

Mechanical Strength Management of Polymer Composites through Tuning Transient Networks

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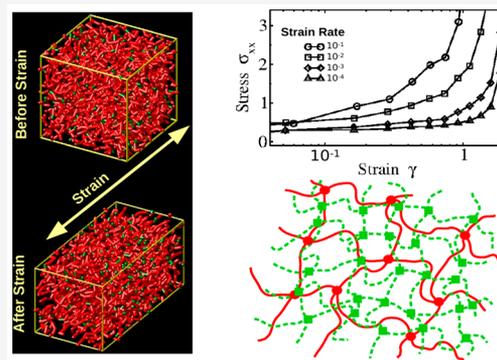
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ABSTRACT: The addition of transient networks to polymer composites marks a new direction toward the design of novel materials, with numerous biomedical and industrial applications. The network structure connected by transient cross-links (CLs) relaxes as time evolves, which results in the stretching release of polymer strands between transient CLs during strain. Using molecular dynamics simulations, we measure directly the stress–strain curves of double polymer networks (DPNs), containing both transient and permanent components, at different strain rates. Lifetime and density of transient CLs control the relaxation spectrum of transient networks and determine the mechanical properties of DPNs. A Rouse mode analysis reveals that at high strain rates the mechanical strength of DPNs is defined jointly by the cross-linking structures of permanent and transient networks. At low strain rates, the cross-linking structure of transient network relaxes, leaving the permanent component of the network as a sole contributor to the mechanical strength of DPNs. The transient network is shown to facilitate a dissipation of energy at higher strain rates and prevents a rupture of the network, while the permanent network preserves the structural integrity of the composite at low strain rates. This study provides computational and theoretical foundations for designing polymer composites with desirable mechanical strength and toughness by means of tuning transient networks.



Composite materials made of polymer networks with targeted mechanical properties are well suited for a wide range of practical applications including wearable electronics, rubber tires, soft robotics, tissue engineering, etc.^{1–3} Biophysical studies have revealed that some tissues, such as skin, muscles, and arteries, have a striking ability of switching between soft and stiff states under strain.^{4,5} This adaptive response to strain enables tissues to accommodate dynamic processes, such as cell proliferation and migration, while rupture is prevented.^{6,7} The strain-dependent stiffening of tissues is mainly facilitated by a collagen-forming fibrillar network, which results in mechanically tunable and structure reversible double polymer networks (DPNs) consisting of a fibrous collagen network mixed within a soft polysaccharide hydrogel.^{8–12} The bioinspired concept of combining different polymer networks to improve mechanical properties has been translated into materials science to develop DPNs as innovative materials with desired mechanical strength and toughness.^{13–20} By mixing rigid and brittle polymer chains, e.g., poly(2-acrylamido-2-methylpropanesulfonic acid) or RAMPS, with flexible and stretchable neutral components, e.g., polyacrylamide (PAAm), the compressive fracture stress of synthesized DPNs is found to be significantly higher than that of conventional single-network gels.²¹ The improved toughness of DPNs is ascribed to the brittleness of the rigid and brittle network serving as “sacrificial bonds” that break and dissipate energy to prevent catastrophic crack propagation, whereas the

stretchable network sustains stress to maintain the integrity of materials.^{22,23} In this case, the network structure of DPN gels is recoverable after rupture of sacrificial bonds, which are essentially transient cross-links (CLs) with certain lifetimes of their bonds.^{24–26} However, the microscopic dynamical mechanism of how a mechanically fragile network, or transiently cross-linked polymer network, can be used to toughen a material as a whole remains to be clarified physically. Little is known about how the mechanical properties of corresponding materials depend on the density and lifetime of the sacrificial bonds, or transient CLs, which dominate the dynamical relaxation of the DPN network structure, due to a lack of experimental methods to quantify binding and unbinding kinetics of transient CLs.

Molecular dynamics (MD) simulations, based on a bead–spring model with each bead representing one monomer, were performed for DPNs at fixed density of permanent CLs and for a wide range of densities of transient CLs. In the model, a finitely extensible nonlinear elastic (FENE) potential was used to define the connectivity, including covalent nearest-neighbor bonds and permanent/transient non-nearest-neighbor CLs, between

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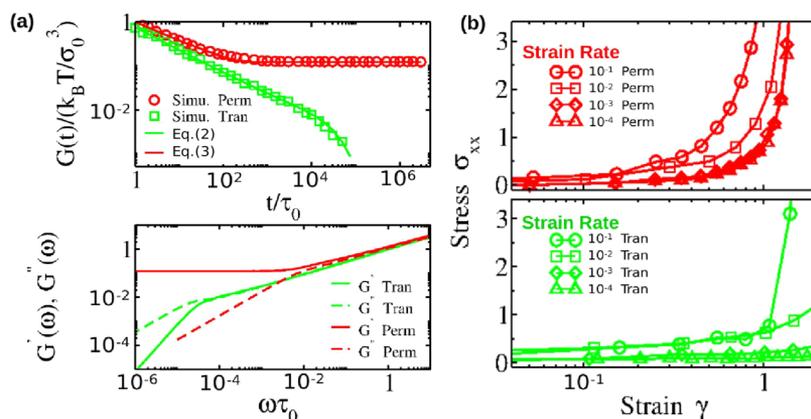


Figure 1. (a) (Upper) Stress relaxation moduli of a polymer network fully consisting of permanently (shown in red) or transiently (green) cross-linked polymer chains. (Lower) Corresponding storage and loss moduli for the permanent and transient networks. (b) Stress–strain curves for the (upper) permanent and (lower) transient networks at different strain rates. σ_{xx} is the uniaxial stress along the stretching direction. Here, we have $n_{pe} = 0.11$ for the permanent network and $n_{Tr} = 0.11$ for the transient network.

monomers (beads).²⁷ Note that a search for new transient CLs and breakage of existing transient CLs are performed continuously as time evolves, with every polymer bead in the transient network being capable of participating in solely one active transient bond at a given time. The lifetime of single-transient CLs is determined by setting the unbinding kinetics through fixing the waiting time and probability for transient bonds to unbind. At a fixed unbinding kinetics, the CL density in the transient network is then tunable through variation of the binding kinetics: a faster binding kinetics results in a higher density of transient CLs.²⁸ The monomer–monomer interaction was modeled as a full range Lennard-Jones (LJ) potential. The equation of motion for the displacement of a monomer is given by the Langevin equation.^{29,30} Transient and permanent networks are homogeneously mixed in the whole system. Note that monomers from polymer chains of the permanent network do not participate in transient cross-linking and vice versa. The volume fraction of monomers $n_m = N_M/V = 0.77$ is adopted to quantify the bulk concentration of polymers, where V and N_M are the system volume and the total number of monomers included in the system, respectively. The polymer chain length in both transient and permanent networks was fixed at $l_c = 128$. The simulations were carried out using the open source LAMMPS MD package.

We first compute the stress relaxation modulus, $G(t)$, of pure transient and permanent networks separately. $G(t)$ is quantitatively computed using a standard protocol of relating $G(t)$ to the stress autocorrelation function of off-diagonal elements of the system stress tensor, based on the Green–Kubo relation^{31–33}

$$G(t) = \frac{V}{3k_B T} [\langle \sigma_{xy}(t)\sigma_{xy}(0) \rangle + \langle \sigma_{yz}(t)\sigma_{yz}(0) \rangle + \langle \sigma_{xz}(t)\sigma_{xz}(0) \rangle] \quad (1)$$

where σ_{xy} , σ_{yz} , and σ_{xz} are the off-diagonal elements of the system tensor. As revealed in the upper panel of Figure 1a, the relaxation modulus of polymer chains in the transient network is analogous to weakly entangled polymer chains, with the corresponding $G(t)$ being well described by the function³⁴

$$G_{Tr}(t) = n_m \cdot k_B T \cdot \left[\left(\frac{t}{\tau_m} \right)^\gamma + g_e \right] \cdot \exp\left(-\frac{t}{\tau_{ter}} \right) \quad (2)$$

in which the fitting parameters are estimated numerically, with $\gamma \approx -0.53$ and $g_e = 0.0058$. The monomeric and terminal relaxation times of single-polymer chains in the transient network are fitted to $\tau_m^{Tr} = 1.0\tau_0$ and $\tau_{ter}^{Rel} = 3.7 \times 10^4\tau_0$, respectively, where τ_0 is the time unit adopted in the simulations. Note that $g_e = 0.0058$ corresponds to an entanglement length of $1/g_e \approx 172$ in the case that the weak plateau is induced by chain entanglements.^{35,36} However, the molecular weight of polymer chains for the studied system is $l_c \ll 172$, indicating that entanglement of polymer chains is absent. A single-mode relaxation was proposed for the cross-linking structure of the transient network in previous stress modulus studies, with its time-dependent stress relaxation modulus decaying exponentially in the form of $g(t - t_0) = \exp[-(t - t_0)/\tau_{Lf}^{TrNet}]$, where τ_{Lf}^{TrNet} represents the lifetime of the transient network.^{37,38} Here we assume that the weak plateau modulus is induced by transient cross-linking and $\tau_{Lf}^{TrNet} \approx \tau_{ter}^{Rel}$, given the single-mode relaxation of transient network's cross-linking structure. Being significantly different from a transient network, $G(t)$ for permanent networks is fitted by a function of the form

$$G_{Pe}(t) = n_m \cdot k_B T \cdot \left(\frac{t}{\tau_{Pe}} \right)^\gamma \cdot \exp\left(-\frac{t}{\tau_{Str}} \right) + G_{Plat} \quad (3)$$

where $\gamma = -0.51$, $G_{Plat} \approx 0.16$ is the plateau modulus, and $\tau_{Str} = 1.2 \times 10^2\tau_0$ is the configurational relaxation time of polymer strands between permanent CLs. The observed plateau modulus on large time scales is induced by the unrelaxed cross-linking structure of the permanent network. From the Fourier transform of $G(t)$, we computed the complex modulus, $G^*(\omega) = G'(\omega) + iG''(\omega)$, from which the storage (elastic) modulus $G'(\omega)$ and loss (viscous) modulus $G''(\omega)$ can be determined, $G'(\omega) = \omega \int_0^\infty G(t) \cdot \sin(\omega t) dt$ and $G''(\omega) = \omega \int_0^\infty G(t) \cdot \cos(\omega t) dt$, where $\omega = 2\pi/t$ is the angular frequency. The results of $G'(\omega)$ and $G''(\omega)$ are shown in the lower panel of Figure 1a. It is obvious that the transient network is a viscous sol due to the cross-linking structure relaxation of the transient network on time scales of $t > \tau_{Lf}^{TrNet}$, whereas the permanent network is a fully elastic gel at small frequencies corresponding to time scales beyond the configurational relaxation of polymer strands between permanent CLs.

The “memory” of the transient network's cross-linking structure at the initial moment of $t = 0$ is lost already at time

scales of $t > \tau_{Lf}^{TrNet}$. Transient CLs are not cross-linked over sufficiently long times to contribute to the hindrance on the configurational relaxation of polymer chains, given the condition that the time scale for the cross-linking structure of the transient network to complete its relaxation is smaller than the configurational relaxation time of polymer strands between transient CLs τ_{Str}^{Tr} , i.e., when $\tau_{Str}^{Tr} > \tau_{Lf}^{TrNet}$ holds. In this case, the configurational relaxation modes of polymer chains in the transient network are not affected by CLs on all length scales, and the corresponding relaxation spectrum is polymer-melt-like without cross-linking. In the opposite case, when $\tau_{Str}^{Tr} < \tau_{Lf}^{TrNet}$ holds, the cross-linking structure of the transient network sustains on time scales of the configurational relaxation of polymer strands between transient CLs, which results in a transient cross-linking-induced hindrance and prevents further configurational relaxation of polymer chains of larger contour lengths. Therefore, the relaxation spectrum of the transient network is then equivalent to that of a permanent network during $\tau_{Str}^{Tr} < t < \tau_{Lf}^{TrNet}$, and the relaxation of polymer chains in the transient network takes place after $t = \tau_{Lf}^{TrNet}$. Above all, τ_{Str}^{Tr} and τ_{Lf}^{TrNet} are the two critical time scales that balance the characteristic mechanical contributions of the transient network that is added to DPNs.

The cross-linking structure of the transient network relaxes as time evolves, which leads to a continuous readjustment of the cross-linking structure, thereby dissipating the resisting energy against the prestrain during a stress–strain process. A weaker stress is thus observed at a given strain for a transient network with fast relaxation of its cross-linking structure. Increasing the strain rate for a given system accelerates the prestrain-induced deformation of polymer strands between the transient CLs, while the relaxation dynamics of the cross-linking structure of the transient network remains invariant. This results in an increase of stress, just as a slowdown of the relaxation dynamics of transient polymer networks at a given strain rate. The crossover from the linear to the nonlinear regime in the stress–strain curve of the transient network shifts to a smaller values while increasing the strain rate and/or delaying the dynamical relaxation of its cross-linking structure. The stress–strain deformation curves for transient and permanent networks are shown separately in the Figure 1b. Starting from equilibrium phases of pure transient or permanent networks, the stretching simulation reproduced the experimental strain ramp protocol in which the stress is measured as a function of an applied strain that increases linearly with time. During the uniaxial deformation at a constant volume, the simulated system expanded in one direction (along the x -axis) while it simultaneously contracted in the other two directions (along the y - and z -axes). The simulation results, as shown in Figure 1b, confirm the dependences of the stress–strain curves on the configurational relaxation of polymer strands between transient and permanent CLs, as well as the cross-linking structure relaxation of the transient network. On the basis of the relaxation time of that cross-linking structure, we can determine the minimal strain rate, $dy/dt = [(I_{Str}^{Tr} - r_g^{Tr})/r_g^{Tr}] \cdot (1/\tau_{Lf}^{TrNet}) \approx 10^{-4}$, below which the transient CLs no longer contribute to the mechanical strength of the transient network. The transient network behaves mechanically like a CL-free polymer melt at strain rates of $dy/dt < 10^{-4}$ because the relaxation of the original cross-linking structure is completed before the strain induces a full stretching of the polymer strands between transient CLs. In contrast, the transient cross-linking structure remains unchanged at the maximum stretching of strands between CLs

when $dy/dt > 10^{-4}$, which results in a crossover from the linear to the nonlinear regime in the corresponding stress–strain curve as the strain increases. Simultaneously, as shown in the upper panel of Figure 1b, the stress–strain curve of the permanent network displays dependence on the strain rate as long as the strain-induced stretching of polymer strands between permanent CLs progresses slower than their conformational relaxation. Note that the crossover of the stress–strain curve from its linear to nonlinear regime shifts toward smaller strain values in the case that the strain-induced stretching of polymer strands between CLs progresses faster than their configurational relaxation. This occurs in Figure 1b within the parameter range between $dy/dt = 0.1$ and 0.01 . The fact that an increase of the strain rate results in an earlier onset of the nonlinear stress–strain behavior of nonentropic nature is in qualitative agreement with experimental data.³⁹

When a transient network is added to mix with a permanently cross-linked polymer network, as sketched in Figure 2, the CL

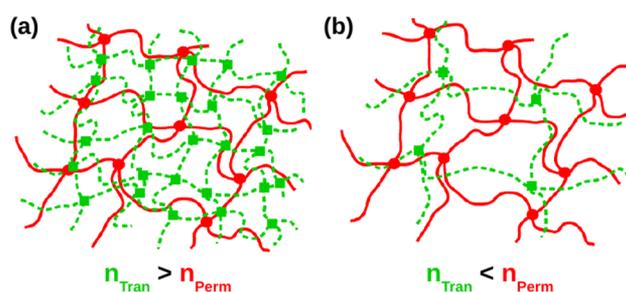


Figure 2. Sketches of DPNs consisting of transiently and permanently cross-linked polymer networks with their chains and CLs shown in red and green curves/symbols, respectively. Here, n_{Tr} and n_{Pe} represent the number densities of transient and permanent cross-links, respectively.

density of the transient network, n_{Tr} , can be either larger or smaller compared to the permanent network, n_{Pe} . This implies either longer or shorter contour lengths of the polymer strands between permanent CLs, l_{Str}^{Pe} , as opposed to the corresponding transient l_{Str}^{Tr} . The case $l_{Str}^{Pe} < l_{Str}^{Tr}$ holds if $n_{Pe} > n_{Tr}$, and $l_{Str}^{Pe} > l_{Str}^{Tr}$ if $n_{Pe} < n_{Tr}$, respectively. The conformations of polymer strands between CLs relax as time evolves, and the time scale for a polymer strand to relax depends on its contour length as $\tau_{Rel} = C_{kT}^b \zeta_b^b l_{Str}^{Pe}$, where ζ_b is the monomeric friction coefficient of a polymer bead and C_{kT}^b is a constant determined by the system temperature kT and the bead size b .⁴⁰ Note that in the current study with our focus on the effects of transient CLs, we do not consider effects of varying Kuhn lengths between transiently and permanently cross-linked polymer chains, i.e., $b^{Pe} = b^{Tr}$. It is assumed that transient and permanent networks are well mixed and transient CLs are thus homogeneously distributed in the DPNs. Consequently, there exist no differences in monomeric mobility between permanently and transiently cross-linked polymer chains; hence, $\zeta_b^{Pe} = \zeta_b^{Tr}$. Therefore, the ratio of relaxation times of chain strands connecting neighboring CLs in permanent and transient networks yields $\tau_{Rel}^{Pe}/\tau_{Rel}^{Tr} = (l_{Str}^{Pe}/l_{Str}^{Tr})^2$.

After completion of the conformational relaxation of polymer strands between permanent CLs, the cross-linking structure of the permanent network in DPNs remains steady at any time scale of $t > \tau_{Rel}^{Pe}$, which creates the unrelaxed modes of polymer strands with contour lengths beyond l_{Str}^{Pe} . Applying an external strain to DPNs induces extension and reduces the conformational entropy of individual polymer chains by stretching. There exists a reversible elastic response of entropic nature of polymer

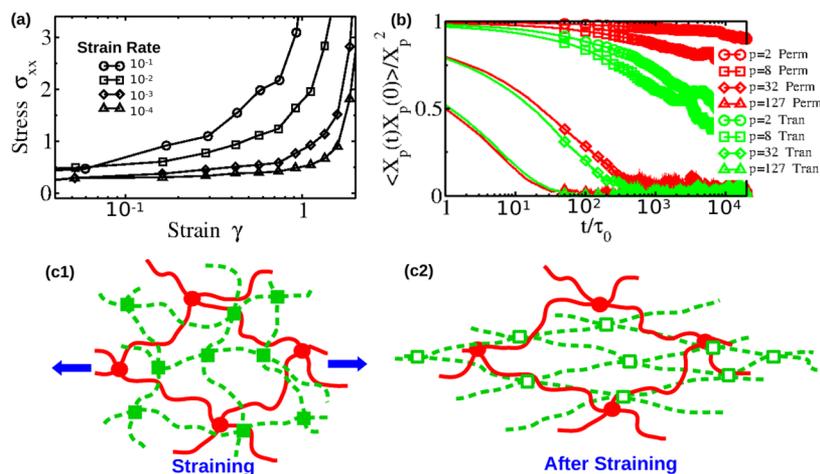


Figure 3. (a) Stress–strain curves of DPNs consisting of transiently and permanently cross-linked polymer chains at different strain rates. (b) Time-dependent autocorrelation functions of Rouse modes of permanently and transiently cross-linked polymer chains in the studied DPNs. (c) Sketches showing a structure of a DPNs, which has a higher density of transiently cross-linked chains than the permanently cross-linked ones, prior to and after stretching of polymer strands between transient CLs, respectively. Here, we have $n_{Tr} = 0.12$ and $n_{Pe} = 0.037$ for the double network.

chains in the small deformation limit, in which the local tension magnitude depends linearly on strain. The maximum deformation of permanent networks inside of the elastic response regime is reached when polymer strands between permanent CLs are fully stretched. Beyond that, a nonlinear response of nonentropic nature emerges in the corresponding stress–strain curve once the deformation of DPNs is sufficiently large to have polymer strands between permanent CLs fully stretched. The transient network makes no contribution to the mechanical strength of DPNs if $l_{Str}^{Pe} < l_{Str}^{Tr}$ holds, given that the maximum stretch of polymer strands between permanent CLs is reached before the strands between transient CLs are stretched out. In this case, the permanent network in DPNs dominates the critical value of the strain, $\gamma_{Cr} = (l_{Str}^{Pe} - R_g^{Pe})/R_g^{Pe}$, above which the stress–strain response of DPNs crosses over into the nonlinear regime, where R_g^{Pe} is the averaged radius of gyration of polymer strands between permanent CLs. Therefore, a density of transient CLs higher than that of the permanent ones, i.e., $l_{Str}^{Pe} > l_{Str}^{Tr}$, is a prerequisite for the transient network to dominate the mechanical strength of DPNs. At increasing strain rates, the mechanical performance of DPNs is first dominated by the permanent network prior to a crossover at $d\gamma/dt = \gamma_{Cr}^{Tr}/\tau_{Lr}^{TrNet}$ with $\gamma_{Cr}^{Tr} = (l_{Str}^{Tr} - R_g^{Tr})/R_g^{Tr}$, after which transient and permanent networks contribute jointly to the mechanical characteristic of DPNs.

The nonlinear rheological characteristics of DPNs in which the density of transient CLs exceeds the density of permanent CLs combine the mechanical strengths of both transient and permanent networks. As shown in Figure 3a, there exists a crossover from the linear to nonlinear regime in the stress–strain curve even at the lowest strain rate of $d\gamma/dt = 0.0001$, in which case the mechanical strength of DPNs is maintained by the permanent network, while the transient network makes no contribution due to the fully completed relaxation of its cross-linking structure on time scales larger than $\tau_{TrNet}^{Rel} \approx 6 \times 10^4 \tau_0$. When the strain rate exceeds $1/\tau_{TrNet}^{Rel}$, such as $d\gamma/dt = 0.1$ and 0.01 , the cross-linking structure of the unrelaxed transient network dominates the mechanical strength of DPNs with $n_{Tr} > n_{Pe}$. In order to clarify the dependence of the stress–strain curve on the relaxation of the cross-linking structure and the conformational relaxation of polymer chains, we performed a

Rouse mode analysis. It was theoretically predicted and verified in simulations that the averaged autocorrelation function of the p th mode, representing the relaxation dynamics of a polymer subchain including $(N - 1)/p$ beads, can be well described by a

stretched exponential, $X_p(t) \cdot X_p(0) = \langle X_p^2 \rangle \exp\left[-\left(\frac{t}{\tau_p}\right)^{\beta_p}\right]$,^{41,42} in

which τ_p and β_p are the relaxation times of the p th mode and the corresponding stretching factor, respectively. As shown in Figure 3b, there is almost no relaxation difference between polymer strands in transient and permanent networks on small length scales, corresponding to large values of p , such as $p = 32$ and 127 , confirming that transient/permanent CLs do not affect the conformational relaxation spectrum of polymer strands between CLs. However, the conformational relaxation of polymer strands in the permanent network is considerably slower than that in the transient network in the case of lower modes, such as $p = 2$ and 8 , corresponding to large contour lengths.

The Rouse mode analysis confirms that the conformational relaxation dynamics of polymer strands in the permanent network is hindered on length scales larger than the contour length between permanent CLs, which results in unrelaxed modes, as shown in Figure 3b for $p = 2$ and 8 . On the contrary, polymer chains in the transient network are relaxed for all modes, i.e., on all contour length scales. This implies that the conformational relaxation is not prevented by transient CLs, which however delay the relaxation of modes corresponding to large contour lengths. The stretching energy imposed by external strain is generally very high at high strain rates. As sketched in Figure 3c, it is primarily the strands between transient CLs that are stretched when an external strain is applied at high strain rates, which prevents a strong stretching of strands between permanent CLs. In this way, the permanent network is mechanically protected by the transient CLs, which dissipate the induced stretching energy at high strain rates. On the other hand, the permanent cross-linking structure with its entropic elasticity facilitates recovery of the transient network to its original structure after the external strain is released. Note that the relaxation time of the transient network's cross-linking structure depends on the density and the lifetime of individual transient CLs in DPNs. The stress–strain curves for DPNs at

different densities of transient CLs and fixed density of permanent CLs, as shown in Figure 4, confirm that the

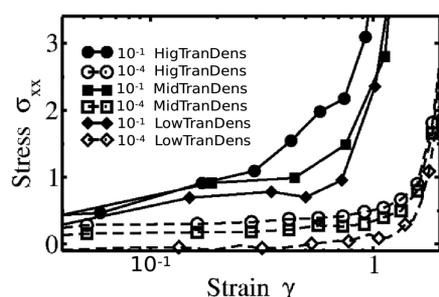


Figure 4. Stress–strain curves for DPNs at high and low strain rates, constant density of permanent CLs, $n_{pe} = 0.037$, and varying density of transient CLs, $n_{Tr} = 0.0020$ (low), 0.037 (middle), and 0.12 (high).

mechanical strength of DPNs increases, and the crossover from the linear to the nonlinear regime shifts toward lower strain when the density of transient CLs is increased.

In summary, on the basis of MD simulations, we provide physical understanding of how the mechanical strength and toughness of polymer composites consisting of DPNs are dependent on the dynamical relaxation of cross-linking structure of transient networks. By measuring directly the stress–strain curves and by performing a Rouse mode analysis of DPNs consisting of homogeneously mixed permanent and transient networks, we verify that transient CLs enhance the mechanical strength of DPNs at high strain rates, in which case the cross-linking structure of the transient network has insufficient time to relax, and the transient network simply adds another contribution to the strength of the permanent network. At low strain rates, corresponding to time scales that exceed the relaxation of the cross-linking structure in the transient network, the mechanical properties of the DPNs display no difference from the pure permanent network in the absence of transient CLs. In DPNs in which the density of transient CLs exceeds that of the permanent CLs, the transient network can prevent strain-induced rupture of the network by dissipating stretching energy at high strain rates, whereas the permanent component of the network prevents the formation of macroscopic cracks and maintains the integrity of the polymer composite. The relaxation spectrum of the cross-linking structure of the transient network, and thereby the mechanical strength of DPNs, is a function of the lifetime and density of transient CLs in the corresponding DPNs. Note that these parameters are controllable through tuning the chemical properties and the composition of DPNs' ingredients;^{43–45} therefore, it appears achievable to design polymer composites with desirable mechanical strength and toughness through introducing transient networks.

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Notes

The authors declare no competing financial interest.

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