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

Claudia Sandoval[a], Cristian Castro[a], Ligia Gargallo[a], Deodato Radic[a,*], Juan Freire[b,**]

[a]*Departamento de Química Física, Laboratorio de Macromoléculas, Facultad de Química,*
Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile
[b]*Departamento de Ciencias y Técnicas Fisicoquímicas, Facultad de Ciencias,*
Universidad Nacional de Educación a Distancia (UNED), Senda del Rey s/n, 28040 Madrid, Spain

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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. $-CH_2OH$ or $-NH_2$, 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.

Keywords: Molecular dynamic simulation; Radial distribution function; Polymer blend

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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* Corresponding author. Tel.: +56 2 6864741; fax: +56 2 68647444.
E-mail addresses: dradic@puc.cl (D. Radic), jfreire@invi.uned.es (J. Freire).

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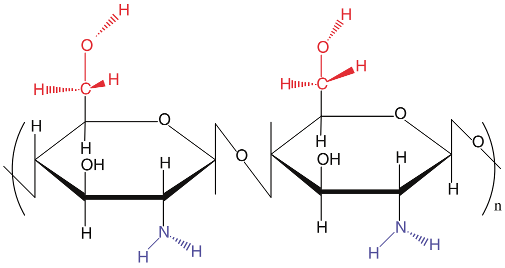


Scheme 1.

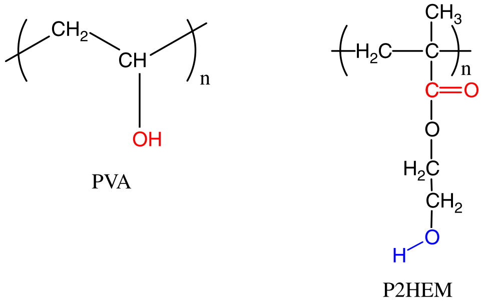
the modification of this natural polymer seems to have a great potential interest.

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



PVA

P2HEM

Scheme 2.

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.

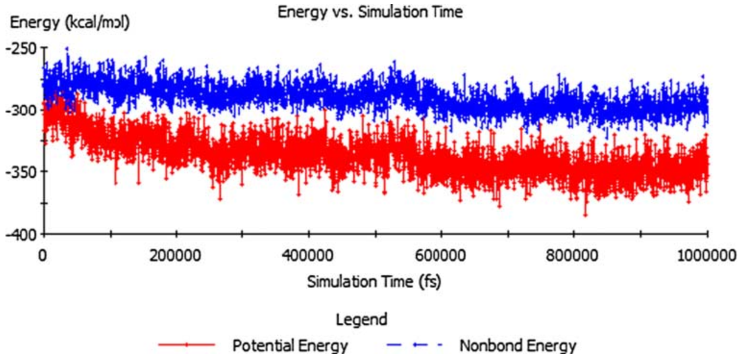
For MDS of the CS/PVA 80/20, 50/50 and 20/80 blends, the number of monomer units were 4/10, 2/22 and 2/36, respectively. For CS/P2HEM 80/20, 50/50 and 20/80 blends the number of monomer units were 8/6, 2/8 and 2/24, respectively.

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.

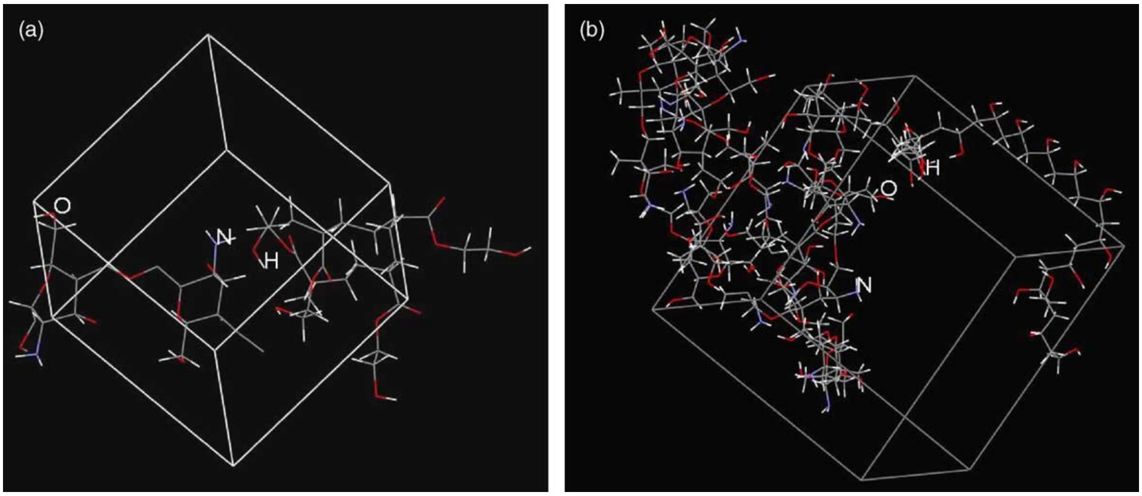
These simulation results can explain the differences in the displacements observed in the experimental FTIR spectra, for the different blend compositions of CS/PVA. A larger displacement indicates a stronger interaction



Scheme 3.

between the polymers [17,18]. Table 1 summarizes the wavelength for the hydroxyl band of PVA as function of the blend composition and the displacements of these bands relative to the pure components. For the 20% composition of PVA, the displacement is larger than that for the 80% composition of PVA. This result is in good qualitative agreement with our simulation. Thus, the RDF curves for the 20% composition of PVA indicate that the interaction is mainly with hydroxyl group of CS and not with the amino group, being the latter interaction weaker. On the contrary the 80% composition of PVA shows a lower displacement, what should indicate that the interactions predominant for this composition are weaker. The RDF curves for this case indicates that the interaction of the –OH group is equally probable with the amino group and with the hydroxymethyl group. However, for the 50% composition the displacement is the same that for 20% of PVA. Nevertheless, this result does not mean that the interaction of the –OH group of the PVA is established preferentially with the hydroxymethyl group of CS. At this composition the contribution of hydroxymethyl groups in CS or in PVA to the interaction are similar. This way the interaction of the –OH group of PVA is with the $–NH_2$ group and with the $OHCH_2–$ group of the CS. In Table 1 a large displacement are observed for the 50% composition, but the FTIR spectroscopy cannot discriminate the molecule to which the interacting atom belong. Therefore, our MDS results are consistent with the experimental data.

The CS/P2HEM blends follow a similar behavior. Fig. 2(a) shows the RDF for the 80/20 composition of CS/P2HEM blend. A larger probability of the interaction of the hydrogen atoms of the hydroxyl group of P2HEM with the oxygen atoms of hydroxymethyl group of CS is observed relative to the nitrogen atoms of the amino groups. This result is in agreement with the displacements shown in Table 2, for the 20% composition of P2HEM. Thus, we observe the largest displacement at this composition ($30.6\ cm^{-1}$). Therefore, the interaction among the groups $OHCH_2–$ of CS and –OH of P2HEM is strong. A different behavior is observed in the compositions 50/50 and 20/80 (Fig. 2(b) and (c)), since an evident interaction arises with the amino group of CS. When the probability of interaction with the amino group of CS is high, the interaction between the polymers is weaker [17,18]. This is reflected in the smaller experimental displacement observed by FTIR at these compositions in Table 2, showing a weaker overall interaction. However, the interaction with the hydroxymethyl group of CS is not disregarded, at these compositions.



Scheme 4.

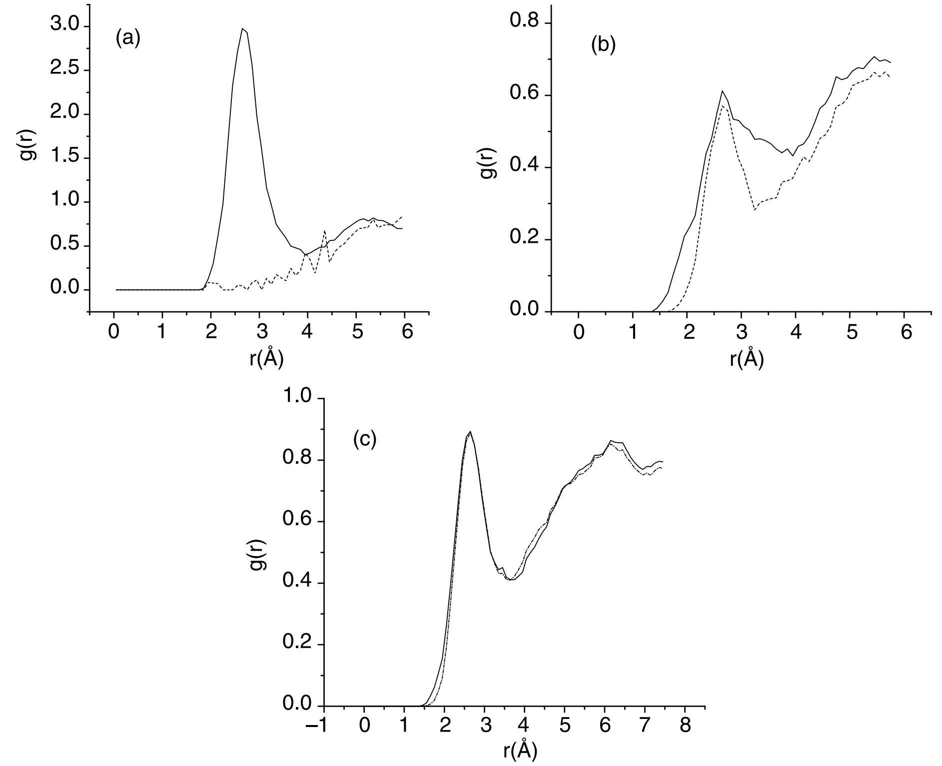


Fig. 1. Radial distribution function (RDF) calculation for the CS/PVA blends: (a) 80/20, (b) 50/50 and (c) 20/80, using as reference: (—) oxygen atom of the hydroxyl methyl group of CS and (- - -) nitrogen atom of the amino group of CS relative to the distance of the hydrogen atom of the hydroxyl group of PVA.

The RDF curves for CS/P2HEM shows two peaks located in the same range of distances where the single peak of the CS/PVA systems appears (2–3 Å). It should be considered that PVA repeat units are smaller than in P2HEM and, their hydroxyl groups are closer to the backbone. Consequently, several hydroxyl groups of PVA can approach simultaneously to the hydroxymethyl groups of CS. Due to the overlap of these close interactions, the RDF curves for OH/OHCH$_2$ only show a single peak. However, the hydroxyl groups of P2HEM are further apart from each other and, when one of them interacts with the different hydroxymethyl group of CS, the presence of another equivalent –OH group is not probable. Hence, the groups tend to interact at more specific positions.

We also calculated the RDF for the oxygen atoms of the carbonyl group of P2HEM and the hydrogen atoms of the hydroxymethyl and amino groups of the CS. Fig. 3 show that a higher interaction exists between oxygen of the carbonyl and hydrogen of the hydroxymethyl group relative to the interaction with the amino group of CS. These calculations are in good agreement with the experimental displacement obtained by FTIR spectra, shown in Table 3. Fig. 3(a) shows the RDF for the 80% composition of P2HEM. The interaction probability is smaller than that for the 50 and 20% compositions Fig. 3(b) and (c), respectively.

Table 1
FTIR absorptions and the displacements of the –OH band of PVA for the CS/PVA blends

Blend from HAc %PVA	–OH band (cm^{-1})	Displacement PVA (cm^{-1})
0	3384.1	–
20	3423.7	47.1
30	3422.7	46.1
50	3423.7	47.1
60	3423.4	46.8
70	3423.7	47.1
80	3418.2	41.6
100	3376.6	–

Table 2
FTIR absorptions and the displacements of the –OH band of P2HEM for the CS/P2HEM blends

Blend %P2HEM	–OH band (cm^{-1})	Displacement P2HEM (cm^{-1})
0	3384.1	–
20	3444.6	30.6
30	3441.4	27.4
40	3442.7	28.7
50	3441.0	27.0
60	3443.1	29.1
70	3441.8	27.8
100	3414.0	–

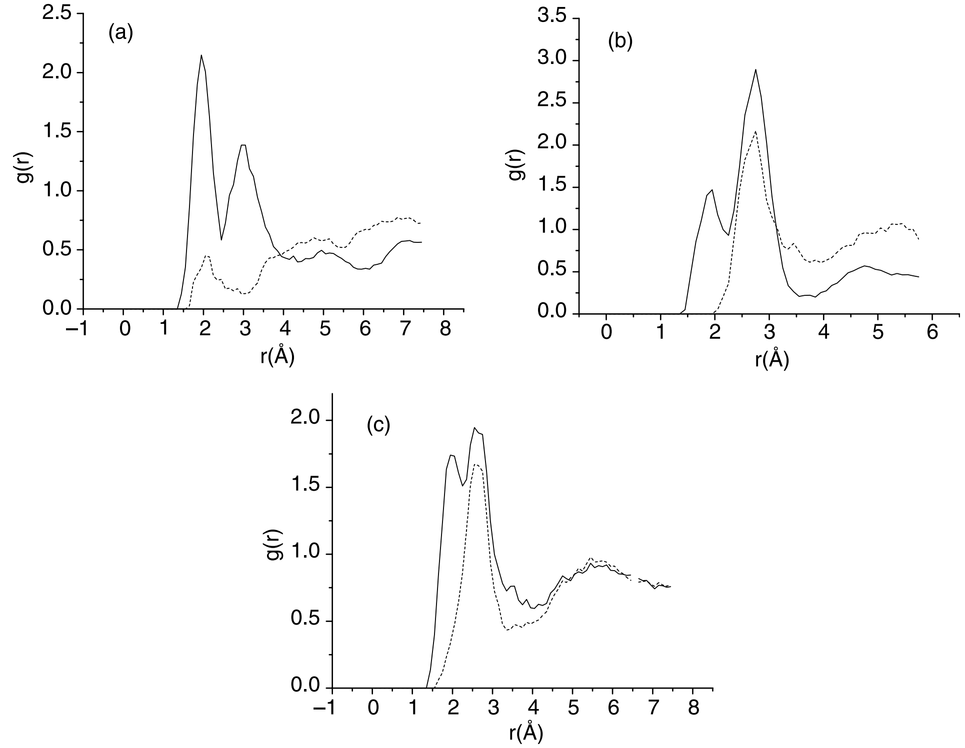


Fig. 2. RDF calculation for the CS/P2HEM blends: (a) 80/20, (b) 50/50 and (c) 20/80, using as reference: (—) oxygen atom of the hydroxyl methyl group of CS and (- - -) nitrogen atom of the amino group of CS relative to the distance of the hydrogen atom of the hydroxyl group of P2HEM.

In this case, the highest interaction corresponds to the 50% composition. These results are in good agreement with the experimental FTIR data, presented in Table 3, where the greater displacements are near the 50% composition. However, the RDF calculations do not show a significant probability implying close interaction between the hydrogen of the amino group of CS and the oxygen atom of the carbonyl group of P2HEM.

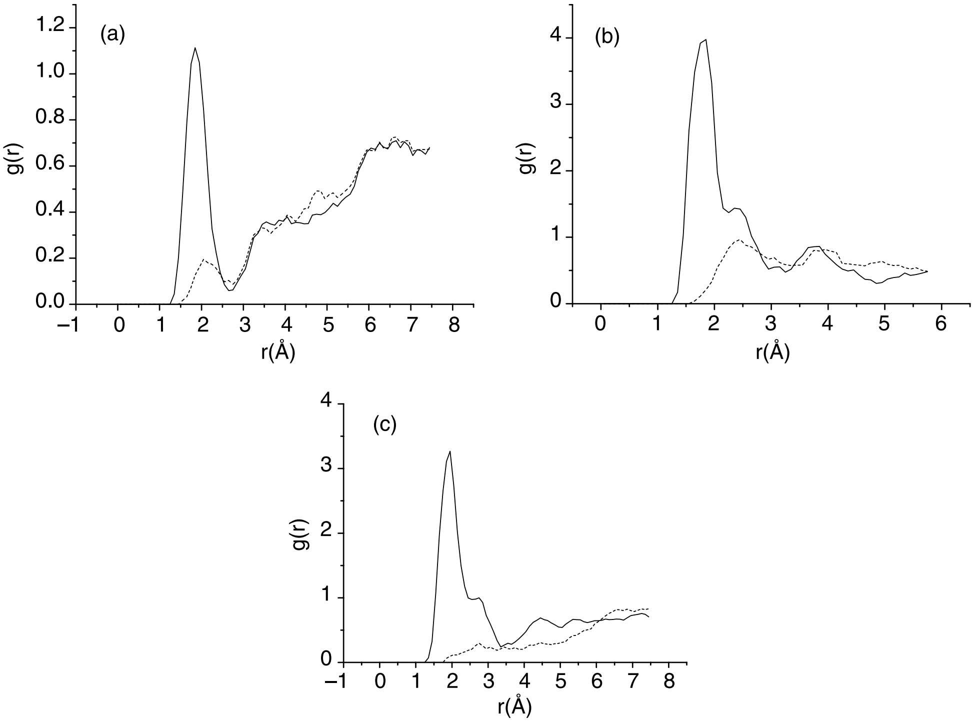


Fig. 3. RDF calculation for the CS/P2HEM blends: (a) 20/80, (b) 50/50 and (c) 80/20, using as reference: (—) oxygen atom of the hydroxyl methyl group of CS and (- - -) nitrogen atom of the amino group of CS relative to the distance of the oxygen atom of the carbonyl group of P2HEM.

Table 3
FTIR absorptions and the displacements of the C=O band of P2HEM for the CS/P2HEM blends

Blend %P2HEM	C=O band (cm^{-1})	Displacement P2HEM (cm^{-1})
0	–	–
20	1729.3	3.5
30	1728.1	2.5
40	1719.4	6.4
50	1729.6	3.8
60	1727.4	1.6
70	1725.8	0
100	1725.8	–

4. Conclusions

From the molecular dynamic simulation carried out in the present work for CS/PVA and CS/P2HEM blends we have characterize different sets of interactions, depending on the composition of the interacting polymer. The calculation shows that for low compositions of PVA and of P2HEM, the interactions are established with the hydroxymethyl group of CS. As the composition in these interacting polymers increases, the amino groups of the CS begin to participate in the interaction. This result shows consistency with the available FTIR experimental data.

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