Original article

**Tensile and water vapour properties of calcium-crosslinked alginate-cashew tree gum films**

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**Summary**

In this study, sodium alginate films were blended with cashew tree gum (CTG) and immersed in CaCl\(_2\) solution. The influence of CTG concentration and immersion time in CaCl\(_2\) on tensile properties, water vapour permeability and water solubility (WS) of alginate films was evaluated. Glycerol-plasticized alginate/CTG films were cast on glass plates, which were then immersed in a 2% CaCl\(_2\) solution to crosslink alginate. CTG concentration in the film solution and immersion time in CaCl\(_2\) bath were varied according to a central composite design. Tensile strength, Young's modulus, WS and water vapour barrier of the films were favoured by higher immersion times in CaCl\(_2\) and lower CTG concentrations. The negative CTG effects on such properties have been attributed to competition between the polysaccharides for interactions with calcium ions, reducing crosslinking density and loosening the film structure. On the other hand, this loosening effect resulted in higher film flexibility at higher CTG concentrations.

**Keywords**

Biodegradable packaging, biopolymer films, gums, polysaccharides.

**Introduction**

Concerns over packaging waste have motivated the development of biodegradable and/or edible packaging films, based on renewable biopolymers such as polysaccharides and proteins (Krochta & De Mulder-Johnston, 1997; Debeaufort et al., 1998). Edible films and coatings are expected to function similar to conventional packaging, acting as barriers against water vapour and gases, and improving mechanical-handling properties of foods. Edible packaging is not meant to entirely replace conventional packaging, but to enhance the efficiency of food protection, reducing packaging requirements and waste. Moreover, edible films can act as barriers between food components, where traditional packaging is unable to function (Krochta & De Mulder-Johnston, 1997).

Sodium alginate is an anionic carbohydrate extracted from various species of brown seaweeds (*Phaeophyceae*). It is a family of unbranched binary copolymers of (1-4)-linked β-δ-mannuronic acid (M) and α-L-guluronic acid (G) residues (Moe et al., 1995). The presence of carboxyl groups in each constituent residue (Ikeda et al., 2000) enables sodium alginate to crosslink with di- or trivalent metal cations, especially calcium ions (Ca\(^{2+}\)), to produce strong gels or films. Although sodium alginate is readily solved in water, the replacement of sodium by Ca\(^{2+}\) produces water insoluble alginates, which is attributed to ionic crosslinkings forming an ‘egg-box structure’ (Nakamura et al., 1995), in which calcium ions are located in cavities linking adjacent guluronic acid chains of alginate (Hambleton et al., 2009). Alginate films have been studied as edible coatings to be applied to a variety of foods such as fruits/vegetables (Raybaudi-Massilia et al., 2008; Fan et al., 2009; Fayaz et al., 2009) and meat products (Marcos et al., 2008; Chidanandaiah et al., 2009), especially as carriers of antimicrobials (Datta et al., 2008; Marcos et al., 2008; Raybaudi-Massilia et al., 2008; Chidanandaiah et al., 2009; Fayaz et al., 2009) and antioxidant compounds (Norajit et al., 2010).

Cashew tree gum (CTG) is a complex water soluble heteropolysaccharide exudated from ducts that appear from leaves, flowers and fruits (Bezerra et al., 2007). Its composition is comprised by galactose (72%), glucose (14%), arabinose (4.6%), rhamnose (3.2%) and glucuronic acid (4.5%) (De Paula et al., 1998). The greatest diversity of cashew tree (*Anacardium occidentale* L.) can be found in northeastern Brazil (Barros et al., 2002), where its culture is a most important agronomic activity (Santos et al., 2007). The cashew tree cultivation is mainly focused on production of cashew nuts (Bezerra...
et al., 2007), whereas CTG has been poorly explored to the moment, although several authors have already mentioned its similarity with gum arabic (De Paula et al., 1998; Mothe & Rao, 2000; Paula et al., 2002). The presence of glucuronic acid (pKa ~3.5) makes CTG to behave as a polyanion at pH > 4.0 (Maciel et al., 2007), making it able to interact with cations. Gyedu-Akoto et al. (2008) and Ofori-Kwakye et al. (2010) reported the presence of high calcium levels in CTG, which suggests that it probably has the ability to interact with anionic sites of other biopolymers. CTG films have been obtained by Carneiro-da-Cunha et al. (2009) in view of their application as edible coatings on apples.

The objective of this study was to evaluate the influence of CTG and CaCl₂ bath on tensile properties, water vapour permeability (WVP) and water solubility (WS) of alginate films.

Materials and Methods

Cashew tree gum purification

Cashew tree gum was extracted from a single cashew tree (Pacajus, CE, Brazil) and purified by a method adapted from that described by Torquato et al. (2004). Basically, the gum was ground, dissolved in distilled water at room temperature (24 ± 1 °C), vacuum filtered and precipitated with commercial ethanol (96°GL) at the ethanol:gum mass ratio of 3:1. The precipitate was drained and placed in Petri dishes to be dried in a fume hood. The dried gum was ground and passed through a 212 μm sieve, producing a fine powder, which is to be referred to henceforth simply as CTG.

Film manufacture

For the film formulation, 1.6 g of sodium alginate (Grindsted® FD175, with 60.5% guluronic acid, provided by Danisco Brasil Ltda., Cotia, SP, Brazil) was mixed with a variable quantity of CTG. Glycerol (Impex, Diadema, Brazil) was added as a plasticizer (at 30% on a sodium alginate + CTG basis), and 0.08 g Tween 80 (Vetec Quimica Farm. Ltda, Rio de Janeiro, Brazil) as a surfactant. The volume was completed to 80 mL with distilled water. The mixtures were maintained at 60 °C in a Fisatom 752A magnetic stirrer (Aaker Solutions Ltda., Porto Alegre, Brazil) while homogenised for 60 min at 200 rpm and vacuum degassed. Dispersions were then cast on 0.3 × 0.3 m glass plates, levelled with a draw-down bar to a thickness of 0.8 mm, and allowed to dry for 6 h on a lab bench (24 ± 1 °C, 76 ± 2% relative humidity). The glass plates with the films on them were then immersed in a 2% CaCl₂ (Vetec Quimica Farm. Ltda) solution to promote interactions of calcium ions with guluronate groups of alginate (by crosslinking) and also with the anionic CTG.

The films were placed on a lab bench (24 ± 1 °C, RH 76 ± 2%) for 24 h to dry. Then, samples were cut and detached from the surface.

Experimental design and analysis of results

The experiment was carried out according to a central composite design, based on Response Surface Methodology, with two variables (Table 1): concentration of CTG in the film solution (based on sodium alginate dry weight) and immersion time in CaCl₂ bath.

Results were analysed using the software Minitab® (Minitab Inc., State College, PA, USA). The regressions to represent the responses were obtained and evaluated in terms of their determination coefficients ($R^2$ values) and the significance of their $F$ values.

Determinations

Prior to film properties determination, the detached, free-standing films were conditioned for 24 h at 25 °C in desiccators containing MgNO₃ saturated solution (50% RH).

Water vapour permeability

The WVP determination, with eight replicates, was based on the method E96-80 (ASTM, 1989) at 24 °C and 85% RH, using silica gel as the desiccant material inside the permeability cells, whereas the bottom of desiccator was filled with 200 mL of distilled water. The internal volume of the permeability cells was 78.54 cm³ (5 cm in diameter, 1 cm in height). The desiccators were

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental conditions of the treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CTG</strong></td>
<td><strong>Unencoded (g per 100 g)</strong></td>
</tr>
<tr>
<td>1</td>
<td>−1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>−1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>−1.41</td>
</tr>
<tr>
<td>6</td>
<td>1.41</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
</tr>
</tbody>
</table>

CTG, concentration of cashew tree gum.

*Based on sodium alginate. Coded values are according to the central composite design, varying from −1.41 to 1.41 (corresponding to 0–100% for CTG concentration and 0–60 s for immersion time in CaCl₂). Uncoded values are the real experimental values of the variables.
25 cm in diameter and 21 cm in height. Eight weight measurements of each cell were carried out within a 24-h period.

**Tensile properties**

Tensile properties of 100 × 15 mm film strips (with six replicates) were measured according to D882-97 (ASTM, 1997), in an Emic DL 2000 Universal Testing Machine with a load cell of 500 N, initial grip separation of 0.05 m and crosshead speed of 10 mm min⁻¹ (1.67 × 10⁻³ m s⁻¹).

**Water solubility**

The measurement of WS of the films (with five replicates) was based on the method proposed by Rhim et al. (1998). Film samples were dried at 105 °C for 24 h to determine initial dry matter. Additional samples were placed in 50-mL beakers containing 30 mL distilled water. The beakers were placed in an environmental chamber at 25 °C for 24 h, and then, the film pieces were removed from the beakers and oven dried (105 °C, 24 h) to determine the insoluble dry matter. The per cent WS was then calculated according to eqn (1).

\[
WS = 100 \times \frac{(S_0 - S)}{S_0},
\]

where \(S_0\) is the initial dry matter and \(S\) the insoluble dry matter.

**Results and discussion**

Table 2 presents the measured properties of the films obtained from different treatments. The regression coefficients for the second-order polynomial equations representing the experimental responses are presented in Table 3. All models were significant \((P < 0.05)\) except for WS, which was slightly non-significant \((P = 0.06)\), and with high determination coefficients \((R^2)\) values. Indeed, overall predicted values were similar to the corresponding observed values (Fig. 1).

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**Table 2** Experimental responses for the properties of the films

<table>
<thead>
<tr>
<th>T</th>
<th>Th (μm)*</th>
<th>TS (MPa)</th>
<th>EB (%)</th>
<th>YM (MPa)</th>
<th>WVP (\times 10^{-11}) g m⁻¹ P⁻¹ a⁻¹ s⁻¹ m⁻²</th>
<th>WS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
<td>Mean</td>
<td>SD</td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>1</td>
<td>18.6</td>
<td>23.5</td>
<td>1.37</td>
<td>4.85</td>
<td>0.259</td>
<td>136</td>
</tr>
<tr>
<td>2</td>
<td>30.1</td>
<td>16.1</td>
<td>1.14</td>
<td>7.99</td>
<td>0.462</td>
<td>103</td>
</tr>
<tr>
<td>3</td>
<td>18.8</td>
<td>24.4</td>
<td>1.42</td>
<td>3.87</td>
<td>0.240</td>
<td>143</td>
</tr>
<tr>
<td>4</td>
<td>29.8</td>
<td>17.9</td>
<td>1.21</td>
<td>5.69</td>
<td>0.287</td>
<td>110</td>
</tr>
<tr>
<td>5</td>
<td>16.7</td>
<td>26.6</td>
<td>1.02</td>
<td>3.79</td>
<td>0.187</td>
<td>157</td>
</tr>
<tr>
<td>6</td>
<td>31.4</td>
<td>18.0</td>
<td>1.23</td>
<td>8.02</td>
<td>0.421</td>
<td>120</td>
</tr>
<tr>
<td>7</td>
<td>25.2</td>
<td>17.6</td>
<td>1.12</td>
<td>7.52</td>
<td>0.398</td>
<td>109</td>
</tr>
<tr>
<td>8</td>
<td>25.7</td>
<td>25.0</td>
<td>1.45</td>
<td>4.79</td>
<td>0.313</td>
<td>143</td>
</tr>
<tr>
<td>9</td>
<td>26.1</td>
<td>24.4</td>
<td>1.38</td>
<td>4.89</td>
<td>0.204</td>
<td>134</td>
</tr>
<tr>
<td>10</td>
<td>24.9</td>
<td>23.8</td>
<td>1.33</td>
<td>4.41</td>
<td>0.269</td>
<td>130</td>
</tr>
<tr>
<td>11</td>
<td>25.6</td>
<td>23.0</td>
<td>1.51</td>
<td>4.04</td>
<td>0.236</td>
<td>141</td>
</tr>
</tbody>
</table>

T, treatment; TS, tensile strength; EB, elongation at break; YM, Young’s modulus; WS, water solubility; WVP, water vapour permeability. *Th: thickness for tensile properties (average of six replicate samples, each one measured eight times). †Thickness for WVP (average of eight replicate samples, each one measured eight times). 

The film disintegrated, and it was not possible to determined WS.

**Table 3** Regression equations (for the coded variables) and statistical parameters of the models for the responses

<table>
<thead>
<tr>
<th>Equations</th>
<th>F</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS = 23.74 - 3.25x - 1.05x² - 1.65y - 1.58y² + 0.21xy</td>
<td>9.40 (P = 0.01)</td>
<td>90.38</td>
</tr>
<tr>
<td>EB = 4.11 + 1.37x + 0.79x² - 0.89y + 0.91y² - 0.33xy</td>
<td>41.05 (P &lt; 0.01)</td>
<td>97.62</td>
</tr>
<tr>
<td>YM = 134.96 - 14.94x - 0.50x² + 7.97y - 6.84y² + 0.02xy</td>
<td>6.22 (P = 0.03)</td>
<td>86.15</td>
</tr>
<tr>
<td>WS = 19.24 + 0.67x - 0.02x² - 1.59y - 0.45y² - 0.08xy</td>
<td>5.62 (P = 0.06)</td>
<td>87.53</td>
</tr>
<tr>
<td>WVP = 6.53 + 0.35x - 0.18x² - 0.76y - 0.19y² + 0.11xy</td>
<td>16.83 (P &lt; 0.01)</td>
<td>94.39</td>
</tr>
</tbody>
</table>

TS, tensile strength; EB, elongation at break; YM, Young’s modulus; WS, water solubility; WVP, water vapour permeability; CTG, concentration of cashew tree gum; IT, immersion time in CaCl₂ solution. x, cashew tree gum concentration (coded values, ranging from -1.41 to 1.41, according to Table 1); y, immersion time in CaCl₂ solution (coded values, ranging from -1.41 to 1.41, according to Table 1).
Figure 2 presents the contour plots for the experimental responses. Tension strength (TS) and Young’s modulus (YM) were favoured by higher immersion times in CaCl₂ bath and lower CTG concentrations. The elongation at break (EB) presented the opposite behaviour, with high CTG concentrations and immersion times in CaCl₂ producing higher EB values.

The effects of increasing immersion time in CaCl₂ on increasing TS and YM and decreasing EB were expected (Wang et al., 2001; Rhim, 2004), presumably due to
increased crosslinking density, as crosslinking sodium alginate with polyvalent cations tends to improve film cohesiveness, rigidity and mechanical resistance (Zactiti & Kieckbusch, 2006), which can be attributed to formation of a denser network with a tightly arranged structure (Roger et al., 2006). On the other hand, the presence of CTG in the film formulations was expected to contribute for increasing TS and YM, because of two reasons. First, the presence of Ca\(^{2+}\) ions in CTG composition indicates the ability of CTG to interact with anionic sites of alginates. Second, calcium divalent cations could link alginate chains to carboxyl groups of glucuronic acid residues of CTG, as suggested by Giannouli et al. (2004) for a pectin-gum arabic system. However, TS and YM were rather reduced by the presence of CTG, which could be explained by a competition between CTG and alginate for interaction with calcium ions, as both polysaccharides are anionic. As a high-guluronic acid sodium alginate was used in this study, it was probably able to form stronger interactions with Ca\(^{2+}\) ions when compared with those formed between CTG and calcium. Then, CTG probably decreased crosslinking degree between sodium alginate and Ca\(^{2+}\) ions, which reduced strength and modulus. On the other hand, this loosening effect on film structure resulted in increased elongation. Considering that high-guluronic sodium alginate is conformationally less flexible than high-mannurionate sodium alginate (Ashikin et al., 2010), and that crosslinking with calcium ions increases brittleness of the films (Silva et al., 2009), the increased flexibility promoted by CTG can make the films more adequate for applications requiring better flexibility, such as applications as edible coatings for fruits and vegetables.

Water solubility and WVP are related concepts, as permeability is a function of solubility. However, water solubility usually refers to water absorption in the film structure itself, whereas WVP is related to water transmission to the food and the consequences associated to food stability. Reducing both WS and WVP of hydrophilic films improves film stability and performance. A high WS may not only cause a film to dissolve when in contact with water, but also affects film tensile properties. Hydrophilic polymers such as sodium alginate tend to progressively absorb water when exposed to high RH environments. The plasticizing effects of the absorbed water lead to reduced inter-chain interactions and increased chain mobility, resulting in a reduction in mechanical strength (Yang & Paulson, 2000). WS (and consequent permeability) of the films were improved by increasing immersion times in CaCl\(_2\), corroborating previous reports (Pavlath et al., 1999; Zactiti & Kieckbusch, 2006), which results from linking polar carboxyl groups of alginate (Pavlath et al., 1999; Rhim, 2004). On the other hand, such properties have been impaired by the presence of CTG, possibly because of competition between both polysaccharides for interactions with Ca\(^{2+}\) ions, unfavouring crosslinking and impairing the water resistance and barrier of the films.

The film with the lowest WVP in this experiment (treatment 3, Table 2) presented better water vapour barrier than alginate films obtained in some previous studies (Rhim, 2004; Zactiti & Kieckbusch, 2006), and WS similar to those reported by Rhim (2004), although its overall tensile properties have been poorer than those reported by the mentioned studies.

Conclusions

Although CTG has calcium ions in its composition, which could interact with anionic sites of alginates, its presence in calcium-crosslinked alginate films impaired their TS, as well as their water resistance and barrier. Such effects probably occurred because of competition between CTG and alginate for interaction with calcium ions from CaCl\(_2\) solution, the high-gulurionate alginate being able to form stronger crosslinking interactions with Ca\(^{2+}\) ions. It has been proposed that the presence of CTG probably reduced the crosslinking density between alginate and Ca\(^{2+}\) ions, which reduced TS, modulus, water resistance and water vapour barrier. On the other hand, CTG favoured elongation of the films, probably because it loosened their structure, keeping a better flexibility.

Acknowledgments

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References


