Introduction

Eco-friendly materials has emerged as one of the most reliable and promising solutions for the food and drug packaging next generation. In this context, thermoplastic starch (TPS) and pectin are promising bases for polymers manufacture due to their wide availability, low cost, renewable character and ability of being produced using traditional processing techniques used in the plastics industry, such as extrusion.

TPS and pectin polymer blends have been successfully developed resulting in good mechanical properties and oxygen barrier properties. Reactive extrusion with edible citric acid and cross linking interactions was evaluated on extruded thermoplastic in natura and cationic starch-pectin blends. Materials water susceptibility and mechanical properties were characterised. Reactive extrusion decreased (up to 75% in natura starch) mechanical properties. Also have decreased (up to 32.4%) both starch polymers water absorption, indicating the possibility of increasing materials water barrier properties but had the opposite effect on the pectin-TPS material, probably related to a cationic-anionic cross linking, resulting in a hydrogel polymer. Reactive extrusion also have negatively affected mechanical properties of both starch polymers, however increased pectin-TPS blends stress and strain at rupture.

Keywords: Extrusion, Bio-based products, Biodegradable packaging, Starch, pectin.
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Water Susceptibility and Mechanical Properties of Thermoplastic Starch–Pectin Blends Reactively Extruded with Edible Citric Acid

ash content of 0.62%, whereas in natura starch containing 28% amylose and 11% moisture. Reagent grade CA, glycerol, high methoxyl pectin (GENU type USP-B, CP Kelco Brasil S/A) were used as received. The chemical structures of CA, pectin and C are provided in Fig. 1.

Processing of thermoplastic starch

To prepare TPS samples, starch (NM and C), pectin, glycerol (30%wt) and AC were premixed to obtain a homogeneous material (see Table 1 for compositions). The mixtures were processed using a single-screw extruder with an 11-mm screw (L/D = 40) from AX Plásticos Ltda (São Paulo, Brazil), with the following zone temperatures from feed to die: 85, 110, 105 and 100 °C at 30 and 27 rpm for the thermoplastic starch, in absence or in presence of the CA, respectively. The processed samples were then hot pressed at 150 °C into 1 mm thick plates.

Fourier transform infrared spectroscopy (FTIR)

Attenuated total reflection (ATR) infrared spectra were recorded on a ThermoScientific Nicolet IR200 spectrophotometer (Rochester, USA). Each spectrum was collected using 64 scans.

Fig. 1. a) High methoxyl pectin (where n is repetitive unity), b) citric acid (CA) and c) cationic starch structures.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Starch Type</th>
<th>CA* (wt%)</th>
<th>Pectin (wt%)</th>
<th>E (MPa)*</th>
<th>WA (%) 43% RH</th>
<th>WA (%) 53% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>N**</td>
<td>0.0</td>
<td>0.0</td>
<td>0.4±0.005 A</td>
<td>9.1±0.7 C</td>
<td>13.6±0.1 H</td>
</tr>
<tr>
<td>B</td>
<td>C***</td>
<td>0.0</td>
<td>0.0</td>
<td>0.4±0.002 A</td>
<td>11.9±0.6 G</td>
<td>13.7±0.5 H</td>
</tr>
<tr>
<td>C</td>
<td>N</td>
<td>1.5</td>
<td>0.0</td>
<td>0.1±0.001 B</td>
<td>7.9±0.4 D</td>
<td>8.7±0.2 I</td>
</tr>
<tr>
<td>D</td>
<td>C</td>
<td>1.5</td>
<td>0.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>E</td>
<td>N</td>
<td>0.0</td>
<td>10.0</td>
<td>0.2±0.04 B</td>
<td>14.1±0.5 E</td>
<td>18.5±0.3 J</td>
</tr>
<tr>
<td>F</td>
<td>C</td>
<td>0.0</td>
<td>10.0</td>
<td>0.1±0.002 B</td>
<td>11.6±0.4 G</td>
<td>13.9±0.5 H</td>
</tr>
<tr>
<td>G</td>
<td>N</td>
<td>1.5</td>
<td>10.0</td>
<td>0.2±0.007 B</td>
<td>11.8±0.6 F</td>
<td>12.5±0.1 K</td>
</tr>
<tr>
<td>H</td>
<td>C</td>
<td>1.5</td>
<td>10.0</td>
<td>0.1±0.003 B</td>
<td>11.6±0.3 G</td>
<td>13.5±0.6 H</td>
</tr>
<tr>
<td>I</td>
<td>---</td>
<td>0.0</td>
<td>100.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

*CA: Citric Acid; **N: in natural (not modified) corn starch; ***C cationic corn starch; *: letter: Tukey test at 95% significance
Dynamic mechanical analysis (DMA)

DMA measurements were performed on a Q-800 dynamic mechanical analyser (TA Instruments, New Castle, USA) in the tension mode. Measurements were performed at a 25 °C with a force rate of 0.5 N/min under flowing synthetic air. 5 samples each composition, with dimensions of 13×5×1 mm cut from the hot pressed plates, were tested. Statistical analysis of variance (ANOVA) and Tukey test were performed at 95% significance level using Tinn-R.

Water absorption (WA)

Prior to the measurements, the samples were dried at 110 ±1 °C for 12 h and then placed in containers with relative humidity (RH) values of 43 and 53% at 25±2 °C, which were obtained using saturated solutions of K\textsubscript{2}CO\textsubscript{3} and Mg(NO\textsubscript{3})\textsubscript{2}, respectively, as stipulated by ASTM E-104. The amount of water absorbed was measured gravimetrically by weighing the samples until a constant mass was reached (at least 3 samples of each composition were tested and the average values were taken).

Results and Discussion

Formulations containing both starches in all investigated concentrations were effective in promoting the plasticisation of the blend and resulted in homogeneous materials. The cationic starch samples prepared under reactive extrusion with citric acid CA (sample D) were too sticky to be hot pressed and were not analysed. 100% pectin samples (sample I) generated a very firm structure during extrusion, and the torque became too high to process it properly. The reactive extrusion of thermoplastic starches in the presence of the CA resulted in a lower viscosity and a higher degree of tackiness, when compared with the material processed in the absence of acids. Such effect may be correlated with the reduction in the molecular mass of starch, indicated by rheological measurements and high performance liquid chromatography\textsuperscript{5,7}. Reactive extrusion in presence of CA produced mixtures that were as clear as the TPS samples, whereas the addition of pectin resulted in clear brown samples, because of the pectin natural colour.

The FTIR spectra (Fig. 2) of TPS prepared with cationic and in natura starches (samples A and B) revealed peaks at 3400-3450 cm\textsuperscript{-1}, indicating hydroxyl groups; 2880-2900 cm\textsuperscript{-1} indicating C-H stretching; and 1150-1085 cm\textsuperscript{-1}, indicating ether\textsuperscript{31,32} presence. Despite some degree of etherification that occurred due to the presence of CA, as observed by Shi et al.\textsuperscript{33}, no significant variations (p<0.05) were found in the spectrum of TPS reactive extruded with CA. These results indicate that starch changes observed in this study were most likely related to chain scission\textsuperscript{5,7}. The major difference between pectin and starch chemical structure were noted for ester carbonyl groups presence. According to Gnanasambandam, Proctor\textsuperscript{34}, the pectin ester carbonyl band area (C=O) observed at a mean frequency of 1756 cm\textsuperscript{-1} exhibits the highest correlation with the mean degree of etherification. However, no differences between the samples blended with or without pectin were observed by FTIR in this band region. These results may be explained due to the low percentage of pectin added to the samples prepared in this study.

The kinetics of the water uptake of starch-pectin blends exhibited an asymptotic increase with time until reaching an equilibrium state, which is a characteristic of several hydrophilic bio-based polymers. Samples containing pectin exhibited statistical increased water absorption properties relative the natura TPS (Table 1). This behaviour may be explained by the higher content of OH groups in the highly methoxylated pectin structures because of its water affinity. When the in natura starch sample was reactively extruded in the presence of citric acid (sample C), a significant (p<0.05) decrease in the water absorption capacity of the TPS films was observed (Table 1). Such decrease may be explained by a breakage in amylose and amylpectin chains, as discussed by Carvalho et al.\textsuperscript{5}; where these chains may become interlaced with other starch chains by intermolecular hydrogen bonding (as opposed to extramolecular hydrogen bonding with water), leading to a lower water uptake capacity. However, in the presence of pectin, all compositions exhibited an increased water uptake. Such results can be explained most likely due to pectin’s galacturonic acid hydroxyl, amide and carbonyl groups. Such groups strongly interact with water by macromolecules binding and also by including it in network voids formed in junction zones (gelling). Pectin-water interactions also may be affected by the pectin monovalent cations, as well as by polymer amorphous properties, particle size, surface and porosity\textsuperscript{35}.

The higher water absorption capacity of the cationic starch obtained through reactive extrusion compared with that of the in natura starch polymers can be explained by the increase in the number of positive charges due to the cationic starch presence. No statistical difference (p<0.05) was observed in the cationic starch samples obtained from reactive extrusion with CA in the presence and absence of pectin, although the sample D was not evaluated (Table 1). This finding suggests that the positive charges in the cationic starch participate in more interactions; thus, the water uptake capacity remained unchanged despite the contribution of additional pectin hydroxyl moieties.

The plots of stress and strain at break are provided in Fig. 3 and Fig. 4, respectively, and the corresponding data for the Young Modulus (E) are summarised in Table 1. The stress-strain plots (not shown) were linear at low strains with high modulus values, which is a characteristic of semi-crystalline
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Materials. TPS starch polymers reactively extruded with CA, in the presence or absence of pectin (C and G samples), did not affect (p<0.05) the materials modulus of elasticity and tension and strain strengths. The addition of pectin, unlike addition of the acid, increased (p<0.05) the water absorption capacity of the films (Table 1) and resulted in a negative effect (p<0.05) on all the modulus and strain at rupture investigated properties (Table 1). The combination of cationic nature of the starch with the anionic nature of pectin can lead to interpolyelectrolyte complexes (IPECs) with a material hydrogel like structure 24,25, resulting in higher hydrophilicity. Such results could be explained due to water plasticizing effect in TPS polymers, which favour intermolecular distance and, consequently, chain mobility. In addition, the pectin polymers may have altered the cationic or in natura TPS polymer matrix interactions due to the presence of the methoxyl groups in pectin, which repelled or hindered bonding between the starch materials, thereby decreasing the mechanical properties of the polymer.

The results observed in this study also demonstrate that reactive extruding in natura or cationic TPS material in the presence of low concentrations of CA (1.5%) can be an interesting way to alter its properties. Although an improvement in the mechanical properties of TPS materials was observed in a previous study of reactive extrusion 5, the same results were not observed for the TPS-pectin blends at the concentrations investigated. However, when reactive extrusion was performed on the cationic starch (H sample), the resulting materials showed a higher hydrophobic character when compared to the in natura TPS.

Conclusions

Reactive extrusion with citric acid was used in in natura or cationic starch-pectin blends and all compositions were effective in promoting the plasticisation of the resulted polymer and produced homogeneous blends. When pectin was blended with cationic starch, no change in the water uptake of the resulting materials was observed. In contrast, the reactive blending of pectin with in natura TPS polymers showed a decrease effect on the mechanical properties and water uptake of the blends. Similarly, reactive extrusion of in natura TPS and in natura TPS-pectin blends with CA exhibited materials with lower stress and strain at break and reduced water absorption capacity. Starch and pectin blends produced under reactive extrusion can result in hydrophilic hydrogel polymers with interesting nontoxic and differentiated properties.

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