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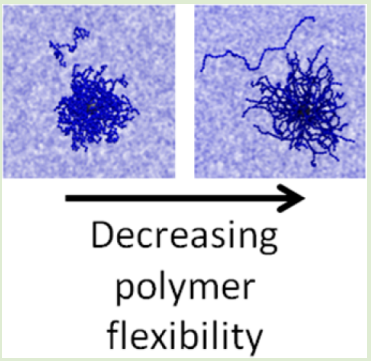
Decreasing Polymer Flexibility Improves Wetting and Dispersion of Polymer-Grafted Particles in a Chemically Identical Polymer Matrix

Brandon Lin,[†] Tyler B. Martin,[†] and Arthi Jayaraman*

Department of Chemical and Biological Engineering, University of Colorado at Boulder, Boulder, Colorado 80309, United States

Supporting Information

ABSTRACT: We present a molecular dynamics simulation study of nanocomposites containing homopolymer-grafted particles in a homopolymer matrix, where the graft and matrix chemistries are identical, to elucidate the effect of polymer flexibility on the wetting of the grafted layer by the matrix and the nanocomposite morphology. Decreasing flexibility of the graft and matrix causes increased wetting of the grafted layer by the matrix. This increased wetting of the grafted layer with decreasing flexibility is more significantly driven by decreasing the graft flexibility than by decreasing the matrix flexibility. This is due to a large increase in mixing entropy of the graft and matrix upon wetting rather than the reduction in conformational entropy loss of matrix upon wetting. Due to this improved wetting with decreasing flexibility of the graft and matrix, we observe increased particle dispersion in the polymer matrix.



Past studies have elucidated the various parameters that govern dispersion/assembly in polymer nanocomposites (PNCs) containing polymer-grafted nanoparticles (PGNs).[1−8] They have mostly focused on PGNs with *flexible* homopolymers that are chemically identical to the matrix homopolymers and shown that polymer grafting density,[3,9] particle curvature,[10] molecular weights, and polydispersity of the graft and matrix[11−15] affect PGN aggregation or dispersion. At high grafting density, aggregation/dispersion is driven largely by dewetting/wetting of the PGN-grafted layer by the matrix. When the molecular weight of the matrix is less than that of the graft, the grafted layer is wet by the matrix, which leads to increased PGN dispersion. At low grafting density, the large molecular weight of the grafts shields the highly curved nanoparticle surface from interparticle attractive interactions and promotes particle dispersion.[16] Decreasing surface curvature decreases the wetting of the grafted layer by the matrix due to increased graft crowding near the surface of the particle. Polydispersity in the graft molecular weight has been shown to eliminate the midrange attractive well in the potential of mean force between PGNs and to stabilize particle dispersion.[11−15] In all of these studies, the impact of polymer flexibility on wetting/dewetting and dispersion/aggregation of PGNs in PNCs has largely been unexplored.

Several studies have focused on semiflexible polymers (in the absence of nanoparticles),[17−32] near surfaces and interfaces,[32−37] as well as on composites of semiflexible polymers and bare particles.[38−41] For example, the effect of semiflexibility on coil to globule transition of the polymer,[20,42] the formation of spherical or toroidal globules,[20,28] and the isotropic−nematic liquid crystalline transitions have been explained.[18,21,22,31] In a composite of semiflexible polymers and bare nanoparticles near substrates, decreasing polymer flexibility causes an increase in polymer density near the surface, resulting in lower nanoparticle density near the substrate compared to flexible polymers.[39] Polymer semiflexibility also impacts the depletion attraction in systems of particles and polymers, with the relative ratio of correlation length and persistence length dictating the depletion thickness and the effects of particle curvature on depletion attraction.[38] These studies point to the importance of changing polymer flexibility on the polymer conformations and effective interactions between the bare particle/surfaces and polymers, and motivate our work here on the role of flexibility in PNCs containing PGNs.

We present a molecular simulation study of PGNs in a chemically identical homopolymer matrix to elucidate the effect of decreasing flexibility in grafts and matrix polymers on wetting of the grafted layer and PNC morphology. Decreasing graft and matrix flexibility leads to increased wetting of the PGNs by the matrix and improved dispersion of particles. Changing the flexibility of the grafts has a more significant effect on improving wetting of the grafted layer than changing the flexibility of the matrix does. We also quantify the effect of decreasing flexibility on the known trends of varying graft and matrix length and grafting density on wetting of the grafted layer by the matrix.

We model PGNs and matrix polymers using a generic coarse-grained (CG) model. Each graft or matrix is modeled as a bead−spring chain,[43] with each bead of size $d = 1\sigma$ ($\sigma \approx 1$ nm) representing a group of monomers on the polymer chain and harmonic springs linking the beads having a force constant of $k_{bond} = 50\ k_BT/\sigma^2$ and a bond rest length of $r_0 = 1\sigma$. We model

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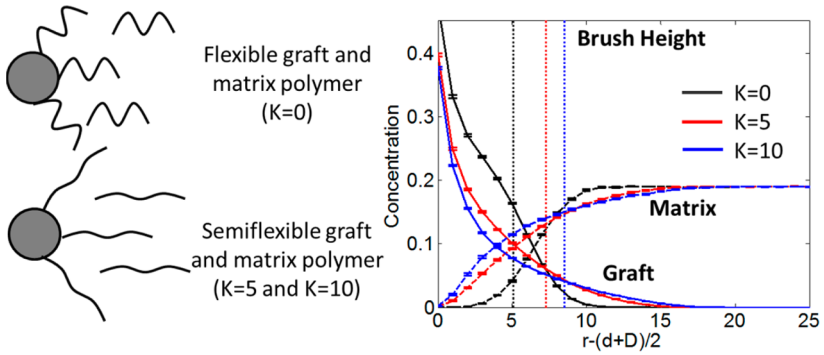

Figure 1. Graft (solid) and matrix (dashed) monomer concentration profiles for a single PGN with grafting density = 0.65 chains/σ^2, N_{graft} = 20, and N_{matrix} = 60, with K = K_{graft} = K_{matrix} = 0 (black), 5 (red), and 10 (blue) k_BT/radians^2. The brush heights are shown as vertical dash-dotted lines.

decreasing flexibility in the graft and matrix through a harmonic angle potential with increasing force constant of K = 0−10 k_BT/radians^2 and a rest angle of θ_0 = π radians.[44] Polymer chains with the values of K studied here would have persistence lengths[45] as shown in Table S1 (calculated using three different methods as described in the Supporting Information). Nanoparticles are modeled as a rigid body of several d = 1σ beads and have isotropically placed grafting sites on the surface. We model a purely athermal system where all pairs of CG beads interact via the Weeks−Chandler−Andersen[46] (WCA) potential. In this study the nanoparticle size is maintained at 5σ and grafting density is varied from 0.25 to 0.65 chains/σ^2, the matrix length, N_{matrix}, from 20 to 100 beads, the graft length, N_{graft}, from 10 to 40 beads, and the angle potential force constant from 0 to 10k_BT/radians^2, with the majority of the results shown for 0 and 5 k_BT/radians^2. Using this CG model, we conduct Brownian dynamics (BD) simulations in the canonical ensemble using the graphical processing unit based HOOMD-blue package.[47,48] We conduct the production simulation runs for 40 million time steps where snapshots of the system are saved every 0.1 × 10^6 time steps. Additional details of the approach are presented in the Supporting Information.

The effect of polymer flexibility on wetting of the grafted layer by the matrix is discussed below. Figure 1 shows that as the graft and matrix flexibility decrease the grafts adopt extended conformations, thereby increasing the brush height from the particle surface. Most importantly, with decreasing polymer flexibility, the matrix concentration profile extends further into the grafted layer, implying increasing wetting of the grafted layer by the matrix chains.

Since we maintain athermal interactions, the wetting/dewetting of the grafted layer by the matrix is driven by the balance of gain in mixing entropy and losses in conformational entropy of the graft and matrix upon wetting. Decreasing flexibility of the *matrix* is expected to decrease its conformational entropy in the bulk and, as a result, decrease the conformational entropy loss the matrix would face upon entering/wetting the crowded grafted layer. As expected, as matrix flexibility decreases, the average end−end distance of the matrix increases (Table S2, Supporting Information); the average and the distribution of end−end distances are a signature of the conformational entropy of the matrix chains. While decreasing *graft* flexibility also reduces the conformational entropy loss of the grafts upon being wet, it is relatively negligible when compared to the matrix due to the grafts being constrained to the particle surface and crowded by other grafts. More importantly, decreasing *graft* flexibility increases the brush height, which increases the grafted layer volume and likely the mixing entropy gain upon wetting. By decreasing the flexibility of the graft and matrix, the conformational entropy losses upon wetting of the grafted layer are reduced, while the gains in mixing entropy are increased, driving the increased wetting of the grafted layer. Next, to understand which of the above factors more significantly drives the increased wetting of the grafted layer by matrix chains with decreasing flexibility, we tune the graft and matrix flexibility individually.

In Figure 2, the matrix concentration at short distances from the particle surface is higher, and thus the grafted layer wetting

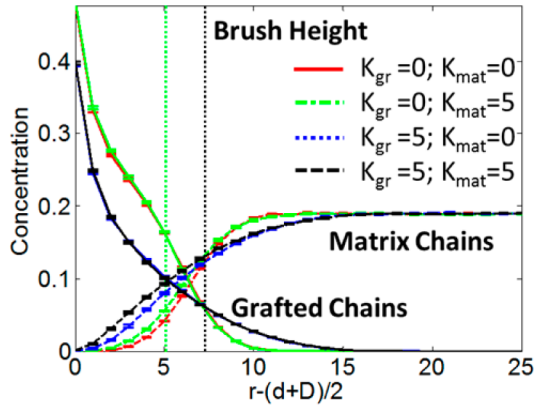

Figure 2. Graft (solid) and matrix (dashed) monomer concentration profile for single PGN with grafting density = 0.65chains/σ^2, N_{graft} = 20, N_{matrix} = 60, and K_{graft} = 0 and K_{matrix} = 0 (red), K_{graft} = 0 and K_{matrix} = 5 (green), K_{graft} = 5 and K_{matrix} = 0 (blue), and K_{graft} = 5 and K_{matrix} = 5 (black). The brush heights are shown as vertical lines, with the two K_{gr} = 0 lines (red and green) and the two K_{gr} = 5 lines (blue and black) overlapping.

is larger for decreased *graft flexibility* (K_{graft} > 0, K_{matrix} = 0) than for decreased *matrix flexibility* (K_{graft} = 0, K_{matrix} > 0). Similarly, the % matrix beads that have wet the grafted layer (denoted as "% wet matrix" in Table 1), calculated as the percent of matrix beads that are within the brush height of any grafted particle (see Supporting Information for details), is significantly more for the case of K_{graft} > 0, K_{matrix} = 0 than that for the K_{graft} = 0, K_{matrix} > 0 case, indicating that decreasing graft flexibility improves wetting more than decreasing matrix flexibility. At constant graft flexibility, decreasing the matrix flexibility has little effect on the brush height and therefore little effect on the grafted layer volume. This means that, when the graft is flexible and matrix is semiflexible, any changes in

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Table 1. Average Percentage of Matrix Beads That Wet the Grafted Layer (% Wet Matrix) as a Function of Graft and Matrix Lengths, Grafting Density, and Flexibility

# of nanoparticles	K_{graft}	K_{matrix}	grafting density (chains/σ^2)	N_{graft}	N_{matrix}	% wet matrix	error
1	0	0	0.65	20	60	0.03%	0.002
1	0	5	0.65	20	60	0.05%	0.002
1	5	0	0.65	20	60	0.49%	0.006
1	5	5	0.65	20	60	0.58%	0.006
1	10	10	0.65	20	60	1.18%	0.007
1	0	0	0.25	20	60	0.10%	0.003
1	5	5	0.25	20	60	0.87%	0.005
1	0	0	0.65	20	20	0.05%	0.002
1	5	5	0.65	20	20	0.63%	0.006
1	0	0	0.65	10	60	0.003%	0.0004
1	5	5	0.65	10	60	0.08%	0.002
1	0	0	0.65	40	60	0.23%	0.005
1	5	5	0.65	40	60	2.81%	0.012
1	0	0	0.65	20	40	0.03%	0.002
1	5	5	0.65	20	40	0.59%	0.006
1	0	0	0.65	20	100	0.03%	0.002
1	5	5	0.65	20	100	0.57%	0.006
20	0	0	0.65	20	100	0.01%	0.0002
20	5	5	0.65	20	100	0.26%	0.0007

wetting come solely from the matrix chains losing less conformational entropy upon wetting the grafted layer. Since the distribution of end−end distances of the matrix upon wetting (Table S2, Supporting Information) is not significantly different for the flexible and semiflexible matrix, the reduced loss in conformational entropy of the matrix with decreasing matrix flexibility is likely small. Conversely, at constant matrix flexibility, decreasing the graft flexibility increases the brush height dramatically and results in significantly higher grafted layer volume, which increases the entropy of mixing of the graft and matrix chains without altering the conformational entropy loss of the matrix. This increased gain in entropy of mixing of the graft and matrix chains is driving the improved wetting behavior, as quantified next.

In Figure 3 we show the gain in mixing entropy of wetting the grafted layer by matrix chains $T\Delta S_{mix}$ versus decreasing flexibility for the graft and matrix. In Figure 3a, where $T\Delta S_{mix}$ is calculated from the simulation trajectories by explicitly counting the number of matrix beads that wet the grafted layer (see Supporting Information), the $T\Delta S_{mix}$ is much larger when the graft flexibility is decreased than when the matrix flexibility is decreased. Furthermore, when the flexibility of both the graft and matrix is decreased, the increase in $T\Delta S_{mix}$ is largest. To minimize the bias introduced by using simulation data in the calculation of $T\Delta S_{mix}$, we recalculated the $T\Delta S_{mix}$ using only the average brush height from each simulation (see Supporting Information). In Figure 3b, we find identical qualitative trends as seen in Figure 3a, with the magnitude of the $T\Delta S_{mix}$ being greater with the approximate method (Figure 3b). Despite the overestimation of $T\Delta S_{mix}$ in Figure 3b (due to the approximation that the density of the matrix beads in the grafted layer is equal to the bulk matrix density), both methods agree that decreasing flexibility increases the $T\Delta S_{mix}$. We can conclusively say that the mixing entropy of the grafted and matrix chains is a primary driving force for wetting/dewetting in this system and that flexibility of the graft and matrix directly tunes this driving force.

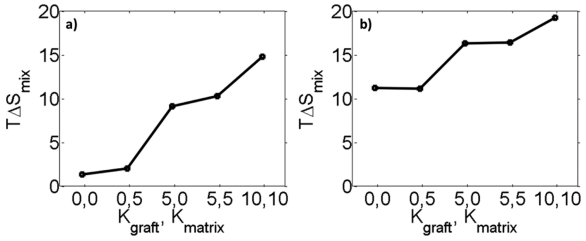

Figure 3. Gain in mixing entropy, $T\Delta S_{mix}$ (in k_BT), as a function of graft and matrix flexibility (a) calculated using simulation trajectory information and (b) estimated approximately with minimal information from simulation (see Supporting Information for details regarding how $T\Delta S_{mix}$ is calculated).

Now we discuss the effect of polymer flexibility on trends of varying grafting density, graft length, and matrix length on wetting/dewetting. For flexible graft and matrix, where the $N_{matrix} > N_{graft}$, as grafting density increases, based on the % wet matrix data in Table 1, wetting of the grafted layer decreases, due to increased crowding in the grafted layer.[4] With increasing grafting density, the percentage change in the number of matrix beads that have wet the grafted layer, normalized by the lower grafting density, shows a drop of 0.70 for $K = 0$ and only a drop of 0.33 for $K = 5$ (Figure 4a). This suggests that the effect of increasing grafting density on wetting of the grafted layer is reduced for a semiflexible graft and matrix. This is because, as the grafting density increases, the change in brush height for semiflexible grafts is lower than that for flexible grafts (Figure S1, Supporting Information), also confirmed by the change in the average radius of gyration of grafts with increasing grafting density being smaller for semiflexible polymers than flexible polymers (Table S3, Supporting Information). In short, decreasing the flexibility reduces the effect of grafting density on the graft conformations and in turn the wetting behavior.

As the N_{matrix} increases at constant N_{graft}, in the case of flexible polymers, the wetting of the grafted layer by the matrix decreases. Decreasing flexibility does not alter how the wetting of the grafted layer by the matrix changes with increasing N_{matrix}. With increasing N_{matrix}, monomer concentration profiles in Figure S1 (Supporting Information) show decreasing

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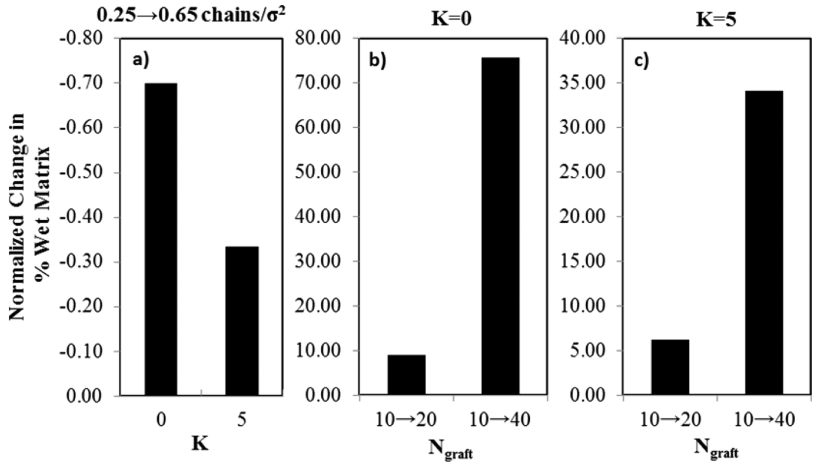

Figure 4. (a) Normalized change in the % wet matrix with increasing grafting density for N_{graft} = 20, (b) normalized change in the % wet matrix with increasing graft length from 10 to 20 and 10 to 40 beads for flexible polymers (K = 0) at high grafting density (0.65 chains/σ^2), and (c) normalized change in the % wet matrix with increasing graft length from 10 to 20 and 10 to 40 beads for semiflexible polymers (K = 5) at high grafting density (0.65 chains/σ^2), for a single PGN with N_{matrix} = 60. The normalized change in the % wet matrix is calculated as $(Y - X)/X$ where Y is the % wet matrix at the higher grafting density or higher graft length and X is the % wet matrix at the lower grafting density or lower graft length.

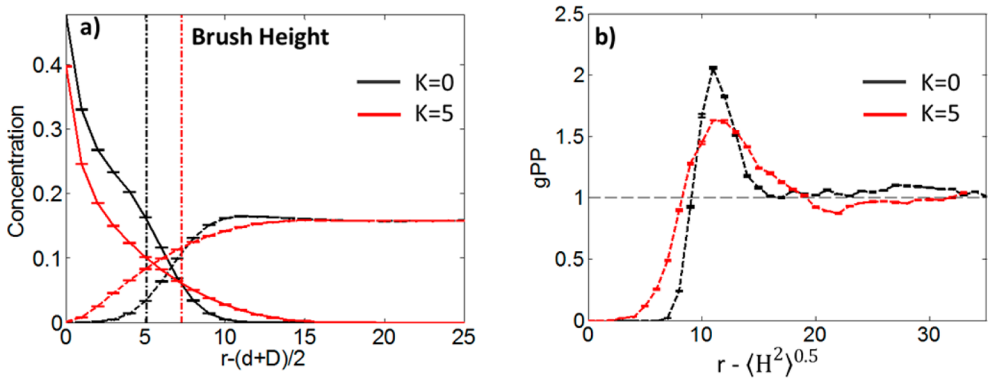

Figure 5. (a) Graft (solid) and matrix (dashed) monomer concentration profile and (b) particle−particle pair correlation function plotted versus the interparticle distance minus the brush height for 20 PGNs with grafting density = 0.65 chains/σ^2 and N_{graft} = 20 and N_{matrix} =100 and increasing values of K = 0 (black) and 5 (red).

penetration of the matrix chains for both K = 0 and K = 5, and the % wet matrix data in Table 1 decrease for both K = 0 and K = 5. As the N_{graft} increases at constant N_{matrix}, in the case of flexible polymers, it is known that the wetting of the grafted layer by the matrix increases. With decreasing flexibility of the graft and matrix, the effect of increasing N_{graft} on increasing wetting of the grafted layer is reduced. For flexible polymers and N_{matrix} = 60, going from graft length of 10 to 20, the normalized change (increase) in % wet matrix is ∼10 and going from 10 to 40 is ∼76 (Figure 4b). In contrast, for semiflexible polymers and N_{matrix} = 60, going from graft length of 10 to 20, the normalized change (increase) in % wet matrix is ∼7 and going from graft length of 10 to 40 is ∼35 (Figure 4c).

We also discuss the effect of polymer flexibility on particle assembly/dispersion at finite filler fraction. Figure 5a shows that, at finite filler fractions, we continue to see the improved wetting with decreasing polymer flexibility that is seen at the dilute filler fraction or single PGN limit. Tables S2 and S3 (Supporting Information) and Table 1 also show that increasing filler fraction does not alter the graft radius of gyration and matrix end−end distance seen for single PGN for both flexible and semiflexible systems. Since increasing wetting of the grafted layer has been connected to increased dispersion for flexible PGNs in past studies,[12−14] we compare the particle−particle pair correlation for the flexible and semiflexible graft and matrix cases. For the semiflexible graft and matrix case, we see a reduced correlation at the contact peak, with the contact peak shifting to larger distances (Figure 5b) when compared to the flexible case. This confirms that reducing flexibility in the graft and matrix improves dispersion of PGNs in a chemically identical polymer matrix, due to increased wetting of the grafted layer by matrix chains.

In summary, the wetting of PGNs by a chemically identical matrix is strongly dependent on the flexibility of the polymer chains. Decreasing flexibility of the grafts more significantly improves the wetting of the grafted layer than decreasing flexibility of the matrix. Finite filler fraction simulations show that decreasing flexibility improves dispersion due to increasing wetting of the grafted layer. These results suggest that in PGN-filled PNCs with larger persistence length polymers (graft and matrix), one would see a larger window in phase space where the particles would be dispersed.

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■ ASSOCIATED CONTENT

Supporting Information

A full description of the methods and analyses used in this study, along with additional data and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: arthi.jayaraman@colorado.edu.

Author Contributions

†B.L. and T.B.M. contributed equally.

Notes

The authors declare no competing financial interest.

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