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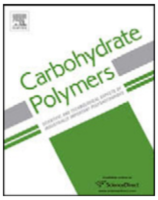

# Blends containing chitosan and poly(sodium-4-styrene sulphonate). Compatibility behavior

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ABSTRACT

The phase behavior of blends containing chitosan (CS) and poly(sodium-4-styrene sulphonate) (PSS) was analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), dielectric spectroscopy (DRS) and atomic force microscopy (AFM). FTIR and DRS analysis seem to indicate the existence of interactions between sulphonate groups of PSS and $-NH_2$ or –OH or both groups of CS. The study of blends by AFM showed a completely different morphology when compared with that of pure components as nanocrystalline domains appeared as globular agglomerates containing more or less spherical particles instead of the independent nanodomains seen in the neat components, possibly as consequence of interactions between both polymers.

## 1. Introduction

Chitosan (CS) is a copolymer of D-glucosamine and N-acetyl-D-glucosamine. It is a pseudo-natural, biodegradable and biocompatible polysaccharide obtained from chitin (Kim, Kim, & Lee, 1996a, 1996b). It has been a subject of intensive research for a long time (Brunel et al., 2009; Dong, Ruan, Wang, Zhao, & Bi, 2004; Nogales, Ezquerra, Rueda, Martinez, & Retuert, 1997; Osman, 2005; Pillai, Paul, & Sharma, 2009; Radhakumary, Nair, Mathew, & Nair, 2005; Rao & Johns, 2008; Sandford & Hutchings, 1987; Skaugrud, 1989; Viciosa, Dionisio, Silva, Reis, & Mano, 2004; Sandford, 1990). The solubility is obtained at pH < 6.5 at pH 4.5 and below, they are completely protonated (Rinaudo, Milas, & Dung, 1993). The effect of the free amino group in partially N-acetylated derivatives play an important role in different phenomena observed in the combination of CS with polymers like polysaccharides (Hirano, Mizutani, Yamaguchi, & Miura, 1978), poly(ethylene oxide) (Mucha, 1998; Wrzyszczynski et al., 1995), and functionalized vinyl polymers (Castro, Gargallo, Leiva, & Radic, 2005; Sandoval, Castro, Gargallo, Radic, & Freire, 2005).

Due to the polyfunctionality of chitosan, its use in polymer blends seems to be interesting in order to obtain biodegradable materials. The fact that CS has –OH and $-NH_2$ free groups, which are able to interact by hydrogen bonding with other functionalized polymers, is a starting point to obtain new biodegradable blends with new properties.

It is well known that polymer blends have been a matter of current interest in the last years (Brus, Dybal, Schmidt, Kratochvil, & Baldrian, 2000; Kono, Iwase, & Kanamori, 2008; Urzúa, Gargallo, & Radic, 2000; Wang, Wang, Zhang, Wan, & Ma, 2008). Blending is a common and potentially versatile way to develop new materials with designed properties, which cannot be reached by using single polymers. The use of polymer blends as a source for new materials is severely limited by the incompatibility of many polymer pairs of interest due to entropic reasons (Brus et al., 2000; Urzúa et al., 2000; Ten Brinke, Karasz, & MacKnight, 1983).

Therefore, in order to reach compatibility, specific interactions are necessary to produce negative heats of mixing (Cowie, Elexpuru, & McEwen, 1991; Jaworska, Sakurai, Gaudon, & Guibal, 2003; Kambour, Bendler, & Boop, 1983; Kim et al., 1996a, 1996b). By this way, the chemical structure of the polymeric components plays an important role in order to enhance interactions which can promote miscibility. The role of polymer–polymer interactions (which determine the phase behavior and final properties of polymer blend materials) is of interest in the prediction of miscibility of polymer blends. The use of functionalized polymers represents a good way to obtain interacting polymers which can produce a single-phase material or a compatible blend with enhanced prop-

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**Table 1**
Glass transition temperatures ($T_g$) of the blends for different CS/PSS compositions (wt%).

| PSS (wt%) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T_g$ (K) | 380 | 412 | 405 | 371 | 386 | 380 | 382 | 377 | 376 | 373 | 371 |

erties. The aim of this work is the study of the compatibility of chitosan with poly(sodium-4-styrene sulphonate) (PSS) using different experimental techniques.

## 2. Materials and methods

Poly(sodium-4-styrene sulphonate) is a commercial polymer from Aldrich with an average molecular weight of 70,000. Chitosan used has a degree of acetylation of around 20%, with a viscometric-average molecular weight of 360,000. This polymer has been obtained from a chemical modification of chitin provided from Federal University of Ceará in Brasil.

Viscometric-average molecular weight of chitosan was estimated by viscosity measurements in acetic acid 0.1 M and NaCl 0.2 M using the viscometric relationship: $K = 1.81 \times 10^{-3}\ \mathrm{Mn}^{0.93}$ (Maghami & Roberts, 1988).

Blends were obtained in solution using dilute aqueous solution of acetic acid (HAc). The acid concentration was 0.5% (v/v) and the pH of the solution was 4.2. Polymer concentration was always around 1.5% (w/w). Composition of blends varied between 10 and 90 wt%. Blends were dried at 35 °C in a vacuum oven during 3 weeks. The water content estimated by TGA is about 7–8%. i.e. seven water molecules per hundred of ionic site.

FTIR spectra of the polymers and blends were recorded in a Bruker Vector 22 spectrophotometer. Spectra were obtained with a resolution of 1 $\mathrm{cm}^{-1}$ and 20 scans.

Thermal degradation of the samples was performed using a TGA/SDTA 851 Mettler–Toledo thermobalance and the data were processed using the STAR$^e$ version 8.1 program from Mettler.

Glass transition temperature ($T_g$) of the samples was determined using a Mettler–Toledo DSC 821-700 calorimetric system equipped with a FRS5 sensor. Thermograms were measured in the range between 233 and 473 K at a scan rate of 20°/min, with dry nitrogen as purge gas.

WAXS measurements were performed on pressed samples irradiated using a Bruker D8 Advance diffractometer operating with Ni-filtered $\mathrm{CuK}_{a1,2}$; $K_b$ radiation source ($\alpha = 1.542$ Å). Powder diffraction spectra were recorded with 40 kV voltage and 40 mA intensity.

Atomic force microscopy characterization of samples was carried out using the tapping mode with a Digital Instruments Nanoscope IIIa Multimode microscope with J scanners of 200 × 200 μm.

A Novocontrol Alpha high resolution dielectric analyzer, connected with a computer and a Novocontrol Novocool cryogenic system for temperature control, was used for dielectric measurements. Blends were measured between 223 and 453 K at a frequency of 1300 Hz. Films were obtained directly by solution casting using a mould of 2.5 cm diameter.

## 3. Results and discussion

Dry and transparent blends of CS and PSS, were measured by DSC. All samples showed single glass transition temperatures. This result, as a first approach, would be indicative of one-phase material. This is true if the presence of a single glass transition is considered as a criterion for miscibility between the components of the blends, but taking into account that pure components show quite similar $T_g$ values, further experiments are necessary to confirm the presence of one-phase material. Table 1 summarizes the obtained values of $T_g$ for CS/PSS blends as function of the blend composition. Scattering of the points and a discontinuous variation of the glass transition temperature with composition are observed. These results suggest the need for using other complementary experimental techniques in order to determine the compatibility level between blend components.

FTIR absorptions of the pure components and blends show some displacements which are summarized in Table 2. In the zone of 3400 $\mathrm{cm}^{-1}$, corresponding to the amino and hydroxyl groups, small shift for the different blend compositions relative to the pure components can be observed. There are shifts until 26 $\mathrm{cm}^{-1}$, relative to the absorption band of pure CS. This result could be interpreted as a consequence of some kind of strong interaction between the components of the blends. Nevertheless, it is necessary to take into account that in this absorption zone the overlapping of the $-\mathrm{NH}_2$ and –OH groups does not allow to clarify in unequivocal way the real response of the polymeric blend. Another absorption zone in the IR spectra that can be useful to get confidence about the interactions between the polymers is that at 1560 $\mathrm{cm}^{-1}$, which corresponds to the absorption of the $-\mathrm{NH}_2$ groups. In this zone of the IR spectra the shift of the bands changed from 4 to 10 $\mathrm{cm}^{-1}$, being larger when the composition of PSS in the blend increased. This result could be attributed to the interaction of the amino group of the CS with the $\mathrm{SO}_3^-$ group of PSS, increasing with the increase of PSS amount. In the same way, the zone of 1160 and 1040 $\mathrm{cm}^{-1}$ of the IR spectra that corresponds to the vibration of the sulphonate groups, showed displacements when compared with pure PSS (see Table 2), that could be attributed to interactions between the sulphonate group of PSS and the $-\mathrm{NH}_2$ or –OH or both groups of chitosan. According to the chemical structure of the polymers, the interaction through hydrogen bonds is highly probable. In fact in previous works dealing with the compatibilization of chitosan with interacting synthetic polymers, the compatibilization process was attributed to hydrogen bonding formation (Castro et al., 2005; Sandoval et al., 2005). The –OH and $-\mathrm{NH}_2$ groups of chitosan are strongly interacting groups by hydrogen bonds, and/or to the interaction between $-\mathrm{NH}_3^+$ and $-\mathrm{SO}_3^-$ in the blend, what could be the reason of the displacements observed in the IR spectra and allow to assume compatibility (Table 3).

**Table 2**
Shifts of FTIR bands ($\mathrm{cm}^{-1}$) for CS/PSS blends in the absorption zones of –OH and $-\mathrm{NH}_2$ groups at different compositions (wt%), and for blends of CS/PSS blends in the absorption zones of the $-\mathrm{S({=}O)}_2$ group.

| PSS (wt%) | –OH and $-\mathrm{NH}_2$ 3400 $\mathrm{cm}^{-1}$ zone | Shifts $-\mathrm{NH}_2$ 1560 $\mathrm{cm}^{-1}$ zone | $\mathrm{S({=}O)}_2$ 1160 $\mathrm{cm}^{-1}$ zone | $-\mathrm{S({=}O)}_2$ 1040 $\mathrm{cm}^{-1}$ zone |
|---|---|---|---|---|
| 0 | – | – | – | – |
| 10 | 2 | 2 | 29 | 5 |
| 20 | 28 | 4 | 29 | 5 |
| 30 | 29 | 4 | 29 | 4 |
| 40 | 28 | 4 | 3 | 4 |
| 50 | 20 | 3 | 3 | 3 |
| 60 | 17 | 10 | 7 | 1 |
| 70 | 25 | 11 | 2 | 1 |
| 80 | 26 | 17 | 5 | 1 |
| 90 | 26 | 12 | 2 | 1 |

**Table 3**
Shifts of FTIR bands for blends CS/PSS blends in the absorption zones of the $-S(=O)_2$ group.

| PSS (%) | $S(=O)_2$ ($cm^{-1}$) | Shifts $S(=O)_2$ ($cm^{-1}$) | $S(=O)_2$ ($cm^{-1}$) | Shifts $S(=O)_2$ ($cm^{-1}$) |
|---|---|---|---|---|
| 10 | 1155 | 29 | 1035 | 5 |
| 20 | 1155 | 29 | 1035 | 5 |
| 30 | 1155 | 29 | 1036 | 4 |
| 40 | 1181 | 3 | 1036 | 4 |
| 50 | 1187 | 3 | 1038 | 2 |
| 60 | 1191 | 7 | 1039 | 1 |
| 70 | 1186 | 2 | 1039 | 1 |
| 80 | 1189 | 5 | 1039 | 1 |
| 90 | 1186 | 2 | 1040 | 0 |
| 100 | 1184 | – | 1040 | – |

According to the results summarized above there is some evidence of interactions, which could allow to assuming compatibility of the polymers in some extent. On the other hand, taken into account the ionic character of the polymers electrostatic interaction could be another contribution to formation of the blend. Nevertheless this information is not enough to get a definite conclusion. For this reason thermogravimetric analysis of the pure components and the blends was also used as another procedure to get more information about the behavior of the blends. Fig. 1 shows the thermogravimetric curves for PSS, CS and blends, represented as the first derivative of the weight loss with temperature ($dm/dT$). This kind of representation is a better way to observe the degradation temperature than the diagrams of pure weight loss versus temperature. The analysis of the thermogravimetric profiles allow to conclude that a 7–7.5% of water molecules relative to the total ionic sites are present, i.e. there are about seven water molecules per hundred of ionic sites. This result was obtained by the comparison of the areas of the peaks in the second derivative of the thermogravimetric profile, and also by the own software of the equipment (STAR$^e$ version 8.1). Thermogravimetric profiles follow a two-stage decomposition process for pure compounds and blends but for blends the process occurs at lower temperatures than that of the pure components. This is an unusual behavior of blends if this thermal behavior is compared with the results reported for blends of CS with other vinyl polymers (Castro et al., 2005; Sandoval et al., 2005), where the thermal degradation of the blends was found at higher temperatures than that of the pure components, what was attributed to the formation of a new material with enhanced thermal properties. This unusual result could be attributed to incompatibility of the polymeric components. Therefore, the experimental results obtained by different experimental techniques are contradictory. A noteworthy point is that the experimental techniques used above are the most commonly reported to decide if a polymeric blend is compatible or not, but as it can be observed in this case the results are not conclusive.

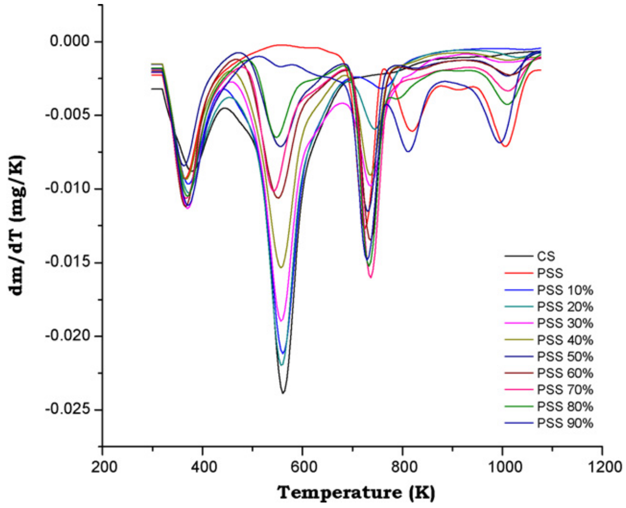

**Fig. 1.** First derivative of the degradation profiles ($dm/dT$) for pure chitosan, poly(sodium-4-styrene sulphonate) and CS/PSS blends of several compositions (wt%).

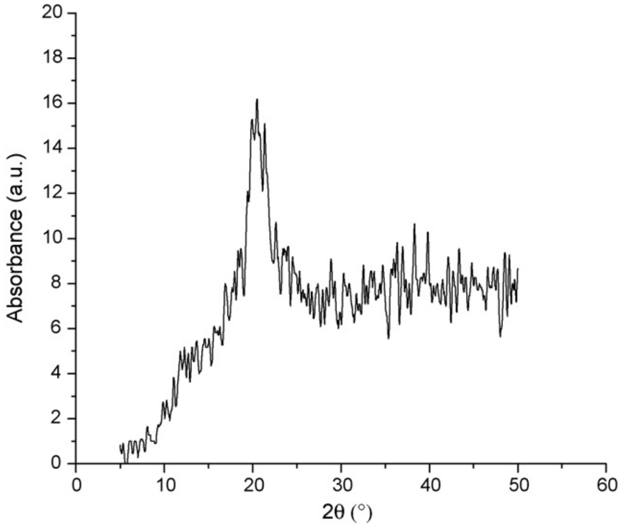

**Fig. 2.** WAXS measurements representation of the powder diffraction spectra of chitosan using Ni-filt $CuK_{a1,2}$; $K_b$ radiation source ($\alpha = 1.542$ Å) at 40 kV voltage and 40 mA intensity.

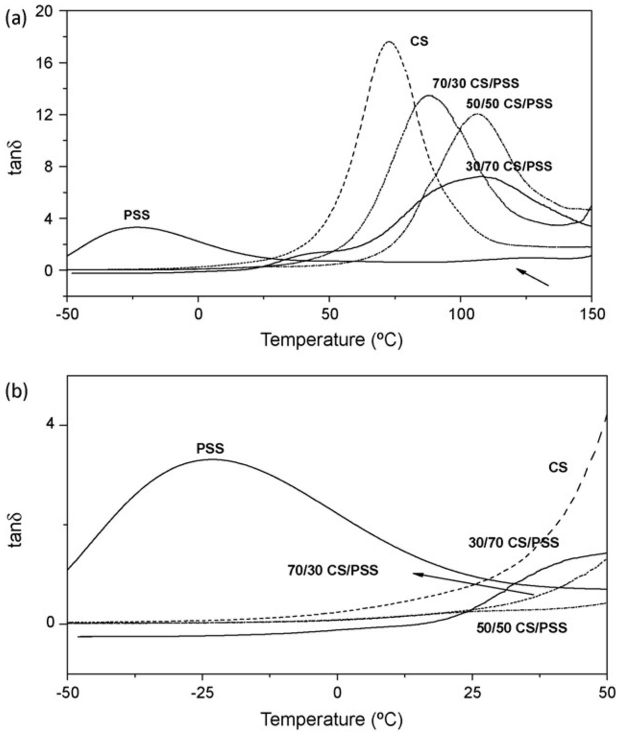

**Fig. 3.** a) Dielectric spectra of tan $\delta$ vs. temperature as measured at 1300 Hz for pure CS and PSS and blend containing 30 and 50 wt% PSS. b) Dielectric spectra of tan $\delta$ vs. temperature as measured at 1300 Hz in the temperature range of secondary relaxation for pure CS and PSS and blends containing 50, 70 and 90 wt% PSS.

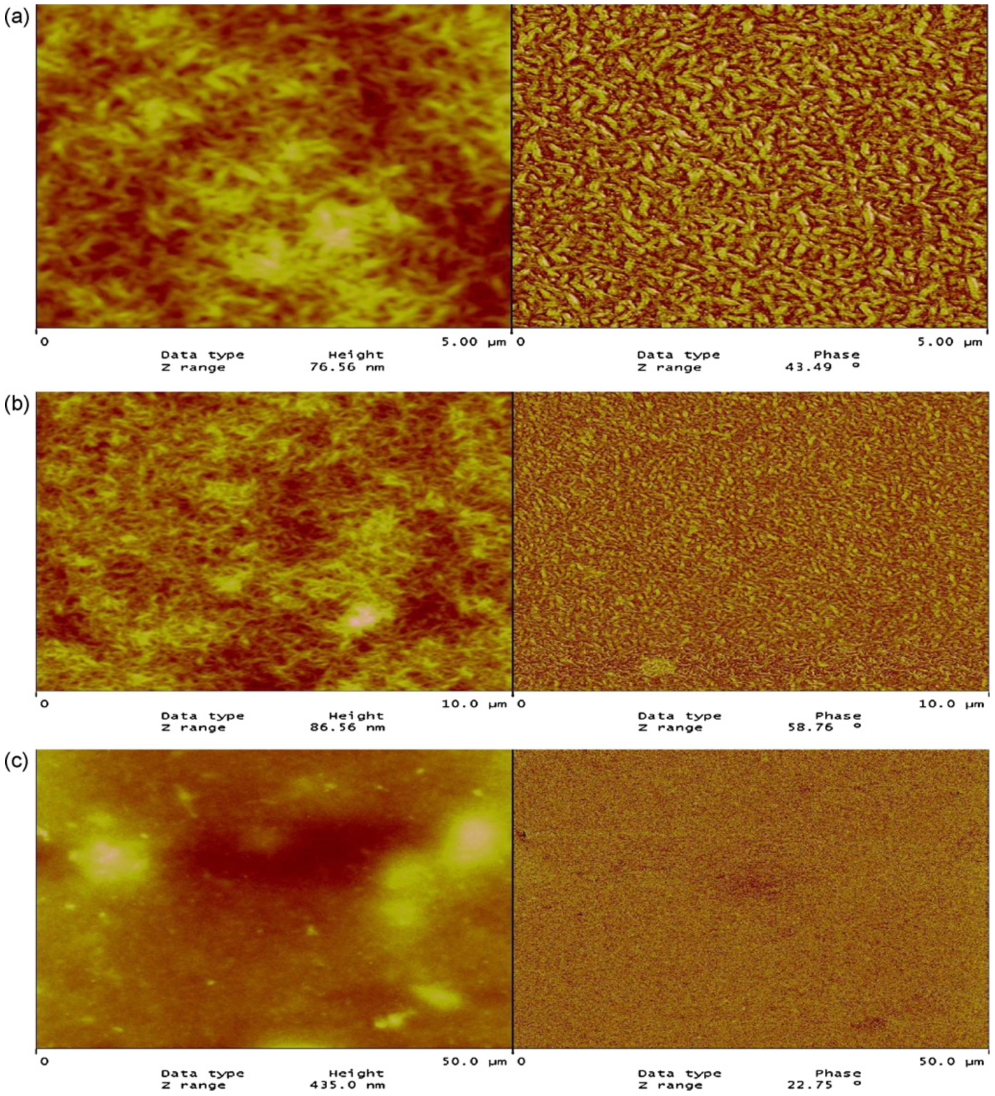

**Fig. 4.** Topography (left) and phase images (right) for films of CS obtained at different magnifications: a) 5 μm, b) 10 μm and c) 50 μm.

As shown in Fig. 2, diffractograms of chitosan exhibited a crystallinity peak whose maximum occurred at the angle $2\theta = 20^\circ$ and a small but broad peaks region corresponding to its amorphous material was also observed. This is a pattern similar to those reported for shrimp material with low crystallinity degree. The crystallinity degree was around 25% as calculated by the ratio of the crystalline peak area and the sum of crystalline and amorphous areas (Jaworska et al., 2003; Kim et al., 1996a, 1996b; Li & Marchessault, 1997).

In order to clarify compatibility behavior, it was necessary to turn to other experimental techniques. Dielectric relaxation spectroscopy (DRS) of the pure components and blends is another way to attempt to clarify the behavior of the blends. DRS has been used by several authors to characterize chitosan, specially for analyzing the effect of water in the molecular motions (Nogales et al., 1997; Viciosa et al., 2004; Viciosa, Dionisio, & Mano, 2006; Stevenson, Kozanecki, & Okrasa, 2005). Moreover, both unmodified PS and sulphonated PSS have been analyzed in terms of DRS (Atorngitjawat, Klein, & Runt, 2006; Costa, Rubinger, & Martins, 2007; Hao, Bohning, & Schonhals, 2007; Wypych et al., 2005), so DRS seems to be a suitable technique for studying the behavior of blends.

Fig. 3a shows the evolution of tan $\delta$ with temperature at a frequency of 1300 Hz for pure CS, PSS and blends with 30, 50 and 70 wt% PSS. For pure CS, a strong relaxation process can be seen, probably related with water desorption mechanism upon heating of the sample (Nogales et al., 1997; Viciosa et al., 2004, 2006). For pure PSS two relaxation processes are detected: the main $\alpha$ relaxation (associated to the glass transition), centered at around 120 °C similar to that shown previously for unmodified PS (Atorngitjawat et al., 2006; Costa et al., 2007; Hao et al., 2007; Wypych et al., 2005), and the secondary $\beta$ relaxation at temperatures below 0 °C, related with the rotation of phenyl groups, that has also been detected for pure polystyrene (PS) (Wypych et al., 2005).

As it can be seen, the secondary relaxation is higher with respect to pure PS, probably due to the ionic species attached to the aromatic ring, while the main relaxation (indicated by an arrow) is weak compared with the $\beta$ relaxation. For CS/PSS blends, the main relaxation process, associated with both processes described for pure components, water desorption of CS and the main relaxation of PSS, is displaced towards the region of the main relaxation of PSS, thus clearly indicating that specific interactions do exist between the components of the blends. The secondary relaxation of PSS is also detected for 30/70 CS/PSS blend. For a better visualiza-

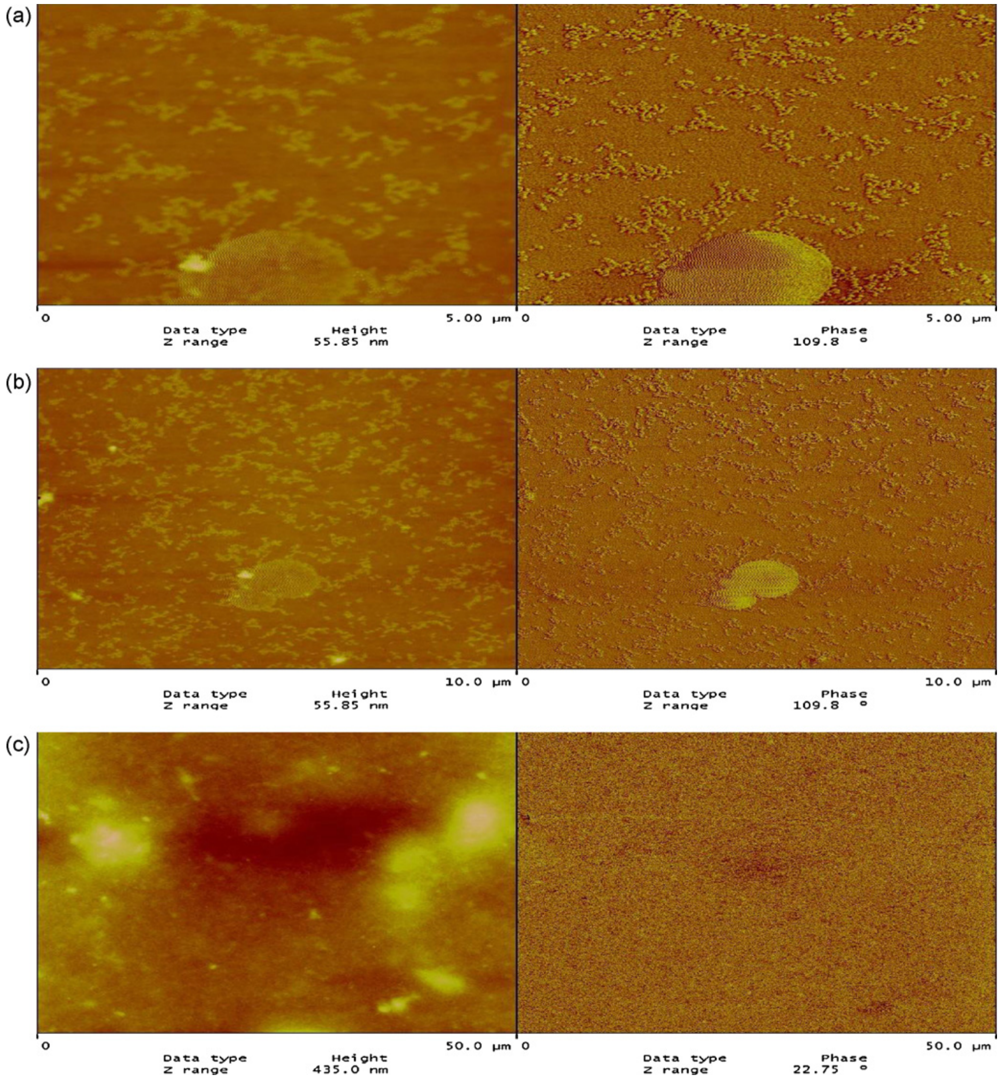

**Fig. 5.** Topography (left) and phase images (right) for films of poly(sodium-4-styrene sulphonate) obtained at different magnifications: a) 5 µm, b) 10 µm and c) 50 µm.

tion, Fig. 3b shows the evolution of tan $\delta$ with temperature in the range of the secondary relaxation. The secondary relaxation is displaced towards higher temperatures and its height significantly decreases with respect to pure PSS as the CS content increases even disappearing for chitosan contents higher than 30 wt%. This fact seems to be related to the interactions between the $-SO_3^-$ group linked to the phenyl group of PSS (responsible of the relaxation) and –OH groups of CS. As it has been shown above by FTIR, DRS seems to confirm the interactions between the components of the blends.

Atomic force microscopy is an experimental technique that could also allow to add interesting information about the compatibility of the blends from a different point of view. Fig. 4a–c shows the AFM topography and phase images for films of pure CS and Fig. 5a–c for pure PSS, obtained with different magnifications. For CS, a fibrous crystalline structure formed by crystalline whiskers can be seen. This structure is also observed after chemical treatments in cellulose extracted from plants. For PSS, also a structure formed by nanosized but also some microsized domains embedded in a smooth flat matrix can be seen. On the other hand, Fig. 6a–c shows both topography and phase images for the 50/50 CS/PSS blend. The morphology is completely different from that observed for pure components and two phases can be clearly distinguished.

The smooth flat phase could correspond to the flat part seen in pure PSS images, while the other one, constituted by individual and interconnected rough and globular domains, containing more or less spherical particles interconnected between them by the other component, could correspond to the rearrangement of the whiskers or worm-like entities seen in 5 µm images of both CS and PSS.

The change in the morphology of the crystalline structure possibly is mainly the consequence of the interactions between the hydroxyl amine groups of chitosan and the sulphonate groups of PSS. These morphological changes could be responsible of the lower temperatures for degradation shown above by TGA.

## 4. Conclusions

CS/PSS blends have been characterized by different experimental techniques in order to analyze their compatibility behavior. The analysis of FTIR spectra of pure components and blends show displacement in several bands, attributed to the interactions between the sulphonate group of PSS and –OH of chitosan.

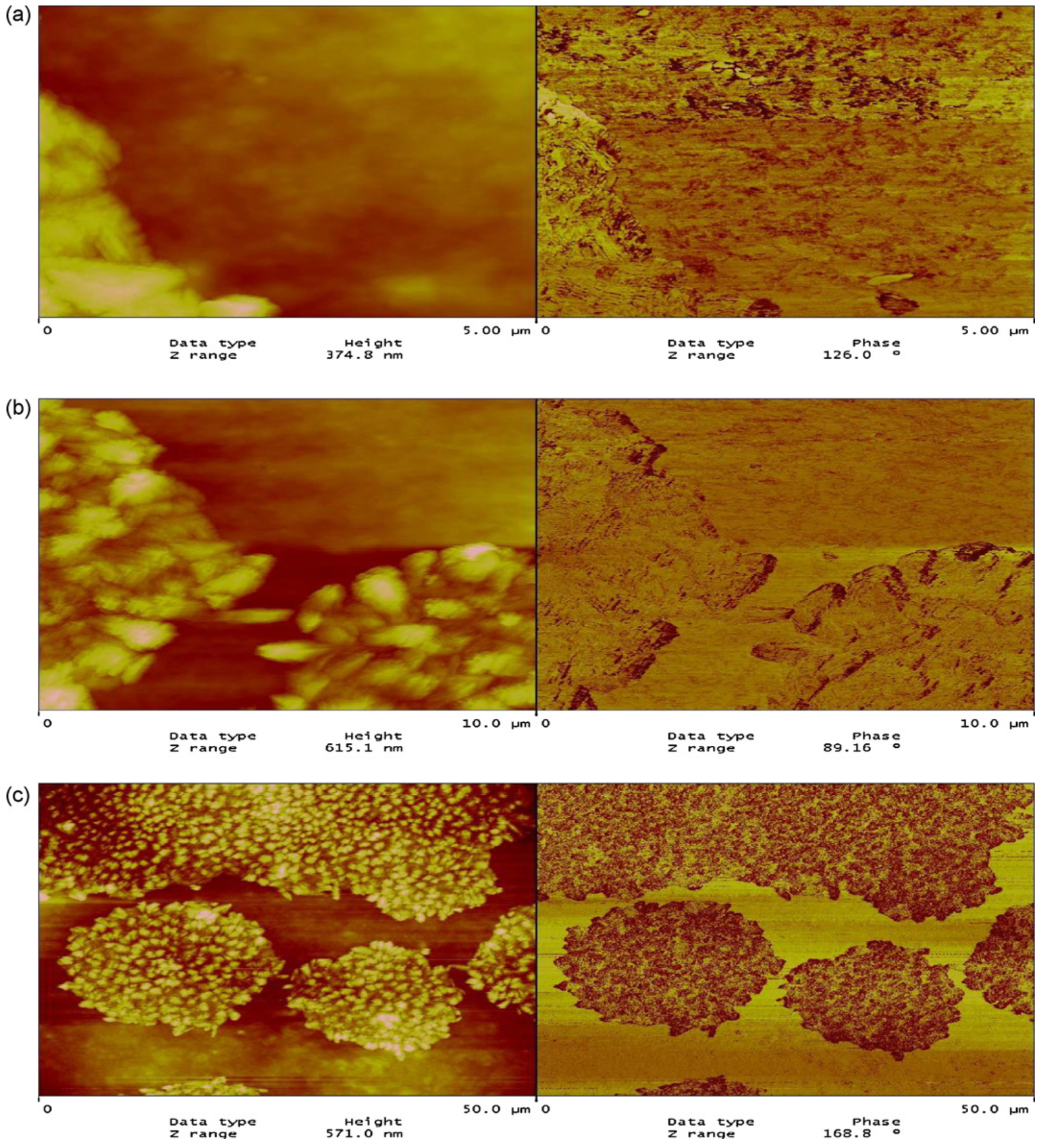

**Fig. 6.** Topography (left) and phase images (right) for films of 50/50 wt% CS/PSS blend obtained at different magnifications: a) 5 µm, b) 10 µm and c) 50 µm.

The thermogravimetric profiles follow a two-stage decomposition process for pure compounds and blends but for blends the process occurs at lower temperatures than that of the pure components. This is an unusual behavior of blends if this thermal behavior is compared with the results reported for blends of CS with other vinyl polymers.

In order to clarify compatibility behavior, blends were characterized by dielectric relaxation spectroscopy and atomic force microscopy. DRS spectra seem to indicate the existence of interactions between the sulphonate groups of PSS and –OH groups of chitosan. The secondary relaxation of PSS (related with the rotation of phenyl groups) is displaced to higher temperatures and its height decreases due to the presence of chitosan as a consequence of polar interactions between specific groups of the components.

As shown by AFM, the morphology of the blends is different from that of pure components. Two phases can be distinguished. One phase is smooth flat and could correspond to amorphous PSS, while the other one, presenting rough and globular interconnected domains, could contain the independent nanocrystalline domains detected for both CS and PSS. The change in the morphology of the crystalline structure leading to the globular agglomeration of nanocrystalline domains seems to be mainly the consequence of the interactions between the hydroxyl groups of chitosan and the sulphonate groups of PSS. These morphological changes could be responsible of the lower temperatures for degradation shown above by TGA.

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