POLYMER SCIENCE

Fracture, fatigue, and friction of polymers in which entanglements greatly outnumber cross-links

Junsoo Kim[1]†, Guogao Zhang[1,2]†, Meixuanzi Shi[1,3], Zhigang Suo[1]*

In gels and elastomers, the role of entanglements on deformation has been studied, but their effects on fracture, fatigue, and friction are less well understood. In this study, we synthesized polymers in which entanglements greatly outnumber cross-links. The dense entanglements enable transmission of tension in a polymer chain along its length and to many other chains. The sparse cross-links prevent the polymer chains from disentangling. These polymers have high toughness, strength, and fatigue resistance. After submersion in water, the polymers swell to equilibrium, and the resulting hydrogels have low hysteresis, low friction, and high wear resistance.

An elastomer consists of cross-linked polymer chains (*1*). The polymer chains fluctuate by thermal motion and can be stretched by a force. The cross-links connect the polymer chains, so that the elastomer recovers its shape when the force is removed. When the elastomer imbibes a solvent, the cross-links prevent the polymer chains from dissolving. The swollen elastomer is called a gel. Dense cross-links stiffen the elastomer and gel but embrittle them (*2*–*5*). This stiffness-toughness conflict is partially resolved in an interpenetrating polymer network where one network is grown within a second one (i.e., a double-network polymer) (*6*–*8*). For example, if one network has prestretched short chains, and the other has stretchable long chains (*6*), when subjected to a small stretch, neither network breaks and the short-chain network stiffens the material. With increasing stretch, the short-chain network will break at isolated spots, while the long-chain network transmits stress and elicits many other short chains to break. The distributed scission toughens the material but causes pronounced hysteresis. Toughness gained from hysteresis is ineffective in applications of cyclic load (*9*).

We resolve the stiffness-toughness conflict, in addition to achieving negligible hysteresis, by fabricating a single-network polymer in which all chains are long and cross-links are greatly outnumbered by entanglements (Fig. 1A). Entanglements function as slip links, which stiffen the polymer. Unlike cross-links, however, entanglements do not embrittle the polymer. When a highly entangled polymer is stretched, before a chain breaks, tension

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[1] John A. Paulson School of Engineering and Applied Science, Kavli Institute for Nanobio Science and Technology, Harvard University, Cambridge, MA 02138, USA. [2] State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China. [3] State Key Laboratory for Strength and Vibration of Mechanical Structures, School of Aerospace Engineering, Xi'an Jiaotong University, Xi'an 710049, China.
***Corresponding author. Email: suo@seas.harvard.edu**
†These authors contributed equally to this work.

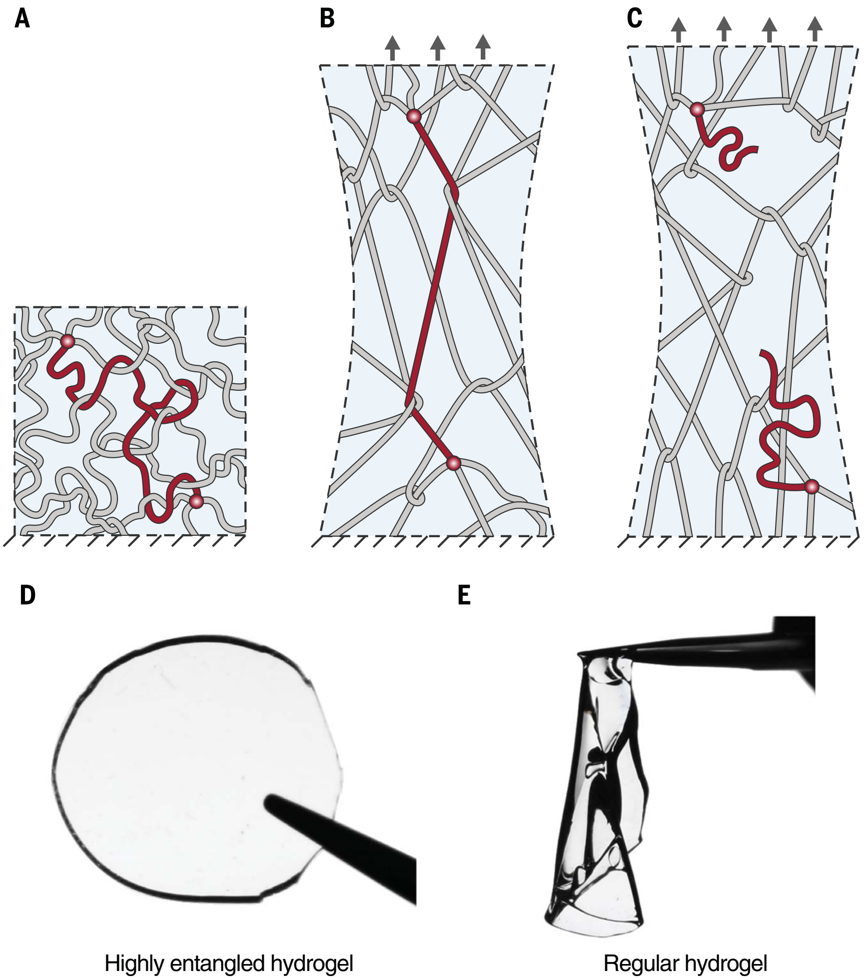

Fig. 1. A gel or elastomer in which entanglements greatly outnumber cross-links. (**A**) Each polymer chain has a large number of entanglements along its length and a cross-link (red dot) at each end. (**B**) A stretched polymer showing transmission of the tension to other chains. (**C**) A broken bond relaxes one chain and partly relaxes the entangled and cross-linked chains. Arrows indicate applied load. (**D**) Highly entangled hydrogel. (**E**) Regular hydrogel.

transmits along the chain and to many other chains through entanglements (Fig. 1B). When the chain breaks at a single covalent bond, the polymer dissipates the elastic energy in many chains, over long lengths (Fig. 1C). Unlike the double-network polymer, this single-network polymer achieves high toughness because all chains are long. Provided that the chains slip with low friction, the polymer has negligible hysteresis.

Whereas how entanglements affect stiffness has been appreciated since the inception of polymer science, how entanglements affect fracture, fatigue, and friction has not. In a polymer melt or solution, the entanglements provide elasticity on a short time scale and viscosity on a long time scale (*10*). In a cross-linked polymer, the entanglements cannot disentangle without chain scission, and they function as additional cross-links that stiffen the polymer (*11*, *12*). The stiffening effect of entanglements is pronounced when the cross-link density is low (*13*).

We ascertain that dense entanglements in hydrogels can be achieved using a precursor of typical ingredients but unusually low amounts of water, cross-linker, and initiator. Crowded monomers result in crowded polymers, which, as one might expect, densely entangle. For the precursor, let W be the water-to-monomer molar ratio, C be the cross-linker-to-monomer molar ratio, and I be the initiator-to-monomer molar ratio. To obtain a well-formed hydrogel, we fix $I/C = 0.4$, so that the initiating points that generate dangling chains are fewer than the cross-links (fig. S1).

We synthesize two polyacrylamide hydrogels using precursors of the same value of C, 3.2×10^{-5}, but different values of W, 2.0 and 25. After the as-synthesized hydrogels are submerged in water and swell to equilibrium, one hydrogel is turgid (Fig. 1D), but the other is flaccid (Fig. 1E and movie S1). The two hydrogels have the same cross-link density. If entanglements were absent, the two hydrogels would swell to the same equilibrium state. The difference in the mechanical behavior of the two hydrogels shows that they have different densities of entanglements. We call the former a highly entangled hydrogel, and the latter a regular hydrogel.

We study the conditions of W and C that form highly entangled hydrogels. Hydrogels of various values of W and C were synthesized and submerged in water. We measured the mass until the hydrogels swelled to equilibrium (fig. S2). The mass ratio of a fully swollen hydrogel to an as-synthesized hydrogel defines the swelling ratio (fig. S3). We plot the equilibrium value of the polymer-to-hydrogel mass ratio, φ, as a function of C and W (Fig. 2A and section 1 of the supplementary text in the supplementary materials). For a hydrogel made of a precursor of $W = 2.0$, in the absence

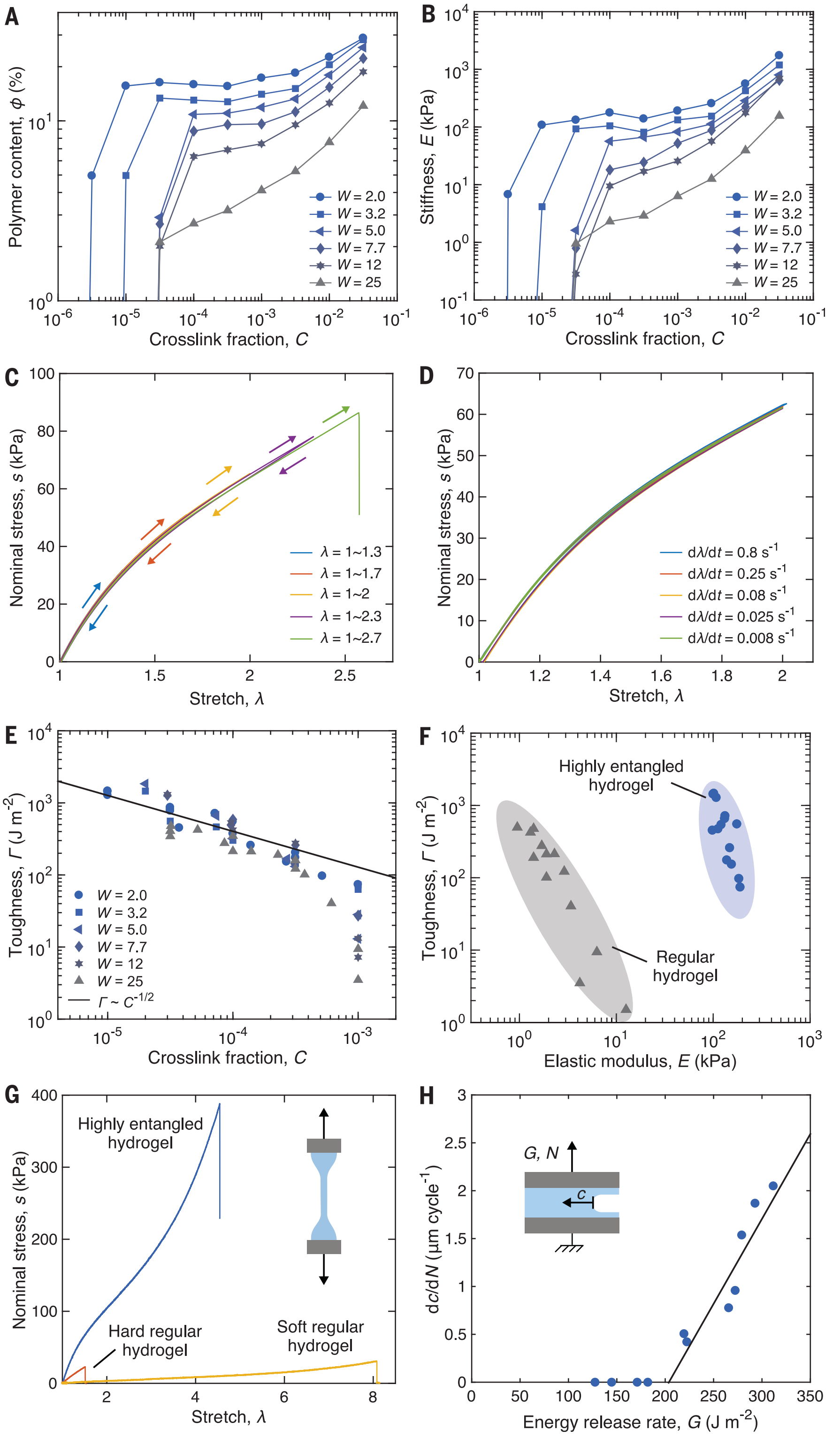

Fig. 2. Mechanical behavior of fully swollen hydrogels. (**A**) The polymer content, φ, of the fully swollen hydrogel. (**B**) The stiffness, E. (**C**) The hydrogel has negligible hysteresis. Arrows indicate loading and unloading. (**D**) The stress-stretch curve is rate-insensitive. (**E**) The toughness, Γ. Also plotted is the Lake-Thomas relation, $\Gamma \sim C^{-1/2}$. (**F**) Two families of hydrogels plotted in the stiffness-toughness plane. Regular hydrogels ($W = 25$) suffer from the stiffness-toughness conflict. Highly entangled hydrogels ($W = 2.0$) resolve this conflict and achieve both high stiffness and high toughness. (**G**) The stress-stretch curves of a highly entangled hydrogel, a hard regular hydrogel, and a soft regular hydrogel, under uniaxial tension. (**H**) The fatigue crack extension, c, per cycle, measured at various amplitudes of energy release rate. For (C), (D), (G), and (H), the highly entangled hydrogel was prepared using a precursor of $W = 2.0$ and $C = 1.0 \times 10^{-5}$.

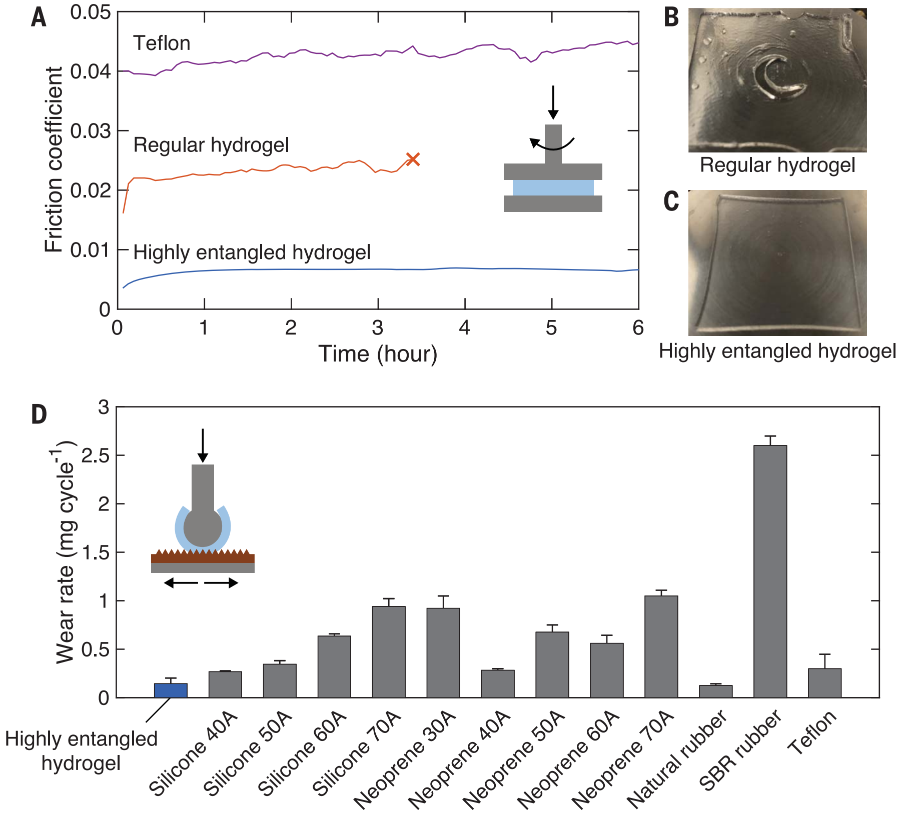

Fig. 3. Friction and wear. (**A**) The friction coefficients of a highly entangled hydrogel, regular hydrogel, and Teflon over time, tested in a rheometer (*29*). The normal pressure is 20 kPa, and the angular velocity is 1 rad/s. (**B**) The regular hydrogel ruptures after 3 hours. (**C**) The highly entangled hydrogel remains intact after 6 hours. (**D**) The wear rates of the highly entangled hydrogel and various materials. Hardness (durometer) is specified. Error bars indicate SEM; *n* = 10 for each group. SBR, styrene-butadiene rubber.

of cross-links, $C = 0$, chains dissolve in water, so that φ is vanishingly small. If C is nonzero but low, the hydrogel does not dissolve but is inelastic and squishy. At a critical value of $C \sim 1.0 \times 10^{-5}$, φ rises steeply. Aided by the dense entanglements, the critical C is low compared with values commonly used in making hydrogels. As C increases beyond the critical value, φ plateaus and is maintained by entanglements. The plateau lasts until $C \sim 10^{-3}$, beyond which φ increases gradually with C, indicating that cross-links are dense enough to prevail over entanglements. The plateau narrows as W increases and disappears when W exceeds about 5. For the same value of C, a precursor of a smaller W leads to a hydrogel of higher φ. The lower the value of W, the denser the entanglements and the lower the critical C. In a polymer network, the entropy of mixing drives swelling, but the entropy of elasticity drives deswelling (*14*). The entanglements function as additional cross-links and drive deswelling.

A similar plateau is also observed for stiffness (Fig. 2B). Such a plateau signifies the existence of entanglements and is used to estimate the density of entanglements (*15*). The stiffness of the hydrogel of $C = 1.0 \times 10^{-5}$ is similar to that of the hydrogel of $C = 1.0 \times 10^{-3}$. We assume that all cross-linkers in a precursor are incorporated into the polymer. Each cross-linker is an end of four chains, and each chain has two ends, so that the average number of monomers per chain is $(2C)^{-1}$. For the hydrogel of $C = 1.0 \times 10^{-5}$, each chain has, on average, $1/(2C) = 10^5/2$ monomers, but the measured stiffness indicates that the entanglements effectively shorten each chain to $10^3/2$ monomers. That is, each chain has entanglements equivalent to 10^2 cross-links.

The highly entangled hydrogel exhibits a high degree of elasticity. Under cyclic stretch to various amplitudes and a fixed rate, the hysteresis is negligible (Fig. 2C). The ratio of the dissipated energy (i.e., the area between the load and unload curves) to the applied work (i.e., the area under the load curve) is less than 1%. Furthermore, the stress-stretch curves are insensitive to the stretch rate over two orders of magnitude (Fig. 2D). The near-perfect elasticity results from several factors. First, although the cross-links are sparse, the dense entanglements aid in maintaining the network configuration when the polymer is stretched. Second, polymer chains are long and do not break before the sample fractures. Third, water has a low viscosity, such that the fully swollen hydrogel has low interchain friction. By comparison, the as-prepared hydrogels have low water content and exhibit pronounced hysteresis (fig. S4). The near-perfect elasticity is consistent with the measurements that the storage modulus is an order of magnitude higher than the loss modulus (fig. S5).

A highly entangled hydrogel behaves like a spring, but a double-network hydrogel behaves like a spring in parallel with a dashpot (*7*). When we hang masses on the highly entangled hydrogel and the double-network hydrogel and pluck, the former vibrates many cycles, but the latter damps to rest immediately (movie S2 and fig. S6A). A steel ball bounces on the highly entangled hydrogel but not on the double-network hydrogel (movie S3 and fig. S6B).

The highly entangled hydrogels exhibit high toughness (Fig. 2E). For hydrogels made from precursors of low C and W, cross-links are sparse, entanglements are dense, and toughness scales as $\Gamma \sim C^{-1/2}$, consistent with the prediction of the Lake-Thomas model (*3*). This consistency indicates that entanglements do not hinder the transmission of tension along the length of the long polymer chains. The toughness of 1460 J/m^2 is comparable to that of a double-network hydrogel (*16*). At small values of W, φ ranges from 8 to 16%. This modest change in φ is consistent with the observed weak dependence of toughness on W. For hydrogels made from precursors of high C and W, however, the cross-links are dense, the entanglements are sparse, and toughness falls substantially below the relation $\Gamma \sim C^{-1/2}$. The toughness observed here, 1 to 10 J/m^2, is consistent with values reported in the literature for regular polyacrylamide hydrogels (*7*).

Regular polymer networks suffer from the stiffness-toughness conflict (*4*, *5*). Stiffness scales with the cross-link density as $E \sim C$ (*2*), and toughness scales with the cross-link density as $\Gamma \sim C^{-1/2}$ (*3*), so that cross-links stiffen the polymers but embrittle them, and this also occurs in regular hydrogels. In the highly entangled hydrogels ($W = 2.0$), the entanglements stiffen polymers but do not embrittle them (Fig. 2F and fig. S7).

Entanglements also markedly strengthen polymers, as illustrated by comparing a highly entangled hydrogel with two types of regular hydrogels (Fig. 2G and section 2 of the supplementary text). The strength is 390 kPa for a highly entangled hydrogel ($W = 2.0$ and $C = 1.0 \times 10^{-5}$), 23 kPa for a hard regular hydrogel ($W = 25$ and $C = 1.0 \times 10^{-2}$), and 31 kPa for a soft regular hydrogel ($W = 25$ and $C = 3.2 \times 10^{-4}$). Entanglements strengthen a hydrogel for several reasons. First, entanglements constrain swell: φ = 16, 7.6, and 3.2% for the

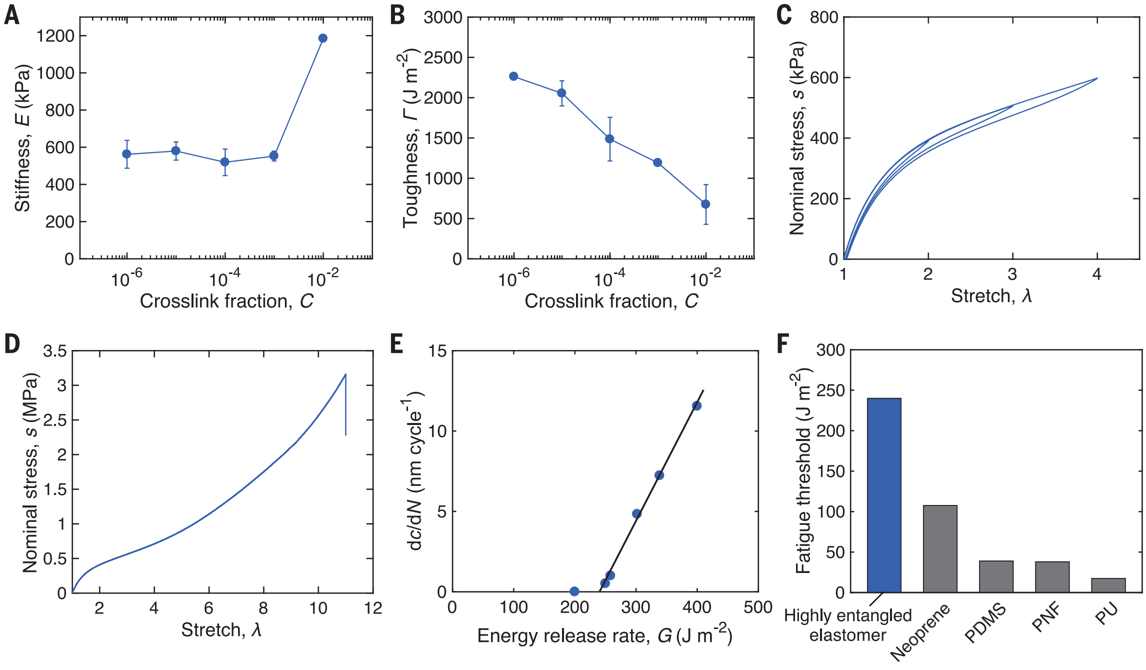

Fig. 4. A highly entangled elastomer. (**A**) At low C, the stiffness plateaus. (**B**) The toughness increases as C decreases. Error bars indicate SEM; n = 3 for each group. (**C**) Subject to load and unload, the highly entangled elastomer exhibits small hysteresis. (**D**) The stress-stretch curves of a highly entangled elastomer under uniaxial tension. (**E**) The fatigue threshold is ~240 J/m^2. (**F**) The highly entangled elastomer has a higher fatigue threshold than regular elastomers of similar stiffness. For (C) to (F), the elastomer is made with $C = 1.0 \times 10^{-5}$.

three hydrogels, respectively, so that the highly entangled hydrogel has more polymers to carry the load than the two regular hydrogels. Second, entanglements readily slip and enable tension to transmit in the chain along its length. Third, entanglements transmit tension between chains, and a highly entangled hydrogel has many more entanglements than a regular hydrogel. When a polymer is stretched, owing to statistical distribution, chains break at different times, which lowers the strength. The strength is increased when entanglements distribute tension both along a chain and between chains. Movie S4 shows that the highly entangled hydrogel lifts a weight at a nominal stress of 73 kPa but the two regular hydrogels do not.

Applications of polymers are often limited not by toughness under monotonic load but by fatigue threshold under cyclic load (*3*). For example, pure natural rubber has toughness of ~10^4 J/m^2 but a fatigue threshold of ~50 J/m^2. The toughness of natural rubber comes mainly from a dissipation process in the bulk (i.e., strain-induced crystallization), and the fatigue threshold comes from breaking chains across the crack plane (*3*). We measure the crack extension per cycle in a highly entangled hydrogel at various amplitudes of energy release rate (Fig. 2H). A linear regression of data estimates a fatigue threshold of ~200 J/m^2. This value is about four times that of natural rubber and about 20 times that of a regular hydrogel (*17*).

A highly entangled hydrogel is slippery and wear-resistant. When a hydrogel slides on a substrate, each polymer chain at the surface of the hydrogel is anchored to the polymer network on one end and mobile on the other end, provided that the polymer chain negligibly adsorbs to the substrate. These dangling and hydrophilic polymer chains stabilize a water-rich layer, which lubricates the surfaces (*18*). The friction decreases as the thickness of the water-rich layer increases, and the thickness scales with the size of the blob of the dangling chains. The highly entangled hydrogel has much longer polymer chains than the regular hydrogel, so that it has a lower friction coefficient. The friction coefficient of the highly entangled hydrogel is 0.0067, about three times lower than that of the regular hydrogel and six times lower than that of Teflon (Fig. 3A). Low friction, together with high toughness and fatigue threshold, leads to a low wear rate (*19*). The regular hydrogel ruptures after 3 hours of slide in a rheometer (Fig. 3B), but the highly entangled hydrogel remains intact after 6 hours of sliding (Fig. 3C). The highly entangled hydrogel has a lower wear rate than Teflon and most elastomers tested by us (Fig. 3D). A polyurethane elastomer and a silica-filled silicone have exceedingly low wear rates, which cannot be accurately determined in our experimental setup. These two materials, however, have friction coefficients much higher than that of the hydrogel.

The highly entangled hydrogels differ from existing hydrogels in other ways. For example, a sliding-ring hydrogel also distributes tension over long chains, but such a hydrogel has a low density of sliding rings and swells enormously, giving a low toughness of 20 J/m^2 and a low strength of 40 kPa (*20*, *21*). The stiffness-toughness conflict has also been resolved in polymers of microarchitectures (*22*–*24*). Unlike such polymers, a highly entangled hydrogel is synthesized in a single step, homogeneous above the scale of the mesh size, and optically transparent.

We next synthesize a highly entangled elastomer from a monomer, without solvent, at room temperature and extremely low C and I. We choose the monomer on the basis of the following considerations: (i) the monomer is a liquid of low viscosity, (ii) the resulting polymer is rubbery, and (iii) the resulting polymer has low entanglement molecular weight, as measured by a rheometer. To demonstrate, we choose ethyl acrylate as the monomer. It is a liquid of viscosity 0.55 mPa·s, even lower than water. Poly(ethyl acrylate) has a glass transition temperature of −21°C and a low entanglement molecular weight (*25*). We synthesize poly(ethyl acrylate) by using various values of C and a fixed value of I/C = 0.1. The polymer creeps below a critical value of $C \sim 10^{-6}$ but is highly elastic above it (fig. S8). As C increases beyond the critical value, stiffness first plateaus and then increases again after $C \sim 10^{-3}$ (Fig. 4A). The plateau confirms that these elastomers are highly entangled. The toughness reaches 2200 J/m^2 at $C = 10^{-6}$ (Fig. 4B). The high toughness is achieved even though the hysteresis is low (Fig. 4C). The low hysteresis can be further reduced by swelling the elastomer with an organic solvent (fig. S9). The highly entangled elastomer has a nominal strength of 3.2 MPa (Fig. 4D). This value corresponds to a true strength of 35 MPa, which is one order of magnitude higher than those of common unfilled acrylic elastomers (*26*). The highly entangled elastomer has a fatigue threshold of ~240 J/m^2 (Fig. 4E), which is much higher than that of regular elastomers at a similar stiffness, including neoprene (*4*), polydimethylsiloxane (PDMS) (*27*), phosphonitrilic fluoroelastomer (PNF) (*27*), and polyurethane (PU) (*28*) (Fig. 4F). Below the fatigue threshold, the crack growth cannot be detected in the highly entangled elastomer after 200,000 cycles of stretch (fig. S10).

A regular polymer has a netlike topology, whereas a highly entangled polymer has a fabric-like topology. In the former, cross-links prevail over entanglements. In the latter, cross-links are outnumbered enormously by entanglements. The different topologies result in different properties. The highly entangled polymers are ideal load-bearing materials: They resolve the stiffness-toughness conflict and simultaneously achieve high toughness and low hysteresis. They are strong, fatigue-resistant, and transparent. Upon swelling, they have low friction and high wear resistance. We have illustrated the behavior of highly entangled polymers using two material systems. Using a similar approach, we have also synthesized and tested a polyacrylic acid hydrogel (fig. S11). Potential applications of highly entangled polymers include swell-tolerant gels, fatigue-resistant adhesives, low-friction coatings, and transparent ionic conductors.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Supplementary Text
Figs. S1 to S13
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Movies S1 to S4

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Fracture, fatigue, and friction of polymers in which entanglements greatly outnumber cross-links

Junsoo KimGuogao ZhangMeixuanzi ShiZhigang Suo

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Longer and stronger; stiff but not brittle
Hydrogels are highly water-swollen, cross-linked polymers. Although they can be highly deformed, they tend to be weak, and methods to strengthen or toughen them tend to reduce stretchability. Two papers now report strategies to create tough but deformable hydrogels (see the Perspective by Bosnjak and Silberstein). Wang *et al*. introduced a toughening mechanism by storing releasable extra chain length in the stiff part of a double-network hydrogel. A high applied force triggered the opening of cycling strands that were only activated at high chain extension. Kim *et al*. synthesized acrylamide gels in which dense entanglements could be achieved by using unusually low amounts of water, cross-linker, and initiator during the synthesis. This approach improves the mechanical strength in solid form while also improving the wear resistance once swollen as a hydrogel. —MSL

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