Role of dynamic bonds on fatigue threshold of tough hydrogels

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Edited by Xiqiao Feng, Tsinghua University, Beijing, China; received January 13, 2022; accepted April 11, 2022 by Editorial Board Member Yonggang Huang

Fatigue threshold ($G_0$) is the energy release rate below which no fatigue crack advances. Understanding the relationship between the static/dynamic structures and $G_0$ of viscoelastic hydrogels is crucial for designing materials exposed to cyclic loading. In this study, we elaborate the role of dynamic bonds in the $G_0$ of tough hydrogels. Using polyampholyte hydrogels possessing abundant ionic dynamic bonds, we adopt a time–salt superposition principle to access a wide range of time scales that are difficult to access in fatigue tests. $G_0$ was found rate-independent in the elastic regime at a low cyclic strain rate, whereas weak power-law relations between $G_0$ and strain rate were first observed in viscoelastic regimes. The former agrees with the molecular explanation of the Lake–Thomas model, and the latter is related to the self-healing property of dynamic bonds in the viscoelastic regime that protects the permanent bonds from breaking. This work modifies the previous consideration that the dynamic bonds only contribute to the fracture toughness and crack resistance but not to the $G_0$.

Viscoelasticity, derived from noncovalent/reversible interactions in covalent polymer networks, is a phenomenon commonly observed in soft materials, such as elastomers (1–4), hydrogels (5–7), and human tissues (8, 9). Viscoelastic dissipation associated with the rheological response of these noncovalent/reversible interactions plays an essential role in toughness enhancement and crack resistance. Moreover, crack advance in the cyclic fatigue test is also found correlated to the rheological response of these noncovalent/reversible interactions. The dynamic bonds have an essential role in toughness enhancement and crack resistance. Moreover, crack advancement in the cyclic fatigue test is also found correlated to the rheological response (10–12). However, whether the viscoelasticity plays roles in the fatigue threshold ($G_0$) for vanishing crack advancing velocities is still an open question.

Studies by Lake and coworkers on rubbers (12, 13) and Suo and coworkers on hydrogels (10, 11, 14) suggested $G_0$ is determined by the covalent network, whereas the noncovalent/reversible interactions make negligible contributions. These studies found that $G_0$ agrees quantitatively well with the Lake–Thomas model (13), which is interpreted by the scission of covalent bonds of the polymer chain lying across the crack plane. Conversely, the $G_0$ values of some viscoelastic soft materials do not quantitatively obey the Lake–Thomas model (15, 16). For example, polyampholyte hydrogels (PA gels) composed of a permanent cross-linking network and dynamic ionic bonds show a stronger relationship between $G_0$ and the mesh size of the permanent network than the scaling relation deduced from the Lake–Thomas model (15). We consider that these discrepancies in the viscoelastic effects might arise from different deformation rates of the fatigue test with respect to the characteristic relaxation times of the viscoelastic materials. However, exploring the fatigue behaviors of the viscoelastic materials over a wide range of strain rates from the elastic regime to the viscoelastic regime is experimentally challenging.

In this work, we study the strain-rate dependence of $G_0$ of viscoelastic hydrogels with ionic bonds. The time–salt superposition principle allows us to tune the dynamics of the ionic bonds and thereby experimentally access a wide range of time scales for fatigue observation at a constant temperature. We show that $G_0$ increases weakly with strain rate in power-law relations in the viscoelastic regime. At the low-frequency limit of the pure elastic regime, where the dynamic bonds are turned off, $G_0$ becomes rate-independent, which can be explained by the Lake–Thomas model. We will discuss a possible mechanism for the role of dynamic bonds on $G_0$ in the viscoelastic regimes. This work provides insight into the relationship between viscoelastic response and fatigue resistance.

Results and Discussion

We adopted covalently cross-linked PA gels as model materials. The PA gels carry equal positive and negative charges that are randomly distributed on the polymer network (Fig. 1). PA gels are dually cross-linked with permanent cross-linking by covalent...
cross-linkers and trapped entanglements and dynamic cross-linking by ionic bonds between opposite charges on the polymer chains (6, 17, 18). The permanent cross-linking density could be tuned by the chemical cross-linker density and monomer concentration for the sample synthesis, whereas the dynamic cross-linking could be switched on and off by equilibrating the synthesized samples in pure water and in high-ionic-strength media, respectively. This is because salt ions screen electrostatic interactions (19, 20), thereby accelerating the dynamics of ionic bonds between opposite charges on the polymer network. In this study, we adopted two sets of samples with different permanent cross-links: a soft (PA-s) loosely cross-linked and a hard (PA-h) densely cross-linked (see details in Materials and Methods and Table 1). The two sets of PA gels were studied in two different states: One was in the as-prepared state, before removing the small counterions (Na\(^+\) and Cl\(^-\)) after synthesis; another was in the water-equilibrated state, after removal of the small ions by dialyzing the gels in water (Fig. 1). The salt-containing gels (as-prepared gels) only showed weak viscoelasticity because of the Debye screening effect of ionic bonds, whereas the salt-free gels (water-equilibrated gels) showed strong viscoelasticity owing to the formation of ionic bonds (Fig. 2 A and C).

Analogous to time–temperature superposition (21) and strain-rate–frequency superposition (22), time–salt superposition is an approach to equivalently probe the rheological behavior of poly-electrolyte complexes at different time scales by varying the salt in the samples at a constant temperature (23, 24). This is because salt accelerates the dissociation processes of ionic bonds, which is equivalent to prolong the observation time scale for salt-free samples and therefore reduces viscoelastic dissipation from ionic bonds. Therefore, the dynamic modulus curve \(G_{\text{salt}}(\omega)\) of salt-containing PA gels at angular frequency \(\omega\) is equivalent to the curve \(G(\omega)\) of salt-free PA gels at \(a_{\text{salt}}\omega\):

\[
G(\omega) = b_{\text{salt}} G_{\text{salt}}(a_{\text{salt}}\omega).
\]

The shift factor \(a_{\text{salt}}\) is determined by superimposing the \(G_{\text{salt}}(\omega)\) curve on the \(G(\omega)\) curve of salt-free PA gels. The modulus shift factor was \(b_{\text{salt}} = \lambda_s^3\) due to polymer density difference in per unit volume, where \(\lambda_s^3\) is the volume ratio of the salt-containing PA gels relative to salt-free PA gels.

Fig. 2 B and D shows the master curves \(G(\omega)\) for salt-free PA gels at 24°C by properly shifting the log-log \(G(\omega)\)–frequency curves of the salt-containing gels to match the curves of the salt-free gels (Fig. 2 A and C). The shift factors used to rescale the as-prepared samples are listed in Table 2. This method allowed us to observe the dynamics of PA gels in a wide frequency range that are otherwise inaccessible under a constant temperature. The plateau regime at the low-frequency side is from the permanent cross-linking where the ionic bonds do not play a role. The increase of storage modulus \(G'\) at high frequency roughly follows \(G' \sim (a_{\text{salt}}\omega)^{0.5}\) and can be attributed to the sticky Rouse motion of associating polymer strands derived from ionic bonds (25). \(G'\) does not reach the plateau modulus at the high frequency limit, indicating that the lifetime of ionic bonds \((\tau_s)\) is short, beyond our observation window \((\tau_s < 10^{-5} \text{ s})\). From Fig. 2 B and D, we can read the transition angular frequency from plateau regime to the viscoelastic regime as \(\omega_* = 0.54\) and 0.15 rad/s for PA-s and PA-h, respectively. The \(\omega_*\) could be related to the sticky Rouse time of associating polymer strands \(\tau_* = \omega_*^{-1} = \tau_s(M_{\text{eff}}/M_s)^2\), where

![Schematic illustration of switch off/on of the dynamic bonds on the polyampholyte network. The dynamic bonds are switched off in the as-prepared state, before removing the small counterions (Na\(^+\) and Cl\(^-\)) after synthesis; another was in the water-equilibrated state, after removal of the small ions by dialyzing the gels in water (Fig. 1). The salt-containing gels (as-prepared gels) only showed weak viscoelasticity because of the Debye screening effect of ionic bonds, whereas the salt-free gels (water-equilibrated gels) showed strong viscoelasticity owing to the formation of ionic bonds (Fig. 2 A and C).](image1)

**Table 1. Sample formulations and obtained structures at water-equilibrated state**

|                 | Total monomer concentration \(C_m\), M | Cross-linker density \(C_{\text{MBAa}}\), mol % | Permanent cross-linking density \(v_{\text{e, eff}}\), m\(^{-3}\) | No. of monomers per strand, \(N_{x, \text{eff}}\) |
|----------------|---------------------------------------|-----------------------------------------------|--------------------------------------------------|-----------------------------------------------|
| PA-s           | 2.0                                   | 0.1                                           | \(2.1 \times 10^{24}\)                           | 1,080                                         |
| PA-h           | 2.5                                   | 1.0                                           | \(1.7 \times 10^{25}\)                           | 130                                           |
Fig. 2. Constructed master curves of mechanical properties of PA gels through time-salt superposition. (A) Frequency sweep curves of the salt-containing and salt-free PA-s by time-temperature superposition at a reference temperature of 24°C. (B) The master curves of frequency sweep constructed from time-salt superposition for PA-s using the curves in A. (C) Frequency sweep curves of the salt-containing and salt-free PA-h by time-temperature superposition at a reference temperature of 24°C. (D) The master curves of frequency sweep constructed from time-salt superposition for PA-h using the curves in C. For time-salt superposition, the salt-free state is taken as the reference state, and the shift factor $a_{salt}$ for frequency is shown in Table 2. The storage modulus $G'$ and loss modulus $G''$ of the salt-containing gels are rescaled by volume change ratio $\lambda_s^3$ due to polymer density difference in per unit volume. Vertical dotted lines in B and D indicate the equivalent angular frequencies $\omega = 2\pi a_{salt} \varepsilon_0$ for the measurements at strain rate $\varepsilon_0 = 0.25$ s$^{-1}$ (a) and 2.5 s$^{-1}$ (b) for the salt-containing gels and $\varepsilon_0 = 0.25$ s$^{-1}$ (a) and 2.5 s$^{-1}$ (b) for the salt-free gels. The $\omega_v$ is the transition angular frequency from plateau regime to the viscoelastic regime. (E) Pure shear test and the geometry $L_0 = 50$ mm, $H_0 = 10$ mm, and $c_0 = 10$ mm used for characterizing toughness ($\Gamma$). (F) The rescaled toughness $\lambda_s^2 \Gamma$ against the dimensionless quantity, $D_i = 2\pi a_{salt} \varepsilon_0 / \omega_v$. $D_i$ denotes the observation strain rate in relative to the longest viscoelastic relaxation rate $\omega_v$. Red sphere: PA-s; blue sphere: PA-h. Data in F are means ± SD, $n = 3$. 

PNAS 2022 Vol. 119 No. 20 e2200678119 https://doi.org/10.1073/pnas.2200678119
Meff and M₁ are the molecular mass of strands between neighboring effective permanent cross-linking points and between neighboring dynamic bonds (Meff > M₁), respectively (25, 26). The very broad viscoelastic regime of PA gels could be attributed to the small M₁ due to the high density of dynamic bonds on the strands. Closer inspection of the master curves reveals differences between the moduli at low frequencies. The G* for PA-h is independent of frequency and much larger than loss modulus (G’) with tan δ on the order of 0.02. As a comparison, the G* of PA-s has a weak frequency dependence at low frequencies, and tan δ is larger than that of PA-h. The latter is a feature of imperfect networks owing to the gradual relaxation of imperfect structures, such as dangling structures (27). From the plateau modulus G* at the low-frequency limit, the effective permanent cross-linking densities were estimated as νc = 2.1 × 10⁻²⁴ and 1.7 × 10⁻²⁵ m⁻³, and the number of monomers per network strand are Nc,eff = 1,080 and 130 for PA-s and PA-h, respectively (Materials and Methods and Table 1). The effective permanent cross-linking results from both chemical cross-linking and trapped entanglements in this PA system, as we have demonstrated that physically trapped entanglements act similarly to chemical cross-links to control the fatigue threshold, i.e., a higher concentration of trapped entanglements induce a lower fatigue threshold (15). However, for the chemical cross-linking hydrogels without dynamic bonds, the fracture energy and fatigue threshold can be improved by entanglements, as suggested by Suo and coworkers (28) and Zhao and coworkers (29). As the weakly cross-linked PA-s still does not reach the plateau modulus at the low-frequency limit, the estimated Nc,eff might be slightly lower than the true value. Also, the αi of PA-s represents the critical frequency entering the strongly viscoelastic region.

Next, we study the fracture behaviors under nominal strain rates ε = v/H₀ = 0.25 and 2.5 s⁻¹, where v is the loading speed and H₀ is the sample height when undeformed. The corresponding measurement positions in the dynamic spectra are indicated by vertical dotted lines in Fig. 2 B and D for PA-s and PA-h, respectively. In the following sections, we use the dimensionless quantity Dᵢ = 2πνc,θiε/λ₀, to denote the observation regime. D₁ > 1 corresponds to the viscoelastic regime, and D₁ < 1 corresponds to the elastic regime. Owing to the time-salt superposition, the two strain rates ε = 0.25 and 2.5 s⁻¹ used in the measurements correspond to a wide dynamic range from the elastic regime (Dᵢ ~ 10⁻²) to viscoelastic regime (Dᵢ ~ 10⁶). Because PA-s exhibits a slight frequency dependence even in the low-frequency limit, weak viscoelasticity may exist even in the low-strain-rate limit.

Fracture energy was measured using a pure shear test (30–32). The prenotched sample was stretched to fracture, and the critical stretch ratio at which the crack propagation started was denoted as λc (Fig. 2 E and SI Appendix, Fig. S1). The fracture energy is calculated from Γ = W(λc)H₀, where W(λc) is the energy density of the unnotched sample stretched to λc. To compare the mechanical properties of the gels in the same state, the Γ and the energy release rate (G) in the following discussion are rescaled by the area swelling ratio λₛ⁻² to correct the chain density per unit area. Fig. 2 F shows that the rescaled fracture energy (λₛ⁻²Γ) increases with Dᵢ = 2πνc,θiε/λ₀, following power-law relations λₛ⁻²Γ ∼ (Dᵢ)⁺α, where α = 0.27 and 0.28 for PA-s and PA-h, respectively. This scaling exponent is consistent with the previously reported value for PA gels in the viscoelastic regime (α = 0.21) (33). We notice that this scaling relation holds for a wide strain-rate range from the elastic regime to the viscoelastic regime. This result indicates that even though the remote deformation is in the elastic regime, complex viscoelastic energy dissipation is involved in the crack advancement.

Next, we investigated the effect of strain rate on the fatigue threshold G₀, following our previous method (34). We performed a cyclic fatigue test under the nominal strain rates ε = 0.25 and 2.5 s⁻¹ using the pure shear geometry shown in Fig. 2 E. The maximum and minimum stretch ratios at each cycle were maintained at the preset values of λmax and 1, respectively. Note that the time-salt superposition approach extends the observation time scale of the fatigue test over four decades in strain rate at room temperature (Di decreases from 10² to 10⁻⁹); otherwise, one complete fatigue test at a low strain rate would take more than 6 years. During cyclic loading, we used a high-resolution digital camera (pixel size ~15 μm) for tracking the crack growth of the prenotched samples, and the crack growth length was denoted as c. The fatigue crack growth per cycle (∆c/∆N) can be obtained from the fitting slope of c in the steady state as a linear function of fatigue cycle number N (SI Appendix, Fig. S2). The energy release rate G, defined as the energy used for fatigue crack growth, is obtained by G = W(λmax)H₀, where W(λmax) is the area under the loading (We) or unloading (Wδ) curves of the unnotched sample that is cyclically loaded to a steady state when the change in loading-unloading curves becomes negligible (Fig. 3 A). Whether the loading or unloading parts should be integrated to obtain W(λmax) remains controversial (35). We will discuss it in this viscoelastic PA system.

We first show the fatigue-resistant curve of PA-s, that is, the plot of ∆c/∆N versus the rescaled energy release rate λₛ⁻²G. Fig. 3 B shows the strong rate dependence of the fatigue-resistance curves. In the large Di regime where viscoelastic effect exists (Di = 2.9 and 29, corresponding to lines a and b in Fig. 2 B, respectively), multimode fatigue resistance occurs, consistent with our previous results (15, 34). That is, a plateau with ∆c/∆N < 0.1 μm per cycle is observed at low λₛ⁻²G above the fatigue threshold, and then ∆c/∆N jumps to several orders of magnitude higher when the λₛ⁻²G becomes large. The slow fatigue mode is attributed to the presence of a mesoscale bicontinuous phase network structure that suppresses crack propagation above the fatigue threshold (15). While in the small Di regime where the viscoelastic effect almost diminishes (Di = 2.9 × 10⁻³ and 2.9 × 10⁻², corresponding to lines a’ and b’ in Fig. 2 B, respectively), ∆c/∆N increases rapidly with λₛ⁻²G above the fatigue threshold, only showing one crack propagation mode. In both regimes, the fatigue-resistant curves shift to larger λₛ⁻²G with increasing Di, suggesting enhancement of fatigue resistance due to an increase in viscoelastic dissipation. As expected, the strong viscoelastic regime shows larger discrepancies in the fatigue-resistant curves using the λₛ⁻²G calculated from Wδ and We than the weak viscoelastic regime.

From the linear plot of ∆c/∆N versus λₛ⁻²G in Fig. 3 C we obtained the fatigue threshold λₛ⁻²G₀ below which the crack did
not grow. In our fatigue test, \( G_0 \) was determined below which the crack growth was undetectable with a resolution of 15 \( \mu m \) for \( n = 50,000 \) cycles (corresponding to a resolution of 3 \( \times \) 10^{-4} \( \mu m \) per cycle). The \( \lambda^2 G_0 \) shows power-law dependence on the \( D_i \) by \( \lambda^2 G_0 \sim (D_i)^\nu \), with \( \nu = 0.18 \) and 0.10 for the \( \lambda^2 G \) calculated from \( W_{ex} \) and \( W_{el} \), respectively (Fig. 3D). This indicates that \( G_0 \) calculated from the loading part depends more strongly on the strain rate than that from the unloading part. In the viscoelastic regime, rate dependence of the fatigue threshold is inevitable due to the fast self-healing of broken ionic bonds. Based on the definition of fatigue threshold, i.e., the energy required to fracture a layer of polymer chains, using the unloading curve to calculate the fatigue threshold would be better than the loading curve. By extrapolating the two power-law relations to low strain rate, we get a better than the loading curve. By extrapolating the two power-law relations and their extrapolations to low strain rate, we get a threshold value in the elastic regime. Here, we discuss why the rate-independent phenomenon has also been observed in PA-s (corresponding to lines a’ and b’ in Fig. 2D), in the elastic regime (corresponding to lines a and b in Fig. 2D), however, there is no difference between the fatigue resistance curves for \( \lambda^2 G \) obtained from either \( W_{ex} \) or \( W_{el} \) because the hysteresis loop no longer exists (SI Appendix, Fig. S3B). Moreover, the fatigue resistance curves are rate-independent, and \( \Delta \sigma \Delta N \) increases with \( \lambda^2 G \) according to the power law of \( \Delta \sigma \Delta N \sim (\lambda^2 G)^{1.2} \). The two power-law relations of the fatigue-resistant curves in viscoelastic and elastic regimes suggest that the viscoelastic dissipation due to ionic bonds can significantly enhance the crack resistance.

The \( \lambda^2 G_0 \) value of PA-h was obtained from the linear regression of the data in Fig. 4A on a linear scale (SI Appendix, Fig. S4). Fig. 4B shows that the \( \lambda^2 G_0 \) increases slightly with increasing \( D_i \) scaling by the power law of \( \lambda^2 G_0 \sim (D_i)^\nu \) with small values of \( \nu = 0.10 \) and 0.04 for \( G_0 \) obtained from \( W_{ex} \) and \( W_{el} \), respectively. The two lines intersect at around \( D_i = 0.16 \), where the pure elastic behavior is observed by rheology test and tensile test. At \( D_i \leq 0.16 \), \( \lambda^2 G_0 \) is rate-independent. The rate-independent phenomenon has also been observed in hydrogels composed of elastic networks (36).

From the above results, in the viscoelastic regime where mechanical hysteresis exists in the steady state (\( W_{ex} > W_{el} \)), \( G_0 \) has a weak strain rate dependence, whereas \( G_0 \) becomes rate-independent in the elastic regime. Here, we discuss why the \( \lambda^2 G_0 \) increases with \( D_i = 2\pi a_{a.d} v/\omega_0 \) in the viscoelastic regime,
where hysteresis loops exist in the steady state. The hysteresis loops are derived from the association–disassociation of dynamic bonds due to fast self-healing rate under cyclic fatigue. These repeated debonding and rebonding of dynamic bonds carry load and dissipate energy and thereby protect the permanent bonds from breaking. We notice that the scaling exponent \( \lambda \) in \( \lambda^2 G_0 \sim (D)^\alpha \) of the fatigue test (Figs. 3D and 4B) is much smaller than \( \alpha \) in \( \lambda^2 T \sim (D)^\alpha \) of the pure shear fracture test (Fig. 2F). The difference could be for three reasons. The first is different ionic bond density: In the fatigue test, only a small fraction of ionic bonds carry load at the steady state, as seen from the shakedown of the hysteresis loop with the increase of cycle (Fig. 3A), while in fracture test all the ionic bonds carry load and dissipate energy.

The second is different crack propagation rate: Crack propagation rate \( (V_c) \) in the fracture test is larger than \( V_c = 5 \times 10^{-5} \mu \text{m/s} \). Given the crack-tip load-transfer length \( I = \Gamma W^\alpha \sim 2 \text{ mm} \) \( [W^\alpha \text{ is the energy density of the unnotched sample stretch up to catastrophic failure (3, 37)] \), the lowest strain rate at the crack tip is \( V_c/I = 25 \text{ s}^{-1} \), which means the local loading rate at the crack tip is much larger than the bulk deformation rate. This also may be the reason that fracture energy in the elastic regime follows the same scaling relation as that in viscoelastic regime (Fig. 2F).

On the other hand, at the threshold condition of fatigue test, the crack advancing was not observed with a resolution of \( \sim 10^{-4} \mu \text{m/s} \). This limit value is eight decades lower than that in the fracture test. The third is different stress singularity conditions: Based on the birefringence observation, the stress singularity around the crack tip is gradually eliminated with increasing fatigue cycles in slow crack propagation mode (15). In contrast, strong stress concentration exists in the fracture test (38).

Finally, we examine if \( G_0 \) in the elastic regime could be explained by the Lake–Thomas model (13). In the Lake–Thomas model, \( G_0 \) is the energy required to rupture polymer strands lying across the crack plane,

\[
G_0 = A \xi \nu_t N_c \varepsilon_b,
\]

where \( A \) is a prefactor, \( \xi \) is the average distance between permanent cross-links, \( \xi = \nu_t^{-1/3} \), and \( \varepsilon_b \) is the bond dissociation energy for a carbon–carbon bond, typically 350 kJ/mol. Substituting the value of \( \nu_t \) and \( N_c \varepsilon_b \) obtained from rheological measurement (Table 1), we get \( G_0 = A \times 10.1 \) and \( A \times 5.1 \text{ J/m}^2 \) for PA-s and PA-h, respectively. Intriguingly, considering that one repeating unit of monomer contains two carbon–carbon bonds, taking \( A = 2 \) to correct the fracture energy for one strand \( (N_c \varepsilon_b \varepsilon_b) \), we obtain a theoretical value of \( G_0 = 10.2 \text{ J/m}^2 \) for PA-h. This value is close to the experiment value of rate-independent \( \lambda^2 G_0 = 9 \text{ J/m}^2 \) at the elastic regime (Fig. 4B), consistent with the observation in nearly elastic hydrogels (39, 40). However, a slightly larger value of \( A = 2.7 \) is required for PA-s to make the theoretical value of \( G_0 \) agree with the experimental value of \( \lambda^2 G_0 = 27.3 \text{ J/m}^2 \) obtained from the intersection of extrapolation of two power-law relations (\( W_{ex} = W_{d0} \)) in Fig. 3D, where no viscous dissipation is involved in the deformation. A more systematic study of the relationship between the permanent cross-linking structure and \( G_0 \) is required in future to quantify the prefactor \( A \) in Eq. 2.

**Conclusion**

We demonstrated that the fatigue threshold \( G_0 \) is weakly rate-dependent in the viscoelastic regime, whereas \( G_0 \) in the elastic regime is rate-independent and agrees with the predicted value from the Lake–Thomas model. In the viscoelastic regime, the dynamic bonds carry load, protecting the permanent bonds from breaking, and thereby contribute to \( G_0 \). Moreover, the fatigue history on dynamic bonds is forgotten due to the self-healing property. By designing dynamic bonds with a relatively long relaxation time so that the observation (working) time window falls in the viscoelastic regime, we can improve the fatigue resistance of soft materials by improving \( G_0 \).

In this work, we discussed the physical features of fatigue resistance of self-healing hydrogels with dynamic bonds from a linear rheology viewpoint. In the viscoelastic regime, the breaking kinetics of dynamic bonds should depend on the stress/strain being experienced by the dynamic bonds, especially at large deformation. This nonlinear rheological effect has been observed in the tensile behaviors of polyampholyte hydrogels (41, 42). How the nonlinear rheology effect influences the fatigue behaviors of self-healing materials is unknown. To address this question, studying the fatigue behaviors in the regime \( \varepsilon \gg \varepsilon_0^{-1} \), where the nonlinear rheology effect could be mostly prominent, is needed. At such a condition, whether the dynamic bonds bring a similar physical effect as that in the short-and- long-chain double network materials or not could be clarified. Using self-healing hydrogels with a relatively long lifetime of dynamic bonds will allow us to study these behaviors.

**Materials and Methods**

**Sample Information**. The PA gels used in this work were prepared following the method in refs. 6, 43, and 44. In short, the precursor solution containing cationic monomer methyl chloride quarternized \( N,N \)-dimethylamino ethylacrylate...
The principle was applied to construct the master curves of frequency sweep of the loosely cross-linked PA-2.0-0.1 (denoted as PA-s) and one densely cross-linked PA-2.5-1.0 (denoted as PA-h). The sodium chloride NaCl concentration (C_{NaCl}) in the as-prepared gels, which is introduced by the crosslinkers on the cationic and anionic monomers, are χ_{C_{NaCl}} = 2.125 and 1.0 M for PA-h and PA-s, respectively. Half of the as-prepared gels were immersed in a large amount of 30 °C deionized water to dialyze for at least 1 month to remove counterions until equilibrium was reached. The deionized water was changed every day. As indicated in our previous work (6), the elemental analysis suggests the water-equilibrated PA-gels prepared at the charge balance point are free of counterions. The water-equilibrated state were taken as the reference state in all the experiments. Taking the length-swelling ratio of the undeformed water-equilibrated gels as 1, the relative length-swelling ratio of undeformed as-prepared gels is χ_{0} (Fig. 1). A pure shear test was used to characterize the toughness of the gels, and cyclic loading was used for fatigue testing using a sample with the pure shear geometry (Fig. 2). The nominal strain rates of ε = v/l_{ls} = 0.25 s^{-1} and 2.5 s^{-1} were applied, where v is the loading speed and l_{ls} is the initial sample height. All of the pure shear and fatigue tests were performed at room temperature. To prevent the sample from dehydrating during the test, we kept the water-equilibrated gels in a water vapor atmosphere during the test as shown in ref. 34, and the as-prepared gels were smeared with silicone oil on the surface layers. The stress (σ)-strain (ε) curves were recorded during the pure shear and fatigue tests, where σ is the force over the initial undeformed cross-sectional area and ε is the ratio between the deformed sample height and the initial sample height. The method to use σ-ε curves to obtain fracture energy (Γ) and energy release rate (G) is shown in SI Appendix, Fig. S1 and Fig. 3A, respectively.

Data Availability. All data are included in the main text and SI Appendix.

ACKNOWLEDGMENTS. We gratefully acknowledge support from Japan Society for the Promotion of Science KAKENHI grantJP17H06144.

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