Nonlinear Viscoelasticity and Toughening Mechanisms in Nanoclay-PNIPAAm Double Network Hydrogels.

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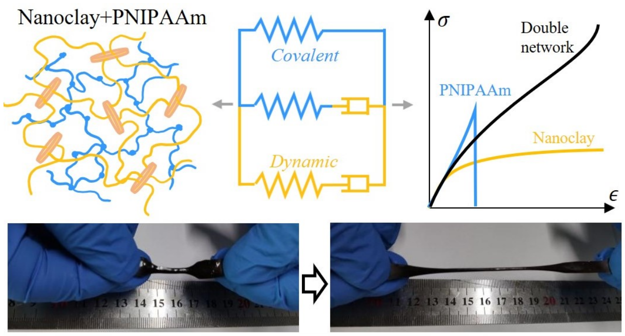
Abstract

We investigate the mechanical properties of a magnetic temperature-sensitive hydrogel at varying concentrations of covalent and physical crosslinking. The hydrogel consists covalently cross-linked Poly(N-isopropylacrylamide) (PNIPAAm), physically interacting nanoclay particles, and magnetic ferric oxide nanoparticles. The physical nanoclay network exhibits strong viscoplastic behavior, and we find that increasing nanoclay content improves both strength and toughness in the double network materials. We investigate the behavior of the gels using a nonlinear viscoplasticity model with a modified rule of mixtures approach and attribute the observed trends to two factors: (a) the yield-stress behavior of the nanoclay network and (b) load-sharing interactions between the PNIPAAm and the nanoclay. Our findings indicate a strong correlation between the mass ratio of covalent crosslinker used and fractional percolation of the PNIPAAm network.



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In recent years, smart hydrogels composed of three-dimensional hydrophilic polymeric networks have shown great promise for use in many developing fields of materials. These gels can be comprised of bio-compatible polymers and typically contain large amounts of water, which regulates their mechanical behavior to be similar to that of biological tissues.[1] Furthermore, they may be chemically modified to sense and react to external stimuli including temperature, light, and magnetic fields.[2–4] One particularly promising class of hydrogels based on poly-N-isopropyl acrylamide (PNIPAAm) display reversible swelling behavior at temperatures near room-temperature,[5,6] which suggests a variety of applications in bionic soft robots,[7,8] smart actuators,[9,10] and drug delivery.[11] Despite this promising feature, their realization in many of these applications relies on increasing the speed of actuation and overcoming their fragile nature.[12,13]

One modification that as been shown to greatly improve the mechanical properties of PNIPAAm gels is nanoclay particles added during synthesis.[8,14,15] In these materials, polymer chains are typically grafted to the nanoclay surface via polar or ionic interactions, creating a secondary physical network within the covalently crosslinked gel.[14,16,17] The topology of the particles, which typically takes the form of platelets or thin rods,[18] is thought to play a role in the secondary network that is created. The resulting toughness and elasticity are observed to be greatly improved in these materials, with stretchability exceeding 1000% in contrast to a covalent PNIPAAm hydrogel, which may fail at closer to 50% stretch.[15,19] This is achieved without affecting the swelling capabilities of the gel at the critical temperature. While the topology of the nanoclay network has been studied in isolation, the role of the hybrid physical-covalent polymer network on the elastic and viscoelastic properties of the material remains largely unknown.[18]

The goal of this study was to understand the interplay between physical bonding and covalent bonding in a double-network thermosensitive hydrogel based on PNIPAAm and Laponite nanoclay. We began by synthesizing five different hydrogels using deionized water as solvent, N-isopropylacrylamide (NIPAM) as temperature-sensitive monomers, N,N'-methylenebisacrylamide (BIS) as the covalent cross-linker, lithium magnesium silicate nanoparticles (Laponite XLG) as the physical cross-linker, and ferric oxide nanoparticles (Fe_3O_4) as magnetic particles, which are added to improve the actuation of the material but do not greatly affect the mechanical properties.[7,20] To assist the synthesis process, tween 20 (TWEEN®20) was used as a surface activator, ammonium persulfate (APS) was used as an initiator, and N, N, N', N'-tetramethylethylenediamine (TEMED) was used as a promoter. The preparation process is shown in Fig. 1a.

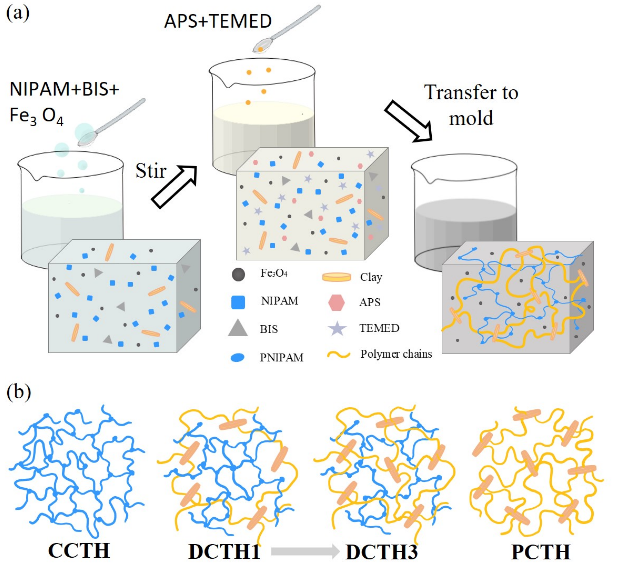

Figure 1: (a) Illustration of the synthesis procedure for magnetic temperature-sensitive hydrogels. (b) Schematic of network architectures with increasing nanoclay content ranging from 0% (CCTH) to 100% (PCTH).

During the preparation process, NIPAM monomers react with the cross-linking agents and create a percolated covalent network consisting primarily of covalent bonds.[21] The internal network of the Laponite nanoclay creates a lamellar structure, which results in large clusters of nanoclay that are physically bonded by polymer chains.[16] By varying the ratio of BIS to nanoclay, we observe a transition from an elastically-dominated material to one that displays strong visco-plastic behavior, which is a function of the percolation of each respective network (Fig. 1b). The resulting double network cross-linked magnetic temperature-sensitive hydrogel (DCTH) thus has a rich variety of behaviors due to its multi-component structure. In this letter, five different ratios of hydrogels were prepared, all of which were identical except for the relative cross-linking agent content. The range of Laponite quantity was swept over 0.1g, 0.2g, and 0.3g, denoted as DCTH1, DCTH2, and DCTH3. To set a control group, we also prepared gels consisting of only covalent crosslinker, which is

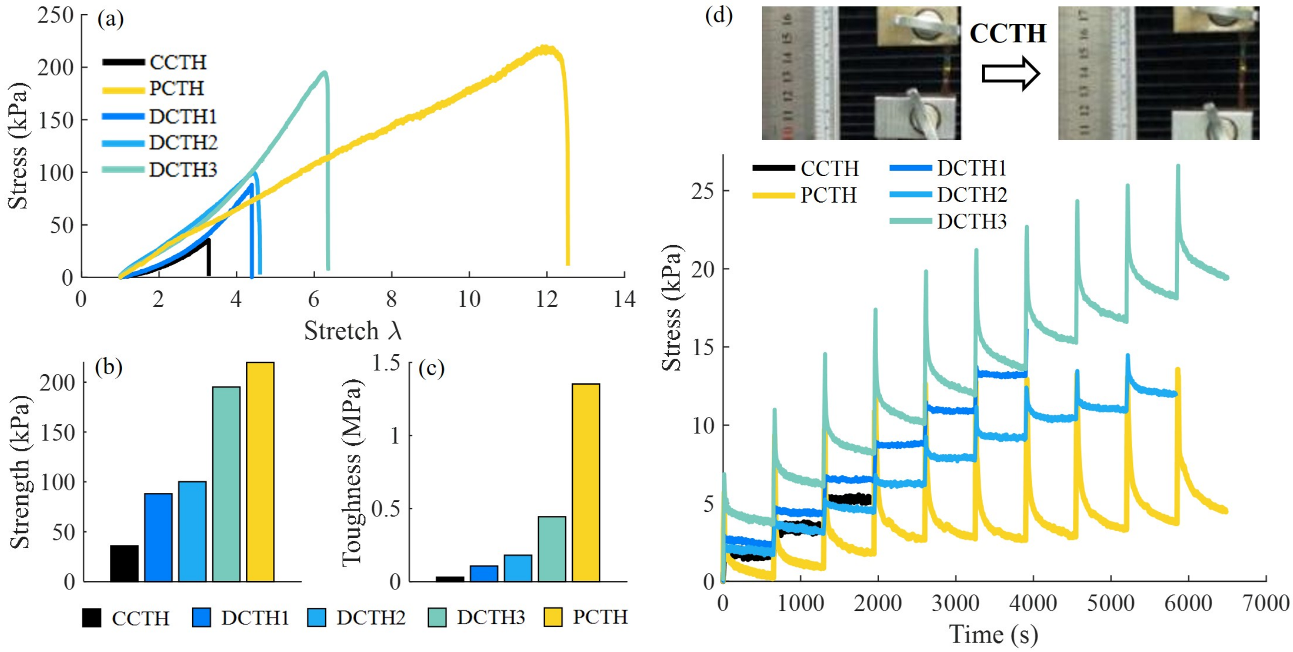

Figure 2: Summary of the mechanical behavior of all five hydrogels. (a) True stress response during uniaxial tension to failure. (b-c) Strength and toughness calculated from uniaxial tension curves (shared legend). (d) True stress response during step-relaxation to failure.

denoted CCTH, and only physical crosslinker (nanoclay), denoted PCTH. For specific details on the synthesis of each sample, see the Supplementary Information.

Following synthesis, the mechanical behavior was investigated using uniaxial tension tests performed to failure. Two behavioral studies were conducted: monotonic loading performed at a constant velocity of 5 mm/min and step-relaxation performed at 20 mm/min, with 600 s relaxation between each step (Figure 2). For further details on the mechanical testing, see the Supplementary Information. Generally, increasing the content of Laponite clay from 0.1g to 0.3g improves both strength and toughness of the material (Fig. 2b-c). The hydrogel with only covalent crosslinking (CCTH) displays both the lowest strength and toughness due to the fragile nature of PNIPAAm hydrogels. In contrast, the gel with only physical crosslinking is highly extendable, but is too viscous to be used for structural applications.

The physical network created by the nanoclay particles sources strong dissipative behavior due to the dynamic nature of the bonds. For instance, we observe the greatest stress relaxation in gels with the highest nanoclay content (Fig. 2d). Two interesting observations are noted: (i) the purely physical network (PCTH) relaxes to a higher equilibrium stress with each loading step and (ii) the only hybrid gel with significant relaxation behavior is DCTH3. From these observations, we predict that the physical nanoclay network behaves viscoplastically and that the observed mechanical behavior is dominated by the percolated network (either covalent or physical), which may be a function of their respective crosslinker concentrations.

To understand the behavior of these gels, we begin by considering the viscoplastic response displayed by the pure nanoclay network (PCTH). In Fig. 3a, we plot the relaxation portion of each loading cycle normalized by its corresponding peak stress σ_0 on a logarithmic scale. If relaxation were characterized by a constant timescale, each curve would be a straight line. Instead, we see that the timescale of relaxation dynamically changes while being held at a constant deformation. Furthermore, the fractional relaxation decreases as more loading steps are performed on the sample, indicating viscoplastic behavior.

To explain the observed relaxation trends, we

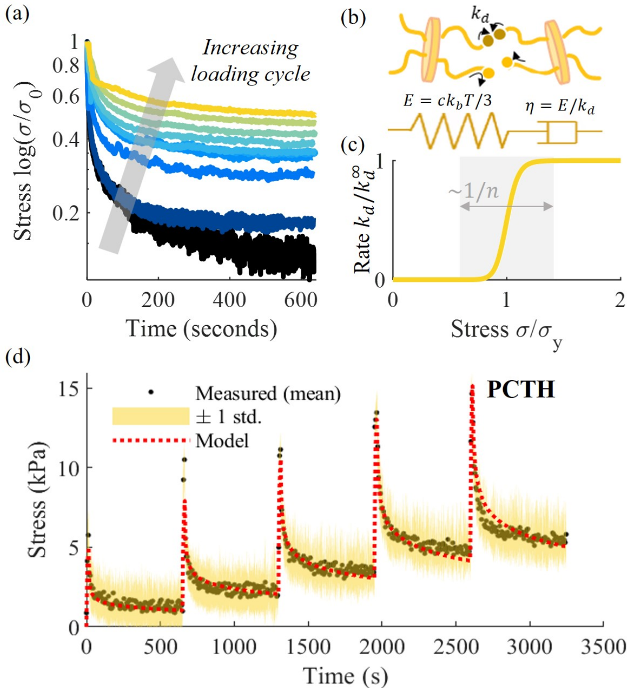

Figure 3: Conceptual illustration of Ellis model with experimental data. (a) Relaxation trends of PCTH plotted on a logarithmic scale. (b) Depiction of dynamic bonding between two nanoclay particles yielding Maxwell behavior. (c) Plot of the detachment rate versus stretch predicted by the Ellis model. (d) Comparison of PCTH step-relaxation data with model prediction.

model the behavior of the PCTH system as a nonlinear Maxwell element shown in Fig. 3b. Following classical rubber elasticity theory,[22] the elastic response of the network is governed by the elastic modulus $E = ck_bT/3$, where c is the number density of polymer chains and k_bT is the thermal energy scale. To determine the viscosity, we consider a network description of the PCTH polymer chains in which bonds connecting adjacent particles are dynamically breaking and reforming at some characteristic rate k_d. In an ideal dynamic network, this rate determines the timescale of relaxation[23,24] and, thus, the effective viscosity η by the relation $\eta = E/k_d$.[25] The experimental data of Fig. 3a implies that this rate is not constant but increases with stress. Motivated by recent work on the nonlinear viscoelasticity of agarose gels,[26] we postulate that the bond exchange rate k_d is bounded between two extremes: an equilibrium detachment rate k_d^0 at low stress and an accelerated detachment rate k_d^∞ when the stress exceeds a 'yield' value σ_y. The Ellis model[27] provides an appropriate form for this relationship as:

$$\frac{k_d - k_d^\infty}{k_d^0 - k_d^\infty} = \frac{1}{1 + (\sigma/\sigma_y)^n}, \tag{1}$$

where n is an exponential factor related to the width of the transition regime (Fig. 3c). In this model, if the equilibrium detachment rate k_d^0 is sufficiently slow, the network would effectively relax to σ_y after each loading cycle. As the experimentally-observed fractional relaxation is increasing, let us consider a simple case in which the yield stress evolves linearly with plastic strain ϵ_p such that:

$$\sigma_y = \sigma_y^0 + h\epsilon_p, \tag{2}$$

where h is an experimentally-measured strain-hardening parameter. Note that the plastic strain ϵ_p is simply the strain recovered from the dashpot element in our Maxwell model. Thus, we postulate that the stress σ_d of the dynamic network (PCTH) evolves with an arbitrary strain rate $\dot{\epsilon}$ as:

$$\dot{\sigma}_d = E_d\dot{\epsilon} - k_d\sigma_d \tag{3}$$

where $E_d = c_dk_bT/3$ and the rate k_d evolves with stress σ_d according to Eq. (1). From Eq. 3, the stress may also take the form $\sigma_d = E_dz(t)\epsilon$, where the function $z(t)$ designates the fraction of elastic strain to plastic strain in the element. At long times, it decays to zero as the dashpot has dissipated all elastic strain. We found that this model was very successful at fitting the experimental trends (Fig. 4b), confirming that the nanoclay-based dynamic network behaves like a "yield fluid" with an equilibrium detachment rate $k_d^0 \approx 0.2$ ms, an accelerated detachment rate $k_d^\infty \approx 0.5$ s, an initial yield stress of $\sigma_y^0 \approx 50$ Pa, and the plastic hardening parameter $h = 1.7$ Pa.

With a clearer understanding of the dynamic network, we then explored the effect of adding a secondary covalent network (PNIPAAm) to the mixture. In contrast to physical bonds, covalent

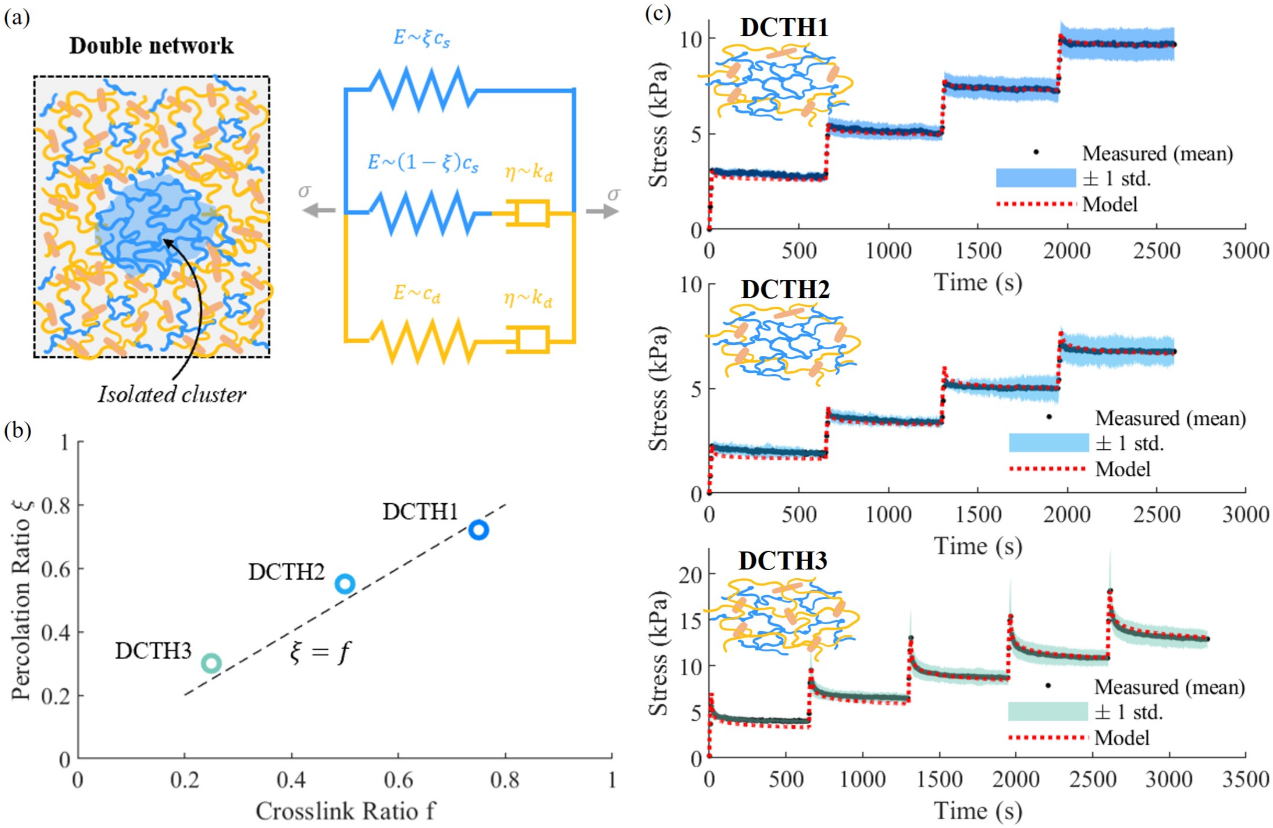

Figure 4: (a) Schematic of isolated clusters in hybrid networks and the corresponding spring-dashpot model depiction. (b) Percolation ratio ξ vs crosslink ratio f found through fitting. The dashed line indicates $\xi = f$. (c) Relaxation fitting for three hybrid networks with increasing nanoclay content.

bonds may break (at large stretches) but do not reform over time.[28] The response of CCTH is thus purely elastic, as observed in Fig. 2d. To quantify the contribution of each network, we introduce the fractional concentration f of static junctions c_s in the network as:

$$f = c_s/(c_s + c_d), \tag{4}$$

where c_d is the concentration of dynamic junctions. With this definition, $f = 1$ corresponds to a purely covalent network while $f \to 0$ converges to a purely dynamic nanoclay network. Following this idea, one may assume that the response of the double network DCTHn follows a rule of mixture, i.e. it reflects the summed contributions of the above two networks as:

$$\frac{\sigma}{E\epsilon} = f + (1 - f)z(t), \tag{5}$$

where the effective elastic modulus is $E = (c_d + c_s)k_bT/3$. Upon attempting to fit experimental data of Fig. 2d, we found however that our double network *does not* follow this simple relation, and that a more intricate force transfer between the two networks must be at play. To understand this discrepancy, we first recall that nanoclay platelets are known to assemble into aggregates,[16] which may contribute to the load-sharing behavior within the material. Given this, we postulate that a phase separation may occur where large regions of nanoclay junctions may exists within regions of static junctions, and vice versa. For the moment, let us focus on aggregates of static crosslinks that may not be percolated with the full covalent network (Fig. 4)a. These 'isolated clusters' likely contribute to the gel's elastic response, but may also relax with the surrounding dynamic network. To formalize this idea, we denote ξ as the fraction of 'stable' covalent junctions, making (1-ξ) the fraction of covalent junctions existing in isolated clusters. Their relative contributions to stress would then follow a hybrid rule of mixtures:

$$\frac{\sigma}{E\epsilon} = f\left[\xi + (1-\xi)z(t)\right] + (1-f)z(t), \qquad (6)$$

where, in the first term of the equation, the contribution of the covalent network was divided into a permanent and a time-relaxing component.[29] This would reflect a generalized Maxwell with three branches as depicted in Fig. 4)a. To gain further insights about the load-sharing mechanisms occurring within the double network, we next sought to determine the relationship between the fraction ξ of percolated static network and its bond fraction f. We proceeded by fitting the experimental data with the modified mixture model (Eq. 6), where we maintained the viscous parameters governing k_d as determined by our fitting of PCTH. The fitting procedure was then carried out on 3-4 experiments for each formulation, treating f and ξ as adjustable parameters. Note that we did not assume to have *a priori* knowledge of the crosslink ratio f, as this may not necessarily correlate with the mass ratio used during synthesis.

In Fig. 4c, we illustrate the relaxation behavior of each double network alongside the prediction of our fitted model. For each curve, we illustrate a shaded range that indicates one standard deviation, showing a very good agreement between experiment and theory. More importantly, we discovered a linear correlation between ξ and f that settled on nearly the exact ratios of crosslinker concentrations used during synthesis. Thus, for the formulation used here, our model indicates that the mass fraction of crosslinkers strongly correlates with the volume fraction f of the corresponding bond. In other words, the ratio ξ of stable covalent bonds (Fig. 4b) can be approximated as $\xi = f$ in equation (6).

The addition of a fraction of dynamic crosslinks into a covalent network is becoming a standardized practice for increasing the toughness of the material.[30,31] Following the successful fitting of our model, we may now consider a simple explanation for the trends of increasing toughness and strength of the double network materials (Fig. 2a-b). First, we note that the failure mechanisms of CCTH and PCTH are fundamentally different. In a covalent network, brittle fracture is expected as localized damage immediately propagates a crack (Fig. 5). In contrast, a dynamic network flows at long timescales, allowing for less localization and creep surrounding the crack tip.[32] For the dual network hydrogel studied here, elasticity can be maintained through the presence of a percolated covalent network, while energy dissipation can be ensured by the dynamic network. The present study also suggests that the improved strength could be explained by network heterogeneity, which could make it less flaw sensitive.[33,34] As shown schematically in Fig. 5, localized cracks within the covalent network could be confined to isolated clusters and halted by the surrounding dynamic network.

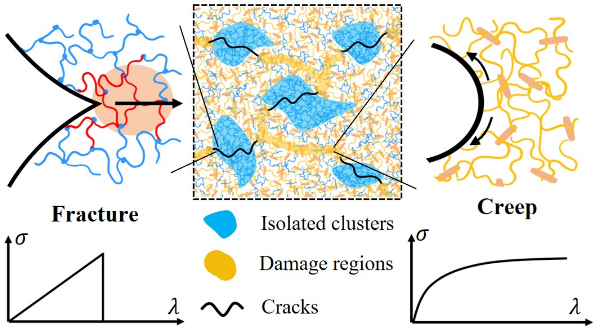

Figure 5: Schematic depiction of crack arrest and toughening due to phase separation in a double network hydrogel

In summary, we presented a simple theoretical framework for understanding the effect of fractional nanoclay content on the mechanics of PNIPAAm hydrogels. We found that adding nanoclay particles to the PNIPAAm gel increases stiffness, toughness, and energy dissipation. The pure nanoclay hydrogel behaves as a dynamic network whose relaxation time increases significantly when the applied stress exceeds a threshold (or yield) value, which was well captured by the Ellis viscoelastic model. When combined with a covalent network, we found evidence that a fraction $1-\xi$ of depercolated covalent bonds remains, which despite being permanent, are able to relax over time following similar characteristics as the dynamic network. Notably, the fraction ξ of stable covalent bonds was found to have a one-to-one correlation with the crosslink ratio f of covalent bonds to total bonds. Taken together, this study provides valuable insights into the nature of force transfer in double networks and may therefore guide the synthesis and control of mechanical parameters for actuating hydrogels, with applications in soft robotics, mechanobiology, and drug delivery.

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Supporting Information Available

Synthesis procedure for each sample and mechanical testing details.

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