Modeling of polyethylene and poly (L-lactide) polymer blends and diblock copolymer: Chain length and volume fraction effects on structural arrangement

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Dissipative particle dynamics (DPD), a mesoscopic simulation approach, has been used to investigate the chain length effect on the structural property of the immiscible polyethylene (PE)/poly(l-lactide) (PLLA) polymer in a polymer blend and in a system with their diblock copolymer. In this work, the interaction parameter in DPD simulation, related to the Flory-Huggins interaction parameter \( \chi \), is estimated by the calculation of mixing energy for each pair of components in molecular dynamics simulation. The immiscibility property of PE and PLLA polymers induces the phase separation and exhibits different architectures at different volume fractions. In order to observe the structural property, the radius of gyration is used to observe the detailed arrangement of the polymer chains. It shows that the structure arrangement of a polymer chain is dependent on the phase structure and has a significantly different structural arrangement character for the very short chains in the homopolymer and copolymers. The chain length effect on the degree of stretching or extension of polymers has also been observed. As the chain length increases, the chain exhibits more stretching behavior at lamellae, perforated lamellae, and cylindrical configurations, whereas the chain exhibits a similar degree of stretching or extension at the cluster configuration. © 2007 American Institute of Physics. [DOI: 10.1063/1.2751498]

I. INTRODUCTION

The self-assembly of polymer systems as a tool for structuring plastics has attracted considerable interest in recent years. This interest arises primarily because these polymer systems exhibit specific functions and performance, with applications such as ultrafiltration membranes, nanopatterned templates, nanowire arrays, and ordered nanoporous polymers. Diblock copolymers, chemically connected end to end, are polymers consisting of two linear blocks of mutually insoluble polymers, whereas polymer blends are constructed by mixing two or more polymers together. Recently, the self-assembly of synthetic polymers by creating either a blend or a diblock copolymer with insoluble properties has been used to create a large number of nanoscale architectures. They have been extensively studied because of their ability to self-assemble into structures with fascinating behavior; i.e., one-, two-, and three-dimensional periodic nanostructures in the bulk state. Compared to the polymer blend, diblock copolymers with two or more polymers exhibit different architectures or a more complex phase behavior because of the constrained degree of freedom.

Polylactide, an aliphatic polyester, was previously used primarily in biomedical applications such as drug delivery systems, medical sutures, and orthopedic materials. It is a biocompatible, biodegradable material, which was produced from lactic acid. Polylactide, containing chiral carbon in each monomer, is produced through the ring-opening polymerization of lactide. This polymer can be produced in different stereochemical structures by polymerizing a mixture of the L and D isomers of lactide, with resultant polymers being poly(D-lactide), poly(DL-lactide), or poly(L-lactide) (PLLA). PLLA, a semicrystalline polymer, is a brittle material with good mechanical properties such as high tensile strength and modulus and a higher end-use temperature. Currently, because of the biocompatibility and biodegradability of PLLA, the modification of PLLA by preparing copolymers and blends has sparked broad investigation. Another widely used polymer material is polyethylene (PE). PE not only has good impact properties but also is saturated and shows high durability. The structural behavior of PE/PLLA blends has attracted broad interest in the industrial and research communities because they display interesting structural behaviors and have useful mechanical properties. Consequently, PE/PLLA diblock copolymer should have a more complex structural behavior and display different structures than PE/PLLA blends.
Computer simulations have been used to study polymer blend\textsuperscript{23-24} and diblock copolymer properties.\textsuperscript{25-27} On a different scale, there are series of well developed simulation techniques such as the molecular dynamics (MD) and Monte Carlo methods on an atomistic level, as well as dissipative particle dynamics (DPD), lattice Boltzmann methods (LBM), and dynamic mean field (MF) theory on a mesoscopic scale. Using atomistic simulation tools, we can analyze the molecular structure and dynamic behavior of molecules. Because they are limited in the time and length scales in simulation and cannot effectively prevent a configuration becoming trapped at a local minimum energy, it is difficult to observe the phase transformation process of a polymer blend and diblock copolymer system. Therefore, atom-based simulations cannot predict more realistic structures on a mesoscopic scale. For structural predictions on this scale, mesoscopic simulations such as DPD, LBM, and MF are effective methods to reflect the mixture process between two or more polymers. Because the simulation methods mentioned above are all focused on a specific scale, it is necessary to use a bridge to gap between atomistic and mesoscopic simulations to compensate for the insufficiency of the time and length scales and gather sufficient data.

Recently, the DPD method has found broad use in many areas, such as the investigation of the immiscibility property of polymer blends,\textsuperscript{28} the formation of micelle in the solvent,\textsuperscript{29} shear force that induces the structural transform of the lamellar phase,\textsuperscript{30} and the viscosity property of polymer.\textsuperscript{31} For bridging the gap between atomistic and mesoscopic simulations, Groot and Warren established a link between DPD and the Flory-Huggins theory for a polymer system, where the Flory-Huggins (FH) parameter ($\chi$) of polymer can be calculated by a microscopic simulation method. The FH parameter ($\chi$) of PHB/PE, PHB/PEO, PEO/PE, and PHB/PEO/PE (Ref. 23) has been calculated by the Monte Carlo simulation, and PS/PE, PE/PS, PP/PS, and HDPE/LLDPE (Ref. 34) by MD simulation. Based on the FH parameter, the DPD method has been used to investigate the morphology of polymer blends,\textsuperscript{25} diblock copolymers,\textsuperscript{25} and surfactants.\textsuperscript{26,35} In this article, because of the importance of PE and PLLA in the industry and in the research community, the hierarchical procedure for bridging DPD and MD methods is used to study the volume fraction $\nu$ effect and chain length effect on the phase and the structural arrangement of PE/PMMA blend and PE-$b$-PLLA diblock copolymer systems. We also compare the difference between the PE/PMMA blend and PE-$b$-PLLA diblock copolymer on the phase structure. The calculation of the gyration radius is used to observe the detailed arrangement of the polymer chain in the mixture polymer system and can then explain the difference between the phase behavior in a PE/PMMA blend and PE-$b$-PLLA diblock copolymer. To understand the conformational property, the ratio of the mean-square radius of gyration ($R_g^2$) to the mean-square end-to-end distance ($R_e^2$) is used as an index to measure the chain conformation. The calculation of this index can indicate whether or not the polymer chain is extend or collapsed in the mixture polymer system.

II. SIMULATION DETAIL

DPD simulations were carried out in order to investigate the phase behavior of PE/PMMA blend and PE-$b$-PLLA diblock copolymer. To explain the interaction behavior in DPD, it is first necessary to obtain the interaction parameter from the MD method. In this section, we first introduce the details of both DPD and MD methods. Finally, we introduce the coarse grain mapping method, which serves as a bridge between the MD and DPD methods.

A. Dissipative particle dynamics simulation method

In the present research, we adopt the DPD simulation method to investigate the chain length effect of a PE/PMMA blend and PE-$b$-PLLA diblock copolymer on the conformational variation; moreover, we also compare the variation between the PE/PMMA blend and PE-$b$-PLLA diblock copolymer. The time evolution is governed by Newton’s equation of motion.

$$\frac{d\mathbf{r}}{dt} = \mathbf{v}_i, \quad (1)$$

$$\frac{d\mathbf{v}}{dt} = \mathbf{f}_i. \quad (2)$$

However, in a DPD simulation, all of the beads in the system are of the same volume regardless of the number of and kinds of different molecules comprising the bead. This assumption is required, because the system must conform to the Flory-Huggins $\chi$-parameter theory.\textsuperscript{36} For simplicity, the masses of all particles in the system are normalized to Eq. (1). The interaction force on bead $i$ is given by the sum of a conservative force $F_{ij}^c$, a dissipative force $F_{ij}^d$, a random force $F_{ij}^R$, and an spring force $F_{ij}^S$. \textsuperscript{37}

$$f_i = \sum_{j \neq i} (F_{ij}^c + F_{ij}^d + F_{ij}^R + F_{ij}^S), \quad (3)$$

where conservative force represents a purely repulsive force, dissipative force represents the friction between DPD beads that reduces velocity differences between the particles, random force works to conserve the system temperature, and the spring force is used to binding the intrapolymer beads. The second and third forces are responsible for the conservation of total momentum in the system. All of the forces act within a sphere of cutoff radius $r_c$, which also defines the system’s length scale. The conservative force with a linear approximation is given by

$$F_{ij}^c = \begin{cases} a_{ij}(1 - r_{ij}/r_c) & (r_{ij} < r_c) \\ 0 & (r_{ij} > r_c), \end{cases} \quad (4)$$

where $r_{ij}$ is the distance between bead $i$ and bead $j$; $a_{ij}$ is the repulsive parameter. For the same kind of the bead in DPD, this repulsive parameter can be determined from the calculation of the dimensionless compressibility.

B. Molecular dynamics simulation

To estimate the DPD interaction parameter, molecular dynamics is employed to estimate dimensionless compress-
of 1150 A3 in the MD simulation, where the PLLA consisted of each chain of PLLA and PE was roughly the same volume as per Sec. II A, the volume parameters in the ENCAD potential are derived from quantum mechanics, spectroscopy, and crystallography. Figure I shows the chemical structure of PLLA and PE. Because DPD assumes that all beads are of the same equilibrium volume in the Flory-Huggins theory as per Sec. II A, the volume of each chain of PLLA and PE was roughly the same volume of 1150 Å3 in the MD simulation, where the PLLA consisted of 6 monomers per chain and PE consisted of 30 monomers per chain.

The procedure used in this study to obtain the equilibrium structure of the PLLA, PE, and PLLA/PE blend simulation models is very similar to that adopted in the study of Jang et al. The PLLA molecules, PE molecules, and PLLA/PE molecules were first arranged in a periodic boundary box with densities of 0.63, 0.48, and 0.5 g/cm³, respectively. The system was relaxed for 30 ps at 600 K temperature, and the system was compressed to the desired density by an expanding rate of 0.1 Å³/fs while the temperature was annealed from 600 to 300 K at a cooling ratio of 50 K/1 ps, where the desired densities of PLLA, PE, and PLLA/PE blends with different volume fractions are shown in Table I. Then, 30 ps of NVT MD simulation was performed to relax the polymer system at 300 K. After the initial equilibrium process, the following steps were used to produce a realistic model. (1) First, the simulation model was gradually expanded to a desired density of 50% by a rate of 0.1 Å³/fs, and then the temperature was increased from 300 to 600 K at a ratio of 20 K/1 ps. (2) NVT MD simulation was performed at this expanded density at 400 K for 20 ps. (3) The system was then compressed to the desired density by an extending rate of 0.1 Å³/fs while the temperature was annealed from 600 to 300 K at a cooling ratio of 50 K/1 ps. (4) NVT MD simulation was performed at the desired density at 300 K for 30 ps. (5) This expansion-compression cycle was then repeated five times. (6) Finally, the NVT MD simulation of 100 ps was performed to equilibrate the simulation system, and then calculate the cohesive energy per unit volume. From the calculations of the cohesive energy per unit volume of the pure PLLA and PE polymer system and the PLLA/PE blend with different volume fractions, the Flory-Huggins parameter \( \chi \) and the repulsive parameter in DPD can then be obtained by the summation of the cohesive energy per unit volume as in Eq. (9).

To determine the dimensionless compressibility of PLLA, the same annealing procedures as described above are performed to obtain an initial equilibrium structure. Then the NPT MD of 100 ps at different target pressures was performed to equilibrate the density and structure of PLLA polymer system. After the NPT MD simulations at different target pressures, the dimensionless compressibility of the PLLA system can be determined from the slope of the pressure and number density in the PE system. Finally, it should be noted that the results of the cohesive energy and the dimensionless compressibility were essentially the same even with annealing cycles greater than the five times used in our current study.

### C. Coarse grain mapping and the solubility parameter

In this simulation, MD is used to calculate the dimensionless compressibility from a pure polymer system, which we then match to the DPD system’s dimensionless compressibility as follows:

\[
\kappa^{-1}\left|_{\text{DPD}}\right. = \frac{1}{k_BT_{\text{DPD}}} \left[ \frac{\partial p_{\text{DPD}}}{\partial \rho_{\text{DPD}}} \right]_T
\]

\[
= \frac{1}{k_BT_{\text{MD}}} \left[ \frac{\partial p_{\text{MD}}}{\partial \rho_{\text{MD}}} \right]_T
\]

\[
= N_m \kappa^{-1}\left|_{\text{MD}}\right., \quad (5)
\]

where \( \rho \) is the number density, \( N_m \) is the coarse graining parameter, \( k_B \) is the Boltzmann constant, and \( T \) is the system temperature. This procedure was repeated five times.

### TABLE I. Desired density of PLLA, PE, and PLLA/PE blend with different volume fractions in MD simulation.

<table>
<thead>
<tr>
<th>( V_{\text{PE}}/V_{\text{PLLA}} )</th>
<th>0:10</th>
<th>1.9</th>
<th>3.7</th>
<th>5:5</th>
<th>10:0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.269</td>
<td>1.239</td>
<td>1.180</td>
<td>1.121</td>
<td>0.972</td>
</tr>
</tbody>
</table>

### TABLE II. Values for the solubility and density of PE and PLLA.

<table>
<thead>
<tr>
<th></th>
<th>Density</th>
<th>Solubility parameter ( a ) (cal/cm³)(^{1/2} )</th>
<th>Solubility parameter ( b ) (cal/cm³)(^{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly((-)lactide)</td>
<td>1.2695</td>
<td>1.25–1.27</td>
<td>9.65</td>
</tr>
<tr>
<td>Polyethlene</td>
<td>0.9721</td>
<td>0.95–0.97</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Values for the solubility parameter of PE and PLLA obtained.

\( a \)Reference values obtained from experiment (Refs. 43 and 44).
temperature. In this study, the \( N_m \) is set 1 in Sec. II B. Then the repulsive parameter \( a_{ij} \) of the same kind of polymers can be determined from the relationship between the dimensionless compressibility, which is found in a reference from Groot and Warren \(^{35} \)

\[
a_{ij} = \frac{(\kappa^{-1} - 1) k_BT}{2 \alpha \rho}. \tag{6}
\]

Groot and Warren’s study shows that the Flory-Huggins parameter \( \chi \) can be mapped to the repulsive interaction parameter \( a_{ij} \) in different kinds of beads. For the case in which the reduced density \( \rho \) is 3, this relationship is as follows:

\[
\chi \approx \alpha (a_{ij} - a_{ii}), \tag{7}
\]

where the constant \( \alpha \) is function of \( \Delta a \) \((a_{ij} - a_{ii})\), which has a linear variation from the range \( 15 \leq \Delta a \leq 115 \). The value is 0.3 at \( \Delta a = 15 \) and the value is 0.2 at \( \Delta a = 115 \) for \( \rho = 3 \). \(^{36} \)

Several different computational methods, such as molecular mechanics, molecular dynamics, and Monte Carlo scheme, are available to estimate the \( \chi \) parameter in solvent-solvent, polymer-solvent, or polymer-polymer systems. \(^{41,42} \) In the present work, we estimated the \( \chi \) parameter of both the PLLA and the PE blend from the mixing energy calculation using an atomistic molecular dynamics simulation. From the calculation of cohesive energies of a pure PLLA system, PE system, and their mixture, the mixing energy and \( \chi \) parameter can be estimated. The \( \chi \) parameter is defined as

\[
\chi = V_{seg} \left( \frac{\Delta E_{mix}}{RT} \right), \tag{8}
\]

where \( V_{seg} \) is the volume of the polymer segment corresponding to the particle size in the DPD. In the DPD simulation, each bead in the system has the same the volume as described above. In our DPD simulation, the volume of each bead is roughly set at 1150 A\(^3\), i.e., the volume of PLLA with 6 monomers is about 1134 A\(^3\) and the volume of PE with 24 monomers is about 1200 A\(^3\). \( R \) is the gas constant; the value of \( \Delta E_{mix} \)—the cohesive energy density—is the total energy of mixing per unit volume, and is defined by the cohesive energy per unit volume for pure components and their blends as in following equation:

\[
\Delta E_{mix} = \phi_A \left( \frac{E_{coh}}{V} \right)_A + \phi_B \left( \frac{E_{coh}}{V} \right)_B - \left( \frac{E_{coh}}{V} \right)_{AB}. \tag{9}
\]

Here, \( \phi_A \) and \( \phi_B \) are the volume fractions of the two components in the blended system. \( V \) is the volume of the simulation model and \( E_{coh} \) is the cohesive energy. From the calculation above, a realistic interaction parameter \( a_{ij} \) between the PE and PLLA pair in DPD can be obtained from a realistic \( \chi \) parameter by using an atomistic simulation.

### III. RESULTS AND DISCUSSION

First the solubility parameters obtained from MD simulations are compared to those from experimental approaches in order to examine if the ENCAD force field can accurately reflect the material properties for PE and PLLA in our simulation model. The solubility parameter values demonstrating the attractive strength between the molecules of the material can be determined through the square root of the cohesive energy density as in the following equation:

**TABLE III.** Cohesive energy density, \( \chi \) parameters, and \( a_{ij} \) for binary polymer blends of PE/PLLA at different volume fractions.

<table>
<thead>
<tr>
<th></th>
<th>PE(1)PLLA(9)</th>
<th>PE(3)PLLA(7)</th>
<th>PE(5)PLLA(5)</th>
<th>PE(7)PLLA(3)</th>
<th>PE(9)PLLA(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E ) (kcal/(mol A(^3)))</td>
<td>57.4</td>
<td>58.9</td>
<td>59.48</td>
<td>59.6</td>
<td>55.6</td>
</tr>
<tr>
<td>( a_{ij} )</td>
<td>34.43</td>
<td>53.18</td>
<td>64.68</td>
<td>88.74</td>
<td>47.91</td>
</tr>
<tr>
<td>( \chi )</td>
<td>6.46</td>
<td>11.2</td>
<td>13.75</td>
<td>18.06</td>
<td>9.9</td>
</tr>
</tbody>
</table>

**TABLE IV.** Morphologies for PE/PLLA systems at different volume fractions, bead numbers, and mixing types (PE/PLLA diblock copolymer and PE/PLLA polymer blends), C and B standing for the PE-\( b \)-PLLA diblock copolymer, and the PE/PLLA polymer blends, respectively.

<table>
<thead>
<tr>
<th>Bead number</th>
<th>PE(1)PLLA(9)</th>
<th>PE(3)PLLA(7)</th>
<th>PE(5)PLLA(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>10</td>
<td>Disorder</td>
<td>Cluster</td>
<td>Gyroid</td>
</tr>
<tr>
<td>20</td>
<td>Cluster</td>
<td>Cluster</td>
<td>Perforated lamellae</td>
</tr>
<tr>
<td>50</td>
<td>Cluster</td>
<td>Cluster</td>
<td>Perforated lamellae</td>
</tr>
<tr>
<td>60</td>
<td>Cluster</td>
<td>Cluster</td>
<td>Perforated lamellae</td>
</tr>
<tr>
<td>100</td>
<td>Cluster</td>
<td>Cluster</td>
<td>Perforated lamellae</td>
</tr>
</tbody>
</table>
\[
\delta = \sqrt{\frac{E_{\text{coh}}}{V}},
\]

where \( V \) is the volume of the simulation model and \( E_{\text{coh}} \) is the cohesive energy. Table II shows the \( \delta \) values of PE and PLLA from both the experimental approach and from our simulation, which shows that the values from our MD simulations are very close to the results obtained by experiment.\(^{33,44} \)

In order to obtain the interaction parameter in DPD, dimensionless compressibility was first obtained from the atomic MD procedure. By MD estimation, the relationship between the number density and pressure of PLLA is obtained, as shown in Fig. 2. As the pressure increases, the number density will increase linearly. The dimensionless compressibility was first obtained experimentally.\(^{43,44} \) In order to obtain the interaction parameter \( \chi \) parameters, and \( a_{ij} \) for binary polymer blends of PE/PLLA at different volume fractions. These values show a slight increase as the volume fraction of PE increases.

Table IV lists the equilibrium structures for PE/PLLA systems at different volume fractions, bead numbers, and mixing types for the PE-b-PLLA diblock copolymer and the PE/PLLA polymer blend. Two capital letters, C and B, stand for the PE-b-PLLA diblock copolymer (C) and the PE/PLLA polymer blend (B) in the concerned system, respectively. Five volume fractions \( (V_{\text{PE}}/V_{\text{PLLA}}=1/9, 3/7, 5/5) \) for PE to PLLA are used for the PE-b-PLLA copolymer and PE/PLLA polymer blend systems. Five different bead numbers, 10, 20, 50, 60, and 100, are considered in this study. For the PE-b-PLLA copolymer (C), these bead numbers represent the total bead number of one PE-b-PLLA copolymer chain, while the bead number of a copolymer chain will be divided into its PE and PLLA fragments for the corresponding blend (B) systems. Taking as an example a bead number of 10 for the PE-b-PLLA copolymer of 1/9 volume fraction, there is one PE bead and nine PLLA beads in one copolymer chain. For the blend system, a PE chain of one bead and a PLLA chain of nine beads are the two components in the simulation model. Six characteristic structures are found for different volume fractions, chain lengths, and polymer mixing types (diblock copolymer or polymer blend systems). These phases include disorder, cluster, gyroid, perforated lamella, cylinder, and lamellae structures, and are illustrated in Figs. 3(a)–3(f), respectively. Figure 3(a) depicts the disorder structure, in which the polymer beads of lower volume fraction distribute randomly in the matrix of polymer beads of higher volume fraction. Disorder structures are only found in the copolymer systems of lowest and highest volume fractions of PE for the shortest copolymer chain. However, for the corresponding blend systems, the polymer beads of lower fractions will form the cluster structure in the polymer bead matrix of higher fractions, as shown in Fig. 3(b). For the shortest copolymer chains of volume fraction of 1/9, one PE bead is connected to PLLA of nine beads. This will constrain the relative distributions of the connected PE and PLLA beads, with the beads of the 1 (of the 1/9 chain) only able to form disordered clustering as in Fig. 3(a), while the 9 (of the 1/9 chain) surround the single (blue) bead cluster of the PE-b-PLLA copolymer. This will form a geometric barrier which prevents beads of other short parts of different copolymer chains from the aggregation and from forming the cluster structure. For longer copolymer chains, as the volumes of the beads of the shorter part increase, the excluded volumes of the beads of the longer part [shown as red beads in Fig. 3(b)] string outward, and are not close enough to form a geometric barrier. Consequently, the beads of the shorter part in different copolymer chains can aggregate together to form a cluster structure for 20, 50, 60, and 100 bead numbers at the volume fractions of 1/9 of PE and PLLA. For the blend system at volume fractions of 1/9, there is no constraint between PE and PLLA beads, and the beads of the lower fractions will form cluster structure for all bead numbers. For the volume fractions of 3/7 of PE and PLLA with the bead numbers more than 10, the blend system will display a cylindrical arrangement as shown in Fig. 3(c), and for the copolymer system, the cluster structure will become a perforated lamella structure shown in Fig. 3(d). For the blend system, the zero-dimensional cluster structure will extend to a one-dimensional cylindrical structure because the polymer beads of lower fractions increase, and no relative distribution for different bead types exists in the blend system. However, for the copolymer system, different bead types are connected by a spring bond, constraining the relative distribution of different bead types. The beads of the longer part of the chain will stay near the beads of shorter part, which will prevent the extension of the cluster structure at 1/9 volume fractions from forming cylindrical structures as in the blend system. These zero-dimensional clusters will arrange to form a two-dimensional perforated lamellae structure. Especially for a bead number of 10, the polymer blend and the diblock copolymer systems display the perforated lamellae phase structure and the gyroid phase structure, respectively, as shown in Fig. 3(e). These structural arrangements of the polymer chain will be explained in more detail in the following paragraphs. For volume fraction of 5/5, the effect of the bead number and the mixing type on the structure is not significant. The arrangement of different polymer beads will be two-dimensional lamellae structures. The case of the polymer blend system at a volume fraction of 5/5 is illustrated in Fig. 3(f).

To study the chain length effect of diblock copolymer and a polymer blend on the orientation and its structure, the mean-square end-to-end distance \( \langle R^2 \rangle \) and the mean-square radius of gyration \( \langle R_g^2 \rangle \) are used to analyze the three spatial properties of the polymer chain. \( \langle R^2 \rangle \) is used to differentiate between an open chain or a compact conformation chain. \( \langle R_g^2 \rangle \) provides information on the mass distribution of the chain in the system, which also plays a central role in interpreting light scattering and viscosity measurements. If all beads have the same mass,

\[
\langle R_g^2 \rangle = \frac{1}{n} \sum_{i=1}^{n} (r_i - r_c)^2,
\]

where \( r_i \) denotes the coordinate of the particle, \( r_c \) denotes
the coordinate of center of mass of the polymer chain, and \( n \) is the bead number in a chain. Additionally, it can be represented as the tensor in different directions as follows:

\[
\langle G_{xy} \rangle = \frac{1}{n} \sum_{i=1}^{n} (r_{ix} - r_{cx})(r_{iy} - r_{cy}),
\]

where \( r_{ix} \) and \( r_{iy} \) denote the position vector of the particle \( i \), whereas \( r_{cx} \) and \( r_{cy} \) denote the position vector of the center of mass of polymer chain. The three eigenvalues of \( G \) are denoted by \( R_g^2 \) (major axial, which is the largest eigenvalue), \( R_g^2 \), and \( R_g^2 \). The summation of \( R_g^2 \), \( R_g^2 \), and \( R_g^2 \) is \( \langle R_g^2 \rangle \), which can be used to roughly determine the structural arrangement of a chain in the system. Their ratios are of interest because if the ratio of another eigenvalue to \( R_g^2 \) is not equal to one, it indicates that the distribution is nonspherical.

Figure 4 depicts the ratios \( R_g^2 / R_g^2 \) and \( R_g^2 / R_g^2 \) of PE.
as a function of bead number (chain length) at the volume fractions of 1/9 of PE and PLLA. It shows that the ratios are very close to one for the blend system even when the bead number is very low, which means that the structure of the PE chain for a polymer blend system displays a spherelike structure in the cluster phase structure of PE, as shown in Fig. 3b. However, for a diblock copolymer system, a value smaller than 1 appears in the case of a bead number of 20, because the connection between the PE and PLLA polymers constrains their degree of freedom of motion. Therefore, the structure expresses a slight ellipsoid structure.

Figure 5 depicts the ratios $R_g^2/R_g^1$ and $R_g^2/R_g^1$ of PE as a function of bead number (chain length) at the volume fractions of 3/7 of PE and PLLA. For the case of the blend system, the ratio shows that the curves of $R_g^2/R_g^1$ and $R_g^2/R_g^1$ of PE are very close to each other when the bead number is greater than 10. As the bead number increases, the curve shows a decrease in the ratios of $R_g^2/R_g^1$ and $R_g^2/R_g^1$ for PE, which indicates that the structure of the PE chains is roughly in an ellipsoid-shaped structure, with two minor and one major ellipsoid axial, as indicated by the white ellipse drawn line in Fig. 6a, and which is gradually elongated in the major ellipsoid axial direction. As is mentioned above, PE at a volume fraction of 3/7 of PE displays a
of PE and PLLA for the polymer blend (the perforated lamella structure) and diblock copolymer systems at the volume fractions of 5/5 of PE and PLLA (the lamella structure). It indicates that the structure of PE also has a dislikle (oblate spheroid) structure in the polymer blend and diblock copolymer systems; moreover, the dislikle (oblate spheroid) structure of the chain gradually becomes more compressed at its minor ellipsoid axial as the bead numbers increase. The major ellipsoid axial direction of dislikle (oblate spheroid) structure is parallel to the lamellar phase structure for copolymer system and the blend system for PE/PLLA blend system, as indicated by the white circles drawn line in Fig. 8(a). This indicates that the major ellipsoid axial direction of dislikle (oblate spheroid) structure which is parallel to the lamellar phase structure has a greater degree of freedom to relax into a stable structure. However, for the bead number of 10 in the diblock copolymer system, the values of $R_g^2/R_g^3$ and $R_g^2/R_g^1$ are very close to each other, which indicates that the structure of PE has an ellipsoid structure, as shown in Fig. 8(b) by white ellipses. The major ellipsoid axial direction is perpendicular to the lamellar phase structure because the constraint of PE and PLLA copolymer limits its degree of freedom of motion.

To understand the conformational property, the ratio of the $\langle R_g^2 \rangle$ to $\langle R_e^2 \rangle$ is one index to measure the chain conformation which is extended or collapsed in the mixed polymer system. A relatively higher value for the ratio indicates a more extended structure, whereas a relative lower value for the ratio indicates a more collapsed structure. Figures 9(a)–9(c) depict the ratio of the $\langle R_g^2 \rangle$ to $\langle R_e^2 \rangle$ as a function of bead numbers for polymer blend and diblock copolymer systems at the volume fractions of 1/9, 3/7, and 5/5 of PE and PLLA, respectively. The ratios for all the blend systems have a higher value than that of the diblock copolymer system, because the higher degree of freedom of polymer blend possesses more flexible properties than that of the copolymer. Consequently, the copolymer exhibits a more compact property. Figure 9(a) shows that the ratio approaches a constant as the bead number becomes greater than 50, and the ratio in the bead number of 20 is slightly higher than that in the bead greater than 50. According to the results mentioned above, we know that as the bead number becomes greater than 50, the structure of the polymer chain forms a clustertype structure; when the bead number is 20, the structure of the polymer chain forms a slight ellipselike structure. Consequently, the ellipselike structure for a bead number of 20 has a relatively more extended structure compared to the clustertype structure for a bead number greater than 20. In Figs. 9(b) and 9(c), the rise in the curve indicates a more extended polymer chain behavior for the blend system and block copolymer system for the cases whose bead number is greater than 10. This phenomenon agrees with our description above that the ratios of mirror to major axial of dislikle (oblate spheroid) (for the diblock copolymer system at $V_{PE}/V_{PLLA}=3/7$ in Fig. 5 and for the diblock copolymer and polymer blend system at $V_{PE}/V_{PLLA}=5/5$ in Fig. 7) and ellipsoid (for the polymer blend system at $V_{PE}/V_{PLLA}=3/7$ in Fig. 5) like structure become lower as the bead number increases. This represents the fact that the polymer chain be-

cylindrical structure, as shown in Fig. 3(c). In Fig. 6(a), we can observe that the major axial direction of the ellipsoid structure of PE (gray bead) is parallel to the axial direction of the cylinder of PE and displays an ellipsoid structure. However, in the case of a bead number of 10, a high (close to one) value in $R_g^2/R_g^1$ and a low value of $R_g^3/R_g^1$ indicate that the structure has a dislikle (oblate spheroid) structure for PE. Therefore, the dislikle (oblate spheroid) structure of the chain leads the phase structure to become a perforated lamella structure.

The case of diblock copolymer shows a significant difference between the curves in $R_g^2/R_g^1$ and $R_g^2/R_g^1$, as shown in Fig. 5, which indicates that the structure of PE is a dislikle (oblate spheroid) structure, with two major and one minor ellipsoid axial, as indicated by the white circle drawn line in Fig. 6(b). As the bead numbers increase, the value of $R_g^3/R_g^1$ gradually decreases, whereas there is only a slight decrease, still very close to a ratio of 1 for $R_g^2/R_g^1$ for PE. This indicates that the dislikle (oblate spheroid) structure of the chain gradually becomes more compressed at its minor ellipsoid axial. The dislikle (oblate spheroid) structure of the chain leads the phase structure to become a perforated lamella structure, a phenomenon very similar to that for the blend system with a bead number of 10. However, the phase structure of PE prefers to form the gyroid structure for the case of a bead number of 10. Comparing that to bead numbers greater than 10 for PE, the values of $R_g^2/R_g^1$ and $R_g^2/R_g^1$ are very close, which indicates that the structure of the PE chain has a slight ellipsoid structure. Therefore, it may be that the constraint of PE and PLLA copolymers and the formative structure of polymer chain lead the phase to form a gyroid structure.

Figure 7 depicts the ratios $R_g^3/R_g^1$ and $R_g^2/R_g^1$ of PE as functions of bead number at the volume fractions of 5/5 of PE and PLLA. It shows a very similar behavior to the case of diblock copolymer system at the volume fractions of 3/7.
comes more extended as the bead number increases. In contrast, the case of a bead number of 10 for blend and copolymer systems displays a falling slope, making evident the fact that this very short chain length affects the flexible property of the chain. The short chain becomes stiffer than the long chain. Consequently, the short chain exhibits a more extended structure. Comparing Figs. 9(b) and 9(c), it can be observed that the rising curve at the volume fractions of 5/5 of PE and PLLA shows a steeper rise than that at the volume fractions of 3/7 of PE and PLLA when the bead number is equal to or greater than 20. This reflects the fact that the PE polymers in the perforated lamella phase are more compact than that in the lamella phase.

IV. CONCLUSION

The DPD simulation method was carried out to investigate the phase behavior and the chain length effect of PE/PMMA blend and PE/PMMA diblock copolymer on different volume fraction ratios. The χ parameter, which bridges the gap between atomistic and mesoscopic simulations, was obtained by molecular dynamics simulation, and was found to be in good agreement with experimental results. The values of the solubility parameters of PE and PLLA are very close to the result obtained by experiment and other simulation studies. For the cases of bead numbers greater than 10, we find that the polymer blend and diblock copolymer of the
same two polymers PE and PLLA have the same phase behavior at a volume fraction of 1/9 and 5/5 of PE/PLLA, which form the cluster phase at a volume fraction of 1/9 of PE/PLLA and lamella phase at a volume fraction of 5/5 of PE/PLLA, respectively. However, our results show a significant difference in the phase structure at a volume fraction of 3/7, where we obtain a perforated lamellae phase in the co-polymer system and a cylindrical phase in blend system.

Polymer chains form a clusterlike structure, ellipsoid structures, and disklike structures in the cluster phase, in the cylinder phase, and in the perforated lamellae phase and lamellae phase, respectively. As the bead number increases, the disklike (oblrate spheroid) and ellipsoidlike structures become a thicker and a thinner structure, respectively, whereas the clusterlike structure maintains the similar structure. However, when the bead number is equal to 10, because of the number of beads in the chain is the fewest in our study, and which makes the chain possess a more stiff behavior, the structure of the short chain may exhibit a different structural arrangement than that of the long chain.

Finally, we found that the ratio of $\langle R_g^2 \rangle$ to $\langle R_e^2 \rangle$ strongly depends on the bead numbers and its structure arrangement in a chain. Because a polymer blend with a higher degree of freedom possesses a more flexible property than that of a copolymer, the copolymer exhibits a more compact property.

FIG. 9. Ratio of $\langle R_g^2 \rangle$ to $\langle R_e^2 \rangle$ to bead numbers for polymer blend and diblock copolymer systems at the volume fractions of (a) 1/9, (b) 3/7, and (c) 5/5 of PE and PLLA, respectively.
Moreover, different volume fractions of PE/PLLA exhibit different phases, such as the cluster, cylinder, and the perforated lamella and lamella structures, with zero-, one-, and two-dimensional phase structures, respectively. This is also one of the factors affecting the structural arrangement of the polymer chain. The higher dimension phase has the more extended structure, whereas the lower dimension phase has the more collapsed structure in the polymer chain.

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