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Molecular dynamics simulation studies of binary blend miscibility of poly(3-hydroxybutyrate) and poly(ethylene oxide)

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Abstract

By means of full atomistic molecular dynamics simulation, the solubility parameters for pure poly(3-hydroxybutyrate) and poly(ethylene oxide) are calculated and the results are in agreement with the literature values. Furthermore, in order to reveal the blend property, the volume–temperature curve of the PHB/PEO blend system (1:2 blends in terms of repeated units) is simulated by employing the united atom approximation to obtain the glass transition temperature. From the volume–temperature curve, the glass transition temperature is about 258 K, which is compared well with the experimental results. It should be pointed out that the two simulated solubility parameters are similar and there is only one glass transition of the blend system, these indicate that the studied blend system is miscible.

Keywords: Molecular dynamics simulation; Poly(3-hydroxybutyrate); Poly(ethylene oxide)

1. Introduction

Recently, much attention has been paid to the environment-friendly materials, such as bacterial polyesters. They fit perfectly well in the ecosystem due to their natural origin and biodegradability [1–4]. Poly(3-hydroxybutyrate) (PHB) is a well known member of the bacterial polyester family and has been commercially available under the trade name Biopol since the early 1980s [5]. However, the commercial exploitation of PHB has been hampered by its high cost, brittleness and narrow processability window [6, 7]. Polymer blending could overcome these drawbacks, and there have been many experiments on miscible blends containing PHB. For example, PHB is miscible with poly(ethylene oxide) (PEO) [8–12], polyepichlorohydrin (PECH) [13,14] and poly(vinyl acetate), etc. [15–18].

In the past decade, molecular modeling has been used to study the polymer blend property [19–28]. They all have pursued with two main objectives: prediction of miscibility and/or miscible blend properties. The main aim of this study is focused on the property of binary blends of PHB with PEO. The compatibility of these blends is estimated by two steps. First, full atomistic molecular dynamics (MD) simulations for pure PHB and PEO are carried out at room temperature. The cohesive energy density of the pure components is calculated, and further the solubility parameter is obtained. Then, by using united atom approximation, the MD simulation of the PHB/PEO blend system (1:2 blends in terms of repeated units) is performed to get the volume–temperature ($V-T$) curve, and from the $V-T$ curve, the glass transition temperature (T_g) of the system is obtained. The energy components against temperature plots are used for analyzing which of them is important during the glass transition process.

2. Simulation details

All the MD simulations are performed by using *Cerius*^{2} software packet of Accelrys Inc., installed on SGI Origin 3800 server. The Dreiding2.21 force field [29] is used throughout. The total potential energy (E_{total}) which is described as the summation of bonding energy (E_{bond}) and

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non-bonding energy ($E_{\text{non-bond}}$) can be expressed as:

$$E_{\text{total}} = E_{\text{bond}} + E_{\text{non-bond}}$$
$$= E_b + E_\theta + E_\phi + E_{\text{vdW}} + E_{\text{Coulomb}} \tag{1}$$

where E_b is the bond stretching energy, E_θ the valence angle bending energy, E_ϕ the dihedral torsion energy, E_{vdW} the van der Waals interaction energy, E_{Coulomb} the Coulombic interaction energy. In our simulation: E_{bond} and $E_{\text{non-bond}}$ are calculated, respectively, in order to analyze the contribution of them to the glass transition.

2.1. Calculation of the solubility parameter

In the first step, homopolymers of PHB and PEO models are constructed, respectively. In each model 100 repeated units are involved. Then 10 amorphous structures of the polymer are generated with periodic boundary conditions. The lengths of each side of the cell are 23.0 Å for PHB and 18.7 Å for PEO. From the 10 structures, we choose the configuration having the lowest energy given by molecular mechanics calculations as the initial configuration. To remove unfavorable interactions in the initial configuration, 5000 steps of energy minimization and anneal for 10 cycles from 300 to 1000 K at intervals of 50 K are performed.

The MD simulation for 2000 ps is fulfilled by using the microcanonical (*NVT*) ensemble with a time step of 1 fs at 300 K. The densities of model systems are maintained as experimental values (densities of amorphous PHB [30] and amorphous PEO [31] are 1.176 and 1.112 g/cm^3 at room temperature, respectively) through the whole simulation. A cutoff distance of 9.0 Å and a buffer of 0.5 Å are adopted to reduce the calculation of the non-bond interactions. Hoover method is employed to keep the constant temperature of the system [32]. Charge of the model is calculated using the charge equilibration method [33]. The MD trajectories are created with a step of 1 fs. When the MD simulations are over, unbuild the cell and begin another MD simulation like above processes to obtain the energy of single chain without the cubic constraint.

2.2. Simulation of the volume–temperature curve

Using the method described above, an amorphous mixture model is generated. The model contains one PHB chain of 100 repeated units and one PEO chain of 200 repeated units and its density is 1.170 g/cm^3. The weight ratio of PHB and PEO is about 1:1. To simplify the calculations, the united atom approximation is adopted.

After initial model construction, 5000 steps of energy minimization and an annealing procedure are performed. The structure is equilibrated at 500 K for 1000 ps using an integration step of 1 fs under *NVT* ensemble. A cutoff distance of 9.5 Å and a buffer of 0.5 Å are fixed to limit calculation time for non-bonded interactions. Then, the system is cooled stepwise to 110 K with the rate of 20 K/350 ps. At each temperature, an *NVT* MD simulation of 100 ps and an *NPT* MD simulation of 250 ps with time step 0.5 fs are carried out.

3. Results and discussion

3.1. Solubility parameters

The solubility parameter is an important quantity, closely related to surface tension, interface tension and miscibility for polymers. It was originally used to polymer/solvent system, particularly in the coatings industry and elastomer industry. The extension to polymer/polymer blend systems was popularized by Bohn [34]. The solubility parameter δ [35] is defined as

$$\delta = \sqrt{\frac{E_{\text{coh}}}{V}} = \sqrt{\frac{(E_s - E_b) \times C}{V_c}} \tag{2}$$

where E_{coh}/V is the cohesive energy density; E_s the single chain energy; E_b the energy of the same chain in periodic system; V_c the volume of the cell in cubic angstrom, C the unit conversion factor.

The values of the MD simulated solubility parameters of PHB ($\delta_{\text{simu-PHB}}$) and PEO ($\delta_{\text{simu-PEO}}$) are listed in Table 1 along with the corresponding values by experiment and other calculations (δ_{PHB} and δ_{PEO}) [10,20,31]. In our calculation of δ, Eq. (2) is used in which $C = 6947.9$ is adopted and the values of E_s and E_b are obtained from the last 500 ps results of dynamics trajectory. $\delta_{\text{simu-PHB}}$ is 8.7 cal$^{1/2}$/cm$^{3/2}$ and $\delta_{\text{simu-PEO}}$ is 9.6 cal$^{1/2}$/cm$^{3/2}$. Avella et al. by using Hoy's group contributions of molar attraction constant method gave the value of δ_{PHB} equal to 9.4 cal$^{1/2}$/cm$^{3/2}$ and δ_{PEO} equal to 9.1 cal$^{1/2}$/cm$^{3/2}$ [10]. For the solubility parameter of PEO, there are other two studies using different methods. One is 9.8 cal$^{1/2}$/cm$^{3/2}$ by using molecular mechanics [20], and another is 9.9 ± 1 cal$^{1/2}$/cm$^{3/2}$ from experiment [31]. Compared with these values, our simulated results are in reasonable agreement with the corresponding literature results.

Mason [36] suggested that if two different polymers have similar value of δ, they will tend to mutually soluble. As the difference value of δ between PHB and PEO in our simulations is 0.9 cal$^{1/2}$/cm$^{3/2}$, it means that PHB and PEO

Table 1
Solubility parameters for PHB and PEO

	MD simulation (cal$^{1/2}$/cm$^{3/2}$)	Reference (cal$^{1/2}$/cm$^{3/2}$)
PHB	8.7	9.4[a]
PEO	9.6	9.1[a] 9.9 ± 1[b] 9.8[c]

[a] Calculated using Hoy's group contributions of molar attraction constant from Ref. [10].

[b] Experimental value from Ref. [31].

[c] Calculated using molecular mechanics from Ref. [20].

tend to soluble, and this is in according with the experimental fact that PHB and PEO have miscible property [8–12].

3.2. Volume–temperature results

The calculated specific volumes of blend system PHB/PEO (1:2 blends in terms of repeated units) as a function of temperature are shown in Fig. 1. The specific volume data at every temperature is calculated from the last 50 ps of *NPT* trajectory file. The curve of volume vs temperature for the blend system shows a distinct break characteristic of vitrification. The extraction of the glass transition temperature (T_g) in this manner is common although only empirically justified [26,38–40]. The calculated T_g shown by Fig. 1 to be about 258 K, and it is a little higher than the experiment values, 230–252 K [8–10,12]. It lies between T_g of PEO (value ranges from 158 to 233 K) and T_g of amorphous PHB (269–274 K measured by dilatometry or 268–278 K tested by dynamic mechanical measurement) [37].

The glass transition is mainly caused by the freezing of the motion of chain segments (local chain movement). It is noted that the time scale for the overall relaxation of a typical chain in an entangle melt is approximately 10^{-6} s. In experiment, T_g is obtained by measuring typical property associated with glass transition over a time scale of seconds or minutes. According to theoretical model and considering other groups' work, the simulation is restricted to the nanosecond time range and in this time range our simulation reaches the equilibrium state. Buchholz's group's [43] and Lyulin's group's [44] studies show the cooling rate dependence of the glass transition temperature of polymer using MD simulation. Other works [26,38–40] used the similar model and simulation time scale to ours and obtained good results of T_g by means of MD simulation. Our simulated T_g value is a little higher than that of experimental values. This is reasonable compared with the experimental glass transition temperature T_g. The MD simulation may be a useful method in predicting T_g of polymers.

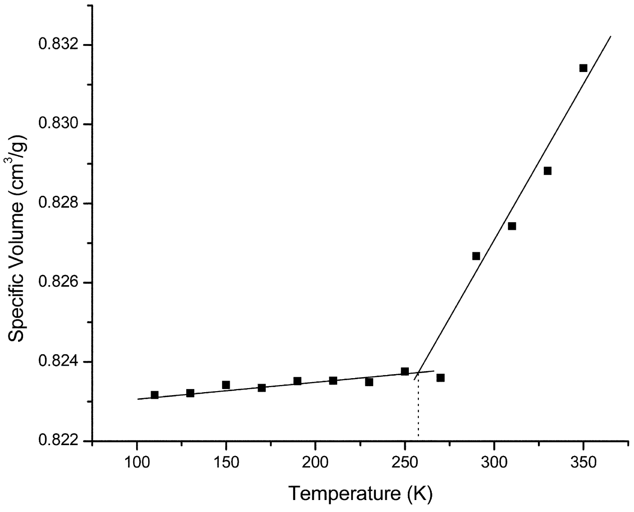

Fig. 1. Specific volume versus temperature using atomistic simulation for blend system PHB/PEO (1:2 blends in terms of repeated units).

3.3. Miscibility of the blend system

The most commonly used method for establishing miscibility in polymer/polymer blends is through determination of glass transition in the blend versus those of the unblended constituents. A miscible polymer blend will exhibit a single glass transition. In case of borderline miscibility, broadening of transition will occur. With cases of limited miscibility, two separate transitions may occur [35]. Our MD simulation shows that PHB/PEO (1:2 blends in terms of repeated units) blend has a single glass transition which is consistent with the experimental results; another immiscible blend system PHB/PE (1:2 blends in terms of repeated units) is studied using the same method and it is found that there are two glass transition during cooling. This indicates theoretically that for an immiscible blend system more than one glass transition may exist. And this result is also in agreement with the experiment fact [45]. Considering the similar solubility parameters of two components and only having one glass transition for our blend system, it can be concluded that the studied blend system PHB/PEO is miscible.

3.4. Roles of the energy components in the glass transition process

Some energy components versus temperature for the blend system are plotted in Fig. 2, which may help us to separate the roles played by the different interacting components in the glass transition process. Roe et al. [41] have shown a characteristic break in a plot of the internal energy per segment versus temperature for a short chain polymethylene analog. In the simulation of the glass transition of PMMA, Soldera [42] also reported small breaks in the plots of total, intramolecular and intermolecular potential energies versus temperature. In our simulation, we also find that there are small breaks in the plots of dihedral torsion energy and non-bond energy versus temperature. Above the glass transition temperature, i.e. $T_g \geqslant 258$ K, the two energy components decrease linearly with temperature decreasing. But below T_g, the two energy components are also decrease linearly with temperature decreasing, the slope is smaller than that above T_g. For other energy components such as bond stretching energy and valence angle bending energy, they decrease linearly with decreasing temperature and there are no noticeable breaks at the glass transition temperature in the plots. This shows that the dihedral torsion energy and non-bond energy play important roles during the glass transition process. It is similar to the pure polymer.

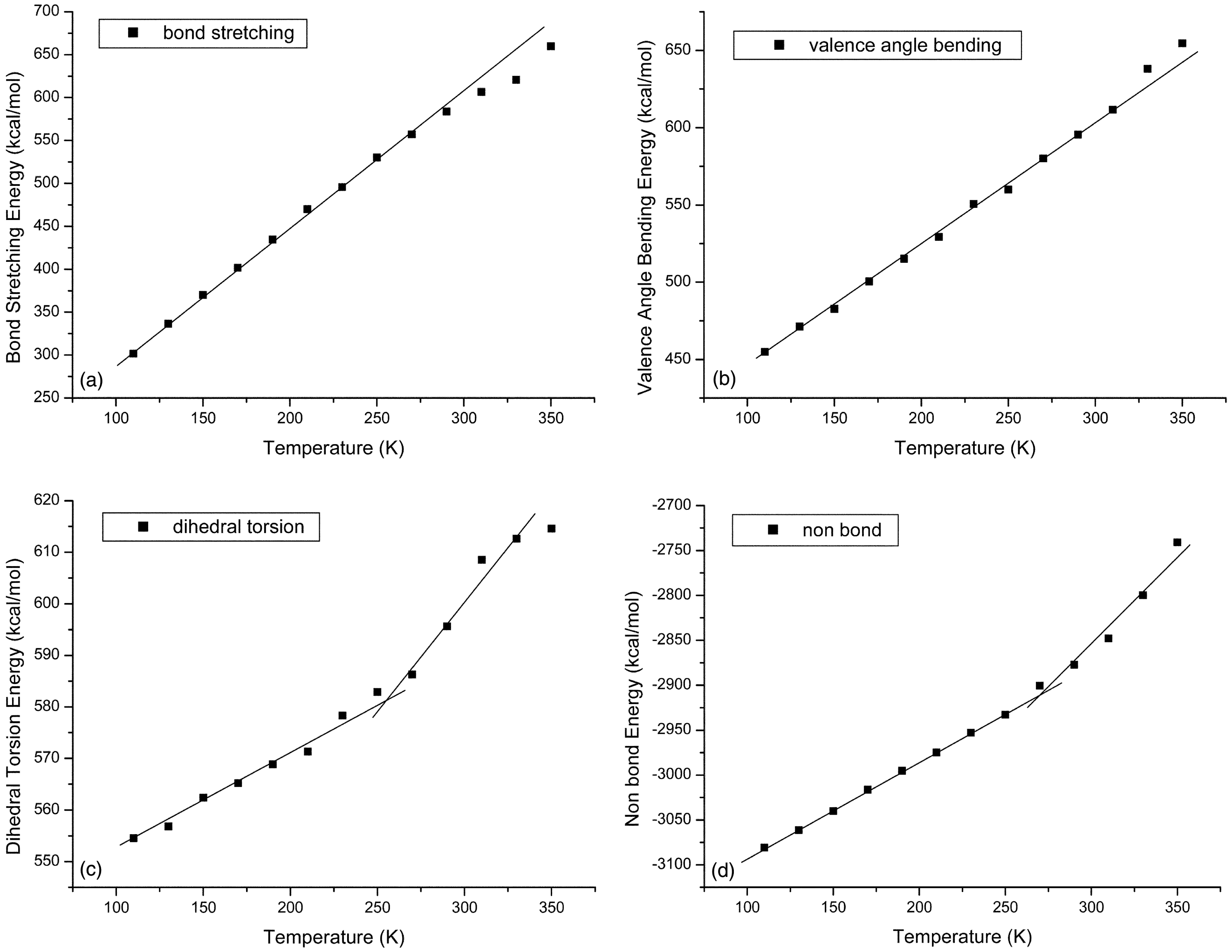

Fig. 2. Plots of some energy components versus temperature for the blend system PHB/PEO (1:2 blends in terms of repeated units): (a) bond energy; (b) angle energy; (c) torsion energy; (d) non-bond energy.

4. Conclusions

In this paper, by means of full atomistic MD simulations, the solubility parameters for two pure polymers (PHB and PEO) are calculated and the results are in agreement with the literature values. Furthermore, the volume–temperature curve of PHB/PEO blend system (1:2 blends in terms of repeated units) is simulated by employing the united atom approximation. From the $V-T$ curve, the glass transition temperature of the blend system is obtained (about 258 K). The glass transition temperature is compared well with the experimental results.

Solubility parameters of PHB and PEO obtained from the simulations have similar values. And we get only one glass transition for the blend system. From above two points, it can be concluded that the blend system is miscible. Energy components such as dihedral torsion energy and non-bonded energy play important roles in the glass transition process of the blend system, as indicated by the plots against temperature from above T_g and below T_g. It seems that MD simulation is a useful method to determine solubility parameter, $V-T$ curve and the glass transition temperature of polymers. Further, the simulated results may be helpful to predict the miscibility of polymer/polymer systems.

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