Supplementary Information

Molecular dynamics simulation of the formation mechanism of the thermal conductive filler network of polymer nanocomposites

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Thermal conductivity of neat polymer

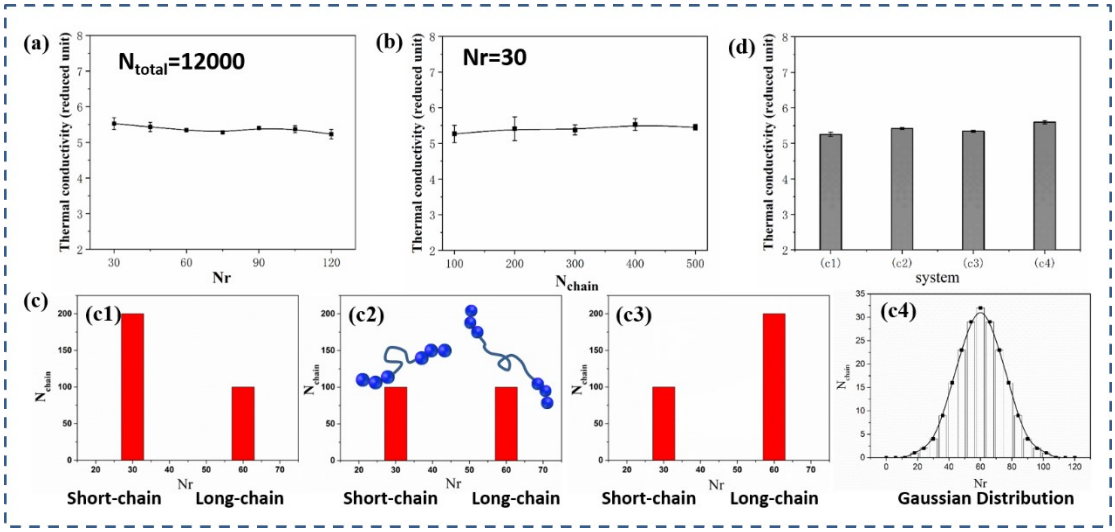

Fig. S1 Thermal conductivity of systems as a function of (a) chain length, Nr and (b) chain number (N_{chain}); (c1-c3) Chain length distribution and (c4) gaussian distribution; (d) Thermal conductivity of systems in (c1-c4).

Fig. S1(a) shows the thermal conductivity (TC), averaged by X, Y and Z directions, of polymer matrix as a function of the chain length (N_r). The total number of polymer beads in the matrix was fixed at 12,000 and N_r is set from 30 σ to 120 σ, corresponding to the chain number N_{chain} is from 400 to 100. The results show that TC of the system ranges from 5.0 to 6.0 (reduced unit) when N_r increases from 30 σ to 120 σ, which indicates that the molecular chain length has a little influence on the TC of the neat polymer. Molecular chain of N_r=30 σ was chosen to investigate the effect of the number of polymer chains (N_{chain}) on the thermal conductivity, and the TC is almost independent of N_{chain} too. Furthermore, for practical polymeric materials, there is always a distribution of the molecular chain length. Several systems were built, which includes three chain length distribution systems (Fig. S1(c1-c3)) combined the chains of N_r=30 σ and N_r=60 σ, and a Gaussian distribution system shown in Fig. S1(c4). Consequently, TC shown in Fig. S1(d) of these systems are similar. Finally, a system with the uniform molecular chain length of 30 σ (N_r=30) was chosen as the matrix for it is simple and representative enough. The box dimensions of these neat polymer systems are 24.01±0.2% σ.

Thermal conduction probability of systems with NPs of D_{NP}=2

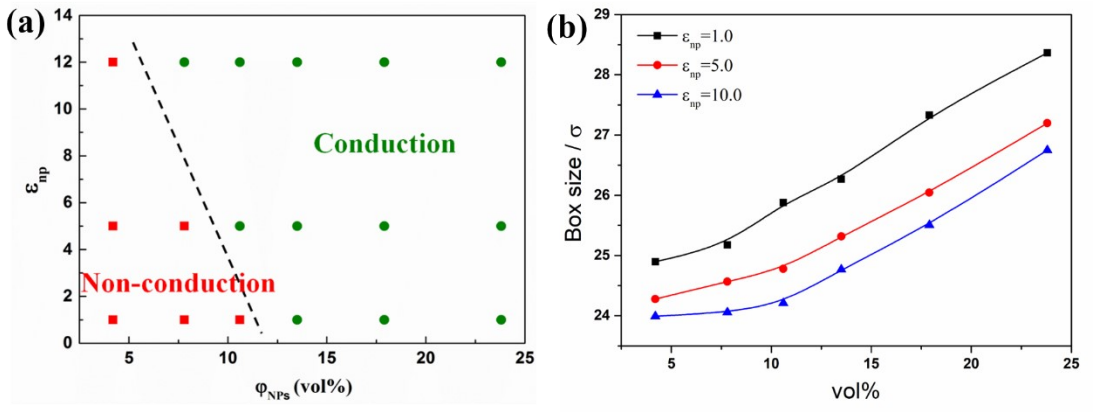

Fig. S2 (a) Phase diagram of thermal conduction probability of systems with filler size of D_{NP}=2 as a function of filling volume fraction. The green dot indicates that the system forms conduction, while the red dot indicates that the system fails to form conduction. (b) The box sizes of D_{NP}=2 systems.

The conduction probability of system with NPs of D_{NP}=2 is always 0 or 1, and there are almost no intermediate states because the assembly behavior is sensitive to ε_{np} due to the high specific surface area. NPs tend to connect to clusters as both packing fraction and physical interfacial interaction increases. The box sizes of filled systems in this work show an increase by up to 18% at most compared to neat polymer systems. Furthermore, the box size of D_{NP}=4 systems is similar to D_{NP}=2 systems, which is not list in detail.

Radial distribution function, $g_{nn}(r)$, of systems with different filler sizes at 23.8 vol%

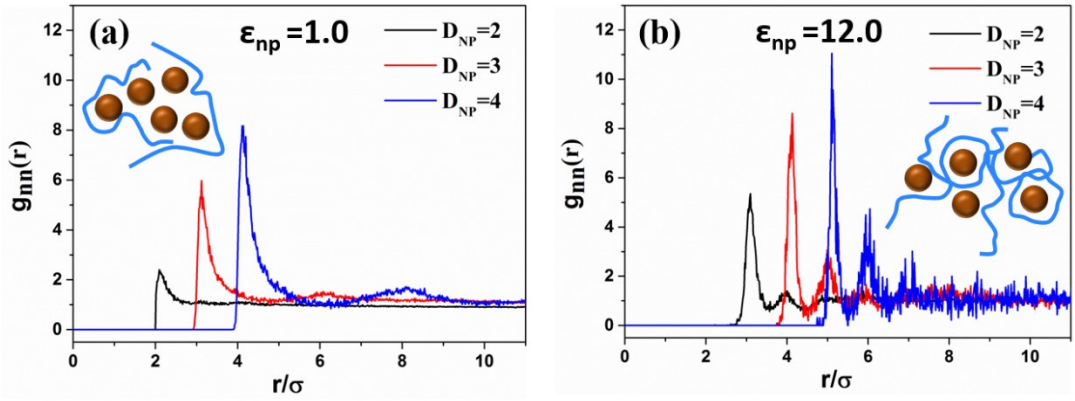

Fig. S3 Radial distribution function of filler-filler, $g_{nn}(r)$, of systems with different filler sizes at 23.8 vol%. (a) contact aggregation; (b) polymer bridging aggregation.

Fig. S3(a) shows that the maximum peak value of any system always appears at $r=(D_{NP,i}/2+D_{NP,j}/2)\ \sigma$, indicating that the fillers are in contact aggregation at $\varepsilon_{np}=1.0$. Where $D_{NP,i}$ and $D_{NP,j}$ represent diameters of the interacting atoms i and j, respectively. While there is no contact aggregation peak in Fig. S3(b), and the maximum peak value appears at $r=(D_{NP,i}/2+D_{NP,j}/2+1)\ \sigma$ corresponding to the polymer bridging aggregation at $\varepsilon_{np}=12.0$.

Radial distribution function, $g_{sn}(r)$, of spherical NPs around the laminar fillers

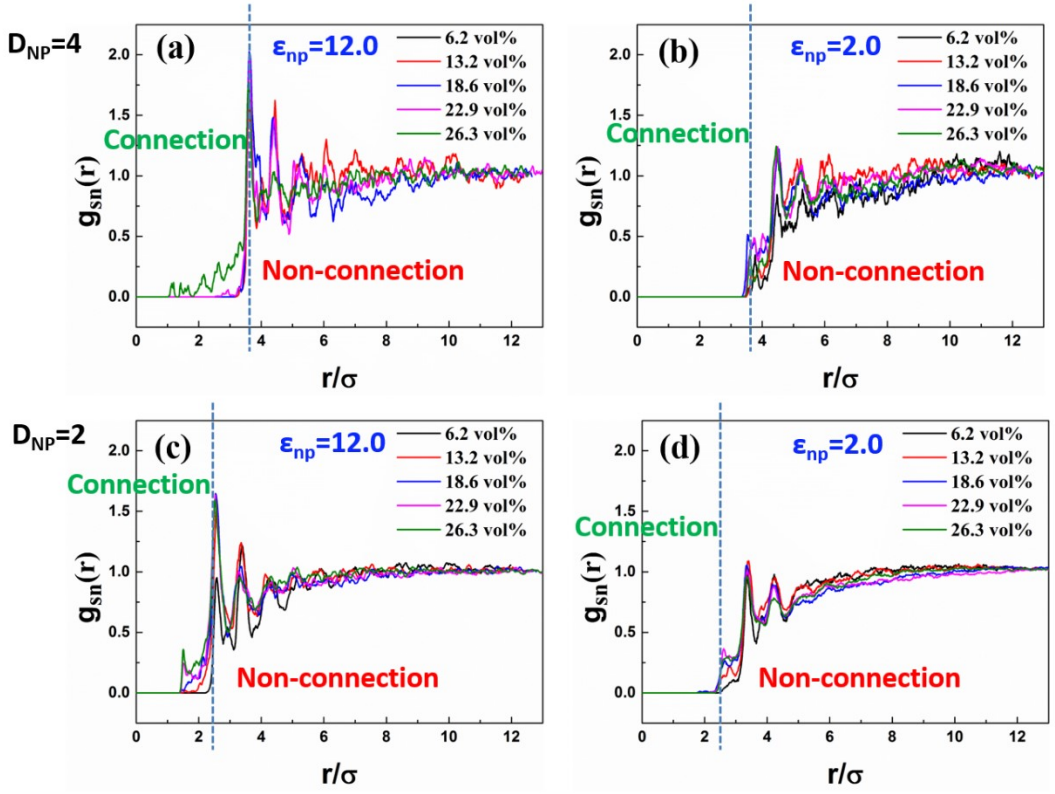

Fig. S4 Radial distribution function, $g_{sn}(r)$, of spherical NPs around the laminar fillers at different ε_{np} and D_{NP}. (a) ε_{np}=12.0, D_{NP}=4; (b) ε_{np}=2.0, D_{NP}=4; (c) ε_{np}=12.0, D_{NP}=2; (d) ε_{np}=2.0, D_{NP}=2.

The radial distribution function of the spherical NPs around the laminar fillers shown in Fig. S4 can qualitatively reflect the degree of overlap of the laminar/spherical filler. The vertical dotted line is the dividing line that determines whether the two fillers are in connection and form an overlapped structure. It is found that in Fig. S4 (a) and (c), a relatively large part appears at the left side of the dotted line. However, in Fig. S4 (b) and (d), only a small portion appears at the left side of the dotted line. It indicates that the strong interface of NPs-polymer (ε_{np}=12.0) is conducive to connect the laminar fillers and spherical fillers compared to the weak interface (ε_{np}=2.0). This is consistent with the law of the conduction probability results shown in Fig. 6(b).

Radial distribution function of hybrid-filled systems after shear

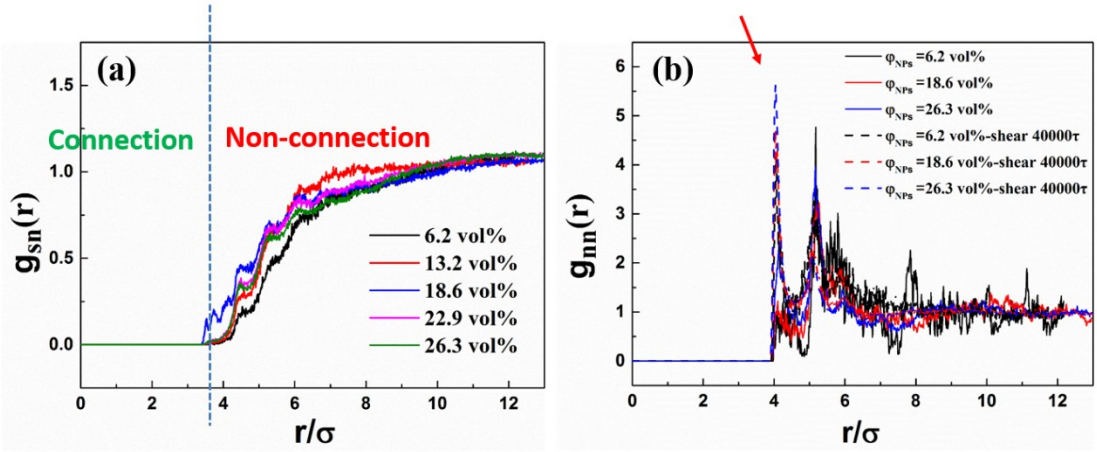

Fig. S5 (a) Radial distribution function of NPs (D_{NP}=4) around laminar fillers, $g_{sn}(r)$, after a shear process of 40000τ; (b) Radial distribution function of NPs around NPs, $g_{nn}(r)$, after a shear process of 40000τ.

Fig. S5(a) shows the distribution of NPs around laminar fillers, and it is found that the content of the NPs in the connected state around laminar fillers is significantly lowered as compared with that in Fig. S4(a), which implies the separation of spherical and laminar fillers. The results of Fig. S5(b) demonstrate that the peak at r=4σ after shear becomes significantly higher, which indicates that oscillatory shear makes more spherical fillers be in close contact with each other.

Incoherent intermediate dynamic structure functions (IIDS)

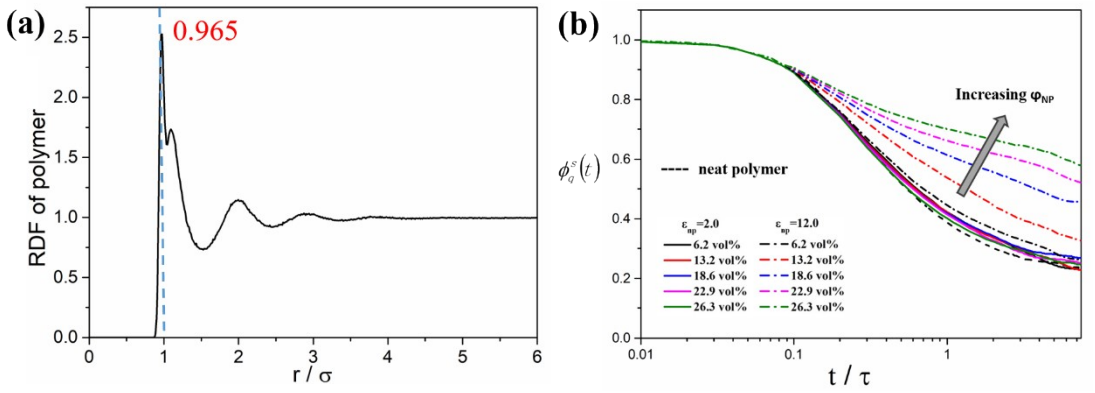

Fig. S6 (a) Radial distribution function of polymer beads; (b) Incoherent intermediate dynamic structure functions (IIDS), of polymers in D_{NP}=4 systems.

$$\phi_q^s(t) = \frac{1}{M}\sum_{m=1}^{M}\left\{\exp\left\langle \mathbf{iq}\cdot[\mathbf{r}_m(t)-\mathbf{r}_m(0)]\right\rangle\right\} = \frac{1}{M}\sum_{m=1}^{M}\left\{\frac{\sin\left\langle q\Delta r_m(t)\right\rangle}{q\Delta r_m(t)}\right\}$$

We calculated the polymer scattering function, incoherent intermediate dynamic structure functions (IIDS). Where q=2π/d, d in this system is equal to 0.965, which is obtained from the position of the first peak of the radial distribution function of polymer, and therefore q=6.51.

Structure evolution of neat polymer with chain length

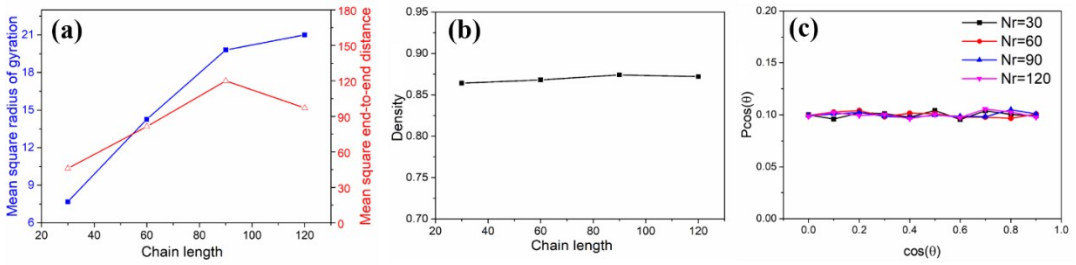

Fig. S7 (a) Mean square radius of gyration and end-to-end distance, (b) density, and (c) bond orientation distribution, of neat polymer systems.

It is generally recognized that the entanglement length N_e is 85 in "Kremer-Grest" bead-spring chains,[1,2] which is within the chain length range that we have chosen (30 to 120). Density, mean square radius of gyration, bond orientation, and mean square end-to-end distance of polymer systems with different chain lengths are shown in Fig. S7. Though the mean square radius of gyration and mean square end-to-end distance increase as the chain length increases, the density of these systems are similar. Pcos(θ) is similar at any cos(θ), which indicates that the probability of bond orientation angle (θ) is the same at all angles. It implies that when the chain length ranges from 30 to 120σ, the chain length does not affect the thermal conductivity, if the polymer chains are in the free entangled structure (no external force applied and no orientation).

1 R. S. Hoy, K. Foteinopoulou, M. Kröger. Topological analysis of polymeric melts: Chain-length effects and fast-converging estimators for entanglement length. *Phys. Rev. E.,* 2009, **80**, 031803.

2 J. X. Hou. Note: Determine entanglement length through monomer mean-square displacement. *J. Chem. Phys*., 2017, **146**, 026101.