

Structure and Dynamics of Polyethylene Nanocomposites

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ABSTRACT: The structure and dynamics of linear monodisperse polyethylene (PE) melts ($C_{160}H_{322}$ and $C_{440}H_{882}$) containing homogeneously distributed spherical nanoparticles were investigated. The PE chains were simulated using a coarse-grained model and a Monte Carlo algorithm. Two variables were considered: (i) the wall-to-wall distance between particles d and (ii) the interaction energy between monomers and particles. The various chain structures changed greatly with d while the monomer–particle interaction had little effect. The average size, shape, and orientation of PE chains did not differ significantly from those of a neat melt. Bridge segments were more stretched relative to segments in the neat melt, and the stretch increased with increasing d . However, the number of bridge segments decreased markedly with increasing d . The chain dynamics were monitored by computing the Rouse relaxation modes and the MSD. The dynamics were slowed by both geometric (confinement by fillers) and energetic (monomer–particle energetic interaction) effects.

Introduction

There has been much attention paid recently to the enhanced properties of polymers containing nanosized filler particles. Many experimental studies have shown improved material properties of polymer nanocomposites over those of the neat polymer.^{1–4} When a small volume fraction of spherical nanoparticles was added to a semicrystalline polyethylene (PE), for example, the tensile strength increased up to 30%, and the tensile modulus nearly doubled in comparison to a structurally similar semicrystalline neat PE.¹ Similarly, for melts and solutions containing small volume fractions of nanosized spherical filler particles, the viscosity may be up to an order of magnitude larger than that of the neat polymer.² The range of volume fractions of nanosized filler particles giving rise to reinforcement was found to be from less than 1% to ~10%—much smaller than normally used in traditional polymer composites, where the fillers have dimensions on the order of micrometers.

The nature of the polymer–filler particle interface defines to a large extent the reinforcement and the viscoelastic properties of the nanocomposites.^{3,4} The interface can be controlled by adjusting the chemistry of the filler surface. Experimentally, it has been observed that when there was little or no adsorption of the polymer to the particle, practically no difference was seen in the storage or loss modulus of the nanocomposite compared to the neat polymer.³ However, the storage modulus increased several orders of magnitude when there was strong adsorption.³ The reinforcement of traditional polymer composites has been extensively studied in the past, and these studies identified the strength of the adsorption of polymers onto the surfaces of the fillers, referred to as bound rubber in the field of composite elastomers, as one of the variables influencing the amount of reinforcement.^{32–34}

Several theories have been proposed for the molecular origins of the reinforcement. An idea proposed previously for filled rubbers suggests that reinforcement is obtained once the filler agglomerates percolate. This idea contrasts with the experimental observation that in filled polymers enhanced properties resulted once good filler dispersion was achieved. An attempt to adapt this idea for nonagglomerated filler structures was based on the assumption that the dynamics of polymer chains located near a surface was slowed down. This led to a confined polymer layer next to the filler, and the thickness of this layer was estimated to be on the order of 1–2 times the radius of gyration (R_g). It was conjectured that the percolation of these layers led to the overall enhancement of properties.⁵ In contrast to this idea is the transient filler network theory which stated that fillers were connected by a network of adsorbed chains forming a “secondary” (i.e., in addition to the entanglements) network. Simple calculations as well as molecular simulations estimated that the network forms once the average filler wall-to-wall distance was on the order of $2R_g$ and smaller. This theory was able to qualitatively explain the nonlinear viscoelastic properties such as the Payne effect seen in nanocomposites.⁴

Many molecular scale simulations have been performed to understand the molecular origins of the reinforcing effect of nanosized fillers, with particular attention devoted to planar interfaces and spherical fillers.^{6–10,12,13,29} Both molecular dynamics (MD) and Monte Carlo (MC) methods were employed, and all studies used an idealized bead–spring representation of the polymer chains. The results seem to support both theories discussed above. The structure of the polymer next to the filler surface is indeed different than in the bulk, and it was confirmed that, provided the wall-to-wall distance is small enough, polymer chains may bridge several neighboring fillers and form a “secondary” network.⁹

The issue whether the fillers perturb the polymer structure depends on the length scale of observation and was investigated previously using a bead–spring model.⁶

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Table 1. Details of the Systems Investigated

system identifier	simulation cell size L [lattice units]	simulation cell size to R_g ratio L/R_g	chain length N	no. of chains N_c	no. of particles N_f	particle diam D_f	wall to wall distance d	vol fraction of filler φ (%)	melt density ρ [g/cm ³]	monomer–particle interaction parameter w
S1	19 × 18 × 18	2.53	80	14	0			0	0.767	
S2	18 × 18 × 18	2.53	80	12	1	1.30 R_g	1.21 R_g	10.6	0.776	1
S3	18 × 18 × 18	2.53	80	13	1	0.70 R_g	1.83 R_g	1.59	0.764	0.1
S4	18 × 18 × 18	2.53	80	13	1	0.70 R_g	1.83 R_g	1.59	0.764	1
S5	18 × 18 × 18	2.53	80	13	1	0.70 R_g	1.83 R_g	1.59	0.764	2
S6	22 × 22 × 22	3.09	80	24	1	0.70 R_g	2.39 R_g	0.87	0.767	1
S7	21 × 21 × 21	2.95	80	20	1	0.70 R_g	2.25 R_g	1.00	0.736	1
S8	27 × 27 × 27	3.79	80	43	8	0.70 R_g	1.19 R_g	3.78	0.766	1
S9	31 × 31 × 31	2.75	220	24	1	0.90 R_g	1.86 R_g	2.56	0.767	1
S10	21 × 21 × 21	2.95	80	20	1	1.30 R_g	1.63 R_g	6.65	0.781	1

The findings were as follows: (a) The orientation of bonds was perturbed only at distances from the wall comparable with the bond length. (b) On the chain scale, the size of the ellipsoidal chains did not change upon confinement; rather, the chains rotated with their long semiaxis in the direction tangential to the wall. (c) The size of the polymer decreased only when confinement became excessive, i.e., when the wall-to-wall distance was smaller than R_g . This effect can be explained on the basis of entropy considerations. The entropy loss associated with rotation was marginal compared to the loss associated with chain size variation. The previous investigation⁶ also showed that the energetic interaction between polymers and fillers has little effect on structure.

The slowing down of the dynamics of chains near a confining surface was also observed in simulations.^{13,29} The slowing down leads to an increase in the glass transition temperature (T_g) of the material.¹⁴ The effect is more pronounced as the interaction becomes more attractive.

This paper investigates the structure and dynamics of an amorphous PE melt containing spherical nanoparticles. Several questions are addressed: (i) Is the static chain structure different in the nanocomposite compared to the neat, and if it is different, on what length scale is the difference seen? (ii) How does the wall-to-wall distance and the monomer–particle interaction control the dynamics of PE chains and on what length scale is the control seen? (iii) To what extent do the results obtained with this polymer specific model differ from those obtained with bead–spring models?

Simulation Setup

The simulations performed in this study used a coarse-grained rotational isomeric state (RIS) model for the PE chains where the chains were represented on a high coordination lattice. The simulations were performed at a temperature of 200 °C, which is above the melting point of PE used in this simulation. The systems represent bulk material with nanosized fillers homogeneously dispersed. In most simulations, one filler particle per simulation cell was considered. Since periodic boundary conditions were used and the simulation box was a distorted cube ($\alpha = \beta = \gamma = 60^\circ$), the filler structure represented a close packing of spherical fillers in space. The image effects were minimized by ensuring the simulation cell size in all three coordinate directions was larger than $2R_g$ in all cases. Several larger systems with eight fillers per simulation cell were also considered. The results from these systems were indistinguishable from those obtained with systems with one filler per cell. The space occupied by the polymer was

filled to a density of ~ 0.76 g/cm³, as appropriate for PE melt at 200 °C.

The simulation method employed in this study used single bead moves that were local and were accepted through the Metropolis Monte Carlo algorithm, which effectively samples the conformational space. The coarse-graining was achieved by combining every two carbon and associated hydrogen atoms on the PE chain into a bead that was located on a second-nearest-neighbor diamond (SNND) lattice. The SNND lattice was created by removing every other site from a diamond lattice resulting in a lattice structure that when a random walk was taken, the path closely approximated the actual angles between carbon atoms belonging to the backbone of a vinyl polymer chain. The RIS model was incorporated into the simulation to calculate the short-range intramolecular conformational potential energy of the chain. The long-range intramolecular and intermolecular interaction potential energies were calculated using a lattice based approximation of the Lennard-Jones potential between monomers and between monomers and filler particle beads. The cutoff radius of the long-range energy was three lattice units (each lattice unit is ~ 0.25 nm).

This simulation method has been incrementally improved over the years^{21–23} and widely used to investigate the properties of PE and other vinyl polymers including their bulk dynamics,^{17,18} mixing of PP and PE,¹⁹ mixing of PP with differing stereochemical compositions,²⁰ and thin films.²⁵ Details of the simulation method and the potentials employed for PE can be found in refs 16 and 25.

Spherical nanoparticles were added to the system by creating a volume of beads on the SNND lattice structure that were uniquely specified as being of filler type. These sites were not accessible to the polymers. The particles were created by identifying all the sites within a specified radius; therefore, the shape of the filler particle was approximately spherical. The fillers were fixed in space during simulation. This approximation was acceptable because the filler mass was much larger than that of the polymer beads. Related to particle size, the filler radius and the distance between fillers were both comparable to the radius of gyration in the neat melt, which was consistent with prior research.^{7,27}

The parameters of the various models considered are listed in Table 1. It must be noted that PE in this model remained amorphous at all times, hence, the issue of how the presence of fillers affected the degree of crystallinity, although important, was not addressed in this study.

The distance between fillers was defined by the filler size and the filler volume fraction. The wall-to-wall

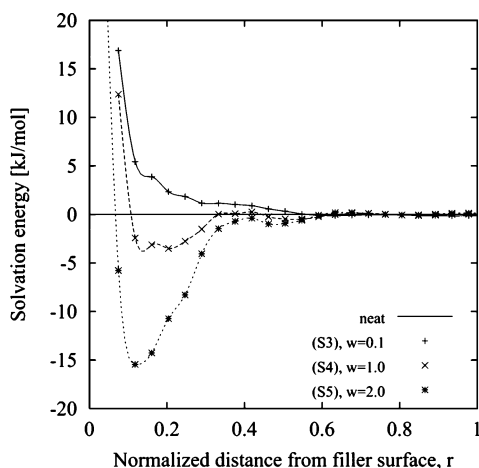


Figure 1. Energy difference between a bead located at distance r from the surface of the filler and a bead in the neat bulk. The distance r is normalized by half of the wall-to-wall distance. Three energetic interactions are shown: (i) $w = 0.1$, repulsive; (ii) $w = 1.0$, neutral; and (iii) $w = 2.0$, attractive.

distance, d , which was defined as the smallest distance between two points located on the surface of two neighboring fillers, ranged from $1.2R_g$ to $2.4R_g$.

The energetic interaction $u(r)$ between polymer beads and particle beads was defined using the same Lennard-Jones potential as was used for the polymer to polymer interactions except it was multiplied by a prefactor w , as shown in eq 1. In this equation, ϵ is the well depth, σ is the location of the well, and r is the distance between bead centers.

$$u(r) = \begin{cases} 4w\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & \text{for } r \geq 0.25 \text{ nm} \\ \text{hard} & \text{for } r < 0.25 \text{ nm} \end{cases} \quad (1)$$

In this study w was taken to be 0.1, 1.0, and 2.0 in separate simulations, representing repulsive, neutral, and attractive interactions, respectively. The case when $w = 1.0$ represented the physical situation when short polymer chains were grafted to the surface of the particle such that the polymer–filler and the polymer–polymer interactions were similar.

Figure 1 shows the solvation energy or the difference in energy of a bead located at a specified distance, r , from the filler surface and its energy in the neat bulk. The depth of the well of the three curves indicates the meaning of the terms repulsive, neutral, and attractive used in this study.

Each system was equilibrated for at least 15 million Monte Carlo steps (MCS); then production runs of 20 million MCS were performed. The equilibration ended once the computed mean-square displacement (MSD) of the representative chain center of mass reached R_g^2 . Each system was replicated three times to improve the statistics.

Results and Discussion

The analysis of the simulation results considers both subchain segments and entire chain segments. The subchain segments include (i) bridges that connect two neighboring fillers, (ii) dangling ends that connect to the filler at one end and the other end is free, (iii) loops that begin and end on the surface of the same filler, and (iv) train segments that snake on the surface of given fillers. Figure 2 illustrates the various types of chain segments

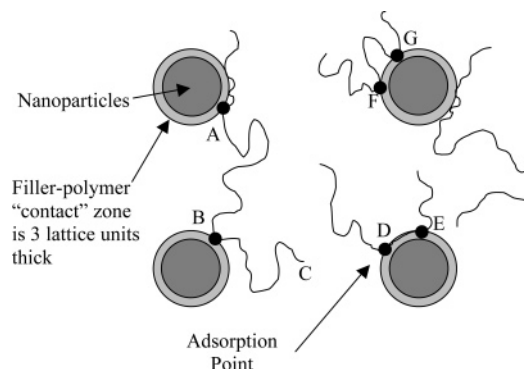


Figure 2. Description of the various types of chain segments investigated. Segment AB is a bridge, segment BC is a dangling end, segment DE is a train, and segment FG is a loop. A monomer is considered attached to a particle if it is within the cut off distance (three lattice units = $7.5 \text{ \AA}$) from the surface.

investigated. A chain is considered attached to a filler particle when at least one of its monomers is within the cutoff distance of the filler particle. This selection of chain subsegments is considered due to the role they are assumed to play in the viscoelasticity of the material. Bridges and dangling segments are important, in particular, since bridges form the secondary network discussed in the Introduction section, while dangling segments are expected to play a significant role in setting the viscosity.

Structure: Subchain Segment Statistics. The first aspect that deserves attention is how frequent the various subchain segments appear in the various realizations of the system considered (S1–S10; see Table 1). This information is presented in Table 2. Table 2 includes the fraction of chains in the systems that form bridges, average number of bridges per filler, fraction of adsorbed beads per chain, and the fraction of chains that have at least one bead adsorbed (one minus fraction of free chains). Because the various systems have different values of d/R_g and w , the data in Table 2 indicate the effect of confinement and stickiness to the filler on these quantities.

The following observations are made by comparing systems S2, S4, and S6, which are described by the same parameters except the wall-to-wall distance, d/R_g , which increases from S2 to S6: (i) The number of bridges decreases rapidly with increasing d . In fact, when $d \geq 3R_g$, no bridges form between fillers. (ii) As d increases, the number of dangling segments increases, this being associated with the decrease in number of bridges. Note that the filler coverage, the fraction of sites on the filler surface occupied by polymer beads, is similar in all systems. (iii) The number of loops and trains remain constant as $d \geq 1.83R_g$. (iv) While in S2, at the smallest d , all chains form bridges, and a large fraction of beads are attached; in S6, 40% of the chains in the system are free. The effect of the monomer–particle interaction prefactor, w , can be observed by comparing systems S3, S4, and S5. It can be seen that this parameter has essentially no effect on these measures of structure.

Structure: Subchain Segment Distributions. The chain segment structure is represented by the probability distribution function (PDF) of the number of monomers, n , in the segment, and the PDF of the end-to-end vector length, R_{ee} . These measures are used as input to rheological molecular models of the viscoelasticity of nanocomposites.²⁶

Table 2. Summary of the Static Chain Structure

system identifier	av no. of segments per filler particle				no. of monomers in segment normalized by the chain length (n/N)				av fraction of chains forming at least one bridge	av no. of bridges per chain that forms bridges	av fraction of chains with at least one bead adsorbed	av fraction of adsorbed beads per chain
	bridge	dangling	loop	train	bridge	dangling	loop	train				
S1												
S2	18.5	16.1	16.1	34.0	0.21	0.16	0.12	0.12	0.86	1.79	1.00	0.37
S3	4.4	18.7	8.3	18.7	0.42	0.37	0.16	0.07	0.31	1.10	0.87	0.14
S4	4.2	19.1	7.7	17.2	0.42	0.36	0.15	0.10	0.30	1.09	0.87	0.17
S5	4.1	19.7	9.2	17.7	0.40	0.34	0.14	0.11	0.29	1.09	0.88	0.19
S6	1.3	24.8	7.9	17.3	0.54	0.43	0.16	0.10	0.05	1.01	0.59	0.13
S7	1.8	23.0	7.2	16.7	0.49	0.41	0.16	0.10	0.09	1.02	0.66	0.14
S9	5.5	33.9	26.9	38.7	0.42	0.36	0.08	0.04	0.21	1.07	0.77	0.10
S10	10.5	30.2	18.7	35.0	0.35	0.29	0.14	0.12	0.45	1.17	0.95	0.24

The distributions of the number of monomers per bridge, dangling end, loop, and train segments normalized by N , and the number of monomers in the chain, $P(n/N)$, are shown in Figures 3, 4, 5, and 6, respectively. Data from systems S2, S3, S4, S5, and S6 are compared in each figure. Systems S2, S4, and S6 have the same monomer–particle interaction prefactor of $w = 1.0$ (neutral) but have a varying wall-to-wall distance, d , between particles, whereas systems S3, S4, and S5 have varying w but the same d .

The bridge and dangling end distributions change substantially as the wall-to-wall distance d varies but are essentially independent of the interaction prefactor, w (see Figures 3 and 4). As expected, the bridge distribution changes from a broad distribution where the mean number of monomers per bridge is approximately one-half of the overall chain ($N/2$) to a sharp distribution of bridge segments containing a small number of monomers. The dangling end segment distribution changes from a nearly constant probability of having any number of monomers between one and N form a dangling end to a highly skewed distribution where there is a high probability of having dangling end segments having $N/2$ or less monomers. This is again consistent with the effect of confinement because in S2 no long dangling ends may exist as they would form bridges.

Figure 3b compares the distribution of the number of monomers per bridge between two systems with similar filler volume fraction and density but with two different chain lengths, $N = 80$ vs $N = 220$. The two distributions are identical as were the other three chain segment distributions. This justifies the use of the smaller but faster simulations based on $N = 80$ chains rather than the $N = 220$ chain systems.

As can be seen in Figures 5 and 6, there is very little variation in the distribution of loop and train segments as the wall-to-wall distance and the monomer–particle interaction prefactor change. This can be explained by the fact that loop and train segments are structures local to the surface of the particle. On average they form with less than $N/6$ monomers in a chain and therefore do not feel the effect of the neighboring particles that are approximately twice as far away as their length.

The question of whether the equilibrium chain structure changes as a result of the presence of nanoparticles is considered next. The issue is studied by probing the PDF of the end-to-end vector length of bridges and entire chains.

The probability distribution of bridge lengths in the nanocomposite is compared to the probability distribution of subchain segments in the neat melt. Figure 7a,b

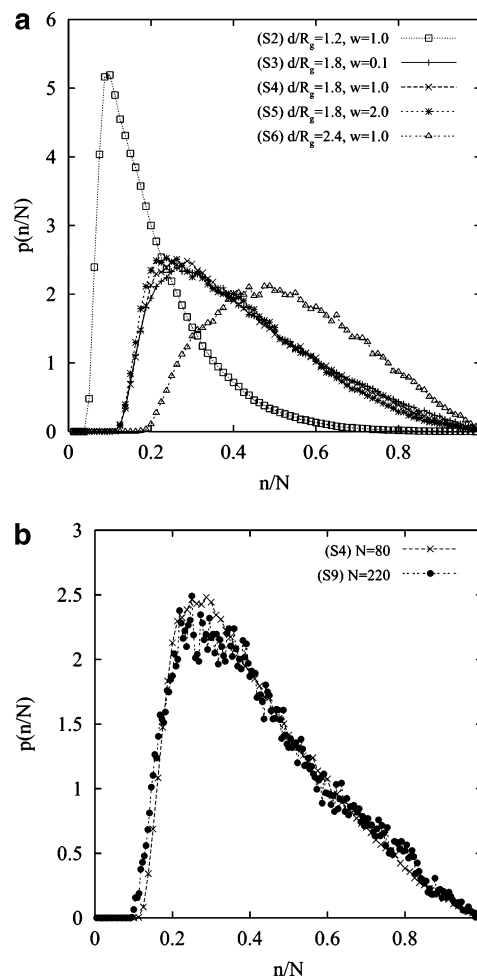


Figure 3. Bridge segment probability distribution function vs the normalized bridge segment length (n/N) for (a) all systems considered (see Table 1) and (b) similar data for different chain lengths.

shows the PDF of $|\bar{\mathbf{R}}_{ee}^b|/(l\sqrt{n})$ for various composite polymer systems, where $\mathbf{R}_{ee}^b$ is the end-to-end vector of a bridge segment, l is the bond length between monomers, and n is the number of monomers in the segment. Also shown is the PDF of segment lengths taken from the neat system simulations. Recall that the neat system is simulated with the same model for the polymer, without fillers, and the distribution is Gaussian. In particular, the neat system is sampled using $P(n/N)$ obtained for bridging segments for the various filled systems (Figure 3), and the resulting distributions of the segment end-to-end vectors are all Gaussian and

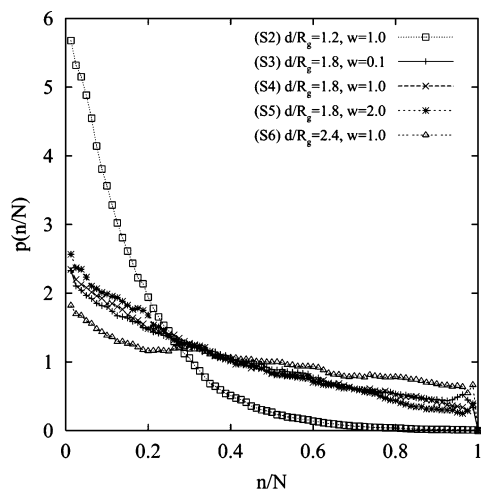


Figure 4. Dangling end segment probability distribution function vs the normalized dangling end segment length (n/N).

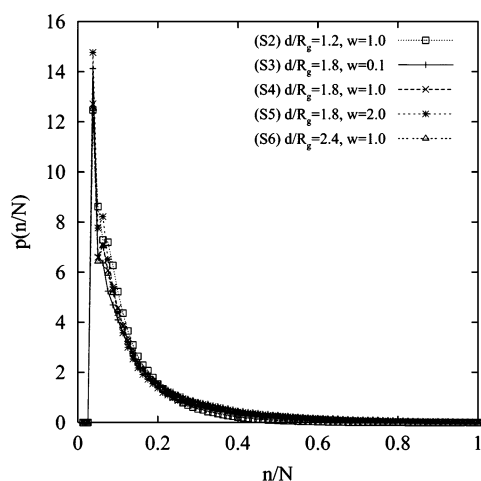


Figure 5. Loop segment probability distribution function vs the normalized loop segment length (n/N).

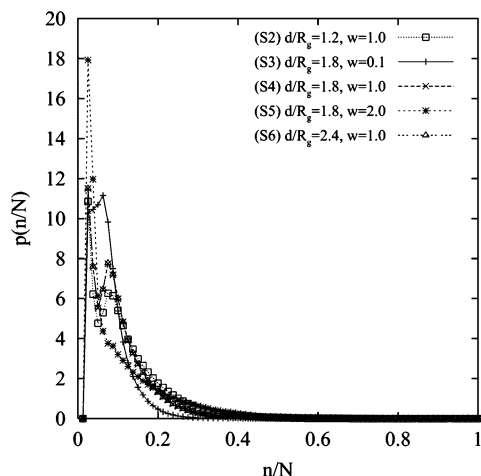


Figure 6. Train segment probability distribution function vs the normalized train segment length (n/N).

superimpose exactly on the similar distribution of the end-to-end vectors of the entire chains.

As the wall-to-wall distance increases, the distributions in Figure 7a shift to the right and become narrower. This indicates that the bridges are stretched compared to similar segments in the neat melt. It is the reduced number of possible chain conformations as the

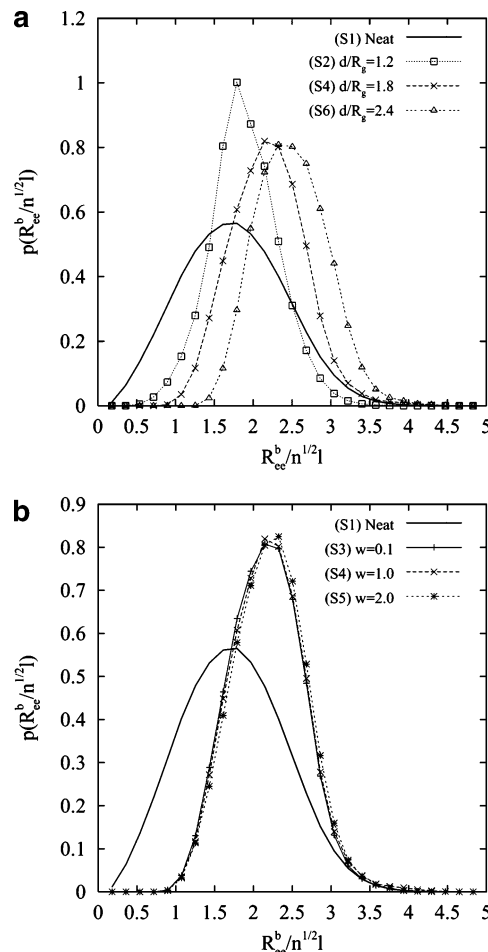


Figure 7. Probability distribution of bridge segments' end-to-end vector length: (a) dependence on confinement, d ; (b) dependence on w .

chain becomes more stretched that causes the narrowing of the distribution seen in Figure 7a. A similar effect was observed in simulations using bead-spring models.²⁷ The apparent stretch of bridge segments compared to segments in the neat is due to the way the distribution of chain subsegments is probed. Let us consider an extreme example. The distribution for the neat system in Figure 7a is identical for chain end-to-end vectors and for end-to-end vectors of chain subsegments; hence, one can replace n by N in this case. If we fix the representative chain at one end to a wall and we bring the other wall at a distance $4l\sqrt{N}$ from the fixed end, then the probability of the free end to reach the wall is very small (as seen in Figure 7a). If one would plot the PDF of only these chains that do reach the wall, assuming that sufficient statistics is accumulated, it would obtain a narrow distribution strongly shifted to the right; only the most stretched chains of the neat distribution manage to reach the wall. A similar effect is observed in the filled system. The farther apart the walls are the fewer bridges exist, and the distribution of bridge end-to-end distances shifts to the right monotonically as the wall-to-wall distance increases.

We would like to comment on the importance of this effect. Stretched chains are stiffer than unstretched ones since the entropic force acting between the two ends follows the Langevin function. This suggests that the filled system is stiffer than the neat material just due to the presence of these segments.³⁰ However, signifi-

cant stretching is observed only when the wall-to-wall distance becomes larger than $2R_g$, situations in which the number of bridges per filler is very small (see Table 2). Hence, an overall stiffening effect exists, but it is not expected to be significant.

The effect of the polymer–particle energetic interaction prefactor, w , is shown in Figure 7b. This parameter changes nothing in the structure of the chain segments as the interaction is local and cannot affect the chain-scale structure. The strength of the interaction is expected to be crucial in dynamics given the energy penalty it imposes during chain detachment from fillers.

Further insight into the structure can be obtained by looking at the statistics for entire chains. If only chains that form bridges are selected, the distribution of the end-to-end vector of the chain, $R_{ee}/(l\sqrt{N})$, is slightly shifted to the right compared with the distribution in the neat melt, indicating a minor stretch. This is obviously an effect of the presence of the bridge. However, when the whole population of chains is considered, the end-to-end distribution is identical to that in the neat melt to within the accuracy of the present calculations. As previously observed for bead–spring systems,^{7,27} the presence of the fillers does not change the structure of the chains if the wall-to-wall distance is larger than R_g , but rather chains remain Gaussian. The stretching of bridges is associated with the sampling of the Gaussian distribution as discussed above.

The conclusion that chains preserve their neat melt structure is reinforced by the evaluation of R_g as well as that of the eigenvalues of the gyration tensor $\lambda_1, \lambda_2, \lambda_3$. Similar to the end-to-end distance, these quantities also are insensitive to d and w for the range of parameters considered. It is expected that if d becomes smaller than R_g , the chain size will decrease, as found for bead–spring systems. The ratios of the three eigenvalues of the gyration tensor ($\lambda_1/\lambda_3:\lambda_2/\lambda_3:\lambda_3/\lambda_3$) are found not to be a function of distance from the particle. This ratio was found to be approximately 14:3:1 for the neat (S1) system. A change in these ratios in the composite systems would imply a change in the shape of the average chain. Again, no change was observed in these ratios as a function of distance from the surface of particle.

To further support the conclusion that chains preserve their neat melt structure, the chain orientation was also investigated by calculating the second Legendre polynomial of the angle between the major semiaxis of the chain and the vector normal to the filler surface passing through the chain center of mass. A similar result to that found for the size and shape of the chains is also found. There is no significant difference in the average orientation of the major semiaxis of the chain ellipsoid as a function of distance from the surface of the particle. This finding, however, is contrary to what was found for the bead–spring model⁶ in which the major semiaxis of the chain ellipsoid rotates tangent to surface of the filler as the distance between fillers decreased. The reason for this discrepancy is likely a result of the relatively smaller size of the particle ($0.7R_g$) used in this investigation compared to previous studies,⁶ where the particle size was $\sim 1.0R_g$, and the large volume occupied by the chains—the chains used in this study occupied a volume ~ 23 times larger than the volume of the filler.

Dynamics: Rouse Modes. The dynamics of the PE chains is investigated by examining both the Rouse

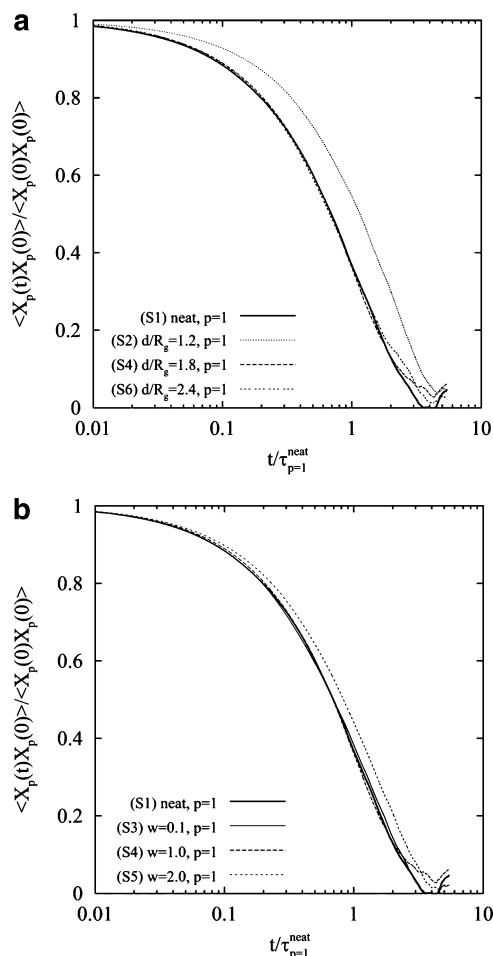


Figure 8. Autocorrelation function for the $p = 1$ Rouse mode normal coordinate: (a) dependence on confinement, d ; (b) dependence on w . The time scale is normalized by the Rouse time of the whole chain in the neat system.

modes and the mean-square displacement of the chain center of mass, $g_3(t)$,³¹ as a function of the number of Monte Carlo steps (MCS). The characteristic relaxation times of the system are determined in the usual way by computing the autocorrelation function of the normal modes. Figure 8 shows the autocorrelation function of the first Rouse mode ($p = 1$) for various systems (see Table 1). Figure 8a shows the effect of confinement by comparing systems S2, S4, and S6 for which $w = 1.0$. As long as d is larger than $\sim 1.5R_g$ (S4 and S6) confinement is too weak to influence relaxation. Slowing down is seen in system S2, for which $d = 1.2R_g$. The relaxation of the neat system (S1) is plotted for reference. The effect of the prefactor w is shown in Figure 8b in which the wall-to-wall distance d is held constant (systems S3, S4, and S5). As expected, increasing polymer–filler adhesion leads to an additional slowdown.

Next, the issue of whether there is a length scale below which the confinement has no effect on Rouse relaxation is investigated. The idea is rooted in the presumption that fillers will only affect relaxation modes with wavelengths comparable to the characteristic length scale of the microstructure, e.g., the wall-to-wall distance. In the limit, one might expect the motion of a single monomer would not be affected by the presence of a particle. To test this hypothesis, all Rouse modes were evaluated. The results are shown in Figure 9 in which the normalization of the two axes

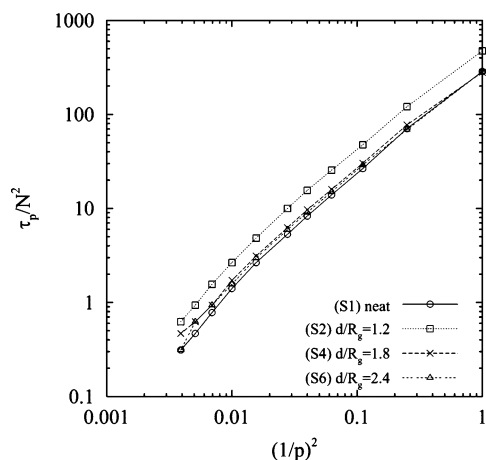


Figure 9. Rouse relaxation times τ_p vs $(N/p)^2$.

reflects the expected Rouse scaling of the relaxation times.²⁸

$$\tau_p = \tau_0 \left(\frac{N}{p} \right)^2 \quad (2)$$

A straight line with a slope of 2 and a y-intercept of τ_0 is predicted by this relation. The data for given system align, which suggests that the Rouse scaling is followed. The lines are shifted in the vertical direction, which is a manifestation of the slowing down also seen in Figure 8a. Interestingly, the assumption made above seems to be false: confinement affects all relaxation modes in the same way, independent of their wavelength. The conclusion remains valid for the data in Figure 8b; the slowing down due to w is similar for all modes. This observation has implications on the modeling of the rheology of the material at larger scales. It implies that the effect of fillers on dynamics (at least Rouse dynamics) may be represented in a mean-field sense by an increase in the average friction the monomer feels. The effective friction coefficient may be calibrated from the intercept of the vertical axis in Figure 9. This mean-field view was taken in the rheological model presented in ref 26.

Dynamics: Diffusion. The dynamics is further analyzed by evaluating the mean-square displacement (MSD) of the chain center of mass, $g_3(t)$, where time t is converted here into number of MC steps. The results are shown in Figure 10. The horizontal axis is normalized by the Rouse time in the neat system. Its selection for normalization is made considering that the Rouse time of the various filled systems is only slightly different than this value.

Figure 10a demonstrates the effect of confinement ($w = 1.0$ in all these cases). The conclusion is similar to that obtained from the Rouse analysis—confinement slows down dynamics. The various g_3 curves are parallel, which indicates that confinement preserves the nature of the diffusion but changes the diffusivity.

Figure 10b shows the effect of the filler–polymer interaction prefactor, w . The curve corresponding to the neutral interaction case ($w = 1.0$) has a slope of 1.0 beyond the Rouse time; i.e., it follows normal simple diffusion dynamics. The system with repulsive interaction ($w = 0.1$) is superdiffusive, while the one with attractive interactions ($w = 2.0$) is subdiffusive (the slope is smaller than 1.0 in the simple diffusion regime).

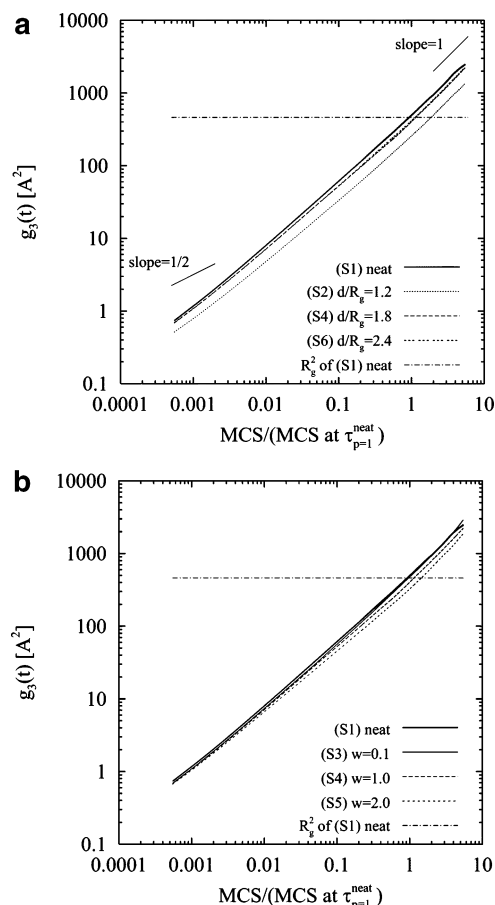


Figure 10. Mean-squared displacement of the chain center of mass vs time (MCS): (a) dependence on confinement, d ; (b) dependence on w . The time scale is normalized by the Rouse time of the whole chain in the neat system. The value of $\langle R_g^2 \rangle$ is shown as a guide.

These findings can be understood by considering an analogy with a random walk. If part of the sites available to the random walker is “stickier” than others, i.e., the walker spends more time there than in other sites, the resulting Levy walk is subdiffusive and is characterized by a scaling exponent smaller than one. If the walker is made to spend less time in a fraction of the available sites, the motion will be superdiffusive and characterized by scaling exponents larger than one. Likewise, if the walk is made in a confined geometry and the walker spends the same amount of time in all sites, the walk is diffusive, but the diffusivity depends on the degree of confinement. The analogy with the polymeric system considered here is obvious. If the polymer–filler interaction is attractive, the representative bead spends more time at the wall than in any other site of the lattice. If the interaction is repulsive, the entropic interaction between chains and fillers pushes the chains away from the filler surface, leading to the creation of a low-density polymer layer in the immediate vicinity of the wall.⁷ As the number of occupied sites is smaller in the depleted layer than in the bulk, the residence time in these sites is shorter, which leads to the superdiffusive behavior.

Conclusions

A series of on-lattice Monte Carlo simulations were performed representing systems of PE chains containing spherical nanoparticles. The purpose of this investigation was to better understand both the static chain

structure and the chain dynamics of a PE nanocomposite by comparing it to neat PE melt system. In addition, we wanted to better understand the length scale over which differences in the chain dynamics are expected. This work concentrated on a polymer system that is chemically defined and was an attempt to simulate real systems as opposed to model (i.e., bead-spring) systems. By using a real system, we hope to study more complicated systems (such as surface modified particles) in the future. In the near future, we will be comparing these PE specific simulations to experiments performed using the nuclear magnetic resonance technique.¹¹

The probability distribution of the number of monomers present in bridge, dangling end, loop, and train chain segments located around and in between spherical particles was presented. The broad distribution of bridges and the nearly uniform distribution of dangling end segments drastically changed to a narrow distribution of a small number of monomers as the distance between particles (d) decreased. Hardly any change was seen in the monomer distribution of loop and train chain segments as d decreased. For all chain segment types investigated, the monomer distribution did not change as a result of varying the monomer-particle interaction energy prefactor, w .

The static chain structure of PE nanocomposites was investigated by examining the following three chain measures—average size, average shape, and average chain orientation—between the composite systems and the comparable neat system. For all three measures no significant variation was observed between values found for the composite systems and those found for the neat system. In addition, no significant variations were found in these measures as a function of distance from the particle for all composite systems investigated.

However, when the structure of bridge segments was examined in detail, it was found that they became more stretched relative to the neat chain segments containing the same number of monomers. The system with the largest wall-to-wall distance between particles had bridge chain segments that were $\sim 40\%$ more stretched when compared to chain segments that contain the same number of monomers in the neat system. The amount of stretch in a bridge segment appeared to decrease as the wall-to-wall distance decreased.

The new information presented in this paper is the effect of the two variables, d and w , on the dynamics of a PE nanocomposite system, specifically, the effect on the Rouse relaxation times and the mean-square displacement. Although the static chain structure investigation using a chemically specific model did not show any differences compared to previous simulations using bead-spring models, this was not obvious at the onset of the investigation. The fact that nearly identically probability distribution functions of chain structures were found using either the polyethylene model or the generic bead-spring model is an interesting result in and of itself and supports the utility of faster, more generic models to investigate chain structure at lengths scales comparable to the radius of gyration of the chains.

The dynamics of the PE chain was found to be different in the composite systems compared to the neat PE. The Rouse relaxation time, τ_p , of the entire chain increased rather suddenly as d decreased below $\sim 1.5R_g$. In addition, τ_p also increased for systems with attractive monomer-particle interaction energy compared to the

systems with neutral and repulsive interactions. The most notable observation was the slowing down in the Rouse dynamics seen on all subsections of the chain no matter how small the subsections were, meaning that on average every monomer feels the confinement of the neighboring particles, slowing the relaxation of every chain subsection.

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References and Notes

- (1) Wei, L.; Tang, T.; Huang, B. *J. Polym. Sci., Part A* **2004**, *42*, 941–949.
- (2) Zhang, Q.; Archer, L. *Macromolecules* **2004**, *37*, 1928–1936.
- (3) Zhang, Q.; Archer, L. *Langmuir* **2002**, *18*, 10435–10442.
- (4) Sternstein, S. S.; Zhu, A. *Macromolecules* **2002**, *35*, 7262–7273.
- (5) Montes, H.; Lequeux, F.; Berriot, J. *Macromolecules* **2003**, *36*, 8107–8118.
- (6) Picu, R. C.; Ozmusul, M. S. *J. Chem. Phys.* **2003**, *118*, 11239–11248.
- (7) Ozmusul, M. S.; Picu, R. C. *Polymer* **2002**, *43*, 4657–4665.
- (8) Vacatello, M. *Macromolecules* **2003**, *36*, 3411–3416.
- (9) Vacatello, M. *Macromolecules* **2001**, *34*, 1946–1952.
- (10) Yuan, Q. W.; Kloczkowski, A.; Mark, J. E.; Sharak, M. A. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1647–1657.
- (11) Ozisik, R.; Zheng, J.; Dionne, P. J.; Picu, C. R.; von Meerwall, E. D. *J. Chem. Phys.*, in press.
- (12) Vacatello, M. *Macromolecules* **2002**, *35*, 8191–8193.
- (13) Smith, K. A.; Vladkov, M.; Barrat, J. L. *Macromolecules* **2005**, *38*, 571–580.
- (14) Starr, F. W.; Schrder, T. B.; Glotzer, S. C. *Macromolecules* **2002**, *35*, 4481–4492.
- (15) Baschnagel, J.; Binder, K.; Doruker, P.; Guse, A. A.; Hahn, O.; Kremer, K.; Mattice, W. L.; Muller-Plathe, F.; Murat, M.; Paul, W.; Santos, S.; Suter, U. W.; Tries, V. *Adv. Polym. Sci.* **2000**, *152*.
- (16) Ozisik, R. Ph.D. Dissertation, University of Akron, Akron, Ohio, 1999.
- (17) Doruker, P.; Mattice, W. L. *Macromol. Theory Simul.* **1999**, *8*, 463–478.
- (18) Ozisik, R.; Doruker, P.; Mattice, W. L.; von Meerwall, E. D. *Comput. Theor. Polym. Sci.* **2000**, *10*, 411–418.
- (19) Clancy, T. C.; Putz, M.; Weinhold, J. D.; Curro, J. G.; Mattice, W. L. *Macromolecules* **2000**, *33*, 9452–9463.
- (20) Clancy, T. C.; Mattice, W. L. *J. Chem. Phys.* **2001**, *115*, 8221–8225.
- (21) Rapold, R. F.; Mattice, W. L. *Macromolecules* **1996**, *29*, 2457–2466.
- (22) Cho, J.; Mattice, W. L. *Macromolecules* **1997**, *30*, 637–644.
- (23) Doruker, P.; Mattice, W. L. *Macromol. Theory Simul.* **1999**, *8*, 5, 463–478.
- (24) Clancy, T. C.; Mattice, W. L. *J. Chem. Phys.* **2000**, *112*, 10049–10055.
- (25) Xu, G.; Lin, H.; Mattice, W. L. *J. Chem. Phys.* **2003**, *119*, 6736–6743.
- (26) Savestani, A. S.; Picu, R. C. *Polymer* **2004**, *45*, 7779–7790.
- (27) Ozmusul, M. S.; Picu, R. C.; Sternstein, S. S.; Kumar, S. *Macromolecules* **2005**, *38*, 4495–4500.
- (28) Rubinstein, M.; Colby, R. *Polymer Physics*; Oxford University Press: New York, 2003.
- (29) Eisenriegler, E.; Kremer, K.; Binder, K. *J. Chem. Phys.* **1982**, *77*, 6296–6320.
- (30) Sternstein, S. S. Rensselaer Polytechnic Institute, private communication.
- (31) Kremer, K.; Grest, G. S. *J. Chem. Phys.* **1990**, *92*, 5057.
- (32) Kamal, M. R.; Mutel, A. *J. Polym. Eng.* **1985**, *5*, 293–382.
- (33) Metzner, A. B. *J. Rheol.* **1985**, *29*, 739–775.
- (34) Malkin, A. Y. *Adv. Polym. Sci.* **1990**, *96*, 69–97.