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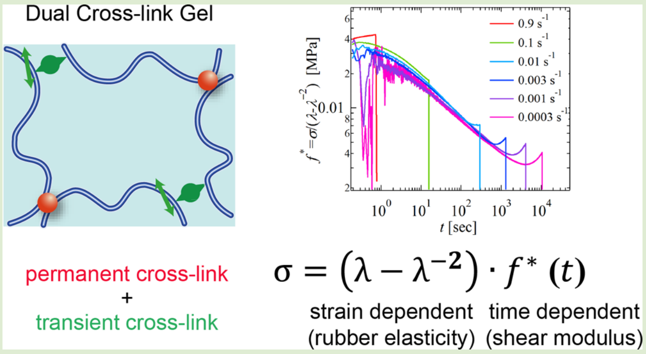
Stress–Strain Relationship of Highly Stretchable Dual Cross-Link Gels: Separability of Strain and Time Effect

Koichi Mayumi, Alba Marcellan, Guylaine Ducouret, Costantino Creton, and Tetsuharu Narita*

Laboratoire SIMM-PPMD, UMR7615, ESPCI ParisTech – UPMC - CNRS, 10 Rue Vauquelin, 75231 Paris, Cedex 05, France

Supporting Information

ABSTRACT: We studied the stress–strain relation of model dual cross-link gels having permanent cross-links and transient cross-links over an unusually wide range of extension ratios λ and strain rates $\dot{\epsilon}$ (or time $t = (\lambda - 1)/\dot{\epsilon}$). We propose a new analysis method and separate the stress into strain- and time-dependent terms. The strain-dependent term is derived from rubber elasticity, while the time-dependent term is due to the failure of transient cross-links and can be represented as a time-dependent shear modulus which shows the same relaxation as in small strain. The separability is applicable except for the strain stiffening regimes resulting from the finite extensibility of polymer chains. This new analysis method should have a wide applicability not only for hydrogels but also for other highly viscoelastic soft solids such as soft adhesives or living tissues.



Hydrogels, i.e., cross-linked polymer networks swollen with water, can be interesting biomaterials for applications such as artificial cartilage, vessels, and prosthetic joints due to their high water content and biocompatibility.[1] Conventional chemical gels, polymer gels cross-linked by covalent bonds, have a low fracture toughness and extensibility, which has limited their biomedical applications. In the past decade, recent developments to finely control the polymer network structure have led to significant improvements in the mechanical strength of hydrogels.[2−14] One of the most successful strategies to toughen hydrogels is to introduce two kinds of cross-links into the polymer network: permanent (strong) and transient (weak) cross-links (Figure 1).[6−14] When these doubly cross-linked gels are deformed, the transient bonds break and dissipate strain energy. The presence of these breakable transient bonds also unloads the main covalent bonds and delays macroscopic rupture. Both these effects contribute to an increase in fracture toughness. Furthermore, during cycling loading, the gels can recover their initial state owing to the elasticity given by the permanent cross-links.

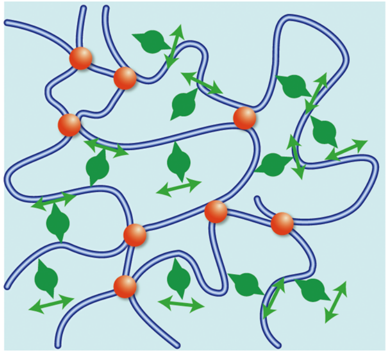


Figure 1. Schematic view of doubly cross-linked gels having permanent crosslinks (circle) and transient crosslinks (circle with stickers).

Since the time-dependent behavior of the doubly cross-linked gels originates from molecular-level breakage of weak bonds, it should depend markedly on both applied strain and strain rate. For highly stretchable doubly cross-linked gels, it is important therefore to investigate the dissipation behavior over a wide range of strains (including the nonlinear regime) and strain rates (above and below the association/dissociation rate of transient cross-links). Although many efforts have been made to create novel types of doubly cross-linked gels with high toughness, there are a few quantitative and systematic studies on the strain and strain rate dependence of the dissipation mechanisms of doubly cross-linked gels. One reason comes from the difficulties in characterizing the mechanical properties of hydrogels compared to elastomers without solvent. Hydrogels can change volume by drying in air and can swell/deswell in response to applied strain in water.[15] The strain rate dependence of the large strain properties of doubly cross-linked gels has only been reported for silica hybrid gels.[7,8] For that system, energy dissipation in large strain is dominated by transient and reversible association between silica particles and polymers and strongly depends on strain rate. However, the

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silica hybrid gels have a complex structure and dynamics resulting in a wide range of relaxation times. This complex dynamics of transient cross-links made it difficult to directly and quantitatively relate molecular dynamics to mechanical properties.

To understand the dissipation mechanism of doubly cross-linked gels, we have developed a model doubly cross-linked gel having a simple chemical structure and only one type of physical interaction between polymer chains. In a previous paper, we have reported the dynamic properties of poly(vinyl alcohol) (PVA) hydrogels cross-linked by covalent (chemical) bonds and transient (physical) bonds between PVA chains and borate ions.[16] The linear viscoelastic properties of this PVA "dual cross-link gel" have been investigated by microrheology based on diffusing-wave spectroscopy (DWS). DWS experiments have indicated that the PVA dual cross-link gels show a typical relaxation time corresponding to the dissociation dynamics of PVA with borate ions. In a range of time scales longer than the characteristic time where the physical cross-links break, we observed an "associative Rouse mode", a slow segmental Rouse mode combined with an intermolecular association/dissociation process, which has been predicted by a linear viscoelastic theory for associating polymers.[17]

In this letter, we report the large strain mechanical properties of highly deformable PVA dual cross-link gels over 4 orders of magnitude of strain rates. We propose a novel method to analyze the large deformation behavior and a simple equation to describe their stress−strain curves. First, we performed shear measurements at a fixed small strain to measure precisely the frequency (strain rate) dependent shear moduli in the linear regime. Second, we conducted uniaxial elongation tests to study the large deformation nonlinear regime at various strain rates. We will show that the nonlinear stress−strain relation of the model dual cross-link gels can be described by strain- and time-dependent terms.

The dual cross-link gels were synthesized by immersing chemically cross-linked poly(vinyl alcohol) (PVA) gels into borax/NaCl aqueous solutions.[16] Details of sample preparation are described in the Supporting Information. We prepared pure chemical gels cross-linked by gultaraldehyde (GA) and dual cross-link gels which have the same chemical cross-linking density and PVA concentration as the pure chemical gels. The PVA concentration was 12 wt %, and the GA concentration in feed was 5.5 mmol/L, corresponding to the molar ratio of GA to monomer units of PVA of 0.002. The borax and NaCl concentrations of the aqueous solutions were 1 and 90 mM, respectively.

The linear viscoelastic properties of the hydrogels were studied by oscillatory shear measurements (see Supporting Information for experimental details). Figure 2(a) shows the frequency dependence of the elastic and viscous moduli, G' and G'', for the pure chemical and dual cross-link gel. The chemical gel exhibits an elastic solid behavior: its elastic modulus G'_C is independent of frequency and much larger than the viscous modulus G''_C. On the other hand, the dual cross-link gel has a much larger viscous modulus showing a peak at $\omega_0 = 0.6$ rad/s. This characteristic frequency corresponds to the dissociation dynamics of physical cross-links in the dual cross-link gel and gives a characteristic relaxation time $\tau_X = 1/0.6 = 1.7$ s.

The elastic modulus of the dual cross-link gel G' can be separated into two contributions resulting from chemical and physical bonds. The contributions of chemical cross-links are given by the moduli of the pure chemical gel G'_C since the chemical and dual cross-link gels have the same chemical crosslinking density. We can estimate the modulus due to the physical bonds G'_P by subtracting the modulus of the chemical cross-links from the total modulus: $G'_P = G' - G'_C$.[16] The frequency dependence of G'_P is shown in Figure 2(b). At frequencies lower than $\omega_0 = 0.6$ rad/s, where physical bonds break to relax stress, the elastic modulus G'_P follows a power-law $G'_P \sim \omega^{0.5}$. As we reported in a previous paper, this frequency dependence is in good agreement with the theoretical prediction of the associative Rouse mode.[16] Indei and Takimoto have suggested that entangled associating polymers with many stickers show a segmental Rouse dynamics retarded by the association of the stickers at longer time scales than the sticker dissociation time τ_X.[17]

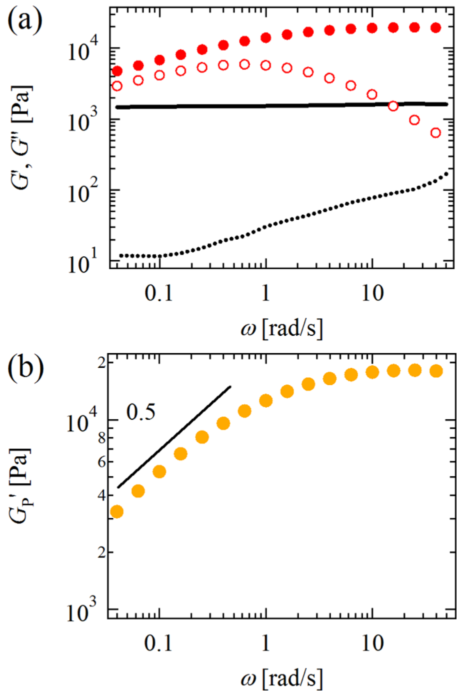

Figure 2. (a) Angular frequency dependence of G' and G'' of the PVA chemical (G': solid line, G'': dotted line) and dual cross-link gel (G': closed circle, G'': open circle). (b) Angular frequency dependence of shear moduli G'_P corresponding to the physical bonds.

We then performed uniaxial stretching experiments to characterize the nonlinear (large strain) behavior of the dual cross-linked gels (see Supporting Information for experimental details). Tensile stress−strain curves (nominal stress vs nominal λ) for the chemical and dual cross-link gels at different initial strain rates are summarized in Figure 3(a). To carry out the tensile tests at strain rates as low as 0.0001 s^{-1} without drying, we tested the gel samples immerged in paraffin oil. The pure chemical gels were quite soft and brittle: they fractured at a value of λ and nominal stress of 2.2 and 7 kPa, respectively. The large strain properties of the dual cross-link gels dramatically change with strain rate. At initial strain rates higher than 0.3 s^{-1}, the dual cross-link gels are fragile because the initial strain rate is too high for physical cross-links to break and reform and hence relax the high stresses at the crack tip. The enhancement in mechanical strength of the dual cross-link gels is only observed at initial strain rates below 0.1 s^{-1}. At lower initial strain rates, the physical bonds in the dual cross-link gels dissociate and reform under deformation entailing a large

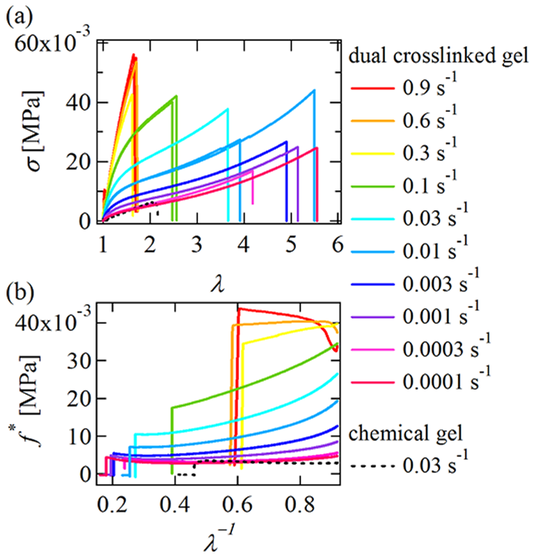

Figure 3. (a) Stress−strain curves for the dual cross-link gels at various initial strain rates. For the comparison, the curve for the chemical gels at an initial strain rate of 0.03 s^{-1} (dashed line) is also shown. (b) Reduced stress f^* as a function of λ^{-1} for the dual cross-link gels at various initial strain rates and the chemical gels at an initial strain rate of 0.03 s^{-1} (dashed line).

energy dissipation, which increases dramatically the fracture stress and strain up to 40 kPa and $\lambda = 5.5$.

The common features of the stress−strain curves can be better visualized by using the reduced stress defined as[7,18,19]

$$f^* = \frac{\sigma}{\lambda - \lambda^{-2}} \tag{1}$$

The reduced stress of an ideal network of Gaussian chains between fixed cross-links is simply its shear modulus and is independent of λ.[19] The reduced stresses of our gels are plotted as a function of $1/\lambda$ in Figure 3(b). As we expected, the reduced stress of the chemical gels at an initial strain rate of 0.03 s^{-1} is almost independent of $1/\lambda$, indicating that, in the absence of physical bonds, there is also little effect of polymer entanglements and their uniaxial deformation is well described by the rubber elasticity model. In the case of the dual cross-link gels, at a high strain rate (0.6 s^{-1}), physical bonds do not rupture, and so the reduced stress is almost constant like for chemical gels. At even higher strain rate (0.9 s^{-1}), the reduced stress increases with strain even at small strains. The strain stiffening may be attributed to the finite extensibility of polymer networks with a higher cross-linking density rather than the pure chemical gels: physical cross-links behave like permanent cross-links at short times, and the physical cross-linking density is about ten times larger than the chemical cross-linking density according to the elastic modulus shown in Figure 2(a). At lower strain rates, the dual cross-link gels show a concave-up curve in Figure 3(b). The reduced stress decreases with strain because of the progressive breakage of physical bonds and then increases due to the finite extensibility of chemically cross-linked networks.

The relaxation process of the reduced stress f^* is governed by two factors: extension ratio λ and time t (or strain rate $\dot{\varepsilon}$). Figure 4(a) shows the dependence of the reduced stress f^* on time t (= $(\lambda - 1)/\dot{\varepsilon}$). Surprisingly, all the curves overlap except for the strain stiffening regimes where the reduced stress increased rapidly with time. As far as we know, it is the first time that a master curve based on reduced stress has been derived directly from stress−strain curves. The deviation from the master curve in a longer time regime comes from the strain stiffening due to the finite extensibility of polymer chains which clearly depends mainly on λ. The reduced stress f^* at shorter times is independent of extension ratio λ and depends only on time t. It can be seen as a time-dependent elastic shear modulus $f^*(t)$ during uniaxial stretching. In the absence of entanglements between cross-links, $f^*(t)$ is proportional to the density of active elastic chains $\upsilon(t)$ at a time $t = (\lambda - 1)/\dot{\varepsilon}$: $f^*(t) \sim \upsilon(t) k_B T$.[19] As the physical cross-links of the dual cross-link gels rupture during deformation, $f^*(t)$ (and $\upsilon(t)$) decreases. The decrease of $f^*(t)$ (and $\upsilon(t)$) is dominated only by time t and independent of strain, which indicates that strain has no effect on the breakage rate of the physical cross-links for the dual cross-link gels.

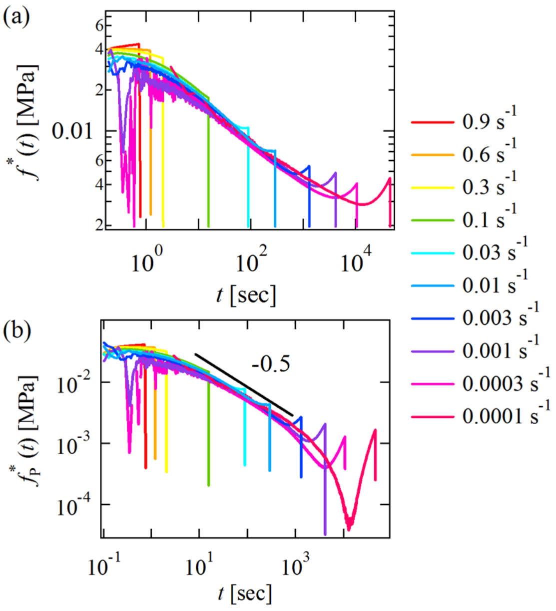

Figure 4. (a) Time dependence of the shear modulus f^* under uniaxial deformation for the dual cross-link gels at various initial strain rates. (b) Time dependence of the shear modulus f^*_P under uniaxial deformation for the physical networks in the dual cross-link gels at various initial strain rates.

The strain independence of f^* suggests the separability of strain- and time-dependent terms of the nominal stress $\sigma(\lambda, t)$.

$$\sigma(\lambda, t) = (\lambda - \lambda^{-2}) f^*(t) \tag{2}$$

The time-dependent shear modulus $f^*(t)$ is a sum of the contributions of chemical cross-links f^*_C (= the time-independent shear modulus of chemically cross-linked network) and physical bonds $f^*_P(t)$. Figure 4(b) shows the shear modulus of physical networks f^*_P (= $f^* - f^*_C$) as a function of time t. At times from 10 s to the onset of the strain stiffening, f^*_P scales with $t^{-0.5}$ in the same manner as the storage component of the linear viscoelastic shear modulus $G'_P \sim \omega^{0.5}$. This suggests that the nonlinear viscoelastic relaxation originates from the same associative Rouse mode as that of the linear viscoelastic relaxation. In the intermediate time regime, the time dependence of $f^*(t)$ and eq 2 results in a simple equation to describe the stress−strain relation of the dual cross-link gels

$$\sigma(\lambda, t) = (\lambda - \lambda^{-2})(a \cdot t^{-0.5} + f^*_C) \tag{3}$$

where a is a prefactor of the time-dependent shear modulus $f_P^*(t)$. The λ-dependent term in eq 3 is derived from the rubber elasticity theory. The time-dependent term is the sum of the shear modulus of chemically cross-linked networks f_C^* and the relaxation modulus of the associative Rouse mode. Equation 3 reproduces well the stress−strain relations of the dual cross-link gels from 0.01 to 0.001 s^{-1} where the energy dissipation of physical bonds enhances efficiently the mechanical toughness as shown in the Supporting Information.

We now discuss the separability of stress into strain- and time-dependent terms. For uncross-linked entangled polymer solutions without strong physical association between polymer chains, the separability has been observed at times longer than 4.5 times the configurational relaxation time and explained theoretically by the reptation model.[20] However, in the case of associating polymer solutions, the validity of this separability is not obvious. Séréro et al. have studied linear and nonlinear stress relaxation of end-functionalized telechelic polymer solutions and reported that chain stretching enhances dissociation of physical bonds and decreases the relaxation time corresponding to the rupture of the physical network bonds.[21] This suggests that the stress of associating polymer networks cannot be separated into strain and time terms. As shown above, our dual cross-link gels demonstrate the separability of stress, which simplifies greatly the stress−strain relation. This is the first work to show this separability for the associating polymer network showing associative Rouse dynamics. The coupling between strain and relaxation time depends on the type of physical cross-linking. In our dual cross-link gels, physical cross-links are not linked covalently to polymer chains and can move freely inside the gels, while the end-functional groups of telechelic polymers are covalently connected to polymer chains. The borate ions can bind to any site on the polymer chains and have negative charges. Because of the electrostatic repulsive interaction between the ionic cross-linkers, when we deform the dual cross-link gels, the physical cross-links move quickly and reach a homogeneous spatial distribution which is not affected by applied strain.

In conclusion, we have shown that the time-dependent stress−strain relation $\sigma(\lambda, t)$ of the highly deformable dual cross-link gels with a well-defined relaxation time can be represented by a simple equation composed of strain- and time-dependent terms except for quite large strains at which strain stiffening occurs due to the finite extensibility of polymer chains. The physical meaning of each term is clear: the strain-dependent term is $\lambda - \lambda^{-2}$ predicted by the classical rubber elasticity theory, and the time-dependent term is the shear modulus $f^*(t)$ which shows the same relaxation behavior as the storage component of the shear modulus in the linear regime. This simple method to analyze the stress−strain relation of the dual cross-link gels by separating strain and strain rate dependent terms and building a master curve of reduced stress vs time gives us the strain- and time-dependent terms at the same time from one set of experimental data, while conventional stress relaxation tests focus only on time dependence and miss the strain-dependent term. It is useful to understand the mechanical properties of many polymer systems including elastomers and other high strength polymer gels which are at the same time nonlinear elastic and viscoelastic.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details (sample preparation, shear measurements and uniaxial tensile tests) and reproduction of stress strain curves by eq 3. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tetsuharu.narita@espci.fr.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Lee, K. Y.; Mooney, D. J. *Chem. Rev.* **2001**, *101*, 1869−1879.

(2) Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 485−487.

(3) Haraguchi, K.; Takehisa, T. *Adv. Mater.* **2002**, *14*, 1120−1124.

(4) Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y. *Adv. Mater.* **2003**, *15*, 1155−1158.

(5) Sakai, T.; Matsunaga, T.; Yamamoto, Y.; Ito, C.; Yoshida, R.; Suzuki, S.; Sasaki, N.; Shibayama, M.; Chung, U. *Macromolecules* **2008**, *41*, 5379−5384.

(6) Lin, W. C.; Fan, W.; Marcellan, A.; Hourdet, D.; Creton, C. *Macromolecules* **2010**, *43*, 2554−2563.

(7) Carlsson, L.; Rose, S.; Hourdet, D.; Marcellan, A. *Soft Matter* **2010**, *6*, 3619−3631.

(8) Rose, S.; Dizeux, A.; Narita, T.; Hourdet, D.; Marcellan, A. *Macromolecules* **2013**, *46*, 4095−4104.

(9) Henderson, K. J.; Zhou, T. C.; Otim, K. J.; Shull, K. R. *Macromolecules* **2010**, *43*, 6193−6201.

(10) Tuncaboylu, D. C.; Sari, M.; Oppermann, W.; Okay, O. *Macromolecules* **2011**, *44*, 4997−5005.

(11) Haque, M. A.; Kurokawa, T.; Kamita, G.; Gong, J. P. *Macromolecules* **2011**, *44*, 8916−8924.

(12) Sun, J. Y.; Zhao, X.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. *Nature* **2012**, *489*, 133−136.

(13) Bakarich, S. E.; Pidcock, G. C.; Balding, P.; Stevens, L.; Calvert, P.; In het Panhuis, M. *Soft Matter* **2012**, *8*, 9985−9988.

(14) Harrass, K.; Krüger, R.; Möller, M.; Albrecht, K.; Groll, J. *Soft Matter* **2013**, *9*, 2869−2877.

(15) Urayama, K.; Takigawa, T. *Soft Matter* **2012**, *8*, 8017−8029.

(16) Narita, T.; Mayumi, K.; Ducouret, G.; Hébraud, P. *Macromolecules* **2013**, *46*, 4174−4183.

(17) Indei, T.; Takimoto, J. *J. Chem. Phys.* **2010**, *133*, 194902.

(18) Bellamine, A.; Degrandi, E.; Gerst, M.; Stark, R.; Beyers, C.; Creton, C. *Macromol. Mater. Eng.* **2011**, *296*, 31−41.

(19) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press: Oxford, 2003.

(20) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986.

(21) Séréro, Y.; Jacobsen, V.; Berret, J. F.; May, R. *Macromolecules* **2000**, *33*, 1841−1847.