Dynamics of Dual Networks: Strain Rate and Temperature Effects in Hydrogels with Reversible H-Bonds

Xiaobo Hu, Jing Zhou, William F. M. Daniel, Mohammad Vatankhah-Vanoosfaderani, Andrey V. Dobrynin, and Sergei S. Sheiko

ABSTRACT: Combining high concentration of reversible hydrogen bonds with a loosely cross-linked chemical network in poly(N,N-dimethylacrylamide-co-methacrylic acid) hydrogels produces dual-network materials with high modulus and toughness on par with those observed for connective tissues. The dynamic nature of the H-bonded cross-links manifests itself in a strong temperature and strain rate dependence of hydrogel mechanical properties. We have identified several relaxation regimes of a hydrogel by monitoring a time evolution of the time-average Young’s modulus \(\langle E(t)\rangle = \sigma(t)/\dot{\varepsilon}\) as a function of the strain rate, \(\dot{\varepsilon}\), and temperature. At low temperatures (e.g., 3 °C), \(\langle E(t)\rangle\) first displays a Rouse-like relaxation regime \((-\frac{t}{\tau^R})\), which is followed by a temporary (physical) network regime \((-\frac{t}{\tau^P})\) at intermediate time scales and then by an associating liquid regime \((-\frac{t}{\tau^L})\) at the later times. With increasing temperature to 22 °C, the temporary network plateau displays lower modulus values, narrows, and shifts to shorter time scales. Finally, the plateau vanishes at 37 °C. It is shown that the energy dissipation in hydrogels due to strain-induced dissociation of the H-bonded cross-links increases hydrogel toughness. The density of dissipated energy at small deformations scales with strain rate as \(U_T \sim \dot{\varepsilon}^{0.53}\). We develop a model describing dynamics of deformation of dual networks. The model predictions are in a good agreement with experimental data. Our analysis of the dual network’s dynamics provides general frameworks for characterization of such materials.

1. INTRODUCTION

The introduction of reversible (physical) cross-links to a permanent (chemical) network allows for effective control of the network mechanical properties in both linear (modulus) and nonlinear (extensibility and toughness) deformation regimes. Such dual polymer networks are employed in a broad range of applications including self-assembly, self-healing, shape-memory, molding, and tissue engineering. This broad variety of applications is driven by the network ability to evolve by breaking and re-forming physical cross-links on experimentally relevant time scales (seconds to hours). Because of the dynamic nature of dual networks, their mechanical properties not only are determined by the network structure but also depend on deformation conditions, i.e., strain rate and temperature.

In strain-rate-controlled experiments, an increase in deformation speed entails faster dissociation of physical cross-links, which requires a higher mechanical stress, resulting in a corresponding increase in network modulus and toughness. If the strain rate, \(\dot{\varepsilon}\), is larger than the inherent (stress-free) dissociation rate constant, \(k_p\), of the physical cross-links (\(\dot{\varepsilon} > k_p\)), the network deformation process leads to significant dissociation of the mechanical energy and an increase of apparent toughness (Figure 1). At slower strain rates, such that \(\dot{\varepsilon} < k_p\), the dissociation–association of physical cross-links does not require any mechanical stimulation, and the amount of energy dissipation is negligible. At these deformation conditions, the same material behaves as a soft elastic network and possesses a low toughness (Figure 1). In other words, dual networks with physical cross-links could be either rigid-and-tough or soft-and-weak depending on the deformation strain rate, \(\dot{\varepsilon}\). Yet, in both cases, the networks remain highly extendable and elastic due to the loose chemical network. A similar level of control over network’s mechanical properties can be achieved by changing temperature, which shifts the dissociation rate constant of the physical cross-links with respect to an applied strain rate. Note that temperature has a dual effect: in addition to changing the thermal energy in the Boltzmann factor, a temperature variation changes the dissociation energy of physical cross-links, which causes the corresponding shifts in the equilibrium constant and concentration of the physical cross-links.

Herein, we report strain rate and temperature dependence of both the small deformation property (modulus) and large deformation properties (strength and toughness) of poly(N,N-dimethylacrylamide-co-methacrylic acid) hydrogels. The de-
signed materials integrate a loose permanent covalent network and a dense H-bonded (physical) network, which undergoes recurrent dissociation and reassociation during deformation.36 Because of the ambiguity of using the time−temperature superposition principle for construction of master curve of the dual networks, our approach is based on analysis of the evolution of time-average Young’s modulus in both linear and nonlinear deformation regimes of hydrogel films undergoing uniaxial extension in broad ranges of strain rates and temperatures.

2. EXPERIMENTAL SECTION

2.1. Materials. N,N-Dimethylacrylamide (DMAA), methacrylic acid (MAAc), ammonium persulfate (APS), and N,N,N,N′-tetramethylethylenediamine (TEMED) were used as received (Sigma-Aldrich). Water was produced by distillation followed by deionization to a resistance of 18 MΩ cm, followed by filtration through a 0.2 μm filter to remove particulate matter.

2.2. Preparation of Dual-Network Hydrogels. The dual-network hydrogels were synthesized by a one-step copolymerization of DMAA and MAAc with a total monomer concentration of 33 wt %. A mixed aqueous solution of DMAA and MAAc monomers with a feeding molar ratio of 4:6, together with 0.5 mol % APS (relative to the total monomer concentration), was degassed with N2 for 20 min. TEMED was added to the solution, and the solution was then transferred to a glass mold with a polydimethylsiloxane (PDMS) spacer to polymerize at room temperature under a N2 atmosphere for 48 h. In this reaction, no additional chemical cross-linker was added. A low fraction of chemical cross-links is produced in situ due to the chain transfer reaction in copolymers with DMAA. Besides, the multiple intermolecular hydrogen bonds were stabilized by the hydrophobic interactions due to the presence of the α-methyl groups of PMAAc.36

2.3. Characterization of Hydrogels. Tensile tests were carried out using dynamic mechanical analysis (RSA-G2, TA Instruments) with an immersion clamps accessory. Samples with a thickness of 1.5 mm were cut into dumbbell-shaped samples (DIN 53504-S3, 2 mm in width with an initial length $L_0$ of 12 mm). The tensile deformation was performed within a broad range of strain rates from 0.00015 to 0.05 s$^{-1}$ at controlled temperature. In order to avoid water evaporation, all of the mechanical tests were carried out in silicone oil. The engineering stress $\sigma$ was estimated from the stretching force divided by the cross-section area of the undeformed sample. The engineering

![Figure 1. Schematic representation of stress−strain curves of dual networks at different strain rates. At low strain rate ($\dot{\varepsilon} < \dot{k}_p$), the network behaves as a loose pure chemical network. With increasing strain rate ($\dot{\varepsilon} > \dot{k}_p$), the deformation process leads to significant dissipation of mechanical energy and, hence, an increase of both apparent toughness and apparent modulus. Higher strain rate results in higher dissipated energy and thus higher toughness and modulus. The dissipated energy due to the dissociation of physical cross-links is measured as the area under the stress−strain curve after subtraction of the elastic energy stored in the chemical network.](image1)

![Figure 2. Tough and elastic dual networks with H-bonds. (a) Chemical structure of dual networks with chemical cross-links and reversible H-bonds. Schematic representation of the initial dual-network state before deformation (i), stretching of polymer chain under mechanical loading (ii), and the dissociation and reassociation of H-bonds during deformation (iii). The chemical cross-links provide shape recovery, while the dissociation/reassociation of H-bonds controls dual-network toughness. (b) Stress−strain curves of tensile tests with repeated loading and unloading cycles ($\dot{\varepsilon} = 0.015$ s$^{-1}$, $\varepsilon_{\text{max}} = 0.5$) of the same hydrogel specimen. All cycles were run at 22 °C in silicone oil. After each cycle, the samples were annealed for 1 h at 22 °C or 3 min at 37 °C in silicone oil. (c) Two loading and unloading cycles ($\dot{\varepsilon} = 0.05$ s$^{-1}$, $\varepsilon_{\text{max}} = 6$) of the same hydrogel sample with 4 h rest at 22 °C in silicone oil. Both cycles were run at 22 °C in air, using samples coated with silicone oil.](image2)
strain ε was estimated from the gap change (ΔL) divided by L₀. Loading–unloading experiments were performed in order to characterize the hysteresis.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties of Dual Networks. Figure 2a shows the chemical structure of the dual-network hydrogel composed of N,N-dimethylacrylamide (DMAA) and methacrylic acid (MAAc) copolymers, which form low concentration of covalent (chemical) bonds and high concentration of H-bonds (physical cross-links). Because of the presence of strong, dense, and reversible H-bonds, hydrogels can have a Young’s modulus of ∼30 MPa and fracture energy of ∼10 kJ m⁻² (at 22 °C, ε̇ = 0.083 s⁻¹), which is similar to the mechanical properties of connective tissues such as ligament and cartilage. As mentioned in the Introduction, these values should be regarded as apparent properties that depend on the deformation conditions including temperature and strain rate. At the onset of deformation (small strains ∼1%), both chemical and hydrogen-bond cross-links are largely intact, and their total density determines the Young’s modulus of the dual-network hydrogel. With increasing deformation, H-bonds start to dissociate and then reassociate with new neighbors relaxing the stress, while the chemical network strands remains strained (Figure 2a, i—iii). Both types of cross-links play distinct roles in the mechanical response: the chemical cross-links control the network elasticity and maintain the sample integrity at large deformations, whereas the recurrent dissociation/reassociation of the H-bonds controls material’s rigidity and toughness by supporting the external stress at a high level. Upon unloading, the stress stored in the strained covalent network facilitates the reverse dissociation/association of the transient H-bonds to restore both the original stress-free shape and mechanical properties (Figure 2a, iii to i). To explore this unique behavior, we performed cyclic loading–unloading tests in a broad range of maximum strains from 50 to 600%. Figure 2b shows the behavior of a sample uniaxially extended up to a relatively low strain of 50% (ε = 0.5). The hydrogel exhibits pronounced hysteresis (0.2 MJ m⁻³) and retains significant deformation (ε = 0.4) after unloading. The large hysteresis can be explained by significant energy dissipation due to the dissociation of H-bonds as illustrated in Figure 2a-iii. After resting in silicone oil at 22 °C for 1 h, the unloaded sample fully recovers its original shape and mechanical properties as evidenced by the second loading–unloading curve lying right on top of the first cycle (Figure 2b). Annealing at a higher temperature of 37 °C allows for much faster sample recovery (3 min) as verified by the third loading–unloading curve shown in Figure 2b. This is consistent with a higher rate of H-bond dissociation with increasing temperature. Both the shape and material properties are fully recovered even after very large deformations. Figure 2c shows an excellent elastic behavior of the rigid hydrogel (E ∼ 10 MPa) extended to a prerupture strain of 600% (ε = 6), which suggests both the robustness of the chemical network and reversibility of deformations, whereas the recurrent dissociation/reassociation of the H-bonds controls material’s rigidity and toughness by supporting the external stress at a high level. Upon unloading, the stress stored in the strained covalent network facilitates the reverse dissociation/association of the transient H-bonds to restore both the original stress-free shape and mechanical properties (Figure 2a, iii to i). To explore this unique behavior, we performed cyclic loading–unloading tests in a broad range of maximum strains from 50 to 600%. Figure 2b shows the behavior of a sample uniaxially extended up to a relatively low strain of 50% (ε = 0.5). The hydrogel exhibits pronounced hysteresis (0.2 MJ m⁻³) and retains significant deformation (ε = 0.4) after unloading. 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the H-bonded cross-links in the physical network during the entire deformation process. In the next section, we analyze individual contributions of both networks at different stages of the deformation process as a function of the strain rate and temperature.

### 3.2. Time-Average Network Modulus

Characterization of the mechanical properties of dual networks is not a trivial task. Unlike the conventional polymer systems, where dynamic properties are determined by one characteristic relaxation time, i.e., characteristic monomer relaxation time, \( \tau_p \), associated with polymer segmental motion, physical networks have an additional relaxation process associated with the lifetime of the physical cross-links, \( \tau_f \). Both relaxation times have different temperature dependences and distinct activation energy barriers. This makes construction of a master curve using the conventional time—temperature superposition approach ambiguous since the physical network structure changes with temperature as well.\(^{20,37} \)

Therefore, to characterize the mechanical properties of the dual networks at small deformations, we use a linear viscoelasticity approximation to calculate evolution of the time-average Young's modulus during uniaxial extension at a constant temperature. At a given strain rate, \( \dot{\varepsilon} \), the tensile stress increases with time as

\[
\sigma(t) = \int_0^t \tau(t') d\varepsilon(t') = \dot{\varepsilon} \int_0^t \tau(t) \, dt = \varepsilon(t) \langle E(t) \rangle
\]

where \( \varepsilon(t) = \dot{\varepsilon} t \) is a strain at time \( t \) and \( \langle E(t) \rangle \) is the time-average network Young's modulus:

\[
\langle E(t) \rangle = \int_0^t \tau(t) \, dt
\]

(1)

In the case of the power law dependence of the relaxation modulus

\[
E(t) \cong E_0 \left( \frac{\tau_0}{t + \tau_0} \right)^{\alpha}
\]

where \( E_0 \) is the Young’s modulus at monomeric time scales; the integration in eq 2 gives the following relation for the time-average modulus as a function of time

\[
\langle E(t) \rangle \cong E_0 \left( \frac{\tau_0}{t} \right)^{\alpha}
\]

(3)

Thus, time-average modulus maintains the same power law as the relaxation modulus in eq 3. However, for an exponential relaxation behavior, \( E(t) \sim \exp \left( -\frac{t}{\tau} \right) \), the time averaging in accordance with eq 2 results in linear decay of the time-average Young’s modulus \( \langle E(t) \rangle \sim t^{-1} \) on the time scales \( t > \tau_0 \). We will apply the outlined formalism of the time averaged Young’s modulus to analyze stress—strain curves obtained for dual networks.

**Figures 3a,c,e** show stress vs strain curves measured in a small deformation range at different strain rates ranging from 0.00015 to 0.05 s\(^{-1} \) and three different temperatures equal to 3, 22, and 37°C. As anticipated from mechanochemistry of physical bonds,\(^{35} \) the stress level decreases with strain rate, resulting in the different stress—strain behaviors. However, we were able to collapse all data sets shown in **Figures 3a,c,e** by plotting the time-average Young’s modulus \( \langle E(t) \rangle = \sigma(t)/\varepsilon(t) \) as a function of time \( t = \varepsilon/\dot{\varepsilon} \) in **Figures 3b,d,f**, respectively. **Figure 3b** (\( T = 37°C \)) displays three different deformation regimes that can be identified by using a scaling model of deformation of an associating network with relatively strong reversible bonds \( (\tau_f > \tau_p) \) as shown in **Figure 4** (eqs S1–S11). It is important to point out that our scaling model for the time average Young’s modulus explicitly considers network relaxation processes at all time scales (see **Figure 4** and Supporting Information for details). In this respect it is different from the recently developed models of the reversible networks dynamics that neglect strands’ Rouse modes.\(^{26,38–40} \) At short time scales \( (t = \varepsilon/\dot{\varepsilon} < 0.1 \, s) \), the modulus decreases with time as \( \langle E(t) \rangle \sim t^{-0.45 \pm 0.03} \), which is attributed to the relaxation of network strands between H-bonded cross-links. This relaxation is consistent with a Rouse dynamics of polymer chains \( (\alpha = 0.5 \) in eq 3), for which the time average network modulus scales with time as \( \langle E(t) \rangle \sim t^{-1/2} \) (eq 4). In the intermediate time range, the modulus relaxation slows down as \( \langle E(t) \rangle \sim t^{-0.14} \), resulting in an apparent plateau due to the presence of a dense physical network of H-bonds. The high cross-linking density results in a high plateau modulus of around 10\(^8 \) Pa, which corresponds to the Young’s modulus of the physical network. After pausing at the temporary network plateau for a certain time, the modulus continues its relaxation through recurring dissociation/reassociation of the H-bonds. In this regime, the system behaves as an associating liquid \( (\langle E(t) \rangle \sim t^{-0.03}) \), where the physical network continues breaking and rearranging into a stress-relaxed configurations. Then the modulus will reach a plateau in the permanent chemical network regime at longer time (**Figure 4**). However, network deformation should be performed at extremely small strain rates to achieve this regime experimentally. At a higher temperature of 22°C (**Figure 3d**), the plateau seen in **Figure 3b** becomes an inflection and shifts to shorter times. This is consistent with the physical network model (**Figure 4**), which suggests a 2-fold effect of a temperature increase: (i) it results in a decrease of the conversion \( p \) of the associating groups, and (ii) it shortens the
lifetime of physical cross-links, $\tau_l$. The decrease in the physical cross-link conversion and lifetime also shifts crossover to the chemical network regime to shorter time scales (Figure 4). The onset of the chemical network plateau at $\langle E(t) \rangle \sim 2 \times 10^5 \text{ Pa}$ is clearly seen in Figure 3d. As the temperature increases to 37 °C (Figure 3f), the time-average modulus decreases with time as $\langle E(t) \rangle \sim t^{-0.55 \pm 0.03}$ at short time scales and then shows a small inflection followed by a faster decay ($\langle E(t) \rangle \sim t^{-0.91 \pm 0.05}$). At longer times (~10 s), the modulus levels off at $\langle E(t) \rangle = 2 \times 10^5 \text{ Pa}$—the modulus of the permanent chemical network (Figure 4). In other words, the H-bonds do not affect the network mechanical properties at high temperatures.

### 3.3. Energy Dissipation in Dual Networks

The combination of the dense physical network and loose chemical network allows dual networks to dissipate large amount of energy upon deformation. In this section, we characterize dual-network toughness as a function of strain and strain rate. Figure 5a displays a series of loading–unloading cycles that were measured at an intermediate strain of $\varepsilon_{\text{max}} = 0.5$ and different strain rates ranging from 0.00015 to 0.05 s$^{-1}$. The hysteresis area between the loading and unloading curves of a gel gives the energy dissipated per unit volume,77 which is directly related to reversible dissociation of the H-bonded cross-links and exhibit strong dependence on the strain rate. As shown in Figure 5b, the hysteresis increases with strain rate at a distinct power law with exponent $\alpha = 0.53$, which directly follows from the time dependence of the time-averaged Young’s modulus $\langle E(t) \rangle$ shown in Figure 3d. Indeed, for deformation at a constant strain rate, we can express stress in a physical network system in accordance with eqs 1–4 as

$$\sigma(\varepsilon) \cong E_0 f_0 \varphi^{0.53} \varepsilon^{0.47} \sim \varepsilon^{0.53}$$

This implies that the hysteresis area obtained from loading–unloading cycle (hysteresis or dissipated energy density) should also scale with the strain rate as $\dot{\varepsilon}^{0.53}$ since

$$U_T = \int_0^\varepsilon \sigma(\varepsilon) \, d\varepsilon \sim \varepsilon^{0.53}$$

The strain rate dependence weakens with the increasing strain rate (Figure 5b and Figure S2), which could be explained by the crossover to the glassy regime at $\dot{\varepsilon} < \dot{\varepsilon}_0$ as shown in Figure 4 and time dependence of the Young’s modulus given by eq 3. In the Supporting Information we have verified that the contribution of the elastic energy due to deformation of the chemical network (Figure 1) to the hysteresis area is negligibly small (Figures S1 and S2).

### 3.4. Yielding Instability and Temperature-Dependent Mechanical Properties

The mechanical properties of the dual network show a strong temperature dependence which controls the dissociation rate of the H-bonds. This is manifested in significant variations of the form of the $\langle E(t) \rangle$ curves upon the temperature increase from 3 to 37 °C as shown in Figure 3. A similar behavior was observed for the yield stress (Figure 6). Figure 6a shows a series of tensile stress–strain curves measured at different temperatures and a constant strain rate of 1 s$^{-1}$. At temperatures lower than 37 °C, the inherent dissociation rate constant, $k_p$, of the hydrogen bonds is much smaller than the strain rate ($k_p \ll \dot{\varepsilon}$). As a result, the higher strain rate tends to enhance the strain localization and thus promote necking, which induces a significant drop in stress.
Lower temperature results in a larger stress decrease. We also conducted loading–unloading measurements at a strain rate of 0.015 s\(^{-1}\) and temperatures between 10 and 37 °C (Figure S3). Similar to the effect of a strain rate decrease, the increase of temperature results in decay of mechanical strength of the dual networks, including yield stress, fracture stress, and toughness (Figure S3). In contrast, the elongation at break exhibits a steady increase with temperature (Figure 6a). All these observations are consistent with the decrease in the conversion of H-bonds and with weakening of their strength at higher temperatures. This in turn results in lower energy dissipation during deformation.

The temperature/strain rate variations of the yield stress and strain can be used to evaluate the mechanochemical parameters of the H-bond cross-links, including dissociation energy and activation volume. We have extended the Eyring model of stress-induced bond dissociation (renormalization of the bond activation volume. We have extended the Eyring model of of the H-bond cross-links, including dissociation energy and strain can be used to evaluate the mechanochemical parameters during deformation.

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Table 1. Yielding Parameters and the Fitting Results

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<th>ε(_f)</th>
<th>E(_p) (MPa)</th>
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The Young’s modulus of the physical network, E\(_p\) at different temperature is estimated from the plateau modulus (inflection point) as shown in Figure 3b,d and Figure S4e (Table 1). By using the obtained values for σ\(_{eg}\) and ε\(_f\) from Figures S4a,b and S5 (Table 1), we plot ln(−ε\(_f\) ln(σ\(_{eg}\)/E\(_p\))) versus σ\(_{eg}\)(1 + ε\(_f\)) based on eq 9. As shown in Figure 6b, the slopes ν/k\(_B\)T are all around 3 MPa\(^{-1}\) for all the temperature, which gives a temperature-independent activation volume ν around 12 ± 1 nm\(^3\) (Table 1). This number is relatively large compared to mechanical activation of individual chemical bonds (∼0.1 nm\(^3\)), which means that yielding instability involves the cooperative movement of a larger number of chain segments, suggesting activation of larger species like clusters of hydrogen-bonds.\(^{41,42}\)

Based on the intercept ln(1/τ\(_l\)) of the fitting curves, the value of lifetime, t\(_l\) can be estimated for each temperature (Table 1), which is in the same order of magnitude to the experimental data in Figure 3. The apparent activation energy E\(_a\) is obtained from the Arrhenius equation, τ\(_l\) = τ\(_0\) exp(E\(_a\)/RT), where R is the gas constant and T is the absolute temperature (see inset in Figure 6b). This energy is lower than the dissociation energy of covalent bond (around 350 kJ mol\(^{-1}\)) but much higher than the dissociation energy of an individual hydrogen bond in water. This suggests formation of clusters of H-bonds that were observed during synthesis of these hydrogels.\(^{36}\)

4. CONCLUSIONS

Unique mechanical properties of dual-network hydrogel and their dependence on the strain rate and temperature are manifestations of the dynamics of reversible hydrogen bonds. In the limit of small deformations, modulus and toughness of hydrogel decrease with decreasing strain rate or with increasing temperature. In this deformation regime, the time-average Young’s modulus (∥ E(t)∥) drops 3 orders in magnitude (from 10\(^6\) to 10\(^5\) Pa) and demonstrates different relaxation regimes (see Figures 3). At low temperatures (3 °C), the time-average Young’s modulus ⟨E(t)⟩ first shows a Rouse-like relaxation of strands between physical cross-links, which is followed by a weaker time dependence due to a temporary plateau of physical network of H-bonds. The physical network plateau is followed by an associating liquid regime with ⟨E(t)⟩ ∼ t\(^{−1}\) as shown in Figure 4. With increasing temperature, both the conversion of the H-bonds and their lifetime decrease, resulting in shift of the crossovers between different network relaxation regimes (see
At lower strain rate or higher temperature, the chemical network dominates the mechanical response, resulting in small hysteresis of stress-strain curves during loading and unloading cycle. This is exactly what one would expect in a regime where the H-bonds relax much faster than the experimental time scale. At higher strain rates and lower temperature, the dual networks exhibit significant energy dissipation due to strain-induced dissociation of the H-bond cross-links, which leads to the corresponding increase in toughness. At small deformations the dissipated energy density first increases with increasing deformation strain rate as $U_T \sim \varepsilon^{6.53}$ and then begin to saturate (see Figure 2b). The analysis of the yielding instability allows to estimate the chemomechanical parameters of the H-bonded cross-links such an activation volume of 12 nm$^3$ and an apparent activation energy of 140 kJ mol$^{-1}$. These values are consistent with the clustering of H-bonds in the studied hydrogels. Our approach to the analysis of mechanical properties of dual networks can be extended to describe other physical networks and guide the design of tough materials for specific applications and environmental conditions.

**REFERENCES**


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