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Blends of chitosan and poly(sodium-4-styrene sulphonate). Compatibilization by lysine and glutamic acid

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ABSTRACT

Polymer blends of chitosan (CS) and poly(sodium-4-styrene sulphonate) (PSS) have been compatibilized using lysine (LYS) and glutamic acid (GLU). Blends of CS/PSS containing LYS and GLU have been studied by thermal analysis. The values of T_g for CS/PSS-LYS blends could not be detected by thermal analysis but one single T_g was found for CS/PSS-GLU blends. Thermogravimetric analysis (TGA) showed that blends decompose at lower temperatures than that of pure components. Displacements in the main absorption bands in the FT-IR spectra were not clear to discern compatibility. Atomic force microscopy (AFM) indicated that addition of lysine or glutamic acid clearly modified the compatibility of the blends. The globular domains existing in the unmodified blend changed to more or less linear and smooth crystalline domains with parallel periodicity. Dielectric analysis revealed that compatibilizer addition changed the secondary relaxation process of PSS to higher temperatures as a result of the modification on interactions. No variation on the segmental dynamics of both polymers was observed as their main relaxations remained unchanged after the addition of lysine or glutamic acid.

1. Introduction

Chitosan (CS) produced from chitin, the most abundant biopolymer after cellulose, by means of an alkaline deacetylation procedure is a natural (poly)aminosaccharide. It is characterized by properties that are unique among natural polymers and is a cationic polymer in acidic solutions (Berth & Datzenberg, 2002). This polymer has been matter of numerous studies and applications as it was described in previous papers (Sandford, 1990; Skaugrud, 1989). It has been extensively studied for applications in areas as diverse as waste-water treatment, paper and textiles, biomedicine and biology (Berth & Datzenberg, 2002). Chitosan is used in low calorie diets and pharmaceuticals as well as antibacteriostatic/anti-fungal agent; as gelling agent in drug delivery systems; as a film, fiber, or gel in wound dressing (Muzzarelli, Jeniaux, & Gooday, 1985; Ratto & Hatakeyama, 1995; Sandford, 1990). Applications of chitosan in photography, ophthalmology, agricultural, and food have been described elsewhere (Beri, Walker, Reese, & Rollings, 1993; Castro, Gargallo, Leiva, & Radic, 2005). These potential applications of chitosan are envisioned primarily as a result of its unique physicochemical properties (Castro et al., 2005; Urzúa, Gargallo, & Radic, 2000). Because of its versatile chemical structure it is possible to assume that CS is a strong interacting polymer because, besides their –OH or –NH_2 groups a minor proportion of amide groups are present which are in general partially hydrolyzed. Therefore some free carboxylic groups are also another interacting functional group (Brannock, Barlow, & Paul, 1991). For this reason the blending process of CS with other interacting synthetic polymers is considered as a new way to obtain materials containing biodegradable moieties. In fact there are several polymeric blends which have several interesting properties, but in the majority of the cases, these blends correspond to synthetic polymers which are not biodegradable and not convenient due to pollution problems. Due to the nature of the functional groups, its compatibilization with other polymers by specific interactions, such as hydrogen bonds, dipole–dipole, acid–base, or complexation between the components is favoured (Paul, Barlow, & Keskkula, 1989). Interactions in these systems give rise to negative heat of mixture favouring the mixing process (Castro, Gargallo, Radic', Mondragon, & Kortaberria, submitted for publication; Sandoval, Castro, Gargallo, Radic, & Freire, 2005; Viciosa, Dionisio, & Mano, 2006). Therefore chitosan can be compatibilized with synthetic polymers obtaining

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Table 1
Glass transition temperatures (T_g) for 50/50 (wt%) blends of CS/PSS-LYS and CS/PSS-GLU.

	PSS (wt%)										
	0	10	20	30	40	50	60	70	80	90	100
CS/PSS-LYS T_g (K)	382	–	–	–	–	–	–	–	–	–	–
CS/PSS-GLU T_g (K)	382	388	384	382	384	383	381	381	383	384	371

Table 2
Displacements of FT-IR bands for 50/50 (wt%) blends of: in the absorption zones of the functional groups: –OH, –NH_2, and –S(=O)$_2$ for: a) CS/PSS-LYS and b) CS/PSS-GLU.

PSS (wt%)	–OH and –NH_2 3400 cm^{-1} zone	Displacement –NH_2 1560 cm^{-1} zone	Displacement –S(=O)$_2$ 1186 cm^{-1} zone	Displacement –S(=O)$_2$ 1040 cm^{-1} zone
(a)				
0	–	–	0	0
10	21	1	31	5
20	20	0	32	3
30	20	0	32	3
40	19	1	4	2
50	18	1	1	2
60	23	0	0	2
70	19	0	1	1
80	20	0	1	0
90	28	0	–	–

PSS (wt%)	Displacement –OH and –NH_2 3400 cm^{-1} zone	Displacements –NH_2 1560 cm^{-1} zone	Displacement –S(=O)$_2$ 1156 cm^{-1} zone	Displacements –S(=O)$_2$ 1040 cm^{-1} zone
(b)				
0	–	–	28	2
10	26	0	31	3
20	20	0	33	2
30	27	0	28	0
40	19	10	26	2
50	22	4	11	2
60	20	0	10	1
70	20	9	9	0
80	20	0	6	1
90	21	1	–	–

blends that could be biodegradable new materials with new properties (Paul et al., 1989; Skaugrud, 1989; Viciosa, Dionisio, Silva, Reis, & Mano, 2004). The compatibilization of chitosan with polyelectrolytes such as poly(sodium-4-styrene sulphonate) (PSS) is not a clear process as it was reported in a previous paper (Castro et al., submitted for publication). The use of small molecules as compatibilizers is a way to obtain new materials containing chitosan and synthetic polymers as new potentially biocompatible polymers. The aim of this work is the study of the compatibility between CS and PSS using lysine (LYS) and glutamic acid (GLU) as small aminoacidic compatibilizers. This study has been performed using the classical thermal and FT-IR techniques, dielectric relaxation spectroscopy (DRS), and atomic force microscopy (AFM).

2. Materials and methods

2.1. Materials

Chitosan (CS) with 20% degree of acetylation and $\bar{M}_V = 360,000$ and commercial poly(sodium-4-styrene sulphonate) (PSS) with $\bar{M}_W = 70,000$ have been previously reported (Castro et al., submitted for publication). Lysine, HOOC-CHNH$_2$-(CH$_2$)$_4$NH$_2$ (LYS), and L-glutamic acid, HOOC-CHNH$_2$-(CH$_2$)$_2$COOH (99%) (GLU), are commercial products from Aldrich.

2.2. Blend preparation

Blends were obtained in solution using dilute aqueous solution of acetic acid (HAc) and stirred for 12 h and yellow films were

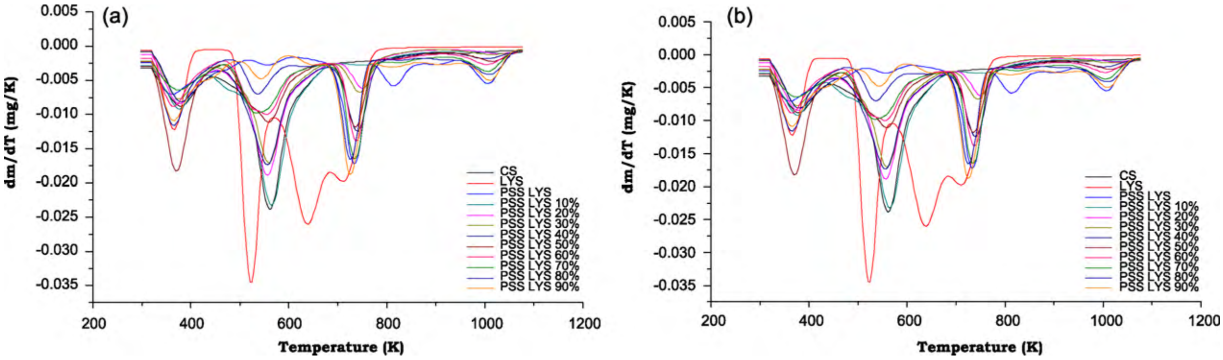

Fig. 1. First derivative of the degradation profiles (dm/dT) for pure chitosan, poly(sodium-4-styrene sulphonate) and blends compatibilized with: a) LYS and b) GLU.

obtained. As the concentration of PSS increases, films are more transparent and more fragile. Concentration of acetic acid solution was 0.5% v/v and the pH of the solution containing chitosan was 4.2. Polymer concentration was always about 1.5% w/w and the compatibilizer concentration of 10% w/w relative to the polymers used in the blend. This concentration would correspond to a 0.15% w/w of the compatibilizer relative to the polymer concentration. Blends were prepared in such a way that the composition varied between 10 and 90 wt% maintaining constant the compatibilizer concentration. Blends were dried at 35 °C in a vacuum oven during three weeks. The water content in the final samples was always about 7–7.5% relative to the ionic sites in the blends.

2.3. Glass transition temperature (DSC) analysis

Glass transition temperatures (T_g) were determined using a Mettler-Toledo DSC 821-700 calorimetric system equipped with a FRS5 sensor. Processing of the data was performed using the STAR^e software version 8.1 from Mettler. The samples were treated as previously reported (Skaugrud, 1989). Several heating cycles were performed i.e. heating from 273 K to 450 K, and maintaining isothermically for 2 min then cooling from 450 K to 248 K and maintaining isothermically for 1 min and finally heating from 248 K to 450 K. Temperatures higher than 450 K allow to degradation of chitosan.

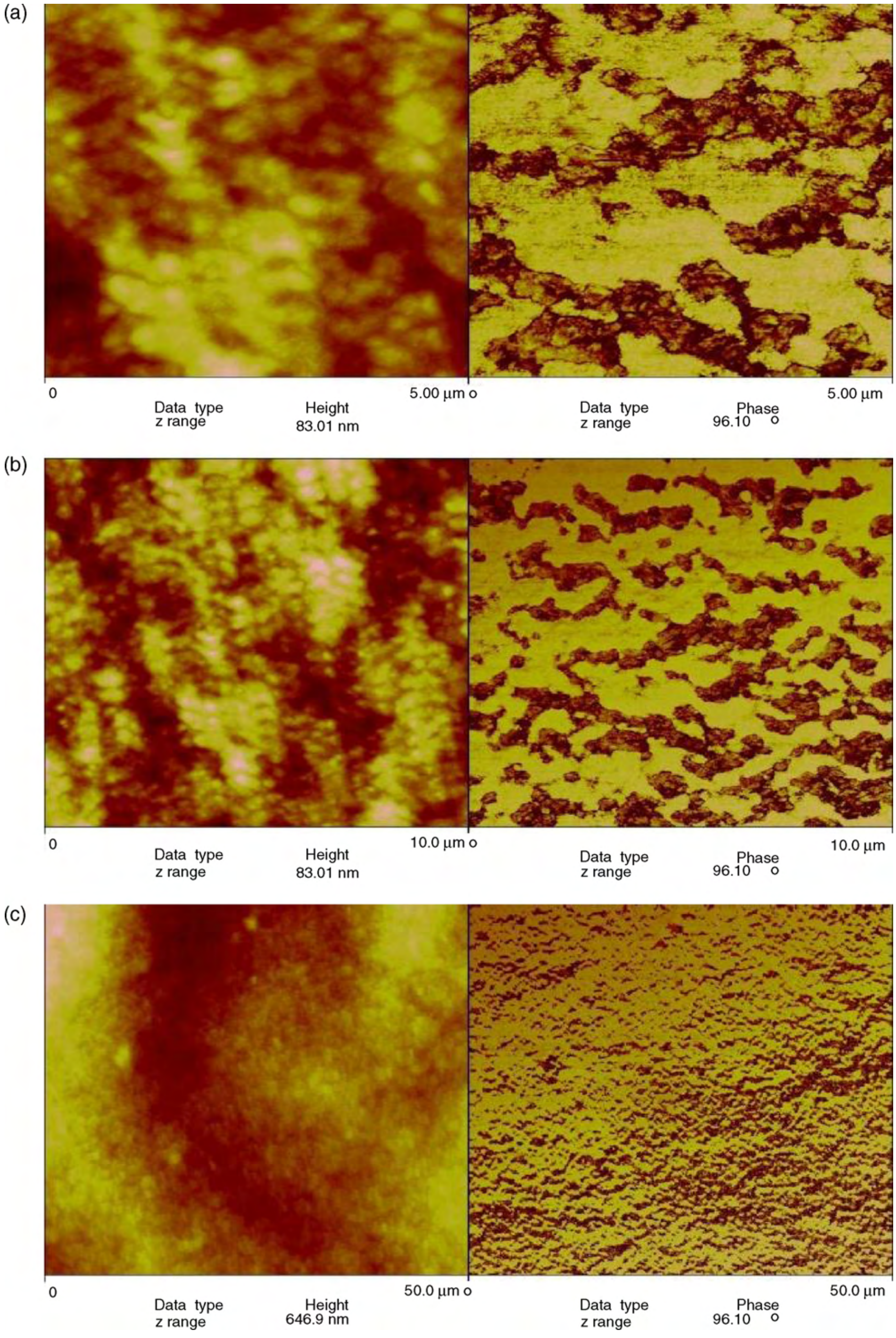

Fig. 2. Topography (left) and phase (right) images for films of CS/PSS-LYS 50/50 (wt%) obtained by AFM: a) 5, b) 10 and c) 50 µm, respectively.

2.4. Thermogravimetric analysis (TGA)

Thermal degradation of the samples was performed using a TGA/SDTA 851 Mettler-Toledo thermobalance. Data were processed using the STAR^e version 8.1 program from Mettler. Samples were heated from 298 K to 1180 K under nitrogen at 20°/min and the weight of the initial sample was 5 mg.

2.5. FT-IR characterization

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

2.6. Atomic force microscopy (AFM)

Sample morphology was analyzed using an atomic force microscope, Digital Instrument Nanoscope IIIa Multimode with scanners of 200 × 200 μm at 1 Hz using the tapping mode.

2.7. Dielectric analysis

A Novocontrol Alpha High Resolution dielectric analyser was used for dielectric measurements of the samples between 3 mHz and 10 MHz, connected with a computer and a Novocontrol Novocool cryogenic system for temperature control. Blends were measured between 223 K and 453 K at a frequency of 1300 Hz. Films

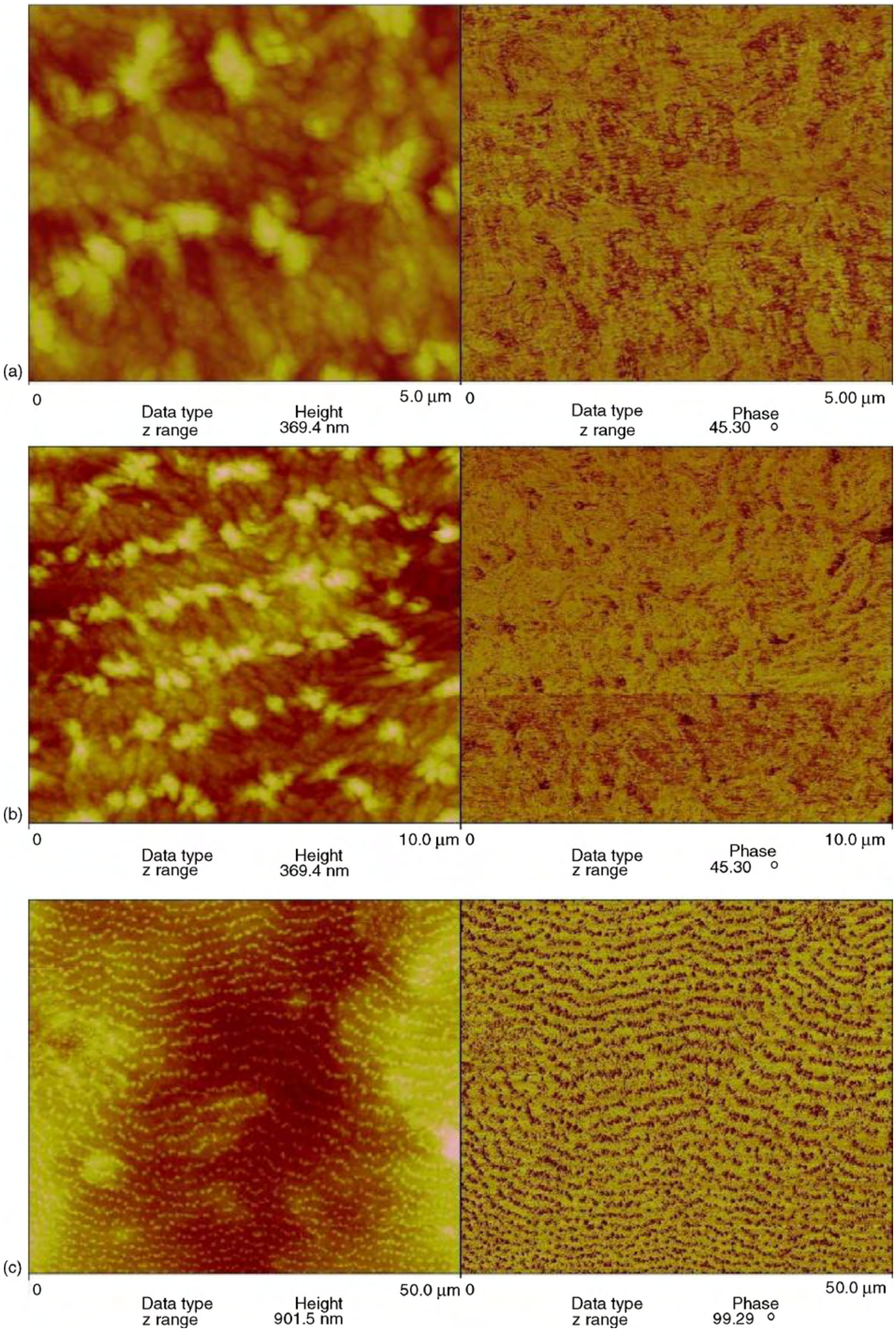

Fig. 3. Topography (left) and phase (right) images for films of CS/PSS-GLU 50/50 (wt%) obtained by AFM: a) 5, b) 10 and c) 50 μm, respectively.

were obtained directly by solution casting using a mold with a diameter of 2.5 cm.

3. Results and discussion

3.1. Calorimetric analysis

Dry samples of blends of chitosan (CS) and poly(sodium-4-styrene sulphonate) (PSS), containing 10 wt% of lysine or glutamic acid (CS/PSS-LYS or CS/PSS-GLU) as compatibilizers were analyzed by DSC measurements. In the case of blends containing LYS, it was not possible to detect the glass transition temperature (T_g). Nevertheless, blends of CS/PSS-GLU showed one single T_g value over the whole range of composition. This result could be considered as a first approach that blends were compatible or at least partially compatible. Table 1 compiles the T_g values obtained for blends of CS/PSS-LYS and CS/PSS-GLU at different compositions.

3.2. FT-IR results

FT-IR analysis in the absorption zones of –OH, –NH$_2$ and –S(=O)$_2$ functional groups at 3400–3440, 1560, 1040–1180 cm^{-1} show differences in the wavenumber with respect to the values for the pure components. The displacements of the different FT-IR signals for CS/PSS blends of different compositions modified with LYS and GLU, respectively are compiled in Table 2. Significant but not continuous displacements of the order of 20–30 cm^{-1} in the absorption zones corresponding to –OH, and –S(=O)$_2$ groups for both types of blends were found. These displacements would suggest that some kind of interactions between the polymers and the compatibilizers are present and could be attributed to a compatibilization process (Paul et al., 1989; Sandford, 1990; Viciosa et al., 2004). In the 3400 cm^{-1} zone displacements attributed to –OH groups of CS are observed as previously reported (Sandford, 1990; Sandford and Hutchings, 1987).

In the zone of the sulphonate groups small displacements were observed for low contents of PSS for the band at 1180 cm^{-1}, but for the band at 1040 cm^{-1} no displacements were detected. This behavior could be attributed to a larger interaction between this group with the –COOH groups of the compatibilizer and chitosan.

Thermogravimetric analysis is an experimental technique which can give some information about the thermal behavior of the blends. Fig. 1 shows the thermogravimetric curves represented as first derivative of the weight loss upon temperature for pure CS, PSS and blends containing LYS and GLU with different blend compositions. The thermal stability of the samples was very similar. The thermogravimetric profiles follow a two-stage decomposition process for the blends. The main observation on these systems is that the decomposition of the blends takes place at lower temperatures than those for the degradation of pure CS and PSS. This degradation temperature is about 15 °C lower relative to the pure components in the case of CS/PSS-LYS blends and lower than 10 °C for blends of CS/PSS-GLU blends. This is an unusual behavior because normally thermal stability increases for related systems (Paul et al., 1989; Sandford, 1990; Viciosa et al., 2004). This behavior is similar to that of blends without compatibilizers (Castro et al., submitted for publication) and it could be related with crystalline and/or morphological variations with respect to those of the pure polymers.

3.3. AFM and DRS analysis

Atomic force microscopy and dielectric analysis are experimental techniques that should allow complementary information to elucidate if blends were compatibilized by LYS and GLU.

As it has been previously shown (Sandford, 1990), phase separation was clearly observed by AFM for films of CS/PSS 50/50 (w/w). However, as shown in Fig. 2, for the 50/50 (w/w) CS/PSS blend modified with LYS compatibilizer, the images at three different magnifications indicate that the blend was compatibilized or at least partially compatibilized by the addition of the compatibilizer. Addition of lysine clearly changed the globular domains existing in the unmodified blend to more or less linearly small aligned and smooth crystallite domains with parallel periodicity. In the case of CS/PSS blend modified with GLU compatibilizer, as shown in Fig. 3, the individual chitosan whiskers appeared individualized showing a pseudo-long range order. This behaviour indicates that strong interactions are promoted by the compatibilizer addition and also that differently pseudo-ordered morphologies can be obtained by changing the amount of ethylene groups of the aminoacidic compatibilizer. Dielectric relaxation spectroscopy (DRS) of the pure components and blends is another way to attempt to clarify the behavior of the blends. As it was remarked in the previous paper (Sandford, 1990), DRS has been used by several authors to characterize chitosan (Costa, Rubinger, & Martins, 2007; Nogales, Ezquerra, Rueda, Martinez, & Retuert, 1997; Viciosa et al., 2006). Moreover, both unmodified PS and sulphonated PSS have been analyzed in terms of DRS (Atorngitjawat, Klein, & Runt, 2006; Hao, Bohning, & Schonhals, 2007; Wypych et al., 2005), so DRS seems to be a suitable technique for studying the behavior of blends.

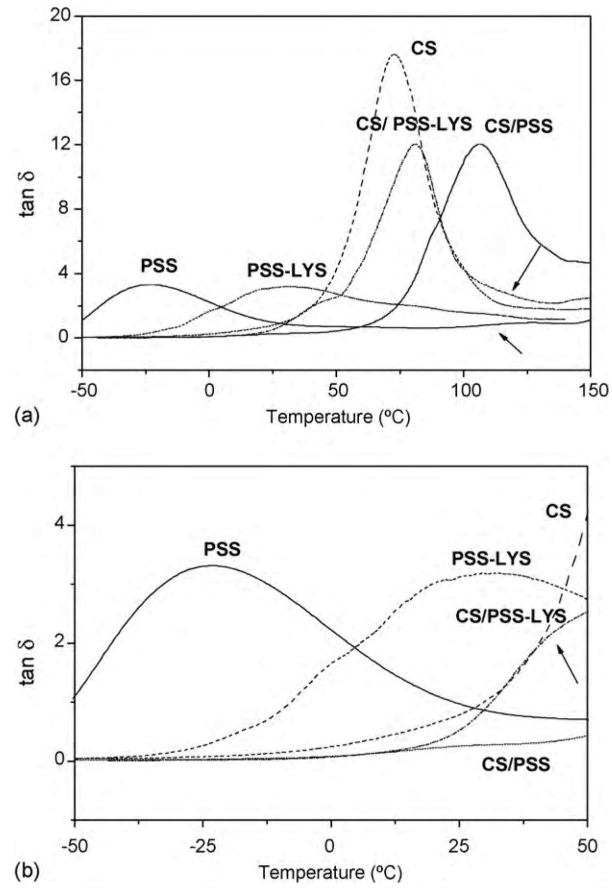

Fig. 4. Evolution of tan δ with temperature at 1300 Hz for: a) pure CS, PSS, PSS-LYS and CS/PSS (50/50) (wt%)-GLU blend between −50 and 150 °C and b) pure CS, PSS, PSS-LYS and CS/PSS-LYS blend 50/50 (wt%) between −50 and 150 °C.

Fig. 4a shows the evolution of tan δ with temperature for pure CS and PSS, PSS-GLU and CS/PSS-GLU blend modified with GLU at a frequency of 1300 Hz. For pure CS, a strong relaxation process can be seen, probably related with water desorption mechanism upon heating of the sample (Costa et al., 2007; Nogales et al., 1997; Viciosa et al., 2006). For pure PSS two relaxation processes are

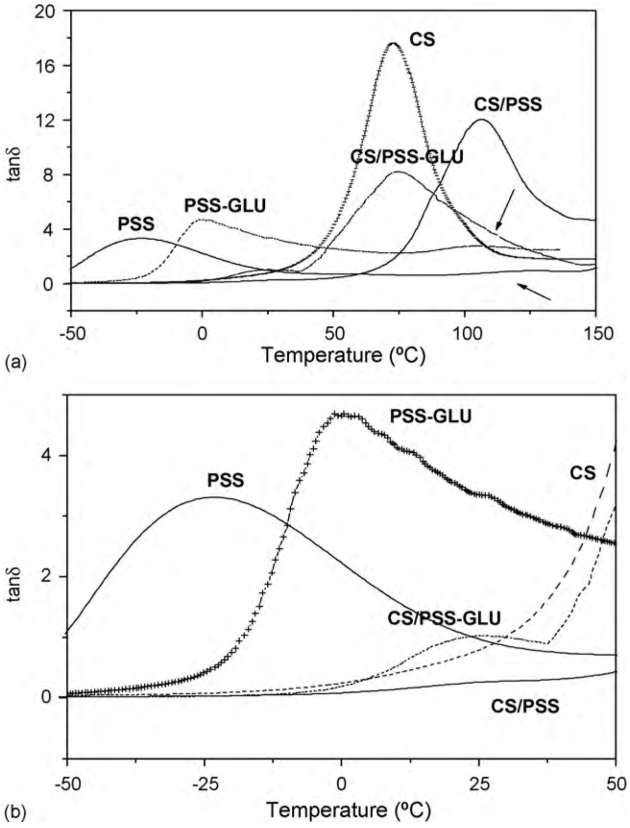

Fig. 5. Evolution of tan δ with temperature at 1300 Hz for: a) pure CS, PSS, PSS-GLU and CS/PSS (50/50) (wt%)-GLU blend between −50 and 150 °C. and b) pure CS, PSS, PSS-GLU and CS/PSS-GLU blend 50/50 (wt%) between −50 and 50 °C.

detected: the segmental α relaxation (associated to the glass transition), centered above 100 °C, similar to that shown previously for unmodified polystyrene (PS) (Atorngitjawat et al., 2006; Hao et al., 2007; Wypych et al., 2005) and the secondary β relaxation at temperatures below 0 °C, related with the rotation of phenyl groups, that has also been detected for pure PS (Atorngitjawat et al., 2006). As it can be seen, the height of the secondary relaxation is increased 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 as it was previously mentioned (Sandford, 1990). For PSS-GLU, the secondary relaxation is even higher than that for neat PSS and it is displaced towards higher temperatures, indicating the effect of the interactions of this compatibilizer with PSS. The main relaxation is again weak compared with the secondary one. For the blend CS/PSS-GLU, the main relaxation associated with both processes described for pure components—water desorption of CS and the main relaxation of PSS can be clearly seen. The main relaxation is broader and the height of the maximum peak of loss factor is lower due to the presence of both components, since the presence of PSS in the high temperature region of the relaxation spectrum (indicated by arrows) is detected. On the other hand, the relaxation appears at lower temperatures with respect to that corresponding to the blend without glutamic acid, which indicates that the compatibilizer interacts with chitosan groups. These interactions should be responsible for the morphological changes shown above by AFM. The secondary relaxation of PSS is also detected for the blends but it is not very clear in Fig. 4a due to the scale used.

For this reason, Fig. 4b shows the evolution of tan δ with temperature in the range of the secondary relaxation. The secondary relaxation is displaced to higher temperatures when compared with pure PSS and PSS-GLU, indicating an increase on interactions between CS, PSS and the compatibilizer with respect to the blend without glutamic acid. Fig. 5a shows the evolution of tan δ with temperature for pure CS and PSS, PSS-LYS and CS/PSS-LYS (w/w) blend at a frequency of 1300 Hz. The displacement of the secondary relaxation of PSS-LYS when compared with neat PSS can be seen again, due to the presence of the compatibilizer. The main relaxation of pure CS and the weak main process of PSS can be also seen. For the blend containing the compatibilizer, the main relaxation process can be again clearly observed. The broadness of the relaxation is now more similar to that of pure CS, and the presence of PSS in the high temperature tail of the spectrum (indicated by arrows) is also confirmed. The small variation with respect to the blend CS/PSS-GLU indicates that despite similar interactions between components do exist, the presence of one more methylene group in the compatibilizer chemical structure can slightly modify the interactions and therefore also the morphological features, as shown above by AFM. The secondary relaxation of PSS is also detected for this blend. Fig. 5b shows the evolution of tan δ with temperature in the range of the secondary relaxation. The secondary relaxation is displaced to even higher temperatures when compared with pure PSS and PSS-LYS, and also with the blend CS/PSS-GLU indicating on one side that interactions between CS, PSS and LYS compatibilizer do exist and on the other that these interactions are modified with respect to those for the other compatibilizer used.

4. Conclusions

DSC, TGA and FT-IR which represent the classical experimental techniques to describe compatibility in polymer blends do not allow to visualize the compatibility between chitosan and poly(sodium-4-styrene sulphonate) using lysine or glutamic acid as compatibilizers. For this reason it was necessary to turn to other techniques like atomic force microscopy or dielectric relaxation spectroscopy. By DRS, the presence of interactions among PSS, CS and compatibilizer was detected by analyzing the secondary relaxation related to the phenyl ring of PSS, which displaced to higher temperatures in the blends with both GLU and LYS compatibilizers. The differences in temperatures of this relaxation indicate that the amount of methylene groups in the aminoacidic compatibilizer is a key factor to control the magnitude of interactions and therefore the morphological features of these blends, as shown by atomic force microscopy. This modification on the interactions between the components of the blend containing the compatibilizer also led to variation on the main relaxation region. The influence of the two carboxylic groups in glutamic acid on the strength of the interaction seems to be a factor to take into account in the compatibilization process.

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