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Supplementary Information for

Stretchable materials of high toughness and low hysteresis

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Other supplementary materials for this manuscript include the following:

Movies S1 to S8

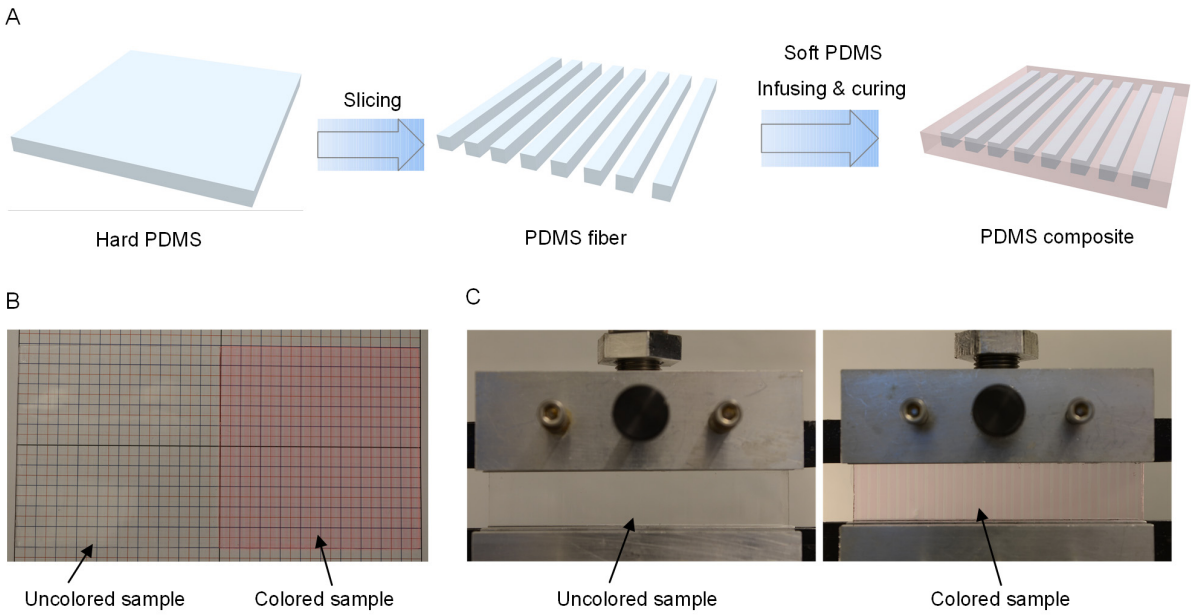

Fig. S1. Fabrication of a composite PDMS. (*A*) We cut film of cured hard PDMS into fibers by a paper cutter, align the fibers in an acrylic mold, pour the PDMS precursor at some ratio of A:B, and cure the composite. (*B*) Samples on the graph paper. On the left is an uncolored composite, which is transparent. On the right is a colored composite. (*C*) Samples mounted on the Instron machine. On the left is an uncolored sample, where the fibers and matrix are visually indistinguishable. On the right, the fiber is uncolored, but the matrix is colored.

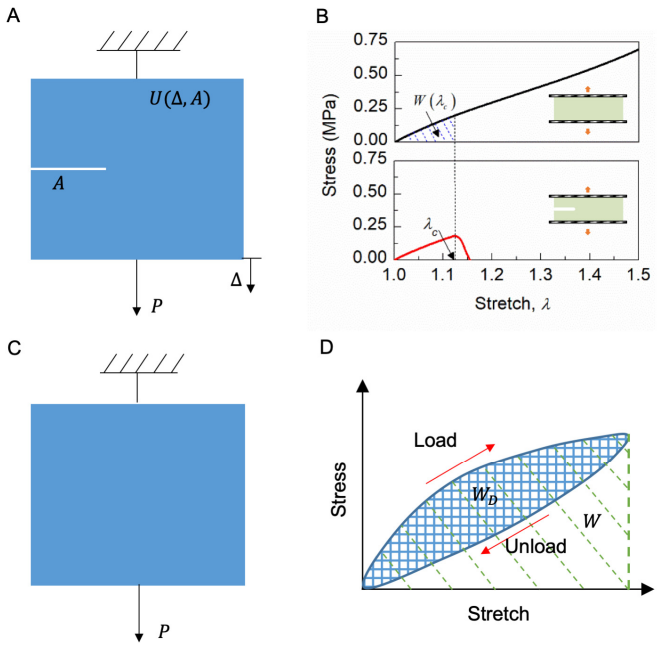

Fig. S2. Definition and measurement of toughness and hysteresis. Toughness and hysteresis both result from energy dissipation, but under different conditions. (*A*) The toughness is defined by the energy dissipated when a crack extends by a unit area. A pierce of material with a crack of area A is loaded by a force P, with the displacement of force Δ. The elastic energy stored in the material is U, which is a function of Δ and A. The work done by the load P is spent on change in the elastic energy and dissipated energy: $Pd\Delta = dU + \Gamma dA$. This equation defines the toughness Γ. (*B*) A method to measure toughness using the stress-stretch curves of two samples of the same material, one containing no crack, and the other containing a precut crack. (*C*) The hysteresis is measured by subject a sample containing no crack to load and unload. (*D*) The hysteresis is defined by W_D/W, where W is the area under the stress-stretch curve measured on loading, and W_D is the area between the loading and unloading curves.

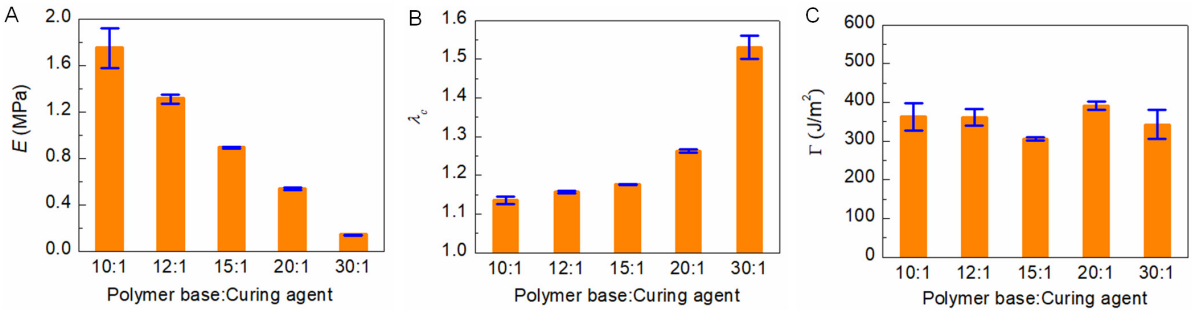

Fig. S3. Data of homogeneous PDMS. (*A*) The elastic modulus of PDMS decreases as the fraction of the curing agent decreases. (*B*) The critical stretch of a sample containing a precut crack increases as the fraction of the curing agent decreases. (*C*) The Sylgard PDMS have toughness ~ 300 J/m^2, insensitive to the A:B ratio within the range tested in this work. (Error bars: S.D., n = 3)

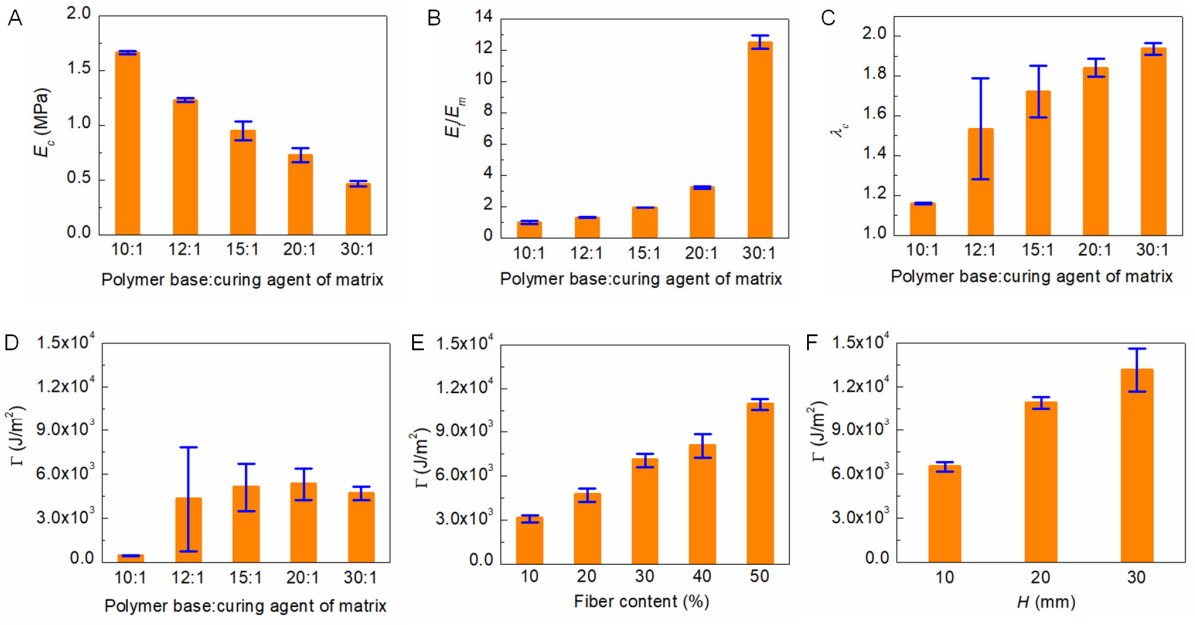

Fig. S4. Data of composite PDMS. (*A*) The modulus of composite decreases as the fraction of curing agent in matrix decreases. The fiber is made of hard PDMS (A:B = 10:1), the polymer base (part A) to curing agent (part B) ratio of matrix varies from 10:1 to 30:1. (*B*) The modulus ratio of fiber to matrix increases as the fraction of curing agent in matrix decreases. (*C*) The critical stretch of a sample containing a precut crack increases as the fraction of curing agent in matrix decreases. When the matrix has moderate fraction of curing agent (A:B = 12:1 and 15:1), the crack cuts the fibers in some samples, but bifurcates into the interface of fiber and matrix in other samples. The measured critical stretch scatters a lot. For matrix of A:B = 30:1, the fiber/matrix modulus contrast is 12. The crack deflects to the edge of samples before the fibers rupture, quite repeatable from sample to sample. (*D*) The measured toughness jumps and then reaches a plateau as the polymer base to curing agent ratio of matrix varies from 10:1 to 30:1. (*E*) When the matrix is fixed at A:B =30:1, the toughness increases almost linearly with the fiber content. (*F*) The measured toughness increases with the sample height within the range of experiment. The composition of matrix is A:B =30:1. (Error bars: S.D., n = 3)

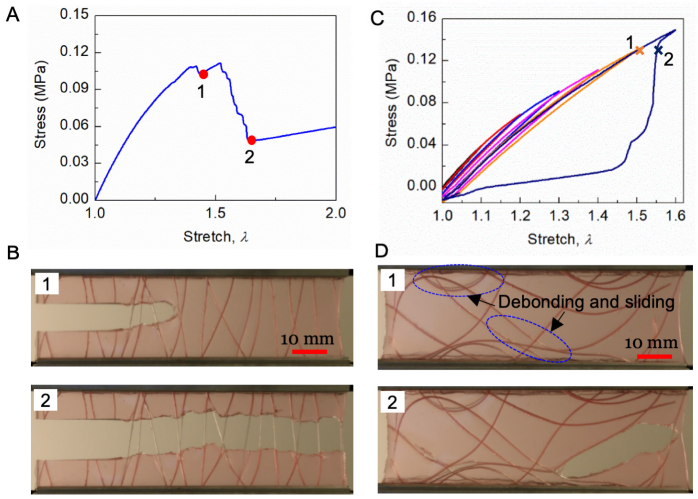

Fig. S5. Weak adhesion between the fibers and the matrix causes deboning and high hysteresis. Spandex fibers are distributed in a PDMS matrix (A:B = 30:1). (*A*) Stress-stretch curve of a precut sample. (*B*) Snapshots corresponding to the two points marked in (*A*). The precrack in the sample starts to grow when the stretch is around 1.4, and propagates through the whole sample gradually. The fibers do not break and slide against the matrix. (*C*) The stress-stretch curve of a sample without precut shows larger hysteresis than that of composites with good bonding. (*D*) Fibers debond and slide against the matrix as the stretch increases. Finally, the debond turns into a running crack.

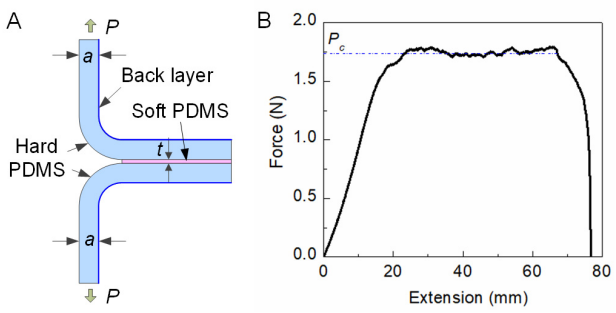

Fig. S6. Peeling toughness. (*A*) The sketch of peeling. The two arms are identical hard PDMS (A:B = 10:1) of thickness a = 3 mm. A flexible but non-stretchable film (Polyester film of 50 microns in thickness, from McMaster-Carr) is glued to each arm using the silicone adhesive (3M Super Silicone Sealant 8661, from McMaster-CARR). The thin middle layer of thickness t = 0.5mm is colored in red and its composition varies from 10:1 to 30:1. Four identical samples are tested for each composition. (*B*) The force-extension curve of a double peeling sample. When the two arms are stretched, the load increases and then reaches a plateau of P_c. The peeling toughness is calculated by $\Gamma_i = 2P_c/w$, where w = 20mm is the width of a sample.

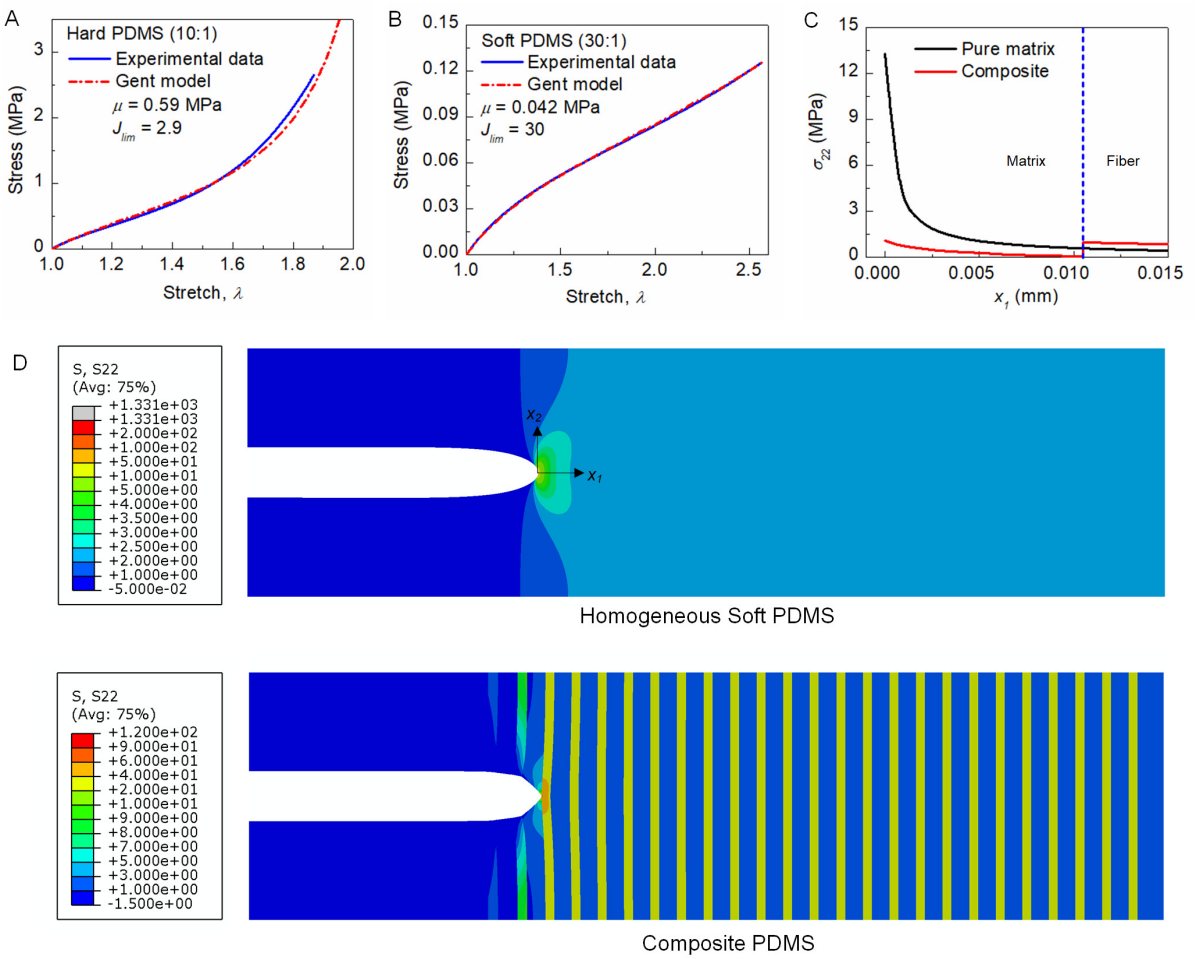

Fig. S7. Finite element Calculation. (*A*) The experimental stress-stretch curve of a hard PDMS is fit to the Gent model. (*B*) The experimental stress-stretch curve of a soft PDMS is fit to the Gent model. (*C*) Stress distribution in front the crack tips of a homogeneous soft PDMS and a composite PDMS. We use ABAQUS and implement the Gent model using UHYPER to calculate the stress state in two materials. We stretch the sample to $\lambda = 1.25$ and calculate the stress distribution (*D*) Stress distribution in the soft PDMS and composite PDMS. The stress is much more concentrated in the homogeneous soft PDMS than in the composite.

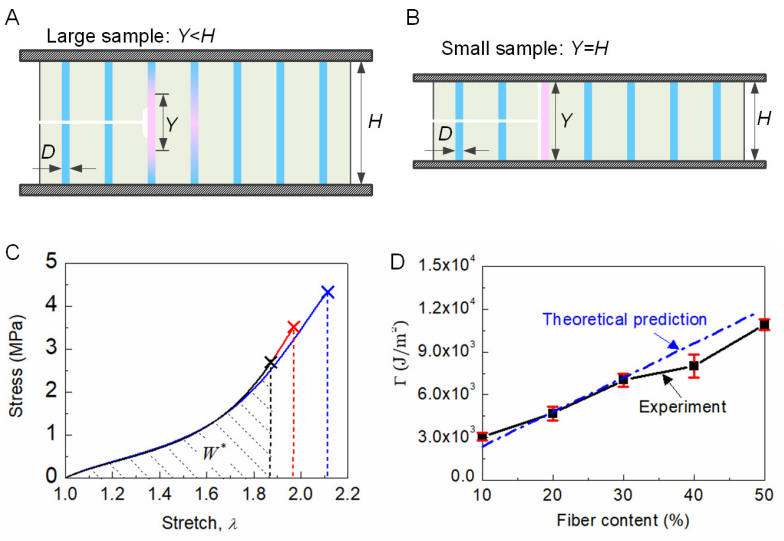

Fig. S8. Theoretical prediction of the toughness of composites. (*A*) When a composite is stretched, the load is mainly carried by the fibers due to the large fiber/matrix modulus contrast. As a crack approaches a fiber, the stress concentration near the crack tip region is alleviated by the stress redistribution and crack deflection. The fiber in front of the crack is almost under uniaxial tension in a length Y in undeformed state. When the fiber ruptures, all the elastic energy stored in this region is released. For a large enough sample, the process zone size Y is limited, smaller than the height of the sample H. (*B*) For a small sample, the process zone size, Y, equals to the sample height H. All the elastic energy in the fibers is released during the fracture process. The toughness is estimated by $\Gamma = W^* H\eta$, where W^* is the work to rupture of the fiber, and η is the fiber content. For composites of large fiber/matrix modulus contrast, the crack deflects to the edge of samples prior to fiber breaking, which means that the process zone is limited by the sample size. In these cases, $Y = H$. (*C*) The work to rupture of a fiber is the area under the stress-stretch curve up to rupture. (*D*) The theoretical predictions agree with the experimental results remarkably well. $W^* = 1.2$ MPa, $Y = H = 20$ mm, fiber content η varies between 10% and 50%.

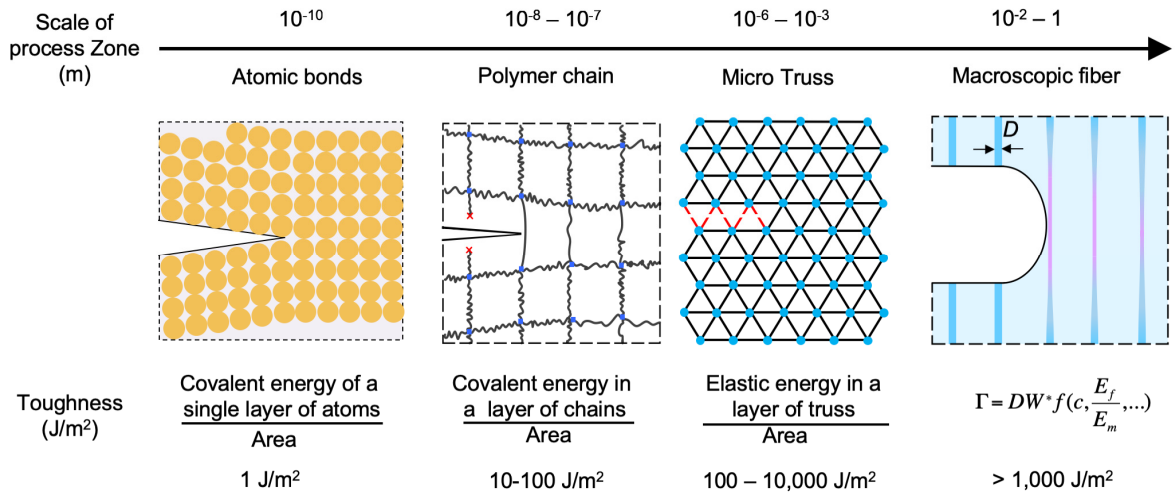

Fig. S9. Hysteresis can be low in materials of constituents of any size and geometry, but toughness increases with the size of the constituents. When a crack extends in a solid like silica, only a layer of atomic bonds breaks, and the atoms off the crack plane remain elastic. The fracture process zone is at the atomic scale and the toughness is the bond energy in a layer of atoms per unit area, on the order of 1 J/m^2. In a single-network elastomer, when a crack cuts a polymer chain, only one bond is broken, but the elastic energy stored in the entire chain is released. The fracture process zone varies between 10-100 nm, and the toughness is the bond energy in a layer of chains per unit area, around 10-100 J/m^2. In a material made of micro trusses, when a crack cut though the material, the energy stored in a layer trusses is dissipated. The fracture process zone is on the order of the length of a truss member, and the toughness is the energy in a layer of truss members per unit area, about 100-10,000 J/m^2, depending on the base material property and the feature size. One can also embed the truss in a soft matrix. For a stretchable composite, the matrix has low elastic modulus, the fibers have high elastic modulus, and the matrix and the fibers form strong adhesion. At a crack front, the soft matrix shears greatly, spreading large stretch in a long segment of each fiber. When a fiber breaks, all the elastic energy stored in the highly stretched segment is released. This process is analogous to that in a single polymer network, but achieves high toughness because rupture releases energy in the length scale of a fiber segment, rather than that of a polymer chain. The process zone is at dimension of fiber size, and the toughness can be easily beyond 1,000 J/m^2. The figure illustrates a few represented architectures of materials. Many other examples can be included, such as a brick-mortar structure, a three-dimensional lattice filled with a soft matrix, a matrix containing short fibers, a laminate of fiber-reinforced sheets.

Movie S1. When a homogeneous hard PDMS with a precut crack is stretched to 1.12 times its original height, the crack runs through the entire sample. The ratio between the base and curing agent is A:B = 10:1. The height of the undeformed sample between the two gripers is 20 mm.

Movie S2. When a composite PDMS of large fiber/matrix modulus contrast ($E_f/E_m \sim 12$) is pulled to a stretch around 1.5, the crack blunts, but remains stable. As the stretch increases, the crack branches near the interface between the matrix and fiber. At a stretch of 1.85, the fibers at location far away from the crack front start to break, and the whole sample ruptures. A:B is 10:1 for the fibers, and is 30:1 for the matrix. We color the matrix in red to see the fibers.

Movie S3. In a composite of identical fiber and matrix composition (A:B = 10:1), the crack cut through the fibers sequentially at a small stretch at around 1.1. The behavior is similar to a crack running in a homogenous hard PDMS (Movie S1).

Movie S4. Spandex fibers and PDMS matrix have weak adhesion. When the composite is pulled to a stretch around 1.4, the crack starts to grow. As the crack runs in the matrix, the fibers remain intact and slide against the matrix. A:B = 30:1 for the matrix.

Movie S5. When a composite of Spandex fibers and PDMS matrix is subject to cyclic loading, fibers debond and slide against the matrix. Finally, the debond turns into a running crack.

Movie S6. When the middle layer of a peeling sample is the hard PDMS (A:B = 10:1), the sample peels along an interface between the middle layer and an arm. The red middle layer is left on one peeled arm, but not on the other.

Movie S7. For a peeling sample of the middle layer of A:B = 15:1, the sample peels through the middle layer, the peeling toughness is almost the same as the bulk toughness (over 300 J/m2), and the middle layer leaves residuals on both peeled arms.

Movie S8. When the middle layer is soft (A:B = 30:1), the sample peels through the middle layer with a wavy pattern.