Physical properties of edible modified starch/carboxymethyl cellulose films

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Novel modified starch/carboxy methyl cellulose (CMC) composite films were prepared by a casting method. The effects of CMC addition on the some physical properties of the resulted blend films were investigated. The blend film composed of 15 W/W CMC /starch, showed the lowest water vapor permeability (WVP) value (2.34×10−7 g/m.h.Pa). The moisture absorption and solubility in water properties of the blend films exhibited similar trends. The addition of CMC at the level of 20 W/W starch caused an increase in the ultimate tensile strength (UTS) by more than 59% in comparison to the pure starch film without any significant decrease in the strain to break (SB). The measurement of color values showed that by the increasing of the CMC content in polymer matrix, the b values (yellowness), YI and ΔE of the blend films decreased and the L values (Lightness) and WI index increased.

Industrial relevance: Ecological concerns have resulted in a renewed interest in natural and compostable materials, and therefore issues such as biodegradability and environmental safety are becoming important. Tailoring new products within a perspective of sustainable development or eco-design, is a philosophy that is applied to more and more materials. It is the reason why material components such as natural fibres, biodegradable polymers can be considered as interesting – environmentally safe – alternatives for the development of new biodegradable composites.

Development of biodegradable materials based on starch has become a very attractive option and production of starch based plastic are gradually obtained considerable concern in the world. In this research, improvement of starch film properties is investigated.

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1. Introduction

In order to solve the problems generated by plastic waste, many efforts have been done to obtain an environmental friendly material. Most of the researches are focused on substitution of the petro-based plastics by biodegradable materials with similar properties and low in cost. Several studies reported the use of starches from different sources to prepare films and coatings with different properties (Bertuzzi, Aramada, & Gottifredi, 2007; Larotonda, Matsui, Sobral, & Laurindo, 2005; Mali, Grossmann, Garcia, Martino, & Zaritzky, 2005; Mali, Sakanaka, Yamashita, & Grossmann, 2005). Starch is the most important polysaccharide polymer that is used to develop biodegradable films because it has capability of forming a continuous matrix and it is a renewable and abundant resource. Nevertheless, starch exhibits several disadvantages such as a strong hydrophilic character (water sensitivity) and poor mechanical properties compared to conventional synthetic polymers, which make it unsatisfactory for some applications such as packaging purposes (Alves et al., 2006; John & Thomas, 2008).

Plasticizers are normally added to the film forming solution before casting and drying procedures, as a way to overcome films brittleness. On the other hand, plasticizers generally increase hydrophilicity of the film which in turn promotes water vapor permeability (Krochta & Mulder-Johnston, 1997; Muller, Yamashita, & Laurindo, 2007). Cross-linking is an efficient method to modify starch. Because of the multi-carboxyl structure of citric acid (CA), it may serve as a cross linking agent. Cross-linking of starch molecules can potentially reinforce the intermolecular binding by introducing covalent bonds and supplements natural intermolecular hydrogen bonds which in turn improves the mechanical properties and water resistibility of the resulted films (Yu, Wang, & Ma, 2005). Furthermore, the edible films made from only one kind of natural film-forming polymer displays good properties in some aspects but are poor in others. An alternative promising strategy to improve the properties of edible films and coatings is through blending of biopolymers. Biocomposite or blend films are usually composed of two or three biopolymers and are prepared by varying methods (Ban, Song, Argyropoulos, & Lucia, 2006; Fama, Gerschenson, & Goyanes, 2009; Gaspar, Benko, Dogossy, Reczey, & Czigany, 2005; Vilaseca et al., 2007). The reports on CMC-modified starch biocomposite films are scarcely found. CMC is a cellulose ether that exhibits thermal gelation and forms excellent films due to its polymeric structure and high...
molecular weight chains. It would be expected that CMC could improve the mechanical and barrier properties of the starch based films due to chemical similarity of starch and CMC, providing good compatibility between them (Ma, Chang, & Yu, 2008).

In current research, the varying levels of CMC were used in modified starch based blend films. The goal of this work was the study of CMC on physical–mechanical properties of starch based composite films intended to be used as edible or biodegradable films.

2. Materials and methods

2.1. Materials

Corn starch (12% moisture) was provided from Glucosan Industry (Ghazvin, Iran). Glycerol, calcium sulfate and potassium sulfate (analytical grade) were purchased from Merck (Darmstadt, Germany). Carboxymethyl cellulose (CMC), with an average molecular weight of 41,000 (practical grade) was purchased from Caragum Parsian Corporation (Tehran, Iran). Citric acid (CA) (food grade) was prepared from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Preparation of films

Starch (5 g) was mixed (25 °C for 5 min) with distilled water (100 mL) and glycerol (40 mL/100 g starch) and 0.5 CA (10% W/W starch). These suspensions were agitated by magnetic stirrer (500 rpm) for 30 min in water bath (90 °C). Carboxymethyl cellulose (0, 5, 10, 15 and 20% W/W starch) was solubilized in 75 ml of distilled water at 75 °C for 10 min. The CMC and starch solutions were mixed together (75 ml CMC-solution + 100 ml starch-CA-solution) and stirred at 75 °C for 10 min (pH = 5.5). Dispersions were then cooled at 40 °C and mixed gently for 20 min to release all air bubbles. Then, about 70 mL of the sample was poured into a Teflon casting tray resulting in films with 0.08 ± 0.01 mm thickness, measured with an Alton M820-25 hand-held micrometer (China) having a sensitivity of 0.01 mm and then dried at 60 °C in an oven to cast the films.

2.3. Water vapor permeability (WVP)

WVP tests were carried out using the standard ASTM (1995) with some modifications (Mali, Grossmann, Garcia, Martino, & Zaritzyk, 2006). Special cups, with an average diameter of 2 cm and a depth of 4.5 cm, utilized to determine WVP of films were cut from each of samples and were mounted between the grips of the machine. The initial grip separation and cross-head speed were set to 50 mm and 5 mm/min, respectively.

2.4. Moisture absorption

Moisture absorption was measured according to the method of Angles and Dufrense (2000). The dried sheets of 20 mm × 20 mm were first conditioned at 0% RH (CsO4) for 24 h. After weighing, they were conditioned in a desiccator containing CaSO4 saturated solution at 20 °C to 25 °C to ensure a relative humidity of 55%. The samples were weighed at desired intervals until the equilibrium state was reached. The moisture absorption of the samples was calculated as follows:

\[
\text{moisture absorption (\%)} = \frac{W_t - W_0}{W_0} \times 100
\]

where \(W_t\) and \(W_0\) are the weights of the sample after \(t\) time at 55% RH and the initial weight of the sample, respectively. All measurements were performed in three replicates.

2.5. Solubility in water

Solubility in water was defined as the percentage of the dry matter of film which is solubilized after 24 h immersion in water (Gontard, Duczé, Cug, & Guilbert, 1994). Film specimens were kept in a desiccator containing dry calcium sulphate till they reached constant weight. Afterward, about 500 mg of each film were immersed in beakers containing 50 ml of distilled water at 23 °C for 24 h with periodical gentle manual agitation. The films were removed from the water and were placed back in the desiccator until they reached a constant weight to obtain the final dry weight of the film. The percentage of the total soluble matter (%TSM) of the films was calculated using the following equation:

\[
\%\text{TSM} = \frac{[\text{initial dry wt} - \text{final dry wt}]}{\text{initial dry wt}} \times 100
\]

TSM tests for each type of film were carried out in three replicates.

2.6. Tensile properties

Ultimate tensile strength (UTS) and strain to break (SB) of the films were determined at 21 °C ± 1 °C using a tensile tester (Zwick/Roell model FR010, Germany) according to ASTM standard method D882-91 (ASTM, 1996). Three dumbbellly forms films (8 cm × 0.5 cm) were cut from each of samples and were mounted between the grips of the machine. The initial grip separation and cross-head speed were set to 50 mm and 5 mm/min, respectively.

2.7. Thermal properties

The thermal properties of the films were determined by differential scanning calorimetry (DSC) (Model F3 200 DSC Netzsch, Germany). The film samples (5 mg ± 3 mg) were cut as small pieces and were placed into a sample pan of DSC equipment. The reference was an empty pan. The glass transition temperature \(T_g\) of the different films were measured at a heating scan rate of 10 °C/min from 30 °C to 250 °C and they were identified as the midpoint temperature of a step-down shift in baseline due to change in heat capacity upon glass transition. Also the melting point \(T_m\) of the films was determined. The \(T_g\) and \(T_m\) of the each film was determined in duplicate and the results were averaged.

2.8. Color

The color values of the films were measured with a colorimeter (made in faculty of agriculture, University of Tabriz, Iran). Film
specimens were placed on a white standard plate (L = 96.86, a = −0.02, and b = 1.99) and the L, a, and b color values were measured. L values range from 0 (black) to 100 (white); a values range from −80 (greenness) to 100 (redness); and b values range from −80 (blueness) to 70 (yellowness). All measurements were performed in three replicates. Total color difference (ΔE), yellowness index (YI), and whiteness index (WI) were calculated as (Bolin & Huxsoll, 1991):

\[ \Delta E = \left[ (L_{\text{standard}} - L_{\text{sample}})^2 + (a_{\text{standard}} - a_{\text{sample}})^2 + (b_{\text{standard}} - b_{\text{sample}})^2 \right]^{0.5} \]  

\[ YI = 142.86b / L \]  

\[ WI = 100 - \left[ (100 - L)^2 + a^2 + b^2 \right]^{0.5} \]

2.9. Statistical analysis

Statistics on a completely randomized design were performed with the analysis of variance (ANOVA) procedure in SPSS (Version 11.5, SPSS Inc., Chicago, IL) software. Duncan’s multiple range test (P < 0.05) was used to detect differences among mean values of films properties.

3. Results and discussion

3.1. Water vapor permeability (WVP)

The WVP of the starch/CMC films diminished with the increase of CMC content as can be seen in Fig. 1. The WVP was 2.62 × 10⁻¹⁰ g/m²h·Pa for the control sample (0% W/W CMC and 10% CA) and decreased significantly to 2.45 × 10⁻¹⁰ g/m²h·Pa and 2.34 × 10⁻¹⁰ g/m²h·Pa for the films containing 10 and 15% W/W CMC, respectively. The film containing 15% W/W CMC has significantly (P < 0.05) the lowest WVP value. However, when the CMC content of the films reached to 20% W/W, the WVP increased not significantly to 2.38 × 10⁻¹⁰ g/m²h·Pa.

Reduction of the WVP with increasing CMC content results in an improvement of the functional properties of these films, considering the hydrophilic characteristics of the matrix. The decrease of the WVP by incorporation of secondary biopolymer is in agreement with results usually reported for polymer blends which are studied for packaging applications (Arvanitoyannis & Biliaderis, 1999; Fama et al., 2009; Ma et al., 2008). Water resistance of CMC biopolymer is better than starch biopolymer (Ma et al., 2008). This could be attributed to the highly crystalline and hydrophobic character of the cellulose fibers in comparison to starch polymer. The addition of CMC could introduce a tortuous path for water molecule to pass through (Kristo & Biliaderis, 2007). At a low content of filler, CMC probably dispersed well in the starch matrix and blocked the water vapor transmission. However, additional amount of CMC might congregate which in turn decreased the effective contents of the CMC and facilitates the water vapor permeation.

3.2. Moisture absorption

Fig. 2 shows the moisture absorption of the starch films as a function of the CMC content. It was observed that the moisture absorption of starch/CMC films was less than that of starch film, at an environmental relative humidity of 55%. These results indicated that the addition of CMC improve the water resistance of the starch matrix. The reason could be that the starch is able to form hydrogen bonds with the hydroxyl and carboxyl groups of the CMC macromolecules and this strong structure could reduce the diffusion of water molecules in the material. With the increase of the CMC contents from 15% to 20%, the moisture absorption increased slightly from 20 to 21.33%. This result indicates that the combination of cellulosic fiber with starch improves water resistance to a certain degree since, as already known, CMC is hydrophilic material, although its hydrophilicity is lower than that of starch (Ma et al., 2008; Mohanty, Misra, & Hinrichsen, 2000). Similar results were obtained by other researchers who observed a reduction in the water absorbed by polymer blends and biocomposites made with addition of cellulosic fiber (Ban et al., 2006), hemi-celluloses (Gaspar et al., 2005) and jute strands (Vilaseca et al., 2007) to starch matrix.

3.3. Solubility in water

The water solubility of the starch/CMC films as a function of CMC content is shown in Fig. 3. Addition of CMC, in all concentrations, decreased the water solubility of starch films. The %TSM was 23.76% for the samples without CMC, which decreased to 21.33 and 20.13% for the films containing 5 and 10% W/W CMC, respectively. However, significant (P < 0.05) decrease in solubility observed at the high levels of CMC. At the level of 20% W/W CMC, the starch films showed the lowest %TSM values at 17.65%.

3.4. Tensile properties

Figs. 4–6 show the relationships between CMC content and the tensile properties of the starch/CMC films. The curves reported in Fig. 4 show an improvement of the mechanical strength with the increase of CMC content. This is in agreement with Ma et al. (2008)
who reported a significant improvement of water resistance and mechanical properties of starch films is achieved by adding relatively small amounts of CMC (till 10%). The UTS and SB as the function of CMC concentration are shown in Figs. 5 and 6, respectively. It was observed an important increase of two and threefold in the UTS when 15 and 20% W/W of CMC was added to the starch, respectively. With increasing CMC concentration from 0% to 20%, the UTS increased significantly ($p < 0.05$) from 6.57 MPa to 16.11 MPa. This was probably due to the interfacial interaction between the matrix and filler due to the chemical similarity (polysaccharide structure) of starch and CMC. It was interesting that with increasing CMC concentration (from 0% to 20%), the UTS increased significantly ($p < 0.05$), however, the SB did not reduce considerably (it reduced only from 66.18% to 58.49%). It seems, CMC could improve the films strength without significant depressing effect on flexibility. The convenient cross linking agents (ex. borax) (Sreedhar, Sairam, Chattopadhyay, Syamala Rathnam, & Mohan Rao, 2005) and plasticizers (polyols) (Arvanitoyannis, Kologiris, Nakayama, Yamamoto, & Aiba, 1997) often do not show the diplex function at relatively high concentration. On the other hand, researchers who examined the effect of cellulosic fibers on the mechanical properties of the starch films, reported different results from these work. The increasing UTS and reducing SB, are the common results that reported as result of incorporation of cellulosic fiber (Ban et al., 2006), hemicelluloses (Gaspar et al., 2005), jute strands (Vilaseca et al., 2007), Manila hemp fiber (Ochi, 2006) and vegetable fibre (Fama et al., 2009) to the starch matrix. Different results in current work may be attributed to cross-linking effect of CA. In the presence of CA, reinforcement effect of CMC is probably weakened, and it cannot interact tightly with starch matrix. Hence, due to creation of limited interactions, the tensile strength of films increased without any significant decreases in their flexibility.

3.5. Thermal properties

Three characteristic thermal transitions may exist for semi-crystalline polymers such as starch: a glass transition for the amorphous fraction, a melting transition for the crystalline fraction and a transition due to crystallization. The DSC thermograms of the starch, starch-CA and starch/CA/CMC films exhibited sharp endothermic peaks (typical of a semi-crystalline polymeric system) at the range of 190 °C to 232 °C. These endothermic peaks have been associated with the melting of crystalline starch and CMC domains reorganized during the retrogradation. The melting peak of starch/CA was around 223.1 °C, i.e. ~13 °C higher than starch film without CA. This difference in melting behavior for starch/CA was attributed to chemically modification in the structure of starch polymer backbone which cause to higher degree of crystallinity.

A weak endothermic peak can be observed in the thermogram of the starch/CA film which may be caused by the melting of the residual CA, since the melt point of the pure anhydrous CA is ~159 °C (Shi et al., 2007).

For starch/CA/CMC polymer blend films, the temperature position of the melting peak decreased from 223.1 °C to 191.7 °C as CMC content increased from 0 to 10% W/W starch, however, higher level of
the CMC increased the position of the peak to 200 °C and 231.7 °C in the samples containing 15 and 20% W/W starch, respectively. The change in the position of this peak indicates that higher CMC contents favor the formation of larger crystal domains and lowers the mobility of the amylopectin (Mondragon, Arroyo, & Romero-Garcia, 2008). The lower level of CMC might be act as lubricant agent and decreased intermolecular interaction and association in starch film matrix which in turn decreases degree of crystallinity.

No glass transition was observed in the thermograms of the plasticized starch films without CMC. The glass transition of plasticized starch films is sometimes difficult to be determined by DSC analysis, because the heat capacity change is quite low at the glass transition.

It could be seen from Fig. 7 that the glass transition phenomena has been more visible when CMC incorporated to starch polymer matrix. Glass transition temperatures were observed in starch/CMC polymer blend films at the range of 130 °C to 150 °C depend on CMC content. This transition probably related to mixed CMC-starch domain in polymer matrix, because glass transition was not observed in specimens without CMC. It could also be seen in the DSC curves of the starch-CMC films (Fig. 7) that the Tg increased when the CMC content increased from 5 to 20% W/W starch, respectively. It could be attributed to increase of the mean molecular weight of polymer in amorphous region of the composite matrix.

Thermograms indicated partial miscibility of CMC and starch in the amorphous phase at the molecular level for any given compositional ratio and both biopolymers remained a homogeneous material throughout the heating cycle, because phase separation (separated glass transition temperature or melting peaks) between two biopolymers in composite films was not observed. If polymer and plasticizers blend or two different polymers are immiscible, the mixture will exhibit two Tg and Tm corresponding to the two pure phases. It is unlikely to blend or two different polymers are immiscible, the mixture will exhibit two glass transition temperature or melting peaks) between two biopolymers throughout the heating cycle, because phase separation (separated amorphous region of the composite matrix.

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3.6. Color

Film color can be an important factor in terms of consumer acceptance of both edible and inedible films. The L, a and b Hunter Lab color values, total color difference (ΔE), yellowness index (YI) and whiteness index (WI) of films are shown in Table 1. The main differences in color values among the starch-CMC films were the increased L values and decreased b values. However no significant (P<0.05) differences in a values was detected among the films. Control sample (0% W/W starch CMC) showed significantly lower L value (darker) and higher b value (yellowish) than polymer blends. This shows that starch produces dark and yellowish films. By increasing CMC content, L values of the films significantly increased (P<0.05). Conversely, b values decreased with incorporation of CMC and continuing to increase CMC content within the starch/CMC films. CMC can produce clearer films than starch (Mohanty et al., 2000), therefore, addition of CMC to starch films, can improve their optical properties and reduce their yellowness.

Color changes due to incorporation of CMC can be more fully described using other color functions (Bolm & Huxoll, 1991), such as ΔE which indicates the degree of total color difference from the standard color plate. YI indicates degree of yellowness, and WI indicates degree of whiteness. The addition of CMC resulted in a significantly decrease (P<0.05) in ΔE (increase clearness). YI showed the same pattern as ΔE. In contrast, WI increased by increasing of CMC content.

4. Conclusions

The addition of CMC to starch-glycerol blends improved the moisture resistance of the resulted starch based composites. At the level of 15%W/W CMC, blend films showed the lowest WVP values at 2.34×10⁻⁷ g/m.h.Pa. However when the CMC content of the blend films reached to 20% W/W starch, the WVP increased to 2.38×10⁻⁷ g/m.h.Pa. By addition of 15%W/W CMC/starch, the moisture absorption and solubility of the films decreased from 24.34% and 23.76% to 20.00% and 19.89%, respectively. Furthermore, CMC had an important influence on the mechanical properties of the resulted composite films. CMC (20% W/W starch) could increase the UTS of starch based composite films by more than 50% compared to the neat plasticized starch film. In the presence of CA, reinforcement effect of CMC was weakened and it probably could not interact tightly with starch matrix. CA (10% W/W starch) increased Tm of the starch based films, however CMC had different effect on Tm, depend on its concentration. By addition of 5 and 10% CMC (W/W starch), Tm decreased however, higher level of the CMC increased the position of the melting peak. In addition, by increasing of CMC content, optical properties of the composite films improved appreciably.

With considering these results, it seems that the CMC-starch biocomposite films show better physic-mechanical properties than starch films and can be potentially replaced of starch films.

Table 1

<table>
<thead>
<tr>
<th>CMC content (%)</th>
<th>L</th>
<th>a</th>
<th>b</th>
<th>ΔE</th>
<th>YI</th>
<th>WI</th>
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<tr>
<td>0</td>
<td>76.41⁺</td>
<td>-1.61⁺</td>
<td>18.38⁺</td>
<td>26.25⁺</td>
<td>34.35⁺</td>
<td>70.05⁺</td>
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<td>-1.56⁺</td>
<td>16.18⁺</td>
<td>23.56⁺</td>
<td>29.58⁺</td>
<td>72.73⁺</td>
</tr>
<tr>
<td>10</td>
<td>78.30⁺</td>
<td>-1.36⁺</td>
<td>13.95⁺</td>
<td>22.12⁺</td>
<td>25.44⁺</td>
<td>74.16⁺</td>
</tr>
<tr>
<td>15</td>
<td>80.00⁺</td>
<td>-1.24⁺</td>
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<td>77.03⁺</td>
</tr>
<tr>
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<td>-1.49⁺</td>
<td>10.48⁺</td>
<td>17.47⁺</td>
<td>18.33⁺</td>
<td>78.82⁺</td>
</tr>
</tbody>
</table>

Means with different letters within a column indicate significant differences (P<0.05).

Fig. 7. Thermogram of the starch films containing different amount of CMC.

References


