

Monte Carlo Simulation of the Structure of Mono- and Bidisperse Polyethylene Nanocomposites*

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Abstract The structure of bidisperse polyethylene (PE) nanocomposite mixtures of 50:50 (by mole) of long and short chains of $C_{160}H_{322}/C_{80}H_{162}$ and $C_{160}H_{322}/C_{40}H_{82}$ filled with spherical nanoparticles were investigated by a coarse-grained, on lattice Monte Carlo method using rotational isomeric state theory for short-range and Lennard-Jones for long-range energetic interactions. Simulations were performed to evaluate the effect of wall-to-wall distance between fillers (D), polymer-filler interaction (w) and polydispersity (number of short chains in the mixture) on the behavior of the long PE chains. The results indicate that long chain conformation statistics remain Gaussian regardless of the effects of confinement, interaction strength and polydispersity. The various long PE subchain structures (bridges, dangling ends, trains, and loops) are influenced strongly by confinement whereas monomer-filler interaction and polydispersity did not have any impact. In addition, the average number of subchain segments per filler in bidisperse PE nanocomposites decreased by about 50% compared to the nanocomposite system with monodisperse PE chains. The presence of short PE chains in the polymer matrix leads to a reduction of the repeat unit density of long PE chains at the interface suggesting that the interface is preferentially populated by short chains.

Keywords: Monte Carlo simulation; Polymer nanocomposites; Bidisperse.

INTRODUCTION

Polymer materials reinforced with nanoparticles have been the subject of interest in both scientific and industrial communities due to their extraordinary and improved performance. The improved properties^[1–7], although very different in nature according to the application of interest and polymers used, are generally termed as the reinforcement effect^[2]. Though an understanding of the reinforcement mechanism behind these improvements is still developing, it is well accepted that the well dispersion of nanoparticles in polymer matrix and the filler spacing between neighboring particles, when it is comparable to the unperturbed chain dimensions, are both factors that play important roles in the property enhancement^[4, 8, 9].

Several theoretical and experimental studies^[2, 4, 10–13] have proposed that the reinforcement is obtained once the neighboring fillers were connected by adsorbed polymer chains forming a “secondary” network, which is also called a polymer-mediated transient network. This network can be formed when the wall-to-wall distance

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(D) between fillers is of the order of several times the radius of gyration (R_g) of the polymer chain. The polymer-filler structure is formed as sequences (subsections) of the chain adsorbing onto the filler particles. The various types of subchain segments in transient network model are illustrated in Fig. 1. This model was successfully used to qualitatively explain the viscoelastic properties of polymer nanocomposites^[10, 14].

Molecular simulations provide an excellent opportunity to directly study the effect of nanoparticles on structure and dynamics of polymer chains, since detailed information on the properties near a nanoparticle surface is difficult to obtain experimentally. The melt structure of polymer chains in the vicinity of the flat and curve solid surfaces has been studied by both molecular dynamics (MD) and Monte Carlo (MC) methods. The results suggest that polymer chains near flat walls do not distort even when they are confined into films as thin as R_g but they are preferentially aligned in the direction parallel to the surface^[14, 15]. In contrast to polymer chains in the presence of curve nanoparticles, polymer chains near flat surfaces were found to be either stretched or compressed depending on the ratio of the chain dimension and the average wall-to-wall distance^[16]. However, recent MC^[17–19] and MD^[20] simulations of polymer melts in the presence of nanosized spherical fillers imply that the chain dimensions are always smaller compared to the bulk at high and moderate filler concentrations. The change in dynamic properties of polymer chains near the interfaces of nanocomposites is also an interesting study. Several computational studies in this area shed light into the issue of the change in the glass transition temperature (T_g) in nanoparticle filled polymers, as well as the effect of surface interactions on melt diffusion and viscosity^[21, 22].

Most computational studies of the structure and dynamics of polymer nanocomposites have been dedicated to monodisperse polymer matrices. However, in reality, polymers are polydisperse. It is well known that the polydispersity of the polymer matrix plays a critical role in defining the properties of polymer nanocomposites but a comprehensive understanding of the effect of polydispersity on polymer chain structure and dynamics in polymer nanocomposites is lacking. Therefore, the study of polydispersity *via* molecular computations is both appealing and timely.

In this work, the structure of bidisperse polyethylene (PE) melts composed of two different chain lengths (long and short) filled with spherical nanoparticles was studied using coarse-grained, on lattice Monte Carlo simulations. The structure of long PE chains was investigated as a function of polydispersity, confinement (as defined by the wall-to-wall distance between nanofillers, D), and polymer-filler interaction strength (as defined by the Lennard-Jones potential well depth prefactor, w). The key questions that the current study aims to address are as follows: (i) What is the nature of the transient polymer network in the presence of short PE chains? (2) How does the polymer-filler interface structure change in bidisperse matrices?

SIMULATION SETUP

Simulations were performed on a high coordination lattice called second nearest neighbor diamond (2nnd or SNND) lattice^[10, 23] employing Metropolis Monte Carlo algorithm^[24]. This simulation method was previously employed by our groups on various types of polymers and geometries (bulk, thin film, polymer droplet) to investigate chain conformation, dynamics, crystallization, *etc.* with success^[10, 14, 25–29]. Although detailed information can be obtained from our previous publications^[10, 25–29], a concise summary is provided here to highlight the basic principles of this method. The high coordination lattice has a lattice constant of 0.25 nm and 60° angles between any unit vectors along the axes. This geometry corresponds to close packing of uniform spheres, and therefore, has 12 nearest neighbors, much greater than the tetrahedral (diamond) lattice onto which polymers with all carbon backbones would fit naturally. To map polymer chains onto the SNND lattice, every two repeat units of polyethylene (PE) are coarse-grained as a single bead on the lattice. With C—C bond length of 0.154 nm and ~109° bond angle, polyethylene chains fit perfectly onto the SNND lattice. The coarse-graining of the polymer chains is reversible; therefore, after simulation is performed on the SNND lattice (or at any stage during the simulation), coarse-grained chains can be mapped back to fully atomistic chains for analysis.

In the current study, simulations were performed for linear polyethylene (PE) chains of $C_{160}H_{322}$, $C_{80}H_{162}$ and $C_{40}H_{82}$. Three different types of systems were studied: neat $C_{160}H_{322}$ (monodisperse system), 50:50 mixtures

of $C_{160}H_{322}:C_{80}H_{162}$, and $C_{160}H_{322}:C_{40}H_{82}$ (by mole). Because the coarse-graining technique used represents a PE repeat unit as a single spherical bead on the simulation lattice, these systems were represented as PE80, PE80/40 and PE80/20, respectively, throughout the remainder of the document. An approximately spherical nanoparticle of varying size (diameter, D_p) was placed at the center of the simulation box. Periodic boundary conditions were employed along all three axes thereby enabling the study of confinement by controlling the distance (D) between the filler (in the parent box) and its images *via* the box size and filler size. Particle size (D_p) and wall-to-wall distance (D) were both kept comparable to the average radius of gyration (R_g) of the PE80 (long) chains. Wall-to-wall distance was defined as the smallest distance between two points located on the surface of two fillers. Wall-to-wall distances of $1.26 \times R_g$, $1.91 \times R_g$ and $2.50 \times R_g$ were investigated in the current study. The simulation method employed in this study used single bead moves that were local and were accepted through the Metropolis Monte Carlo algorithm, which was shown to effectively sample the conformational space. The filler was assumed not to move during the simulations.

The interaction energy used in this model contains a short-range interaction based on the rotational isomeric state (RIS) model and a long-range interaction based on the 6–12 Lennard-Jones (LJ) potential. Energetic interactions, $u(r)$, between polymer-polymer and polymer-filler beads were defined using the same LJ potential. The monomer-filler affinity is controlled by the prefactor (w), as shown in Eq. (1). The w values of 0.1, 1.0 and 2.0 were used corresponding to repulsive, neutral and attractive interactions, respectively. In Eq. (1), ε is the minimum potential energy, σ is the location of the minimum energy, and r is the distance between bead centers.

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

All simulations were performed at 473 K. The space occupied by the polymer was filled to a density of $\sim 0.76 \text{ g/cm}^3$, which is the melt density of PE at 473 K^[10]. After the initial structure was created, an equilibration run was performed for at least 10 million Monte Carlo steps (MCS). Each MCS is defined as an attempt to move each bead (except the filler beads) in the system once. Once the system reached equilibrium, production run of 20 million MCS were performed. Each system was replicated three times with different starting configurations to decrease statistical error. The details of the various simulations performed are provided in Table 1.

Table 1. Details of the various polyethylene nanocomposite simulations performed

System	$l_x \times l_y \times l_z$ (lattice unit)	n	I	N	N_p	D_p/R_g	D/R_g	$\rho (\text{g/cm}^3)$	w
A1	$19 \times 18 \times 18$	80	1	14	—	—	—	0.767	—
A2	$18 \times 18 \times 18$	80	1	12	1	1.38	1.26	0.776	1.0
A3	$18 \times 18 \times 18$	80	1	13	1	0.73	1.91	0.764	1.0
A4	$22 \times 22 \times 22$	80	1	24	1	0.73	2.50	0.767	1.0
A5	$18 \times 18 \times 18$	80	1	13	1	0.73	1.91	0.764	2.0
A6	$18 \times 18 \times 18$	80	1	13	1	0.73	1.91	0.764	0.1
A7	$18 \times 18 \times 18$	80/40	1.124	7/13	1	1.38	1.26	0.776	1.0
A8	$18 \times 18 \times 18$	80/40	1.124	7/13	1	0.73	1.91	0.776	1.0
A9	$18 \times 18 \times 18$	80/20	1.562	7/26	1	1.38	1.26	0.777	1.0
A10	$18 \times 18 \times 18$	80/20	1.562	7/26	1	0.73	1.91	0.777	1.0
A11	$22 \times 22 \times 22$	80/20	1.563	12/48	1	0.73	2.50	0.767	1.0
A12	$18 \times 18 \times 18$	80/20	1.562	7/26	1	0.73	1.91	0.777	2.0
A13	$18 \times 18 \times 18$	80/20	1.562	7/26	1	0.73	1.91	0.777	0.1

l_i : Simulation box size along axis i (each lattice unit equals to 0.25 nm); n : Number of repeat units (also the number of coarse-grained beads per chain); I : Polydispersity index; N : Number of PE chains; N_p : Number of spherical nanoparticles; D_p : Particle diameter; R_g : Average radius of gyration of the PE80 chains; D : Shortest distance between two nanoparticles; ρ : Density of the polymer matrix; w : monomer-particle interaction energy prefactor.

RESULTS AND DISCUSSION

The static (conformational) and dynamic properties of long polyethylene (PE) chains in monodisperse and bidisperse melts containing spherical nanoparticles were investigated *via* coarse-grained, on lattice, Metropolis Monte Carlo simulations. Neat PE melts were used as control and all other simulations were compared to the neat PE simulations when appropriate. The conformational analysis considers both entire chains and subchain segments such as bridges, loops, trains and dangling ends^[2] that could form on the filler. In general, as illustrated in Fig. 1, the polymer chains can be considered as sequences of train segments (subchain segments totally running in the interface shell of a given particle), bridge segments (sequences of non-interface units with the two adjoining units in the interface shells of two different particles), loop segments (similar to bridge segments, but starting and ending in the interface shell of the same particle) and dangling terminal segments.

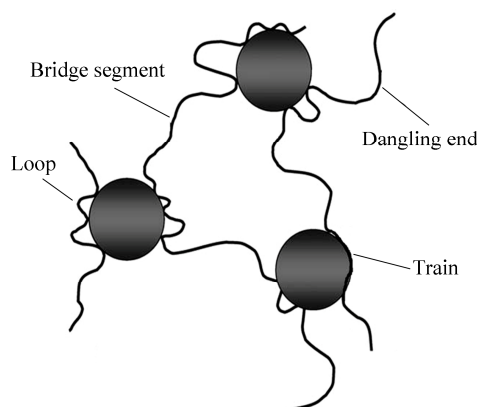


Fig. 1 Schematic representation of various types of subchain segments investigated

Overall Chain Conformation

We first focus our attention on the effect of the nanoparticle on the conformation of PE chains in the melt. Figure 2 shows the probability distribution function of the end-to-end vector (R) of PE80 chains in various systems for different values of D and w parameters. All curves are identical for all conditions indicating that PE80 chains retain the same Gaussian statistics even when they are confined between solid spherical nanoparticles.

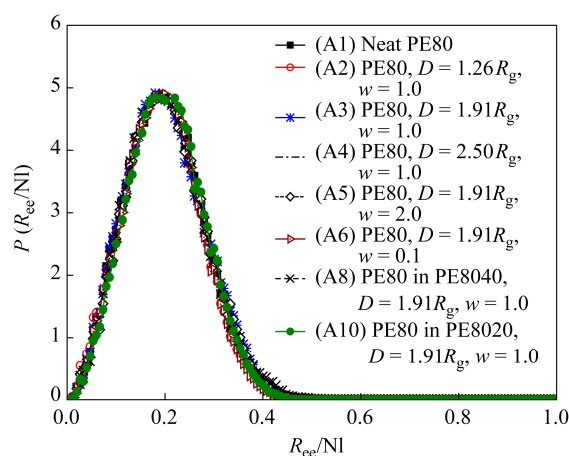


Fig. 2 Probability distribution function of the end-to-end vector of PE80 chains in neat PE80 melt, and monodisperse and bidisperse PE mixtures in the presence of nanofillers

Monomer Density Profile

The bead density of the PE80 chains as a function of radial distance from the nanoparticle surface in both monodisperse and bidisperse systems with different D and w are illustrated in Fig. 3. As can be seen in Fig. 3, all systems considered have a well-defined layered structure. The first layer is generally observed at ~ 1.1 times the lattice constant from the nanofiller surface and is generally the densest layer. The exception to this behavior was observed in systems with repulsive polymer-filler interaction ($w = 0.1$). As the interaction parameter value increased and the system became more attractive, the density of the first layer increased substantially as shown in Fig. 3(a). The density of the first layer did not show a strong dependence on confinement as measured by parameter D as shown in Fig. 3(b). On the other hand, the spacing between layers increased with increasing D values. Figure 3(c) shows the effect of bidispersity on the density profile of PE80 chains. It is important to note that although bidisperse systems contain shorter PE chains, the density profile was plotted for PE80 chains only and as a result, the density profiles change drastically. The density profiles of the PE80 chains in A8 and A10 systems, which have the same number of PE80 chains but have differing short chain molecular weights, are almost the same. When the density profiles are normalized by the number of PE80 chains present in each system (See Fig. 3d), the PE80 chain density profiles look exactly the same. This result shows that even when the system is diluted with shorter chains, the density profile of the long chains as a function of distance from the filler surface does not change.

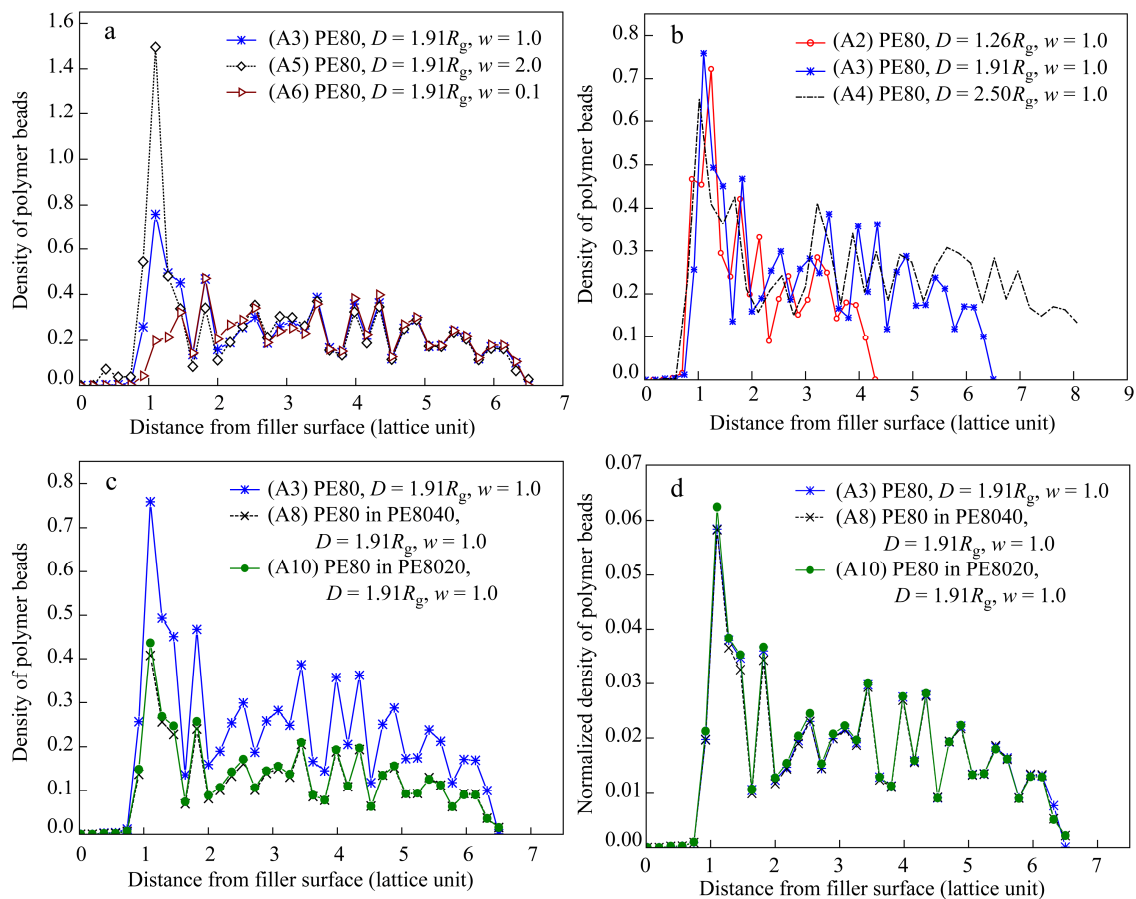


Fig. 3 Monomer density profiles of PE80 chains as a function of radial distance from the filler surface with the variation of (a) polymer-filler interaction parameter (w), (b) confinement (D), and (c, d) polydispersity (In (d) the density profiles from (c) are normalized by the number of PE80 chains in each system.)

Subchain Segment Statistics

An interesting aspect that deserves consideration is how D , w and bidispersity of polymer matrix affect the various types of subchain segments because subchain segments play a critical role in the transient network model. Table 2 presents the average number of bridges, dangling ends, loops and train segments, the average fraction of chains forming at least one bridge segment and the average fraction of free chains that are not involved in any subchain segments. To study the effect of confinement (D) on the average number of subchain segments per filler A2, A3 and A4 systems were considered. It was found that the average number of bridges decreases rapidly with decreasing confinement (increasing distance between fillers, D). Dionne *et al.*^[10] reported that no bridges were formed between nanofillers when $D > 3R_g$. This result is consistent with the observed behavior of the dangling ends: increasing filler-filler distance leads to increased number of dangling ends. On the other hand, the average number of loops and trains remain constant when $D \geq 1.91R_g$ suggesting that the effect of confinement on these types of subchain segments ends at some critical length scale. This observation is logical giving that both trains and loops involve only one filler; therefore, they are local structures and they feel the effect of confinement when it is quite strong.

Table 2. Summary of the statistic chain structure of PE80

Systems	Average number of subchain segments per filler				Average fraction of chains forming at least one bridge	Average fraction of free chains
	Bridge	Dangling	Loop	Train		
A1	—	—	—	—	—	—
A2	18.7	16.1	15.8	33.9	0.87	0.00*
A3	4.3	19.4	7.6	17.3	0.30	0.14
A4	1.8	24.3	7.1	17.3	0.05	0.41
A5	4.3	19.1	9.2	18.2	0.33	0.16
A6	4.3	19.1	8.4	18.9	0.31	0.12
A7	11.1	9.01	10.5	20.4	0.88	0.00*
A8	2.1	10.3	4.2	9.0	0.27	0.13
A9	11.7	9.1	10.6	21.3	0.89	0.00*
A10	2.3	10.5	4.6	9.8	0.30	0.12
A11	0.6	12.5	4.5	9.1	0.05	0.40
A12	2.2	11.2	5.5	10.5	0.29	0.09
A13	2.4	9.9	3.9	9.6	0.31	0.15

* No free chains were found in these systems.

The effect of monomer-filler interactions (w) can be observed by comparing A3, A5, and A6 systems. It can be seen that this parameter has essentially no effect on the average number of subchain segments.

The above observations were made comparing systems that contained only PE80 chains. However, same tendencies were found to be correct for systems containing bidisperse PE chains. The main difference in the bidisperse systems is that the average number of all subchain segments decreased compared to the monodisperse PE80 systems. However, when the PE80 subchain segment averages were normalized by the number of PE80 chains in each system studied, the bidisperse systems showed lower average number of bridges, dangling ends and trains but similar number of loops. This finding suggests that the effect of adding short chains to the system is not simply a dilution effect but rather the short chains are preventing long chains from forming subchain segments particularly bridges, which are important in the formation of the transient network.

In comparison with other MC and MD simulations, another interesting result is that chains and particles do form highly interconnected transient networks in all cases studied, including those with large particles and low filling density in Table 2 of Ref. 2. For instance, even though the average number of bridges per chain is as low as 0.13, the number of bridges per particle is anyway considerable, since each particle is in contact with polymer chains^[2].

Subchain Segment Distributions

The subchain segment structure of the PE80 chains are represented by the probability distribution functions of the number of monomers in the segment (n) normalized by the total number of monomer units (N). The probability distributions, $p(n/N)$, of the number of monomers per bridge, dangling end, loop, and train segments were normalized by the number of monomers in the chain, N , and are shown in Figs. 4(a), 4(b), 4(c) and 4(d), respectively.

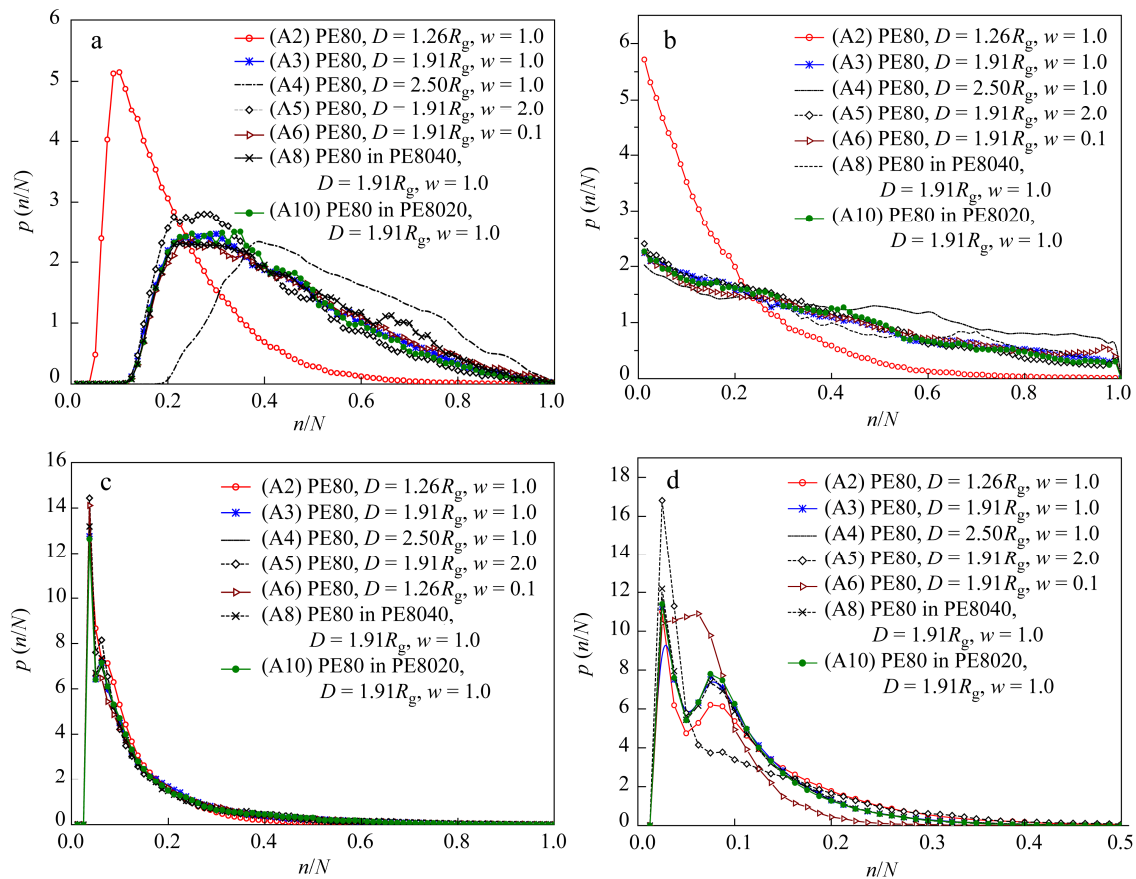


Fig. 4 Probability density distribution functions of the normalized number of bonds of PE80 chains for (a) bridges, (b) dangling ends, (c) loops, and (d) trains of monodisperse and bidisperse PE nanocomposite systems

To investigate the effect of confinement A2, A3, and A4 systems were compared. The number of monomers in bridge and dangling end distributions of PE80 chains were found to be strongly dependent on confinement. With increasing confinement, the bridge distribution becomes narrower indicating that bridge segments were shorter, and therefore, contained less monomers. The dangling end distribution (Fig. 4b) changes from a nearly constant probability to a highly skewed distribution. This observation indicates that dangling ends of any length was almost equally possible when filler-to-filler distance was greater than $\sim 1.3R_g$. However, with the onset of confinement below $\sim 1.3R_g$, only dangling ends with small number of monomers were allowed. This finding is expected because at high confinement ($< 1.3R_g$), long dangling ends would end up forming bridges. As can be seen in Figs. 4(c) and 4(d), the data show little variation in the distribution of loop and train segments with confinement and polymer-filler interaction. Both loop and train segments are structures local to the filler; therefore they are not influenced by confinement, which is happening at much longer length scales^[11]. The polymer-filler interaction parameter showed a strong influence on the loop and train segments compared to confinement because this parameter controls the structure at the interfacial region, local to the filler structure.

The bidispersity effect was investigated via A3, A8 and A10 systems. The results showed that the segment distribution profiles of PE80 chains are almost identical in each of these systems.

CONCLUSIONS

The structure of monodisperse and bidisperse polyethylene melts filled with spherical nanoparticles was investigated by means of a coarse-grained, on-lattice, Monte Carlo method. Bidisperse polyethylene matrix was represented as the mixture of long and short chains. The simulations were performed to evaluate the effect of confinement due to nanofillers, monomer-filler interaction and polydispersity on the behavior of the long polyethylene chains.

In all cases, the long polyethylene chains essentially retained their conformational behavior in the presence of nanofiller, consistent with the notion that it is hard to distort chains in the melt. Polymer-filler structure can be considered as sequences of the chains that are attached to the nanofiller. The subchain segment structures (bridges, dangling ends, loops and trains) were represented by probability distribution functions of the number of monomers in each segment. The distribution of monomers in bridge and dangling end segments drastically changed with increasing confinement. Only small variations in the distribution of local structures (loop and train segments) were observed with confinement. The effect of monomer-filler interaction and polydispersity of polymer matrix were mostly found to be too weak to affect subchain segment structure and their probability distributions.

The statistic chain structure of polyethylene nanocomposites was investigated by examining the average number of subchain segments per filler. The average number of subchain segments per filler in bidisperse polyethylene nanocomposites decreased by about 50%, compared to the monodisperse polyethylene nanocomposite. This result was explained by the observed decrease in bead density of long polyethylene chains at the interface.

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