Supporting Information

Molecular dynamics simulation study of the fracture property of

the polymer nanocomposites filled with grafted nanoparticles

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3.1 Dispersion state of nanoparticles and brush configuration

3.1.1 Dispersion state of nanoparticles

Here, we adopted the radial distribution function (RDF) of nanoparticles (NPs) to characterize their dispersion state in the matrix by tuning the grafting density. The grafting density (Σ) varies from 0.0, 0.1, 0.2, 0.3, to 0.4 while the length of the grafted chain (L_g) is fixed to be 20. As shown in Fig. S2(a), the peak at $r = 4\sigma$ reflects the direct contact structure of NPs. It is found that the peak at $r = 4\sigma$ gradually decreases with increasing Σ . This indicates that the bare NPs intend to form the aggregations in the matrix because of their attractive interaction. With the increase of Σ , the aggregation structure of NPs is gradually broken down, which leads to the uniform distribution of NPs in the matrix. This is attributed to a competition between matrixinduced depletion attraction between NPs and the steric stabilization provided by grafted chains.^{1, 2} Furthermore, we calculated the probability distribution (P_N) of the nearest neighbor NPs surrounding one NP (N_{num}) at a separation less than 5.0σ . As shown in Fig. S2(b), with the increase of Σ , the N_{num} at the maximum P_N gradually decreases from 6.0, 2.0, 1.0, 0.0 to 0.0 respectively at $\Sigma = 0.0$. Meanwhile, the P_N at N_{num}=0.0 gradually increases. These results further reflect that NPs gradually disperse into the matrix and more single NP appears. To better observe the NP dispersion state, their snapshots with different Σ are shown in Fig. S2(c), which clearly presents that the NRs gradually disperse in the matrix.

Then, we turned to the dispersion state of NPs as a function of the L_g by fixing $\Sigma = 0.3$. Here, L_g varies from 0, 10, 15, 20, 25, to 30. Figure S3(a) present the RDF of

NPs for different L_g . With the increase of L_g , NPs tend to stay away from each other, which is evidenced by the decline of the peak at $r = 4\sigma$. However, the difference of the height of this peak for different L_g is smaller than that for different Σ , which indicates that the grafting density dominates the dispersion state of NPs. Similarly, the probability distribution (P_N) of the N_{num} is calculated in Fig. S3(b), which are similar for different L_g . The snapshots of NPs with different L_g are present in Fig. S3(c), which further proves that the dispersion state of NPs is similar for different L_g .

3.1.2 Brush configuration

Here, we characterized the brush configuration to understand the dispersion mechanism of NPs. The monomer density of grafted chains as a function of their distance from the NPs is calculated in Fig. S4(a) for different Σ . It is found that grafted chains are crowded near the NPs and thus extend far from the NPs with the increase of Σ . Then, we presented the RDF between NPs and grafted chains belonging to other NPs in Fig. S4(b). At higher Σ , grafted chains belonging to other NPs become more difficult to penetrate into the brushes. This is because the grafted chains of NPs occupy the space by themselves, which limits the penetration of other grafted chains in Fig. S4(b). In addition, with the increase of Σ , the more matrix chains penetrate into brushes, which induces the wetting of grafted NPs by the polymer matrix in Fig. S4(c). This leads to a broader matrix/brush interface and the inter-locking interaction between them. However, at high Σ =0.3 and 0.4, the brushes are too dense, which prevent the matrix chains from penetration. Thus, the interface between matrix chains and brushes decreases greatly near the NP surface, which reduces the interaction between them. In

total, the dispersion state of grafted NPs gradually improves with Σ .

Then, we continued to investigate the effect of the L_g on the brush configuration at fixed Σ =0.3. First, the monomer density profile of the grafted chains is calculated for different L_g , which is shown in Fig. S5(a). It is found that with the increase of L_g , grafted chains will stretch farther from the NPs to mix with the matrix chains, which is attributed to the entropic effects. The RDF between NP core and the grafted chains belonging to other NPs is presented in Fig. S5(b). This indicates that the extension of grafted chains produces the space between them, which can promote the penetration of grafted chains belonging to other NPs. As shown in Fig. S5(c), the interpenetration between grafted chains and matrix chains also becomes more easily, intrinsically driven by entropy. In total, the dispersion state of NPs is similar for different L_g .



Fig. S1 Snapshot of a nanoparticle (NP). The blue sphere is the NP core, and the bonded red spheres are the virtual surface points which do not occupy space. There are 96 virtual surface points surrounding one NP. (b) Snapshot of the simulated system with grafting density $\Sigma = 0.1$ as an example. The green spheres denote the grafted chains, while the matrix chains are not shown for clarity. (c) The partial snapshot of the end-grafting process. Once the grafting site of the grafted chain has a less than distance (0.5 σ) with one random virtual surface point, a covalent bond between them is generated.



Fig. S2(a) RDF, (b) the probability distribution (P_N) of the nearest neighbor nanoparticles (NPs) surrounding one NP (Nnum) at a separation less than 5.0σ , and (c) the snapshots of NPs with different grafting density Σ where the polymer chains are neglected for clarity. The blue spheres denote the NPs. ($T^* = 1.0$)



Fig. S3(a) RDF, (b) the probability distribution (P_N) of the nearest neighbor nanoparticles (NPs) surrounding one NP (Nnum) at a separation less than 5.0σ , and (c) the snapshots of NPs with different length of grafted chains (L_g) where the polymer chains are neglected for clarity. The blue

spheres denote the NPs. (T^* =1.0)



Fig. S4 Density profiles and RDF in systems with different grafting density (Σ) at fixed length of the grafted chain (L_g =20). (a) Monomer density profile as a function of position from the nanoparticle (NP) core of grafted chains that are grafted to the reference NP. The curves are shifted by the NP radius (R_n). (b) RDF between the NP core and the grafted chains belonging to other NPs. (c) RDF of matrix chains around NPs.





Fig. S5 Density profiles and RDF in systems with different length of grafted chain (L_g) at fixed grafting density ($\Sigma = 0.3$). (a) Monomer density profile as a function of position from the nanoparticle (NP) core of grafted chains that are grafted to the reference NP. The curves are shifted by the NP radius (R_n). (b) RDF between the NP core and the grafted chains belonging to other NPs. (c) RDF of matrix chains around NPs.



Fig. S6 vdW energy change with respect to the strain for systems with different grafting density (Σ). ($T^* = 1.0$)



Fig. S7(a) The stress-strain curves contributed by both matrix chains and grafted chains and (b) the stress by each bead of matrix chains or grafted chains at the strain ≈ 0.12 (the maximum stress) for systems with different grafting density (Σ). ($T^* = 1.0$)



Fig. S8 The bond orientation degree $\langle P_2 \rangle$ of (a) matrix chains and (b) grafted chains for systems with different length of grafted chains (L_g). ($T^* = 1.0$)



Fig. S9 (a) The stress-strain curves contributed by both matrix chains and grafted chains and (b) the stress by each bead of matrix chains or grafted chains at the strain ≈ 0.12 (the maximum stress) for systems with different length of the grafted chain (L_g). ($T^* = 1.0$)



Fig. S10 (a) The number of voids as a function of the strain. (b) The left axis denotes the probability of voids generated (1) at the end beads of chains or (2) at the surface of nanoparticles (NPs), while the right axis represents the probability of voids generated at both (1) and (2) with respect to the length of the grafted chain (L_g) . $(T^* = 1.0)$

Table SI. Beads parameters

| Atom Type | Representation | Bead diameter (σ) | Bead mass (m) |
|-----------|---------------------------|----------------------------|---------------|
| 1 | Nanoparticle cores (NP) | 4 | 64 |
| 2 | Virtual surface points | 0 | 1 |
| 3 | Grafting sites | 1 | 1 |
| 4 | Grafted chains (except 3) | 1 | 1 |
| 5 | Matrix chains | 1 | 1 |

Table SII. Grafting density parameter

| Grafting density (Σ) | 0 | 0.1 | 0.2 | 0.3 | 0.4 |
|-----------------------------------------------|---|-----|-----|-----|-----|
| Number of grafted chains per NP $(N_{\rm g})$ | 0 | 5 | 10 | 15 | 20 |

| Table SII | I. Parameters | s of each | simul | ated system |
|-----------|---------------|-----------|-------|-------------|
| | | | | 2 |

| System | Σ | L_g/L_m | N_g/N_m |
|--------|-----|-----------|-----------|
| 1 | 0 | 20/100 | 0/499 |
| 2 | 0.1 | 20/100 | 5/399 |
| 3 | 0.2 | 20/100 | 10/299 |
| 4 | 0.3 | 20/100 | 15/199 |
| 5 | 0.4 | 20/100 | 20/99 |
| 6 | 0.3 | 10/100 | 15/199 |
| 7 | 0.3 | 15/100 | 15/199 |
| 8 | 0.3 | 20/100 | 15/199 |
| 9 | 0.3 | 25/100 | 15/199 |
| 10 | 0.3 | 30/100 | 15/199 |

Grafting density Σ , the length of the grafted chain L_g , the length of the matrix chain L_m , the number of grafted chains N_g , the number of matrix chains N_m .

References

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