

# Molecular Dynamics Simulations on the Blends of Poly(vinyl pyrrolidone) and Poly(bisphenol-A-ether sulfone)

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**ABSTRACT:** Molecular simulations are the most important tools to predict the properties of polymers and their blends. In this work, we have predicted the blend incompatibility of poly(*n*-vinyl pyrrolidone) (PVP) and poly(bisphenol-A-ether sulfone) (PES). Atomistic simulations were performed to compute the Flory-Huggins interaction parameter over all the compositions ranging from 90 to 10% of the individual polymers, which confirmed that the blends are incompatible (Bhattacharya et al., *J Membr Sci* 2003, 227, 23). Kinetics of phase separation was examined

via density profiles calculated using MesoDyn approach. For incompatible blends, the critical value of 0.32 computed from the Flory-Huggins theory agreed with the value of 0.29, suggesting the validity of our approach. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3572–3576, 2008

**Key words:** molecular dynamics; cohesive energy density; Flory-Huggins theory; interaction parameter; blend compatibility

## INTRODUCTION

Poly(vinyl pyrrolidone) (PVP) and poly(bisphenol-A-ether sulfone) (PES) are the most widely used polymers in drug delivery and separation science.<sup>1,2</sup> X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicated that these polymers are incompatible.<sup>1</sup> Blend compatibility/incompatibility of polymers can be studied by innumerable experimental techniques,<sup>3,4</sup> because readily miscible polymer blends are seldom obtained. However, it is important to determine the properties of the blends before their intended applications. Despite the progress made in experimental tools to study the blend compatibility, theoretical studies are somewhat rare.<sup>5–9</sup> Atomistic simulations would provide reliable predictions on the blend properties of polymers provided accurate experimental parameters are used in the simulations. Self-consistent field theory (SCFT) has led to the investigation on the microphase separation of diblock and triblock copolymers.<sup>10</sup> In contrast, molecular dynamic (MD) simulations would permit the modeling of polymeric chains during the

phase separation. On the other hand, mesoscopic<sup>11,12</sup> (MesoDyn) and dissipative particle dynamic (DPD) methods<sup>13</sup> treat the polymeric chains in a coarse-grained (mesoscopic) level by grouping the atoms together up to the persistence length of the polymer chains. This treatment can also be extended to length and time scales by several orders of magnitude compared to the atomistic simulations. MesoDyn deals with the dynamic mean field density functional theory in which dynamics of phase separation is described by the Langevin-type equations to investigate polymer diffusion.

This study is a continuation of our earlier work<sup>14–18</sup> in predicting blend compatibility/incompatibility of polymers. In this study, atomistic and mesoscopic calculations have been performed on PVP and PES polymers to confirm their immiscibility through the calculations of Flory-Huggins<sup>19</sup> interaction parameter. The computed results are in agreement with the experimental observations<sup>1</sup> of immiscible behavior of these polymers in solid film forms investigated by XRD and SEM techniques along with theoretical predictions based on the Flory-Huggins theory. Our present MD simulations also suggested that the blends of PVP and PES are immiscible in the entire range of their compositions. Even though the exact reason for this type of behavior is not fully explored, our predicted results and published experimental data agreed that the presence of aromatic rings and bulky CH<sub>3</sub> group in PES might restrict the free rotation around C–C bond of its backbone, thereby hindering the chain mobility. On the other hand,

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nitrogen group in PVP is small compared to aromatic and  $\text{CH}_3$  groups in PES and hence, PVP would crystallize much faster than PES. In this study, blend incompatibility was examined through an approach that treated, hierarchically, different lengths, and time scales.

To the best of our knowledge, no MD simulations were attempted before on the blends of PVP and PES. In this article, MD simulations of oligomeric forms of these polymers were performed at ambient temperature over several ranges of blend compositions. Cohesive energy density (CED) of pure polymers in the blend was estimated to compute the solubility parameter,  $\delta$ , of the blends as a function of blend composition. Flory-Huggins interaction parameter,  $\chi$ , was calculated to understand the energetics in the mixing of polymers, which indicated unfavorable interactions. Interaction parameters obtained from MD simulations along with other structure-dependent (monomer number and length, characteristic ratio, etc.) parameters were subsequently supplied into the mesoscopic simulations. The coarse-grained representation of the systems permitted us to study the blends of high molecular weight and to extend time scales for the observation of phase separation. The computed results indicated close agreements with the reported literature data<sup>1</sup> as well as with our internal simulation findings.

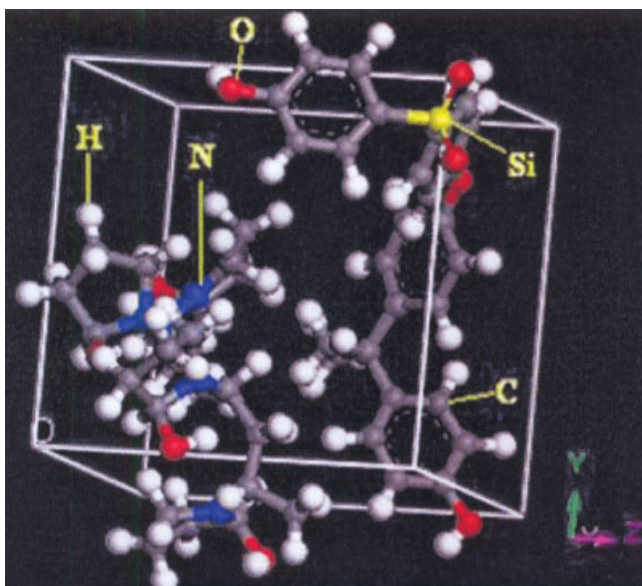
### Simulation results

All the simulations were carried out at ambient temperature (298 K) with the Discover molecular mechanics and dynamics simulation module<sup>20</sup> obtained from Accelrys, USA, and Materials Studio Modeling (Version 4.0) installed on Windows XP 2002. Initially, bulk phases were constructed with the amorphous cell program, which uses the combined use of the arc algorithm developed by Theodorou and Suter<sup>21</sup> and the scanning method of Meirovitch.<sup>22</sup> Glassy amorphous phase was constructed in two stages. Chain conformations were assumed to resemble those of the unperturbed chains with significant probability in the bulk. Initially, the proposed structure was generated using the rotational isomeric state model of Flory,<sup>23</sup> describing the conformations of unperturbed chains. To avoid excessive overlaps between the chains, modified conditional probabilities were used, which accounted for nonbonded interactions between the atoms to be placed and rest of the system. Initial structures were minimized by turning on the potential interactions in such a way that the more severe overlaps are relaxed such that the minimum is reached gradually by switching on the full potential. In the scanning method, all possible continuations of the growing chain were considered while computing

conditional probabilities. For the good "blending" of different component polymers, amorphous phases were checked for filling space regularly after construction of the initial amorphous cell. If two component chains were not well "mixed" (sufficient intermolecular contacts) in the initial configuration, then it was discarded and a new one was attempted. Minimization was achieved using conjugate gradient method (CGM) until the energy reached minimum. The CGM used in this study works on the Polak-Ribiere algorithm with a convergence level of 0.1 kcal/mol/Å. Initial configurations were refined by the dynamics of 50 ps after the amorphous cell was generated. The COMPASS<sup>24</sup> (condensed-phase optimized molecular potentials for the atomistic simulation studies) force field was used for modeling the interatomic interactions. This is the widely used all-atom force field optimized to predict structural, conformational, and thermophysical condensed phase properties of polymers. COMPASS is based on PCFF (polymer-consistent force field). The combination of valence terms, including diagonal and cross-coupling terms for bond stretching, bond angle bending, and dihedral angle distortions, a Coulombic term for electrostatic interactions and a Lennard-Jones 6-12 potential for van der Waals interactions comprised the energy expression.

The cell multipole method<sup>25-27</sup> was used for calculating the nonbonded interactions. This method is quite efficient to simulate bigger systems, because it scales linearly with the number of atoms,  $N$  (compared to the cutoffs that scale as  $N^2$ ), but it requires a modest memory. Here, the periodic box is divided into  $M$  cubic cells with  $M \approx N/4$ . In each cell, cells in the nearest neighborhood contributed to the near-field potential, while others to the far-field potential (short and long-range interactions). Interactions between atoms in the near-field cells were calculated directly for each pair of atoms. Interactions for atoms in the far-field cells were computed via expansions of multipole moments (charge, dipoles, quadrupoles, and octapoles) around the center of each cell.

The snap shot of 1 : 1 blend system is shown in Figure 1. Density of polymers as taken from literature was  $\rho(\text{PVP}) = 1.040 \text{ g/cm}^3$  and  $\rho(\text{PES}) = 1.240 \text{ g/cm}^3$ . The system consisted of 135 atoms for 1 : 1 blend combination. The cell size was 11.205 Å. The carbon atoms are gray, hydrogen white, and oxygen red in color. Detailed model construction procedure is described by different ratios of the number of chains of PES to the number of chains of PVP in the unit cells. The number of chains per unit cell, chain length, and density values are summarized in Table I. Density of the blend was calculated from the density of individual polymers and volume fraction of each polymer. As mentioned earlier, configurations were generated individually for each system and relaxed (this was checked visually and by the system



**Figure 1** Snapshot of amorphous unit cell for 1 : 1 blend of PVP/PS. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

energy) to compute the CED. MD simulations under constant temperature and density (NVT ensemble) were performed for each configuration using the Discover program. A time step of 1 fs was used, and the temperature was controlled by Anderson Thermostat. Energy of the system was monitored to ensure that it fluctuated around the average value, and this was considered as criterion for having “equilibrated” the system to the desired temperature, wherein trajectories were stored periodically for later processing. Arithmetic averages over the configurations stored in each trajectory and over all trajectories generated for each system were estimated. Thermal fluctuations were taken into account, which gave reliable estimates of properties at the chosen temperature during the simulation step.

It is important to choose an appropriate force field to obtain valuable information on the structure dynamics of the blends. COMPASS force field was used to compute the solubility parameters of PVP and PES to match these values with the reported literature data. The total energy,  $E_T$ , of the system was considered to be sum of bonding and nonbonding interactions given by:

$$E_T = E_b + E_0 + E_\phi + E_{oop} + E_{pe} + E_{vdw} + E_q \quad (1)$$

Here, the first four terms represent the bonded interactions, which correspond to energies associated with the bond,  $E_b$ , bond angle bending,  $E_0$ , torsion angle rotations,  $E_\phi$  out of loop,  $E_{oop}$  and potential energy,  $E_{pe}$ . The last two terms represent nonbonded interactions, which consist of van der Waals term,  $E_{vdw}$  and the electrostatic force,  $E_q$ . In COMPASS,

$E_{vdw}$  is invariably described by Lennard-Jones 6-12 potential, whereas the electrostatic energy is calculated from partial charges of atoms in the system as estimated by charge-equilibration method.<sup>28</sup> Electrostatic interaction was calculated by the Ewald summation method,<sup>29</sup> because it calculated long-range interactions more accurately.

Systems were built with 3D periodicity and equilibrated in the NVT ensemble at 298 K. In general, initial amorphous structure was in a relatively high-energy state. Therefore, before performing MD calculations, we performed the energy minimization; when the system became close to minimum, the CGM was used.<sup>30</sup> In the NVT ensemble, MD simulations were performed for each blend. Nose dynamics<sup>31</sup> was used to create the canonical MD trajectories, and a time step of 1 fs was used to ensure the stability of the simulation. Because the simulation time depends on the number of atoms in the system, simulation was carried out until total energy of the system was stabilized. The last few hundred ps of the trajectory file were used to calculate Hildebrand solubility parameter defined as square root of CED as well as Flory-Huggins interaction parameter,  $\chi$  given by:

$$\chi = \frac{z\Delta E_{mix}}{RT} \quad (2)$$

Here,  $z$  is coordination number, whose value for cubic lattice model was taken as six,  $R$  is molar gas constant (cal/mol), and  $T$  is temperature in kelvin, at which the simulation was performed. The energy of mixing,  $\Delta E_{mix}$  needed to compute  $\chi$  was calculated as

$$\Delta E_{mix} = \phi_A \left( \frac{E_{coh}}{V} \right)_A + \phi_B \left( \frac{E_{coh}}{V} \right)_B - \left( \frac{E_{coh}}{V} \right)_{mix} \quad (3)$$

In the above equation, subscripts  $A$ ,  $B$ , and  $mix$  represent the CED values of PVP, PS, and their blends, respectively, by considering the identity:  $CED \equiv \frac{E_{coh}}{V}$ . Symbols  $\phi_A$  and  $\phi_B$  represent volume fractions of PVP and PES, respectively. Using the calculated value of energy of mixing for both the polymers,  $\chi$  was calculated using eq. (2).

**TABLE I**  
Simulation Details of PS/PVP Blends for Different Ratios

No. of chains per unit cell	Composition (wt % PVP)	Density (g/cm <sup>3</sup> )	$\chi$ [eq. (2)]
Pure PES	0	1.240	N/C
9 : 1	10	1.190	0.540
7 : 3	30	1.107	0.636
5 : 5	50	1.080	0.450
3 : 7	70	1.058	0.542
1 : 9	90	1.045	0.539
Pure PVP	100	1.040	N/C

N/C, not calculated.

To understand whether both PVP and PES are miscible or immiscible, we have computed the critical value of  $\chi$  using

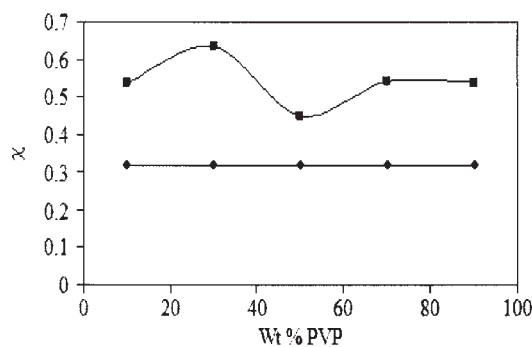
$$(\chi_{AB})_{\text{critical}} = \frac{1}{2} \left( \frac{1}{\sqrt{m_A}} + \frac{1}{\sqrt{m_B}} \right)^2 \quad (4)$$

Here,  $m_A$  and  $m_B$  represent the degree of polymerization (actual number of repeating units) of  $A$  and  $B$ . Note that the blends are miscible if  $\chi_{AB}$  is  $<$   $(\chi_{AB})_{\text{critical}}$ . If  $\chi_{AB}$  is considerably greater than the critical value, then the components are totally immiscible (i.e., they form two separate phases) and vice versa for miscibility. If the value of  $\chi_{AB}$  is slightly greater than the critical values, then the blends are partially miscible in which case, two phases are present with both the components in both the phases.

## DISCUSSION

The method generally used to estimate polymer-polymer compatibility is by measuring  $T_g$  of the blend and compare it with  $T_g$  of component polymers. If one of the components is crystalline, then the depression in  $T_m$  is used to investigate the blend compatibility.<sup>4</sup> In an earlier report,<sup>1</sup> XRD and SEM methods were used to investigate that PVP and PES blends are immiscible throughout their composition range. However, attempts to make stable films in our laboratory for performing differential scanning experiments were not successful. Hence, we resorted to the computational aspects to understand the problem. The  $T_m$  of PVP is 160°C, whereas that of PES, it is 185°C, and both the polymers are hydrophobic in nature; hence, one cannot expect them to be compatible in solid form. The variations in  $T_m$  of PVP in the blend would have been the best way to assess the blend compatibility, but since we could not prepare blend films, this approach was not pursued. Our computations, therefore, rely heavily on the published data.<sup>1</sup> The coexistence of two phases in the blend of PVP and PES was predicted<sup>1</sup> using Flory-Huggins theory, which also confirmed the immiscibility of the blends. Additional support comes from a comparison of our calculated value of  $\chi_{\text{critical}} = 0.29$  with that of 0.32 with the published data.<sup>1</sup>

The present MD simulation results on blends of PVP and PES were used to understand the interactions between individual polymers by calculating  $\chi$  values using eq. (2); these are displayed in Figure 2 as a function of composition of PVP. All the data points are above the critical  $\chi$  data line at 0.32 computed from eq. (4), which confirmed beyond doubt that both the polymers are immiscible. Small variations in  $\chi$  with varying wt % of PVP above the critical line are attributed to variations due to hydrophobic domains of the individual polymers with varying composi-



**Figure 2** Flory-Huggins interaction parameter versus weight fraction of PVP.

tions of the blend system. Thus, the absence of favorable interactions between PVP and PES chains strongly suggest that these polymers are immiscible.

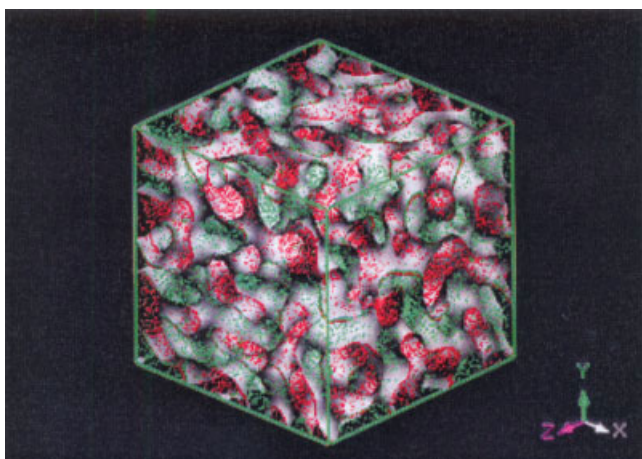
Polymer chain lengths were determined from the degree of polymerization and characteristic ratios of the polymers. The expression for MesoDyn chain length ( $N_{\text{meso}}$ ) is given by

$$N_{\text{Meso}} = \frac{M_p}{M_m C_n} \quad (5)$$

where  $M_p$  is polymer molecular weight,  $M_m$  is monomer molecular weight, and  $C_n$  is characteristic ratio. MesoDyn input parameter is related to Flory-Huggins interaction parameter through the equation:

$$v^{-1} \varepsilon_{ij} = \chi_{ij} RT \quad (6)$$

where  $\chi_{ij}$  parameter is taken from atomistic simulations performed for each blend at each composition (as discussed earlier),  $R$  is molar gas constant (8.314 J/mol K), and  $T$  is 298 K. To account for numerical stability, the time step for simulation was chosen in such a way that dimensionless time step,  $\tau$ , used by the program was 0.5 (i.e., between 0 and 1), and bond length was 1.154 nm throughout. Thus, 200  $\mu$ s was the time step used for PVP/PES blend at 50/50 composition. A constant noise parameter of 75.002 was maintained during the entire simulation (because too high or too low value would lead to system instability), which was applied to shorter chains with longer statistical units. The grid dimensions were  $32 \times 32 \times 32$  nm, and size of the mesh over which density variations were plotted using the Grid spacing field of 1 nm. Bond length was 1.1543 Å times the cell length to guarantee the isotropy of all the grid-restricted operators. The temperature 298 K corresponds to the temperature at which  $\chi$  was calculated for the total simulation time of 200  $\mu$ s. Hence, the chemistry of the system was determined by the values included for external potentials. After performing the calculation of energy of mixing using atomistic simulation, the energy of mixing was related to  $\chi$  parameter by the equation:



**Figure 3** Density profile slices showing the unmixed 1 : 1 blend of PVP/PS for 200  $\mu$ s, green color represents pristine PVP, red color for pristine PS, and gray color for the shaded pockets, which correspond to the interface between them. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$$\chi = \frac{\Delta \tilde{E}_{\text{mix}}}{RT} V_{\text{mon}} \quad (7)$$

Notice that there are alternative routes to obtain  $\chi$  parameter, that is, vapor pressure or interfacial tension experiments. However, in mesoscopic simulation, after setting up the initial configurations, the systems were led to evolve toward equilibrium to observe either phase separation or mixing.

Blend compatibility was predicted through the calculation of order parameter,  $P_i$  defined as the volume average of the difference between local density squared and the overall density squared as given by the integral:

$$P_i = \frac{1}{V} \int [\eta_i^2(r) - \bar{\eta}_i^2] dr \quad (8)$$

where  $\eta_i$  is the dimensionless density (volume fraction) for species  $i$ . It may be noted that phase separation proceeds via diffusion of the components through the interfaces. The density profile data displayed in Figure 3 suggest that both the phases are separated, which is in good agreement with the published results.<sup>1</sup>

## CONCLUSIONS

This article demonstrates the use of COMPASS force field approach for predicting the blend immiscibility of PVP/PES through calculations of solubility parameter and Flory-Huggins interaction parameters. Atomistic and mesoscopic simulations confirmed blend immiscibility at all compositions. The concentration dependence of  $\chi$  calculated from the MD cal-

culations matched with the Flory-Huggins theoretical calculations.<sup>1</sup> The  $\chi$  values for blends above 0.32 of  $\chi_{\text{critical}}$  confirm the blend immiscibility, which also indicates that atomistic simulation is in agreement with the mesoscopic simulation. Notice that critical interaction parameter value of  $\chi = 0.32$  calculated in this work is in agreement<sup>1</sup> with the value of 0.29 from the theoretical computations using Flory-Huggins approach, which suggests the validity of our approach. Mesoscopic density slices (regions) (Fig. 3) confirmed the phase separation between PVP and PES, which supported our atomistic simulation protocol used in this study.

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