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Polymer 44 (2003) 1979–1986

polymer

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Molecular dynamics and thermal analysis study of anomalous thermodynamic behavior of poly (ether imide)/polycarbonate blends☆

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Received 27 July 2002; received in revised form 1 January 2003; accepted 15 January 2003

Abstract

Molecular dynamics simulation used to study the binary polymer blend of poly (ether imide) (PEI) and polycarbonate (PC) showed that these polymer blends are immiscible. The Flory-Huggins interaction parameter, χ, calculated from simulation reached a minimum value at 80 wt% PEI. The simulation results showed that the concentration dependence of χ was mainly due to electrostatic interaction and van der Waals force. The simulation results were supported by differential scanning calorimetry (DSC) measurements. The DSC measurements showed that there are two distinct glass transition temperatures for all the blends' concentrations. However, at 80wt % PEI, the T_g of PEI-rich phase reached a minimum while that of the PC-rich phase was comparable to its pure form indicating that there is some partial miscibility of PC in the PEI rich phase, but no PEI is incorporated in the PC rich phase. From simulations, the χ versus concentration plot shows the same trend as the experimentally measured glass transition temperature versus concentration plot.

Keywords: Polymer blends; Molecular dynamics simulation; Glass transition temperature

1. Introduction

Polymer blends and alloys constitute an important part of plastics consumption and continue to grow at a rate of 9% per year [1]. An important polymer blend is the blend of poly(ether imide) (PEI) and polycarbonate (PC). PEI and PC are high performance engineering thermoplastics. The chemical structures of PEI and PC are shown in Fig. 1. PEI/PC blends can be used for aircraft interior components and household applications. The PEI/PC blends, Ultem LTX™ series, have been available commercially since 1990 from GE Plastics. PEI/PC blends combine the high temperature resistance and intrinsic flame resistance of PEI with the good impact strength and ease of processing of PC. Blending PC into PEI also dilutes the cost of PEI, and reduces PEI's notch sensitivity [2].

PEI has been blended with several other polymers such as liquid crystalline polymer (LCP), poly ether ether ketone (PEEK), liquid crystalline polyimide (PI-LC) and nitro-substituted polybenzimidazole (NO_2–PBI) [3–8]. The blends of PC with epoxy, PMMA, high performance polystyrene, and poly(styrene-co-methacrylic acide) have been studied in recent years [9–12]. There are few papers published on PEI/PC blends. Chun et al. [13] studied the thermal properties and morphology of PEI/PC blends and found that the blends exhibited two distinct glass transition temperatures. Moreover, they found that the glass transition temperature of the PEI-rich phase changes at different loadings of PC, while that of PC-rich phase stays constant. However, the reason for this behavior was not fully explored.

The primary objective of this paper is to use molecular dynamics simulation (MD) to delineate the molecular processes that lead to the anomalous observation. To this end, the Hildebrand solubility parameters of PEI and PC and Flory-Huggins interaction parameter of the blends at various concentrations are computed. In addition, blends at several concentrations are made and analyzed using differential scanning calorimetry (DSC) to obtain the full T_g versus concentration curves to validate previous results.

To our knowledge, no molecular dynamics simulations have been done for PEI/PC blends, but some simulation work has been done on pure PEI and pure PC. Shih et al.

☆ Portions presented at the IUPAC conference (2002).

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doi:10.1016/S0032-3861(03)00054-5

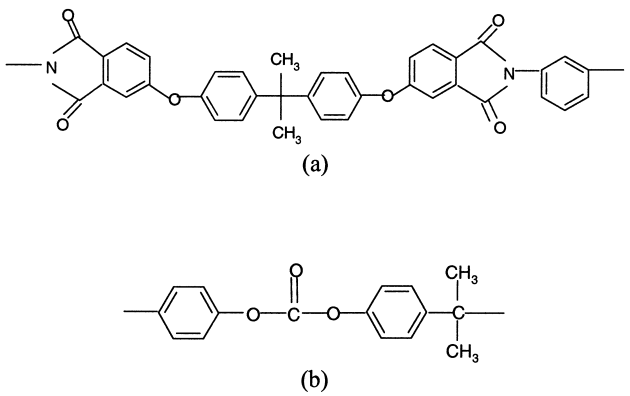

Fig. 1. Chemical structure of (a) PEI repeating unit and (b) PC repeating unit.

performed molecular dynamics simulation of BPA-PC using the TRIPOS5.2 force field [14]. They found that the carbonate group undergoes rotation more easily than that of the isopropylidene group. Fan et al. [15] investigated the structure factor and some mechanical properties of BPA-PC using MD simulation with the Dreiding2 force field. Ballone et al. [16] simulated PC based on a density functional force field. They calculated the structure factor of PC and compared it with the experimental results obtained from spin-polarized neutron scattering. Eichinger et al. determined the cohesive energy of PEI using the COMPASS force field [17].

2. Experimental

2.1. Materials

The polymers used in this study were obtained from commercial sources. The PEI was ULTEM 1000 provided by GE Plastics. The PC was LEXAN 101, also from GE Plastics. All materials were provided in pellet form. The physical properties of these polymers are given in Table 1.

2.2. Experimental methods

The PEI/PC blends were prepared in a Haake Rheocord 90 series 600 batch mixer with roller blades. Before blending, the pellets were dried overnight at a temperature of 90 °C in a vacuum oven to remove any traces of volatile materials. The mixer was preheated to 340 °C before adding the pellets. The component weight was calculated by using the desired weight percent of each component and by requiring the total melt volume of materials to be kept at 78% volume of the mixing chambers. It was shown by Sundararaj et al. that at this loading there is optimum material exchange between the two chambers of the mixer and there are no stagnant areas in the mixer center due to overfilling [18]. After the mixture reached the desired temperature, PEI pellets were added through the chute into the chambers first, and after 2 minutes, PC pellets were added. The ram was then placed over the top opening of the chambers and a 5 kg weight was then placed on top of the ram. The PEI/PC blend ratios were: 90/10; 87.5/12.5; 85/15; 82.5/17.5; 80/20; 75/25; 70/30 and 60/40. The total mixing time was 10 min. After this time, the motor was stopped and a sample was taken from the indents of the roller blades and quenched in the liquid nitrogen.

A differential scanning calorimeter, TA Instruments DSC 2910 equipped with Thermal Analyst 2200 software was used to determine the glass transition temperature(s), T_g, of the samples. DSC scans were obtained from 7–12 mg samples placed in a nitrogen atmosphere at a heating rate of 20 K/min. The measured glass transition temperature depends on the heating rate used, but since all measurements were done at the same heating rate, they can be compared with each other.

3. Simulation methodology

Molecular dynamics (MD) simulations were carried out using a commercial software package, Cerius2, version 4.6, from Molecular Simulation Inc. (now Accelrys Inc.) on a Silicon Graphics OCTANE workstation. Choosing the appropriate force field is considered to be the most important factor in obtaining valuable simulation results. There are a large number of force fields available in literature; they are parameterized for different physical systems. In the first part of the work, three commonly used force fields for polymers, namely Drieding2.21 [19], PCFF and COMPASS [20] were used to compute the Hildebrand solubility parameters (δ) of pure PC and PEI to check which force field best matched the solubility parameters of the polymers reported in literature. This force field was then used for simulations of blends of the two polymers. Here, Dreiding2.21 gave the most accurate estimation of solubility parameters of the present systems (see Table 2), and therefore, it was used for the subsequent simulation work on polymer blends. This is not surprising since Dreiding2.21 has been found to give fairly accurate estimation of

Table 1
Properties of PEI and PC used in the current work

Polymer (Abbreviation)	Source	Molecular weight (M_w)	Specific heat (C_p, J/Kg/K)	Density (ρ, kg/m^3)	T_g (°C)
Poly(ether imide): ULTEM 1000 (PEI)	GE plastics	30,000	1650 (220 °C)	1,270 (25 °C)	219
Polycarbonate: Lexan 101 (PC)	GE plastics	31,600	1580 (150 °C)	1,200 (25 °C)	150

Table 2
Solubility parameter of pei and pc simulated by different force field

Name	Repeating units	MWT	Solubility parameter ($MPa^{0.5}$)			
			Dreiding2.21	PCFF	COMPASS	Experimental
PC	23	5851	19.9	22.0	19.2	19.65[a], 20.3[b]
PEI	10	5928	21.7	25.9	19.7	19.01–23.92[c]

[a] Calculated from group contribution
[b] Ref. [35]
[c] Ref. [29]

solubility parameter values of various systems [21–23] using the NVT ensemble. It should be noted that this force field is not suitable for a NPT ensemble because it cannot reproduce the experimental density. It should also be noted that when we use the NVT ensemble with the Drieding2.21 force field, the simulation often yields relatively large pressures.

In the Dreiding2.21, the total energy of a system is represented by the sum of bonding and non-bonding interactions:

$$E = E_b + E_\theta + E_\phi + E_{inv} + E_{VDW} + E_Q \quad (1)$$

The first four terms represent bonded interactions, which correspond to the energy associated with bond stretching (E_b), bond angle bending (E_θ), tortion angle rotations (E_ϕ), and tetrahedral center inversions (E_{inv}). The last two terms represent non-bonded interactions, which consist of van der Waals (E_{vdw}) and electrostatic (E_Q) energies. In Dreiding2.21, E_{vdw} is described by a Lennard–Jones 12–6 potential. The electrostatic energy is calculated based on the partial charges of the atoms in the system estimated by the charge-equilibration method [24]. The electrostatic interaction was calculated by the Ewald summation method since it calculates long-range interaction forces more accurately.

The bulk amorphous state of the pure polymers and their blends were built using cubic unit cells subjected to periodic boundary conditions. A typical example for the initial configuration of PEI/PC blends is shown in Fig. 2. The unit cell volume was determined by the number of atoms and the bulk density of the material (the unit cell is shown in Fig. 2). The detailed model construction procedure is described elsewhere [25]. For the PEI/PC blend simulation, the concentrations of the blends were controlled by including different ratios of the number of chains of PEI to the number of chains of PC in the periodic boundary unit cells. The number of chains, chain sizes and densities are summarized in Table 3. The density of the blend system was calculated from the density of the pure polymer and the concentration of each polymer assuming that the components' volumes are additive [26].

In general, the initial amorphous structure is in a relatively high energy state. Therefore, before MD, we need to do an energy minimization. When the system is far from the thermodynamic equilibrium, the steep descendent method is most efficient. However, when the system is close to the minimum, the conjugate gradient method is the best [27].

The NVT ensemble simulations were carried out for all the structures. Nose dynamics coupled with a Verlet Leapfrog numerical algorithm was used to create the canonical molecular dynamics trajectories, and a time step of 1 femto-second was used to ensure the stability of the simulation. The simulation time depends on the number of the atoms in the system, and it is usually carried out until the total energy of the system stabilizes. The last few hundred pico-seconds of the trajectory file were used to calculate the physical properties of interest.

One of the properties, the Hildebrand solubility parameter (δ) is defined as the square root of cohesive energy density. That is:

$$\delta = \sqrt{\frac{(E_{vac} - E_{bulk})\rho}{M}} \quad (2)$$

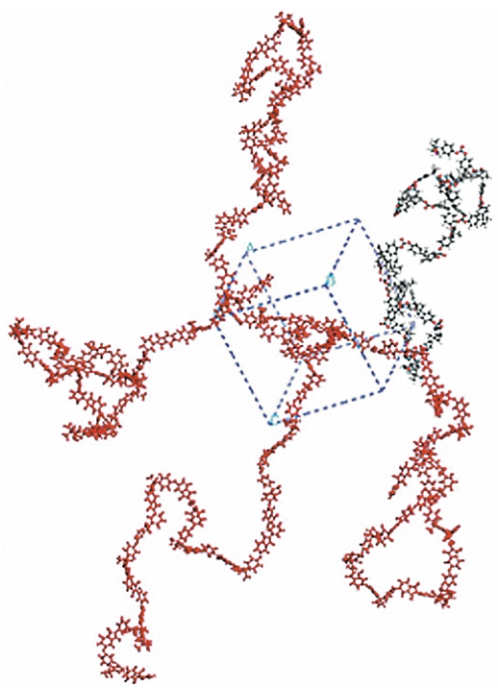

Fig. 2. Initial conformation of PEI/PC blends with 4 chains of PEI (red) and 1 Chain of PC (black). Note unit cell (dark blue).

Table 3
Simulation details for PEI-PC blend system

System number	Number of chains per unit cell	Composition (volume PEI %)	Density of the system (g/cm^3) at 340 °C	Molar volume (cm^3/mol)	χ
1	1 PC chain	0	1.040	5626	N/A
2	1PEI chain	100	1.107	4876	N/A
3	4PC chains, 1PEI chain	19.3	1.053	5571	2.35
4	2PC chains, 1PEI chain	32.4	1.062	5533	2.46
5	1PC chain, 1PEI chain	48.9	1.073	5489	2.30
6	1PC chain, 2PEI chains	65.7	1.084	5445	2.30
7	1PC chain, 4PEI chains	79.3	1.093	5410	0.89
8	1PC chain, 6PEI chains	85.2	1.097	5394	3.96

where E_{vac} is the potential energy in the vacuum state, E_{bulk} is the potential energy in the amorphous state, ρ is the density of the polymer and M is the molecular weight of the polymer. The MD simulation was used to calculate E_{vac} and E_{bulk}, and these energies were subsequently used to calculate δ. Once the solubility parameter of the two polymers had been obtained, the Flory-Huggins interaction parameter χ was calculated by:

$$\chi = \frac{V_0(\delta_1 - \delta_2)^2}{RT} \tag{3}$$

Here, R is the universal gas constant. V_0 is a reference volume. The choice of V_0 is rather arbitrary. In the original Flory-Huggins theory, one should chose the smallest among the molar volume of the solvent and the molar volumes of the repeating units of the polymers comprising the mixture. Since the molar volume of the PC repeating unit is smaller than that of PEI, the PC repeating unit is taken as V_0. It should be noted that we can only obtain positive χ values from this equation and, in addition, concentration dependence cannot be studied.

Two polymers, with degrees of polymerization m_A and m_B defined based on the same reference volume (really like number of segments of the polymer in the lattice), will be miscible if their χ_{AB} values are less than $(\chi_{AB})_{critical}$ which is given by

$$(\chi_{AB})_{critical} = \frac{1}{2}\left(\frac{1}{\sqrt{m_A}} + \frac{1}{\sqrt{m_B}}\right)^2 \tag{4}$$

It should be pointed out that a blend exhibiting a χ_{AB} value which is smaller than the critical value would mean that the components in the blend are completely miscible. In other words, the system meets both miscibility criteria that are a negative ΔG_m and a positive second derivative of ΔG_m with respect to the concentration of either component. When χ_{AB} is considerably greater than the critical value, the components are totally immiscible and form two separate phases and only one component is found in each phase. However, if the measured χ_{AB} is slightly greater the critical value, the blend exists as in a so-called partially miscible mixture in which there are two phases but both components can be found in both phases. So long as the measured χ_{AB} and the corresponding critical value are calculated based on the same reference volume, comparing the measured χ_{AB} with the critical value will give a good indication about the degree of miscibility of the blend. Therefore, polymer researchers have been using χ_{AB} rather than enthalpy change of mixing (ΔH_m) to characterize miscibility of polymer solutions and blends. It is important to note that knowledge of ΔH_m alone cannot predict whether a system is miscible or not. This is simply because the entropy change of mixing (ΔS_m) has to be considered.

The most direct approach to obtain the Flory-Huggins interaction parameter for binary polymer blends is to measure the corresponding enthalpy change on mixing; however, it is too small to be measured experimentally. Based on the MD simulation, one can readily calculate the heat of mixing by comparing the enthalpies of the blends and pure polymers as shown in the following equation:

$$\Delta H_m = H_{mixture} - \sum n_i H_i \tag{5}$$

where n_i and H_i are the moles and specific enthalpy of component i in its pure component state, $H_{mixture}$ is the enthalpy of the blend system. The linear thermal expansion coefficients of PEI and PC are 5.58×10^5 cm/cm/K and 6.84×10^5 cm/cm/K, respectively. Since they are very close to each other, we feel justified not to include the $\Delta(PV)$ effect and ΔH_m is assumed to be the equal to ΔE_m. The Flory-Huggins interaction parameter can be calculated from the following equation for ΔH_m:

$$\Delta H_m = \chi RT \phi_1 \phi_2 \tag{6}$$

where ϕ_1 and ϕ_2 are the volume fractions of polymers 1 and 2. In this way, we can study the concentration dependence for the Flory-Huggins interaction parameter.

4. Results and discussion

Similar to what Chun et al. [13] observed, we also observed two distinct T_g's for the PEI-PC blends (see Fig. 3), one corresponding to the PEI-rich phase and the other to the PC rich phase. The existence of two distinct T_g's indicates that these two polymers are immiscible. Fig. 4 shows that the T_g of the PC-rich phase in the blends is identical to that of pure PC. On the other hand, Fig. 5 shows

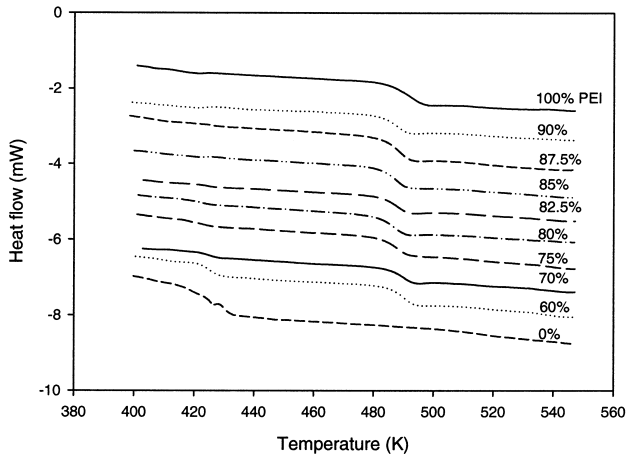

Fig. 3. Heat flow versus temperature of PEI-PC blends. The curves are shifted vertically to avoid overlap.

that the T_g of the PEI-rich phase first decreased with increasing overall PC content up to 20 wt%; the T_g of the PEI-rich phase then reached a minimum value at 20% PC; and finally the T_g of PEI-rich phase increased at higher overall PC contents and approached the T_g of pure PEI. The maximum T_g decrease was about 6 °C, which occurred at 80% PEI. The error bar was obtained using three independent measurements of the same sample. Chun et al. [13] also reported a similar phenomenon for the PEI/PC blends; however, in their case, the minimum T_g of the PEI-rich phase occurred at 90% overall PEI content. It should be noted that the concentration intervals they used to determine the concentration dependence of the T_g of the PEI-rich phase were not as fine as in this work. In addition, their blend samples were prepared by single screw extrusion and solution casting, whereas we used melt blending in an intensive batch mixer. They also found from scanning electron microscopy that the size of the minor component domains for the PEI/PC blend ratio with the lowest T_g is small compared with the size of the minor component for the other blend ratios. They suspected that this might be due to the difference in the viscosity of the two polymers. In

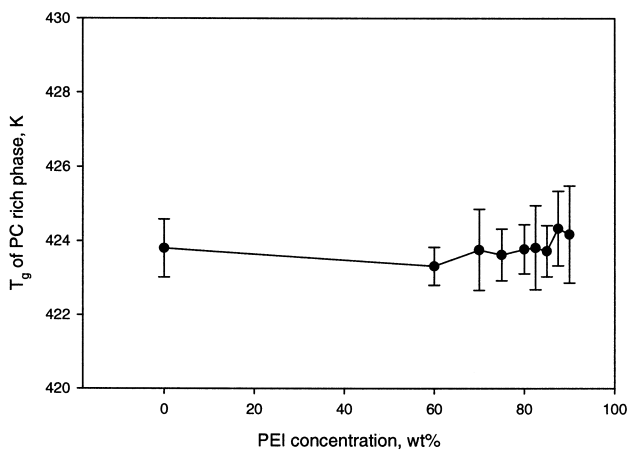

Fig. 4. Concentration dependence of T_g of PC in PEI-PC blends.

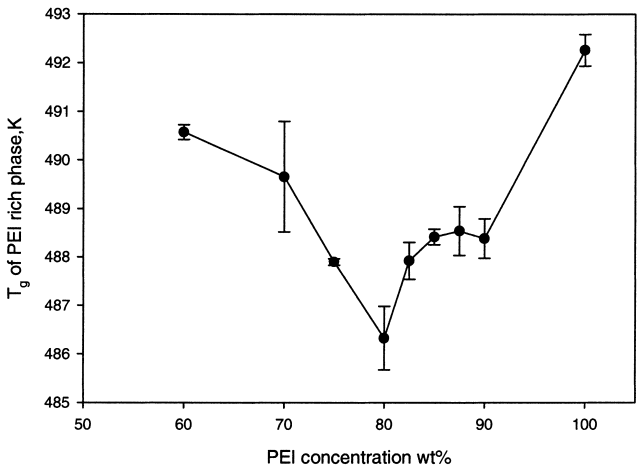

Fig. 5. Concentration dependence of T_g of PEI in PEI-PC blends.

other work, Lin and Sundararaj [28] show micrographs which showed incorporation of PC in the PEI rich phase but no PEI in the PC phase.

We performed molecular dynamics simulation of these binary polymer blends to determine the reason for this thermodynamic behavior on a molecular level. The solubility parameters calculated from MD simulations using the three different force fields are shown in Table 2. The solubility parameter results using PCFF force field did not match with the results obtained from the other two. It yielded a much larger δ value than those obtained from Dreiding2.21 and COMPASS force field. The calculated solubility parameters using the Dreiding2.21 and the COMPASS force fields are in fairly good agreement with experiment (see Table 2). However, there is significant variation in the experimental values reported [29]. Since the two force fields yielded comparable results, and because the COMPASS force field takes about 7–10 times longer CPU time than the Dreiding2.21 force field to do the same time scale simulation, the Dreiding2.21 force field was chosen for subsequent simulations.

Because of computer data storage space limitations, the simulation work could not be done using the actual size of the polymers. However, to some extent, the size of the molecule used in the model is important in order to calculate accurate thermodynamic properties. Therefore, it is necessary to study what minimum molecular size is sufficient to represent the real polymer. To determine this minimum size, the solubility parameter of PEI and PC at different molecular weights was studied until the point when increasing molecular weight did not change the solubility parameter value. Fig. 6 shows that the solubility parameter of PC decreases sharply at first as the number of repeating units increases, but levels off when the number of repeating units is greater than 10 ($M_n = 2545$).

For PEI, Fig. 7 shows that the solubility parameter for PEI has a similar trend and δ starts to approach a constant value when the number of repeating units is greater than 8 ($M_n = 4742$). For the remainder of the simulations, 23

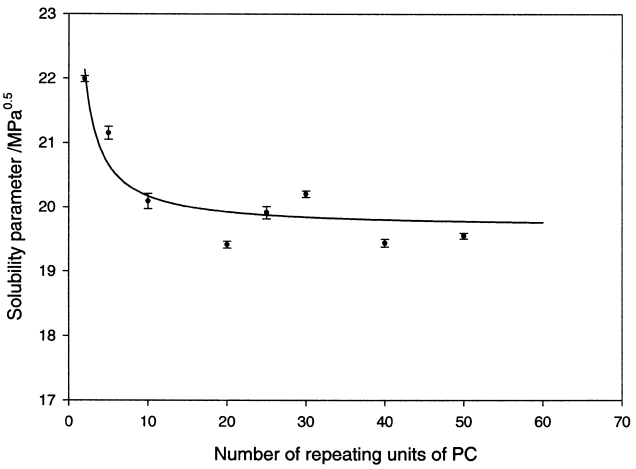

Fig. 6. Computed solubility parameter of PC versus number of repeating units.

repeating units ($M_n = 5851$) were chosen for the PC molecule while 10 repeating units ($M_n = 5928$) were chosen for the PEI molecule. Just like the actual polymers used in the experiment, the PC and PEI molecules used in the simulation had similar molecular weights. Fan et al. [15] found that using 21 repeating units for PC was sufficient for their simulations.

The NVT molecular dynamics trajectory files were created for each structure. The time required for equilibrium depends on the size of the system, and the time was determined by running the simulation until a stable energy was attained for the system. The mean potential energies of the bulk and the vacuum states were then calculated by using the time average of the potential energy values over the last 100 ps of the trajectory.

Once the average total energy values were obtained for each system, ΔH_m can be calculated for the blend systems using the fact that ΔH_m is approximately equal to ΔE_m in these systems. The energy change during mixing for each type of energy was also calculated and these are summarized in Table 4. Fig. 8 is the plot of molar enthalpy change, ΔH_m and Gibbs free energy change upon mixing, ΔG_m, versus blend concentration. The ΔG_m was calculated from ΔH_m using the combinational entropy changes, ΔS_m^{comb} from Flory-Huggins theory for mixing the two materials:

$$\Delta G_m = \Delta H_m - T\Delta S_m^{comb} \quad (7)$$

Fig. 8 showes that the ΔH_m and the ΔG_m curves are similar. However, polymer researchers usually use χ instead of ΔH_m. The χ values calculated using Eqs. (5) and (6) are plotted versus concentration of PEI in Fig. 9. The χ value are positive and larger than the critical χ value (from Eq. (4)) calculated based upon the chain lengths of the components used, which indicated that these two polymers were immiscible. From Table 4, we can see that the torsion energy and inversion energy contribute to the miscibility of the blend while the other energies tend to drive the blend away from miscibility. It seems that the present results, which are based on the use of Dreiding2.21 force field, indicate that the immiscibility of this binary polymer blend could be due to the bond stretching energy, bond angle bending energy and electrostatic energy. Another noteworthy point is that the composition dependence of χ at around 80% of PEI is not smooth and monotonic-this is not consistent with what is predicted by the Flory-Huggins theory. This is mainly attributed to the fact that the simulations were carried out with the incorporation of the local concentrations of the polymers and the shapes of their repeating units. In other words, the mean field approximation, which is required in the original Flory-Huggins theory, was not used here.

The concentration dependence of χ calculated from simulation (Fig. 9) has the same trend as the concentration dependence of the glass transition temperature of the PEI rich phase (Fig. 5). The change in χ with concentration was due mainly to the van der Waals and electrostatic energy. The value of χ calculated in this paper using MD is greater than that calculated by Chun et al. [30]using measured glass transition temperatures. The χ values from Chun et al.

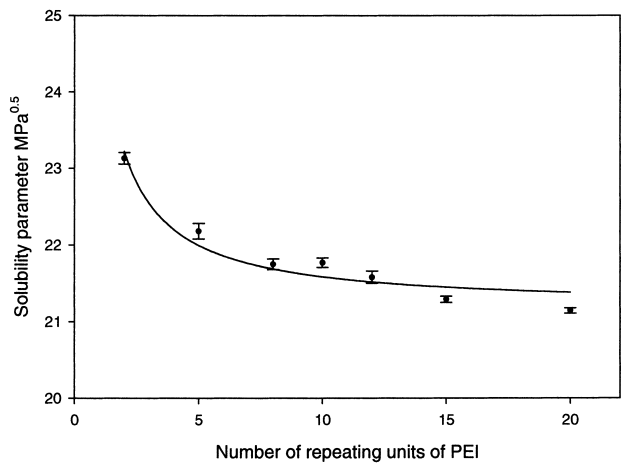

Fig. 7. Computed solubility parameter of PEI versus number of repeating units.

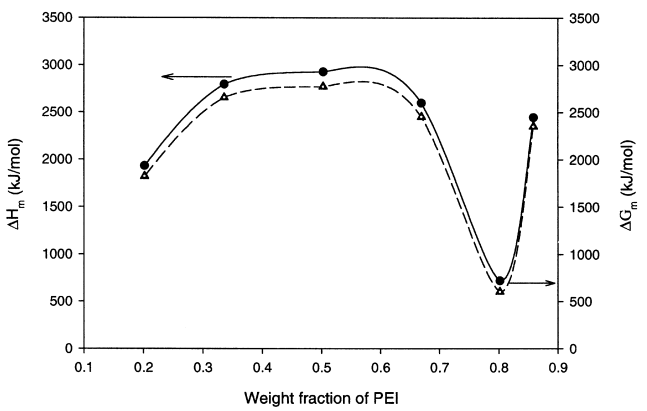

Fig. 8. Molar enthalpy and Gibbs free energy change upon mixing versus weight fraction of PEI.

Table 4
Energy change upon mixing for PEI/PC blend systems

System number	ΔE_b (kcal/mol)	ΔE_θ (kcal/mol)	ΔE_ϕ (kcal/mol)	ΔE_{inv} (kcal/mol)	ΔE_{vdw} (kcal/mol)	ΔE_Q (kcal/mol)
3	28.95	11.64	−8.81	0.40	4.70	14.01
4	17.50	19.13	−12.58	−0.68	6.38	14.75
5	14.11	10.19	−0.044	−1.90	−1.43	10.62
6	15.93	7.98	−12.74	−3.25	15.87	18.79
7	27.76	12.40	−11.20	−2.28	−2.84	−4.07
8	32.04	17.63	−3.59	2.54	8.00	38.00

ranged from 0.198 to 0.271 whereas our values are an order of magnitude larger. The method used by Chun et al. to calculate the Flory-Huggins interaction parameter is delineated in Kim et al. [31–34]. For most concentrations, the χ calculated from MD in our work is also greater than that calculated from Eq. (3) using the δ from the MD ($\chi = 1.053$). Again, it should be kept in mind that there is no concentration dependence for the χ value determined from Eq. (3). At 80 wt% PEI, the χ calculated directly from the energies obtained from MD is smaller than the one calculated using Eq. (3). There are several reasons that may contribute to the quantitative disagreement between Chun et al.'s values and our values. First of all, the χ from experimental data was based on the apparent volume fractions of the blend system, while the χ calculated from simulation was based on the atomic level volume fraction. Secondly, for PEI/PC blends, because they are immiscible, there is no specific interaction between these two polymers, and the entropy effects may have an influence; but entropy effects are not included in the MD simulation calculation. Usually, entropy effects can be ignored. Thirdly, Dreiding2.21 is a generic force field, and some parameters in this force field may need to be modified to make it suitable for our system. It was encouraging that the solubility parameters obtained using the Dreiding 2.21 force field in this work were comparable to literature results which used other force fields such as COMPASS which is claimed to be more comprehensive.

5. Conclusions

The thermal analysis showed that the PEI/PC blends are immiscible, and that there is some anomalous thermodynamic behavior in these blends. From the T_g measurements, there seems to be some level of PC in the PEI rich phase, but no incorporation of PEI in the PC rich phase. Based on Dreiding2.21 and COMPASS force fields, the NVT MD simulation of PEI and PC yielded δ values that are in good agreement with the experimental values in literature. Using Dreiding2.21 force field, the molecular dynamics simulation of PEI/PC blends showed these two polymers are immiscible and the concentration dependence of χ calculated from simulation has the same trend as the concentration dependence of the glass transition temperature measurements. However, the χ calculated from simulation does not quantitatively match the value obtained using experimental data. The NVT MD simulation proved to be a useful way to understand the underlying forces that are responsible the miscibility of PEI/PC blends. Because the polymer blend system studied was a very large system with complex molecules, the MD

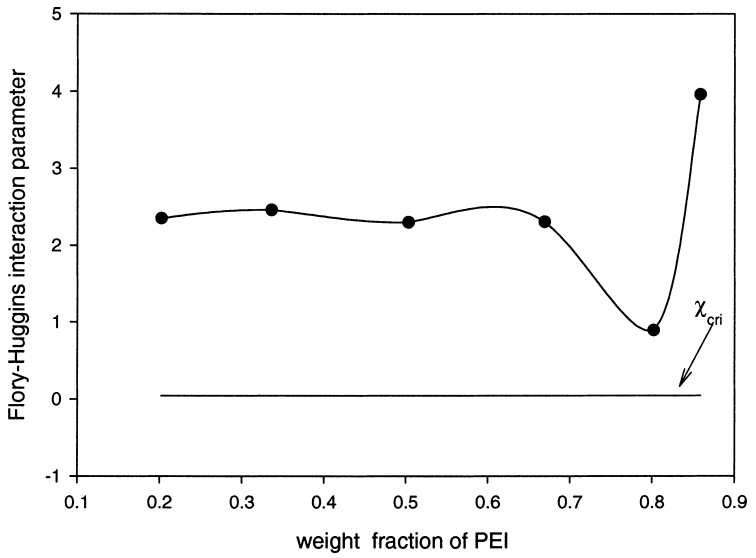

Fig. 9. Flory-Huggins interaction parameter versus weight fraction of PEI.

simulation consumed significant computer resources. A more efficient integration algorithm will improve our ability to do efficient MD simulation of these engineering polymer blends.

Acknowledgements

The authors would like to thank NSERC (the National Science and Engineering Research Council of Canada) for financial support.

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