

Supporting Information

Effect of nonaffine displacement on the mechanical performance of degraded PCL and its graphene composite: an atomistic investigation

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S1 The degree of swelling and the loss of weight in the erosion model

The degree of swelling (DoS) and the loss of weight (LoW) are calculated for the light erosion (LE) model and the heavy erosion (HE) model. The calculation method is the same as the experiment, based on the weight w of the material.^[1]

$$\text{DoS} = \frac{w_{wet} - w_{dry}}{w_{dry}} = \frac{w_{water}}{w_{PCL}}$$

$$\text{LoW} = \frac{w_0 - w_{dry}}{w_0} = \frac{w_0 - w_{PCL}}{w_0}$$

w_0 is the weight of predegraded PCL; w_{water} and w_{PCL} is the weight of water and PCL in the degraded structure respectively. The DoS is close to the LoW, which matches the PCL hydrolytic degradation in the experiment.

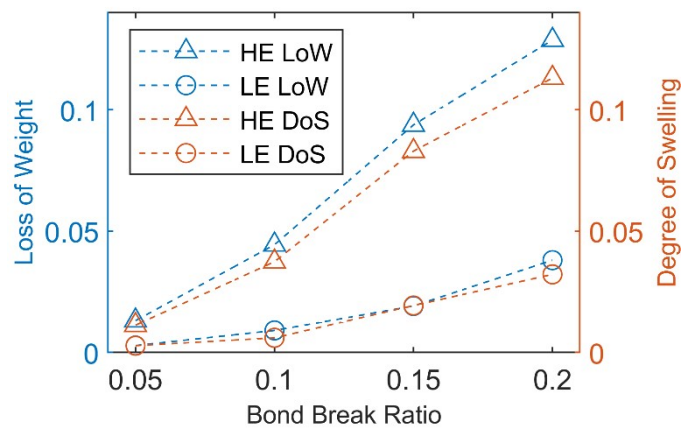


Figure S1 The loss of weight and the degree of swelling for the heavy erosion models and light erosion models.

S2 The R-square from the theoretical linear prediction and stress-strain history

As the stress history is influenced by the thermal noise significantly, the R^2 value of the initial data is small. To determine the linear region, the R^2 theoretical prediction from a linear signal with noise assumption is compared with real history. The prediction aligns well with data at the small strain, and starts to diverge later (Figure S2). The proportional limit is determined when the difference reaches 0.005.

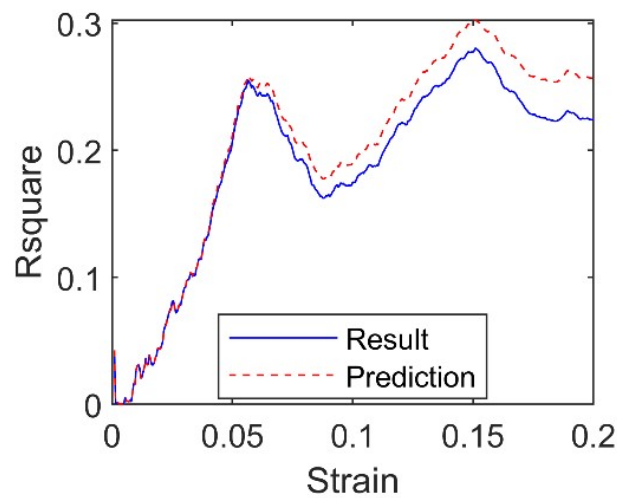


Figure S2 The R-square history of the PCL tensile test with a strain rate of 10^{-4} ps⁻¹

S3 The Young's modulus influenced by the PCL diffusion rate at different stages.

The MSDs of PCL at three tensile rates and equilibrium are shown in **Figure S3**. Usually, the relation between MSD and time τ can be described by the power law $MSD = K\tau^\alpha$. For the typical particle Brownian motion, $\alpha = 1$. However, for large molecules, the local confinement and viscoelasticity can cause subdiffusion, where $\alpha < 1$.^[2] For the highest strain rate in the low strain rate region ($5 \times 10^{-4} \text{ ps}^{-1}$), the subdiffusion stage can be observed and the affine displacement starts to dominate the MSD in the subdiffusion stage. For the lowest strain rate in the high strain rate region ($5 \times 10^{-3} \text{ ps}^{-1}$), the affine displacement takes effect before the subdiffusion region, and the subdiffusion region cannot be observed. For the strain rate at the transition region ($1 \times 10^{-3} \text{ ps}^{-1}$), the MSD difference caused by the affine displacement is less than 1% at the end of picosecond relaxation.

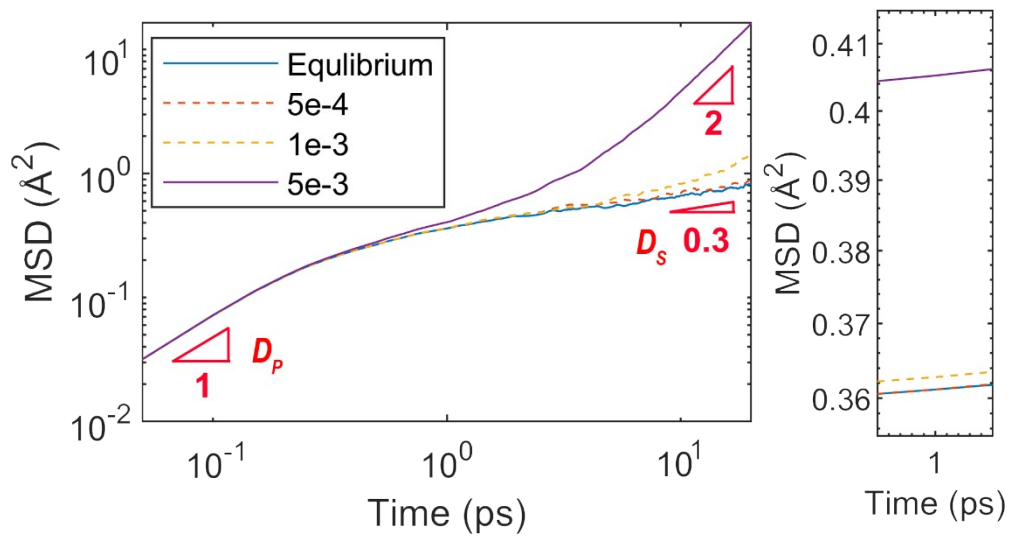


Figure S3 The MSD of PCL under different strain rates. The right panel is the zoomed-in version for $1 \pm 0.005 \text{ ps}$.

S4 The molecule volume change during the tensile deformation

The molecular volume is recorded for CS20% during the tensile test. The molecular volume has an ignorable change during the tensile deformation.

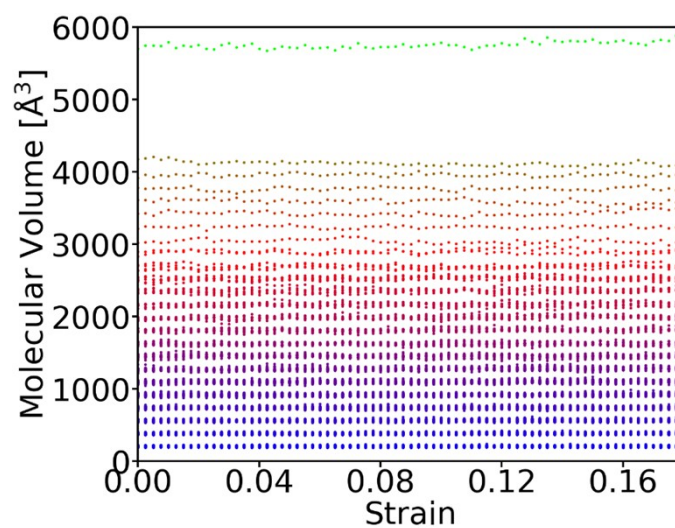


Figure S4 The average molecular volume for each molecular weight in the CS20% model during the tensile simulation, colored by molecular weight.

S5 The radial distribution function and the local strain of graphene

The radial distribution function (RDF) of the graphene during the composite tensile test is tracked. The initial RDF is colored in blue, which changes into red by gradient according to the composite strain. The RDF does not have a noticeable shift, even when the composite strain reaches 0.2. Only the distribution becomes a bit narrow when the strain increases. The overall strain does not change into the local strain of graphene on the same scale.

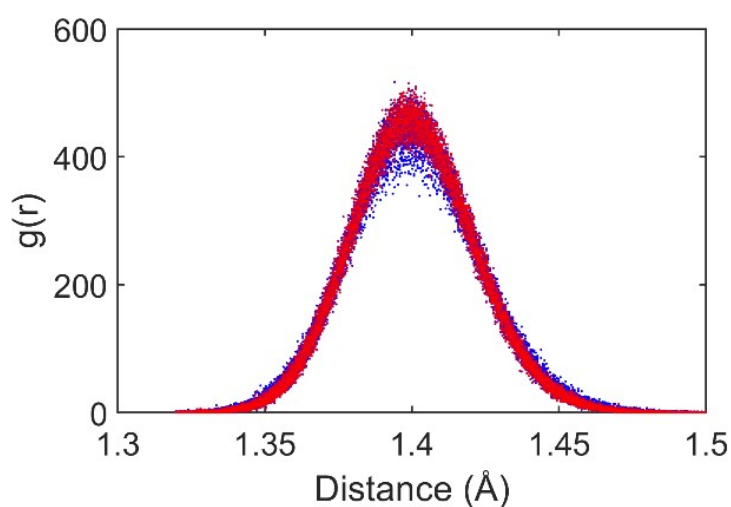


Figure S5 The radial distribution function of graphene during the composite tensile deformation.

S6 The average pressure of each molecular weight in CS20%

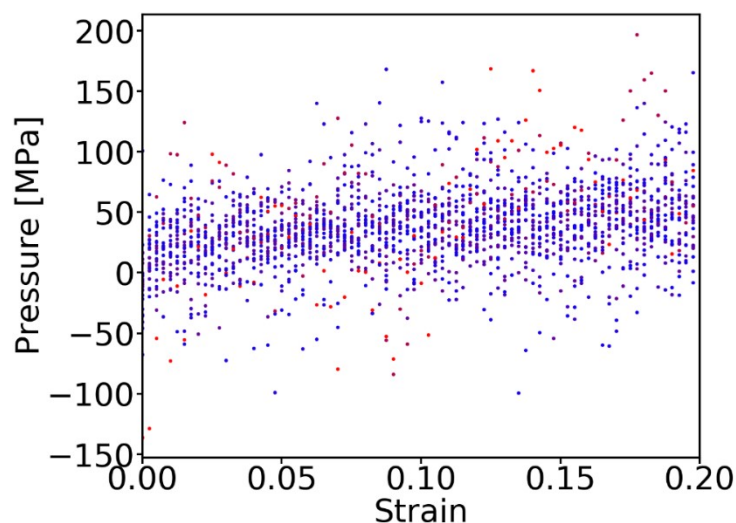


Figure S6 The average pressure for each molecular weight in CS20% has more noise and less increment.

Table S1. The potential settings of atoms in OPLS potential.

| Atom type | Potential | Mass [Da] | Charge [e] | Sigma [Å] | Epsilon [kJ mol ⁻¹] |
|----------------------------|-----------|-----------|------------|-----------|---------------------------------|
| Alcohol at the end | | | | | |
| Alcohol C | opls_157 | 12.0110 | 0.145 | 3.50 | 0.276144 |
| Alcohol O | opls_154 | 15.9994 | -0.683 | 3.12 | 0.711280 |
| Alcohol H | opls_155 | 1.0080 | 0.418 | 0.00 | 0 |
| Alkane and ester | | | | | |
| Alkane H | opls_140 | 1.0080 | 0.060 | 2.50 | 0.125520 |
| Methylene C | opls_136 | 12.0110 | -0.120 | 3.50 | 0.276144 |
| Ester C | opls_465 | 12.0110 | 0.510 | 3.75 | 0.439320 |
| Double bond O | opls_466 | 15.9994 | -0.430 | 2.96 | 0.878640 |
| Single bond O | opls_467 | 15.9994 | -0.330 | 3.00 | 0.711280 |
| Methoxy H | opls_469 | 1.0080 | 0.030 | 2.42 | 0.062760 |
| Methoxy C | opls_468 | 12.0110 | 0.160 | 3.50 | 0.276144 |
| Carboxyl at the end | | | | | |
| H | opls_270 | 1.0080 | 0.450 | 0.00 | 0 |
| Single bond O | opls_268 | 15.9994 | -0.530 | 3.00 | 0.711280 |
| Double bond O | opls_269 | 15.9994 | -0.440 | 2.96 | 0.878640 |
| C | opls_267 | 12.0110 | 0.520 | 3.75 | 0.439320 |

References

- [1] I. Castilla-Cortázar, J. Más-Estellés, J. M. Meseguer-Dueñas, J. L. Escobar Ivirico, B. Marí, A. Vidaurre, *Polym. Degrad. Stab.* **2012**, 97, 1241.
- [2] S. C. Weber, J. A. Theriot, A. J. Spakowitz, *Phys. Rev. E* **2010**, 82, 011913.