Effect of Amylopectin Content on Mechanical, Barrier and Thermal Properties of Plasticized Starch/Chitosan Films

Marilia M. Horn, Virginia C. A. Martins and Ana M. G. Plepis

Abstract: Mechanical, barrier, and thermal properties of films based on blends of corn starch and chitosan plasticized with ethylene glycol, glycerol, and sorbitol were investigated. Starch amylopectin variation was explored, and contents of 100% and 73% were employed to blend with chitosan and polyols. The findings showed that high amylopectin content has a significant effect ($p < 0.05$), resulting in films with lower tensile strength (TS) and reduced water vapor permeability (WVP). On the other hand, the incorporation of polyols showed a significantly high ($p < 0.05$) elongation at break (EB) for films plasticized with glycerol and sorbitol at high amylopectin content. For chitosan/73% amylopectin film, the addition of plasticizers exhibited no significant difference ($p < 0.05$) among the samples for TS and WVP results. The amylopectin content played no influence in the degradation stability of the films measured by thermogravimetry (TGA). However, amylopectin content influences the endothermic peak temperature observed by differential scanning calorimetry (DSC) analysis. A reduction of about 15°C was noticed for the film prepared with high amylopectin content, a behavior correlated to its amorphous structure, capable of retaining more water than a crystalline region.

Keywords: chitosan; starch; amylose; films

1. Introduction

As an alternative to fossil-based raw materials, polysaccharides obtained from natural sources are being considered in developing films for packaging [1], as drug carriers [2], or for wound dressing [3]. These polymers with biodegradable properties are described as eco-friendly materials due to their life cycles, participating in the fixation of CO$_2$ after degradation. This property meets the current pollution concerns, promoting sustainable development of new materials [4].

Starch is a known non-toxic biopolymer, usually applied as an alternative natural source instead of ongoing plastics. Starch consists of two polysaccharide chains: the linear α-(1,4) linked D-glucose amylose and the α-(1,4) bonds but with α-(1,6) bonds at branching points amylopectin [5]. Due to this characteristic, interaction with other polymers is strongly affected, as a more or less packed network structure can be obtained. In fact, pure starch films are described to exhibit poor mechanical strength and high moisture features. Then, a combination with another biopolymer is essential to overcome these limitations. In the literature, mixtures of gelatin and starch [6], and nano-cellulose and starch [7] are examples of associations to produce films with enhanced properties.

Chitosan is the principal derivative of chitin, mainly isolated from crustacean and mollusk exoskeleton. It is a linear polymer composed of β-(1 → 4)-2-acetamido-2-deoxy-d-glucopyranose and of β-(1 → 4)-2-amino-2-deoxy-d-glucopyranose residues [8]. Due to its good film-forming properties associated with its biodegradability, non-toxicity, and being a renewable material enable chitosan in the production of sustainable films. Chitosan films are highly sensitive to humidity conditions [9], which limits their application.
The synergetic effect between chitosan and starch can modify the structure and properties of films, affecting mainly mechanical and water barrier properties [10]. Even though this association is described in the literature [11–14], it is not possible negligence that junction zones of phase separation can be observed even for polymers interacting in a high extension. This is responsible for chitosan/starch films displaying a brittle characteristic. The ability of low molecular weight molecules to reduce polymer interactions reflected in soft and flexible films is confirmed by previous research [15]. Usually, the ability of plasticizer agents is related to their molecular configuration, number of hydroxyl groups, and compatibility with the polymer system [16]. Choosing the appropriate plasticizer is essential to produce films with enhanced mechanical and barrier properties, as an inaccurate selection can cause the obtention of brittle films, as observed by Veiga et al. [17] in starch films plasticizer with sucrose.

This study addresses the use of corn starch with two different amylopectin content (73% and 100%) to evaluate how the branched structure of the starch affects the intermolecular hydrogen bonds between the amino and hydroxyl groups of chitosan and the hydroxyl groups of the starch, respectively. Furthermore, polyols with different amounts of hydroxyl groups were selected to analyze the changes in these direct associations.

2. Materials and Methods

2.1. Materials

Corn starch with two contents of amylopectin was purchased in Sigma-Aldrich. One is composed of 73% amylopectin and 27% amylose, while the second essentially contains amylopectin (100%), as described by the supplier. Starch gelatinization was performed to break the crystalline structure of the starch molecules, exposing their hydroxyl groups and increasing the swell ability and solubility of the starch [5]. The starch powder was heated up to 90 °C for 30 min in excess of water and let to cool down until room temperature.

The chitosan used in this study was extracted from a waste source, squid pens (Doryteuthis spp.) following the procedure previously described [18]. The molecular weight of 403 KDa and the degree of acetylation of 9% were determined for the obtained chitosan. Analytical grade glycerol (GL) was supplied by Aldrich. Sorbitol (SO) and ethylene glycol (EG) were purchased by Merck. All other chemicals were analytical grade.

2.2. Films Preparation

A series of preliminary studies (not discussed in this text) allowed the optimization of the process for obtaining the films, such as mixing time, polysaccharide ratio, and quantity of polyols. The objective was to achieve homogeneous mixtures without precipitates or undissolved materials.

Gelatinized corn starch solution was prepared at 2% (w/v) in deionized water. The extracted chitosan (1 g) was dissolved in 1% (v/v) acetic acid using a constant overnight stirring. A 2:1 ratio (w) was used to blend starch and chitosan solutions. Higher amounts of the starch solution produce heterogeneous mixtures as seen in the preliminary studies. The samples were labeled CS73 and CS100, regarding the quantity of amylopectin present in corn starch.

For the plasticizer samples, the same molar amount of EG, GL, and SO was used in the composition. The blends were prepared by mixing chitosan/starch/plasticizers in a 1:2:1 ratio (w). The solution was homogenized for 30 min under magnetic stirring and labeled CS73EG, CS73GL, CS73SO, CS100EG, CS100GL, and CS100SO, depending on the amount of amylopectin and the plasticizer type.

All the obtained blends were poured into Teflon molds using a constant amount (0.35 g cm⁻²) to allow solvent evaporation. The drying process was performed for 24 h at 25 °C and in the absence of pressure. The casted films were peeled and maintained at a controlled humidity of 65% before analysis.
2.3. Characterization

2.3.1. Thermal Analysis

The thermal stability of the films under heating was evaluated by thermogravimetry (TGA) and differential scanning calorimetry (DSC). A TGA-2050 (TA Instruments, New Castle, DE, USA) was employed to analyze the weight loss behavior when 10 mg of samples were heated between 25 °C and 800 °C at 10 °C min⁻¹ in a synthetic air atmosphere. For the DSC measurement, samples of about 6 mg were heated at the rate of 10 °C min⁻¹ from 25 °C to 450 °C under a dynamic synthetic air atmosphere in a DSC-2010 (TA Instruments).

2.3.2. Film Thickness

A micrometer (Model M110-25, Mitutoyo MFG. Co. Ltd., Kawasaki, Japan) was employed to measure the thickness of the films at 10 different points. The mean values were calculated and adopted for the water vapor permeability (WVP) determination and for the tensile tests.

2.3.3. Water Vapor Permeability (WVP)

The procedure was performed in triplicate and following the ASTM E96, with slight modifications [19]. A wide-mouth cup (7 × 10⁻³ m² area) was filled with 1 g of calcium chloride (anhydrous) to simulate 0% humidity. The cup was sealed with the film, weighed, and placed in a chamber with a controlled humidity of 75%, established by a supersaturated sodium chloride solution. At predetermined times, the flask was removed, and the weight gain was recorded. Due to the different humidity conditions between both sides of the film, there is a partial pressure gradient that produces a driving force allowing the water diffusion through the film. As the cup contains anhydrous calcium chloride, the flow of water causes an increase in the cup weight. This is used to plot a graphic over time and the obtained slope is applied for the calculation of the water vapor transmission rate (WVTR), according to Equation (1):

\[
WVTR = \frac{m}{t \times 1/A}
\]

where \( m/t \) is the slope of the graphic of the weight gain against time and \( A \) is the area of the sample permeation (m²). The water vapor permeability was calculated employing Equation (2):

\[
WVP = \frac{WVTR \cdot d}{vp(RH_1 - RH_2)}
\]

where \( d \) is the thickness (mm), \( vp \) is the water vapor pressure at 25 °C (3139 Pa), \( RH_1 \) is the relative humidity inside the chamber (75%) and \( RH_2 \) is the relative humidity inside the cup (0%). The experiment was performed in triplicate.

2.3.4. Solubility

The solubility was determined using pieces of 1 × 1 cm dried overnight at 60 °C and then weighed for the initial dry mass (\( I_{mass} \)). Films were immersed in 5 mL of deionized water and stirred at low speed (50 rpm) for 24 h at 25 °C. The film piece was removed and dried at 60 °C until constant weight to determine the final dry mass (\( F_{mass} \)). The soluble matter was calculated using Equation (3):

\[
Solubility(\%) = \frac{(I_{mass} - F_{mass})}{I_{mass}} \times 100
\]

The test was conducted in triplicate.

2.3.5. Tensile Tests

Tensile tests were carried out using a DMA 2980 (TA Instruments, New Castle, DE; USA) at a test speed of 1 N min⁻¹. Tensile strength (TS) and maximum elongation at break (EB) were evaluated using the results of three independent measurements with each film (15 × 6.3 mm). Tensile strength was expressed in megapascals (MPa) and calculated by
dividing the maximum load (N) by the specimen’s initial cross-sectional area (m²). EB was determined by the ratio of the final length (sample rupture) to the initial length of the specimen and expressed as a percentage.

2.3.6. Statistical Analysis

Film thickness, water vapor permeability, solubility, and tensile test results were statistically treated using analysis of Variance (ANOVA) and Tukey’s test with a significance level set at 5%.

3. Results and Discussion

Polysaccharide films are generally colorless [20]. All the chitosan/gelatinized starch films prepared in this study were homogeneous and opaque in appearance. Adding polyols provided more flexible and less brittle films, as expected, allowing easy peeling from the molds. Figure 1 shows the representative photo of the films prepared with 73% amylopectin/chitosan and the different polyols. The samples composed of chitosan/100% amylopectin exhibited a similar appearance.

![Figure 1. Image of the chitosan/starch prepared in this study. In (A), CS73; in (B), CS73EG; in (C), CS73GL and in (D), CS73SO.](image)

3.1. Thermal Analysis

The thermogravimetric technique provides reliable information about the moisture of the films and their decomposition temperature. Since the films are composed of polysaccharides and polyols, composed of plenty of hydrophilic groups, they generally interact with water molecules. Depending on the type of polyol used and the branched structure of starch, distinct thermal properties can be observed.

Figure 2 displays the TGA curves of CS100 and their respective films with polyols. The results for the CS73 film and with the polyols are shown in the Supplementary Materials (Figure S1).

Thermogravimetric curves were used to determine the thermal stability of the films and the effect of polyols on this property. Typically, polysaccharides exhibit three defined stages of weight reduction characterized by water loss (25–200 °C), polymeric chain decomposition (200–400 °C), and carbonization (400–750 °C). The percentage of weight loss for the films is listed in Table 1.

The degradation temperature represents the point where the polymer networks start to decompose. It is affected by changes in polymer intramolecular interactions and reflects the stability of the associations, and was determined by the T_onset point in the decomposition step (Table 1).
As the first weight loss is related to the water present in the polymeric film, the amylopectin content seems to have any effect, as similar values were obtained for CS73 (9.2%) and CS100 (10.0%). Similarly, adding ethylene glycol or sorbitol causes no alteration in the water content. Considering the sample temperature range, CS73GL, and CS100GL, however, displayed distinct behavior. The DTG curves assist the interpretation of the thermogravimetric curves, as two peaks were observed between 25–200 °C. This is probably associated with the water loss and part of the glycerol that did not interact with the polysaccharides. Indeed, analyzing the TGA/DTG curves of the pure polyols (Supplementary Material, Figure S2), the glycerol shows a one-step decomposition around 137 °C. Then, the decomposition of this polyol results in an increase and observation of the two peaks in the derivative DTG curve. Nevertheless, this effect is more pronounced in the CS100GL than in CS73GL due to a strong interaction between chitosan and starch amylopectin 100%, which hinders the interaction of all the added glycerol.

The second stage of the weight loss curve reflects the point wherein the molecular structure of the polymer film begins to degrade through functional group decomposition, interpreted by the T\textsubscript{onset}. The amylopectin content played no influence in the degradation stability of the films, as a difference of around 3 °C was observed, comparing CS73 and CS100. It is likely that the starch sources exhibit a high influence on the thermal decomposition of films than the amylopectin content. For chitosan/potato starch Mathew et al. [21] described a T\textsubscript{onset} value of 308 °C, while for sugar palm starch/chitosan, a decomposition temperature of 184 °C was measured [22].

Independent of the amylopectin content, films with ethylene glycol and glycerol exhibited similar T\textsubscript{onset} values. However, CS73SO and CS100SO showed lower degradation

<table>
<thead>
<tr>
<th>Film</th>
<th>1st Stage (25–200 °C)</th>
<th>2nd Stage (200–400 °C)</th>
<th>3rd Stage (400–750 °C)</th>
<th>T\textsubscript{onset} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS73</td>
<td>9.2</td>
<td>50.4</td>
<td>38.9</td>
<td>270.4</td>
</tr>
<tr>
<td>CS73EG</td>
<td>8.4</td>
<td>51.4</td>
<td>39.3</td>
<td>264.8</td>
</tr>
<tr>
<td>CS73GL</td>
<td>5.1/11.8</td>
<td>50.8</td>
<td>32.3</td>
<td>269.7</td>
</tr>
<tr>
<td>CS73SO</td>
<td>11.4</td>
<td>54.4</td>
<td>33.8</td>
<td>258.4</td>
</tr>
<tr>
<td>CS100</td>
<td>10.0</td>
<td>50.6</td>
<td>38.5</td>
<td>267.3</td>
</tr>
<tr>
<td>CS100EG</td>
<td>7.8</td>
<td>50.5</td>
<td>10.8</td>
<td>267.4</td>
</tr>
<tr>
<td>CS100GL</td>
<td>4.7/21.0</td>
<td>45.5</td>
<td>27.8</td>
<td>265.4</td>
</tr>
<tr>
<td>CS100SO</td>
<td>9.7</td>
<td>56.8</td>
<td>32.7</td>
<td>256.3</td>
</tr>
</tbody>
</table>
temperature values, attributed to an increase in the free volume of the system. Sorbitol, as a molecule composed of six OH groups, increases the space and consequently, reduces the polysaccharides chain interactions. It results in a less stable network structure and an impact of around 12 °C in the T_{onset} point.

The DSC was employed to evaluate the temperature of the endothermic peak (around 100 °C) attributed to the water evaporation (Supplementary Material, Figures S3 and S4). As polysaccharides, chitosan and starch show a high-water affinity due to their chain structure composed of hydroxyl groups. These hydrogen bonds are strongly affected by the intramolecular interaction between the polymer and when additives are incorporated in polymeric mixtures. Additionally, polyols interfere with these associations as they also contain OH groups in the structure. The values of Table 2 represent the temperature of the endothermic peak and the enthalpy (ΔH) associated with this thermal event.

### Table 2. Endothermic peak temperature and the associated enthalpy for the films.

<table>
<thead>
<tr>
<th>Film</th>
<th>Temperature (°C)</th>
<th>ΔH (J g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS73</td>
<td>106.3</td>
<td>362.9</td>
</tr>
<tr>
<td>CS73EG</td>
<td>111.1</td>
<td>298.7</td>
</tr>
<tr>
<td>CS73GL</td>
<td>119.1</td>
<td>206.4</td>
</tr>
<tr>
<td>CS73SO</td>
<td>119.9</td>
<td>230.6</td>
</tr>
<tr>
<td>CS100</td>
<td>91.6</td>
<td>334.8</td>
</tr>
<tr>
<td>CS100EG</td>
<td>97.1</td>
<td>268.2</td>
</tr>
<tr>
<td>CS100GL</td>
<td>125.3</td>
<td>322.9</td>
</tr>
<tr>
<td>CS100SO</td>
<td>116.3</td>
<td>316.4</td>
</tr>
</tbody>
</table>

The amylopectin content influences the temperature of the endothermic peak since a reduction of about 15 °C was noticed for CS100 compared to CS73. This may be related to the presence of amyllose chains in the starch structure. Since both the amorphous part (amylose) and the crystalline part (amylopectin) of starch are responsible for water retention. Nevertheless, the amorphous phase, which is where most of the amylose is distributed, is a less dense region, which allows for greater water absorption [23].

The plasticizers influence the temperature at which the endothermic peak is observed, as there is a shift to higher temperatures related to an increase in the interaction of water with the polysaccharides and the polyols. Then, it is possible to assume that the polyols are involved in the intramolecular interaction in the network system, especially due to their hydrophilic character. A comparable analogy is observed for the enthalpy involved in this thermal transition. Adding polyols reduces the energy necessary to evaporate the water from the polymeric system. It is coherent with the effect of plasticizers, as they interfere in the polymer–polymer associations and reduce their interaction.

Special attention to the film CS100GL must be considered. A high endothermic peak (125.3 °C) and enthalpy (322.9 J g⁻¹) were observed. This phenomenon could be related to the presence of glycerol that did not interact with the polymeric system, as observed by the thermogravimetric measurements. Then, the free glycerol can interact with the surrounding water, increasing both analyzed parameters.

### 3.2. Thickness and Solubility

Film thickness was determined to calculate the water vapor permeability and tensile properties of films. Higher film thickness indicates a higher resistance, gas permeability, and mechanical properties [4]. Factors such as chemical structure, preparation method, and the association between the polysaccharides and plasticizers affect this feature. The use of starch with high amylopectin content significative decreased the thickness of the film, as CS73 showed a value of 0.066 mm in comparison to 0.042 mm measured for CS100 (Table 3). A significant difference was seen among the group of films prepared with different content of amylopectin. In general, high values were obtained for those formulated with 73% amylopectin. Comparable characteristic was previously observed by Wang et al. [24] for...
films of maize starch/gelatin. The same pattern was observed for the films containing polyols, confirming that this property is directly affected by the amylopectin content but not by the presence of plasticizers. Al-Hassan et al. [25] described thickness between 0.05 to 0.07 mm for films of sago starch/gelatin without the influence of plasticizers.

Table 3. Thickness and solubility values for the films.

<table>
<thead>
<tr>
<th>Film</th>
<th>Thickness (mm)</th>
<th>Solubility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS73</td>
<td>0.066 ± 0.006 a,b</td>
<td>9.66 ± 0.43 c,f</td>
</tr>
<tr>
<td>CS73EG</td>
<td>0.080 ± 0.006 a</td>
<td>15.90 ± 0.63 d</td>
</tr>
<tr>
<td>CS73GL</td>
<td>0.068 ± 0.003 a</td>
<td>50.58 ± 0.93 a</td>
</tr>
<tr>
<td>CS73SO</td>
<td>0.081 ± 0.005 a</td>
<td>22.34 ± 0.79 c</td>
</tr>
<tr>
<td>CS100</td>
<td>0.042 ± 0.003 c</td>
<td>7.32 ± 0.54 f</td>
</tr>
<tr>
<td>CS100EG</td>
<td>0.045 ± 0.003 c</td>
<td>12.61 ± 0.60 d,e</td>
</tr>
<tr>
<td>CS100GL</td>
<td>0.050 ± 0.002 b,c</td>
<td>32.50 ± 0.90 b</td>
</tr>
<tr>
<td>CS100SO</td>
<td>0.050 ± 0.003 b,c</td>
<td>34.59 ± 0.93 b</td>
</tr>
</tbody>
</table>

Same letter in the column means no statistical significance.

The moisture content of a film is dependent on its composition and can also indicate biodegradability properties [26]. The solubility of the films was calculated using Equation (3), and the values are listed in Table 3. The films CS73 and CS100 exhibited the lowest solubility values. This behavior is expected for polysaccharide films due to their large molecular weight. The inclusion of hydrophilic compounds, such as polyols, disrupts this direct association between the polymeric chains, leading to more space between them. This is responsible for improving the water access to the polymeric system, enhancing the solubility.

The possibility of controlling and obtaining films with a range of solubility values is mainly associated with their applicability. As high solubility implies the missing film structure in a high-humidity environment. For example, packaging materials that are in contact with food or films for sensor application [27] must keep their integrity for long periods in high-moisture conditions. On the other hand, materials that can be easily washed off can be applied as a temporary coating product.

3.3. Water Vapor Permeability (WVP)

Weight gain of the cup sealed with the film and placed in a chamber with a difference in humidity was recorded as a function of time. The slope was evaluated by linear regression ($R^2 > 0.99$), and the water vapor transmission rate (WVTR) and water vapor permeability were calculated according to Equations (1) and (2).

As shown in Figure 3, the WVP of the films showed significant differences regarding the amylopectin content. Higher WVP was observed for CS73 than for CS100. Since amylose is more hygroscopic than the starch-branched structure, the affinity for water molecules was higher in this film, resulting in an increment in water diffusion. Truly, all the films prepared with 73% amylopectin content exhibited high WVP without any significant difference between the values. This means that the plasticizers showed a low effect on water diffusion.

On the other hand, when plasticizers were incorporated in films prepared with 100% amylopectin, distinct behavior was observed depending on the type of plasticizer. Compared to CS100, the addition of ethylene glycol and sorbitol decreased the WVP, being statistically different for CS100SO. Nevertheless, the CS100GL film showed an increase in WVP, a value similar to those calculated for films with low amylopectin content. As previously observed in thermal characteristics, this film showed that some glycerol was not interacting with the polymeric system. This leads to free small molecules able to interact with water, increasing their permeability.
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Figure 3. Water vapor permeability for the films prepared with different content of amylopectin and plasticizers. Same letter in the bar plot means no statistical significance.

The literature described a range of values and behavior depending on the type of starch and association [25,28] and plasticizer [29]. Arvanitoyannis et al. [30] reported that the ratio between the components influences the WVP, as values ranged from $1.1 \times 10^{-13}$ to $167.6 \times 10^{-13}$ g m$^{-1}$s$^{-1}$Pa$^{-1}$ when the starch weight ratio increased from 5 to 40%.

Additionally, the permeability of films was influenced by the existence of steric hindrance and tortuosity for the diffusion of water molecules [26].

3.4. Tensile Test

The elongation at break and tensile strength of the films depends on the amount of amylopectin associated with chitosan and the presence of polyols. The stress-strain curves are shown in the Supplementary Materials (Figures S5 and S6). Table 4 summarizes the calculated tensile strength and elongation at break for the films. For non-plasticizer films, the elongation at break was slightly reduced for CS100 compared to CS73, but the difference was not statically significant. However, the tensile strength decreased from 57.10 MPa (CS73) to 14.75 MPa (CS100), confirming that distinct associations are involved in chitosan starch association due to the absence or presence of amylose.

Table 4. Tensile strength, elongation at break and Young’s modulus values for the films.

<table>
<thead>
<tr>
<th>Film</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at Break (%)</th>
<th>Young’s Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS73</td>
<td>57.10 ± 0.92$^a$</td>
<td>3.04 ± 0.15$^{b,c}$</td>
<td>20.94 ± 0.98$^c$</td>
</tr>
<tr>
<td>CS73EG</td>
<td>60.03 ± 2.72$^a$</td>
<td>4.70 ± 0.20$^{b,c}$</td>
<td>26.89 ± 1.42$^b$</td>
</tr>
<tr>
<td>CS73GL</td>
<td>22.78 ± 2.27$^c$</td>
<td>7.39 ± 0.40$^b$</td>
<td>6.70 ± 0.36$^d$</td>
</tr>
<tr>
<td>CS73SO</td>
<td>32.04 ± 2.87$^b$</td>
<td>6.87 ± 0.59$^b$</td>
<td>6.41 ± 0.51$^d$</td>
</tr>
<tr>
<td>CS100</td>
<td>14.75 ± 0.32$^d$</td>
<td>2.66 ± 0.11$^{b,c}$</td>
<td>48.04 ± 0.64$^a$</td>
</tr>
<tr>
<td>CS100EG</td>
<td>13.51 ± 1.08$^d$</td>
<td>2.04 ± 0.39$^c$</td>
<td>27.21 ± 1.23$^a$</td>
</tr>
<tr>
<td>CS100GL</td>
<td>2.54 ± 0.16$^e$</td>
<td>20.13 ± 0.29$^a$</td>
<td>0.17 ± 0.01$^e$</td>
</tr>
<tr>
<td>CS100SO</td>
<td>14.03 ± 0.72$^d$</td>
<td>16.43 ± 1.76$^a$</td>
<td>2.04 ± 0.07$^e$</td>
</tr>
</tbody>
</table>

Same letter in the column means no statistical significance.

For the group of samples of chitosan/73% amylopectin, a reduction in the TS was registered after glycerol and sorbitol were included. However, CS73EG showed a non-significant difference in relation to CS73. This behavior is associated with the presence of polyols in the polymer system. Glycerol ad sorbitol disrupts the associations of the polysaccharides, reflecting a decrease in the intramolecular interactions, reducing the TS. As ethylene glycol is a small molecule and contains only two OH groups, its effect is less
pronounced in the polymer–polymer association, and the TS remains comparable to CS73. Similar behavior was observed in the EB values: even though they were not statistically significant, a tendency to increase the flexibility properties in CS73GL and CS73SO in comparison to CS73 was observed.

The TS displayed a reduction in the values when the content of amylopectin increased due to the amorphous nature of this branched structure [31]. Nevertheless, no significant difference was observed after the inclusion of the plasticizers, as TS was around 14 MPa for CS100, CS100EG, and CS100SO. An unexpected reduction was obtained for CS100GL due to the poor incorporation of glycerol in the polymeric system. Once more, ethylene glycol exhibited a low interference in EB behavior compared to the control film, CS100. The elongation at break of CS100GL (20.13%) and CS100SO (16.43%) films was significantly higher than that of CS100 film. The significant increase in the plasticizer films might be related to the interactions of polysaccharides and polyols or, in the case of the glycerol, due to the high amount of water that was detected in TGA measurements. Truly, water is considered a plasticizer [5], and its presence can change the network association, improving the flexibility of the films and also barrier properties, which was also observed in the WVP results (Figure 3).

Young’s modulus is an indicator of film rigidity, as greater modulus values are observed for more rigid materials. The amylopectin content influences this characteristic, as CS100 displayed a high value (48.04 MPa) compared to CS73 (20.94 MPa). This effect can be related to the presence of linear amylose chains in the last sample, which shows more mobility and, consequently, influences the elastic character of the samples. As expected, the addition of plasticizers reduced this property due to the interference effect of polyol in the polymer–polymer associations, producing a polymeric system with more mobility.

As described for WVP, the literature describes a range of TS and EB values. Bourtoom et al. [29] found for rice starch/chitosan 1:1 plasticized with sorbitol, TS, and EB values of 35% and 7%, respectively. In a study of sago starch/gelatin films plasticized with glycerol and sorbitol, Al-Hassam [25] found TS values of 9.87 MPa and 25.03 MPa and EB of 17.11% and 4.33%, respectively.

In fact, the mechanical behavior of the films is strongly correlated to the plasticizer, the nature of starch, and the ratio between the components. In this study, it is noticeable that the amylopectin content or the absence/presence of amylose plays an important role in the properties of the films.

4. Conclusions

Changing the amylopectin content in films associated with chitosan and polyols modifies their properties. As the same ratio and molar content between the components was adopted, the alteration in features was directly related to the studied formulation. The thermal stability determined by thermogravimetry showed no influence related to the amylopectin content, and it is likely that it is more often correlated to the starch source. The DSC was employed to evaluate the temperature of the endothermic peak, showing a dependence on the amylopectin amount, as a reduction of around 15 °C was observed for the endothermic peak related to the water evaporation. Similar behavior was detected in the film thickness and tensile strength, as a high content of amylopectin promotes a significant reduction from 0.066 to 0.042 mm and 57.10 to 14.75 MPa, respectively.

On the other hand, the reduction from 9.66 to 7.32% in the solubility properties and elongation at break (3.04% for CS73 compared to 2.66% for CS100) exhibited no significant difference. In addition, the study showed that the polyols affected the polysaccharide associations distinctly. In general, they are associated with an increase in solubility and in elongation at break. Remarkable influences were observed in chitosan/100% amylopectin films containing sorbitol, wherein films with low WVP ($1.35 \times 10^{-9}$ g m$^{-1}$ s$^{-1}$ Pa$^{-1}$) and high EB (16.43%) were obtained.
**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/polysaccharides4030015/s1, Figure S1: Thermogravimetric (solid line) and DTG (dash line) curves of films (synthetic air and heating rate 10 °C min⁻¹); Figure S2: Thermogravimetric (solid line) and DTG (dash line) curves of the polyols (synthetic air and heating rate 10 °C min⁻¹); Figure S3: DSC curves of films (synthetic air and heating rate 10 °C min⁻¹); Figure S4: DSC curves of films (synthetic air and heating rate 10 °C min⁻¹); Figure S5: Representative curve of stress-strain of the films; Figure S6: Representative curve of stress-strain of the films.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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