Distinct Mechanical Properties of Nanoparticle-Tethering Polymers

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1. Effect of interaction strength $\varepsilon_{np}$ on the stress-strain behavior of nanoparticle-tethering polymers

The pair correlation function $g(r)$ was applied to further verify the packing structures of nanoparticles obtained by BOD. The peak position ratio of typical peaks in $g(r)$ can determine the packing geometry.\textsuperscript{S1} The results of $g(r)$ at various $\varepsilon_{np}$ are shown in Figure S1. There is only one strong peak in $g(r)$ at $\varepsilon_{np} = 1.0$, while several peaks are exhibited at $\varepsilon_{np} = 5.0$ and 12.0. The typical peaks are numbered for larger $\varepsilon_{np}$. The position ratio of typical peaks at $\varepsilon_{np} = 5.0$ and 12.0 is about $1 : \sqrt{2} : \sqrt{3} : 2$, indicating that the nanoparticles are packed approximately in a FCC manner (in accordance with the BOD results).

![Figure S1. Pair correlation functions $g(r)$ between the nanoparticles at various $\varepsilon_{np}$. The typical peaks are numbered as 1, 2, 3, and 4 for larger $\varepsilon_{np}$.](image-url)
Figure S2 shows the diffusion coefficients of nanoparticles as a function of time at various $\varepsilon_{np}$. As can be seen, the diffusion coefficient decreases and finally arrives at a plateau for any $\varepsilon_{np}$ with the evolution of time. The effect of $\varepsilon_{np}$ on the diffusion coefficient of nanoparticles can be also viewed. At lower $\varepsilon_{np}$ ($\varepsilon_{np} = 2.0$), the diffusion coefficient is larger, and decreases more slowly with the time. With increasing $\varepsilon_{np}$, the diffusion coefficient decreases. At higher $\varepsilon_{np}$ ($\varepsilon_{np} = 12.0$), the diffusion coefficient is so small that the nanoparticles can be considered to be frozen.

**Figure S2.** Diffusion coefficients of nanoparticles as a function of time at various $\varepsilon_{np}$. 
2. Effect of polymer length $L$ on the stress-strain behavior of nanoparticle-tethering polymers

Figure S3a and S3b shows the BOD of nanoparticles and the pair correlation function $g(r)$ between the nanoparticles for various $L$, respectively. It can be seen that for $L = 4$, six point groups are distributed on the hexagon vertices and four point groups are located on the square vertices in the BOD, suggesting the nanoparticles approximately adopt a hexagonally closed packing manner.$^{S2, S3}$ For $L = 36$, the diagonal and square distribution of points in the BOD implies a FCC packing of nanoparticles, similar to the case of $L = 24$ (Figure 2c). As shown in Figure S2b, for $L = 4$ and 36, the $g(r)$ has the typical peak position ratios $1 : \sqrt{2} : 2 : \sqrt{5}$ and $1 : \sqrt{2} : \sqrt{3} : 2$, respectively. Therefore, the hexagonally closed packing of nanoparticles for $L = 4$ and the FCC packing of nanoparticles for $L = 36$ were further confirmed.

Figure S4 shows the change of nonbonding potential $\Delta E_{\text{pair}}$ between deformed and undeformed states with respect to the strain for various $L$. It can be seen, at smaller strain the nonbonding potential $E_{\text{pair}}$ increases more remarkably for smaller $L$, resulting in larger enthalpy gain for smaller $L$. Therefore, the interaction enthalpy as well as the conformation entropy makes important contribution to the higher stress and modulus for smaller $L$. At larger strain, the value of $\Delta E_{\text{pair}}$ for smaller $L$ is still larger than that for larger $L$. Therefore, the enthalpy gain is still larger for smaller $L$. However, the entropy loss first increases then decreases with increasing $L$. It is shown that at larger strain, the stress first increases and then decreases with increasing $L$ (Figure 5a). Therefore, the stress is dominated by the entropy for smaller $L$, while it is controlled by the cooperative action of entropy and enthalpy for larger $L$. 
Figure S3. (a) BOD of nanoparticles for $L = 4$ and $L = 36$. The solid lines indicate the BODs of ideal hexagonally closed packing and FCC packing structures. (b) Pair correlation functions $g(r)$ between the nanoparticles for various $L$. The typical peaks are numbered as 1, 2, 3, and 4 for $L = 4$ and $L = 36$. 
Figure S4. Change of nonbonding potential $\Delta E_{\text{pair}}$ between deformed and undeformed states with respect to the strain for various $L$. 
3. Effect of particle size $d$ on the stress-strain behavior of nanoparticle-tethering polymers

Figure S5a shows the pair correlation functions $g(r)$ between the nanoparticles for various $d$. The insert shows the BOD of nanoparticles for $d = \sigma$ and $d = 4\sigma$. In the BOD for $d = \sigma$, the projected points are approximately distributed in the form of point groups along the four-fold directions, indicating a non-perfect cubic-like packing for nanoparticles. This can be verified by the typical peak position ratio of $1 : \sqrt{2} : 2$ in $g(r)$. With increasing $d$ to $4\sigma$, there is no typical peak position ratio in $g(r)$, and the projected points are located randomly on the sphere surface in the BOD. Therefore, the nanoparticle packing is not ordered enough for $d = 4\sigma$.

In Figure 7a, the stress-strain curve for large nanoparticles ($d = 4\sigma$) has an obvious yield point, exhibiting a glassy or crystalline feature. To explain this phenomenon, we examined the glass transition temperature for $d = 4\sigma$. The total volume $V(T)$ as a function of $T$ for $d = 4\sigma$ is plotted in Figure S5b. As can be seen, the $V(T)$ increases linearly with increasing $T$ below or above a certain temperature. According to the intersections of fitted lines, the $T_g$ is obtained to be about 1.1, which is higher than the examined temperature ($T = 1.0$). Therefore, the stress-strain curve for $d = 4\sigma$ exhibits a glassy feature.
Figure S5. (a) Pair correlation functions $g(r)$ between the nanoparticles for various $d$. The insert shows the BOD of nanoparticles for $d = \sigma$ and $d = 4\sigma$. (b) Plot of the total volume $V(T)$ versus $T$ for the nanoparticle-tethering polymers with $d = 4\sigma$. 
4. Comparison with neat polymers and nanoparticle/polymer blends

We examined the glass transition temperatures for the neat polymers, nanoparticle/polymer blends, and nanoparticle-tethering polymers. Figure S6a shows the $V(T)$ as a function of $T$ for the neat polymers, nanoparticle/polymer blends, and nanoparticle-tethering polymers at $T = 1.0$ and $P = 0.0$. By linear fitting, the $T_g$ were estimated to be 0.45, 0.65, and 0.66 for the three systems. The $T_g$ are all lower than 1.0, therefore these systems are in rubbery states at $T = 1.0$.

Figure S6b shows the changes of nonbonding potential $\Delta E_{\text{pair}}$ between undeformed and deformed states for the neat polymers, nanoparticle/polymer blends, and nanoparticle-tethering polymers at $T = 1.0$. The $E_{\text{pair}}$ almost has no increase for neat polymers, but increases rapidly with the strain at smaller strain for nanoparticle/polymer blends and nanoparticle-tethering polymers. The increase in $E_{\text{pair}}$ for the nanoparticle/polymer blends and nanoparticle-tethering polymers are almost the same at smaller strain, but the $\Delta E_{\text{pair}}$ for the nanoparticle-tethering polymers is larger than that for the nanoparticle/polymer blends. The larger $\Delta E_{\text{pair}}$ leads to larger enthalpy gain. The enthalpy together with the entropy contributes to the highest stress for the nanoparticle-tethering polymers as shown in Figure 9a.
Figure S6. (a) $V(T)$ versus $T$ for the neat polymers, nanoparticle/polymer blends, and nanoparticle-tethering polymers at $T = 1.0$ and $P = 0.0$. (b) $\Delta E_{\text{pair}}$ versus the strain for the three systems. The polymer length was set to be 24, and the nanoparticle diameter was set to be $2\sigma$. The interaction strength between nanoparticles and polymers was $\varepsilon_{np} = 5.0$. 
References

