Electronic Supplementary Material (ESI) for Nanoscale.

Tough and Strong Bioinspired Nanocomposites via Interfacial Cross-links

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1. The origin of the saw-tooth shape of the stress-strain curve

Figure S1 shows the number of broken cross-links and the stress-strain response simultaneously for the sample with 23.69% cross-links. Evidently, the dramatic drops in the stress-strain curve are always accompanied by the breakage of cross-links.

2. Energy evolution during the tensile test for different cross-link stiffness

Figure S2 shows the energy evolution in terms of types of interactions during the tensile test when the cross-link density is equal to 24.11 percent. Note that because of the thermal fluctuation of the system, the energy change ratio in the very beginning is not reasonable. To avoid confusion, we choose 0.04 as the start value of strain. Results indicate that as the stiffness of the cross-links increases, the proportion of the van der Waals energy variation in the total energy increase decreases while that of inter-chain energy, especially bond and angle energy, increases; this implies that the polymer chains are more stretched for samples with stiffer cross-links. The increasing stiffness of the cross-links enhances the ability of load transfer and energy absorption for the composite. However, here comes the question: do the cross-links play an important role in energy absorption? **Figure S3** shows the energy variation classified according to types of components and interactions during the tensile test. It indicates that the energy variation of the cross-links is negligible compared with those of the polyethylene matrix and graphene fibers. Another conclusion can be drawn that the polyethylene matrix, rather than graphene fibers, plays the major role in energy absorption.

3. Structural probability distribution variation for different cross-link stiffness

Figure S4 shows the structural distribution of polyethylene matrix from samples with 24.11 percent cross-link density, the stiffness of which is equal to 965kJ.mol^{-1}.Å^{-2}. As we can see, for bonds and angles, there is only one peak, located at 1.54Å and 112.8^{o} respectively. The shapes of the curves change slightly as deformation continues. Unlike the probability distribution of bond and angle, there are three peaks, two big ones at positive and negative 120 degrees and a small one at 0 degrees. During the tensile test, the middle peak is flattened while the remaining two only undergo minor fluctuations. **Figure S5** shows the structural distributions of polyethylene matrix from samples with 24.11 percent cross-links with a stiffness of 3860kJ.mol^{-1}.Å^{-2}, which exhibit similar features to Figure S4. However, there are some differences we can see from the bond and angle probability distributions. Unlike Figure S4, we can see from Figure S5 that as the deformation progresses the peaks in bond and angle distribution become even, indicating that the intra-chain configurations change dramatically. These findings are in accordance with the conclusion in the main text that as the

cross-link stiffness increases, bond and angle energy play an important role in enhancing the energy-absorption ability.

Figures

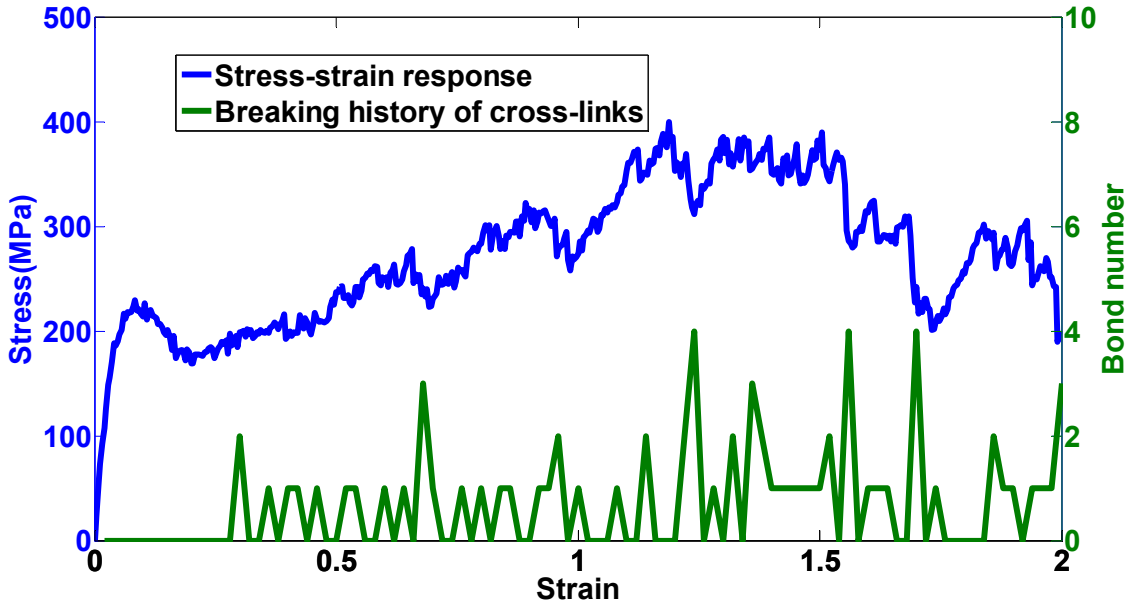

Figure S1. Stress-strain curve and the number of broken cross-links during the tensile test (cross-link density is equal to 23.69%).

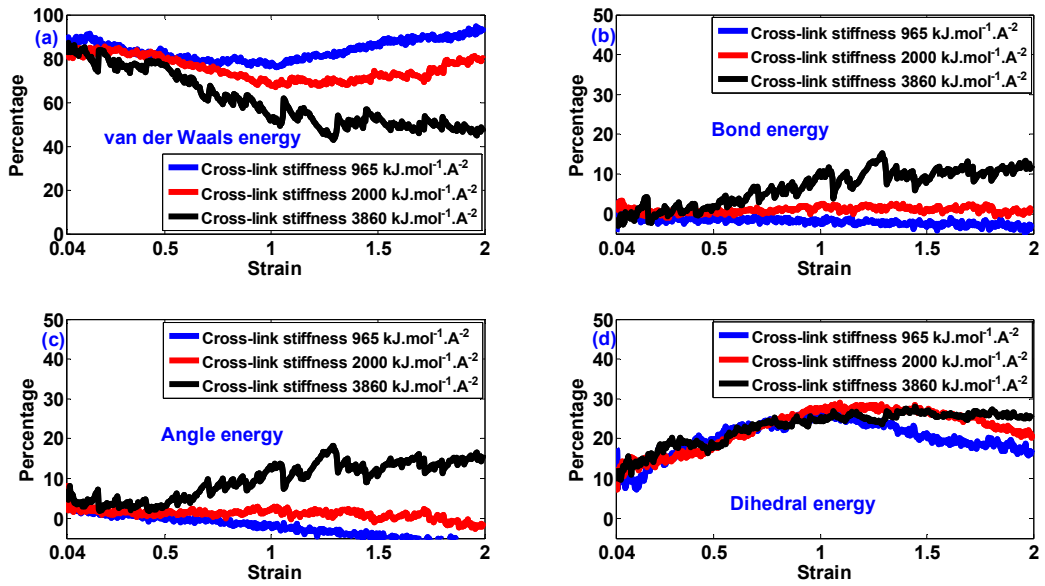

Figure S2. Percentage variation of energy evolution during the tensile test for different stiffness of cross-links when the cross-link density is 24.11% (a) van der Waals energy; (b) Bond energy; (c) Angle energy; (d) Dihedral energy.

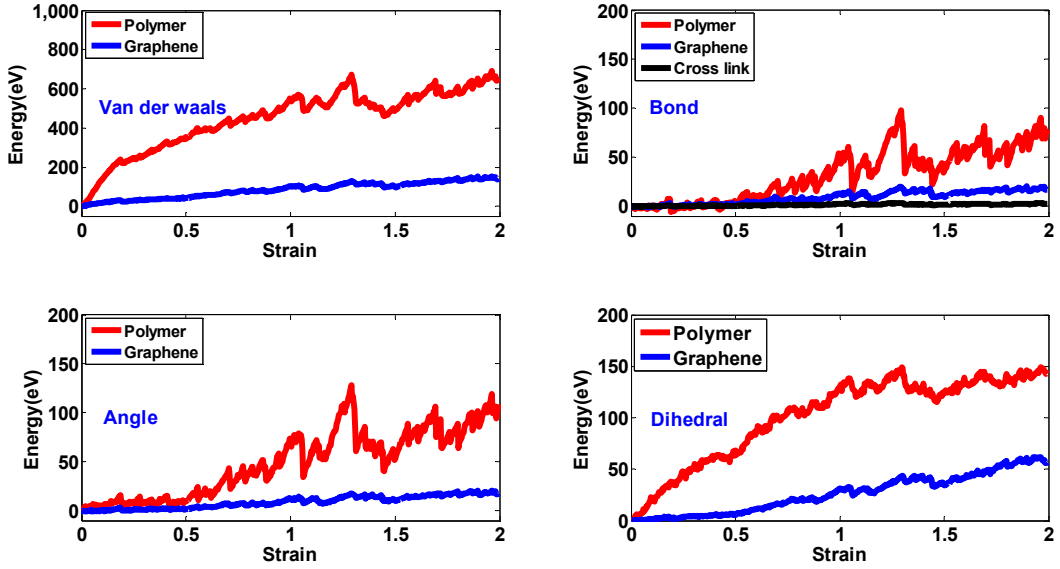

Figure S3. Energy evolution with respect to different types of interactions during the tensile test when the stiffness and density of cross-links are 3860 kJ.mol^{-1}.Å^{-2} and 24.11%, respectively.

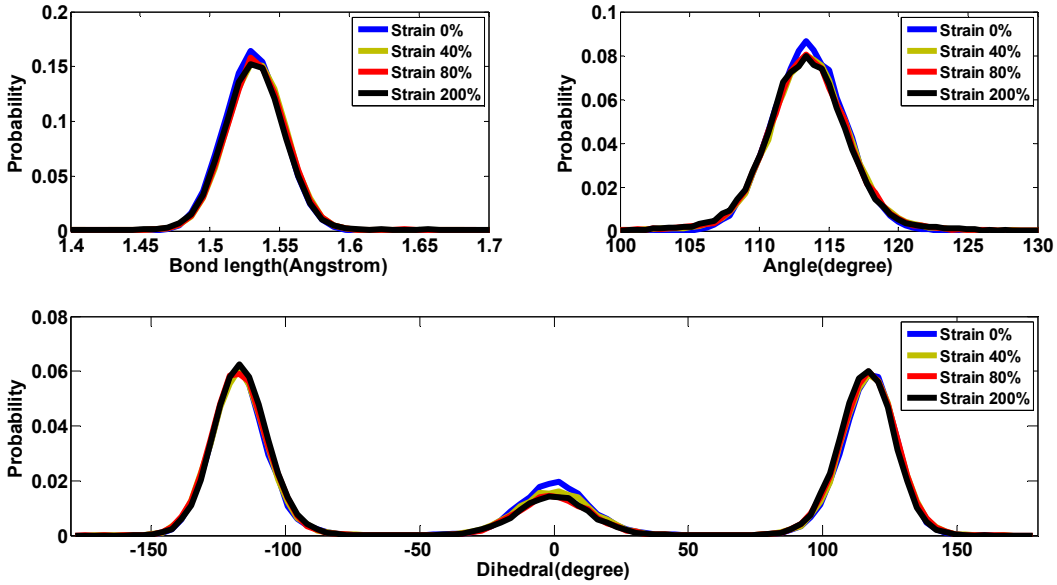

Figure S4. Structural probability distribution of the polyethylene matrix during the tensile test when the cross-link stiffness and density are 965 kJ.mol^{-1}.Å^{-2} and 24.11%, respectively.

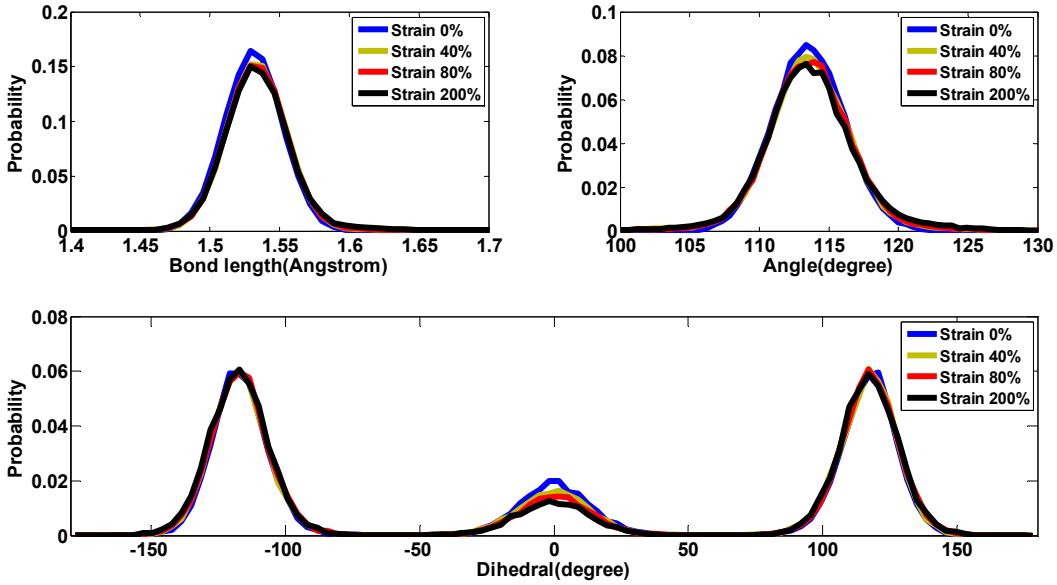

Figure S5. Structural probability distribution of the polyethylene matrix when the cross-link stiffness and density are 3860 kJ.mol^{-1}.Å^{-2} and 24.11%, respectively.

Tables

Table S1. Summary of the polynomial fittings of the relations between mechanical properties and density of cross-links

Mechanical properties	Fitting forms and parameters(ρ is the density of cross-links)
Young's modulus(E) (unit: MPa)	$E = a_1\rho^2 + a_0$ a_1=0.8290, a_0= 4127.1
Ultimate strength(σ_u) (unit: MPa)	$\sigma_u = a_1\rho^2 + a_0$ a_1=0.3394 , a_0=215.42
Toughness(T) (unit: $MJ.m^{-3}$)	$T = a_1\rho^2 + a_0$ a_1=0.3618 , a_3=299.97