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Molecular dynamics simulations of the enthalpy of mixing of poly(vinyl chloride) and aliphatic polyester blends

Sukmin Lee[a,*], Jung Goo Lee[a], Hosull Lee[a], Stephen J. Mumby[b]

[a]Kumho Chemical Laboratory, Hwaam dong 57-1, Yuseong ku, Taejon 305-348, South Korea
[b]Molecular Simulations Inc., 9685 Scranton Road, San Diego, CA 92121, USA

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Abstract

A molecular dynamics (MD) study was performed to analyze the enthalpy of mixing between poly(vinyl chloride) (PVC) and various aliphatic polyesters. The enthalpy of mixing was calculated from the computed cohesive energy densities of: (1) pure PVC; (2) aliphatic polyesters with a molar ratio of CH_2/COO groups from 2 to 14; and (3) mixtures of these components. In order to validate the calculation method, mixtures of homologue model compounds with low molar-masses were also examined. An immiscible *n*-octane/methyl acetate pair having a 50/50 volume ratio showed an enthalpy of mixing of $+3.43$ cal/cm^3 at 298 K, whereas the miscible 2,3-dichlorobutane/diethyl acetate pair of a 50/50 volume ratio showed the enthalpy of mixing of -3.20 cal/cm^3 at 298 K. The calculated results for model compound mixtures also showed good agreement with empirical observations from the literature. The cohesive energy density of pure aliphatic polyesters, as the CH_2/COO value of polymer chains is increased, decreases gradually owing to the reduced polarity of aliphatic polyesters. The binary interaction parameter (B) of PVC and aliphatic polyester mixtures predicts a maximum miscibility around a CH_2/COO ratio of 6, where the calculated B was equal to -3.85 cal/cm^3. These results are in semi-quantitative agreement with experimental values from the literature. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular dynamics; Enthalpy of mixing; Polymer blends

1. Introduction

A negative Gibb's free energy of mixing is a necessary condition for polymer blends to form a miscible phase. The entropy change during mixing may be negligible when the molecular weights of polymers become large. In the case of the blends having strong intermolecular interactions, particularly, the miscibility can be simply determined from the enthalpy change of mixing instead of Gibb's free energy of mixing. An exothermic enthalpy of mixing is indicative of a miscible blend. Accordingly, a knowledge of the enthalpy of mixing of blends is important in determination and comprehension of miscibility, although its accurate measurement is not straightforward.

Several methods to predict the enthalpy of mixing have been proposed [1–6]. One experimentally available method is the direct measurement of enthalpy of mixing using analogue compounds of low molar-masses, in which the error due to end effects from small molecules should be considered. Alternatively, the enthalpy of mixing can be determined from Hess's law [7] by measuring the heat of polymer solution in a mutual solvent. An indirect way to infer the enthalpy of mixing is to employ an equation that relates the binary interaction energy density (B) with enthalpy of mixing, i.e. $\Delta H_{mix}/V = B\phi_1\phi_2$, where V is the total volume of blend, and ϕ_i is the volume fraction of component i. Here it is assumed that B has only enthalpic considerations, which infers a negligible entropy of mixing. The interaction parameter can be estimated by the melting point depression method for crystallizable systems [8–11]. Also, either the gas/vapor sorption method [12–14] or inverse-phase gas chromatography [15,16] employing small molecule probes can be used to determine the interaction parameter. Small angle neutron scattering [17,18] and forward recoil spectrometry [19] have also been used to estimate interaction parameters.

There have been attempts to perform theoretical prediction [20–23] using thermodynamic models such as the universal quasi-chemical (UNIQUAC) and modified Guggenheim quasi-chemical (MGQ) models. Both models are group contribution methods to adopt a concise representation of mixing process by considering the locally nonrandom distribution of interacting species in equilibrium mixtures. The latter uses a single fluid approximation that

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[*] Corresponding author.

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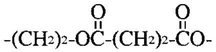
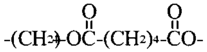
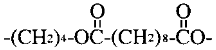
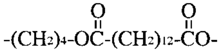
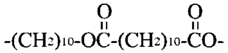
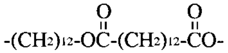
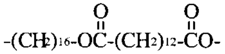
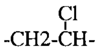
Table 1
Characteristics of polymers used

Name	Repeating unit	Code	Density (g/cm^3)	CH_2/COO	Number of chains in a cell	Number of atoms in a cell	Size of a cell (Å)
Poly(ethylene succinate)	 $-(CH_2)_2-O\overset{O}{\overset{\parallel}{C}}-(CH_2)_2-\overset{O}{\overset{\parallel}{C}}O-$	PES	1.320	2	6	1 092	22.19
Poly(butylene adipate)	 $-(CH_2)_4-O\overset{O}{\overset{\parallel}{C}}-(CH_2)_4-\overset{O}{\overset{\parallel}{C}}O-$	PBA	1.130	4	7	1 064	21.13
Poly(butylene sebacate)	 $-(CH_2)_4-O\overset{O}{\overset{\parallel}{C}}-(CH_2)_8-\overset{O}{\overset{\parallel}{C}}O-$	PBS	1.136	6	8	1 024	21.81
Poly(butylene dodecamethylene dicarboxylate)	 $-(CH_2)_4-O\overset{O}{\overset{\parallel}{C}}-(CH_2)_{12}-\overset{O}{\overset{\parallel}{C}}O-$	PBD	1.085	8	10	1 100	23.95
Poly(decamethylene decamethylene dicarboxylate)	 $-(CH_2)_{10}-O\overset{O}{\overset{\parallel}{C}}-(CH_2)_{10}-\overset{O}{\overset{\parallel}{C}}O-$	PDEDE	1.001	10	16	1 088	21.43
Poly(dodecamethylene dodecamethylene dicarboxylate)	 $-(CH_2)_{12}-O\overset{O}{\overset{\parallel}{C}}-(CH_2)_{12}-\overset{O}{\overset{\parallel}{C}}O-$	PDODO	0.982	12	14	1 120	21.62
Poly(hexadecamethylene dodecamethylene dicarboxylate)	 $-(CH_2)_{16}-O\overset{O}{\overset{\parallel}{C}}-(CH_2)_{12}-\overset{O}{\overset{\parallel}{C}}O-$	PHEDO	0.968	10	12	1 104	21.43
Poly(vinyl chloride)	 $-CH2-\overset{Cl}{\overset{\mid}{C}}H-$	PVC	1.385	–	12	1 040	23.12

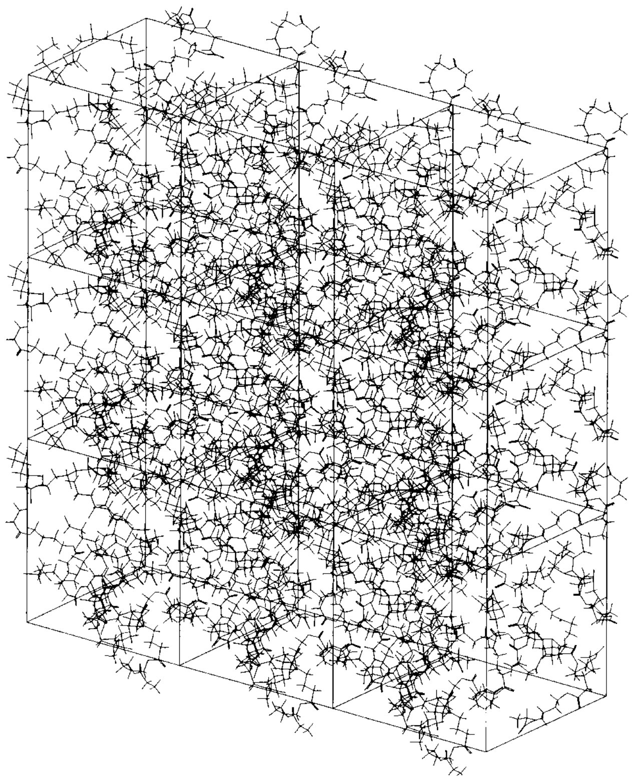


Fig. 1. A periodic amorphous cell model of poly(vinyl chloride)/poly(butylene succinate) mixture of a volume ratio of about 50/50.

the exchange energy of interacting pairs is symmetrical, while the first is a two-fluid model. The MGQ model has been applied to several blend systems, and appears to predict the enthalpy of mixing quantitatively well in the several blends containing polar components.

In this work, we attempt to determine the enthalpy of mixing using molecular dynamics (MD) simulation in order to analyze the miscibility of polymer blends, which has been attempted only a few times before. [24–26] For this, the enthalpy of mixing could be computed,

$$\Delta H_{\mathrm{mix}} \cong -\left[\frac{E_{\mathrm{coh}}}{V}\right]_{\mathrm{blend}} + \phi_1\left[\frac{E_{\mathrm{coh}}}{V}\right]_1 + \phi_2\left[\frac{E_{\mathrm{coh}}}{V}\right]_2 \quad (1)$$

from this simple relation containing the cohesive energy (E_{coh}) of each component and mixture. The relation assumes no change of volume during mixing. The E_{coh} of pure polymer components and of mixtures can be calculated with MD simulations, although the experimental measurement of the E_{coh} for polymer mixtures is not practical.

The blend system under investigation in this work was PVC mixed with linear aliphatic polyesters [27–29]. These blends are known to show a miscibility window depending on the CH_2/COO ratio in polyesters, with a sharp immiscibility–miscibility boundary around a value of this ratio of 3 or 4, and a relatively broad boundary at the other end. The interaction of the local dipoles between chlorines in PVC and the ester carbonyl groups in polyesters is thought to dominate the miscibility in this blend system [27,30]. The details of the miscibility window being determined by the extent of specific intermolecular interactions as the ratio of CH_2/COO in polyesters is changed, and reflected in the enthalpy of mixing.

In this study, homologue model compounds and polymeric segments of PVC and several aliphatic polyesters were employed to determine the enthalpy of mixing and interaction parameters, and the miscibility behaviour of blends were examined using MD simulations [31].

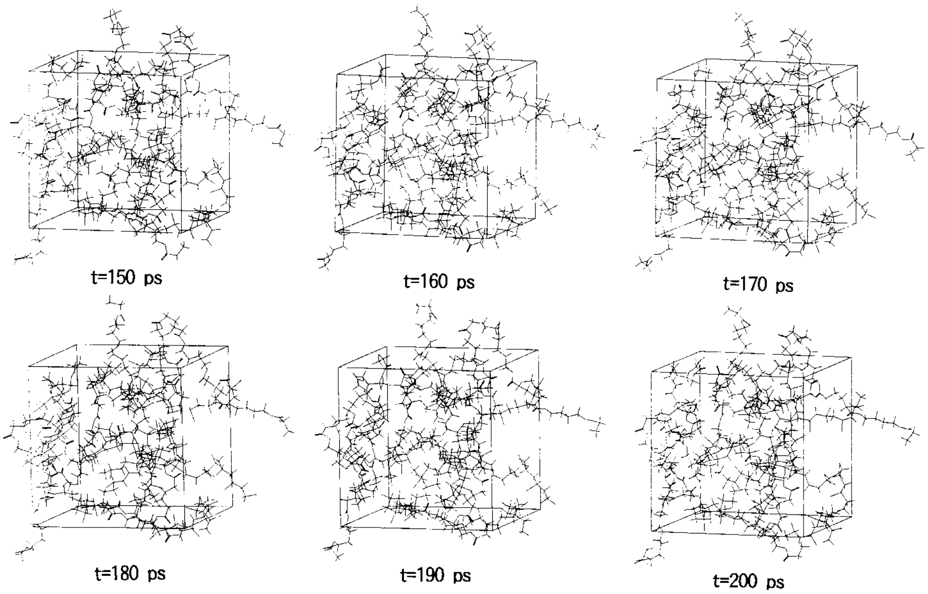


Fig. 2. Snapshots of an amorphous cell containing poly(vinyl chloride)/ poly(butylene succinate) mixture, changing as a function of the annealing time during the molecular dynamics at 358 K.

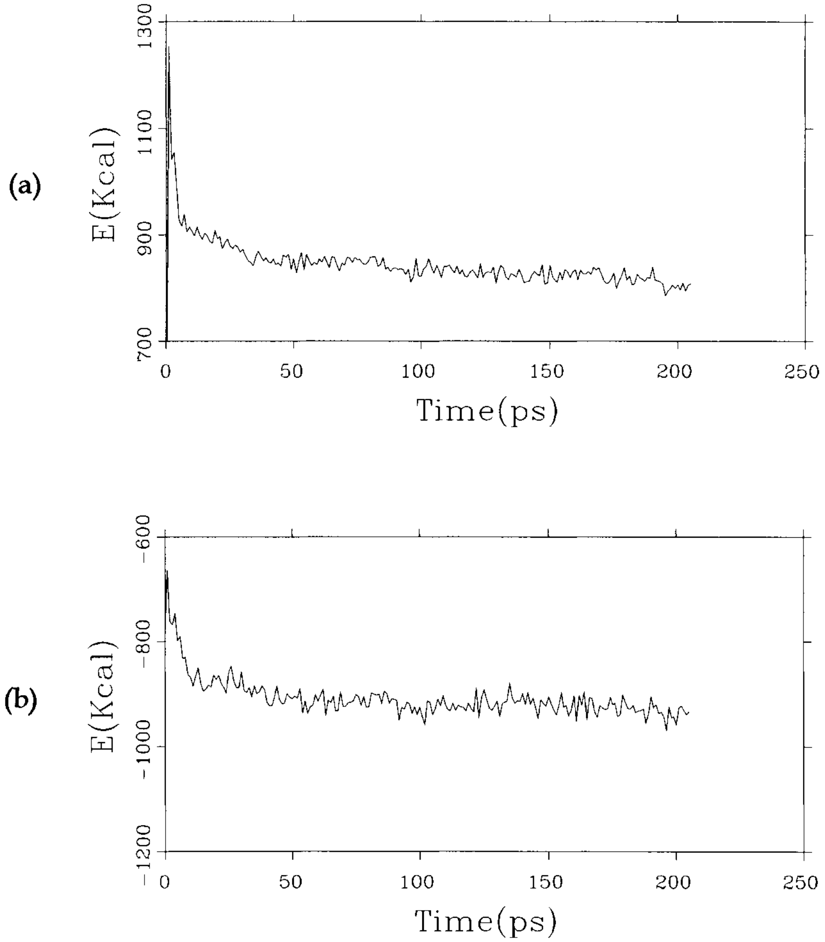


Fig. 3. Variation of (a) the total energy and (b) the non-bonded interaction energy as a function of time for the poly(vinyl chloride)/poly(butylene succinate) mixture (a 50/50 volume ratio) during a 200 ps MD simulation at 358 K.

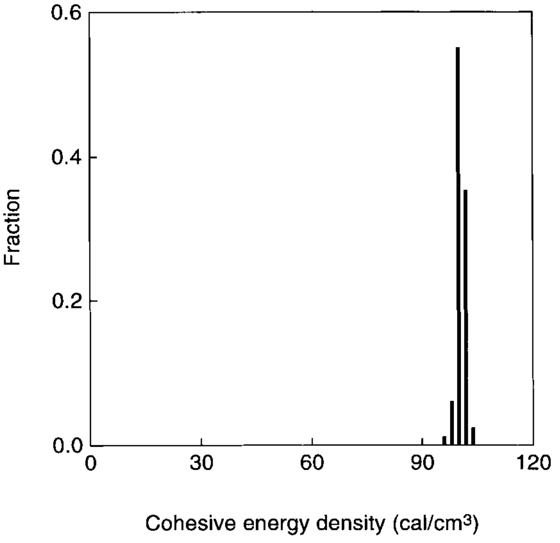


Fig. 4. Distribution of the frame cohesive energy density calculated from the configurations collected every 5 ps, for the poly(vinyl chloride) and poly(butylene succinate) mixture (about 50/50 volume ratio).

2. Calculation methods

For molecular simulations, we employed a commercial force field of MSI, pcff [32–36], which has been parameterized for organic polymers. A force field describes the interaction energy between the molecules as well as the energetic variation of the intramolecular motions of a molecule. The interaction energy here is written as the sum of atom-pair interactions from Coulombic energy and van der Waal's energy in type of Lennard–Jones potential as follows

$$E_{\mathrm{int}} = \sum_{i>j} \frac{q_i q_j}{\varepsilon r_{ij}} + \sum_{i>j} \frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6} \qquad (2)$$

where q_i is the partial charge on atom i, r_{ij} is the distance between the two atoms i and j, A_{ij} and B_{ij} are determined from the force field parameters for atoms i and j, and ε is the dielectric constant.

Model systems containing 1000–1200 atoms of the corresponding molecules of model compounds or polymer segments were employed. Cubic cells of initial configurations were generated, using the amorphous cell module adopting the modified rotational isomeric state (RIS)

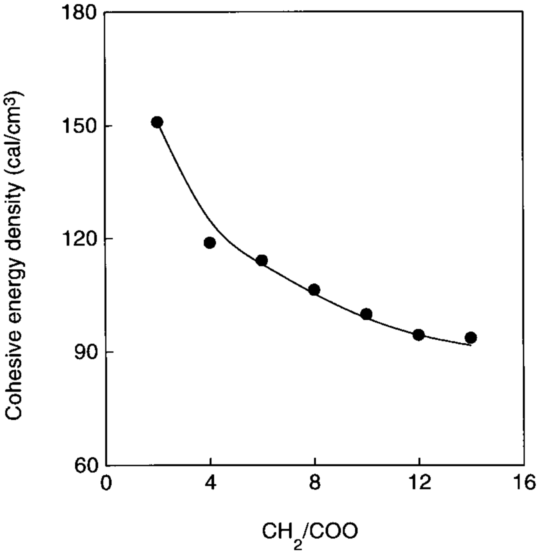


Fig. 5. Cohesive energy density as a function of CH_2/COO value for various aliphatic polyesters from a 200 ps MD simulation at 358 K.

method, which prohibits intermolecular overlaps. The length of each side of the cell is about 21–24 Å. To remove unfavourable interactions in the initial configuration, 500 steps of energy minimization were performed using the steepest descent method. The MD simulation was performed using the (N,V,T) ensemble, and the periodic boundary condition. The density of model systems was maintained as experimental or calculated values through the whole MD simulation. Velocity rescaling, coupled with the Verlet velocity algorithm [37], was used to create the MD trajectories with a dynamic step of 1 fs. Velocity rescaling is well established and used widely [35,36], even though it does not correspond to a true ensemble. Equilibration for 5 ps at the given temperature was followed by the MD simulation of 100 ps for the model compounds with low molar-masses, and 200 ps for polymer segments.

The E_{coh} for pure compounds or mixtures was calculated from the 15–17 configurations obtained from every 5 ps during the MD simulation after equilibration was reached. The E_{coh} was obtained by the quantity:

$$U_{intra} - (U_{calc} + dU_{tail}) \tag{3}$$

where U_{intra} denotes the intermolecular energy of the parent molecules, U_{calc} is energy given by the simulation with a sharp cutoff of the non-bonded potential, 8 Å in this study, and dU_{tail}, expressed as follows [38]

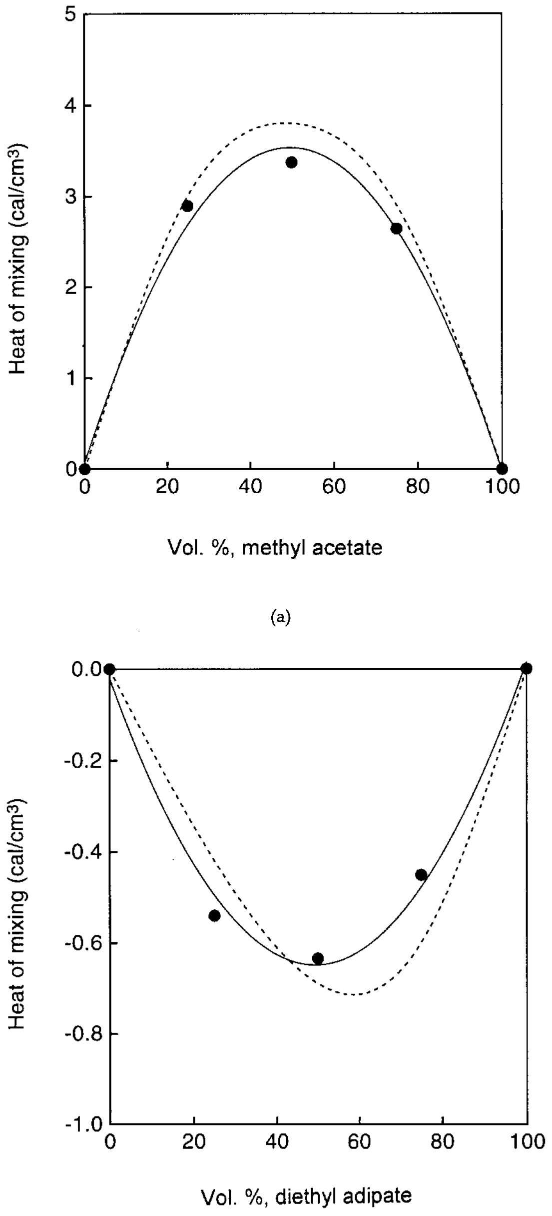
$$\delta dU_{tail} = \frac{1}{2}\sum_{\alpha=1}^{\nu} N_{\alpha} \sum_{\beta=1}^{\nu} \rho_{\beta} 4\pi \int_{r_c}^{\infty} r^2 g_{\alpha\beta}(r) U_{\alpha\beta}(r) dr \tag{4}$$

where α and β are the chemical types of the atom at the origin and the atom at distance r, respectively, ρ is the density, N is the number of atoms, $g_{\alpha\beta}(r)$ is the radial distribution function, and r_c is the cutoff length, 8 Å in this work. The computations were performed using a Cray-C94A and an R8000 Silicone Graphics workstation.

3. Results and discussion

In polymer blends, it is not practical to measure the accurate enthalpy of mixing, although knowing it is most efficient to determine the miscibility. We investigated model compound mixtures as well as polymer mixtures to quantitatively compare experiments and calculations of the enthalpy of mixing. The pairs as model compound mixtures we used were methyl acetate/*n*-octane, and 2,3-dichlorobutane/diethyl adipate, of which experimental enthalpies of mixing are available in the literature [21]. The *n*-octane and 2,3-dichlorobutane can be regarded as homologue compounds for polyethylene and PVC, respectively, while methyl acetate and diethyl adipate are homologues of aliphatic polyesters. As for aliphatic polyesters, we employed polyesters with even values of CH_2/COO ratios from 2 (poly(ethylene succinate) or PES) to 14 (poly(hexadecamethylene dodecamethylene dicarboxylate) or PHEDO), where the factor influencing the miscibility is not the sequence of the groups, but the overall ratio of CH_2/COO group in the polyesters [27]. The physical characteristics of polymer segments used are listed in Table 1. The densities in Table 1 were experimental values from the literature, except for poly(decamethylene decamethylene dicarboxylate) (PDODO), poly(dodecamethylene dodecamethylene dicarboxylate) (PDEDO), and PHEDO, of which densities were calculated by the connectivity indices method [39]. For the density prediction of polymers using MD simulations, the pcff force field is known to be able to predict well within an error of 1% [35,36]. However, this requires considerably longer simulation times than the PVT calculation we employed in this study. Here we focused on the miscibility of this blend system.

Individual configuration cells generated as initial structures contain 40–110 molecules for model compounds, and 6–17 molecules for polymer segments. For polymer segments, the number of atoms in main backbones is 24–80, depending on the size of single molecules. We constructed a single initial configuration for each blend system for MD simulations. A typical example as an initial configuration for PVC and poly(butylene succinate) (PBS) mixture is shown in Fig. 1. The cubic cell is surrounded with identical cubes. It illustrates part (3 × 1) of the array of an amorphous cell model obtained by applying periodic boundary conditions; only skeletal bonds are depicted and the identities of atoms are not displayed. To obtain configurations at given temperatures, MD annealing was performed for each pure compound and mixtures with volume-averaged densities from those of homopolymers in Table 1. For a PVC/poly(butylene adipate) (PBA) (about 50/50 volume ratio) mixture, a series of snapshots collected every 10 ps during MD simulation at 358 K is shown in Fig. 2. Local



(a)

(b)

Fig. 6. Enthalpies of mixing of (a) methyl acetate/*n*-octane mixtures at 298 K: —●—, calculated; - - -, experiment; and (b) 2,3-dichlorobutane/diethyl adipate mixtures at 298 K: —●—, calculated; - - -, experiment [21].

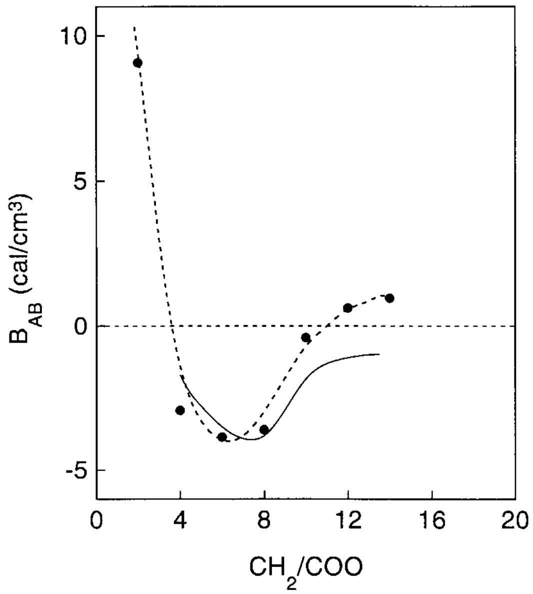


Fig. 7. Comparisons of the binary interaction parameters at 358 K for poly(vinyl chloride) and aliphatic polyesters containing various CH_2/COO values: –●–, calculated; ——, experiment [21,27].

changes of the chain configuration due to molecular motions caused by thermal energy may be noticed with overall shape not changed severely within the simulation time.

For time variation of total energy and non-bonded interaction energy of PVC/PBA (about 50/50 volume ratio) mixture, as shown in Fig. 3a and b, total energy spiked up to 1260 kcal/mol at the beginning of thermal annealing, and then decreased gradually. Around 50 ps, it reached an equilibration state by showing a leveling off in the energy. In the non-bonded interaction energy, the mixture showed a reduction in energy by 200 kcal/mol, and it took about 50 ps to reach the equilibration of molecular motions. For PBA, as an example of a pure polymer, the initial increase of total energy was 1070 kcal/mol, and the reduction of non-bonded interaction energy was 100 kcal/mol after annealing for 25 ps. It may be seen that the bulk of the reduction in energy is attributed to secondary interactions such as Coulombic and van der Waals interaction and that molecular segments are more strongly attracted by secondary interactions in the mixture.

The statistical ensemble for calculation of the cohesive energy density was generated. During MD simulations, the statistical configurations were collected every 5 ps during the equilibration stage after the initial dynamic for 50 ps. These configurations could be regarded completely uncorrelated to one another due to an adequate time interval of configuration collections. A typical example of the narrow distribution of 16 frame cohesive energy densities for PVC/PBS (about 50/50 volume ratio) mixture is shown in Fig. 4. It showed fluctuation with a standard deviation range within

Table 2
Enthalpies of mixing and binary interaction parameters of poly(vinyl chloride) and various aliphatic polyester blends

CH_2/COO	ϕ_{PVC}	ΔH_{mix} (cal/cm^3)	B (cal/cm^3)
2	0.498	2.267	9.07
4	0.517	− 0.731	− 2.93
6	0.512	− 0.981	− 3.85
8	0.484	− 0.900	− 3.60
10	0.492	− 0.101	− 0.40
12	0.494	0.157	0.63
14	0.483	0.240	0.96

0.1%. To obtain the narrower distribution of cohesive energy density, the outliers of distributions were eliminated.

The cohesive energy densities of several pure aliphatic polyesters at 358 K are summarized in Fig. 5. The cohesive energy density decreases due to the reduced polarity of polymers as the CH_2/COO ratio is increased. It should show a trend of approaching ultimately the cohesive energy density of polyethylene having infinity of the CH_2/COO value. On the other hand, the experimental cohesive energy density of *n*-octane is 58.2 cal/cm^3 at 298 K, while the calculated value was 58.79 cal/cm^3. For PVC, the experimental cohesive density is 88 to 117 cal/cm^3 at 298 K, and the calculated value is 82.99 cal/cm^3 at 358 K. This is quite reasonable if we admit the temperature dependency of the cohesive energy. The quantitative accuracy of calculated cohesive energy depends mainly on theoretical model, force field, and limitation of the method itself [26]. From the accuracy of the cohesive energy densities of model compounds and polymers, the calculation method was confirmed to be quite reasonable.

The enthalpies of mixing for various mixtures were calculated using Eq. (1) for comparison with experimental values shown in the literature [27,28]. Lai et al. used group contribution methods such as the MGQ and UNIQUAC models [21]. In these methods, the group interaction parameters obtained from the heats of mixing for various esters, alkanes, and chlorinated hydrocarbon liquids were used to predict the heats of mixing for the monomeric units of aliphatic polyesters and PVC. Particularly, for the MGQ model, liquid mixtures of ester, alkane, and chlorinated hydrocarbon showed accuracy within a 9% relative error. Although we have discussed our computational results by comparing with theoretical predictions from the MGQ or UNIQUAC methods as well as experimental results, it was not our intention in this study to compare the pros and cons of these methods, which are based on different levels of computational approximations. The MGQ method uses a thermodynamic model like the group contribution method coupled with a single fluid approximation with the well defined group interaction parameters obtained from experiments, while the MD simulation employing force fields including energetic parameters is based on a relatively simple thermodynamic equation for calculating the enthalpy of mixing. The accuracy of the MGQ method depends on the deliberate choices of structural groups and the precise estimation of surface parameters of the groups involved, whereas the molecular simulation requires a high quality of force field describing intermolecular energies, particularly, electrostatic and van der Waals energies responsible for hydrogen bondings in these systems. Within the frame of calculation adopted, the force field, i.e. pcff [32–34], used in this study gives a good estimation of cohesive densities with relative errors within about 5%. The less polar molecules appear to show better agreement between experimental and calculated cohesive energy.

Fig. 6a and b show enthalpies of mixing for methyl acetate/*n*-octane and 2,3-dichlorobutane/diethyl adipate mixtures, respectively. The methyl acetate/*n*-octane system is immiscible, having a positive enthalpy of mixing, and the 2,3-dichlorobutane/diethyladipate system is miscible, showing a negative enthalpy of mixing. The calculated enthalpies of mixing are close to experimental values. At a 50/50 volume ratio of methyl acetate/*n*-octane mixtures, the calculated value is $+3.37$ cal/cm^3 at 298 K, while the experimental value was $+3.8$ cal/cm^3. On the other hand, the MGQ and UNIQUAC method predicted about $+4.3$ cal/cm^3 and $+2.5$ cal/cm^3, respectively for the enthalpy of mixing.

For blends of PVC and aliphatic polyesters, interaction parameters calculated from the enthalpy of mixing at 358 K were compared with literature experimentals [21,27], as summarized in Fig. 7. The binary interaction parameter (*B*) was calculated from calculated enthalpies of mixing using the equation, $\Delta H_{\text{mix}}/V = B\phi_1\phi_2$. According to the calculated results shown in Fig. 7, the blends show a miscibility window between $CH_2/COO = 4$ and 10. There are two types of hydrogen bonding governing the miscibility between PVC and polyesters; one is the interaction between hydrogen of methylene and chlorine of PVC, and another is the interaction between a hydrogen of PVC and carbonyl group of polyester. It is difficult to separate quantitatively two attractive interactions, which increase and approach to zero as CH_2/COO increases.

Upon overall consideration, at low values of the CH_2/COO ratio, there is a strong attractive interaction within polar polyester molecules and the self-association results in blend immiscibility. As the value of CH_2/COO ratio is increased, the intermolecular interaction between PVC and aliphatic polyesters begins to overcome the self-association energy of polyesters. Although the energy should be definitely weak, since the interaction intramolecular in polyesters is not usually classified as strong self-association, the energy should be stronger at the lower CH_2/COO ratio. The blends with a value of the CH_2/COO ratio between 5 and 7 show an optimum of intermolecular interactions. The maximum miscibility appears at a CH_2/COO ratio of 6, where the *B* was equal to -3.85 cal/cm^3. At higher values of the CH_2/COO ratio, the interaction energy becomes weaker due to the scarcity of the interaction, and correspondingly begins to show immiscibility. This means that the interaction present does not become weaker rather the number of favourable interactions decreases. It has been reported [28] for this blend system that the immiscibility at high carbonyl content may be due to an unfavourable balance of intramolecular and intermolecular interactions mostly occurring between methylene and carbonyl groups. In the immiscible region, due to the lack of the favourable interactions, entropy effects such as unfavourable free volume effect should become more prominent, which were not considered at all in the calculation. The detailed results of the calculation from this study are shown in Table 2.

The trend of interaction parameters from MD simulations in this study is generally in accordance with those by the

MGQ method, except that the minimum of the *B* values in this study is located at a CH_2/COO value of 6, while the minimum by the MGQ method is located around a CH_2/COO value of 3. At the high CH_2/COO value as in the MD method, the MGQ method also predicted a positive *B* value, where only the enthalpic change is considered. Coleman et al. used a solubility parameter method modified with an added term to account for the presence of favourable intermolecular interactions in polymer blends [40]. For a given system, the optimum miscibility is located at a CH_2/COO ratio of 3.5. In the framework of a miscibility guide they suggested, the miscibility is dependent on the balance between the favourable strong interactions, like hydrogen bonds, and the physical interactions, in general unfavourable. This latter one is resumed by solubility parameters. As the pure polymer solubility parameters difference increases stronger interactions are needed in order to achieve the miscibility for this system.

Experimentally, the maximum miscibility by the melting point depression method [27] is located around a CH_2/COO ratio of 7, as indicated by a solid line in Fig. 7. Riedl et al. have reported [28] that for the thermodynamic study of this blend system by inverse-phase gas chromatography at 393 K, the *B* values are dependent upon the methylene to carbonyl ratio, reaching a minimum for a value of 5, which is corresponding to PVC/poly(caprolactone) blends. On the other hand, for the mixtures of small analogue compounds, the minimum of *B* was observed at a CH_2/COO ratio of 6.

When calculated *B* values are compared with experimental ones, it should be remembered that the empirical method unavoidably takes entropic effects of mixing into consideration, since free volume effects may be a major influence on the miscibility in the case of the interactions being weak or in conditions close to the immiscibility boundary, although the contribution from the ideal or combinatory term is quite small for high polymer blends. Thus, the experimental *B* should presumably include the error to some extent from the genuine *B* considered in calculations. It is thus surmised that the entropic effects of mixing induces a large difference between *B* values from calculation and experiment at the high values of CH_2/COO ratio, where the entropic effects of mixing rather than enthalpic effects play a relatively important role.

Good agreements were generally observed among miscibility behaviours predicted from the calculations of this MD study and the MGQ method, and those observed empirically through the melting point depression method and high temperature inverse-phase gas chromatography. It is argued that the MD calculation may be used as a good method to obtain the quantitative evaluation of enthalpy of mixing of polymer blends.

4. Conclusion

The MD simulation to calculate the enthalpy of mixing as a criterion of the polymer miscibility was performed in this study. The method consists, using a commercial module, of a amorphous cell construction and MM/MD simulations for the calculation of pairwise cohesive energy densities and the consequent enthalpies of mixing. The results of calculation with model compound mixtures and polymer systems compare well with literature experimental data. For comparison with experiment as in this study, a highly precise experimental enthalpy of mixing is required. The accuracy of this calculation depends on theoretical construction of the model, force field, and the limitation of the method itself [26]. The absolute values of cohesive energy density obtained in the calculation show some deviations from the experimental values. The calculation may need enormous computation time to obtain more accurate results by demanding a larger system or MD simulation steps. It may require the adjustment of force field for better prediction. Despite these facts, the difference between the cohesive energy density before and after mixing could be applied efficiently to determine the enthalpy of mixing within an acceptable accuracy. It demonstrates the positive results with the prediction of the enthalpy of mixing by MD simulations. Other examples of polymer blends are under investigation for further research.

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