_∞ from 1.0 to 0.05. This change occurred because the active chains are formed beyond the gelation threshold ($p \sim 0.4$ for the tetra-PEG gel) and the number of the

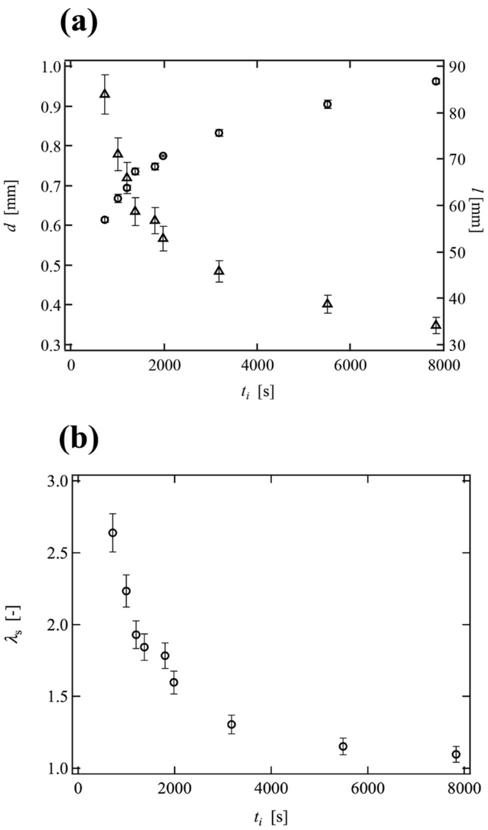


Fig. 5 **a** Diameter (circles) and length (triangles) of the samples **b** permanently set for the doubly crosslinked gels against t_i

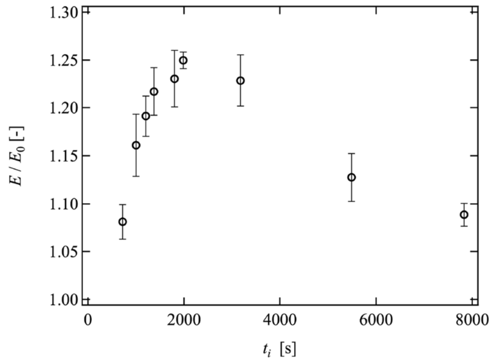


Fig. 6 Normalized Young's modulus for the doubly crosslinked gels against the stretching time (t_i)

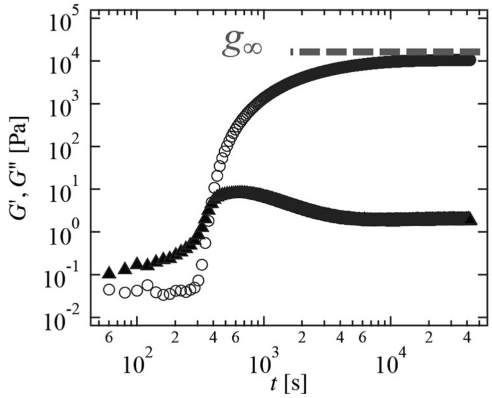


Fig. 7 Time development of the storage (G', circles) and loss (G'', triangles) moduli during the gelation reaction

active chains does not increase linearly with increasing p. The increasing rate is more rapid at the low p region than that at the high p region, which can be explained by the Bethe approximation written in ref. [44]. Figure 4b shows the stress-elongation curves normalized by E. The dashed line represents the prediction of the classical rubber theory. All the experimental curves overlap each other, suggesting that connectivity has a limited impact on the finite extensibility within the region of p examined. In other words, the connectivity (p) and the network strand length (N) are decoupled as reported previously [42]. In addition to this finding, the curves well agree with the prediction of the classical rubber theory in the region $\lambda < 2.5$. According to these experimental results, we conclude that the tetra-PEG gel system has a robust W function obeying the classical rubber theory.

Effect of time for imposition of the stretching on the gels during the gelation reaction

We prepared a series of doubly crosslinked networks using the tetra-PEG gel system ($l_0 = 1.0$ mm, $d_0 = 32$ mm, $\lambda_{\mathrm{i}} = 2.6$). Figure 5a shows the diameter (d) and length (l) for the doubly crosslinked gels against t_i. As t_i increased, d decreased, and l increased. Figure 5b shows the t_i-dependence of the residual strain (λ_s). λ_s decreased with increasing t_i and asymptotically approached unity from 2.6. Figure 6 shows the Young's modulus (E) for the doubly crosslinked gels against t_i. All the data were normalized by the modulus of the unstretched gel (E_0). The E/E_0 value increased with increasing t_i, reached a maximum value at $t_i = 1980$, and then decreased to unity. These results qualitatively corresponded to the prediction of the two-network theory.

To experimentally estimate the value of g_1/g_∞, we performed an oscillatory measurement during the gelation reaction for the network "at ease" and obtained the relationships between the storage modulus (G') and the reaction time, as shown in Fig. 7. Prior to the experiments, we had checked that g_1 and g_∞ corresponded to the value of the plateau modulus and had little frequency dependence. Figure 8 shows the relationships between λ_{s} and g_1/g_∞ with the prediction of Eq. 7 (dashed line). The two-network theory well reproduced the experimental results. Furthermore, the normalized Young's modulus was well reproduced by the prediction of Eq. 8 (Fig. 9). Based on these results, we confirmed the validity of the two-network theory in the case of the constant stretching ratio.

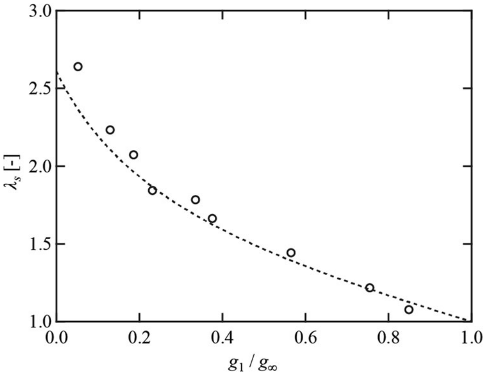


Fig. 8 Residual strain for the doubly crosslinked gels against the ratio of the first network component (g_1/g_∞)

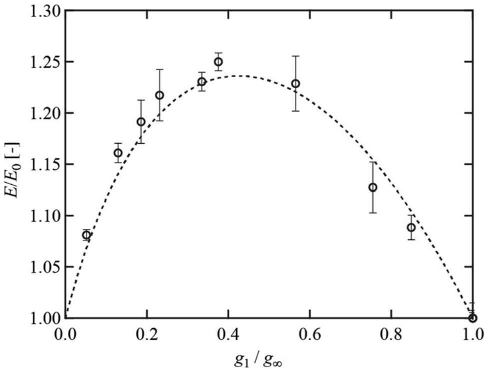


Fig. 9 Normalized Young's modulus for the doubly crosslinked gels against the ratio of the first network component (g_1/g_∞)

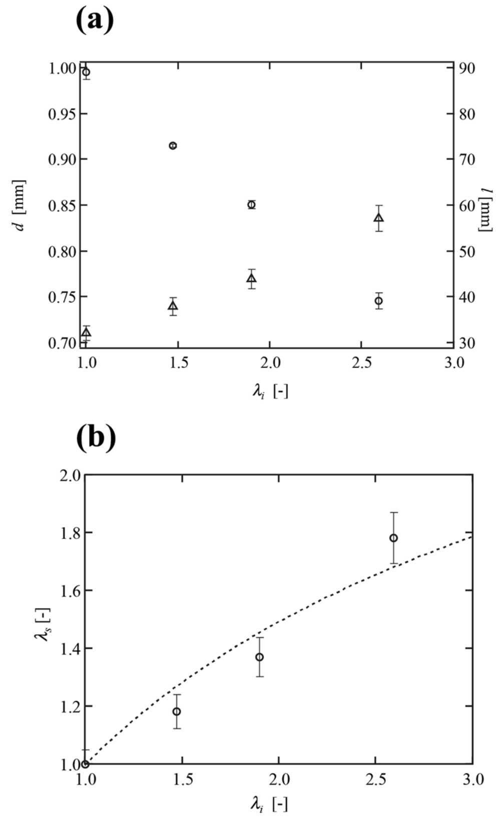


Fig. 10 **a** Diameter (circles) and length (triangles) of the samples and **b** residual strain for the doubly crosslinked gels against λ_i. The dashed line represents the prediction of Eq. 7

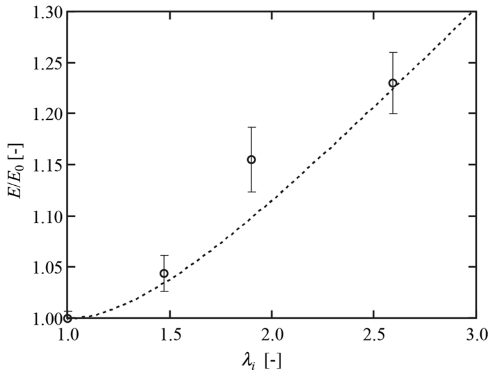


Fig. 11 Normalized Young's modulus for the doubly crosslinked gels against the stretching ratio (λ_i)

Effect of the stretching ratio

In the previous section, we changed the fraction of the first network by tuning t_i. Here, we changed the imposed stretching ratio (λ_i) with maintaining $t_i = 1800$ s, which resulted in tuning λ_i with a constant g_1/g_∞. As shown in Fig. 10a, d decreased, while l increased with increasing λ_i. As a result, λ_s monotonically increased with increasing λ_i (Fig. 10b). The prediction of Eq. 7 (dashed line) well reproduced the experiments as well. Good agreement was also observed for the normalized Young's modulus and prediction of Eq. 8 (Fig. 11). These results strongly suggest that the two-network theory is valid for the chemically crosslinking-dominant networks and that the simple sum rule of the strain energy density function is reasonable to describe the mechanical properties of anisotropic materials.

Conclusion

In this study, we fabricated doubly crosslinked networks using the tetra-PEG gel with near-ideal network structures. We investigated the Young's modulus and residual strain as a function of the time for the imposition of the stretching of the gels (t_i) and the stretching ratio (λ_i) during the gelation reaction. The results showed that (1) the residual strain decreased with increasing t_i; (2) the Young's modulus had a maximum value accompanied with t_i; and (3) the Young's modulus and the residual strain increased with increasing λ_i. These results are quantitatively reproduced in the framework of the two-network theory, which models the balance of strain energy between the first and second networks.

Based on these observations, we for the first time succeeded in quantitatively validating the two-network theory.

Acknowledgements This work was supported by the Japan Society for the Promotion of Science (JSPS) through the Grants-in-Aid for the Graduate Program for Leaders in Life Innovation (GPLLI), the International Core Research Center for Nanobio, the Core-to-Core Program A. Advanced Research Networks, the Grants-in-Aid for Young Scientists (A) Grant Number 23700555 (to TS), and Scientific Research (S) Grant Number 16746899 (to UC). This work was also supported by the Japan Science and Technology Agency (JST) through the Center of Innovation program (to UC) and the PREST (to TS).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Hikmet RAM, Lub J, Broer DJ. Anisotropic networks formed by photopolymerization of liquid-crystalline molecules. Adv Mater. 1991;3:392–4.
2. Kumpfer JR, Wie JJ, Swanson JP, Beyer FL, Mackay ME, Rowan SJ. Influence of metal ion and polymer core on the melt rheology of metallosupramolecular films. Macromolecules. 2012;45:473–80.
3. de Haan LT, Schenning APHJ, Broer DJ. Programmed morphing of liquid crystal networks. Polymer. 2014;55:5885–96.
4. Pei Z, Yang Y, Chen Q, Terentjev EM, Wei Y, Ji Y. Mouldable liquid-crystalline elastomer actuators with exchangeable covalent bonds. Nat Mater. 2013;13:36.
5. Xia Y, Yang P, Sun Y, Wu Y, Mayers B, Gates B, Yin Y, Kim F, Yan H. One-dimensional nanostructures: synthesis, characterization, and applications. Adv Mater. 2003;15:353–89.
6. Ruoff RS, Lorents DC. Mechanical and thermal properties of carbon nanotubes. Carbon. 1995;33:925–30.
7. Tobolsky AV, Takahashi Y, Naganuma S. Effect of additional crosslinking of continuous chemical stress relaxation of cis-polybutadiene. Polym J. 1972;3:60–&.
8. Andrews RD, Tobolsky AV, Hanson EE. The theory of permanent set at elevated temperatures in natural and synthetic rubber vulcanizates. J Appl Phys. 1946;17:352–61.
9. Berry JP, Scanlan J, Watson WF. Cross-link formation in stretched rubber networks. T Faraday Soc. 1956;52:1137–51.
10. Kaang S, Nah C. Fatigue crack growth of double-networked natural rubber. Polymer. 1998;39:2209–14.
11. Meng Y, Yang J-C, Lewis CL, Jiang J, Anthamatten M. Photoinscription of chain anisotropy into polymer networks. Macromolecules. 2016;49:9100–7.
12. Mott PH, Roland CM. Mechanical and optical behavior of double network rubbers. Macromolecules. 2000;33:4132–7.
13. Singh NK, Lesser AJ. A physical and mechanical study of prestressed competitive double network thermoplastic elastomers. Macromolecules. 2011;44:1480–90.
14. Wang J, Hamed GR, Umetsu K, Roland CM. The Payne effect in double network elastomers. Rubber Chem Technol. 2005;78:76–83.
15. Flory PJ. Elasticity of polymer networks cross-linked in states of strain. T Faraday Soc. 1960;56:722–43.
16. Fricker HS. The effects on rubber elasticity of the addition and scission of cross-links under strain. Proc R Soc Lond Ser A. 1973;335:267–87.
17. Shibayama M, Takata S, Norisuye T. Static inhomogeneities and dynamic fluctuations of temperature sensitive polymer gels. Phys A. 1998;249:245–52.
18. Allen G, Kirkham MJ, Padget J, Price C. Thermodynamics of rubber elasticity at constant volume. Trans Faraday Soc. 1971;67:1278–92.
19. Candau S, Peters A, Herz J. Experimental-evidence for trapped chain entanglements—their influence on macroscopic behavior of networks. Polymer. 1981;22:1504–10.
20. Flory, PJ. *Principles of polymer chemistry*. (Cornell University Press, Ithaca, 1953).
21. Wall FT. Statistical thermodynamics of rubber II. J Chem Phys. 1942;10:485–8.
22. Kawamura T, Urayama K, Kohjiya S. Multiaxial deformations of end-linked poly(dimethylsiloxane) networks 5. Revisit to Mooney-Rivlin approach to strain energy density function. Nihon Reoroji Gakkaishi. 2003;31:213–7.
23. Kawamura T, Urayama K, Kohjiya S. Multiaxial deformations of end-linked poly (dimethylsiloxane) networks. III. Effect of entanglement density on strain-energy density function. J Polym Sci Pol Phys. 2002;40:2780–90.
24. Kawamura T, Urayama K, Kohjiya S. Structure and mechanical properties of bimodal pdms networks in the swollen state. J Soc Mater Sci Jpn. 1998;47:113–6.
25. Kawamura T, Urayama K, Kohjiya S. Multiaxial deformations of end-linked poly(dimethylsiloxane) networks. 1. Phenomenological approach to strain energy density function. Macromolecules. 2001;34:8252–60.
26. Urayama K, Kawamura T, Kohjiya S. Multiaxial deformations of end-linked poly(dimethylsiloxane) networks. 2. Experimental tests of molecular entanglement models of rubber elasticity. Macromolecules. 2001;34:8261–9.
27. Urayama K, Kawamura T, Kohjiya S. Structure-mechanical property correlations of model siloxane elastomers with controlled network topology. Polymer. 2009;50:347–56.
28. Urayama K, Kawamura T, Kohjiya S. Multiaxial deformations of end-linked poly(dimethylsiloxane) networks. 4. Further assessment of the slip-link model for chain-entanglement effect on rubber elasticity. J Chem Phys. 2003;118:5658–64.
29. Rubinstein M, Panyukov S. Elasticity of polymer networks. Macromolecules. 2002;35:6670–86.
30. Everaers R. Constrained fluctuation theories of rubber elasticity: general results and an exactly solvable model. Eur Phys J B. 1998;4:341–50.
31. Rottach DR, Curro JG, Grest GS, Thompson AP. Effect of strain history on stress and permanent set in cross-linking networks: aA molecular dynamics study. Macromolecules. 2004;37:5468–73.
32. Rottach DR, Curro JG, Budzien J, Grest GS, Svaneborg C, Everaers R. Molecular dynamics simulations of polymer networks undergoing sequential cross-linking and scission reactions. Macromolecules. 2007;40:131–9.
33. Sakai T, Matsunaga T, Yamamoto Y, Ito C, Yoshida R, Suzuki S, Sasaki N, Shibayama M, Chung UI. Design and fabrication of a high-strength hydrogel with ideally homogeneous network structure from tetrahedron-like macromonomers. Macromolecules. 2008;41:5379–84.
34. Sakai T. Gelation mechanism and mechanical properties of Tetra-PEG gel. React Funct Polym. 2013;73:898–903.
35. Sakai T. Experimental verification of homogeneity in polymer gels. Polym J. 2014;46:517–23.

36. Matsunaga T, Sakai T, Akagi Y, Chung U, Shibayama M. Structure characterization of tetra-PEG gel by small-angle neutron scattering. Macromolecules. 2009;42:1344–51.
37. Akagi Y, Katashima T, Katsumoto Y, Fujii K, Matsunaga T, Chung U, Shibayama M, Sakai T. Examination of the theories of rubber elasticity using an ideal polymer network. Macromolecules. 2011;44:5817–21.
38. Akagi Y, Gong JP, Chung U-I, Sakai T. Transition between phantom and affine network model observed in polymer gels with controlled network structure. Macromolecules. 2013;46:1035–40.
39. Nishi K, Fujii K, Chijiishi M, Katsumoto Y, Chung U, Sakai T, Shibayama M. Kinetic study for AB-type coupling reaction of tetra-arm polymers. Macromolecules. 2012;45:1031–6.
40. Lange F, Schwenke K, Kurakazu M, Akagi Y, Chung UI, Lane M, Sommer JU, Sakai T, Saalwachter K. Connectivity and structural defects in model hydrogels: a combined proton NMR and Monte Carlo simulation Study.Macromolecules. 2011;44: 9666–74.
41. Katashima T, Urayama K, Chung U-I, Sakai T. Probing the cross-effect of strains in non-linear elasticity of nearly regular polymer networks by pure shear deformation. J Chem Phys. 2015;142: 174908.
42. Akagi Y, Katashima T, Sakurai H, Chung U-I, Sakai T. Ultimate elongation of polymer gels with controlled network structure. RSC Adv. 2013;3:13251–8.
43. Flory PJ, Rehner J. Statistical mechanics of cross-linked polymer networks I Rubberlike elasticity. J Chem Phys. 1943;11:512–20.
44. Akagi Y, Matsunaga T, Shibayama M, Chung U, Sakai T. Evaluation of topological defects in Tetra-PEG gels. Macromolecules. 2010;43:488–93.