

Specific interactions in blends containing Chitosan and functionalized polymers. Molecular dynamics simulations

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Abstract

Chitosan (CS)/poly(vinyl alcohol) (PVA) and Chitosan/poly(2-hydroxyethyl methacrylate) (P2HEM) blends have been studied through molecular dynamic simulations. In a previous work it was found miscibility between these polymers and it was attributed to hydrogen bonding formation. However, the experimental information obtained was not enough to know which of the interacting groups of Chitosan, i.e. $-\text{CH}_2\text{OH}$ or $-\text{NH}_2$, are responsible of the interaction. Therefore, we have performed molecular dynamics simulation runs of 1 ns in order to calculate radial distribution functions (RDF) for the groups tentatively involved in the interaction. The results are correlated with our previous experimental data. This way, we have obtained a more precise conclusive information about the interactions involved as function of the blends composition. For low compositions of PVA and P2HEM the interaction is predominantly with the hydroxymethyl groups of CS while as the composition of PVA and P2HEM increases, the interaction with the amine groups increases.

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1. Introduction

The chemical structure of the side chain of vinyl polymers plays an important role in the miscibility behavior of polymer blends containing this kind of polymeric material.

Polymer blends have been a matter of current interest in the last years. The increasing concern is mainly due to polymer blending is a common and potentially versatile way to develop new materials with designed properties, which cannot be reached by using single polymers [1,2]. Polymer blends have been used widely since they often show different properties which are better than the single homopolymers. The main trouble in the compatibilization of polymer blends is that in general these kinds of materials

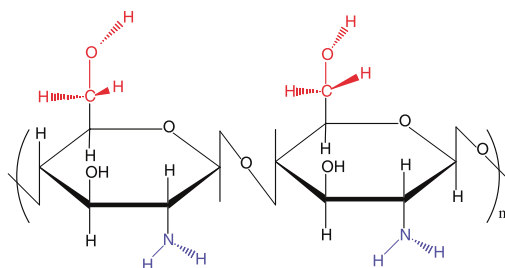
are immiscible because of entropic reasons. Nevertheless, miscibility can be reached when interacting groups are inserted in the polymers to be blended. Therefore, polymers containing interacting groups are good candidates to form miscible blends [3,4]. In these systems specific interactions are the driving force to obtain one phase system [1–3,5–7].

Chitosan (CS) is a natural polymer that is mainly obtained from the mollusk shell. Its chemical structure as (1 → 4)-2-amino-2-deoxy- β -D-glucan, contains *N*-deacetylated derivatives of Chitin, (1 → 4)-2-acetamido-2-deoxy- β -D-glucan [8–10] (Scheme 1).

In fact CS has four hydroxyl groups, an amine group and in a minor proportion an amide groups, which are in general partially hydrolyzed and, therefore, some carboxylic acid groups can be present. The importance and applications of CS in photography, ophthalmology, agricultural, medical, food and cosmetic industries have been described elsewhere [11,12]. Modification of CS by compatibilization with other polymeric materials could be of interest for different applications. CS can be considered as strongly interacting polymer, which may allow obtaining compatible polymer blends. Although blends containing CS are not common,

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Scheme 1.

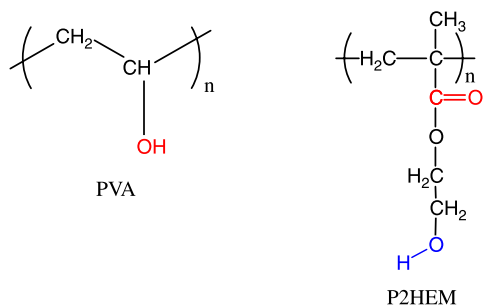
the modification of this natural polymer seems to have a great potential interest.

In a previous work, [13] we have reported the experimental results dealing with the interaction of CS with commercial polymers like poly(vinyl alcohol) (PVA) and poly(2-hydroxyethyl methacrylate) (P2HEM) (Scheme 2).

Compatibility in these systems was attributed to hydrogen bonding formation between the $-OH$ and $-NH_2$ groups of CS with the $-OH$ of PVA or P2HEM. However, it was very difficult to know which of the functional groups, $-OH$ or $-NH_2$, of CS were actually responsible of the interaction. The aim of this work is to perform molecular dynamics simulations in order to elucidate this point and, more specifically, to discern which of the functional groups of CS are present in the apparent hydrogen bonding of the particular systems. With this end, we compare our simulation results with the experimental data previously reported.

2. Methodology

All our molecular dynamic simulations (MDS) were performed by the program MS-Modeling (Accelrys). The force field used was PCFF [14] and a time step of 0.001 ps was used. The molecular equilibration was done by using dynamic module of Discover, running dynamics of 500 ps for each sample, in the NVT ensemble. MDS runs of 1 ns were subsequently carried out under periodic boundary conditions (PBC), using samples prepared for each composition of the blends through the Amorphous Cell [15] module. The analysis of results was carried out in the



Scheme 2.

interval from 600 to 1000 ps of simulations, where the dynamic shows a stable behavior (Scheme 3).

The simulated systems were CS/PVA and CS/P2HEM at the 20/80, 50/50 and 80/20 compositions, for each of the pair blends.

For MDS of the CS/PVA 80/20, 50/50 and 20/80 blends, the number of monomer units were 4/10, 2/22 and 2/36, respectively. For CS/P2HEM 80/20, 50/50 and 20/80 blends the number of monomer units were 8/6, 2/8 and 2/24, respectively.

From the trajectory coordinates, we have performed calculations for the radial distribution function (RDF), $g(r)$, between different types of possibly interacting pairs of atoms. This function measures the point probability of finding one of the atoms at a distance r from the other atom [16]. For our RDF calculations, we have considered the interaction between oxygen atom of hydroxymethyl group and nitrogen atom of amino groups of CS with the hydrogen atoms of hydroxyl groups of P2HEM and PVA (Scheme 4(a) and (b), respectively). Also, we have obtained $g(r)$ for the interaction of the mentioned groups of CS with the oxygen atoms of carbonyl group of P2HEM.

3. Results and discussion

The miscibility between CS and PVA or P2HEM, is attributed mainly to hydrogen bonding formation [13]. These polymers can interact by $OHCH_2-$ and/or $-NH_2$ of CS, because of the presence of hydroxyl group in PVA and P2HEM monomer units. Fig. 1(a) shows the RDF for 80/20 CS/PVA blend. It can be observed that the presence of the $-OH$ groups of CS in the neighbourhood of the $-OH$ of PVA 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 $-OH$ of PVA is almost zero (dotted line in Fig. 1(a)), indicating no significant interaction between them. This can be explained taken into account that the hydroxymethyl groups in CS have free rotation; therefore, it is more available for interaction with the hydroxyl group of PVA. Fig. 1(b) shows the RDF for 50/50 CS/PVA blend. An important change can be observed in comparison with the results shown for the 80/20 composition. According to this figure interactions are now shown both for the hydroxymethyl and amino groups of CS with the hydroxyl group of PVA. An even clearer peak of interaction is also observed for the 20/80 blend (Fig. 1(c)). This feature can be attributed to the fact the availability of the $-OHCH_2$ groups of CS to interact with $-OH$ group of PVA is lesser in these compositions and, therefore, the latter groups begin to interact with the amino group of CS.

These simulation results can explain the differences in the displacements observed in the experimental FTIR spectra, for the different blend compositions of CS/PVA. A larger displacement indicates a stronger interaction

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