Effects of Chain Length on the Structure and Dynamics of Polymer-NP Composites

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Introduction

The addition of nanoparticles (NP) as fillers to glass-forming polymer materials can substantially change the mechanical, dynamical, electrical, and optical properties of the material, thus understanding polymer-NP composite is important for developing new materials. Previous work from the Starr lab has shown that the changes to the glass transition in the dilute NP limit arise from modifications to the interfacial dynamics of monomers[2]. In many applications of these materials, the case is more complex due to higher NP concentrations and longer chain lengths relative to the NP separation. The dilute and concentrated limits have been thoroughly studied, and it has been proposed that there is an intermediate regime, in which NPs can affect each other through chains that bridge between them[1]. Therefore, using computational approach, we focus on the intermediate regime, aiming to investigate the chain length dependence of its properties as well as the potential bridging phenomenon.
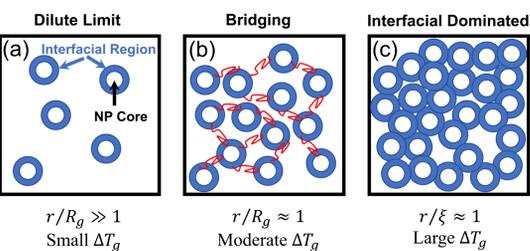
Fig.1 Three schematic regimes of polymer-NP composites[1].

Simulation Setup

We use LAMMPS Molecular Dynamics Simulator to model the polymer composites as an ideal, uniform dispersion of NP surrounded by polymer melts. An icosahedron shaped NP is fixed at the center of a simulation box and surrounded by polymer chains of varying lengths (5, 10, 15, 20, 30, 40 beads); by periodic boundary condition, this simulates an ideal dispersion of NP. For each chain length, we simulate three NP concentrations (2.8%, 5.5%, 10.4%) by varying the total number of polymer chains. For systems with longer chains ($N \geq 30$ in ϕ = 2.8%, 5.5%, and $N \geq 20$ in ϕ = 10.4%), we use larger simulation cells with 8 fixed NPs surrounded by 8 times the number of polymer chains that were present in the 1 NP systems. These larger simulations ensure that the simulation cell size is always more than double the chain dimension, and allow observation of bridging chains between different NPs. Simulations are performed in an NVT ensemble along an isobaric path with pressure P = 0.1 and temperatures ranging from 0.42 to 0.80, in reduced Lennard-Jones units $T^* = K_b T/\epsilon$, where ϵ is the polymer-polymer interaction strength.
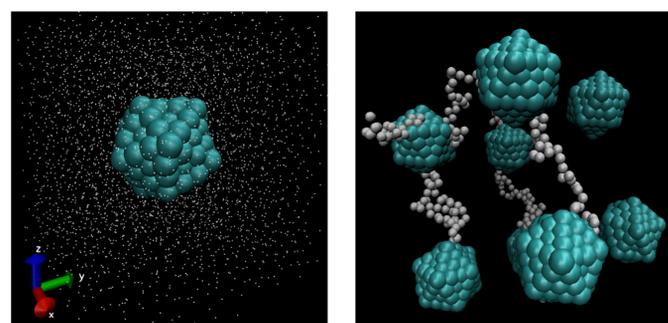
Fig.2 Simulation Setup:
(a) 1 NP in polymer melts; (b) 8 NPs and bridging chains.

References

1. Emamy, H., Kumar, S.K., & Starr, F.W. (2018). Diminishing Interfacial Effects with Decreasing Nanoparticle Size in Polymer-Nanoparticle Composites. *Physical review letters, 121* 20, 207801.
2. Starr, F. W., Douglas, J. F., Meng, D., & Kumar, S. K. (2016). Bound layers "cloak" nanoparticles in strongly interacting polymer nanocomposites. *ACS nano, 10*(12), 10960-10965.

Chain Structure and Orientation
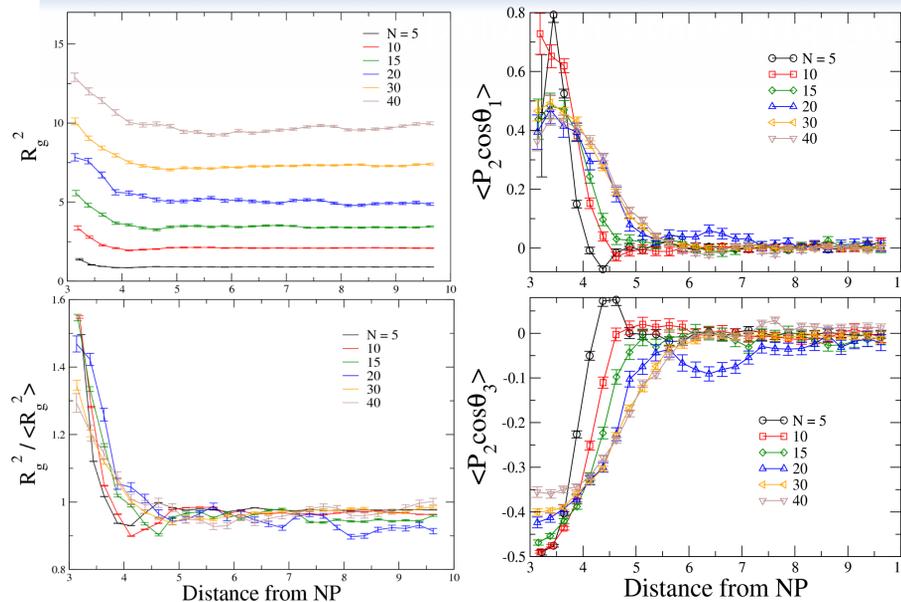
Fig.3 (a) R_g^2 and (b) normalized R_g^2.

Fig.4 (a) $\langle P_2 \cos\theta_1 \rangle$ and (b) $\langle P_2 \cos\theta_3 \rangle$.

We first examine the gyration tensor to characterize the chain dimension. Fig. 3a shows that the radius of gyration R_g^2 increases near the NP surface, meaning that chains elongate approaching the NP. When we scale R_g^2 by the corresponding average for each chain length $\langle R_g^2 \rangle$ (Fig. 3b), we show that this effect is independent of chain length. We also evaluate the orientational parameters $\langle P_2 \cos\theta_1 \rangle$ and $\langle P_2 \cos\theta_3 \rangle$ (Fig.4), which are associated with the shortest and longest rotational axis of the chain. Near the NP surface, $\langle P_2 \cos\theta_1 \rangle$ increases while $\langle P_2 \cos\theta_3 \rangle$ decreases, demonstrating that chains tend to align their shortest axis normal to the NP surface, and the longest axis along the NP surface. Also, the orientational changes extends farther from the NP as chain length increases.

When differentiating bridging chains from others, we find that bridging chains extend along the direction connecting NPs (Fig. 6). However, the differences are only significant when NP separation is large and bridging chains have to stretch, in which cases the bridging chains are rare (see Fig. 5 for the fraction of bridging chains).
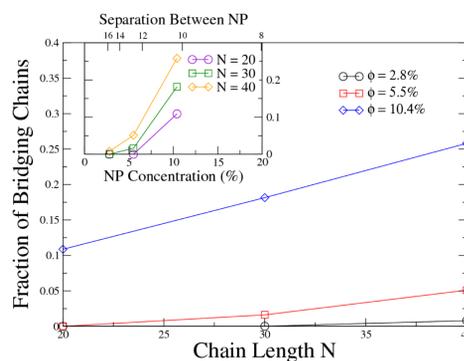
Fig.5 Fraction of bridging chains.
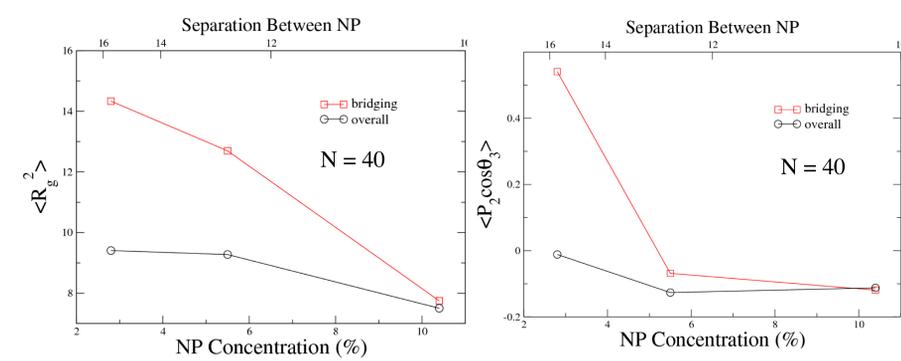
Fig.6 (a) $\langle R_g^2 \rangle$ and (b) $\langle P_2 \cos\theta_3 \rangle$ of bridging chains compared to the overall.

Chain Dynamics and T_g

Fig.7 Relaxation time τ (N) for different types of chains.
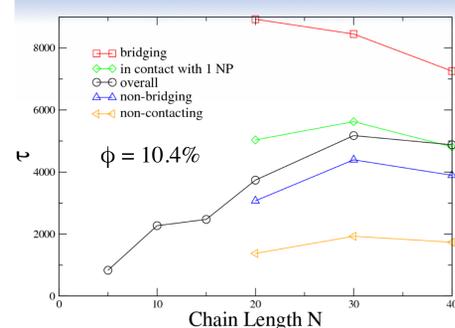
To evaluate the effect of bridging on the dynamics, we compare the relaxation time τ of bridging chains with that of other chains (Fig.7). Bridging chains have a longer relaxation time compared to the average over all chains and all other subtypes. However, as chain length and the bridging fraction increase, the difference between τ of bridging and that of the average decreases. In other words, the dynamics of bridging chains only differ significantly when bridging between NP requires that chains are significantly expanded. In this case, there are relatively few bridging chains, thus their effect on the average is minimal.

We then evaluate how chain length and bridging influence the dynamical glass transition temperature T_g of composites, based on the composite relaxation time. We show that T_g of composites follows the trend in pure polymer systems (Fig.8). Independent of ϕ, T_g increases with chain length and saturates at $N \approx 20$, consistent with previous experiments and simulations of pure polymer systems; we also show that T_g follows a generally linear relationship with $1/N$. Since the relaxation of bridging chains only differs from the overall significantly when the fraction of bridging chains is small, the dynamical T_g is not significantly affected by bridging.

Fig.8 (a) T_g (N) and (b) T_g (1/N) for all different ϕ.

Conclusion

- Bridging chains can have significantly altered conformations and relaxation, but their effects on the composite are minimal.
- Chain length does not have a significant impact on the chain structure at the NP interface, but NP interfacial effects on chain alignment extend farther from the NP surface as chain length increases.
- T_g of composites increases and saturates with chain length, an effect that stems from the chain length effect found in pure polymer systems.