

Contents lists available at ScienceDirect

Extreme Mechanics Letters



journal homepage: www.elsevier.com/locate/eml

Constitutive modeling of bond breaking and healing kinetics of physical Polyampholyte (PA) gel



Sairam Pamulaparthi Venkata^{a,1}, Kunpeng Cui^{b,1}, Jingyi Guo^a, Alan T. Zehnder^a, Jian Ping Gong^{b,c,d}, Chung-Yuen Hui^{a,c,*}

^a Field of Theoretical and Applied Mechanics, Department of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY, 14853, United States

^b Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo 001-0021, Japan

^c Soft Matter GI-CoRE, Hokkaido University, Sapporo 001-0021, Japan

^d Faculty of Advanced Life Science, Hokkaido University, Sapporo 001-0021, Japan

ARTICLE INFO

Article history: Received 15 November 2020 Received in revised form 14 January 2021 Accepted 14 January 2021 Available online 26 January 2021

Keywords: Self-healing Hydrogel Large deformation Nonlinear viscoelasticity

ABSTRACT

A three-dimensional finite strain nonlinear viscoelastic model is developed to study the mechanical behavior of a physically cross-linked Polyampholyte (PA) gel. The time dependent behavior of this gel is due to the ionic interactions of oppositely charged monomers randomly distributed along the chain backbone. In this work, we divide the physical cross-links broadly into weak and strong bonds, depending on their survival and reformation characteristics. Our constitutive model connects the strain dependent bond breaking and reforming kinetics in the microscopic regime to the deformation of the gel at the continuum level. We compare the predictions of our model with uniaxial tension, tensile-relaxation, cyclic, and small strain torsional relaxation tests. The material parameters in our model are obtained using least squares optimization. Our theory agrees well with the experimental behavior of the gel.

© 2021 Elsevier Ltd. All rights reserved.

1. Introduction

A hydrogel is a three-dimensional network of cross-linked hydrophilic polymer chains swollen in water. The large water content allows hydrogels to be biocompatible. For example, hydrogels are used as scaffolding materials in tissue engineering [1–3] and as self-regulatory vehicles in drug delivery systems [4,5]. Polyelectrolyte hydrogels have been explored as a replacement to artificial muscles, cornea, and cartilage [6,7]. For hydrogels to be substitutes for load-bearing structural biomaterials, properties such as mechanical strength, stiffness, resistance to wear, shock-absorption, high toughness, and self-healing properties are desired. Traditional hydrogels are too brittle and are not ideal candidates for bio-structural materials. The synthesis of double network (DN) hydrogels has shown promising results for development of highly extensible gels with high fracture toughness property.

Double network hydrogels consist of two interpenetrating networks of brittle and ductile polymers. The first network is densely

E-mail address: ch45@cornell.edu (C.-Y. Hui).

https://doi.org/10.1016/j.eml.2021.101184 2352-4316/© 2021 Elsevier Ltd. All rights reserved. cross-linked, easily breakable, and is brittle in nature, while the second network is loosely cross-linked, highly extensible, and is ductile in nature [8-11]. When the DN hydrogel is subjected to mechanical loading, the first network carries most of the load and undergoes internal fracture, acting as a sacrificial network. The second network, being highly extensible, prevents the formation and propagation of macroscopic cracks and a sudden failure of the gel under mechanical loading. Due to the continuous damage of the first network under loading, energy is effectively dissipated, and the toughness of the material is improved [12-15]. In DN hydrogels with only covalent type of bonds, the rupture of the first network is permanent which lowers fatigue resistance. To address this limitation, the chemical bonds in the sacrificial network can be replaced with physical bonds which can break and re-attach [16–18]. These reversible physical bonds help the gel to recover partially or fully, depending on the resting period [19,20]. As a result, the gel can maintain its fatigue resistance, high extensibility, and toughness for cyclic tests. Due to the breaking and healing kinetics of reversible bonds, the mechanical properties of these gels are time dependent, and the gel behaves like a viscoelastic material [21].

Many researchers have been successful in synthesizing tough self-healing hydrogels, but the quantitative understanding of bond breaking and healing kinetics of these viscoelastic gels is still in progress [22–31]. In our previous works, we developed

^{*} Corresponding author at: Field of Theoretical and Applied Mechanics, Department of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY, 14853, United States.

¹ These authors contributed equally to this work.

constitutive models to study time-dependent mechanical behavior of a dual cross-linked polyvinyl alcohol (PVA) gel, where PVA chains form physical cross-links with borax ions and chemical cross-links with glutaraldehyde ions [32–34]. The PVA gel has simpler bond kinetics as the chemical bonds do not break under mechanical loading and the kinetics of physical bonds are not dependent on the applied strain. Therefore, understanding the microscopic interactions of bond kinetics of PVA gel through macroscopic mechanical models help us in dealing with more complex gels, where the kinetics of temporary bonds are time, rate, and strain dependent.

In most polymeric materials, the dissociation and association of physical bonds is dependent on the strain/stress experienced by the bonds [35–38]. The rate of dissociation is expected to be high when the force acting on these bonds or the stretch is high. In this paper, we study the strain-dependent bond breaking and healing kinetics of a physically cross-linked polyampholyte (PA) gel synthesized by Gong's group [39]. We develop a finite strain constitutive model to quantitatively understand the bond kinetics of the PA gel.

The purely physical PA gel is synthesized by random copolymerization of oppositely charged ionic monomers. In each polymer chain, the positive and negative charged monomers are randomly distributed along the chain backbone. PA gel has a phase-separated structure composed of soft and stiff phases, with a structure length of ~ 100 nm [40–43]. The soft and stiff phases differ in polymer densities, where the soft phase has a low polymer density, and the stiff phase has a high polymer density. As the ionic interactions depend on polymer density [39], the ionic bonds can be divided into two types: strong bonds and weak bonds. These bonds serve as sacrificial structure and enhance the fatigue [44] and fracture resistance, self-healing behavior [45], and shock absorbance of PA gel. We adopt a similar principle to DN gels, using rupture of sacrificial bonds to dissipate energy and enhance the toughness of the overall material.

The PA gels have 50–70 wt% of water content at an equilibrium state, much less than that of conventional hydrogels (> 80 wt. %). These gels are strongly viscoelastic (due to dynamics of physical bonds), have high toughness (fracture energy of 4000 J m⁻²), and can recover completely. These gels show yielding-like behavior at a critical strain [39], which suggests that the kinetics of physical bonds are sensitive to strain. The wide range of mechanical properties, high toughness, and the healing behavior motivates us to study the behavior of PA gel, as the gel exhibits promising properties that can be utilized in real world applications. For example, these PA gels show adjustable adhesion to charged surfaces in water [46], and dramatically improve the toughness of glass-fiber-reinforced soft composites when used as a matrix [47].

This paper is organized as follows. In Section 2, we describe our constitutive model for purely physically cross-linked PA gel and state the assumptions considered in our model. The straindependent bond breaking function and the survivability function are introduced. The strain energy density function of undamaged network and total strain energy density of the gel are mentioned. Finally, a nominal stress-strain relationship which depends on the history of loading is presented for different types of mechanical tests. In Section 3, an experimental procedure for the synthesis and mechanical tests of our PA gel is laid out. In Section 4, we estimate few material parameters from experiments. In Section 5, a least squares optimization method is proposed to capture all the material parameters involved in our constitutive model. During this optimization process, multiple data sets of material parameters are obtained. We select one data set of material parameters based on physical intuition and the estimates computed in Section 4. In Section 6, we present the results and discuss the accuracy of our model for different types of loading histories using the data set of material parameters chosen in Section 5. We observe that our model captures the mechanical behavior of physically cross-linked PA gel reasonably well. Conclusions are in Section 7.

2. Theoretical model

We state the basic assumptions of our theory here, many of which are similar to those in our previous PVA gel work [33,34] and in Guo [48]. For the sake of clarity, these assumptions are restated here.

2.1. Assumptions

- 1. The polymer network consists of chains connected by physical bonds.
- 2. In reality, physical bonds have a distribution of interaction strengths, and bond breaking/reforming kinetics. For simplicity, we categorize these interactions into two groups of bonds: weak and strong bonds.
- 3. Both weak and strong bonds can break and reattach according to breaking and healing kinetics. The breaking kinetics are specified by two survivability functions ϕ_{B_i} (i = 1 refer to weak bonds, i = 2 refer to strong bonds), where ϕ_{B_i} is the fraction of bonds that survived from the time of their birth, τ to the current time, t.
- 4. We assume that the stress sustained by a chain is instantaneously relaxed when it breaks, and immediately after a chain is reattached, it is in a relaxed state and carries no strain energy. The deformation of a chain reconnected at time τ can be described by the deformation gradient tensor $\mathbf{F}^{\tau \to t}$. The superscript $\tau \to t$ indicates that the chain experiences the deformation history from its birth (reattachment) at time τ to the current time *t*. The special case of $\tau = 0$ applies to the chains that are connected before mechanical loading. We assume that before loading, the gel has been rested sufficiently long that the physical bonds achieve dynamic equilibrium. Dynamic equilibrium results in a constant molar fraction of connected and broken temporary chains and a constant reforming rate which is equal to the breaking rate.
- 5. The healing kinetics for weak and strong bonds are specified by the reattachment rates χ_i (i = 1, 2) which *represents* the fraction of weak/strong bonds reattached per unit time per unit reference volume. Physically, the healing rate must increase with the number of broken bonds. Here we use the simplest assumption that healing rate is directly proportional to the number of broken bonds divided by a characteristic healing time. This is a reasonable assumption since healing is achieved by the bonding of opposite charges to the number of available sites, so the reaction rate should be proportional to the number of broken bonds. The reforming rate $\chi_i(t)$ is assumed to be proportional to the number of broken or unconnected bonds $N_{h_i}(t)$ per unit reference volume. Specifically, let $\hat{\chi}_i(t) = \chi_i(t)N_0$ be the number of weak/strong bonds reattached per unit time per unit reference volume, where N_0 is the total number of physical bonds per unit reference volume, then

$$\hat{\chi}_i(t) = N_{b_i}(t)/t_{H_i}, \text{ or } \chi_i(t) = \frac{1}{t_{H_i}} \frac{N_{b_i}(t)}{N_0},$$
 (1)

where t_{H_i} is the characteristic healing time of *i*th type of physical bonds. Here, we simplify notation by writing χ_i as a function of time *t* only, whereas it also depends on the entire loading history.

- 6. We assume strong and weak bonds break and heal independently. Specifically, breaking and healing kinetics are completely specified by ϕ_{B_i} , χ_i .
- 7. In the continuum scale, the gel is incompressible and isotropic. Since chains connecting by physical bonds are identical, the same strain energy function applies to network connected by weak and strong bonds.

The following notations are introduced to describe our PA gel model:

- The total number of weak (strong) bonds per unit reference volume is denoted by $N_i = \omega_i N_0$ where ω_i is the molar fraction, weak bonds and strong bonds are referred to i = 1 and i = 2 respectively. Note $\omega_1 + \omega_2 = 1$ and that both ω_1, ω_2 are constants, independent of time. However, it is important to note that not all weak or strong bonds are connected after the synthesis of the gel, even under no applied load or deformation.
- The total number of weak or strong bonds that are connected per unit reference volume at time *t* is given by $N_{c_i}(t)$. Similarly, the total number weak or strong bonds that are broken per unit reference volume at *t* is denoted by $N_{b_i}(t)$. Therefore, we have $N_i(t) = N_{c_i}(t) + N_{b_i}(t)$.

2.2. Survivability function

The concept of a survivability function, $\phi_B(\tau, t)$ was introduced in our previous works to study the breaking kinetics of a PVA hydrogel [33,34]. A surprising aspect of the PVA gel is that $\phi_B(\tau, t)$ is *independent* of the force acting on the physical bonds. This result leads us to propose that the breaking rate for the PVA gel is given by

$$-\frac{\partial\phi_B}{\partial t} = \frac{1}{t_B}\phi_B^{\alpha_B},\tag{2}$$

where t_B is a characteristic breaking time for physical bonds and $2 > \alpha_B > 1$ is a material constant that specifies the rate of decay of ϕ_B . For the PA gel system, Eq. (2) is inadequate since the bond breaking is sensitive to the stretch experienced by the bond. To reflect this effect, we modify Eq. (2) by allowing the rate of bond breaking to be dependent on the stretch experienced by a bond from its birth at time τ to the current time $t > \tau$. In the affine model, this stretch is characterized by the first invariant of the right Cauchy–Green tensor, given by $H(\tau, t) = \text{trace}\left[\left(\mathbf{F}^{\tau \to t}\right)^T \mathbf{F}^{\tau \to t}\right]$. Thus, for the PA gel, we modify Eq. (2) to

$$-\frac{\partial\phi_B}{\partial t} = \frac{1}{t_B}\phi_B^{\alpha_B}f\left[H(\tau,t)\right],\tag{3}$$

where *f* is the accelerating breaking function. Physically, we expect *f* to increase monotonically with *H*. Also, for small deformations we have $f(H^{\tau \to t} \approx 3) \approx 1$. Consistent with the tension test results in Fig. 2 we allow *f* to increase rapidly after some critical deformation, I_c . When the sample is loaded beyond this critical deformation, the gel shows yielding-like behavior due to the acceleration of breaking kinetics. Experiments (see Fig. 2) show that although the "yielding" stress increases rapidly with the applied loading rate, the "yielding" strain characterized by I_c is insensitive to the loading rate. Eq. (3) can be integrated to obtain

$$\phi_B(\tau, t, H^{\tau \to t}) = \left[1 + \frac{\alpha_B - 1}{t_B} \int_{\tau}^{t} f\left(H^{\tau \to s}\right) ds\right]^{\frac{1}{1 - \alpha_B}}.$$
(4)

It is important to note that the survivability function depends on the time τ when the bond is formed, current time *t*, and the deformation history $H(\tau, s) \equiv H^{\tau \to s}$ for $s \in (\tau, t]$. In the following, we simplify notations by writing $\phi_B(\tau, t, H^{\tau \to t}) \equiv \phi_B(\tau, t)$. A more detailed discussion on the physics of Eqs. (2) and (3) is given in supporting information (SI, see Section S1).

The accelerating breaking function $f_i(I_1)$ used in this work is

$$f_i(I_1) = \exp\left\{ \left(1 + \frac{I_1 - 3}{I_c - 3} \right)^{m_i} - 1 \right\}, I_c = \lambda_c^2 + \frac{2}{\lambda_c},$$
(5)

where I_c is the first invariant of the right Cauchy–Green tensor calculated at the critical stretch λ_c , after which the bond breaking kinetics accelerate, and m_i is a material parameter. When chains are stretched beyond their critical strain limit, $f_i(I_1)$ increases significantly and this accelerated bond breaking phenomenon results in macroscopic softening of the gel. The critical strain related parameter I_c is assumed to be same for the weak and strong bonds. An estimate of I_c can be obtained from tensile test data, where the slope of nominal stress versus nominal strain decreases rapidly (see Fig. 2). When the deformation is small compared to the critical strain, i.e., $|I_1 - 3| \ll |I_c - 3| f_i(I_1) \approx 1$, we recover our previous PVA constitutive model where breaking kinetics is independent of strain/stress.

Since the breaking rate of physical bonds is dependent on the deformation applied, we can no longer use the steady-state assumption of dynamic equilibrium once loading starts. In other words, once loading starts, the breaking and healing rates are history dependent and not necessarily equal. The healing rate is considered next.

2.3. Healing rates for physical bonds

For each type of bonds, the number of bonds per unit reference volume reattached between τ and $\tau + d\tau$ which survive until $t > \tau$ is

$$\phi_{B_i}(\tau, t)\hat{\chi}_i(\tau)\,d\tau. \tag{6a}$$

The total number of reattached bonds of type *i* from when the gel is synthesized ($\tau = -\infty$) to the current time, $N_{c_i}(t)$ is

$$N_{c_i}(t) = \int_{-\infty}^t \phi_{B_i}(\tau, t) \hat{\chi}_i(\tau) d\tau.$$
(6b)

By Eq. (1), the total number of unconnected bonds is $N_{b_i}(t) = \hat{\chi}_i(t)t_{H_i}$. Since $N_i = N_{b_i}(t) + N_{c_i}(t)$, we have

$$\omega_{i}N_{0} = \hat{\chi}_{i}(t)t_{H_{i}} + \int_{-\infty}^{t} \phi_{B_{i}}(\tau, t)\hat{\chi}_{i}(\tau)d\tau \Leftrightarrow \omega_{i} = \chi_{i}(t)t_{H_{i}} + \int_{-\infty}^{t} \phi_{B_{i}}(\tau, t)\chi_{i}(\tau)d\tau.$$
(7)

Eq. (7) states that the healing rate χ_i depends on the loading history and can be obtained by solving an integral equation.

Eq. (7) can be simplified since we assume loading starts at t = 0. Before loading starts, the bonds are in a state of dynamic equilibrium so $\chi_i(t) = \chi_i^{ss}$ for t < 0. The steady state healing rate χ_i^{ss} can be found by setting t = 0 in Eq. (7). In SI (Section S2), we show that

$$\chi_i^{ss} = \frac{\omega_i}{t_{H_i} + \frac{t_{B_i}}{2 - \alpha_{B_i}}}.$$
(8)

We use Eq. (7) along with $\chi_i(t) = \chi_i^{ss}, \forall t \leq 0$ and $\int_{-\infty}^0 \phi_{B_i}(\tau, t) \chi_i(\tau) d\tau = \chi_i^{ss} \frac{t_{B_i}}{2-\alpha_{B_i}} \left[\phi_{B_i}(0, t) \right]^{2-\alpha_{B_i}}$ to derive

$$\omega_{i} - \chi_{i}^{ss} \frac{t_{B_{i}}}{2 - \alpha_{B_{i}}} \left[\phi_{B_{i}}(0, t) \right]^{2 - \alpha_{B_{i}}} = \chi_{i}(t) t_{H_{i}} + \int_{0}^{t} \phi_{B_{i}}(\tau, t) \chi_{i}(\tau) d\tau.$$
(9)

Eq. (9) allows us to find the reattachment rates given the loading history.

2.4. Strain energy

The total strain energy of the PA gel is the sum of strain energies carried by the network connected to both the weak and strong bonds. In the following Section 2.5, we assume that the strain energy density W_0 of the undamaged network depends only on the invariant $I_1 = \text{trace}(\mathbf{F}^T \mathbf{F})$. The total strain energy density of the gel W is

$$W = \sum_{i=1}^{2} \int_{-\infty}^{t} \phi_{B_{i}}(\tau, t) \chi_{i}(\tau) W_{0} [H(\tau, t)] d\tau$$

= $\left\{ \sum_{i=1}^{2} \chi_{i}^{ss} \frac{t_{B_{i}}}{2 - \alpha_{B_{i}}} \left[\phi_{B_{i}}(0, t) \right]^{2 - \alpha_{B_{i}}} \right\} W_{0} (I_{1}(t))$
+ $\sum_{i=1}^{2} \int_{0}^{t} \phi_{B_{i}}(\tau, t) \chi_{i}(\tau) W_{0} [H(\tau, t)] d\tau.$ (10)

The first term on the RHS of Eq. (10) corresponds to the strain energy of physical bonds that survive to current time t from the start of the loading (t = 0). The second term on the RHS of Eq. (10) represents the increase in strain energy due to the reattachment of broken bonds during the loading phase. Note, we have used assumption 4 which states that when a chain is reattached, it carries no energy or attaches in a relaxed state. The assumption is reflected in the argument of W_0 in Eq. (10). Specifically, $\phi_{\rm Bi}(\tau, t)\chi_i(\tau)d\tau$ is the fraction of bonds that are reattached between the time τ and $\tau + d\tau$ and survive until the current time *t*. Since these bonds carry energy from their birth at τ , the argument of W_0 is $H(\tau, t) = \text{trace}\left[\left(\mathbf{F}^{\tau \to t}\right)^T \left(\mathbf{F}^{\tau \to t}\right)\right]$.

2.5. Strain energy density function

PA gels are highly stretchable as shown in Fig. 2. In this work, we use a three term Yeoh's strain energy function to capture the network's strain hardening behavior

$$W_0(I_1) = \sum_{i=1}^{3} c_i (I_1 - 3)^i,$$
(11)

where $\mu \equiv 2c_1$ is small strain shear modulus of the undamaged PA gel. The hardening behavior is controlled by the parameters c_2 and c_3 which have dimensions of stress. The first term in the Eq. (11) is the classical neo-Hookean strain energy density, so there is no significant difference between a Yeoh and a neo-Hookean solid at small stretches.

2.6. Nominal stress

Following the Coleman-Noll procedure [49] (see SI, Section S3), the first Piola-Kirchhoff stress is given by

$$\mathbf{P}(t) = -p \left(\mathbf{F}^{0 \to t}\right)^{-T} + \left\{ \sum_{i=1}^{2} \chi_{i}^{ss} \frac{t_{B_{i}}}{2 - \alpha_{B_{i}}} \left[\phi_{B_{i}}(0, t) \right]^{2 - \alpha_{B_{i}}} \right\} \\ \times \left. 2 \frac{dW_{0}}{dI_{1}} \right|_{I_{1}(t)} \mathbf{F}^{0 \to t} \\ + \sum_{i=1}^{2} \int_{0}^{t} \phi_{B_{i}}(\tau, t) \chi_{i}(\tau) 2 \left. \frac{dW_{0}}{dI_{1}} \right|_{I_{1} = H(\tau, t)} \mathbf{F}^{\tau \to t} \left(\mathbf{F}^{0 \to \tau} \right)^{-T} d\tau,$$
(12)

where *p* is the Lagrange multiplier which enforces the incompressibility condition.

Of particular interest are the relations between nominal stress and stretch ratio in uniaxial tension and relaxation tests. In uniaxial tension, the nominal stress **P** is related to the stretch ratio λ (*t*) in the loading direction (see Section S3.1 for derivation) bv 2-00 -

$$P(t) = \left| \sum_{i=1}^{2} \chi_{i}^{ss} \frac{t_{B_{i}}}{2 - \alpha_{B_{i}}} \left[1 + \frac{\alpha_{B_{i}} - 1}{t_{B_{i}}} f_{i}(I_{1}(t)) t \right]^{\frac{1 - \alpha_{B_{i}}}{1 - \alpha_{B_{i}}}} \right| \\ \times 2 \frac{dW_{0}}{dI_{1}} \Big|_{I_{1}(t)} \left(\lambda(t) - \lambda(t)^{-2} \right) \\ + \sum_{i=1}^{2} \int_{0}^{t} \chi_{i}(\tau) \phi_{B_{i}}(\tau, t, H(\tau, t)) \\ \times 2 \frac{dW_{0}}{dI_{1}} \Big|_{H(\tau, t)} \left[\frac{\lambda(t)}{\lambda^{2}(\tau)} - \frac{\lambda(\tau)}{\lambda^{2}(t)} \right] d\tau,$$
(13)

where $I_1 = \lambda^2 (t) + \frac{2}{\lambda(t)}$. In an *ideal* tensile-relaxation test, the stretch ratio is increased suddenly (at t = 0) to $\lambda_0 > 1$ and held constant for all t > 0.

The nominal stress P decreases with time. Using Eq. (13), P in the direction of stretch is given by dW

$$P(t) = 2 \left(\lambda_0 - \lambda_0^{-2}\right) \frac{dw_0}{dI_1} \Big|_{I_1(\lambda_0)} \\ \times \left\{ \sum_{i=1}^2 \rho_i \left[1 + \frac{\alpha_{B_i} - 1}{t_{B_i}} f_i \left(I_1(\lambda_0)\right) t \right]^{\frac{2 - \alpha_{B_i}}{1 - \alpha_{B_i}}} \right\},$$
(14a)

where

$$I_1(\lambda_0) = \lambda_0^2 + \frac{2}{\lambda_0}, \, \rho_i = \frac{\chi_i^{ss} t_{B_i}}{2 - \alpha_{B_i}}.$$
 (14b,c)

Here ρ_i is the molar fraction of attached weak/strong bonds when the gel is in dynamic equilibrium. In an actual relaxation test, the stretch ratio is increased at a rapid but finite rate to reach λ_0 . As a result, Eq. (14a) needs to be modified (see SI, Section S3.2).

In the SI (Section S4), we show that the relaxation modulus G in the small strain regime for a torsional relaxation test is given by

$$G = \mu \left\{ \sum_{i=1}^{2} \chi_{i}^{ss} \frac{t_{B_{i}}}{2 - \alpha_{B_{i}}} \left[1 + \frac{\alpha_{B_{i}} - 1}{t_{B_{i}}} t \right]^{\frac{2 - \alpha_{B_{i}}}{1 - \alpha_{B_{i}}}} \right\}.$$
 (15)

3. Experimental procedure

Materials: Anionic monomer p-styrenesulfonate (NaSS), cationic monomer 3-(methacryloylamino)-propyl-trimethylammonium chloride (MPTC), and photoinitiator α -ketoglutaric acid (α -keto) were purchased from Wako Pure Chemical Industries, Ltd., Japan. All chemicals were used without further purification, and deionized water was used in all experiments.

Gel Synthesis: The preparation process of tough PA gel was described in detail in our previous work [39]. In brief, the gel was synthesized by one-step random copolymerization of cationic and anionic monomers at a high concentration with balanced charges. First, an aqueous solution containing NaSS, MPTC, and α -keto was prepared at 50 °C. The total monomer concentration, $C_{\rm m}$, was 2.1 M, and the molar ratio of NaSS/MPTC was 0.525:0.475. The concentration of α -keto was 0.25 mol %, relative to $C_{\rm m}$. Then the solution was injected into a reaction cell consisting of two glasses separated by a 2 mm-thick spacer. UV polymerization was performed in an argon atmosphere for 11 h with a 365 nm UV light. The resulting gel was put into a large amount of water longer than one week to remove the counterions and unreacted small chemicals. The equilibrated gel has a water content around 50 wt% and has high toughness.

Uniaxial Tensile Test: Gel samples for uniaxial tensile test were cut into a dumbbell-like shape according to JIS K 6261-7 standard. The gauge length, width, and thickness of samples were

٦

12, 2, and 1.75 mm, respectively. Samples were loaded in tension by a Shimadzu autograph machine with a 100 N load cell. The measurement was conducted in a water vapor environment to prevent gel dehydration. Six strain rates were used: 0.0014, 0.0042, 0.014, 0.042, 0.14, and 0.42/s. A maximum stretch ratio of 4.0 was used to avoid the structure damage to the phase structure [40]. Here, the nominal stress *P* is defined as the tensile force divided by the cross-section area of the undeformed sample. The stretch ratio λ is defined as the displacement divided by the gauge length of the undeformed sample. The stretching speed divided by the gauge length of the undeformed sample.

Tensile Cyclic Test: The tensile cyclic test was performed with the same sample geometry and experimental device as that in the uniaxial tensile test. The samples were clamped and stretched to a predetermined λ of 3.0 at a constant strain rate. Then the clamp returned to the original position with a same or different constant strain rate without stopping at the peak stretch ratio. Six cyclic tests were performed with different combinations of loading/unloading rates: 0.14/0.14, 0.14/0.014, 0.14/0.0014, 0.0014/0.0014/s.

Large Strain Tensile Relaxation Test: The large strain relaxation test was performed with the same sample geometry and experimental device as that in the uniaxial tensile test. Samples were stretched to a prescribed stretch ratio at a constant strain rate of 0.14/s and then were held, and stress change was recorded. Four stretch ratios were used: 1.51, 2.01, 3.01, and 4.01.

Small Strain Torsional Relaxation Test: Gel samples for small strain relaxation test were cut into a disk shape with a diameter of 15.0 mm and a thickness of 1.75 mm. Samples were sheared to a strain (λ -1) of 0.5% within 0.03 s and then held fixed by an ARES rheometer in a parallel plate geometry. Samples were adhered to two plates by superglue to prevent them from slipping and surrounded by water to prevent dehydration during the measurement. Prior to measurement, the built-in autostrain function of the ARES rheometer was used to minimize compression on the sample.

Finally, it should be noted that the hydrogels we used in this work are in water-equilibrated state. So, there is no excess water flow between gel and water or water vapor during the measurement.

4. Estimate of material parameters

Our PA gel constitutive model has 13 unknown independent material parameters in total. These unknown parameters are listed below in Table 1.

Some of the material parameters in Table 1 can be estimated using uniaxial tension and tensile-relaxation experimental data. These estimates serve as initial conditions or bounds for the least square optimization process discussed in Section 5. The least squares method provides us multiple local optimums; these estimates guide us in selecting an optimal parameter set which is close to the physical properties of the gel.

Once the material parameters in Table 1 are found, molar fractions of the connected physical bonds in dynamic equilibrium (ρ_1 or ρ_2), steady state healing rates of the physical bonds (χ_1^{ss} or χ_2^{ss}), and small strain instantaneous shear modulus of PA gel ($\mu\rho_1 + \mu\rho_2$) can be determined using Eqs. (8) and (14c). In the following Section 4.1, we show how a relaxation test can be used to estimate $\mu\rho_1 + \mu\rho_2$. An estimate of the critical stretch ratio λ_c or I_c can be determined from tensile data. The procedure to determine these estimates is described below.

4.1. Estimate for small strain shear modulus

The nominal stress in uniaxial tension test is given by Eq. (13). For small times and small strains, the fraction of physical bonds connected in the material are almost the same as their steady state fractions (ρ_1 or ρ_2), and the very few newly formed bonds hardly carry any load. Mathematically, this means that integral term in the Eq. (13) is small in comparison with the first term. Since strains are small at short times, we neglect strain hardening and strain dependent breaking, resulting in

$$P(t) \approx \left(\sum_{i=1}^{2} \rho_{i}\right) \mu \left(\lambda(t) - [\lambda(t)]^{-2}\right),$$

as $2 \frac{dW_{0}}{dI_{1}}\Big|_{I_{1}(t)} \approx \mu(\text{at low strains}),$
$$\approx \left(\sum_{i=1}^{2} \rho_{i}\right) 3\mu\varepsilon,$$
(16)

for short times and sufficiently fast loading rate. Eq. (16) implies that the instantaneous Young's modulus E_0 , measured using the initial slope of the nominal stress–strain curve, is related to $\mu \sum_{i=1}^{2} \rho_i by$

$$E_0 = 3\mu \sum_{i=1}^{2} \rho_i.$$
 (17)

Hence, we can use the loading portion of relaxation test to determine $\mu \sum_{i=1}^{2} \rho_i$. This is illustrated in Fig. 1.

4.2. Estimate for critical stretch ratio λ_c

Fig. 2 shows that the slope of nominal stress versus nominal strain decreases rapidly after a critical strain around 15% is reached. The inset shows that although stress increases rapidly with the strain rate, the critical strain where "yielding" occurs is insensitive to strain rate. This behavior is reflected in Eq. (5) where we propose that breaking kinetics is controlled by strain experienced by the network. The procedure of determining the estimate of critical stretch ratio λ_c is mentioned in SI (Section S6). We found that λ_c lies between 1.1 to 1.3. Within this range, the fitting result of nominal stress is not particularly sensitive to λ_c .

The inset in Fig. 2 seems to suggest that the instantaneous modulus E_0 is dependent on the loading rate. In theory, all the curves in Fig. 2 at very short time should have the same slope. In practice, the loading rate needs to be sufficiently fast for the strains to be measurable. The strains in the insert in Fig. 2 are too large to see this effect. In Fig. 1, all the tensile-relaxation tests for different stretch ratios are loaded at *a fast rate* of 0.14/s, and we notice that at *small strains* (in the order of 10^{-3}) all the curves fall on the same line suggesting the accuracy of data.

5. Least squares error optimization method

We use least squares error optimization to determine the 13 unknown material parameters in Table 1. First, we select data from three data sets (simple tension, relaxation, and cyclic tests). Fig. 3 shows some representative data. In these plots, loading and unloading rates are denoted by LR and UR respectively. Experimental data are solid black lines. The basic idea is to choose parameters so that model prediction of nominal stress minimizes the least squares error at selected points, indicated by blue dotted circles in Fig. 3. More data points are chosen in regions where the slope of the stress–strain curve changes rapidly. In cyclic and simple tension tests, *xdata* is a vector consisting of selected nominal stretch values and *ydata* is the corresponding experimental nominal stress values. In tensile-relaxation tests, *xdata* is a



Fig. 1. Fitting the initial slope of nominal stress-nominal strain plots from three tensile-relaxation tests carried out at three stretch ratios λ_0 (solid lines). The experimental plots shown here are from the loading part of three tensile relaxation tests of the same data set. Note that all three relaxation tests fall on the same line at small strains (less than 0.3%). The small strain instantaneous shear modulus is $\mu\rho_1 + \mu\rho_2 \approx 1.87$ MPa (1/3 of the slope of the dotted blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Uniaxial tension test data for purely physical PA-gel for different strain rates ($\dot{\varepsilon} = \dot{\lambda}$).

| Table 1 | | | | | | |
|---------|-------------|------------|--------|-----|--------------|--------|
| Summary | of material | parameters | for PA | gel | constitutive | model. |

| Steady state | e parameters | | | | | |
|-----------------------|------------------|-----------------------|-------------------|-----------------------|-----------|--------------------------|
| α_{B_i} | t_{B_1} | t_{H_1} | α_{B_2} | t_{B_2} | t_{H_2} | ω_1 or ω_2 |
| Strain depe | ndent accelerate | d breaking functi | on parameters, f | r | | |
| <i>m</i> ₁ | | <i>m</i> ₂ | | λ_c | | |
| Undamaged | network strain | energy density f | unction, Yeoh's n | nodel, W ₀ | | |
| $c_1 \equiv \mu/2$ | | c_2/c_1 | | c_{3}/c_{1} | | |
| | | | | | | |

vector storing selected time points and *ydata* is the corresponding experimental nominal stress values. Let η denote a vector of 13 material parameters, our goal is to determine η which minimizes the objective function:

$$\sum_{i} (F(\eta, xdata_{i}) - ydata_{i})^{2}, \quad lb \le \eta \le ub.$$
(18)

The lower and upper bonds on η are denoted by *lb* and *ub* respectively. The notation F refers to the solution of the nominal

stress equation in either loading–unloading or simple tension or tensile-relaxation test. $F(\eta, xdata_i)$ in Eq. (18) is determined using a *lsqcurvefit* inbuilt function with *trust-region-reflective* algorithm in *MATLAB 2018a* version. In the optimization process, it is possible to find multiple data sets that have similar least squares error (less than 10 percent average error between simulated result and experimental stress data).

We find a set of optimal parameters by replacing the history dependent reattachment rates ($\chi_1(t)$ or $\chi_2(t)$) with the steady



Fig. 3. Selected plots from three data sets: (a) cyclic tests, (b) tensile-relaxation tests, and (c) simple tension tests. We optimize 13 material parameters in Table 1 to get the minimum least squares error in nominal stress from all these plots (see SI, Section S5 for the entire data set use in optimization). Here LR and UR denotes loading and unloading rates respectively.

state values $(\chi_1^{ss} \text{ or } \chi_2^{ss})$. This reduces the computing time of $F(\eta, xdata_i)$, as we avoid solving the integral equation (Eq. (9)). Using this set of optimal parameters, we recalculate $F(\eta, xdata_i)$ using the full theory (solving the Eq. (9)) to check whether the results are within the error bound (less than 10 percent average error between simulated result and experimental stress data). Details of these calculations are given in the SI (Section S5). In all

cases, we found that these assumptions give material parameters that are consistent with experimental data.

Table 2 summarizes the parameters we determined using the optimization process. We notice from Table 2 that the characteristic breaking time of strong bonds is almost ten times the breaking time of weak bonds. Furthermore, the characteristic healing time of the strong bonds is almost twice the characteristic



Fig. 4. Nominal stress *P* (MPa) vs nominal stretch λ for loading and unloading tests with different strain rates. (a), (b), and (c): The upper plots have a loading rate (LR) of 0.14/s and unloading rates (UR) of 0.14/s, 0.014/s, and 0.0014/s from left to right respectively. (d), (e), and (f): Similarly, the lower plots have a loading rate of 0.0014/s and unloading rates of 0.14/s, 0.014/s, and 0.0014/s from left to right respectively. Experiments are shown as solid black lines and dashed blue lines are model predictions using parameters in Table 2.

Table 2

| The independent material parameters determined using least squares optimization p | rocess. |
|---|---------|
| Steady state parameters | |

| $\alpha_{B_i}=1.7712$ | $t_{B_1} = 0.0031 \text{ s}$ | $t_{H_1} = 0.1276s$ | $\alpha_{B_2} = 1.7441$ | $t_{B_2} = 0.0324 \text{ s}$ | $t_{H_2} = 0.2038 \text{ s}$ | $\omega_1 = 1 - \omega_2 = 0.5016$ |
|--|------------------------------|---------------------|-------------------------|------------------------------|------------------------------|------------------------------------|
| Strain dependent accelerated breaking function parameters, f | | | | | | |
| $m_1 = 0.4606$ | | $m_2 = 0.5845$ | | $\lambda_c = 1.1226$ | | |
| Undamaged network strain energy density function, Yeoh's model, W ₀ | | | | | | |
| $\overline{c_1 \equiv \mu/2 = 4.69}$ | 29 MPa | $c_2/c_1 = 0.4485$ | | $c_3/c_1 = 0.2100$ | | |

| 1 | Га | h | e | 3 |
|---|-----|---|---|---|
| | ••• | | | |

| The dependent material parameters determined | ined using values from Table 2. |
|---|---|
| Steady state healing rates (from Eq. (8)) | |
| $\chi_1^{ss} = 3.5583 \ s^{-1}$ | $\chi_2^{ss} = 1.5088 \ s^{-1}$ |
| Molar fraction of connected physical bonds | in dynamic equilibrium (from Eq. (14c)) |
| $ \rho_1 = 0.0476 $ | $ \rho_2 = 0.1908 $ |
| Small strain shear modulus | |
| $\mu \rho_1 + \mu \rho_2 \equiv \frac{E_0}{3} = 2.2376 \text{ MPa}$ | |

healing time of weak bonds. We also note from Table 3 that the healing rate of strong bonds is less than half of healing rate of weak bonds. This is reasonable as the strong bonds break and reattach at a slower pace. As a consequence, using Eq. (14c) we get $\rho_2 > \rho_1$ (see Table 3). Table 2 also shows $m_1 < m_2$, which implies that the breaking of weak bonds is less dependent on strain when compared to the strong bonds.

Using the material parameter values in Table 2, the rest of the parameters are computed and shown below.

As a check on the validity of the parameters, we note that the values of small strain instantaneous shear modulus ($\mu(\rho_1 + \rho_2)$) and critical stretch ratio (λ_c) from Tables 2 and 3 are consistent with the estimates obtained from experimental data in Section 4.

6. Results and discussion

We compare modeling results with experimental data from cyclic tension, tensile relaxation and simple tension tests. Modeling results are determined using parameters in Table 2 and solving Eqs. (9) and (13) for the nominal stress and the healing rates respectively.

6.1. Cyclic tests

Fig. 4 compares experimental data with model. Experiments consists of uniaxial tension cyclic test with different loading (LR) and unloading rates (UR). Fig. 4 shows that our model predicts



Fig. 5. Nominal stress *P* (MPa) vs time *t* (s) for tensile-relaxation tests with different nominal stretch ratios. Experiments are solid black lines and dashed blue lines are model predictions using parameters in Table 2. Insets show the loading part of the test. Relaxation tests are carried out using 4 stretch ratios (a) $\lambda_0 = 1.51$, (b) $\lambda_0 = 2.01$, (c) $\lambda_0 = 3.01$, and (d) $\lambda_0 = 4.01$.



Fig. 6. Nominal stress *P* (MPa) vs nominal stretch λ for simple tension tests with 5 loading rates (LR) (a) 0.0014/s, (b) 0.0042/s, (c) 0.014/s, (d) 0.042/s, (e) 0.14/s, and (f) 0.42/s. The Solid black lines are experiments and dashed blue lines are model predictions using parameters in Table 2.

the experimental data well for all cases. For very small loading rates of 0.0014/s, our model slightly overestimates the nominal stress in the loading phase.

6.2. Tensile-relaxation tests

Fig. 5 plots show that our model (blue dashed lines) is in excellent agreement with experimental data in both the loading and the relaxation phases ($\lambda_0 \approx 1.5 - 4$).

6.3. Simple tension

Fig. 6 presents simple tension tests with 6 different loading rates covering 2 decades. Our model predicts the experimental data very well for the loading rates of 0.0042/s, 0.14/s, and 0.42/s

cases. For the loading rates 0.0014/s and 0.014/s, the model did not do as well. Nevertheless, for LR = 0.0014/s, the relative error between theory and experiment is less than 10%. For LR = 0.042/s, we slightly underestimate the stress, the relative error between theory and experiments is less than 6%.

6.4. Time dependent healing rate $(\chi_1(t) \text{ or } \chi_2(t))$

The time evolution of the healing rate during the mechanical loading for select loading–unloading and tensile-relaxation tests is shown in Fig. 7. Red and blue lines denote the healing rates for weak and strong bonds respectively. These results are obtained by solving the integral equation (Eq. (9)) using the material parameters in Table 2. For both tests the healing rate increases until the end of loading and then starts to decrease.



Fig. 7. Healing rate $(\chi_1(t) \text{ or } \chi_2(t))$ (/s) for weak (red dotted lines) and strong bonds (blue dotted lines) vs time (s) for two types of mechanical testing. (a) and (b): The two upper plots are loading–unloading tests with a loading rate (LR) of 0.14/s and unloading rate (UR) of 0.014/s. (c) and (d): The two lower plots are tensile-relaxation tests with a nominal stretch ratio of $\lambda_0 \approx 3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. Stress contributions from physical bonds computed using our model for different loading histories: (a) simple tension, (b) tensile-relaxation, and (c) cyclic test. The tensile test is carried out using a loading rate (LR) of 0.14/s. The stretch ratio in the tensile-relaxation test is $\lambda_0 \approx 3$. The cyclic test has a loading rate (LR) of 0.14/s and an unloading rate (UR) of 0.014/s. Experimental data is indicated by solid black lines, the stress contribution from weak bonds are red dotted lines, the stress contribution from strong bonds are green dotted lines, and total stress contribution from physical bonds (weak + strong) are blue dash-dotted lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7 plots show that the time dependent healing rates for both weak ($\chi_1(t)$) and strong bonds ($\chi_2(t)$) for cyclic and tensilerelaxation loading histories. Here we present only two loading histories, but the general behavior is similar for other loading histories: the healing rate of weak or strong bonds increases until maximum load and there is a drop in the healing rate after that. During unloading, less chains are stretched which decreases the breaking rate of bonds and less increase in the fraction of the broken bonds during this phase. Therefore, the healing rates for both strong and weak bonds change only slightly during the unloading phase. During relaxation, bonds are broken and healed, but the newly healed bonds do not carry load, so the stress carried by physical bonds gradually decreases (see also Fig. 8(b)). These results suggest a simple way to improve the efficiency of the optimization procedure. Since solving the integral equation is time consuming, one may assume that the healing rate is given by the steady state healing rate in the optimization process. We found this procedure hardly changes the fitting.

6.5. Load bearing characteristics of strong and weak bonds

The stress contributions from strong and weak bonds are shown in Fig. 8 for different loading histories. The general trend can be captured by selecting one case from each of the three loading histories (simple tension, relaxation and cyclic). Tables 2 and 3 indicate that $m_1 < m_2$, implying that the breaking of weak bonds depend less on strain when compared to strong bonds. Also, since $\chi_1^{ss} > \chi_2^{ss}$, weak bonds heal more than twice as fast



Fig. 9. The sample is sheared to a strain of 0.005 in a torsional relaxation test. (a) Shear strain vs time for short times. This figure shows that the desired strain is achieved at 30-40 milli seconds. (b) Relaxation modulus, *G* (MPa) vs time, *t* (s) is shown. The solid lines are experiments (same test repeated) and the dashed blue line is model prediction Eq. (15) based on Table 2.

as strong bonds. These suggest that the stress contribution from weak bonds is higher than strong bonds at higher stretch ratios and lower at low stretch ratios, as shown in the simple tension data (Fig. 8(b)). This is because at high stretch ratios, the number of broken strong bonds increases much faster than the number of broken weak bonds (see SI, Section S7). On the other hand, the weak bonds heal much faster than the strong bonds, so they bear more of the applied load. A similar trend can be observed for different types of loadings (tensile, tensile-relaxation and cyclic test).

6.6. Small strain torsional relaxation test

The constitutive model is expected to work for multi-axial state of stress and strain. Although the main focus of this work is on uniaxial tension behavior, it is interesting to see whether the same parameters in Table 2 can capture the shear stress measured in a small strain torsional rheology test, which is commonly used to study viscoelastic behavior. Fig. 9 shows two small strain relaxation tests in torsion (solid lines). In this test, the sample is twisted rapidly to a shear strain of $\varepsilon_0 = 0.005$. The relaxation modulus G(t) of two experiments are shown as solid lines in Fig. 9. These experimental results are compared to the small strain relaxation modulus given by Eq. (15) which is plotted as a blue dashed line.

Our model underestimates the modulus for t < 0.1s. This is because we used Eq. (15) which models an ideal relaxation test where the desired strain ($\varepsilon_0 = 0.5\%$ in Fig. 9) is achieved instantaneously. However, in the experiment, this strain is achieved at around 30–40 milli-seconds. The discrepancy of Eq. (15) and experimental data during short times can be attributed to this finite rate effect.

7. Conclusions

We developed a rate and strain dependent bond breaking/ reforming constitutive model to quantify the mechanical behavior of a physically crosslinked PA gel. The predictions from our model are validated by comparing with uniaxial tension, tensilerelaxation, cyclic (loading–unloading), and small strain rheology tests. The comparisons between the theoretical predictions and experimental data are generally good. We found some discrepancies between theory and experiment in simple tension tests where the loading is slow. As noted by an anonymous reviewer, this discrepancy can be caused by the fact that the critical stretch ratio is not exactly a constant or independent of strain rate. Another possibility could be our choice of accelerated breaking function which tends to shift the "yielding point" slightly depending on the loading rate and this contradicts the assumption the critical stretch is a constant. These are possibilities that we will consider in the future.

The main difficulty is that there are 13 material parameters in our model and there is no simple experimental procedure to determine all of them. There are also limitations in our model. For example, we assume the stress sustained by a temporary chain is instantaneously relaxed when one of the connecting bond breaks, and that immediately after a temporary chain is reattached, it is in a relaxed state and carries no strain energy (Assumption 4). This scenario may not be true at high loading rates where newly broken bonds may still carry load and newly reattached chains may still carry some strain energy. In addition, most of our experiments are performed in uniaxial tension so our model may not work well in multi-axial loading. An extensive validation of our theory will be conducted in future works by subjecting the gel to more complex multi-axial loading histories.

CRediT authorship contribution statement

Sairam Pamulaparthi Venkata: Numerical simulations. **Kunpeng Cui:** Experimental data. The theory was jointly developed by Venkata, Guo and Hui with input from Zehnder. All the experimental work was done by Cui and supervised by Gong. All authors participated in the writing of paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This material is based upon work supported by the National Science Foundation, USA under Grant No. CMMI-1903308. J.P.G. acknowledges support from the Japan Society for the Promotion of Science, Japan KAKENHI (grant no. JP17H06144). K.P.C. acknowledges support from the Japan Society for the Promotion of Science, Japan KAKENHI (grant no. JP19K23617). J.P.G. and K. P. C. acknowledge support from the Institute for Chemical Reaction Design and Discovery by World Premier International Research Initiative, MEXT, Japan. The authors would like to thank two anonymous reviewers for suggestions.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eml.2021.101184.

References

- [1] L.J. Suggs, E.Y. Kao, L.L. Palombo, R.S. Krishnan, M.S. Widmer, A.G. Mikos, Preparation and characterization of poly(propylene fumarate-co-ethylene glycol) hydrogels, J. Biomater. Sci. Polym. Ed. 9 (1998) 653–666, http: //dx.doi.org/10.1163/156856298X00073.
- [2] C.K. Kuo, P.X. Ma, Ionically crosslinked alginate hydrogels as scaffolds for tissue engineering: Part 1. Structure, gelation rate and mechanical properties, Biomaterials 22 (2001) 511–521, http://dx.doi.org/10.1016/S0142-9612(00)00201-5.
- [3] K.Y. Lee, D.J. Mooney, Hydrogels for tissue engineering, Chem. Rev. 101 (2001) 1869–1880, http://dx.doi.org/10.1021/cr000108x.
- [4] Haesun Park, Kinam Park, Waleed S. Shalaby, Biodegradable hydrogels for drug delivery, 1993.
- [5] Y. Qiu, K. Park, Environment-sensitive hydrogels for drug delivery, Adv. Drug Deliv. Rev. 64 (2012) 49–60, http://dx.doi.org/10.1016/j.addr.2012.09. 024.
- [6] H.J. Kwon, K. Yasuda, J.P. Gong, Y. Ohmiya, Polyelectrolyte hydrogels for replacement and regeneration of biological tissues, Macromol. Res. 22 (2014) 227–235, http://dx.doi.org/10.1007/s13233-014-2045-6.
- H.J. Kwon, Tissue engineering of muscles and cartilages using polyelectrolyte hydrogels, Adv. Mater. Sci. Eng. 2014 (2014) 1–7, http://dx.doi.org/ 10.1155/2014/154071.
- [8] J.P. Gong, Y. Katsuyama, T. Kurokawa, Y. Osada, Double-network hydrogels with extremely high mechanical strength, Adv. Mater. 15 (2003) 1155–1158, http://dx.doi.org/10.1002/adma.200304907.
- [9] A. Nakayama, A. Kakugo, J.P. Gong, Y. Osada, M. Takai, T. Erata, S. Kawano, High mechanical strength double-network hydrogel with bacterial cellulose, Adv. Funct. Mater. 14 (2004) 1124–1128, http://dx.doi.org/10. 1002/adfm.200305197.
- [10] Y.-H. Na, Y. Tanaka, Y. Kawauchi, H. Furukawa, T. Sumiyoshi, J.P. Gong, Y. Osada, Necking phenomenon of double-network gels, Macromolecules 39 (2006) 4641–4645, http://dx.doi.org/10.1021/ma060568d.
- [11] R.E. Webber, C. Creton, H.R. Brown, J.P. Gong, Large strain hysteresis and mullins effect of tough double-network hydrogels, Macromolecules 40 (2007) 2919–2927, http://dx.doi.org/10.1021/ma062924y.
- [12] H.R. Brown, A model of the fracture of double network gels, Macromolecules 40 (2007) 3815–3818, http://dx.doi.org/10.1021/ma062642y.
- [13] J.P. Gong, Why are double network hydrogels so tough? Soft Matter. 6 (2010) 2583–2590, http://dx.doi.org/10.1039/b924290b.
- [14] X. Wang, W. Hong, Pseudo-elasticity of a double network gel, Soft Matter. 7 (2011) 8576, http://dx.doi.org/10.1039/c1sm05787a.
- [15] T. Nakajima, T. Kurokawa, S. Ahmed, W. Wu, J.P. Gong, Characterization of internal fracture process of double network hydrogels under uniaxial elongation, Soft Matter. 9 (2013) 1955–1966, http://dx.doi.org/10.1039/ C2SM27232F.
- [16] K.J. Henderson, T.C. Zhou, K.J. Otim, K.R. Shull, lonically cross-linked triblock copolymer hydrogels with high strength, Macromolecules 43 (2010) 6193–6201, http://dx.doi.org/10.1021/ma100963m.
- [17] W.-C. Lin, W. Fan, A. Marcellan, D. Hourdet, C. Creton, Large strain and fracture properties of poly(dimethylacrylamide)/silica hybrid hydrogels, Macromolecules 43 (2010) 2554–2563, http://dx.doi.org/10.1021/ ma901937r.
- [18] M.A. Haque, T. Kurokawa, G. Kamita, J.P. Gong, Lamellar bilayers as reversible sacrificial bonds to toughen hydrogel: Hysteresis, selfrecovery, fatigue resistance, and crack blunting, Macromolecules 44 (2011) 8916–8924, http://dx.doi.org/10.1021/ma201653t.
- [19] J.-Y. Sun, X. Zhao, W.R.K. Illeperuma, O. Chaudhuri, K.H. Oh, D.J. Mooney, J.J. Vlassak, Z. Suo, Highly stretchable and tough hydrogels., Nature 489 (2012) 133–136, http://dx.doi.org/10.1038/nature11409.
- [20] K. Mayumi, A. Marcellan, G. Ducouret, C. Creton, T. Narita, Stress-strain relationship of highly stretchable dual cross-link gels: Separability of strain and time effect, ACS Macro Lett. 2 (2013) 1065–1068, http://dx.doi.org/10. 1021/mz4005106.

- [21] T. Narita, K. Mayumi, G. Ducouret, P. Hébraud, Viscoelastic properties of poly(vinyl alcohol) hydrogels having permanent and transient cross-links studied by microrheology, classical rheometry, and dynamic light scattering, Macromolecules 46 (2013) 4174–4183, http://dx.doi.org/10.1021/ ma400600f.
- [22] N.M. Ames, V. Srivastava, S.A. Chester, L. Anand, A thermo-mechanically coupled theory for large deformations of amorphous polymers. Part II: Applications, Int. J. Plast. 25 (2009) 1495–1539, http://dx.doi.org/10.1016/ j.ijplas.2008.11.005.
- [23] L. Anand, N.M. Ames, V. Srivastava, S.A. Chester, A thermo-mechanically coupled theory for large deformations of amorphous polymers. Part I: Formulation, I. J. Plast. 25 (2009) 1474–1494, http://dx.doi.org/10.1016/j. ijplas.2008.11.004.
- [24] X. Zhao, A theory for large deformation and damage of interpenetrating polymer networks, J. Mech. Phys. Solids. 60 (2012) 319–332, http://dx.doi. org/10.1016/j.jmps.2011.10.005.
- [25] H. Cho, R.G. Rinaldi, M.C. Boyce, Constitutive modeling of the ratedependent resilient and dissipative large deformation behavior of a segmented copolymer polyurea, Soft Matter. 9 (2013) 6319–6330, http: //dx.doi.org/10.1039/c3sm27125k.
- [26] X. Zhao, Multi-scale multi-mechanism design of tough hydrogels: building dissipation into stretchy networks, Soft Matter. 10 (2014) 672–687, http: //dx.doi.org/10.1039/C3SM52272E.
- [27] Y. Liu, H. Zhang, Y. Zheng, A micromechanically based constitutive model for the inelastic and swelling behaviors in double network hydrogels, J. Appl. Mech. 83 (2016) http://dx.doi.org/10.1115/1.4031897.
- [28] T. Lu, J. Wang, R. Yang, T.J. Wang, A constitutive model for soft materials incorporating viscoelasticity and mullins effect, J. Appl. Mech. 84 (2017) http://dx.doi.org/10.1115/1.4035180.
- [29] Y. Mao, S. Lin, X. Zhao, L. Anand, A large deformation viscoelastic model for double-network hydrogels, J. Mech. Phys. Solids 100 (2017) 103–130, http://dx.doi.org/10.1016/j.jmps.2016.12.011.
- [30] V.N. Khiêm, T.-T. Mai, K. Urayama, J.P. Gong, M. Itskov, A multiaxial theory of double network hydrogels, Macromolecules 52 (2019) 5937–5947, http: //dx.doi.org/10.1021/acs.macromol.9b01044.
- [31] R. Huang, S. Zheng, Z. Liu, T.Y. Ng, Recent advances of the constitutive models of smart materials – Hydrogels and shape memory polymers, Int. J. Appl. Mech. 12 (2020) 2050014, http://dx.doi.org/10.1142/ S1758825120500143.
- [32] R. Long, K. Mayumi, C. Creton, T. Narita, C.Y. Hui, Time dependent behavior of a dual cross-link self-healing gel: Theory and experiments, Macromolecules 47 (2014) 7243–7250, http://dx.doi.org/10.1021/ ma501290h.
- [33] R. Long, K. Mayumi, C. Creton, T. Narita, C.-Y. Hui, Rheology of a dual crosslink self-healing gel: Theory and measurement using parallel-plate torsional rheometry, J. Rheol. 59 (2015) 643–665, http://dx.doi.org/10. 1122/1.4915275.
- [34] J. Guo, R. Long, K. Mayumi, C.Y. Hui, Mechanics of a dual cross-link gel with dynamic bonds: Steady state kinetics and large deformation effects, Macromolecules 49 (2016) 3497–3507, http://dx.doi.org/10.1021/ acs.macromol.6b00421.
- [35] A. Ghatak, K. Vorvolakos, H. She, D.L. Malotky, M.K. Chaudhury, Interfacial rate processes in adhesion and friction, J. Phys. Chem. B 104 (2000) 4018–4030, http://dx.doi.org/10.1021/jp9942973.
- [36] M.K. Beyer, H. Clausen-Schaumann, Mechanochemistry: The mechanical activation of covalent bonds, Chem. Rev. 105 (2005) 2921–2948, http: //dx.doi.org/10.1021/cr030697h.
- [37] S.R. Lavoie, R. Long, T. Tang, A rate-dependent damage model for elastomers at large strain, Extrem. Mech. Lett. 8 (2016) 114–124, http://dx. doi.org/10.1016/j.eml.2016.05.016.
- [38] K. Yu, A. Xin, Q. Wang, Mechanics of self-healing polymer networks crosslinked by dynamic bonds, J. Mech. Phys. Solids 121 (2018) 409–431, http://dx.doi.org/10.1016/j.jmps.2018.08.007.
- [39] T.L. Sun, T. Kurokawa, S. Kuroda, A. Bin Ihsan, T. Akasaki, K. Sato, M.A. Haque, T. Nakajima, J.P. Gong, Physical hydrogels composed of polyampholytes demonstrate high toughness and viscoelasticity, Nat. Mater. 12 (2013) 932–937, http://dx.doi.org/10.1038/nmat3713.
- [40] K. Cui, T.L. Sun, X. Liang, K. Nakajima, Y.N. Ye, L. Chen, T. Kurokawa, J.P. Gong, Multiscale energy dissipation mechanism in tough and self-healing hydrogels, Phys. Rev. Lett. 121 (2018) 185501, http://dx.doi.org/10.1103/ PhysRevLett.121.185501.
- [41] K. Cui, Y.N. Ye, T.L. Sun, L. Chen, X. Li, T. Kurokawa, T. Nakajima, T. Nonoyama, J.P. Gong, Effect of structure heterogeneity on mechanical performance of physical polyampholytes hydrogels, Macromolecules 52 (2019) 7369–7378, http://dx.doi.org/10.1021/acs.macromol.9b01676.
- [42] K. Cui, Y.N. Ye, T.L. Sun, C. Yu, X. Li, T. Kurokawa, J.P. Gong, Phase separation behavior in tough and self-healing polyampholyte hydrogels, Macromolecules 53 (2020) 5116–5126, http://dx.doi.org/10.1021/acs. macromol.0c00577.

- [43] K. Cui, Y.N. Ye, C. Yu, X. Li, T. Kurokawa, J.P. Gong, Stress relaxation and underlying structure evolution in tough and self-healing hydrogels, ACS Macro Lett. (2020) 1582–1589, http://dx.doi.org/10.1021/acsmacrolett. 0c00600.
- [44] X. Li, K. Cui, T.L. Sun, L. Meng, C. Yu, L. Li, C. Creton, T. Kurokawa, J.P. Gong, Mesoscale bicontinuous networks in self-healing hydrogels delay fatigue fracture, Proc. Natl. Acad. Sci. USA. 117 (2020) 7606–7612, http://dx.doi.org/10.1073/pnas.2000189117.
- [45] A.B. Ihsan, T.L. Sun, T. Kurokawa, S.N. Karobi, T. Nakajima, T. Nonoyama, C.K. Roy, F. Luo, J.P. Gong, Self-healing behaviors of tough polyampholyte hydrogels, Macromolecules 49 (2016) 4245–4252, http://dx.doi.org/10. 1021/acs.macromol.6b00437.
- [46] C.K. Roy, H.L. Guo, T.L. Sun, A.B. Ihsan, T. Kurokawa, M. Takahata, T. Nonoyama, T. Nakajima, J.P. Gong, Self-adjustable adhesion of polyam-pholyte hydrogels, Adv. Mater. 27 (2015) 7344–7348, http://dx.doi.org/10. 1002/adma.201504059.
- [47] D.R. King, T.L. Sun, Y. Huang, T. Kurokawa, T. Nonoyama, A.J. Crosby, J.P. Gong, Extremely tough composites from fabric reinforced polyampholyte hydrogels, Mater. Horiz. 2 (2015) 584–591, http://dx.doi.org/10. 1039/C5MH00127G.
- [48] Guo Jingyi, Constitutive modeling and fracture mechanics of a self-healing hydrogel with chemical and physical cross-links, 2019, http://dx.doi.org/ 10.7298/V58W-4H93.
- [49] G.A. Holzapfel, Nonlinear Solid Mechanics: A Continuum Approach for Engineering, Wiley, Chichester, New York, 2000.