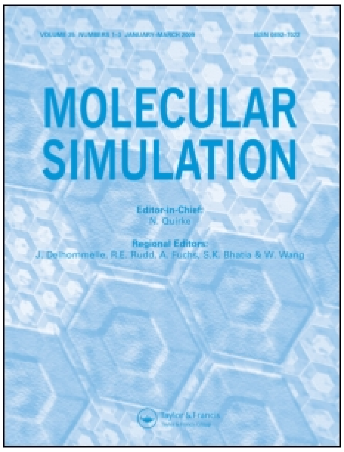

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A molecular simulation of the compatibility of chitosan and poly(vinyl pyrrolidone)

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A molecular simulation of the compatibility of chitosan and poly(vinyl pyrrolidone)

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The compatibility of chitosan (CS) and poly(vinyl pyrrolidone) was investigated by molecular dynamic (MD) simulations using the Flory–Huggins theory. The specific interactions in blends were studied by the radial distribution function (RDF). The Flory–Huggins interaction parameter, χ, was calculated at 298 K to assess the blend compatibility at different component ratios in the polymers. Miscibility was observed for blends with more than 50% of CS in the molar fraction, while immiscibility was prevalent at the molar fraction of CS between 10 and 50% of CS. Miscibility between poly(*N*-vinyl-2-pyrrolidone) (PVP) and CS polymers is attributed to the hydrogen bond formation of the $-C{=}O$ group of PVP and the $-CH_2OH$ groups of CS. This was further confirmed by MD simulations of RDFs for groups or atoms that are involved in interactions. These results are correlated well to obtain more realistic information on interactions involved as a function of blend composition.

Keywords: chitosan; poly(vinyl pyrrolidone); compatibility

1. Introduction

In recent years, the blends of natural polymers with synthetic ones were used for the development of new biomaterials with better mechanical properties and biocompatibility [1–5]. Chitosan (CS) is a polysaccharide derived from deacetylation of chitin, which has been used in a wide variety of fields owing to its good biocompatibility, biodegradability and capacity to form membrane, fibre, gel, cotton and microparticles [6–8]. Interest in the biomaterial prepared by CS mixed with synthetic polymer and natural polymers has attracted many attentions [9]. As a water-soluble polymer, poly(*N*-vinyl-2-pyrrolidone) (PVP) has been used as a main component of temporary skin covers or wound dressing [10]. PVP blending with other polymers played a significant role in a series of PVP hydrogels as biomedical materials [11]. Blends of CS and PVP (Figure 1) have been investigated using a variety of experimental techniques [12–14]. More specifically, Yeh et al. [12] tested the compatibility using techniques such as Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis and evaluated the incompatibility that occurs when the quantity of CS exceeded 75%. However, Marsano et al. [13] examined the binary blend compatibility of CS and PVP by viscosity, DSC and FTIR and found that the blends were compatible in the solid states and incompatible in third component as solution. In all of these papers, the experimental results are contradictory to each other. In order to distinguish which experimental results are true, the molecular simulation was used to investigate the compatibility of CS and PVP.

A number of different modelling techniques are available for studying polymer miscibility, ranging from quantitative structure-property-relationship methods and simple lattice-based models to state-of-the-art statistical mechanics approaches. These molecular simulations have led to achieving important properties of polymeric blends with a high accuracy [15–17] that are otherwise difficult to study experimentally or for which experimental data are not available or often when such results are conflicting [18]. Among the several theoretical tools used to study polymer/polymer blend compatibility, Flory–Huggins theory [19] is the classical theory for calculating the free energy of mixing. The theory was expanded to model polymer systems by assuming that the polymer consisted of a series of connected segments, of which each segment occupied one lattice site. Assuming that the segments are randomly distributed in the original theory, the mixing entropy was assumed to be purely combinatorial. However, it has been known for many years that non-combinatorial contributions are also important in polymer systems. These are variously known as the free-volume effect, the equation-of-state effect and the packing effect. Once the Flory–Huggins chi parameter (which, in classical Flory–Huggins theory, includes only the enthalpy contributions

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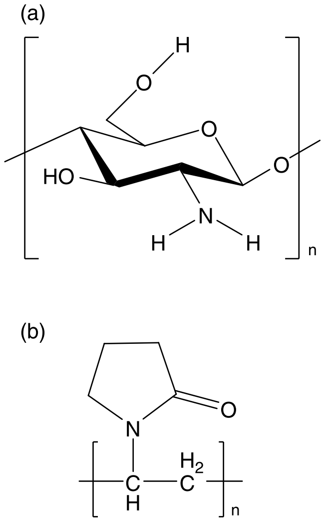

Figure 1. The molecular structure of (a) chitosan and (b) poly(*N*-vinyl-2-pyrrolidone).

to the free energy of mixing) is known, the entire phase behaviour of the system can be evaluated.

In this paper, molecular dynamics (MD) simulations of oligomers of PVP and CS were conducted at room temperature for a wide range of compositions. The cohesive energy density (CED) of the pure components and mixtures was calculated. The χ interaction parameter was derived as a function of composition for the different blends. The χ values indicate the favourable interactions for specific mixtures. Compatibility in these systems was attributed to hydrogen-bond formation between the —OH and —NH_2 groups of CS with the carbonyl group of PVP [20]. However, it is very difficult to know which functional groups of CS are actually responsible for the interaction. This aspect was further investigated by calculating the radial distribution function (RDF) of polymeric chains. Our work provides some useful information to understand the structures of CS/PVP blends at the molecular level.

2. Simulation details

2.1 System

The systems under consideration were binary blends of PVP with CS in different compositions. To choose the polymer chain length in MD simulations, individual CS and PVP polymers were subjected to minimisation. Dynamics was performed to find δ plotted versus the number of repeating units of the polymer. When a stable value of δ was obtained, it confirmed that the number of repeating units is sufficient for the simulation. In the present work, syndiotactic CS of 20 units and PVP consisting of 30 repeating units were used to generate the amorphous cell for the different composition. Density of the chosen polymers was taken from the literature [21] as $\rho_{(\mathrm{PVA})} = 1.04\,\mathrm{cm}^{-3}$ and $\rho_{(\mathrm{CS})} = 0.670\,\mathrm{g/cm}^3$. The density and χ of different composition were listed in the Table 1. All the simulations were conducted at room temperature ($T = 298\,\mathrm{K}$).

2.2 Molecular simulations

MD simulation has provided a powerful tool to understand the dynamics of a polymer at molecular level, which can lead to significant insights into the atomic motions [22,23]. The initial structures of polymer blends were constructed using Amorphous Cell modules of Materials Studio program (MS, version 4.1 Accelrys Software Inc., San Diego, CA, USA). The energy minimisation and MD simulations of blends were conducted with the polymer-consistent force field (PCFF). PCFF was developed based on CFF91 and is intended for application to polymers and organic materials [24–26]. The structures of blends were subject to the energy-minimisation calculations by Smart minimizer method with 5000 iterations to be used as starting lowest energy structures for the forthcoming structure discussion. After the minimisation, the molecular equilibration was done using the dynamic module of Discover, running dynamics of 50 ps for each sample, in the NVT ensemble. MD runs of 1000 ps were subsequently carried out under periodic boundary

Table 1. Simulation details for PNIPAM/CS blend.

System no.	Number of chains per unit cell	Composition (wt% CS)	Density (g/cm^3)	χ (Equation (1))
1	10 PVP chain	0	1.040	not applicable
2	1 CS + 9 PVP chain	10	1.003	0.1136
3	2 CS + 8 PVP chain	20	0.966	0.4173
4	3 CS + 7 PVP chain	30	0.929	0.2833
5	4 CS + 6 PVP chain	40	0.892	0.2178
6	5 CS + 5 PVP chain	50	0.855	0.0558
7	6 CS + 4 PVP chain	60	0.818	0.0484
8	7 CS + 3 PVP chain	70	0.781	0.0183
9	8 CS + 2 PVP chain	80	0.744	0.0145
10	9 CS + 1 PVP chain	90	0.707	0.0317
11	10 CS chain	100	0.670	not applicable

conditions using samples prepared for each composition of the blends through the Amorphous Cell module. The snapshot of unit cells (ball and stick model) for 50% composition of PVP blend is shown in Figure 2.

2.3 Calculation methods [18]

After the dynamic equilibration, the CED and solubility parameter (δ) values were found out using the last 600–1000 ps of the trajectory files. The Flory–Huggins interaction parameter, χ, could be given by:

$$\chi = \frac{z \cdot \Delta E_{\text{mix}}}{RT}, \tag{1}$$

where z is the co-ordination number taken to be six for the cubic lattice model, R is the molar gas constant (cal/mol), and T is temperature in Kelvin, at which the simulation was performed. Energy of mixing, ΔE_{mix} needed to calculate χ was calculated as:

$$\Delta E_{\text{mix}} = \phi_A \left(\frac{E_{\text{coh}}}{V}\right)_A + \phi_B \left(\frac{E_{\text{coh}}}{V}\right)_B - \left(\frac{E_{\text{coh}}}{V}\right)_{\text{mix}} \tag{2}$$

In the above equation, subscripts A, B and mix represent CED values of PNIPAM, CS and PNIPAM/CS blends, respectively, by considering the identity: CED $\equiv (E_{\text{coh}}/V)$. Symbols ϕ_A and ϕ_B represent the volume fractions of PNIPAM and CS, respectively. Using the calculated value of the mixing energy for CS and PNIPAM, χ was calculated from Equation (1). The calculated results of χ in different compositions are listed in Table 1.

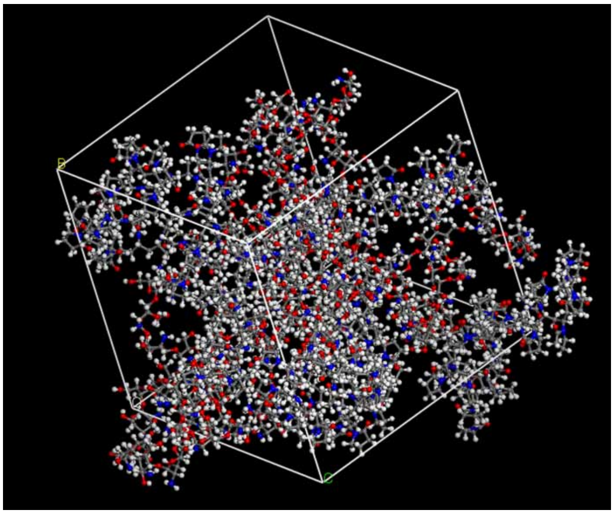

Figure 2. Snapshot of unit cell for 50% composition of PVP blend.

2.4 Radial distribution function

From the trajectory co-ordinates, we have also evaluated the radial distribution function (RDF). The RDF is a measure of the probability of an atom within an arbitrary reference frame located in a spherical shell with an infinitesimal thickness at a distance r from a reference atom. The resulting function is given by the symbol, $g_{AB}(r)$, which was calculated by averaging over the static relationship of every given pair of particles, AB as follows:

$$g_{AB}(r) = \frac{\langle n_{AB}(r) \rangle}{4\pi r^2 \Delta \rho_{AB}} \tag{3}$$

where $\langle n_{AB}(r) \rangle$ is the average number of atom pairs between r and $r + \Delta r$ and ρ_{AB} is the density of atom pairs of type AB. The total RDF, $g(r)$, which gives a measure of spatial organisation of atoms about the central atom, can be used to demonstrate a long-range order of the structure. Therefore, $g(r)$ was used to distinguish between amorphous and crystalline structures of the polymers. RDF was calculated for various pairs of atoms of molecules, since it gives an insight as to how the atoms pack in an amorphous structure. To perform RDF calculations, we have considered the interactions between the hydrogen atom in the —OH and —NH$_2$ groups of CS and the oxygen atom of carbonyl group in PVP.

3. Result and discussion

3.1 Flory–Huggins interaction parameter

As a first step, it is of interest to understand what minimum molecular size is sufficient to represent the real polymer chain. To determine this minimum size, solubility parameters of CS and PVP at carefully chosen different molecular weights have been computed up to a point even if the increase of polymer molecular weight did not change the solubility parameter. As displayed in Figure 3, the solubility parameter curve of PVP varies within a narrow range and then levels off beyond 30 repeating units of PVP.

Computed values of δ are plotted versus repeating units of CS (up to 100 monomer units) in Figure 4. It is observed that the δ values do not vary much beyond 20 monomer units. In the present work, the tendency of PVP and CS polymers to mix at a specific composition was examined by calculating the CED of the blends and of pure components. It is, therefore, realised that the solubility parameter of individual polymers (PNIPAM or CS) exerts an influence on their blend miscibility.

As a further test of the compatibility behaviours of PNIPAM and CS polymers, we have computed the critical value of χ using the following equation [27]:

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

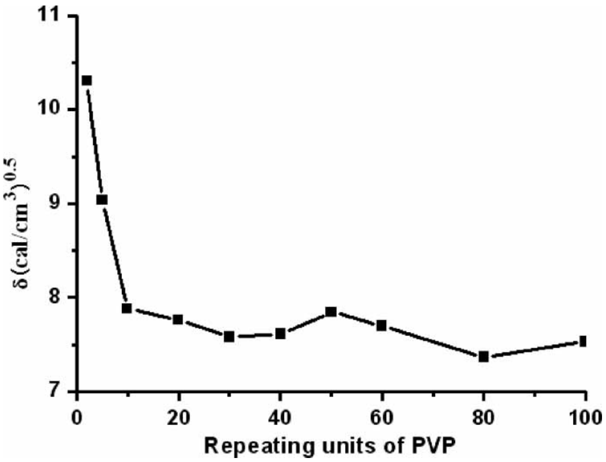

Figure 3. Solubility parameter of PVP versus repeating units of PVP.

where m_A and m_B represent the degree of polymerisation (actual number of repeating units) of A and B. It may be noted that even though the χ parameter has been discussed at various levels to depend on the mixture compositions, it was realised that composition dependence of χ led to further computational problems in the present research. Hence, the calculated values of χ parameter are good enough to obtain the reproducible data. Notice that blends are miscible if χ is smaller than $(\chi_{AB})_{critical}$. If χ is considerably larger than the critical value, then blends are immiscible (i.e. they form two separate phases). If the value of χ is slightly greater than the critical value, then the blends are partially miscible in which case both the phases are present, one for each component of the blend. So long as the measured χ and the corresponding critical values are calculated based on the same reference volume, comparison of the measured χ with the critical values would provide a good indication of the degree of blend miscibility. Therefore, one can use χ_{AB} to characterise blend miscibility [28]. Results of χ versus the molar fraction of CS calculated from Equations (1) and (2) are displayed in Figure 5.

From Figure 5, we could find that the value of χ lies below the χ critical line in the composition range from 50 to 90%, which indicates that the blend is miscible. For compositions below 50%, the value of χ lies above the critical value indicating blend immiscibility. The value of χ critical is around 0.49, which represents the limiting line for the blend to be miscible. All of the data calculated from the simulation indicate that the blends are miscible when the composition of CS is higher than 50% (Figure 5).

3.2 *Radial distribution function*

RDF is useful in the structural investigations of both solid and liquid packing (local structure) for studying specific interactions such as hydrogen bonding. Figure 6 displays the RDF for the different CS/PVP blends of hydrogen atom of CS relative to the distance of the oxygen atom of PVP. The peaks of $g(r)$ indicate the presence of definite correlation between atoms within that radius, while the absence of any peaks beyond 6 Å distance indicates that there is no long-range interaction in the systems. It can be observed that the presence of the $-HOCH_2$ groups of CS in the neighbourhood of the $-C{=}O$ of PVP is significantly more probable, with $g(r)$ about 3.0, which indicates a strong interaction between these groups. On the other hand, the probability for the $-NH_2$ of CS in the proximity of the $-C{=}O$ of PVP is about 0.5 indicating almost no significant interaction between them. This can be explained on the basis of free rotation of hydroxymethyl groups of CS which may interact with the groups of PVP. The probability of interaction between $-NH_2$ of CS and $-C{=}O$ of PVP would be small at these compositions.

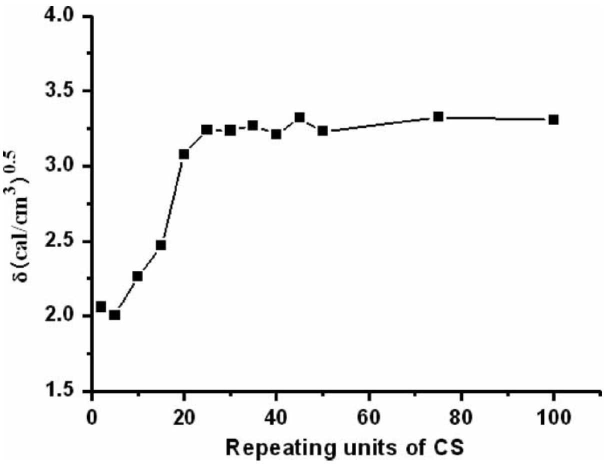

Figure 4. Solubility parameter of CS versus repeating units of CS.

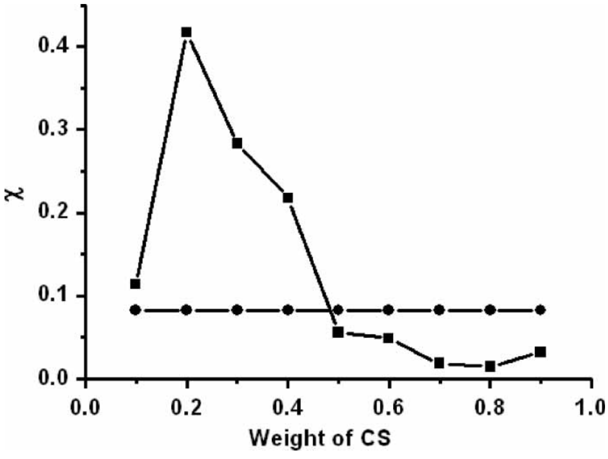

Figure 5. Flory–Huggins interaction parameter versus composition per cent of CS.

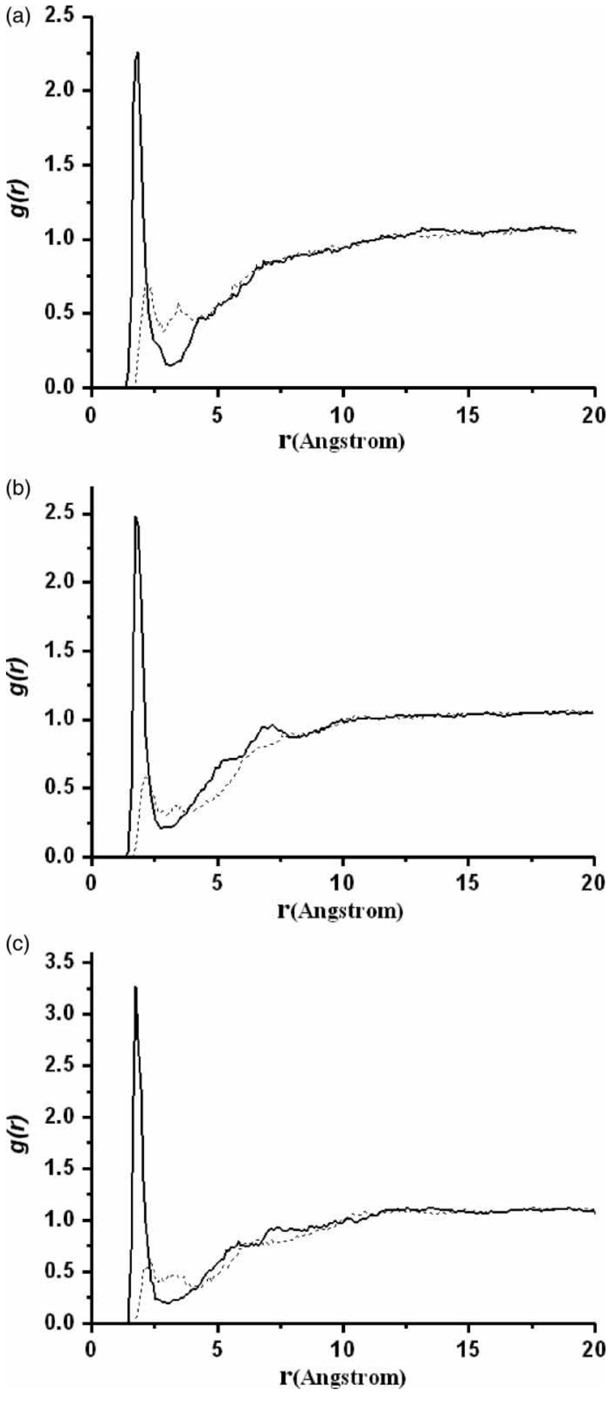

Figure 6. RDF calculation for the CS/PVP blends: (a) 20/80, (b) 50/50, (c) 80/20, using as reference:(—) hydrogen atom of the hydroxyl methyl group of CS and (...) hydrogen atom of the amino group of CS relative to the distance of the oxygen atom of the carbonyl group of PVP.

The compatibility of CS and PVP also can be explained by the RDF of the $-HOCH_2$ groups of CS in the neighbourhood of the $-C{=}O$ of PVP relatively. Figure 6(a) shows the RDF for the 20% composition of CS. The interaction probability is smaller than that for the 50 and 80% compositions in Figure 6(b) and (c), respectively. In this case, the lowest interaction corresponds to the 20% composition, indicating their immiscibility. These results are in good agreement with the calculated data derived from the Flory–Huggins interaction parameter.

4. Conclusion

The compatibility of CS and poly(vinyl pyrrolidone) can be predicted to a significant extent by MD simulations. MD simulations indicated that the molar fraction of CS below 50% is immiscible, since χ is higher than χ_{critical}, for these systems, whereas 10:90–50:50 blends of PVP:CS are miscible. The RDF calculations show that at higher compositions of CS, interactions of hydrogen bond are established between the hydroxymethyl group of CS and the carbonyl group of PVP. Our study provides some useful information for understanding experimental results on CS/PVP blends at the molecular level.

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