ABSTRACT

The use of nanoparticles as reinforcement loads may be an interesting alternative to improve the properties of gelatin films. Thus, the objectives of this study were the development of nanocomposite gelatin-based films by spreading, and the study of the effect of the nanoparticle concentration on the mechanical properties of those films. The nanocomposite-forming solutions (NFS) were prepared with 5g gelatin/100g NFS, 30g glycerol/100g gelatin and 0, 5 and 10g montmorillonite (MMT)/100g gelatin. The NFS were applied on the support using an automatic spreader (spreader height= 1.5 mm; spreader speed= 35 mm/s; base temperature= 20ºC) and dehydrated at 30ºC. The nanocomposite films were characterized immediately after drying (DN), and after 7 days-conditioning (CN) in 58% relative humidity at 25ºC, to determine the mechanical properties by tensile tests, moisture, thickness and phase transitions by differential scanning calorimetry (DSC). The increase in MMT concentration (CMMT) increased the thickness of the films, with slightly higher effect for the CN than for the DN, and provoked decrease in the moisture of films as function of CMMT. Regarding the mechanical properties, the tensile strength of the DN and CN increased with CMMT, indicating reinforcement of the biopolymeric matrix by the nanoparticle load. Similar behavior was observed for the elastic modulus. The lower values of resistance and rigidity for the CN must be attributed to the plasticizing effect of the absorbed moisture during conditioning. Besides, the elongation at break (%) increased with the CMMT for the DN but decreased for the CN. The nanoparticles affected the phase properties, which demonstrated the plasticizing effect of the absorbed moisture, according to the DSC results. Thus, the montmorillonite contributed to reduce the susceptibility of the nanocomposite material to the environmental relative humidity, and to enhance the mechanical properties, notably resistance and rigidity.

Keywords: biodegradable films; nanoparticle; resistance; physical properties.

INTRODUCTION

Studies involving production and characterization of biopolymer-based films have increased in the last decades as a consequence of the increased awareness of the environmental impact of synthetic packaging [1]. These films are normally produced with macromolecules of biological origin, such as the gelatin, capable of forming a continuous matrix. Amongst the proteins, gelatin has been well studied because of its excellent film forming properties [2,3]. In overall, these films have limited mechanical resistance compared to synthetic films and are sensitive to the relative humidity of the air, due to the hygroscopic character of the biopolymer and the plasticizers [4,5].

An alternative to overcome the poor mechanical properties shown by biopolymers-based films, including gelatin-based films, is their blending with nanoparticles, which act as reinforcement by enhancing the strength and stiffness of the resulting nanocomposite structures, if the nanoparticles are well dispersed in the biopolymer matrix. The main reason for this improvement in the mechanical properties of nanocomposite films is the stronger interfacial interaction between the matrix and layered nanoparticles due to the vast surface exposed of the nanoparticle layers [6].

Several types of nanoparticles has been used on the development and characterization of biopolymer-based nanocomposite, but the montmorillonite is the most utilized one [6,7,8,9], including gelatin-based nanocomposite [10,11,12]. The montmorillonite is among the most commonly used nanoparticle because it is environmentally friendly and readily available in large quantities with relatively low cost [6]. The platelet-like geometry of MMT makes it ideal as a property-enhancing additive [10]. Nevertheless, there are controversial results among these works, with of course, positive effect of the montmorillonite on the mechanical properties of the films, but with negative or neutral effect too. So, more research must be done on development of nanocomposite.
Thus, the objectives of the present study were the development of nanocomposite gelatin-based films charged with montmorillonite, by spreading, and the study of the effect of the nanoparticles concentration on the mechanical properties of those films.

MATERIALS & METHODS

To prepare the nanocomposite-forming solutions (NFS), gelatin (Cg= 5g of gelatin/100g of NFS) was hydrated for 30 min, and then dissolved and held at 70ºC for further 30 min., using a thermostatic bath (Marconi, Model TE 184). Complimentary water was used to prepare a dispersion of the montmorillonite (MMT) using an ultraturrax (25000rpm). Glycerol (30g glycerol/100g of gelatin) was added in this dispersion. This dispersion was mixed with the gelatin solution, always under magnetic stirring (Tecnal-TE085), and maintained at 60°C for further 10 min.

The nanocomposite-forming solutions were spread on the Plexiglas support using an automatic spreader (Model Speed II, TKB Erichsen) (spreader height= 1.5 mm; spreader speed= 35 mm/s; support temperature= 20ºC) and dehydrated inside air-circulating chamber (30ºC) [5]. After that, the films were characterized immediately after drying (DN) and after 7 days of conditioning (CN) at 58% relative humidity and 25ºC.

The mechanical properties of the films were determined using a texture analyser TA.XT2i (SMS, Surrey,UK) controlled by the Texture Expert V.1.15 software (SMS). Tensile tests were run using rectangular samples of 100 mm x16 mm, initial grips separation of 80 mm and cross-head speed of 0.9 mm/s [13]. The moisture was determined by drying in a forced air oven at 105ºC for 24 h., and the thickness of the films was measured with a digital micrometer (Mitutoyo).

The phase transition temperatures of the films were determined using a differential scanning calorimeter DSC TA 2010 controlled by a TA 5000 module (TA Instruments, New Castle, DE, USA) according to Sobral et al. [5,14]. The films (~10mg) were conditioned on aluminium pans. The temperature range used was -120 to 100ºC with a heating rate of 5ºC/min in an inert atmosphere (45 mL/min of N₂), twice. The glass transition (mid-point) temperature (Tg) and the melting (peak) temperature (Tm) were calculated using the Universal Analysis V1.7F software (TA Instruments).

All characterizations were at least carried out in triplicate.

RESULTS & DISCUSSION

The nanocomposites produced in this work were homogeneous, transparent and with an overall good visual aspect as it can be observed in the Figure 1.

![Figure 1. Photography of samples of gelatin-based nanocomposite with 5% (left) and 8% (right) of montmorillonite.](image-url)
The MMT reduced the sensibility of the material to environmental humidity. The increase on MMT concentration reduced moisture of DN \((y=-0.533x+13.1, \text{R}^2=0.945)\) and CN \((y=-0.312x+20.2, \text{R}^2=0.956)\) \(\text{Figure 3}\), being that the moisture difference among CN and DN samples must be credited to water absorption by gelatin and glycerol, as they are hygroscopic. Tunc et al. [7] also observed similar behavior working on nanocomposite produced using gluten and montmorillonite. These authors explained that the reduction in water sensitivity with the increasing on MMT concentration can be explained by a tortuous pathway limiting water molecules penetration in the nanocomposite due to the high aspect ratio of the layered MMT if they are correctly dispersed in the matrix.

Regarding the mechanical properties, it was observed that the tensile strength of the DN \((y=1.2x+46.7, \text{R}^2=1.000)\) and CN \((y=0.8x+25.0, \text{R}^2=0.684)\) increased with MMT concentration \(\text{Figure 4}\), indicating reinforcement of the biopolymer matrix by the nanoparticle load. Similar behavior was observed for the elastic modulus \(\text{Figure 5}\). These results may suggest that the nanoparticles were well dispersed in the gelatin matrix, and agree with Cyras et al. [6] and Rao [10], who also observed good improvement in mechanical properties of starch-based and gelatin-based nanocomposite, respectively. Rao [10] observed that at a loading of 5% of MMT, the Young’s modulus increased by 75%, and the tensile strength increased by 25%. Also working on gelatin-based nanocomposites, Bae et al. [11] observed that increasing the MMT content increased the tensile strength and made the films more brittle. But, these authors, who tested several MMT concentrations between 0 and 9%, observed the higher value of tensile strength for 5% MMT. Similarly, Luecha et al. [9], working on zein-based nanocomposite with 0 to 10% of MMT, observed maximum tensile strength for samples charged with 5% of MMT (2.5 times greater than 0% MMT) and Tunc et al. [7] also observed the maximum occurring at 5% of MMT in a gluten matrix. For Jang et al. [12], working on gelatin-agar nanocomposite, the maximum of the tensile strength was observed for 3% of MMT. These results indicated the casting technique has a critical MMT percentage where the dispersion of MMT is better [9].
Contrarily to the results described above, Sothornvi et al. [8] observed that all the tensile properties of the whey protein isolate-MMT nanocomposites films decreased significantly, and explained these results by the incomplete dispersion of the MMT into the protein matrix, which was caused by the incompatibility of hydrophobic nanoparticles with hydrophilic biopolymer.

Besides, the elongation at break, increased with the MMT concentration for the DN (y=0.8x+25.5, R²=0.996), but decreased for the CN (y=-1.1x+47.8, R²=0.905) (Figure 6). This inverted behavior suggests that the plasticizing effect of moisture was more considerable than the reinforcement effect of the nanoparticles concerning the elongation at break. Bae et al. [11] observed that increasing the MMT content reduced the elongation at break of the gelatin-MMT nanocomposites. Similar results were found by Cyras et al. [6], Rao [10], and Jang et al. [12].
Again, the lower values of resistance (Figure 4) and rigidity (Figure 5) and the high values of elongation at break (Figure 6) for the CN compared to DN must be attributed to the plasticizing effect of the absorbed moisture during conditioning [4,5]. The nanoparticles affected the phase properties, which demonstrated the plasticizing effect of the absorbed moisture, according to the DSC results (Figure 7). These thermograms were similar to others obtained for gelatin-based films [5] and for gelatin-based nanocomposite [10]. During the first heating scan of DN and CN, a glass transition (Tg), associated to a glycerol rich fraction was observed at very low temperature, at -65 to -61°C for DN, and -74 to -75°C for CN (Table 1). After that, another glass transition was observed in both scans. This Tg must be associated to the gelatin rich fraction charged with the MMT. In the first scan, the MMT reduced this Tg, but in the second scan, the presence of the MMT slightly increased Tg (Table 1). Similar behavior was observed by Rao [10], which stated that the Tg of the gelatin-based nanocomposites appeared to be similar to that of pure gelatin, and by Luecha et al. [9], which observed that the Tg of the zein-MMT nanocomposites remained around 36°C.

Considering just the first scan, an endothermal phenomenon associated to the melting of gelatin crystals [14], appeared after the glass transitions (Figure 7). The melting temperature, calculated as the peak temperature, increased with the MMT, principally for DN (Table 1). This behavior agrees with that observed by Rao [10], working on gelatin-based nanocomposite: the melting temperature slightly increased with the addition of MMT, indicating that the crystallinity is depressed by the addition of nanoparticles.

Considering now the second heating scan, no endothermal phenomenon was observed (Figure 7). The heating of samples during the first scan provoked the melting of the crystalline region and the gelatin-based nanocomposites behaved as a molecularly dispersed molten plastic and then, when this dispersion was submitted to the cryogenic cooling, the formation of the junctions between the adjacent macromolecules was avoided [14]. Thus, the material was completely amorphous and just one Tg was observed shifted to low temperatures [5], as it can be observed in the Table 1. The Tg of the glycerol rich fraction is not affected by the crystallinity of the gelatin. It can be observed in the work of Rao [10] that no thermal transitions were detected in the second heating scan. According to this author, this suggests that during the first heating, gelatin crystals were melted and the molten gelatin molecules were not able to reorganize into a crystalline phase in the presence of strong interacting MMT upon cooling.

![Figure 7. Examples of DSC curves obtained with DN (a,b,c) and CN (d,e,f) with 0% MMT (a,d), 5% MMT (b,e) and 10% MMT (c,f): first scan (left) and second scan (right).](image)

<table>
<thead>
<tr>
<th>C_{MMT} (%)</th>
<th>1st Tg (°C)/1st scan</th>
<th>2nd Tg (°C)/2nd scan</th>
<th>Tm (°C)</th>
<th>1st Tg (°C)/1st scan</th>
<th>2nd Tg (°C)/2nd scan</th>
<th>1st Tg (°C)/1st scan</th>
<th>2nd Tg (°C)/2nd scan</th>
<th>Tm (°C)/1st scan</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-65.3</td>
<td>---</td>
<td>71.2</td>
<td>-66.7</td>
<td>40.8</td>
<td>-73.8</td>
<td>31.5</td>
<td>66.9</td>
</tr>
<tr>
<td>5</td>
<td>-61.0</td>
<td>40.0</td>
<td>82.1</td>
<td>-52.3</td>
<td>23.5</td>
<td>-73.8</td>
<td>33.6</td>
<td>69.1</td>
</tr>
<tr>
<td>10</td>
<td>-61.0</td>
<td>20.1</td>
<td>75.6</td>
<td>-57.7</td>
<td>40.5</td>
<td>-75.3</td>
<td>32.0</td>
<td>68.9</td>
</tr>
</tbody>
</table>

Table 1. Results of DSC analysis.
Finally, it must be explained that the effect of conditioning, lowering both transitions temperatures (Table 1), was due to the water plasticization of films, also observed for the Tg of the glycerol rich fraction obtained in the second scan.

CONCLUSION

Montmorillonite contributed to reduce the sensibility of the gelatin nanocomposite material to environmental relative humidity, and to enhance the mechanical properties, notably the resistance and rigidity. The phase properties were also affected by the nanoparticles.

REFERENCES


Acknowledgements: to CAPES, for the Dr fellowship of MFCJ, to CNPq, for the grant (PJAS), to USP, for the IC fellowship of SFN, and to FAPESP, for the Post-Doc fellowship of FMV.