MECHANICAL PROPERTIES OF NOVEL ACTIVE CHITOSAN-NANOCALY BIONANOCOMPOSITE

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Summary: Montmorillonite (MMT) and rosemary essential oil (REO) were incorporated into chitosan to improve physical and mechanical properties as well as antimicrobial and antioxidant behavior. MMT weight percent relative chitosan was varied from 1 to 5 and activated by three REO levels (0.5%, 1%, and 1.5% v/v) and their impact on barrier properties, solubility, water gain, and tensile strength of the chitosan films was investigated. Microstructure of chitosan/MMT-REOS nanocomposites was characterized X-ray diffraction (XRD) and Fourier transform infrared (FTIR). The results showed that incorporating MMT and REO into chitosan improves water vapor permeability, solubility and water gain of the chitosan film more than 50%. It was also shown that the combine effect of clay and REO improves significantly tensile strength and elongation of chitosan. The study of chitosan/MMT-REO nanocomposites structure using XRD and FTIR confirmed that the improvement of physical and mechanical properties relates to the MMT exfoliation and good interaction between chitosan and MMT in the presence of REO. It was found based on experimental results that synergistic effects of MMT and REO make chitosan/MMT-REO nanocomposite an interesting material with several potential applications in food packaging industry.
1. Introduction

Biopolymers have been widely investigated over the last two decades because they can be a viable solution to the waste disposal of plastic food packaging materials. These biodegradable materials can also improve food quality and extend the shelf-life through minimizing microbial growth in the product. Furthermore, biopolymer films are excellent vehicles for incorporating a wide variety of additives, such as antioxidants, antifungal agents, antimicrobials, colors, and other nutrients [1-2].

Chitosan, a deacetylated derivative of chitin, is the second most abundant polysaccharide found in the nature after cellulose. It was found to be non-toxic, biodegradable, biofunctional, and biocompatible [3-5]. Chitosan bring some advantages over other biomolecule-based active polymers used as packaging materials because of its antibacterial behavior and bivalent minerals chelating ability [6]. However, poor mechanical, gas barrier properties and also low thermal stability and hardness of chitosan and especially weak water resistance because of its hydrophilic nature, limit its application particularly in the presence of water and humidity[7-8].

As for other biopolymers, many strategies have been explored to improve the barrier and mechanical properties of chitosan-based biodegradable films. These include the addition of plasticizers, salt addition, chemical modification of hydroxyl groups, cross-linking of polysaccharides, the use of suitable solvent, the change of pH and the addition of different polysaccharides [9-13].

Recently, polymer-clay nanocomposites have received significant attention as an alternative to conventional filled polymers. Because of their ability for nano-scale dispersion, which bring significant improvement in mechanical and physical properties compared to micro-scale polymer composites. Several studies have reported amelioration of mechanical properties [14, 8], thermal stability [15, 7], functional properties [16], barrier properties [17], and water solubility [17] of chitosan films via incorporation nanocly into chitosan in the range of 1-5 wt%.
Although several reports on chitosan/clay nanocomposites have been appeared in the literature, to the best of our knowledge there are no reported data on the combined effect of nanoclay and antioxidant/antimicrobial compounds like EOs. It seems that the combination of nanoclay and an antimicrobial/antioxidant compound in chitosan films can be suitable due to its acceptable structural integrity and barrier properties imparted by the nanocomposite matrix, and the antimicrobial/antioxidant properties contributed by the natural antimicrobial/antioxidant agents impregnated within. In addition, such nanocomposite films prepared based upon natural biopolymers are environmental-friendly with all the benefits one may expect from biopolymer and nanocomposite packaging materials [1]. In the present study the combined effects of montmorillonite nanoclay and rosemary essential oil as a natural antioxidant/antimicrobial compound-on the structural, mechanical, physical, and barrier properties of chitosan have been investigated.

2. Materials and methods

2.1. Materials
Crab shell chitosan (medium molecular weight (190–310 kDa), 75–85% deacetylated, Sigma-Aldrich Chemical Co., USA) and Na-Montmorlonite (MMT) from Southern clay, USA were used as received. Glacial acetic acid and Tween 80 were purchased from Merck, Germany. Rosemary essential oil was obtained from Pars Atran Co., Iran.

2.2. Sample preparation
2.2.1. Preparation of chitosan/clay-rosemary solutions
Aqueous solution of chitosan was prepared by dissolving 20 g of chitosan powder in 1000 mL of aqueous acetic acid solution (1%, v/v), using a magnetic stirring plate at 90 °C and 1250 RPM for 20 min and then cooled to room temperature. Nanocomposite samples were prepared according to methods reported by Xu et al. (2006). Selected amounts of clay (1, 3, and 5 w% on solid chitosan) were dispersed in 100 mL of 1% (v/v) aqueous acetic acid solution and vigorously stirred for 24 h. Afterward 150 mL of chitosan solution was added to clay solutions and the mixture was stirred for 4 h. then 0.2 % w/v of Tween 80, as an emulsifier,
was added to the mixture and stirred in 40 °C for 30 min. Finally appropriate amount of rosemary essential oil (REO) was added to the solution, to reach a final concentration of 0.5, 1, 1.5% v/v and homogenized with Ultra Turrax (IKA T25-Digital Ultra Turrax, Staufen, Germany) at 7000 RPM for 2 min. After cooling of resultant mixture at room temperature, it was degassed under vacuum for 5 min in order to remove all bubbles.

2.2.2. Preparation of nanocomposite films

The chitosan/clay-rosemary solutions (160 mL) were casted in simple cubic mold made from Teflon coated steel with dimension of 25.5 × 28.5 cm², then dried for 72 h at ambient conditions (25 °C) to prepare nanocomposite films. Dried films were then peeled and stored in a desiccator at 25°C and 50% (Containing saturated magnesium nitrate solution) relative humidity until evaluation.

2.3. Sample Characterization

2.3.1. X-Ray diffraction characterization (XRD)

The structure of nanoparticle and its nanocomposites was evaluated by XRD measurement. XRD patterns were taken with a Philips X’ Pert MPD diffractometer (Netherlands), with Co Ka radiation at a wavelength of 1.544 nm, at 40 kV and 30 mA. Chitosan/clay-rosemary films were scanned over the range of diffraction angle 2θ = 1–12°, with a scan speed of 1°/min at room temperature.

2.3.2. Fourier transform infrared spectra (FTIR)

FTIR spectra were collected in transmission mode by using a Bruker (EQUINOX 55, England) FTIR spectrophotometer in the range of 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹.

2.3.3. Measurement of film thickness

The thickness of the samples was determined with a manual digital micrometer (0.001 mm, Mitutoyo, japan). Measurements were repeated in ten different region of each sample. Average values were calculated and used in Water vapor permeability and tensile properties calculation.
2.3.4. Determining of moisture Content
Film samples (0.1 g) were weighed and dried at 105 °C in an oven for 24 h. Moisture content was determined as a percentage of the initial film weight lost during drying and was reported on a wet basis.

2.3.5. Mechanical properties
Tensile strength (TS) and elongation at break (E%) of the film samples were determined according to ASTM standard method D 882–02 (ASTM 2002) with an Instron Universal Testing Machine (model 200, Hiwa, Iran). The film samples were cut in rectangular specimens (2.54 × 10 cm). Initial grip separation was set at 50 mm, and cross-head speed was set at 50 mm/min. This test was repeated five times for each specimen to confirm the repeatability.

3. Results and discussion
3.1. XRD analysis of chitosan nanocomposites
XRD characterization of chitosan and chitosan/MMT nanocomposite has been carried out under previously mentioned procedure and the results are shown in Figure 1. The crystalline structure of chitosan is strongly dependent on its processing treatment, as well as its origin and molecular constitution, such as degree of deacetylation and molecular weight [16]. However, the data reported in Figure 1 shows that the crystallinity of chitosan is slightly reduced by the addition of the MMT. This agrees with previously reported results with Lavorgna et al. [14]. MMT had a characteristic peak at 20 = 8.56° (d_{001} = 11.93 Å). With addition of 1 and 3 wt% MMT to chitosan, the reflection peak disappeared, indicating formation of an exfoliated structure, which was disordered and not detectable by XRD. Further increasing the amount of MMT to 5 wt% gave a broad peak at 20 = 5.82° (d_{001} = 17.59 Å). This was much lower than that of pristine MMT, suggesting that intercalation occurs together with some exfoliation [8]. The figure shows that the structure of nanocomposites is not affected by the presence of the REO. These results are in good agreement with those obtained by other investigators [14, 16, 8]. It was shown that inorganic and hydrophilic MMT in low concentration (1-5%) can easily dispersed in the chitosan
solution to form a favorable interaction with hydrophilic chitosan. Strong polar interactions, especially hydrogen bonding, critically affect the formation of intercalation and exfoliated hybrids [18].

3.2. FTIR analysis of chitosan/clay nanocomposites

The Figure 2 shows the FTIR spectra of chitosan and chitosan/MMT nanocomposite films. It is important to note that the peaks between 3500 and 3000 cm\(^{-1}\), corresponding to stretching vibration of free hydroxyl and to asymmetric and symmetric stretching of the N-H bonds in amino group [21], respectively. These are stronger in neat chitosan film compared to those incorporated with clay and REO. The bands appearing between 2750 and 3000 in the spectrum of chitosan film is due to stretching vibrations of C–H bond in –CH\(_2\) (\(\nu = 2930\) cm\(^{-1}\)) and –CH\(_3\) (\(\nu = 2870\) cm\(^{-1}\)) groups, respectively (Paluszkiewicz et al. 2010). In addition, two strong bands at 1541 and 1403 cm\(^{-1}\), associated with OH in-plane bending, are less discernible in the films incorporated with clay and REO. These peaks became more flattened with incorporating clay and REO. These may due to hydrogen bonding between the –OH group in MMT and functional groups in REO ingredients and the -NH and –OH groups in chitosan [19].

In the spectra of the nanocomposites, the N-H bonded to O-H vibration band at 3209 cm\(^{-1}\) in chitosan shifted towards lower frequency (\(\nu = 3202\) cm\(^{-1}\)) in nanocomposite with 1% MMT. This fact indicates that -NH\(_2\) and -OH groups of chitosan formed hydrogen bonds with the -OH group of MMT [20]. It is further shifted to lower frequency (\(\nu = 3130\) cm\(^{-1}\)) for chitosan/clay 1% nanocomposite containing 1% REO which shows hydrogen-bonding interaction between chitosan and clay is enhanced in the presence of REO in accordance with other results [19].

A shift towards lower frequency in the absorption bands at 3209 in the FTIR spectra was coincidental with the decrease in peaks at 3500-3000, 1530 and 1440 cm\(^{-1}\). This observation presents an assumption that there could be a particular arrangement in the films due to the interactions of MMT and REO ingredients functional groups with hydroxyl and amino groups in chitosan matrix[21].
Figure 1. XRD patterns of MMT powder and chitosan-based nanocomposite films.
3.3. Mechanical properties
Mechanical properties of chitosan based films are presented in Table 1. The result showed that the tensile strength (TS) of chitosan film increased significantly by incorporating MMT into chitosan up to 3W% and then decreased by adding more MMT. As can be seen from Table 1 TS increased about 20% and 15% when concentration of MMT was 3 and 5w%, respectively. However, for similar samples Elongation (E%) decreased slightly. Xu et al. [8] and Lavorgna et al. [14] also found that the TS of the chitosan film containing various concentrations of MMT was significantly higher than that chitosan. This improvement in TS of nanocomposite in low amount of MMT may be attributed to the uniform dispersion of MMT in chitosan matrix and strong interaction between chitosan and MMT. The decrease in TS at high concentration of MMT may caused by some aggregation of MMT particles with high surface energy [8].

TS of nanocomposite improved significantly by incorporating REO even at low amount of REO. The highest TS was observed for nanocomposite with 5% of MMT and 0.5% of REO. TS value for this nanocomposite is about 38% higher than pure chitosan film. The E%
increased significantly by incorporating REO up to 44% and it seems that REO has showed a plasticizing ability. As described for moisture sorption the maybe the presence of REO in low amount changes the hydrogen-bonding network within the material and allows a better interaction between nanofiller and matrix.

Table 1. Summary of water vapor permeability, mechanical and physical properties for chitosan-based nanocomposite films.

<table>
<thead>
<tr>
<th>Factors</th>
<th>TS (MPa)</th>
<th>E (%)</th>
<th>Moisture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT (%w/w chitosan)</td>
<td>REO (%v/v)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>0</td>
<td>60.80±8.60</td>
<td>3.79±0.54</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>63.74±3.38</td>
<td>3.56±0.54</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>72.02±6.98</td>
<td>4.28±0.53</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>74.66±2.90</td>
<td>3.91±0.74</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>64.86±1.47</td>
<td>5.47±0.71</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>72.54±1.46</td>
<td>3.44±0.22</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>73.48±4.39</td>
<td>4.11±0.11</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>71.45±3.78</td>
<td>4.31±0.27</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>71.33±5.34</td>
<td>4.83±0.49</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>69.33±5.22</td>
<td>3.01±0.52</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>83.00±3.47</td>
<td>4.10±0.61</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>65.71±7.48</td>
<td>3.42±0.09</td>
</tr>
<tr>
<td>5</td>
<td>1.5</td>
<td>74.71±4.84</td>
<td>4.31±0.47</td>
</tr>
</tbody>
</table>

Different superscripts within a same column indicate significant differences among formulations (P < 0.05).

4. Conclusion

It was shown that incorporation of very low amount of nanoclay into chitosan improves significantly physical and mechanical properties. XRD pattern showed MMT exfoliation and FTIR spectra demonstrated good interaction between chitosan and MMT. The compatibility of REO with chitosan/MMT nanocomposite was confirmed in order to produce an active bionanocomposite for food packaging. In addition, it is expected chitosan nanocomposites containing REO exhibit some antioxidant and antimicrobial properties which make them very
interesting for food preservation. The results of antimicrobial and antioxidant aspect of chitosan nanocomposites will report near future by our group.

Referentes

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