Supporting Information

The design of highly conductive and stretchable polymer conductors with low-load nanoparticles

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Model and simulation details

In this study, we simulated an isothermal system that exploits specific interaction potential, drag, and thermal noise terms to implicitly describe solvent effects by using Langevin dynamics. The equation of motion for each coarse-grained bead in the system is governed by the Langevin equation,

$$m_i \ddot{\mathbf{r}}_i(t) = \mathbf{F}_i^{\mathbf{C}} (\mathbf{r}_i(t)) + \mathbf{F}_i^{\mathbf{R}}(t) - \gamma_i \mathbf{v}_i(t).$$
 S1

Here, m_i is the mass of the bead *i*, **r** and **v** are the position and velocity of the bead, respectively, $\gamma = I/D$ is the coefficient of friction, where D is the diffusion coefficient of the bead. We fixed $\gamma = 1.0$ by assuming that the friction coefficient has no spatial and temporal fluctuations. F^C is the conservative force derived from the summation of bonding and nonbonding potential energies. The action of the solvent is implicitly handled by a random force (F^R) that satisfies the fluctuation dissipation theorem,

$$\langle \mathbf{F}_{i}^{\mathrm{R}}(\mathbf{t})\mathbf{F}_{i}^{\mathrm{R}}(t')\rangle = 6\gamma k_{B}T\delta_{ij}\delta(t-t').$$

Here, k_B is the Boltzmann constant and T is the temperature. The coupled action of friction and random forces constitutes an efficient thermostat.

The nanoparticle model consists of 90 coarse-grained beads with a diameter of σ , and these beads are uniformly arranged on a spherical surface with a diameter of 5σ . The motion and rotation of nanoparticle are tackled by rigid body method in which the rotation is integrated by quaternion algorithm¹. Each polymer chain consists of 500 coarse-grained beads. For polymer chains, the interaction potential between adjacent bonded beads is represented by a harmonic potential,

$$U_{\text{harmonic}}(r) = \frac{1}{2}k(r - r_0)^2.$$
 S3

where k is the force constant, k=1000.0 ε/σ^2 .

In the simulation process, the degree of aggregation between nanoparticles is characterized by calculating the radial distribution function between particles. The radial distribution function describes the probability of finding pairs of nanoparticles within a certain distance r, and is calculated as

$$g(\mathbf{r}) = \frac{v}{N^2} < \sum_i \sum_{j \neq i} \delta(r - r_{ij}) >, \qquad S4$$

where N is the total number of nanoparticles in the system and V is the volume of the simulation box.

The chain-like structure formed by the self-assembly of nanoparticles in the conductive nanocomposite system is driven by the stress and will gradually orient along the stretching direction when the system is stretched. At a fixed strain rate, the orientation of the nanoparticle's chain-like structure can be calculated by

$$P_2 = (3 < \cos^2 \alpha > -1)/2,$$
 S5

where α is the angle between the vector formed by the two nanoparticles in direct contact and the reference direction (refers to the stretch direction z direction). The calculation of Equation S5 requires statistics and averaging of adjacent nanoparticles in all chain-like structures in the system. The adjacent nanoparticles in all chain-like structures in the system are counted and averaged. Therefore, we can obtain the change process of the orientation of the chain-like structure formed by the self-assembly of nanoparticles during the stretching process.

All simulations were performed in a cubic simulation box of length 80 σ with periodic boundary conditions under a canonical (NVT) ensemble, we use affine deformation to change the box length in three orthogonal directions, but keep the constant volume, to describe the actual tensile strain under the tensile simulation. The reduced density of polymer beads is fixed at $\rho^* = 0.85$. The temperature is fixed at T^{*} = 2.5. Velocity-Verlet algorithm is applied to integrate the equations of motion with a time step $\delta t = 0.002$. All simulations were carried out with an in-house package².

The mixtures of polymers and nanoparticles are simulated at least 6×10^7 time steps to obtain an equilibrium configuration. Following, irreversible cross-linking is randomly introduced to change the topological connection by adding new bonds between adjacent beads from different chains, forming polymer elastomers. Six independent samples of equilibrium structures were averaged to reduce statistical errors. We maintained a fixed stretching rate during the tensile strain process, and the initial zdirection simulation box length (80σ) of the system was uniaxially stretched along the z-axis direction within the 2×10^7 simulation time step, and finally reached 400 σ . To reduce statistical error, we performed 30 independent simulations of the stretching process of the system, and averaged the percolation probability and orientation results.

- 1. Nguyen, T. D.; Phillips, C. L.; Anderson, J. A.; Glotzer, S. C., Rigid body constraints realized in massively-parallel molecular dynamics on graphics processing units. *Comput. Phys. Commun.* **2011**, *182* (11), 2307-2313.
- Zhu, Y. L.; Liu, H.; Li, Z. W.; Qian, H. J.; Milano, G.; Lu, Z. Y., GALAMOST: GPUaccelerated large-scale molecular simulation toolkit. *J. Comput. Chem.* 2013, 34 (25), 2197-211.



Figure S1 Percolation probability as a function of the volume fraction of NPs with different polymer contents for 10% and 30% cross-linking degree (CD), respectively. The cross-linking degree is defined as $2*N_c/N_b$, where N_c is the number of cross-linking bonds and N_m is number of polymer beads.



Figure S2 Structures of 10 vol% NPs-20 vol% polymer systems under different tensile strains: (a) equilibrium state; (b) 80% strain; (c) 160% strain; (d) 240% strain; (e) 320% strain; (f) 400% strain, respectively.