Effect of individual and combined physical treatments on the properties of corn starch

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ABSTRACT. Native starch has wide use in the food industry although some of its characteristics are limited and require modification. This study aimed to make individual and combined physical changes in corn starch and to investigate starch changes, the single-screw extruder efficiency and possible applications for the modified starch. Starch was modified by annealing (ANN), heat-moisture treatment (HMT) and extrusion (E) treatment. Physicochemical, crystalline, thermal and morphological properties were assessed. Modified starches that did not undergo the extrusion process had the swelling index higher than the extruded ones and the inverse occurred with solubility. The starches pasting transparency decreases over time of the analysis. Starches modified by ANN, HMTA and HMT showed type A crystallinity and the extruded ones, V type. The modification of starch by single-screw extruder combined with the ANN methods HMT and HMTA was efficient, modified its structure and functional properties, providing technological and nutritional benefits.

Keywords: physical modification; extrusion; physical analyses.

Efeito dos tratamentos físicos individuais e combinados nas propriedades do amido de milho

RESUMO. O amido nativo tem ampla utilização na indústria alimentícia, porém, algumas de suas características são limitantes e necessitam de modificação. O objetivo do trabalho foi avaliar modificações físicas individuais e combinadas no amido de milho e verificar as alterações do amido, a eficiência da extrusora mono-rosca e as possíveis aplicações para o amido modificado. O amido foi modificado pelos tratamentos annealing (ANN), heat–moisture treatment por estufa (HMT) e por autoclave (HMTA), e extrusão (ENAT), individualmente, e ANN, HMT e HMTA combinados com extrusão, produzindo EANN, EHMT e EHMTA, respectivamente. Foram avaliadas propriedades físico-químicas, cristalinas, térmicas e morfológicas. Os amidos modificados que não passaram pelo processo de extrusão tiveram o índice de inchamento maior do que aqueles que foram extrusados e o inverso aconteceu com a solubilidade. A claridade dos amidos diminuiu com o passar do tempo da análise. Os amidos modificados por ANN, HMTA e HMT apresentaram cristalinidade do tipo A, e os extrusados cristalinidade do tipo V. As amostras extrusadas apresentaram baixa temperatura de pasta e baixa viscosidade. A modificação do amido através da extrusora mono-rosca combinado com os métodos ANN, HMT e HMTA foi eficiente, modificou sua estrutura e propriedades funcionais, proporcionando benefícios nutricionais e tecnológicos.

Palavras-chave: modificação física; extrusão; análises físicas.

Introduction

Corn is a source of vitamins, minerals and functional elements that meets the nutritional needs of the world. Common corn starch has about 25% amylose and 75% amylopectin. This carbohydrate has great industrial and food use.

Generally, food produced with native starches has low process tolerance for commercial production and shelf stability unsuitable for distribution. Thus, it is necessary to make changes by physical, chemical or enzymatic processes to provide specific functional properties (Klein et al., 2013). Physically modified starches can be considered as a natural product and a safe ingredient, therefore, by legislation their addition in food follows the same criteria as native starch and not as modified starch, a great advantage compared to chemical and enzymatic modified starches.

Heat-moisture treatment (HMT) and annealing (ANN) are physical modifications that alter the physicochemical properties of the starch without destroying its granular structure (Jacobs & Delcour, 1998, Adebowale, Afolabi, & Olu-Owolabi, 2005,
Hormdok & Noomhorm, 2007, Maache-Rezzoug, Zarguili, Loisel, Queveau, & Buléon, 2008). Both processes require a controlled starch-moisture, temperature and heating time ratio (Chung, Liu, & Hoover, 2009). HMT is performed under low moisture content (10-30%) and at higher temperatures (90-120°C), while ANN requires a high water content (50-60%) and relatively low temperatures, those below gelatinization point (at most 50°C) (Maache-Rezzoug et al., 2008).

Extrusion has been widely used in recent years to produce puffed snacks, breakfast cereals and animal feed. The high temperature and the short extrusion time have a significant modification effect on the physical-chemical properties of the starch-based raw material. The final product quality highly depends on the source of the raw material, but also on the processing parameters, such as, extruder type (single or double screw), screw configuration, temperature profile, screw speed, moisture and feed rate (Fellows, 2000, Baik, Powers, & Nguyen, 2004).

The combined modifications have been successfully studied regarding HMT-ANN combinations, but when it comes to combined treatment with extrusion, there is a lack of studies, principally using a single-screw extruder. Thus, this work aimed to evaluate the individual and combined physical modifications of corn starch through its physicochemical, crystalline, thermal and morphological properties and investigate changes in starch, the efficiency of the single-screw extruder and best applications for the modified starch produced.

**Material and methods**

**Material**

Corn starch was purchased at a popular market in the city of Maringá, state of Paraná, Brazil. The only solvent used for the modifications was distilled water.

**Methods**

The starches underwent four independent and three combined modifications. The independent variables were: heat-moisture treatment by oven-dry (HMT), heat-moisture treatment by autoclave (HMTA), annealing (ANN) and extrusion (E). The combined modifications were the same as before, but followed by extrusion: HMT followed by extrusion (EHMTE), HMTA followed by extrusion (EHMTA) and ANN followed by extrusion (EANN). Native starch was used as standard. Table 1 shows the acronyms of all samples and their respective descriptions for better understanding.

<table>
<thead>
<tr>
<th>Acronyms</th>
<th>Samples description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAT</td>
<td>Native Starch</td>
</tr>
<tr>
<td>ANN</td>
<td>Annealing</td>
</tr>
<tr>
<td>HMT</td>
<td>Heat-Moisture Treatment (oven-dried)</td>
</tr>
<tr>
<td>HMTA</td>
<td>Heat-Moisture Treatment (autoclaved)</td>
</tr>
<tr>
<td>ENAT</td>
<td>Native Extruded Starch</td>
</tr>
<tr>
<td>EANN</td>
<td>Annealing + Extrusion</td>
</tr>
<tr>
<td>EHMT</td>
<td>Heat-Moisture Treatment (oven-dried) + Extrusion</td>
</tr>
<tr>
<td>EHMTE</td>
<td>Heat-Moisture Treatment (autoclaved) + Extrusion</td>
</tr>
</tbody>
</table>

**Heat–Moisture Treatment (HMT)**

For modification HMT by oven-dry and autoclave, the starch moisture adjustment to 25±0.5% was necessary. Oven-dry modification was carried out with some modifications according to Franco, Ciacco, and Tavares (1995) at 110°C for 16 hours. The autoclave modification was performed according to Pinto et al. (2015) at 121°C for 1 hour. After modifications, samples were oven dried at 40°C for 24 hours.

**Annealing (ANN)**

Modification ANN method was performed by dispersing the starch in distilled water in a ratio of 1: 4. The dispersion remained under heating at 50±2°C and constant stirring for 16 hours. After cooking period, the sample was oven-dried at 40°C for 24 hours (Pinto et al., 2015).

**Pre-treating for extrusion**

Prior to extrusion, a sample pre-treatment was necessary to increase the starch granules allowing as best as possible, the extrusion cooking. First, the starch was dispersed in a tray with excess distilled water and taken to the oven at 40°C for 24 hours, this step granted the starch to remain in blocks. Furthermore, the moisture was adjusted to 20±2% with gentle homogenization and rest for 24 hours under refrigeration for moisture equalization. With the established moisture, the starch passed through 14 and 16 mesh sieves to obtain larger granules. After this process, the starch was extruded.

**Extrusion cooking (E)**

After the pre-treatment, the starch was extruded by an Imbra RX50 extruder (Inbramaq, RibeirãoPreto - SP), equipped with a single screw of 0.05 m in diameter and 0.2 m in length, a screw speed of 41.89 rad s⁻¹ and feed rate of 42 kg hour⁻¹.
After extrusion, the sample was oven dried at 40°C for 24 hour, grinded and stored.

**Swelling power and solubility**

The starch swelling power and solubility were determined according to Leach, Mccowen, and Schoch (1959) described method with some modifications. The determination was carried out by dispersing starch in water followed by heating and centrifugation.

**Pasting transparency**

The starch paste transparency was performed according to Morikawa and Nishinari (2000) that determines the transmittance percentage (T%) of a starch solution (0.001 kg 0.1 L⁻¹) measured every 24 hours in UV/VIS spectrophotometer at 650 nm after heating (95°C/ 30 min) and subsequent cooling (1 hour/ 25°C).

**X-ray diffraction**

Starch X-ray diffractograms were obtained using an X-ray diffractometer (D8 Advance-Bruker). The diffraction scanning region ranged from 5 to 30° 2θ and scan rate of 1° min⁻¹ (Pinto et al., 2015).

**Pasting properties**

The samples pasting properties were determined according to Pumacahua-Ramos et al. (2015) using a RVA-4 fast viscosity analyser (Newport Sci., Australia). Suspensions with 8% (w w⁻¹) starch were used with 28 g of distilled water underwent a controlled heating and cooling cycle under constant shear (16.75 rad s⁻¹). It was held at 50°C for two min, heated from 50 to 95°C at 6°C min⁻¹, and held at 95°C for 5 min, cooled to 50 at 6°C min⁻¹ and held at 50°C for two min. The reported values are the means of duplicates.

**Granules morphology**

Morphology of the starch granules was evaluated by scanning electron microscopy (SEM) (Shimadzu, SS-550). Samples were putter coated with gold and examined in the SEM under a 15 kV acceleration voltage.

**Statistical analysis**

All analyses were performed in at least a duplicate. The data were evaluated by analysis of variance (ANOVA) and expressed as mean values and significant differences were assessed by the Tukey test (p < 0.01) using Assistat software (Federal University of Campina Grande, Campina Grande, state of Pernambuco, Brazil) 7.7 beta version (Silva & Azevedo, 2016).

**Results and discussion**

**Swelling power and solubility**

The swelling power and solubility results are shown in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solubility (%)</th>
<th>Swelling (g g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAT</td>
<td>2.05±0.08</td>
<td>9.08±0.02</td>
</tr>
<tr>
<td>ANN</td>
<td>2.20±0.07</td>
<td>9.25±0.00</td>
</tr>
<tr>
<td>HMT</td>
<td>2.64±0.19</td>
<td>7.93±0.03</td>
</tr>
<tr>
<td>HMTA</td>
<td>2.12±0.11</td>
<td>7.73±0.01</td>
</tr>
<tr>
<td>ENAT</td>
<td>6.60±0.08</td>
<td>5.31±0.01</td>
</tr>
<tr>
<td>EANN</td>
<td>9.85±0.47</td>
<td>4.86±0.07</td>
</tr>
<tr>
<td>EHMT</td>
<td>8.24±2.50</td>
<td>4.86±0.04</td>
</tr>
<tr>
<td>EHMTA</td>
<td>11.63±2.74</td>
<td>5.33±0.27</td>
</tr>
</tbody>
</table>

Same lower case letters signify samples in a column that do not differ based on Tukey’s test (p < 0.01).

NAT and ANN starches presented higher swelling power than the other treatments (< 0.01). NAT starch had no initial changes and the ANN treatment used a low temperature (50°C) that was not enough to change the swelling properties. This fact may have occurred because when starch molecules get in contact with excess water and undergo heating, breakdown of the crystalline structures occurs and the molecules build hydrogen bonds between amylose and amylopectin, causing hydroxyl groups exposure increasing starch granule swelling (Singh, Singh, Kaur, Sodhi, & Gill, 2003).

The treatments with extrusion (ENAT, EANN, EHMT e HMTA) had lower swelling power than the non-extruded. This may have occurred because starch molecules get in contact with excess water and undergo heating, breakdown of the crystalline structures occurs and the molecules build hydrogen bonds between amylose and amylopectin, causing amylose molecules leaching (Zavareze et al., 2009).

On the other hand, we could observe that the starches that went through the extrusion process had greater solubility compared to those that were not extruded. This solubility difference probably occurred because starch granules from not extruded samples were destroyed and more starch particles
were retained for the extrusion treatment due to the lower moisture content, causing the starch structure to become more stable. This fact was observed by Zhang et al. (2016) that studied the extrusion effects on the corn starch properties with high amylose content.

Swelling and solubility information helps the industry to choose the starch type to use in products manufacturing. Starches with lower swelling power and solubility, such as those studied in this research, are desirable in noodles, canned foods and for filling manufacture (Zavareze & Dias, 2011).

**Pasting transparency**

The transparency results are shown in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transmittance %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 hour</td>
</tr>
<tr>
<td>NAT</td>
<td>0.61±0.046</td>
</tr>
<tr>
<td>HMTA</td>
<td>0.64±0.01</td>
</tr>
<tr>
<td>HMT</td>
<td>0.64±0.01</td>
</tr>
<tr>
<td>HMTA</td>
<td>0.62±0.02</td>
</tr>
<tr>
<td>ENAT</td>
<td>5.40±0.20</td>
</tr>
<tr>
<td>EANN</td>
<td>6.30±0.10</td>
</tr>
<tr>
<td>EHMT</td>
<td>10.60±0.10</td>
</tr>
<tr>
<td>EHMTA</td>
<td>7.13±0.15</td>
</tr>
</tbody>
</table>

*Small letters: comparison of each in relation to the analysis time. Same small letters signify samples in a line that do not differ based on Tukey’s test (p < 0.01). **Capital letters: comparison between samples in the same period of analysis. Same capital letters signify samples in a column that do not differ based on Tukey’s test (p < 0.01).

Observing Table 3, when the samples are compared to each other at each time, we can observe that the transmittance percentage presented similar behaviour for the samples NAT, ANN, HMTA and HMT during the entire analysis. Observing similarly the ENAT and EANN samples showed similar behavior after 48 and 96 hours, and EANN had transmittance similar to EHMTA sample after 96 hours.

The implication of ANN on starch transparency can be explained by the swollen granules fragility. Starch pastes with more disintegrated granules cause greater transmittance to light than those with granules that are more swollen. The paste transparency is a result of swollen granules ruptures (Craig, Maningat, Seib, & Hoseney, 1989).

As observed in Table 3, the starches that did not undergo the extrusion process showed lower transmittance than those that were extruded. In general, the starches with the highest retrogradation, which in this study were those that did not undergo the extrusion process as seen in Table 4, setback viscosity, produced more pastes that are opaque. Those that have undergone the extrusion process and that have presented greater transmittance have moderately transparent paste, because of the loss of the granular structure due to the extrusion. The lower the transmittance, the more opaque the starch paste. The percentage of transmittance is directly linked to the clarity of the starch paste, i.e. if the light passes without any absorption, the absorbance is zero and the transmittance is 100%. However, if the light is fully absorbed the transmittance is zero and the absorbance is infinite. The higher the transmittance, the greater the clarity of the paste (Craig et al., 1989, Mendes, Ribeiro, & Almeida, 2015).

**X-ray diffraction**

Starches are classified as type A, B and C according to their crystallinity profile.

Starch NAT, ANN, HMT and HMTA showed strong peaks at 15.2 and 23.2° 2θ, and a hesitant doublet between 17.9 and 18.1°, indicating type A starch (Cai, Cai, Man, Zhou, & Wei, 2014). After the modifications, the ANN, HMT and HMTA starches presented crystallinity similar to NAT starch. However, the modified HMTA starch had more intense peaks than other samples. This fact can be attributed to the structural rearrangement within the crystalline property of the starch granules, where the moisture and thermal energy applied during the modification process could cause a double helices displacement of the starch structure between the starch crystals, generating a tightly packed and more ordered crystalline arrangement than native starch and the others. The fact also reported by Hoover (2010). The lower intensity of diffraction peaks from ANN and HMT samples may have occurred due to the loss of crystalline arrangement by hydrogen bonding breakdowns; this fact may cause the adjacent double helices displacement and orientations rearrangement that are not perfectly parallel (Hoover & Vasanthan, 1994).

After the extrusion process, the appeared double peak between 17.9 and 18.1° 2θ collapsed originating a singlet around 18.4° 2θ. At 7.0, 12.1 and 13.2° 2θ small peaks emerged in all extruded samples, losing their characteristic of type A starch and presenting characteristic of type V starch.

Type V formation can be ascribed to simple amylose helices that are very close, including the existing lipid complexes (Kibar, Gönenc, & Us, 2010). Zhang et al. (2016). It was also observed the common corn starch degradation that before the extrusion presented type A pattern changed to type V, and the high amylose corn starch that had type B pattern started to present the type V. The extrusion cooking promoted disorder of the double helices of the starch macromolecules and new arrangements.

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took place with inclusion of lipids that are present in corn starch. The low pasting temperatures showed in the Table 4 for the extruded starches confirm the changes that were promoted during extrusion. This new starch conformation acquired after extrusion can be associated with nutritional benefits mainly due to increase of slowly digestible starch (Zortéa-Guidolin, Carvalho, Godoy, Demiate, & Scheer, 2017).

### Pasting properties

The pasting properties results are shown in Table 4. HMTA presented pasting temperature compared to NAT. This fact was also reported by Klein et al. (2013) in a study of the HMTA combination at different temperatures. Pasting temperature is related to the starch onset paste formation. The high pasting temperatures in starches under going the different heat-moisture treatments indicate that there is more strength and crosslinks in the starch granules that requires higher heating temperature for structural breakdown and paste formation (Zavareze & Dias, 2011).

Reduction of the NAT starch paste temperature from 81.40 to 48.20°C when the starches undergo the extrusion process, shows that there has been a weakening of the starch bonds due to modification, demanding a lower temperature to swell the starch granules (Karim et al., 2008). It can be seen that even with increasing temperature and over the time, extruded starches showed low viscosity because the extrusion gelatinizes the starch and also damages the granules, thus reducing the viscosity. Heat and moisture treatments, such as extrusion, may limit the swelling capacity of starch granules, which also contributes to the viscosity reduction (Zhang et al., 2016).

Breakdown is the difference between the maximum and minimum viscosity during heating, and ranged from 324.50 to 659.50 cP. A larger breakdown indicates rupture or a low tendency of the granule to withstand the shear forces during the heating (Karim et al., 2008). However, the decrease in breakdown indicates that the treatments improved starches mechanical and thermal stability (Watcharatewinkul, Puttanlek, Rungsardthong, & Uttapap, 2009). This stability can be a consequence of the starch molecules reorientation by strengthening the bonds between amylose and amyllopectin side chains (Zavareze & Dias, 2011).

Except for the ANN treatment, there was a certain degree of degradation of the starch granules that was evidenced by the lower profile of viscosity during the viscoamylographic analysis (Table 4). From technological point of view, the physical modified starches may be used to take advantage of those new pasting properties. In the case of extruded samples, the starch can be used for instant soups, creams and convenient foods due to the destructivity of starch granules that became soluble in cold water (Tomaszewska-Ciosk et al., 2012).

### Granules morphology

Figure 1 (from A to D) shows the corn starch that did not undergo extrusion cooking formed agglomerates with spherical and polygonal granules. It can be observed in Figure 1B that ANN starch granules are more polygonal and smooth with few pores. The HMT and HMTA samples, in image C and D, present less uniform and more porous granules.

The structure of the starches after extrusion was partially destroyed, giving rise to irregular, relatively large, rough and almost amorphous particles. These images agree with the results of the other analyses, especially the X-ray diffraction and the pasting properties, which showed that the extruded starches were considerably degraded.

### Conclusion

The ANN, HMT and HMTA modifications did not show significant differences compared to NAT starch. The extrusion modified more intensely, besides pregelatinizing, altered the starch crystallinity profile and viscoamylografics properties.

Thus, the production of pregelatinized starch through single-screw extrusion and the combination with the ANN, HMT and HMTA methods were efficient in the starch manufacturing with new characteristics. The new conformation of the starch after extrusion provides nutritional benefits by increasing the slow digestible starch, and technological benefits by the new properties viscoamylografics acquired, characteristics that allow the industry improvement and development of new products.

### Table 4. Viscoamylographic profile of the modified samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pasting Temperature (°C)</th>
<th>Peak Viscosity (cP)</th>
<th>Setback Viscosity(cP)</th>
<th>Breakdown viscosity(cP)</th>
<th>Final Viscosity(cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAT</td>
<td>81.40 ±2.62</td>
<td>1537.50 ±68.59</td>
<td>1008.00 ±14.14</td>
<td>529.50 ±82.73</td>
<td>1568.00 ±48.08</td>
</tr>
<tr>
<td>ENAT</td>
<td>84.47 ±0.53</td>
<td>1406.50 ±17.68</td>
<td>936.50 ±21.92</td>
<td>470.00 ±39.60</td>
<td>1431.00 ±106.07</td>
</tr>
<tr>
<td>HMT</td>
<td>81.12 ±0.53</td>
<td>773.50 ±7.78</td>
<td>449.00 ±39.60</td>
<td>324.50 ±47.38</td>
<td>822.50 ±10.61</td>
</tr>
<tr>
<td>HMTA</td>
<td>87.25 ±0.00</td>
<td>1151.50 ±70.31</td>
<td>493.00 ±73.54</td>
<td>659.50 ±33.23</td>
<td>1212.00 ±27.78</td>
</tr>
<tr>
<td>EANN</td>
<td>48.20 ±0.00</td>
<td>446.00 ±8.49</td>
<td>27.50 ±2.12</td>
<td>418.50 ±11.31</td>
<td>745.00 ±9.19</td>
</tr>
<tr>
<td>EHMT</td>
<td>48.20 ±0.00</td>
<td>456.00 ±19.80</td>
<td>33.50 ±14.85</td>
<td>422.50 ±34.65</td>
<td>825.00 ±9.19</td>
</tr>
<tr>
<td>EHMTA</td>
<td>48.20 ±0.00</td>
<td>395.50 ±64.35</td>
<td>23.50 ±0.71</td>
<td>372.00 ±63.64</td>
<td>35.50 ±2.12</td>
</tr>
</tbody>
</table>

Same lower case letters signify samples in a column that do not differ based on Tukey’s test (p < 0.01).
Figure 1. Scanning electron micrographs of modified and native starches at different amplitudes. A) NAT 2400 x; B) ANN 4000 x; C) HMT 4000 x; D) HMTA 4000 x; E) ENAT 100 x; F) EANN 43 x; G) EHMT 100 x; and H) EHMTA 100 x.

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