Molecular dynamics modelling for the analysis and prediction of miscibility in polylactide/polyvinilphenol blends

Inger Martinez de Arenaza [a], Emilio Meaurio [a], Borja Coto [b], Jose-Ramon Sarasua [a],*

[a] School of Engineering, University of the Basque Country (EHU-UPV), Alameda de Urquijo s/n, 48013 Bilbao, Spain
[b] Tekniker, Tribology Unit, Otaola 20, 20600 Eibar, Spain

ABSTRACT

This paper analyzes the miscibility state of Poly(L-Lactide) (PLLA) and Poly(DL-Lactide) (PDLLA) with Poly(styrene) (PS) and Poly(vinyl phenol) (PVPh) by means of Molecular Dynamics (MD) simulations performed using the COMPASS force-field. Immiscibility was found in polylactide/PS blends while miscibility was the result in polylactide/PVPh blends, both previsions agreeing with the experimental behaviour. The values calculated for the Flory-Huggins interaction parameter, χ, have been compared with the experimental results and with estimations based on existing miscibility models. Even though the dependence of χ with composition and the prediction of miscibility is correct, both the solubility parameters and the interaction parameters obtained prove that molecular modelling tends to underestimate the strength of the interactions. The observed differences are explained in terms of the absence of cooperativity effects for oligomeric chains used in molecular modelling of high molecular weight polymer blends.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Blending of existing polymers is an interesting route towards the development of new polymeric materials. In the past decades only experimental investigation methods have been available; blends were prepared in the laboratory and subsequently analyzed at different temperatures to obtain the phase behaviour of the systems. Unfortunately, the experimental study of polymeric blends can be cumbersome, and contradictory results can be found in the literature for certain systems. For example in case of blends prepared by solvent casting, the so called $\Delta\chi$ effect [1] can revert a phase separated system into a completely miscible one [2,3]. In case of blends prepared from the melt in which one of the partners undergoes depolymerisation reactions at high temperatures, the reduction of molecular weight can improve the miscibility of otherwise immiscible polymer systems. In other cases, blending from the melt can result in degradation reactions modifying the miscibility behaviour of the system [4]. In recent years molecular modelling is gaining acceptance as a reliable technique to analyze the miscibility behaviour of polymer materials [5]. Its main advantage is to allow the prediction of the miscibility regardless of the availability of the polymers to be investigated.

Nowadays, COMPASS (condensed phase optimized molecular potentials for atomistic simulation studies) is one of the most recent and powerful force fields developed for the study of condensed phase systems [6]. Compared to earlier force fields, the most important difference is that non-bonded terms (such as the Lennard-Jones 6–9 potential) have been parametrized using condensed phase properties such as densities and cohesive energies of low molecular weight liquids [6]. Consequently, the valence parameters had to be also reparametrized due to the coupling between the valence and non-bond parameters [1]. Condensed phase properties of polymers were not included in the parametrization perhaps because their cohesive energies are hard to measure and many of the reported experimental values usually rely in arguable approximations [7–11]. Finally, the COMPASS force-field was validated for low molecular weight compounds using properties such as the enthalpy of vaporization (related to the cohesive energy) [6]. Hence, the COMPASS force-field is assumed a good approximation for condensed phase systems, which include polymer systems by extension [6]. In fact, several polymer systems have been investigated using this force-field, and the phase behaviour has been correctly anticipated [5]. However, accurate quantitative works comparing experimental and molecular modelling results are scarce since most of the studies focus on the analysis of miscibility using exclusively one of the two approaches.

Polylactides (PLA) are biodegradable materials that have attracted considerable research effort in the biomedical field in recent

---

* Corresponding author.
  E-mail address: jr.sarasua@ehu.es (J.-R. Sarasua).

years [12]. The presence of asymmetrical carbon atoms in the polylactide chain leads to the existence of different stereoisomers. Optically pure polylactides, poly(L-lactide), hereafter called PLLA, and poly(D-lactide), PDLA, show stereoregular moiety distribution along their main chain and therefore are semicrystalline polymers. If however there is only some degree of regularity in the LL/DD moiety distribution then polylactides can be regarded as copolymers whose crystallization ability decreases with decreasing optical purity [13]. Finally, optically non-active polylactides, denoted as PDLLA result from racemic or meso monomers and so they can be regarded as *atactic* copolymers with random moiety distribution in the chains and because of this structural irregularity PDLLA is an amorphous polymer. The range of applications for these materials is continuously growing, and blending is among the most promising routes to develop new materials. However, only a few miscible counterparts of high molecular weight have been reported so far, including poly(methyl methacrylate), poly(methyl acrylate), poly (vinyl acetate), poly(ethylene oxide) and poly(vinyl phenol) [2]. Indeed, the analysis of the miscibility of some systems has been controversial. For example, only partial miscibility was initially reported for blends of Polylactides with Poly(vinyl phenol) (PVPh), however in a later study those preliminary results were attributed to the $\Delta \chi$ effect, and complete miscibility was probed for the PLA/PVPh blends [2–4].

To our knowledge up to date only qualitative comparisons have been possible in polymer blends on the basis of their miscibility behaviour determined both experimentally and by molecular modelling. The aim of this paper is to gain a deeper comprehension of the miscibility state in polymer blends based on specific interactions by using molecular modelling analysis. The PLLA/PVPh and PDLLA/PVPh systems studied here are of special interest because the Flory-Huggins interaction parameter was experimentally obtained in two previous works as a function of composition using different techniques [2,3], hence the interest of predicting miscibility in polymer blends is not only technological but also fundamental because in this case it will be possible to perform a direct comparison between the experimental and calculated parameters accounting for miscibility. Finally, a theoretical model is also used to estimate values of χ and to aid in the interpretation of the composition dependence observed for the interaction parameter.

2. Simulation details

The miscibility state of Poly(L-lactide) (PLLA) with Poly(vinylphenol) (PVPh) has been investigated using Molecular Dynamics (MD) simulations performed at room temperature (298 K). The Discover molecular mechanics and dynamics simulation module of the Materials Studio (v. 4.0) software package obtained from Accelrys was used for this task. The bulk phases were generated using Amorphous Cell program, which uses the combined use of the arc algorithm developed by Theodorou and Suter [14] and the scanning method of Meirovitch [15].

Initial structures were built using the rotational isomeric state (RIS) model of Flory [16] that describes the conformations of the unperturbed chains. A 5000 step minimization was subsequently carried out using the conjugate gradient method (GCM), which utilizes the Polak-Ribiere algorithm. The minimized amorphous structures were inspected for proper space filling and for a correct number of contacts. Whenever inappropriate blending was suspected, new cubic cells were attempted, replacing the former structures in case of lower energy after minimization (in most cases initial cells were however the best option since they were built from the unperturbed statistics).

The COMPASS (Condensed phase Optimized Molecular Potentials for Atomistic Simulation Studies) force-field has been used in

this research, as it has been specially optimized to provide accurate condensed phase equation of state and cohesive properties for molecules containing a wide range of functional groups [6,17]. COMPASS is based on PCFF (Polymer Consistent Force-Field), and is the first ab initio force-field used for modelling interatomic interactions [17]. The potential energy of a system can be expressed as a sum of valence (or bond), crossterm, and non-bond interactions:

$$E_{total} = E_{valence} + E_{crossterm} + E_{nonbond} \qquad (1)$$

the energy of valence interactions, $E_{valence}$, comprises bond stretching (E_{bond}), valence angle bending (E_{angle}), dihedral angle torsion ($E_{torsion}$), and inversion (also called outof plane interactions and denoted as $E_{inversion}$ or E_{oop}) terms. In addition, modern force fields like COMPASS include a Urey–Bradley term (E_{UB}) to account for interactions between atom pairs in 1–3 configurations (i.e., atoms bound to a common atom):

$$E_{valence} = E_{bond} + E_{angle} + E_{torsion} + E_{oop} + E_{UB} \qquad (2)$$

cross terms included in $E_{crossterm}$ increase the accuracy of the force-field by introducing correction factors to the valence energy to account for the interdependence existing between different valence terms. For example, the term named $E_{bond-bond}$ considers stretch–stretch interactions between two adjacent bonds. Similarly, the COMPASS force-field includes stretch–bend, bend–bend, stretch–torsion, bend–torsion and bend–bend–torsion terms. Finally, the non-bond interaction term, $E_{non-bond}$, accounts for the interaction between non-bonded atoms (also called secondary interactions) and includes the van der Waals energy, E_{vdW}, the Coulomb electrostatic energy, $E_{Coulomb}$, and the hydrogen bond energy, E_{Hbond}, as:

$$E_{non-bond} = E_{vdW} + E_{Coulomb} + E_{Hbond} \qquad (3)$$

in COMPASS E_{vdw}, is described by Lennard-Jones 6–12 potential. The partial charges of atoms are estimated by charge-equilibration method and electrostatic energy is calculated by Ewald summation method, highly accurate in the calculation of long-range interactions [19]. An accuracy of 0.0001kcal/mol with an update width of 5 Å were applied to evaluate electrostatic interactions.

After generation and minimization, all the systems were refined by molecular dynamics calculations. 3D periodicity was configured using cubic unit cells. The density of the blends is calculated from the densities of individual polymers and the composition of the blend (Table 2). The sizes of the amorphous cubic cells, calculated by the Amorphous Cell module according to the number of chains located into the cell and the density of the blend, range from 11.85 Å for the PVPh cubic cell to 22.47 Å for the cell containing 85.7 wt% of PLLA (system 10 in Table 2). The number of atoms involved in the simulations range from 175 for neat PVPh to 1100 for system 10. MD simulations were performed with the "Discover" molecular mechanics and dynamics module, and were equilibrated for 200 ps under constant temperature and density (NVT ensemble). The time step of 1 fs is used to ensure the stability of simulation.

3. Results and discussion

The solubility parameters of the pure polymers, PLLA, PDLA, PVPh and PS exert tremendous influence on blend miscibility [20]. Therefore, the Hildebrand solubility parameter [21], δ, has been calculated for different chain lengths to obtain the minimum representative polymer chain length. The solubility parameter is defined as the root of the cohesive energy density (CED), where the CED is the ratio between the calculated cohesive energies, E_{coh}, and volumes, V, according to equation (4):

$$\delta = \sqrt{CED} = \sqrt{\frac{E_{coh}}{V}} \qquad (4)$$

The solubility parameter describes the attractive strength between the molecules of the material [22]. Fig. 1 shows the values of δ obtained by simulation vs the number of repeat units for the polymers studied in this paper. The length above which the solubility parameter reaches a nearly constant value can be assumed as the minimum molecular size representing the real polymer chain. As can be seen, PLLA and PDLA reach a clear plateau for chain lengths of about 20 units; while in case of PS the plateau appears at only about 10 repeat units. On the other hand, the trend of solubility parameter of PVPh is less clear, probably due to the difficulties involving the modelling of Hydrogen bonds. For this polymer, the solubility parameter varies only very smoothly for chains above 10 repeat units, and this length has been chosen to model the PVPh chains. Table 1 lists the solubility parameters calculated for the representative lengths and compares them with the experimental values obtained by solubility testing experiments, considered the most reliable technique for the determination of δ [11]. As can be seen, calculated values are in all cases about 10−20% below the experimental values, indicating that molecular modelling underestimates the strength of the attractive interactions in the neat polymers. The deviations observed should not be attributed to the difference in length between the modelled and the real chains, because other authors have also found similar negative deviations in spite of using large molecular models. For example, Gestoso et al. [36] investigated the amorphous PVPh chain using a model with up to 250 repetitive units and obtained a solubility parameter of 8.7 ± 1.2 (cal/cm³)^(1/2). Negative deviations have also been found for other pure polymers [5,18].

The calculation of the CED (E_{coh}/V) values for the blends by means of atomistic simulations allows the determination of the energy of mixing, ΔE_{mix} (approximately equivalent to the so called interaction energy density, B), according to equation (5) [5]:

$$\Delta E_{mix} = \phi_A \left(\frac{E_{coh}}{V}\right)_A + \phi_B \left(\frac{E_{coh}}{V}\right)_B - \left(\frac{E_{coh}}{V}\right)_{mix} \qquad (5)$$

where the terms in parenthesis represent the cohesive energies of the pure polymers (**A** and **B**) and the blend (**mix**), and φ_A and φ_B represent volume fractions of the polymers in the blend.

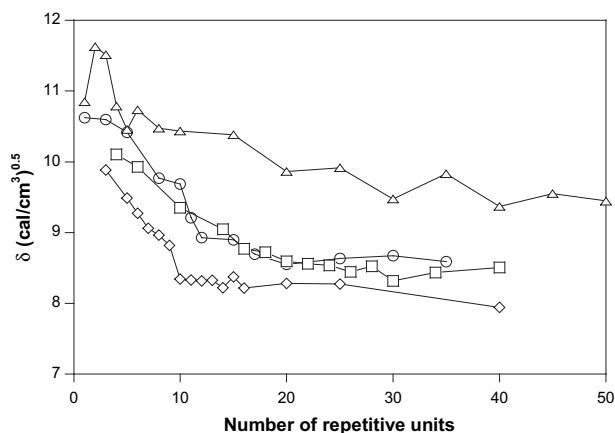Finally, the Flory-Huggins interaction parameter χ, can be calculated from ΔE_{mix} according to [25]:

Fig. 1. Calculated solubility parameter versus number of repeat units for ($\triangle$) PVPh, ($\square$) PLLA, ($\bigcirc$)PDLLA and ($\diamond$) PS.

Table 1
Calculated and experimental solubility parameters for the polymers studied in this paper.

Polymer	MD Calculations			Experimental values[a]	
	Repeat units	Molecular weight	δ_{MD} (cal/cm³)^0.5	δ_{exp} (cal/cm³)^0.5	Reference
PLLA	20	1440	8.5	10.6	[23]
PDLLA	20	1440	8.6	10.6	[23]
PVPh	10	1200	10.4	12.0	[24]
PS	10	1040	8.4	9.4	[11]

[a] All the experimental values have been obtained by solubility testing experiments, considered the most reliable technique for the determination of δ [11].

$$\chi = \left(\frac{\Delta E_{mix}}{RT\phi_A\phi_B}\right)V_m \qquad (6)$$

where V_m is the molar volume of the repeat unit chosen as reference (PLA). This value is $V_m = M/\rho = (72 \text{ g/mol})/(1247 \text{ g/cm}^3) = 57.7$ cm³/mol, R is the molar gas constant and T is the temperature of the simulation in Kelvin. A positive value of the Flory-Huggins interaction parameter indicates immiscibility for blends of high molecular weight polymers, but in general the critical value of χ obeys equation (7):

$$(\chi_{AB})_{critical} = \frac{1}{2}\left(\frac{1}{\sqrt{m_A}} + \frac{1}{\sqrt{m_B}}\right)^2 \qquad (7)$$

where m_A and m_B represent the degree of polymerization of the pure polymers. If the interaction parameter of the blend is smaller than $\chi_{critical}$ the system is miscible in the whole composition range. If χ is slightly larger than the critical value, the blend exhibits partial miscibility: two phases coexist containing both components. For larger values of χ, the components are completely immiscible. By comparison of the values of χ calculated by atomistic simulation with the critical value (equation (7)) the miscibility behaviour of the system can be predicted [5].

We will first discuss the results obtained for blends with polystyrene, (systems PLLA/PS and PDLLA/PS), because a simpler analysis can be expected due to the lack of specific interaction. Fig. 2 shows snapshots for PDLLA/PS blends of different composition. As can be observed, in the molecular dynamics simulations, the minimized structures tend to favour self contacts over intermolecular contacts, suggesting the immiscibility of the system.

Similar results (not shown here) have also been found for the system PLLA/PS. In addition, from the values of ΔE_{mix} calculated for the amorphous cells of Fig. 2, a tentative value can be calculated for χ using equation (6) and then compared to $\chi_{critical}$ calculated by equation (7). The value of $\chi_{critical}$ for the chains simulated in this paper is 0.1457 and the values of χ obtained from the amorphous unit cells in Fig. 2 are in all cases above this critical value, indicating the immiscibility of the system.

It is noteworthy that, according to the Flory-Huggins model, χ is a measure of the strength of intermolecular contacts in intimately (randomly) mixed blends. Since miscible systems usually show certain non-randomness, χ includes both an enthalpic and an entropic contribution (the latter correcting for the departure from randomness). Nevertheless, a large number of contacts can be assumed in any miscible blend because miscibility implies homogeneity at a small scale. In case of amorphous cell modelling of an immiscible system, simulations will tend to increase the fraction of intramolecular contacts and reduce the intermolecular contacts. In these cases, the situation is far from random mixing and the values obtained for χ using molecular modelling cannot be compared with those provided by theoretical approaches assuming random mixing (such as Hildebrands approach, see later in this paper). Also
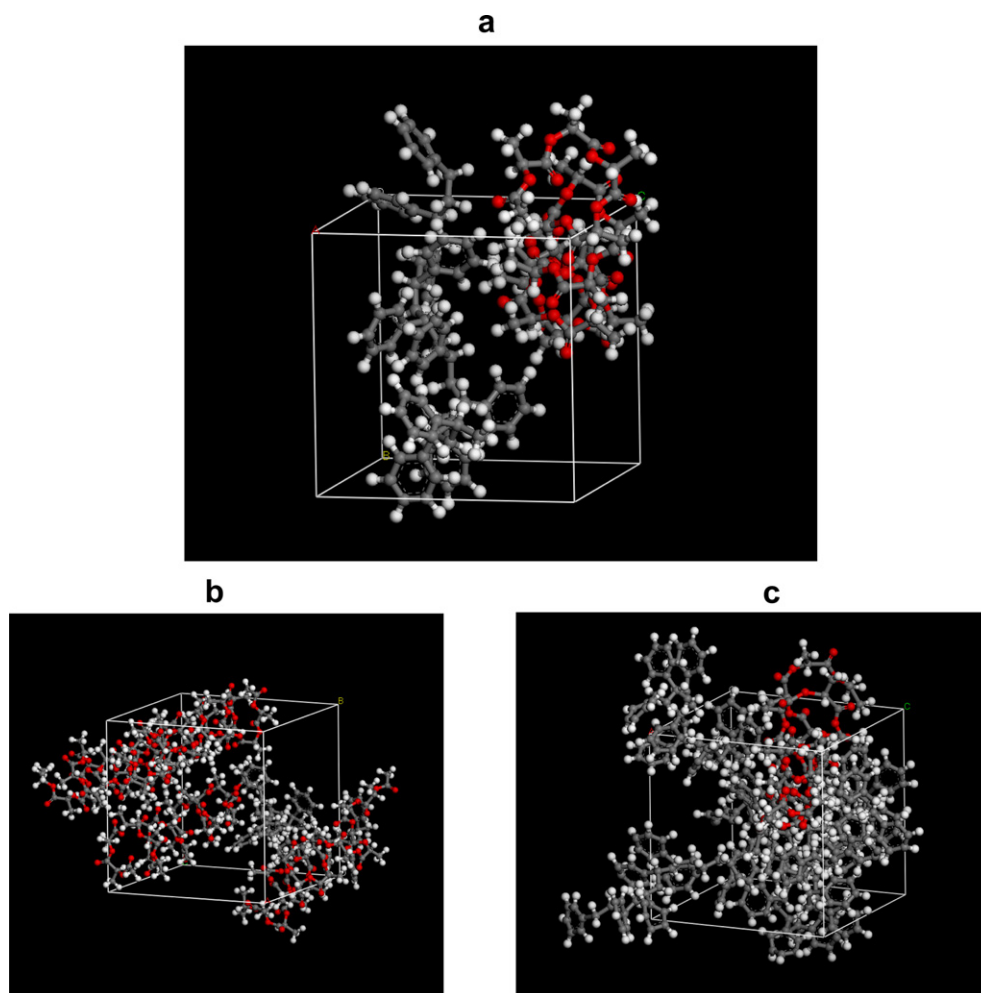
a

b   **c**

Fig. 2. Snapshot of the amorphous unit cells for PDLLA/PS blends of different composition, containing a) 1-1, b) 4-1 and c) 1-4 chains of PDLLA-PS.

experimental values are not available for the PLLA/PS system. Since the basic significance of the χ values obtained for this system is the prediction of immiscibility, they have been omitted [26].

Consequently we will focus on polylactide blends with PVPh where the occurrence of specific interactions due to the presence o hydroxyl groups has already been proven [2,3]. Fig. 3 shows the snapshots of PLLA/PVPh blends of different composition. Compared to the polylactide blends with PS, a larger ratio of intermolecular contacts is observed in PLLA/PVPh suggesting the presence of a significant amount of attractive hydrogen bonding interactions between OH groups of PVPh and C=O groups of both PLLA and PDLLA. Fig. 3d and e sample some of the hydrogen bonds detected by the Discovery module; Fig. 3d displays the hydrogen bond between the hydroxyl group of PVPh and the C=O group of PLLA and Fig. 3e shows the hydrogen bond between different hydroxyl groups of PVPh. Therefore, the molecular modelling simulations performed in this work apparently capture correctly the specific interactions actually present in these systems.

A similar analysis has been performed for the PDLLA/PVPh system, and similar qualitative results have been obtained. Table 2 lists detailed information for the modelled blends, including molar ratio, weight percentage, density, molar volume and the Flory-Huggins interaction parameter calculated from ΔE_{mix} values and equation (6).

Fig. 4 compares the interaction parameters obtained by simulation analysis with the experimental values according to references 2 and 3. This figure also includes estimated values (according to the

assumptions indicated later on), valuable to understand the dependence of χ on composition. The experimental interaction parameter for the PLLA/PVPh system [2] included in Fig. 4a was obtained from melting point depression studies, hence this value corresponds to the equilibrium melting temperature of PLLA (about 210° C). In addition, PLLA was observed to crystallize only in the range of compositions from 70/30 to pure PLLA [2] and therefore the measured value can be considered a mean value within that range of compositions. Also, high molecular weight samples were used for the experimental study, but as long as the interaction parameter is assumed to reflect exclusively the strength of the interactions, this should be a minor concern for the comparison performed in Fig. 4. As can be seen in Fig. 4a, the molecular modelling calculations underestimate the magnitude of the interaction parameter. In addition, noting that UCST behaviour is typical in systems for which miscibility can be attributed to the occurrence of attractive specific interactions, we should expect an even larger experimental negative value for χ at room temperature, and therefore a larger difference.

Fig. 4b compares the calculated values for the PDLLA/PVPh system with the experimental results taken from reference 3. For this system, mixing enthalpies were measured directly by DSC at a temperature of about 140° C, and the interaction parameter was therefore obtained at that temperature for different compositions [3]. However, it must be noted that the mixing exotherm was found to overlap with the glass transition temperature of PVPh, and some overestimation of χ can expected, specifically for the blends with
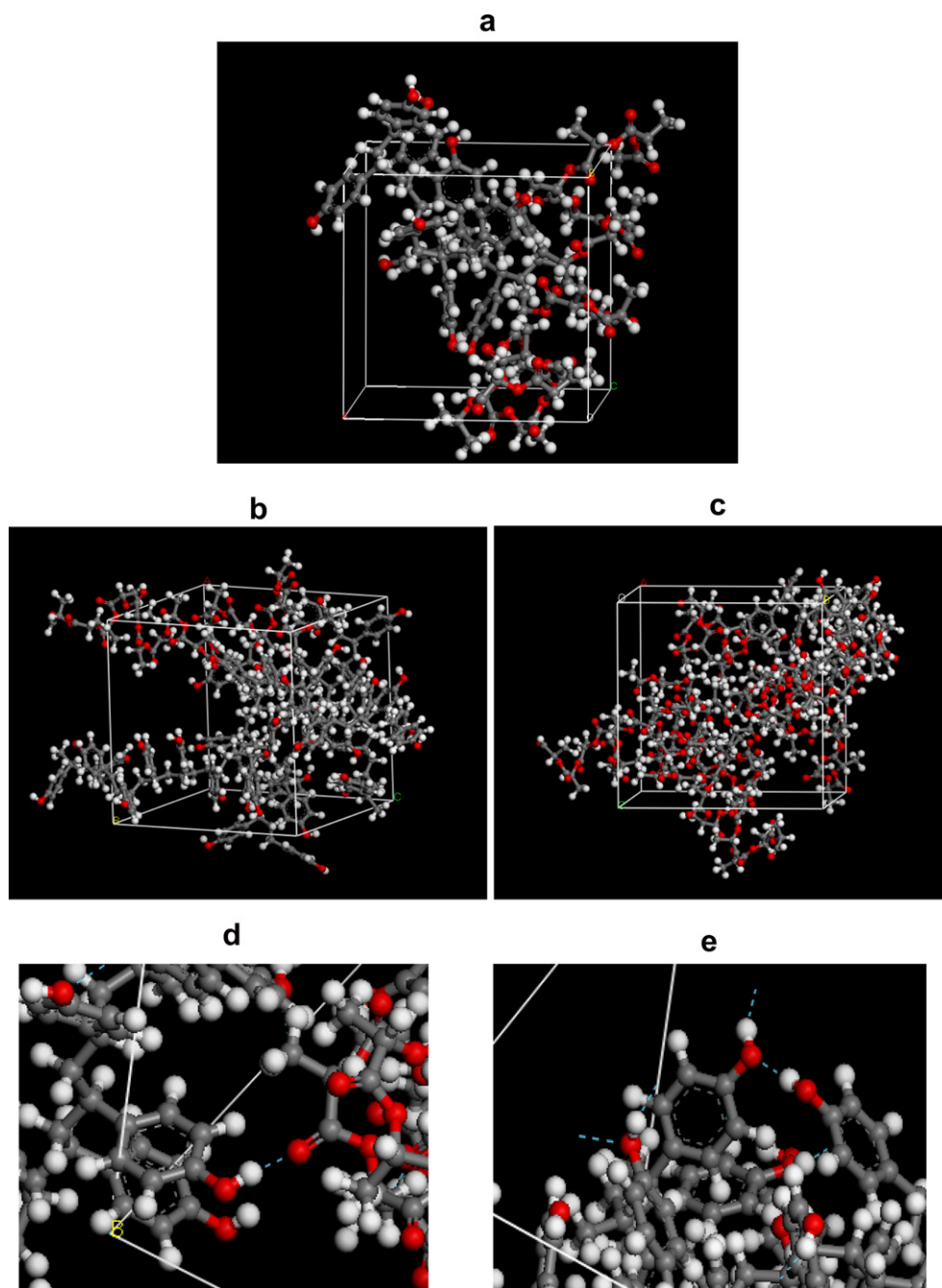
a

b

c

d

e

Fig. 3. Snapshot of the amorphous unit cells for PLLA/PVPh blends of different composition, containing a) 1-1, b) 1-4 and c) 4-1 chains of PLLA-PVPh. Snapshots d) and e) display respectively O−H⋯O=C and O−H⋯O−H hydrogen bonds.

larger PVPh contents [3]. As can be seen in Fig. 4b, the calculated values are again smaller in magnitude than the experimental results. However, the dependence on composition is very similar for both sets of results; in both cases χ shows a strong dependence on composition and its magnitude increases as the content of PVPh in the blend increases.

To summarize, both the solubility parameters presented in Fig. 1 and the interaction parameters shown in Fig. 4 suggest that molecular modelling tends to underestimate the strength of the interactions. Certain part of the difference could be attributed to incompletely equilibrated systems. Polymer blends are highly entangled systems that during the MD simulations can remain trapped in local minima instead of evolving to the global minimum.

This point can be specifically applied to the calculated points deviating upside in Fig. 4; probably they would shift downside in better equilibrated systems. But even if those points were corrected, calculated values would remain smaller than the experimental results; this is especially true recalling that the experimental values at room temperature should be larger than those plotted in Fig. 4, which were measured at high temperatures. The exact reason is not straightforward, but the parametrization of the COMPASS force-field using low molecular weight compounds may exclude features specific to polymeric chains arising from repeat unit linking; for example Cooperative Hydrogen Bonding by the proximity effect mechanism [28,29]. This is a well known mechanism in the formation of interpolymer complexes [28], but is not restricted to that kind

Table 2
Detailed results obtained from the simulations of the modelled PLLA/PVPh and PDLLA/PVPh blends.

System number	PLA molar ratio (%)	Number of PLA–PVPh chains in the cell	wt% PLA	Density [a] (g/cm^3)	$\chi_{PLLA/PVPh}$	$\chi_{PDLLA/PVPh}$
1	0	0–1	0	1.25	–	–
2	28.6	1–5	19.3	1.2495	−0.75	−0.87
3	33.3	1–4	23.1	1.2494	−0.58	−0.44
4	40	1–3	28.6	1.2492	−0.67	−0.41
5	57.1	2–3	44.4	1.2488	−0.34	−0.22
6	66.7	1–1	54.5	1.2485	−0.66	−0.06
7	75	3–2	64.3	1.2482	−0.40	−0.05
8	80	2–1	70.6	1.2480	−0.29	−0.13
9	88.9	4–1	82.7	1.2476	−0.29	−0.08
10	90.9	5–1	85.7	1.2475	−0.63	−0.11
11	100	1–0	100	1.2470	–	–

[a] densities calculated from the values corresponding to the individual polymers [27].

of materials and has been proven to exist by quantum mechanical calculations even when a dimmer bonds to a polymeric chain [29]. According to this mechanism, if two chains bond each other, the formation of the first bond is accompanied by a favourable enthalpic contribution and an unfavourable entropic contribution because the second chain losses the translational degrees of freedom [28]. If the neighbouring repeat unit forms a second bond, the additional enthalpic contribution is the same as for the first bond, but the unfavourable entropic contribution is smaller because the freedom degrees for this unit were already restricted. Therefore, the formation of two neighbouring bonds is accompanied by a larger change in the free energy of mixing (in molar basis), and hence by a larger value of χ. As the number of bonds increases, the unfavourable entropic contribution decreases, because the formation of each new bond decreases translational or rotational degrees of freedom. Hence, the free energy increases with the number of bonds, even though the largest variation occurs for the formation of the second bond. This effect cannot be accounted for using single functional low molecular weight analoges, because the formation of each bond is accompanied by identical enthalpic and entropic contributions.

In addition, Fig. 4 also includes the values of χ estimated as described below. According to the Flory-Huggins theory [30], the free energy of mixing per mole of lattice sites for a mixture of polymer A and polymer B is:

$$\frac{\Delta G_{mix}}{RT} = \left(\frac{\phi_A}{N_A}\right)\ln\phi_A + \left(\frac{\phi_B}{N_B}\right)\ln\phi_B + \chi\phi_A\phi_B \quad (8)$$

where N_i is the number of segments in polymer i. For systems in which only dispersive interactions can be expected, χ can be calculated using the approach proposed by Hildebrand [31]:

$$\chi = \frac{V_m(\delta_A - \delta_B)^2}{RT} \quad (9)$$

According to this approach, interaction parameters can only adopt positive values, in agreement with the repulsive nature of the dispersive interactions. In systems containing also specific interactions (attractive interactions), their contribution can be introduced using the model proposed by Painter and Coleman [32]:

$$\frac{\Delta G_{mix}}{RT} = \left(\frac{\phi_A}{N_A}\right)\ln\phi_A + \left(\frac{\phi_B}{N_B}\right)\ln\phi_B + \chi_{dis}\phi_A\phi_B + \frac{\Delta G_H}{RT} \quad (10)$$

where the term on χ_{dis} accounts for the contribution of the dispersive interactions and is calculated using equation (9) and "special" solubility parameters that exclude the effect of specific interactions to the cohesive energy; and the last term accounts for the contribution of the specific interactions to the energy of mixing. Comparing equations (8) and (10), the interaction parameter for the PLA/PVPh blends can be calculated according to:

$$\chi\phi_A\phi_B = \chi_{dis}\phi_A\phi_B + \frac{\Delta G_H}{RT} \quad (11)$$

The values of the "dispersive" solubility parameters for PLA and PVPh are respectively 10.1 and 10.6 (cal/cm^3)$^{0.5}$ according to group contribution methods [7]; hence $\chi_{dis} = 0.0244$ (equation (9)), indicating a small dispersive contribution. The last term in equation 11 can be estimated considering the following approximations, justified in the next paragraphs:

i) The entropic contribution to ΔG_H is neglected.
ii) The autoassociation of PVPh is considered to remain almost unchanged upon the addition of the polyester.
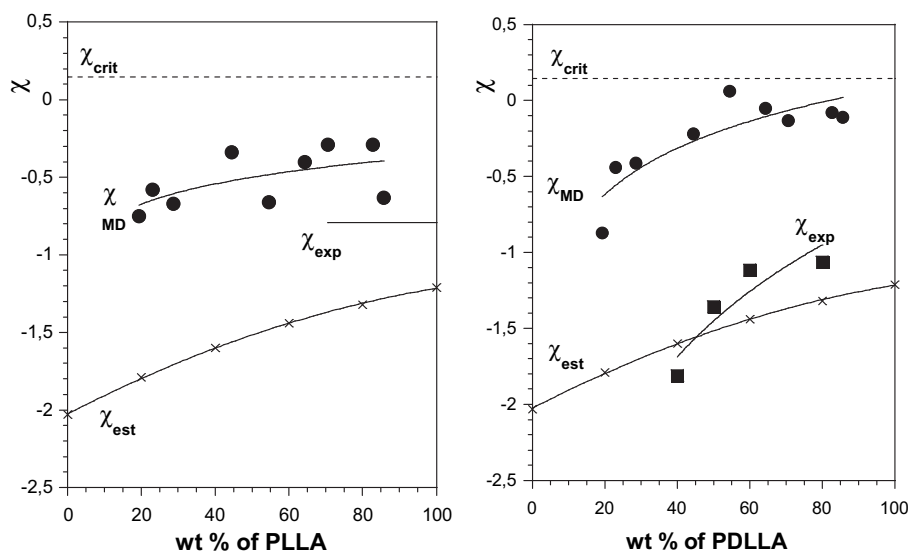

Fig. 4. Interaction parameters for the PLLA/PVPh system (left) and PDLLA/PVPh system (right). Temperature is 298K for the calculated (χ_{MD}) and estimated (χ_{est}) values, 483K for χ_{exp} PLLA/PVPh and 413K for χ_{exp} PDLLA/PVPh.

iii) The extent of the interassociation is assumed proportional to the product of the molar fractions.

Neglecting the entropic contribution to ΔG_H is a minor approximation, equivalent to assuming that the blend behaves as a regular solution to a good approximation. Therefore, the term on ΔG_H only includes the enthalpic contribution.

The second assumption is supported by the association behaviour observed on similar blends, such as the PMMA/PVPh system [33]. To explain why the autoassociation of PVPh was observed to remain almost constant regardless of the content of Poly(methyl methacrylate) at least two factors can be considered. The first factor is the lower strength of the $C=O\cdots H-O$ hydrogen bonds compared to the $O-H\cdots O-H$ ones: the enthalpy of hydrogen bonding for the former bond ($h_A = -3.8$ kcal/mol) is smaller than the enthalpies corresponding to the formation of hydroxyl dimers ($h_2 = -5.6$ kcal/mol) or multimers ($h_B = -5.2$ kcal/mol) [32]. Another factor is known as intramolecular screening [34]. In the amorphous state, polymer chains adopt a statistical coil conformation where the chain bends back to itself favouring self contacts. A significative reduction in the autoassociation of PVPh should be accompanied by a change in conformational statistics, and by an unfavourable conformational energy contribution. In other words, the linkage of monomeric units in a polymeric chain restricts the chances of changes of interassociation upon blending, compared to low molecular weight substances. These two factors that can explain why the autoassociation remains nearly constant in the PMMA/PVPh system also hold for the PLA/PVPh systems, and therefore we will assume that both systems perform similarly regarding to the autoassociation of PVPh.

The third assumption is apparently straightforward. The number of contacts in a lattice model is given by the product of the volume fractions ($\varnothing_A\varnothing_B$) basically because the number of "dispersive" contacts depends on the surface area of the monomeric unit, proportional to its molar volume to first approximation, and therefore volume fractions are adequate to measure the number of dispersive contacts. However, in the case of specific interactions in systems containing a single interacting group per repeat unit, the number of contacts theoretically achievable assuming random mixing is given by the product of molar fractions, $x_A x_B$. In addition, the fact that hydrogen bonds can only be established within certain ranges of distances and orientations of the interacting groups provides additional restrictions that will decrease the number of actually hydrogen bonded groups. The analysis by FTIR of the $C=O$ stretching band has shown that the percentage of hydrogen bonded $C=O$ groups at high dilution approaches 80% in systems with low steric hindrances [32,35]. Also, as the autoassociation of PVPh is assumed to remain unperturbed, only the free hydroxyl groups (x^F_{OH}) present in the (pure) PVPh fraction will be available for hydrogen bonding. Hence, the fraction of interassociated OH groups in the blend (x^I_{OH}) can be estimated as $0.8(x_{C=O})(x^F_{OH})$. The fraction of the free OH groups in the blend will be the remaining difference to the total OH groups.

Using the preceding assumptions, and recalling also that the content of autoassociated OH groups in pure PVPh is about 60% according to FTIR measurements [33] and molecular modelling simulations [22], the association extents before and after blending have been calculated in Table 3. This table also includes the values calculated for χ according to equation 11. For this purpose, the variation of ΔG_H has been considered a pure enthalpic contribution, ΔH_H, according to our first assumption. Because the autoassociation is assumed to remain unchanged, the only contribution to consider is the formation of the interassociation (x^I_{OH}). Finally, recalling that equation 11 is written for one mol of lattice sites and that Table 3 provides the amount of hydrogen bonds for blends containing

Table 3
Estimated molar fractions for the autoassociated (x^A_{OH}), interassociated (x^I_{OH}) and free (x^F_{OH}) hydroxyl groups.

Composition		Association before blending		Association after blending			Interaction parameter
φ_{PLA}	x_{PLA}	x^A_{OH}	x^F_{OH}	x^A_{OH}	x^I_{OH}	x^F_{OH}	χ
0	0	0.6	0.4	0.6	0	0.4	−2.03[a]
0.2	0.294	0.424	0.283	0.424	0.066	0.216	−1.79
0.4	0.526	0.285	0.190	0.285	0.080	0.110	−1.60
0.6	0.714	0.172	0.114	0.172	0.065	0.049	−1.44
0.8	0.869	0.078	0.052	0.078	0.036	0.016	−1.32
1	1	0	0	0	0	0	−1.21[a]

[a] calculated at high dilution (but not exactly $x_{PLA} = 0$ or 1).

a total amount of 1 mol of polymer, values of ΔG_H have been calculated according to:

$$\Delta G_H = (\phi_{PLA} + \phi_{PVPh}r)x^I_{OH}h_A \qquad (12)$$

where r is the fraction of molar volumes, $r = V_{m,PLA}/V_{m,PVPh} = 0.60$; the term $(\varphi_{PLA} + \varphi_{PVPh}r)x^I_{OH}$ represents the molar number of interassociated hydrogen bonds within one mol of lattice sites, and h_A is the enthalpy of hydrogen bond formation corresponding to the interassociation ($h_A = -3.8$ kcal/mol) [32].

This estimative model and Table 3 provide simple answers to the miscibility behaviour of the system. Miscibility can be attributed to the presence of free OH groups in pure PVPh, available for the formation of $C=O\cdots H-O$ bonds, which provide a favourable contribution to the free energy of mixing. Recalling the negligible strength of the dispersive interactions in this system (compared to the strength of specific interactions), the table also provides a simple explanation to the dependence of χ with composition. If one PLA unit is introduced in a pure PVPh matrix, it will occupy a single lattice site and the strength of the hydrogen bond formed (which, of course, also depends on its probability of formation) belongs entirely to the single lattice site. On the other hand, if one PVPh unit is introduced in a pure PLA matrix, it will occupy $1/r$ lattice sites and the hydrogen bond formed (of the same strength as above) will spread over $1/r$ lattice sites. Therefore, χ is larger in PVPh rich systems, and the variation of χ with composition arises mainly from the difference in molar Volumes. Note that the variation of χ with composition ($1.21/2.03 = 0.6$) is almost equal to r.

4. Conclusions

The ability of molecular modelling based on the COMPASS force-field to predict selected critical properties for the miscibility behaviour of polymer systems has been investigated in this paper. The solubility parameters Poly(L-Lactide), Poly(D-Lactide), Poly(vinylphenol) and Poly(styrene) have been first calculated using molecular dynamics. The calculated values have been compared with experimental results obtained exclusively by solubility testing which is considered the most reliable experimental procedure to measure δ. In all cases, calculated values showed negative deviations in the 10−20% range with regard to the experimental values.

The miscibility state of Polylactide blends with PS and PVPh has been subsequently investigated using molecular modelling. The phase behaviour has been correctly predicted for both PLA/PS and PLA/PVPh systems, and the dependence of the interaction parameter on composition has also been correctly simulated. However, following the same trend observed for the autoassociation interactions in the pure homopolymers, the strength of the intermolecular interactions is underestimated. The interaction parameters

estimated using known miscibility models with some simple assumptions provide a closer approach to the experimental results. The fact that the COMPASS force-field is parametrized using low molecular weight compounds may explain some of the observed deviations since polymer specific features such as cooperativity effects [28,29] are not expected to occur in those compounds.

Acknowledgements

References

[1] Kelts LW, Landry CJT, Teegarden DM. Macromolecules 1993;26:2941–9.
[2] Meaurio E, Zuza E, Sarasua JR. Macromolecules 2005;38:1207–15.
[3] Meaurio E, Zuza E, Sarasua JR. Macromolecules 2005;38:9221–8.
[4] Zuza E, Meaurio E, Etxeberria A, Sarasua JR. Macromol Rapid Commun 2006;27:2026–31.
[5] Jawalkar SS, Aminabhavi TM. Polymer 2006;47:8061–71.
[6] Sun H. J Phys Chem B 1998;102:7338–64, <http://www.scripps.edu/rc/softwaredocs/msi/cerius45/compass/COMPASSTOC.doc.html>.
[7] Coleman MM, Serman CJ, Bhagwagar DE, Painter PC. Polymer 1990;31:1187–203.
[8] Galin M. Polymer 1983;24:865.
[9] Huang JC. J Appl Polym Sci 2003;91:2894–902.
[10] Kong M, Silveira MDLV, Zhao L, Choi P. Macromolecules 2002;35:8586–90.
[11] Hansen CM. Hansen solubility parameters: a user's handbook. Boca Raton, Florida: CRC Press; 2000.
[12] Auras R, Harte B, Selke S. Macromol Biosci 2004;4:835–64.
[13] Sarasua JR, Prud'homme RE, Wisniewski M, LeBorgne A, Spassky N. Macromolecules 1998;31:3895.
[14] Theodorou DN, Suter UW. Macromolecules 1985;18:1467–78.
[15] Meirovitch H. J Chem Phys 1983;79:502–8.
[16] Flory PJ. Statistical mechanics of chain molecules. Munich, Germany: Hanser; 1989.
[17] Eichinger BE, Rigby D, Stein J. Polymer 2002;43:599–607.
[18] Mu D, Huang XR, Lu ZY, Sun CC. Chem Phys 2008;348:122–9.
[19] Jawalkar SS, Nataraj SK, Raghu AV, Aminabhavi TM. J Appl Polym Sci 2008;108:3572–6.
[20] Jawalkar SS, Adoor SG, Sairam M, Nadagouda MN, Aminabhavi TM. J Phys Chem B 2005;109:15611–20.
[21] Zhang M, Choi P, Sundararaj U. Polymer 2003;44:1979–86.
[22] Gestoso P, Brisson J. Polymer 2003;44:2321–9.
[23] Agrawal A, Saran AD, Rath SS, Khanna A. Polymer 2004;45:8603–12.
[24] Arichi S, Himuro S. Polymer 1989;30:686–92.
[25] Case FH, Honeycutt JD. Trends Polym Sci 1994;2:259–66, <http://accelrys.com/resource-center/case-studies/archive/misc/misc.html>.
[26] Zuza E, Lejardi A, Ugartemendia J, Monasterio N, Meaurio E, Sarasua JR. Macromol Chem Phys 2008;209:2423–33.
[27] Sarazin P, Favis BD. Biomacromolecules 2003;4:1669–79.
[28] Papisov IM, Litmanovich AA. Adv Polym Sci 1988;90:139–79.
[29] Kriz J, Dybal J. J Phys Chem B 2007;111:6118–26.
[30] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.
[31] De Gennes PG. Scaling concepts in polymer physics. Ithaca, NY: Cornell University Press; 1979.
[32] Coleman MM, Graf JF, Painter PC. Specific interactions and the miscibility of polymer blends. Lancaster, PA: Technomic Publishing, Inc; 1991.
[33] Li D, Brisson J. Polymer 1998;39:793–800.
[34] Painter PC, Berg LP, Veytsman B, Coleman MM. Macromolecules 1997;30:7529–35.
[35] Meaurio E, Katime I. Macromol Mat Eng 2005;290:1166–75.
[36] Gestoso P, Brisson J. Comp Theo Polym Sci 2001;11:263–71.