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Thermal Analysis of Chitosan Based Networks

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Abstract

In this work two kinds of material were studied: chitosan cross-linked with glutaraldehyde and in a blend with PEO. The resulting products as well as chitosan and PEO raw materials, were analyzed by TG/DTG, DSC and DMTA to determinate the influence of cross-linking and PEO addition on thermal properties of the resulting materials. It was observed by thermogravimetry that the water-polymer interaction will be different for the cross-linked material compared to the blend, according to the specific site availability. The influence of such modifications (cross-linking and PEO addition), on chitosan thermal stability was also studied. The DSC results showed a good agreement with the TG/DTG results, reinforcing the interpretation given for TG/DTG results. DMTA results indicate that glass transition temperature is around 50 °C for the polymer under study.

Keywords: Chitosan; Thermal analysis; Blends

1. Introduction

Nowadays, there is a growing interest in the production and use of new materials from renewable sources. Natural polymers are replacing synthetic polymers in different applications (Majeti & Kumar, 2000; Wood, 2001). Partly because the waste from natural polymers is normally biodegradable. Chitosan is the *N*-deacetylated derivative of chitin, a natural polysaccharide widely found in crustaceans and insects. It is widely used because of its biodegradability and its structural properties (Dodane & Vilivalam, 1998). Chitosan hydrogels can be used as carriers for the release of drugs and bio-active molecules. Recently some chitosan-based cross-linked networks were studied. In this case, the amine group of each glucosamine residue within the chitosan chain can serve as a reactive site for a reductive amination with glutaraldehyde forming an imine link between linear chitosan chains (Capitani, Crescenzi, de Angelis, & Segre, 2001; Monteiro & Airoldi, 1999). Hydrophilicity is a very important characteristic for this material and it is, in part, due to the presence of the amine groups. Therefore, is a promising way to prevent dissolution in acid media and also achieve resistance to chemical and long-term biological degradation without sacrificing chitosan hydrophilicity since most of the amine groups will be preserved.

Another relatively common chitosan modification is the preparation of blends as, for instance, chitosan–poly(vinyl alcohol) (Srinivasa, Ramesh, Kumar, & Tharanathan, 2003), chitosan-polyurethane (Lin-Gibson, Walls, Kennedy, & Welsh, 2003) and chitosan–poly(ethylene oxide) (Amiji, 1995; Khoo, Frantzich, Rosinski, Sjostrom, & Hoogstraate, 2003; Patel & Amiji, 1996). The latter system was chosen because poly(ethylene oxide)(PEO) is a water soluble polymer available at different molecular weights that exhibits useful properties, such as low toxicity and immunogenicity. Because of the useful biological activities of chitosan and PEO, a combination of these two polymers may have beneficial effects on the biological characteristics of the resulting membrane.

It is well known that water content has a significant influence on chitosan physical properties. The chitosan water content is affected by the number of ionic groups in the material as well as their nature. The important binding sites for water molecules in chitosan are the hydroxyl and amine groups present in the polymer. Several studies have been performed to obtain an understanding of the adsorption

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mechanism and the characteristics of the water molecules adsorbed to a polymer system (Khalid, Agnely, Yagoubi, Grossiord, & Courrazze, 2002; Qu, Wirsen, & Albertson, 2000). However, most of this work was done with hydrogels. According to the results, water in hydrogels can generally be classified into three species: freezable water, non-freezable water and freezable bound water. A problem related to hydrogels is that the probable similarity between water–water and water–polymer interactions makes studies of the latter ones a difficult task, although some spectroscopic methods have been found to be useful (Rueda, Secall, & Bayer, 1999). At higher polymer concentrations, however, the number of water molecules and polymeric unit can be comparable. For example, at 10% water content, chitosan contains one water molecule per polymeric unit. In this concentration range, therefore, chitosan–water interactions should be highly significant and amenable to study. A second reason for studying chitosan membranes at low water contents (below 25%) is the considerable interest in the thermal, mechanical and structural properties of this type of material.

Thermal methods such as thermogravimetry (TGA), differential scanning calorimetry (DSC) and dynamical mechanical thermal analysis (DMTA) have emerged as powerful thermo analytical techniques to monitor physical and chemical changes in both natural and synthetic polymers (Appelqvist, Cooke, Gidley, & Lune, 1993; Cardenas, Bernal, & Tagle, 1992; Ratto, Hatakeyama, & Blumstein, 1995). These methods yield curves that are unique for a particular composition of matter and some changes in chemical structure and composition, or molecular architecture may bring about discrete and reproducible variations in the thermograms. Further, some of these changes involve the loss of material in the volatilization, which can be quantitatively measured by TGA.

In the present work the feasibility of using TGA, DSC and DMTA to monitor the physical and chemical changes occurring during two different modifications of chitosan (cross-linking and PEO addition) is further explored.

2. Materials and methods

Chitosan was supplied by Polymar (Brazil) with a deacetylation degree of 85% according to the supplier. Polyethylene oxide (PEO) was purchased by Sigma (USA) with a MW = 1,000,000 g/mol. All others chemicals were analytical grade reagents and used as received.

2.1. Membrane preparation

2.1.1. Chitosan raw material

Chitosan was dissolved in a 2.0 wt% aqueous acetic acid solution for 24 h under stirring. The resultant solution was filtered using a Millipore Millex filter, cast on a glass plate and dried in an oven at 50 °C for 12 h. The membrane was then immersed in sodium hydroxide (NaOH) solution 0.5 M for 2 h to be neutralized. Then it was repeatedly washed with distilled water and allowed to dry at room temperature.

2.1.2. Cross-linked chitosan

Water-conditioned membranes were treated with 0.01%(w/v) glutaraldehyde (Vetec-Brazil) solution for 48 h at room temperature. Subsequently, the membrane was rinsed with distilled water and allowed to dry at room temperature.

2.1.3. Chitosan/PEO blend

PEO was dissolved in an acetic acid aqueous solution 2.0%(v/v) for 24 h under stirring in order to obtain a 1%(w/v) PEO solution. An appropriate amount of chitosan solution, prepared as above, was added to PEO solution at a ratio of 95:5, respectively, and stirred for 1 h. Afterwards, the solution was cast on a glass plate, dried using an oven, rinsed and allowed to dry in the same way as used for pure chitosan.

All dry membrane thicknesses were measured with a digital micrometer. Each membrane was measured at 10 different points (5 points each side) and only the ones with a relative standard deviation smaller than 10% were used. The membrane thicknesses were in the range of 30–40 μm.

2.2. Thermogravimetric analysis (TG, DTG)

Thermogravimetric (TG) analysis and differential (DTG) thermogravimetric analysis were carried out with a Netzsch TG 209 C Iris system. All analyses were performed with a 5 mg sample in aluminum pans under a dynamic nitrogen atmosphere between 30 and 900 °C. The experiments were run at a scanning rate of 10 K/min.

2.3. Differential scanning calorimetry (DSC)

DSC was performed using a Netzsch DSC 204 Phoenix. Accurately weighted (5 mg) samples were placed into aluminum cups and sealed. A small hole was done at the top of the cup in order to allow the release of water. An empty cup was used as reference. The experiment consisted of two runs. The first one from -100 to 200 °C and the second one from -100 to 400 °C. The experiments were run at a scanning rate of 10 K/min.

2.4. Dynamical mechanical thermo analysis (DMTA)

Dynamical mechanical measurements were carried out with a Netzsch DMA 242 instrument operated in the tensile mode, at a frequency of 1 Hz and a heating rate of 5 K/min, from -120 to 180 °C. In this DMTA instrument, a film sample is longitudinally deformed by a small sinusoidal stress and the resulting strain, which lags behind the applied force by a phase angle δ, is measured. The technique yields values of dynamic storage modulus E'

(in-phase component), loss modulus E'' (out-of-phase component), and mechanical loss tangent tan $\delta = E''/E'$.

3. Results and discussion

3.1. Thermogravimetric analysis

Fig. 1 exhibits the DTG curves for pure chitosan (CHI), pure PEO and bidistilled water (H_2O), as well as cross-linked chitosan (CG/CHI) and chitosan blended with PEO (CHI/PEO). For pure PEO it can be observed that no significant degradation occurred before 300 °C. The total degradation of PEO was observed in a single stage and was completed at 425 °C. For chitosan, weight loss took place in two stages. The first one starts at 60 °C with a weight loss of 10%. The second stage starts at 240 °C and reaches a maximum at 380 °C with a weight loss of 41.4%. This result is similar to the ones of Nieto, Peniche-Covas, and Padron (1991) and Tirkistani (1998). The first stage is assigned to the loss of water. The second one, corresponds to the decomposition (thermal and oxidative) of chitosan, vaporization and elimination of volatile products. According to the literature (Nieto et al., 1991), pyrolysis of polysaccharides starts by a random split of the glycosidic bonds, followed by a further decomposition forming acetic and butyric acids and a series of lower fatty acids, where C2, C3 and C6 predominate. Cross-linked chitosan and chitosan modified by PEO are also degraded in two stages. Table 1 presents TG data for chitosan, PEO and the prepared samples.

Considering the first stage of degradation, which is related to water loss, one can see from DTG curves that their shapes are not similar. Polysaccharides usually have a strong affinity for water and therefore, may be easily hydrated, resulting in macromolecules with rather disordered structures. As it is known, the hydration properties of these polysaccharides depend on the primary and supramolecular structure (Kittur, Prashanth, Udaya Sankar, & Tharanathan, 2002). Therefore, variations on the peak area and/or position related to water loss are expected to reflect physical and molecular changes caused by cross-linking and PEO addition. Close examination of Fig. 1 reveals that there are differences in peak area and position, indicating that these systems differ in their water holding capacity and strength of water-polymer interaction. Comparing the peak for pure water with the one for pure chitosan, one can realize that the chitosan peak presents an asymmetry from the high temperature side. For the cross-linked sample, one can observe that the peak tends to be split into two and, finally, for the chitosan–PEO blend it is possible to observe that the peak increases in intensity and becomes more symmetric.

Considering the chitosan structure, it can be seen that water molecules can be bound by two polar groups, hydroxyl and amine, present in this macromolecule. Rueda et al. (1999) made some infrared investigations and found that the interaction of water with the hydroxyl groups is stronger than with the amine groups. They also found that the relative amount of water molecules bound to the two polar groups of chitosan changes during the water sorption process. By using infrared analysis, they showed that for low water content the intensity of the band corresponding to N–H vibration is larger than the band corresponding to O–H vibration.

Comparing the asymmetry and width of the peak for pure chitosan with the one obtained for pure water, it could be stated that the removal of a considerable amount of water from chitosan occurs at temperatures below 100 °C, that, for

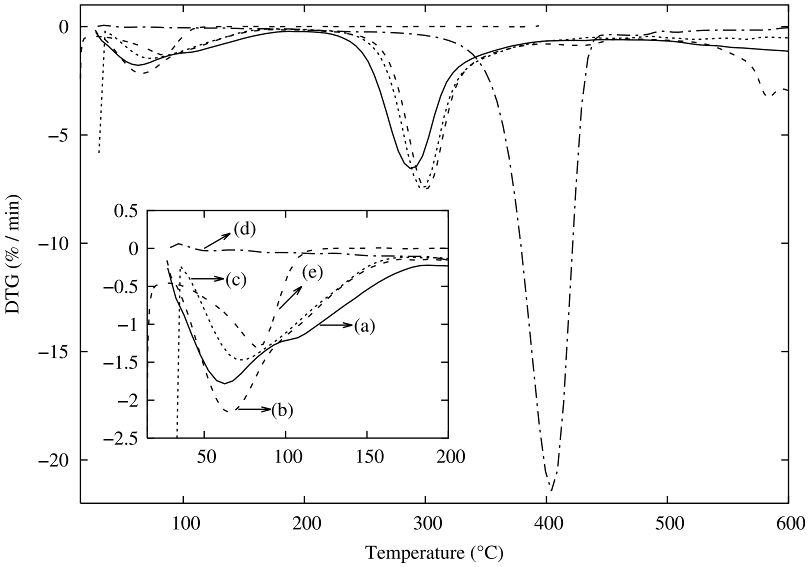

Fig. 1. DTG curves for: (a) cross-linked chitosan (CG/CHI), (b) chitosan in blend with PEO (CHI/PEO), (c) pure chitosan (CHI), (d) pure PEO (PEO) and (e) distilled water.

chitosan, water molecules interact with two different polar groups and that the interactions with amine groups are weaker than those with hydroxyl groups. Since a considerable amount of water is released at temperatures below 100 °C, it can be concluded that, at low water contents, the water molecules should be predominantly bound to the amine groups. Consequently, it might be thought that, in the case of pure chitosan, water molecules bound to amine groups could be more easily removed (at lower temperature) than those molecules bound to hydroxyl groups. This results is in good agreement with the ones found by Rueda et al. (1999), described above.

In the case of the DTG curve for the cross-linked sample, one can see that the splitting is now more evident and that there is a peak with maximum at around 60 °C. Considering that during cross-linking reaction some amine groups are transformed into imine ones, one can assume that, for a cross-linked chitosan sample, there will be a smaller number of amine groups available to interact with the water molecules. Therefore, some water molecules that would be bound to amine groups will now be bound to hydroxyl groups. As a consequence, an increase in intensity of the peak located at 100 °C is observed.

Furthermore, the decrease in ordered structure, due to chemical modification caused by cross-linking, may significantly contribute towards an increase in the content of sorbed water, as showed in Table 1.

The third DTG curve to be discussed is the one related to the chitosan–PEO blend. As Fig. 1 shows the peak is now more symmetric, with a maximum at 64.7 °C and the shoulder at 100 °C is not so evident. One can argue that the narrow and more symmetric peak observed for chitosan–PEO blend is just due to the fact that, once the polymers are mixed (in solution) the terminal hydroxyl groups of PEO will preferentially interact with the hydroxyl groups of chitosan forming intermolecular hydrogen bonds. So, in this case, the sorbed water will be bound to the amine groups and, considering that this interaction is weaker than the one with the hydroxyl groups, the water molecules will be released at lower temperatures. In other words, the peak related to the water–hydroxyl interactions is not present because, in this case, such groups are already bound to the terminal hydroxyl groups of PEO and therefore are not available to bind water molecules.

Table 1
Results of thermogravimetric analysis

Sample	First stage		Second stage		Weight remaining after 500 °C (%)
	T (°C)	Weight loss (%)	T (°C)	Weight loss (%)	
CHI	72.7	10.0	297.3	41.5	48.5
CG/CHI	62.7	14.9	288.8	46.0	39.1
CHI/PEO	64.7	13.7	300.7	44.3	42.0
PEO	404.9	90.6	–	–	9.4

The second stage of degradation displayed in Fig. 1 and Table 1 shows that the PEO addition tends to shift the peak maximum to higher temperatures. Such a shift to higher temperature is attributed to an increase in thermal stability. On the other hand, the cross-linked sample maximum peak was shifted to lower temperature indicating a decrease in sample thermal stability. Some studies have shown that the addition of PEO to chitosan greatly influences its properties (Amiji, 1995; Khoo et al., 2003; Patel & Amiji, 1996; Zhang, Li, Gong, Zhao, & Zhang, 2002). As a result of different interactions, according to the composition, two different types of hydrogen bonds are formed in blends of PEO and chitosan. Some of them are intra-molecular hydrogen bonds and others are intermolecular hydrogen bonds (attractive bonds) that physically cross-link the blend. For lower amounts of PEO, the intermolecular interactions predominate and, as a consequence, the blend is compatible. As the amount of PEO is increased, the intra-molecular interactions between the terminal hydroxyl groups of PEO predominate, the attractive bonds are inhibited, the blend becomes incompatible and, as a consequence, some properties may tend to deteriorate rather than improve. In this study, since the blend has a very small amount of PEO (1%) one can suppose that the attractive bonds would be maximized: This fact could explain the increase in thermal stability.

In general, an increase in the amount of glutaraldehyde leads to an increase in the decomposition temperature, since new covalent bonds cross-link the molecules. However, in our study, the DTG curves shows that the cross-linked sample starts to decompose at lower temperature indicating that the cross-linked sample is less stable than the uncross-linked one. Similar results were also found by Glico-Kabir, Penhasi, and Rubinstein (1999) and Kim and Lee (1993) when working with cross-linked samples of guar gum and chitosan, respectively. The authors found that very low degree of cross-linking tended to reduce sample stability and, as the cross-linking agent concentration increased beyond a certain value, there was an increase in the decomposition temperature. Since the glutaraldehyde concentration used in this work was quite low (0.01%) and the cross-linking reaction was heterogeneous, one can assume that, in this work, the cross-linking degree was quite low. A possible explanation for the decrease of thermal stability at low degree of cross-linking would be the formation of intra cross-linking reactions between polysaccharides chains, which by its turn interferes with previously existing attractive hydrogen bonds, in those regions where cross-linking occurred. As a consequence, the cross-linked polymer's structure weakened, reducing its thermal stability.

3.2. *Differential scanning calorimetry*

Fig. 2-I and II shows, respectively, the first and second run DSC curves for chitosan and PEO raw materials as well

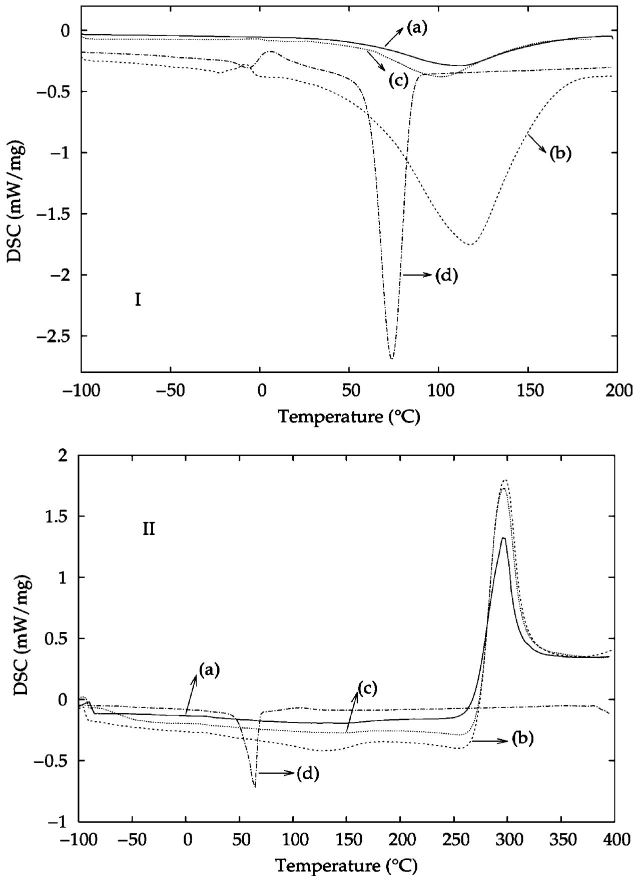

Fig. 2. DSC first (I) and (II) second run curves for (a) cross-linked chitosan (CG/CHI), (b) chitosan in blend with PEO(CHI/PEO), (c) pure chitosan (CHI) and (d) pure PEO(PEO).

as cross-linked chitosan and chitosan blended with PEO. All samples were stored in a desiccator before analysis. The temperature range used on the first run was from −100 to 200 °C. The maximum temperature of 200 °C was selected in order to limit possible chitosan degradation. As expected, the melting of water was not observable since, as already showed by thermogravimetric analysis, the samples water content ranged from 10 to 14% and, according to the literature (Qu et al., 2000), at this water content, only non-freezable water is present. The second observation is that all samples presented an apparently endothermic event. For pure PEO the peak was centered at about 70 °C and, according to some authors (Khalid et al., 2002), it is related to its melting. For pure chitosan the peak was centered around 100 °C and for both networks (cross-linked chitosan and blended with PEO) they were above100 °C. A further general property of this event is that, except for pure PEO, on immediate reheating, such a peak was not perceptible anymore (Fig. 2-II), supporting the view that water evaporation occurred during the first DSC run. These results confirm the previous one obtained by TG analysis and suggest that the samples were not truly anhydrous and that some bound water was not completely removed by drying in the desiccator.

A closer examination of Fig. 2-I reveals differences in the peak area and position of endotherm, indicating that these macromolecules differ in their water holding capacity and strength of water-polymer interaction. In the case of the cross-linked sample, the peak position was shifted to higher temperature, indicating that the water interaction with this network is stronger than with chitosan raw material. This result is in agreement with the previous one obtained by TG analysis and therefore the explanation for that could be the same one already discussed. In brief, the cross-linking reaction occurs between the glutaraldehyde and the amino groups of chitosan. So, the cross-linked material will have less amino groups available to form hydrogen bonds with water molecules. As a consequence, most of water molecules will be bound to chitosan hydroxyl groups instead of amino groups and, since the hydrogen bonds with the hydroxyl groups of chitosan are stronger than the ones with the amino groups, one could expect that a higher temperature would be necessary to remove such water molecules.

For chitosan–PEO sample the figure shows that the endothermic peak area increased, indicating that the sample has a higher water content. This result is also in agreement with the previous one obtained by TG analysis. That is, with PEO addition, new hydrophilic centers are formed, i.e. the terminal hydroxyl groups of PEO bind a higher number of water molecules and hence increase the content of bound water. Furthermore, the decrease in ordered structure due to chemical modification may significantly contribute toward the increase in the content of sorbed water. The DSC second run, obtained from −100 to 400 °C is shown in Fig. 2-II. As already stated, the first point to note is the absence of a peak around 100 °C, confirming that this peak is related to water molecules that were eliminated in the first run. It is also shown that the sample blended with PEO still had some residual water compared with the two others (pure chitosan and cross-linked chitosan), confirming that in this system water molecules seem to be strongly bound to the polymer hydrophilic groups. The main event of these calorimetric curves is an exothermic peak at approximately 300 °C, present in all analyzed samples and due to the degradation of the main chain, as already discussed on the TG section. Although the differences in peak positions are not so evident as on DTG curves, the differences in peak intensities are in good agreement with the weight loss values showed in Table 1. Comparing the results of DSC and TG/DTG we can conclude that they are in very good agreement. However, from DTG curves, it was possible to obtain more information about how the water molecules are bound to the polymer chain. This might be explained as a result of the higher sensitivity of the thermogravimetric method.

The glass transition temperature (T_g) can usually be obtained by DSC. The glass transition temperature of chitosan is still a subject of controversy. The main reason may be that, being a natural polymer, some properties like crystallinity, molecular weight and deacetylation degree, can present wide variations according to the source and/or method of extraction and will influence the T_g. Ratto et al. (1995) observed the chitosan glass temperature at 30 °C for water contents ranging from 8 to 30%. Lazaridou and Biliaderis (2005) found T_g ranging from −23 to 67 °C, according to the water content, indicating, in both cases, the plasticizing effect of water. On the other hand, Sakurai, Maegawa, and Takahashi (2000) observed the T_g of chitosan at 203 °C, while Kittur et al. (2002) found no evidence for T_g suggesting that T_g for chitosan could lies at a higher temperature, where degradation prevents its determination. In the present study the DSC measurements showed no significant stepwise increase in specific heat, showing, therefore, no evidence in favor of the occurrence of a glass transition temperature.

3.3. Dynamical mechanical thermo analysis

The thermo-mechanical behaviors of pure chitosan, the cross-linked sample and its blend with PEO were examined by DMTA. The results are presented in Fig. 3. A very broad temperature range was used in order to cover all the T_g's range found in literature (from −23 to 203 °C). It was observed that after the first run, the samples presented a dark yellow coloration indicating that the heating has caused degradation of chitosan molecules. Therefore, a second run was not carried out.

Mucha and Pawlak (2005) have recently published some DMTA data using pure chitosan as well as in blend with another polymers. According to the authors, the chitosan glass transition is observed between 156 and 170 °C (according to deacetylation degree). As one can see from Fig. 3 such an event was not observed in our study. The reason for that could be the residual water present in all 'dry' samples acting as plasticizer and lowering chitosan's T_g in such way that, water evaporation at around 100 °C could cover the glass transition of chitosan. Besides the glass transition, they also found some others molecular relaxation at −21, 24 and 43 °C.

Considering Fig. 3 one can see that the main event observed is a relaxation at 50 °C, that according to Mucha is related to reorganization of packing of chitosan molecules due to an increase of residual water mobility. Another possibility is that such a relaxation is due to the local molecular motion in a pseudo-stable state in the presence of water, as proposed by Sakurai et al. (2000).

The second observed event is a relaxation at around −20 °C, that can be clearly observed for pure chitosan. According to literature such relaxation is recognized as β-relaxation associated with local motions of side groups in chitosan. Another relaxation around −75 °C, has already been found in literature. It occurred for the three samples in study with a shift to higher temperature in the case of the blend with PEO. According to some authors (Pizzoli, Ceccorulli, & Scandola, 1991), this relaxation is called γ-relaxation and its origin is a local motion of the backbone of dry chitosan, such as small amplitude oscillations of the sugar rings around the glycosidic bonds.

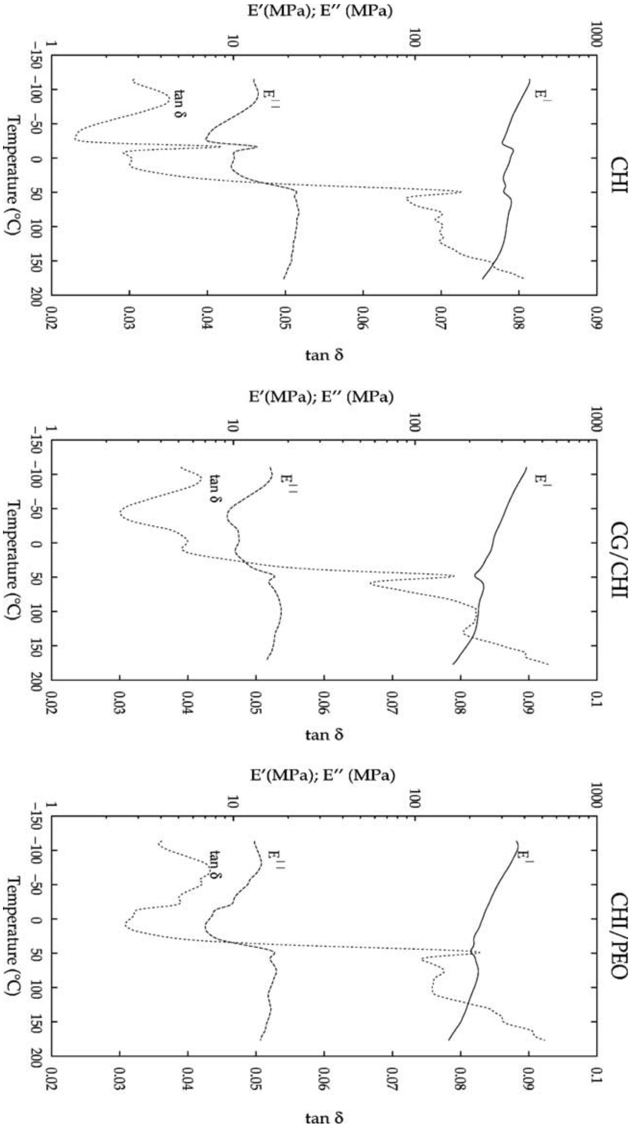

Fig. 3. DMTA curves for pure chitosan (CHI), cross-linked chitosan (CG/CHI), and chitosan in blend with PEO(CHI/PEO).

4. Conclusion

Three different materials were thermally analyzed: pure chitosan, chitosan cross-linked with glutaraldehyde and chitosan blended with PEO. From thermogravimetric analysis it was concluded that the three samples presented some differences in the strength of water-polymer interaction. For pure chitosan, at low moisture content, water was predominantly bound to the amine groups of chitosan while for cross-linked chitosan the peak related to water bound to the polymer hydroxyl groups was also evident. The chitosan/PEO blend presented the most symmetric peak, indicating that one interaction is preferential in this case.

As the peak is located below 100 °C one can assume that, for the blend, water molecules are bound to the amine groups as in pure chitosan. The main difference between pure chitosan and in blend with PEO is the peak intensity. From these data it was concluded that the blend was the more hydrophilic material probably because the reduction in crystallinity caused by the mixture that would facilitate the access of water molecules to the amine groups. In terms of thermal stability, it was concluded that PEO increases chitosan thermal stability while the cross-linking process tended to decrease it.

DSC results were in good agreement with those obtained by TG/DTG curves and therefore confirmed all the conclusions cited above. According to the results one can conclude that TG analysis is more sensitive for this kind of analysis than the DSC. From the DSC curves it was not possible to observe the chitosan glass transition temperature. The analysis of DMTA spectra indicated a few molecular relaxations existing in pure chitosan as well on the cross-linked material and in its blend with PEO. DMTA results showed that, due to chitosan's hydrophilic nature, the residual absorbed water has a strong effect on the macromolecular mobility.

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