Stepwise Elastic Behavior in a Model Elastomer

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Monte Carlo simulations of an entanglement-free cross-linked polymer network of semiflexible chains reveal a peculiar stepwise elastic response. For increasing stress, step jumps in strain are observed that do not correlate with changes in the number of aligned chains. We show that this unusual behavior stems from the ability of the system to form multiple ordered chain domains that exclude the cross-linking species. This novel elastomer shows a toughening behavior similar to that observed in biological structural materials, such as muscle proteins and abalone shell adhesive.

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In this Letter, we describe a model material that shows a behavior similar to that of some very tough natural materials. We report results from Monte Carlo (MC) simulations of idealized cross-linked polymer networks that show unusual deformation properties leading to greater toughness. Cross-linked polymer elastomers are in widespread use primarily due to their excellent elasticity and ease of synthesis or fabrication. A variety of methods exists to enhance the toughness of elastomers, including the use of nanocomposites [1], networks with bimodal chain distributions [2], associating polymers [3], and, more recently, hybrid organic-inorganic composites [4]. Such approaches usually rely on generating regions within the elastomer that resist any applied deforming force. The elastic response remains qualitatively similar even as quantities such as modulus and toughness change. We describe here an alternative approach to toughness enhancement wherein the nature of elastic behavior under stress itself is different.

We take advantage of the fact that semiflexible polymer chains are known to undergo isotropic-nematic transitions under the right conditions of temperature, density, and chain stiffness [5]. It has been theoretically predicted that such semiflexible chains in a cross-linked form can undergo strain-induced phase transitions to ordered states [6]. A previous study [7] found that the theoretical predictions failed to account for trapped entanglements that cause a significant fraction of the network chains to remain unaligned even at very high strains, thus preventing a discontinuous transition to an ordered nematic state. In the current study, we have removed all the trapped entanglements by using an ideal network architecture. This architecture, combined with stiff chains, results in a stress-strain curve that has an unusual staircaselike shape, and the area under the curve (which corresponds to the toughness or the energy required to break) is greater than that of the equivalent disordered elastomer. We show that this combination improves elastomer toughness by undergoing a stepwise rather than continuous extension under stress.

Such a stepwise elastic response has been observed in natural materials that are unusually tough. Single molecule

atomic-force microscope (AFM) studies on the muscle protein titin [8] have shown that its molecular structure has many folded domains that unfold successively and individually in response to force, giving rise to a sawtooth-type force-extension curve. Similar mechanisms make abalone shells, which are composed mainly of calcium carbonate, orders of magnitudes tougher than pure calcium carbonate crystals [9]. The shells consist of organic material (containing proteins) sandwiched between calcium carbonate plates; this organic material also shows a modular elastic response. In both cases, during an extension experiment, the pulling force rises quickly to a large value, one that is still less than the breaking force, and then oscillates, resulting in a large area under the forceextension curve. This means that more energy is required to ultimately break this molecule as compared to a simple short or long molecule. Here, we report for the first time a similar reinforcing effect in a polymeric system that is closely related to man-made elastomers.

Our simulation system is an idealized form of an endlinked elastomer with tetrafunctional cross-links known as a "diamond network" [10]. It is an entanglement-free cross-linked polymer network in which all cross-links are saturated and would lie at the nodes of a diamond lattice if all the chains were fully stretched. We have used semiflexible polymer chains that can undergo isotropicnematic-like transitions under certain conditions. The network is made up of unit cells that contain eight cross-links and 16 chains each. We have used systems with eight unit cells and a chain length of 20 monomers. Periodic boundary conditions were used in all directions to mimic bulk conditions. The deformation simulations to measure the elastic response were carried out in continuum space. The chain monomers and the cross-linking species were modeled as spherical beads of diameter σ_{LJ} with the bond length fluctuating within a range: $\sigma_{LJ} \pm 0.2 \sigma_{LJ}$. Nonbonded beads interact via a cut-shifted Lennard-Jones (LJ) potential with a cutoff of $r_c = 1.2\sigma_{\rm LI}$ (that gives a small attractive well) and an overlap distance of $r_0 = 0.85\sigma_{\rm LJ}$. We used a reduced temperature $k_B T/\varepsilon =$ 0.675 (where k_B is the Boltzmann constant, T is the temperature, and ε is the LJ energy parameter). Chain stiffness was introduced using a bond-angle bending potential [11] of the form $E_b/k_BT = k_b(1 + \cos\psi)$, where k_b is an adjustable bending parameter that determines the chain stiffness, and ψ is the bond angle. We used $k_b = 5$ (corresponding to a persistence length of $\sim 5\sigma_{LJ}$) for our primary model and $k_b = 3$ for a reference model because the latter, while very similar to the former, lacks a discontinuous isotropic-nematic transition.

The system relaxation was done via MC moves that mimic diffusive dynamics. Networks were deformed using highly efficient cluster volume [12] moves. The networks were first equilibrated at a meltlike density ($\rho = 0.9$, where $\rho = N_t/V$ is the network bead number density, N_t is the total number of sites in the system, and V is the simulation box volume) by performing isotropic NPT simulations. The pressure corresponding to $\rho = 0.9$ was found to be $P^* = 1.95$. To induce uniaxial stretching, a smaller pressure is applied in the z direction (P_z) , while the pressures along the x and y directions, P_x and P_y , are kept unchanged (= P^*). The net stress σ along the z direction is $|P^* - P_z|$, and the choice of z axis is arbitrary. To achieve meltlike densities in our system, a relatively large P^* is needed because of the lack of strong van der Waals attractions in our model. However, the manner in which tensile stress is applied (with $P_z < P^*$) is the same even if $P^* \rightarrow 0$; i.e., σ must act as a negative (outward) force relative to P^* . The strain, λ , is given by $\lambda = L_z/L_{z,0}$, where $L_{z,0}$ and L_z are the z dimensions of the network



before and after deformation. The stress values reported here for σ have been made dimensionless by multiplying them by σ_{LJ}^3/k_BT . To summarize, we imposed increasing amounts of stress on the systems and then measured the resulting deformation. The net orientation of chain segments along the strain axis can be detected by the average segmental order parameter *S* that is calculated as S = $\langle (3\cos^2\theta - 1)/2 \rangle$, where θ is the angle between the orientation of chain segments and the strain axis, and the average is over all the chain bonds. S = 1 corresponds to complete order and S = 0 to random disorder.

Figure 1 shows the stress-strain data for networks with $k_b = 5$ (main system) and $k_b = 3$ (reference system). It is immediately evident that the $k_b = 5$ network data points are limited to narrow intervals of strain, indicating that the network deforms in steps. The staircaselike nature of the data can be seen to increase the area under the curve, as compared to the reference system. The inset shows the extent of ordering in the same system as a function of strain. Ignoring the first datum which corresponds to $\sigma = 0$, S is seen to slowly increase from 0.4 to 0.7 and eventually level off ($S \sim 0.5$ can be regarded as the threshold of an ordered phase). Simulation data (not shown) for systems with different sizes are consistent with those in Fig. 1.

Figure 2 shows snapshots of all the chains in the network at various stresses along with the locations of cross-links for the same conditions. The chains seem to be in a stretched conformation regardless of the stress or strain



FIG. 1 (color online). Stress vs strain data for the semiflexible chain diamond network ($k_b = 5$) during extension and compression (dashed lines are drawn to emphasize the staircaselike nature of the data). Also shown are extension data for the reference (more flexible) diamond network (with $k_b = 3$). The inset shows the order parameter *S* as a function of strain during extension for $k_b = 5$.

FIG. 2 (color online). Intermediate snapshots of the diamond network equilibrated with a different number of ordered chain domains and cross-link aggregates (where the lines represent chain backbones and the dots represent the cross-links): (a) $\sigma = 0.05$, $\lambda = 5.02$; (b) $\sigma = 0.0175$, $\lambda = 3.74$; (c) $\sigma = 0.0075$, $\lambda = 2.52$; (d) $\sigma = 0$, $\lambda = 1.0$.

and exist in ordered but separate domains. Cross-link pictures show that these separations between ordered domains correspond to the regions where the cross-linking species aggregate. The extension mechanism for this system then is not the progressive stretching of chain conformations, but rather the increase in the number of ordered chain domains. Overall values of the order parameter change moderately with strain because the chains are always in an extended and ordered state. In fact, the distance between the cross-link aggregates is about 80%-85% of the contour length of the chains. Assuming that the chains are connected to two cross-links in different groups (not strictly true as explained later), one can come up with a prediction of $S \sim 0.46-0.6$ for the system order parameter, which lies within the range of values found in simulation.

This ability to maintain the extent of order while changing exterior dimensions is absent in entangled systems. Our simulations with realistically entangled end-linked networks [7] have shown that, under stress, the entangled sections of chains are prevented from aligning completely. In all unstrained network systems, chains connected to different cross-links are interdispersed. In entangled networks, some of this interdispersion unravels to allow stretching, but trapped entanglements prevent complete unraveling-two possible scenarios are depicted in cartoon form in Figs. 3(a) and 3(b). Diamond networks, on the other hand, allow the chains to stretch while remaining interdispersed. During additional deformation, this interdispersion can be stepwise reduced as new ordered domains form until the maximum extension of the system as a whole is reached. A small section of the diamond network



FIG. 3. Schematic of chain interdispersion in networks (spheres represent cross-linking sites and chains are represented by lines): (a),(b) trapped entanglements in entangled networks that prevent complete separation of interdispersed chains and (c) separation of interdispersed chains in diamond networks (cross-links divided into two groups split to become a part of three groups).

system is sketched in Fig. 3(c) undergoing separation of intermixed chains. This gradual (and eventually complete) unraveling of chain interdispersion is key to the unique stepwise extension mechanism. Simulations on realistic end-linked networks with the minimum possible amount of entanglements (cross-linked at just above the overlap concentrations) have revealed that their elastic behavior is not stepwise [13]. Therefore, just the absence of entanglements is not sufficient to cause the microsegregation of cross-links. Regular connectivity, as seen in the diamond network, also appears to be important.

The noncontinuous elastic behavior is caused by the abrupt increase in the number of ordered domains during extension. Under a particular amount of applied stress, an equilibrated state of the system corresponds to the existence of a number of ordered domains that occur only in a very narrow strain interval. Any intermediate strain represents a nonequilibrated condition which leads to a staircaselike force-extension data exhibiting ranges of strain that are not visited by the system. During the transition from one equilibrium state to another (e.g., extension from two to three ordered chain domains), it was seen with the aid of numerous intermediate snapshots that the segregated structure is first destroyed so that the cross-links are roughly uniformly distributed in the system volume [14]. In such a state, the network is more "deformable" and can extend in the direction of the applied force. The next equilibrium state is then formed if the deformation rate is slow enough. It was observed that the cross-links always divide themselves in almost equal numbers among the segregated groups, regardless of the number of such groups. Depending on the initial conditions, two crosslinks connected to the same chain may end up in the same group. In such cases, the chain in question exists in a U-shaped configuration. Such behavior is exhibited by a small minority of the chains; most of the chains exist in a stretched conformation that spans two neighboring crosslink groups. Reduction in stress does not result in a corresponding reduction of strain, as the structure with the ordered domains is favored by the system. This leads to significant hysteresis as shown in Fig. 1.

Our results here are qualitatively similar to the behavior of titin and other similar materials. The sawtooth forceextension data seen there is the result of measuring the extension force (via AFM) as a function of the extension. Once a modular system is in its equilibrated state (when a folded domain has just been unfolded in the protein or when ordered chain domains are completely formed in the system under consideration here), the force required to hold it at that particular strain is much less than the force required to reach that strain. Accordingly, the measured force falls off repeatedly after reaching peaks. In our case, since strain is measured as a function of deforming force, we observe only the recurring sharp increases in stress at almost constant strains. The vertical falloffs are not seen; the sharp upswings are connected horizontally instead (Fig. 1). In place of progressively unfolding protein domains, the diamond networks extend by unraveling interdispersed chains to form successively more ordered domains along the extension direction. Thus two different mechanisms yield the same end result: toughness enhancement caused by a stepwise elastic response. In both cases, such steps are due to changes in the number of stable microdomains. In titin, the number of stretched regions increases with strain; in our network, the number of ordered domains increases with strain. In titin, its modular design is most apparent in the unstrained state; in our network, its modular nature is apparent in highly stretched states. These systems are two examples of inherently modular polymeric materials with an associated periodic energy minima as a function of deformation; materials with similar characteristics should be good candidates to exhibit a stepwise elastic response.

The segregation of the cross-linking species on application of stress is of potential interest. The cross-links are similar to the chain monomers in all respects except that they are connected to four other beads. Connectivity and stress combine to segregate these otherwise similar species. The cross-links have a relatively larger number of connected neighbors; this extensive branching hinders the alignment of nearby segments. The presence of stiff chains that tend to align and stretch eventually excludes the disorder-inducing cross-links from the ordered domains, despite the associated loss of mixing entropy.

In conclusion, we have observed in a model material a toughness improving elastic behavior, similar to that seen in some tough natural substances. We found that, under stress, semiflexible chain diamond networks form domains in which the chains are ordered and from which the crosslinks have been excluded. The cross-links segregate between the ordered regions. The extension mechanism of the networks is through the successive rearrangement of the ordered structure, wherein interdispersed chains unravel and the number of ordered domains increases in the strain direction without changing the amount of ordered material. This results in a stepwise elastic behavior and a greater area under the stress-strain curve and overall toughness.

Some other possible entanglement-free network architectures include a planar "hexagonal" network with trifunctional cross-links and a three-dimensional "cubic" network with hexafunctional cross-links. The cubic network may even be better than the diamond network at forming ordered chain domains as a result of the increased branching around the cross-linking sites. Experimental networks can also be made that approach the ideal zeroentanglement limit, e.g., by adopting strategies such as reducing the molecular weight between cross-links and by carrying out the cross-linking reaction in solution [15]. Energetic interactions could also be harnessed to induce aligned packing of chains. Such interactions appear to be at work in the formation of a semicrystalline mesophase in poly(diethylsiloxane) elastomers. By combining some of the above strategies, it may be possible to experimentally reproduce diamond networklike behavior in elastomer systems. Furthermore, the bicontinuous network structures of block copolymers (such as the double gyroid [16] and double diamond [17]) have been used as templates to synthesize mesoporous inorganic structures [18] and could potentially be used to generate entanglement-free regular polymeric structures.

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