Properties of baked starch foam with natural rubber latex

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Abstract

Petroleum-based synthetic plastics used for making consumer articles constitute the largest non-renewable source of municipal solid waste in the United States. Containers and packaging products represent the largest group within plastic waste in municipal landfills. Efforts are being made worldwide to search for renewable and biodegradable substitutes for non-biodegradable plastics. Starch from surplus commodity crops has been investigated as a possible replacement, but it does have some disadvantages such as its susceptibility to water owing to its highly hydrophilic nature. To improve the water resistance of starch-based products, we incorporated natural rubber latex into baked starch foams based on wheat, potato, and waxy corn starches. While latex increases the density of the foam, it also improves the flexibility of the product. Stabilization of the latex with non-ionic additives helped prevent irregularities in the foam product. The flexural properties of these foams are comparable with commercial products and can be “tuned” by varying the starch type and adjusting the latex concentration. Latex also decreases the equilibrium moisture content and decreases the effect of higher humidity on the foam products.

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1. Introduction

The U.S. Environmental Protection Agency reported in 2003 that 24.2 million tonnes of municipal solid waste (MSW) was plastics (U.S. Environmental Protection Agency, 2005). While plastics was the fourth largest MSW category, it was the largest category containing mostly non-renewable resources. (The first three categories were paper, yard trimmings, and food scraps.) Containers and packages represent the largest group within the plastic MSW. Due in part to the large volume of non-renewable plastic waste and because many plastics also do not degrade within a reasonable period, researchers have searched for renewable and biodegradable substitutes for petroleum-based plastics (Lipinsky, 1981; Narayan, 1994).

One of the commodities that researchers have studied extensively is starch. Starch is not only renewable and biodegradable, it is also inexpensive and abundant (Whistler et al., 1984). Baked starch foams have thermal insulation properties comparable with commercial containers (Glenn et al., 2001a). However, the replacement of baked starch foams for plastics such as polystyrene has shortcomings. Thermally processed or hydroplastic starch behaves differently under varying moisture conditions. At high moisture levels, the baked starch foam product is flexible and has low strength, but at low moisture levels, the product tends to be brittle (Shogren et al., 1998). When starch foams are immersed in water, they quickly lose shape and become slimy. A solution to the susceptibility of starch to moisture is to form a...
thin hydrophobic film on the starch (Glenn et al., 2001b; EarthShell, 2002).

Baked starch foams have recently been intensely explored for use in disposable single-use packaging items. This technology, which uses an aqueous batter that foams due to the steam generated by heating of the batter, was initially developed by Tiefenbacher et al. (1994) and has since been commercialized (Andersen and Hodson, 1999a,b). Increasing amylose content and starch concentration produced denser and stronger foams; however, denser foams provided less flexibility (Shogren et al., 1998a,b). Increasing amylose content and starch concentration produced denser and stronger foams; however, denser foams provided less flexibility (Shogren et al., 1998). Using high-amylopectin starches resulted in the lightest foams, but they had low strength (Lawton et al., 1998). Using high-amylopectin starches resulted in the lightest foams, but they had low strength (Lawton et al., 1998). Using high-amylopectin starches resulted in the lightest foams, but they had low strength (Lawton et al., 1998). Using high-amylopectin starches resulted in the lightest foams, but they had low strength (Lawton et al., 1998). Using high-amylopectin starches resulted in the lightest foams, but they had low strength (Lawton et al., 1998). Using high-amylopectin starches resulted in the lightest foams, but they had low strength (Lawton et al., 1998).

Baked starch foam technology of potato, wheat, and waxy corn starches by incorporating natural rubber latex and compared these with commercially available products. Because of conflicting reports (Glenn et al., 2001a; Kiatkamjornwong et al., 2001), the effect of calcium carbonate on these formulations was also investigated.

2. Materials and methods

2.1. Materials

Native potato starch as PenCook 10 and Potato Starch Superior were from Penford (Englewood, CO) and Emsland (Emlichheim, Germany), respectively; wheat starch, Midisol 50, was from MGP Ingredients (Archbold, OH); waxy corn starch was from Penford. Pre-gelatinized starch was from Penford (PenPlus UM) and Emsland (Emjel E 70). Fiber, PL416, was from Weyerhaeuser (Federal Way, WA). Calcium carbonate, GSP-30, was from Imerys (Roswell, GA). Magnesium stearate, 905-G, was from Whittaker, Clark, and Daniels (South Plainfield, NJ) and from Aldrich (St. Louis, MO). Hevea latex, Dynatex GTZ LA, was from Guthrie latex (Tucson, AZ). Glycerol, sodium chloride, Triton X-100 (a non-ionic detergent/surfactant), and sodium hydroxide were purchased from Fisher Scientific (Hampton, NH), and calcium nitrate tetrahydrate was purchased from Aldrich and Fisher Scientific. Samples of Nexton D2500W and Natrosol 250HBR PA were provided by Hercules (Wilmington, DE). Nexton is a water-soluble non-ionic, hydrophobically modified hydroxyethylcellulose additive used to control texture in cement, gypsum, and latex products. Natrosol is hydroxyethylcellulose used to control the viscosity of latex paints. The panel press was from Hebenstreit GmbH (Mörfelden-Walldorf, Germany) with the dimensions of 110 mm × 165 mm × 1.8 mm. The temperature controllers were Series 93 from Watlow (St. Louis, MO); Paperboard and Styrofoam were from McDonald’s (Oak Brook, IL) and Target (Minneapolis, MN), respectively. The batter mixer was Model N50A obtained from Hobart (Troy, OH). Three point bend flexural testing were done with an Instron 5500R (Canton, MA), and the software used was Series IX. Moisture content (MC) was determined on a Mettler Toledo Halogen Moisture Analyzer model HR73 (Columbus, OH).

2.2. Sample preparation

Batter ingredients were mixed in a Hobart similar to previous description (Glenn et al., 2001a,b). Pre-gelatinized starch was used so that the cooking of the starch was not necessary. The batter contained water with fiber (7.7 wt%), magnesium stearate (2.3 wt%), native starch (46 wt%), and pre-gelatinized starch (6.5 wt%). All weight percent values are based on the amount of added water in the formulation. When required, latex was added last and mixed for 5 min before the batter was ready for baking. The amounts of added latex and calcium carbonate are listed in the tables.

The panel press was preheated to between 190 and 200 °C and the batter was baked for 1 min. Bacter load was determined by the minimum amount of batter that consistently foams to fill the mold.
2.3. Instron testing and moisture analysis

The starch foams were cut into 25.4 mm widths with a Delta band saw (Jackson, TN) and equilibrated in approximately 50% relative humidity (saturated solution of calcium nitrate tetrahydrate) at ambient temperatures for at least one week before testing. Similarly, MC was determined after equilibration with the temperature on the halogen moisture analyzer set at 105°C for 30 min. Tests of statistical significance on physical and mechanical properties were done using t-tests on Microsoft Excel (Redmond, WA). Generally, density and MC differences of >0.01 g/cm³ and >0.2%, respectively, are significant (95% confidence).

3. Results

3.1. Foam with potato starch

Addition of latex into the batter (with and without CaCO₃) provided a foam product with improved flexibility as evidenced by the increase of the strain at yield (samples P-1 to P-8 of Table 1). Not surprisingly, the stress at yield as well as the modulus also decreased with increased latex addition. The largest change in the flexural properties of the foam appears to occur between latex concentrations of 9 and 18 wt% of water (with and without CaCO₃). The addition of CaCO₃ at 9 wt% of water had little or no impact on foam properties compared with foams without CaCO₃ (Table 1). The foam density increased with increased latex content in the batter, which was not surprising, as latex does not foam upon baking. CaCO₃ did not affect the density of the product, but lowered the MC of the foams. Furthermore, MC decreased with increased latex content.

3.2. Foam with wheat starch

Unlike potato starch, the strain at yield in wheat starch-based foam decreased with increased latex amounts until 18 wt% of water (samples W-1 to W-8 of Table 1). At 27 wt% of latex to water, the strain at yield increased compared with 18 wt% of latex to water. These observations remained consistent with or without CaCO₃ present in the batter. The stress at yield and modulus generally decreased with increased amounts of latex, as seen in Table 1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Native starch</th>
<th>Latex (wt% of water)</th>
<th>CaCO₃ (wt% of water)</th>
<th>Strain at yield (%)</th>
<th>Stress at yield (MPa)</th>
<th>Modulus (MPa)</th>
<th>Density (g/cm³)</th>
<th>MC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1 Potato 0 0</td>
<td>1.74 ab</td>
<td>3.22 c</td>
<td>241 d</td>
<td>0.15</td>
<td>9.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-2 Potato 9 0</td>
<td>1.72 a</td>
<td>2.44 b</td>
<td>185 c</td>
<td>0.16</td>
<td>9.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-3 Potato 18 0</td>
<td>2.29 c</td>
<td>2.65 b</td>
<td>163 b</td>
<td>0.20</td>
<td>7.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-4 Potato 27 0</td>
<td>2.78 d</td>
<td>1.82 a</td>
<td>105 a</td>
<td>0.21</td>
<td>7.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-5 Potato 0 9</td>
<td>1.78 ab</td>
<td>2.64 b</td>
<td>192 c</td>
<td>0.16</td>
<td>8.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-6 Potato 9 9</td>
<td>1.94 b</td>
<td>2.44 b</td>
<td>187 bc</td>
<td>0.16</td>
<td>7.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-7 Potato 18 9</td>
<td>2.48 cd</td>
<td>1.75 a</td>
<td>108 a</td>
<td>0.19</td>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-8 Potato 27 9</td>
<td>2.79 d</td>
<td>1.77 a</td>
<td>98.6 a</td>
<td>0.20</td>
<td>6.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-1 Wheat 0 0</td>
<td>3.05 j</td>
<td>4.08 h</td>
<td>190 gh</td>
<td>0.20</td>
<td>8.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-2 Wheat 9 0</td>
<td>2.82 hj</td>
<td>3.10 fg</td>
<td>157 fg</td>
<td>0.20</td>
<td>7.6</td>
<td></td>
<td></td>
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<tr>
<td>W-3 Wheat 18 0</td>
<td>2.51 h</td>
<td>3.16 f</td>
<td>172 g</td>
<td>0.21</td>
<td>7.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-4 Wheat 27 0</td>
<td>2.78 hj</td>
<td>2.77 f</td>
<td>140 f</td>
<td>0.22</td>
<td>6.6</td>
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<tr>
<td>W-5 Wheat 0 9</td>
<td>2.28 g</td>
<td>3.70 gh</td>
<td>225 h</td>
<td>0.21</td>
<td>8.2</td>
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<tr>
<td>W-6 Wheat 9 9</td>
<td>2.24 g</td>
<td>3.53 gh</td>
<td>218 gh</td>
<td>0.23</td>
<td>7.5</td>
<td></td>
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<tr>
<td>W-7 Wheat 18 9</td>
<td>2.04 f</td>
<td>3.03 f</td>
<td>199 h</td>
<td>0.23</td>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-8 Wheat 27 9</td>
<td>2.48 gh</td>
<td>2.72 f</td>
<td>159 fg</td>
<td>0.24</td>
<td>6.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-1 Waxy corn 0 0</td>
<td>2.11 m</td>
<td>2.34 pq</td>
<td>142 n</td>
<td>0.13</td>
<td>9.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-2 Waxy corn 9 0</td>
<td>2.10 n</td>
<td>2.35 mpq</td>
<td>147 mn</td>
<td>0.15</td>
<td>8.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-3 Waxy corn 18 0</td>
<td>2.56 o</td>
<td>2.16 sq</td>
<td>119 m</td>
<td>0.18</td>
<td>8.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-4 Waxy corn 27 0</td>
<td>2.50 e</td>
<td>2.12 s</td>
<td>109 m</td>
<td>0.20</td>
<td>6.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-5 Waxy corn 0 9</td>
<td>1.80 m</td>
<td>1.84 mn</td>
<td>133 mn</td>
<td>0.14</td>
<td>8.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-6 Waxy corn 9 9</td>
<td>2.04 mm</td>
<td>1.63 m</td>
<td>108 m</td>
<td>0.15</td>
<td>7.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-7 Waxy corn 18 9</td>
<td>2.30 o</td>
<td>2.21 sq</td>
<td>120 mn</td>
<td>0.17</td>
<td>6.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-8 Waxy corn 27 9</td>
<td>2.50 o</td>
<td>2.11 nmp</td>
<td>118 m</td>
<td>0.19</td>
<td>6.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values within columns followed by a different lower case letter statistically have a <5% probability of being the same. Samples containing different native starches were not statistically compared.
in foams prepared with potato starch. However, these decreases for wheat starch were not as drastic as found with potato starch (Table 1). Also, the increase in the density resulting from increased latex content in the batter was comparatively much lower than foams with potato starch. The addition of CaCO₃ to the formulation appears to decrease strain at yield while slightly raising the modulus and density. As with potato starch, MC decreased with increased latex, and there was a small difference in MC between foams with or without CaCO₃.

### 3.3. Foam with waxy starch

The strain at yield of the waxy corn starch foam increased upon increasing latex content, and the stress at yield and modulus decreased with increased latex content for the formulations without CaCO₃ (samples C-1 to C-8 of Table 1). These changes were similar to potato starch, but to a smaller extent. The stress at yield and modulus remained unchanged for waxy corn in the presence of CaCO₃, whereas the strain at yield increased. Because the waxy corn starch has a better foaming property than the other native starches (Lawton et al., 1999), it produced a product that has the lowest density. An increase in the amounts of latex increased the density of the foamed product similar to the other starch types. The largest change in the properties of the waxy corn starch product appears to be between latex at 9 wt% of water and latex at 18 wt% of water similar to potato starch (with and without CaCO₃) (Table 1). MC again exhibited a decrease with increased latex content. Unlike the wheat starch and similar to the potato starch, the CaCO₃ appears to decrease the MC of the foam product.

For the three different native starches, wheat starch foams also exhibited the highest strain at yield, stress at yield, and density before the addition of latex. Wheat starch foams also were the most brittle (unpublished results) and contained the least amount of equilibrium MC. Wheat starch also had the highest stress at yield, modulus, and density than the other starches with the same additives. This behavior is expected because wheat starch does not foam as well as the other starches, and denser products are known to produce stronger starch-based foams (Shogren et al., 1998). Native potato starch appears to be most affected by the addition of and increasing amounts of latex. Due to this, the flexural properties of the native potato starch formulations overlap those of waxy corn starch. That is, the strain at yield with potato starch starts lower (at no latex) and ends higher (at 27 wt% latex) than waxy corn starch. Similarly, the stress at yield and the modulus both starts higher (with no latex) and ends lower (at 27 wt% latex) for potato starch than with waxy corn starch.

### 3.4. Effect of latex stabilizers and CaCO₃

A typical foam product based on the formulation shown in Table 1, sample P-7, contains, upon careful inspection, little white spots. These spots, which occur when the batter is lumpy or 'heterogeneous' (Kiatkamjornwong et al., 2001), are due to the coagulation of latex before baking. Thus, latex stabilizers were included into the batter to determine the effect of latex coagulation on the product and to make the product more appealing. These results are shown in Table 2, where all samples contained 18 wt% latex and 9 wt% CaCO₃ with respect to water. Coagulation was still observed in the butters of samples A-5 (Natrosol at 0.44 wt% of water) and A-7 (Nexton at 0.09 wt% of water), but the extent of coagulation was considerably less. Only a Triton X-100 concentration of ≤0.05% was needed to prevent coagulation of the latex in the batter for all three different native starches. No changes in flexural properties were observed for the potato starch formulation with (sample A-2 of Table 2) and without Triton X-100 (sample P-7 of Table 1). Similarly, there was no significant difference

### Table 2

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Additive</th>
<th>Additive (wt% of water)</th>
<th>Native starch</th>
<th>Strain at yield (%)</th>
<th>Stress at yield (MPa)</th>
<th>Modulus (MPa)</th>
<th>Density (g/cm³)</th>
<th>MC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>Triton X-100</td>
<td>0.44</td>
<td>Potato</td>
<td>2.96 bc</td>
<td>1.48 a</td>
<td>77.7 ab</td>
<td>0.19</td>
<td>7.3</td>
</tr>
<tr>
<td>A-2</td>
<td>Triton X-100</td>
<td>0.00</td>
<td>Potato</td>
<td>2.63 ab</td>
<td>1.61 ab</td>
<td>88.3 abc</td>
<td>0.19</td>
<td>7.4</td>
</tr>
<tr>
<td>A-3</td>
<td>Triton X-100</td>
<td>0.00</td>
<td>Wheat</td>
<td>2.76 b</td>
<td>2.23 cd</td>
<td>119 cd</td>
<td>0.21</td>
<td>6.5</td>
</tr>
<tr>
<td>A-4</td>
<td>Triton X-100</td>
<td>0.00</td>
<td>Waxy corn</td>
<td>3.27 c</td>
<td>1.45 a</td>
<td>64.4 a</td>
<td>0.17</td>
<td>6.6</td>
</tr>
<tr>
<td>A-5</td>
<td>Natrosol</td>
<td>0.44</td>
<td>Potato</td>
<td>2.36 a</td>
<td>2.36 d</td>
<td>142 d</td>
<td>0.19</td>
<td>6.8</td>
</tr>
<tr>
<td>A-6</td>
<td>Nexton</td>
<td>0.44</td>
<td>Potato</td>
<td>2.70 b</td>
<td>1.99 bc</td>
<td>112 c</td>
<td>0.18</td>
<td>6.7</td>
</tr>
<tr>
<td>A-7</td>
<td>Nexton</td>
<td>0.00</td>
<td>Potato</td>
<td>2.91 b</td>
<td>1.82 abc</td>
<td>102 bc</td>
<td>0.18</td>
<td>6.8</td>
</tr>
</tbody>
</table>

All samples contained latex and CaCO₃ at 18 and 9 wt% of water, respectively. Values within columns followed by a different lower case letter statistically have a <5% probability of being the same.
between the potato starch formulation with (sample A-6 of Table 2) and without Nexton (sample P-7 of Table 1). However, potato starch formulations with Triton X-100 (samples A-1 and A-2) are significantly different from formulations with Natrosol (sample A-5) and to some extent with Nexton (samples A-6 and A-7). These differences can partially be attributed to the difference in MC of the samples, because higher MC is known to make the foams weaker and more flexible (Shogren et al., 1998). Natrosol appears to make the foam product stiffer and stronger, countering the effect of added latex.

The flexural properties of the wheat and waxy corn starch formulations with added Triton X-100 (samples A-3 and A-4 of Table 2) were substantially different from samples without the additive (samples W-7 and C-7 of Table 1). Specifically, these wheat and waxy corn formulations have a higher strain at yield with lower stress at yield and modulus. This shows that the stabilized latex in the formulation produced foams that were more flexible. The added stabilizers did not change the density or the equilibrium MC of the products.

CaCO$_3$ addition appears to promote latex coagulation when a stabilizer is not present. This observation is not surprising because CaCO$_3$ is not soluble in water, and thus, acts as an abrasive in the batter. Nevertheless, data from Table 1 suggest that CaCO$_3$ does not substantially affect the properties of the baked foam products.

3.5. Comparison with commercial products

The same flexural tests for commercial products are listed in Table 3. The results show that starch foam products are not substantially different from commercial products. In fact, strain at yield is higher for starch-based products.
foams, whereas stress at yield, modulus, density, and equilibrium MC typically falls between Styrofoam and paperboard. Furthermore, Tables 1 and 2 reveal the fact that the properties of the starch foam product can be ‘tuned’ by a mixture of different starches with varying concentrations of latex.

3.6. Impact of moisture content

Foam panels were equilibrated at 75% relative humidity (saturated NaCl solution) and tested on the Instron to determine the effects of moisture (Table 4). For native potato starch, the stress at yield and modulus decreased to a smaller extent when latex was present in the formulation. However, no significant difference was observed between the formulations with and without latex. For waxy corn starch, the foam products behaved similar to potato starch where the stress at yield and modulus decreased to a smaller extent when latex was present in the formulation. These results suggest that, for potato and waxy corn starch-based formulations, the addition of latex into the batter reduced the effect of relative humidity on the flexural properties. The flexural properties of the foam panels at 75% relative humidity generally have a smaller standard deviation than those equilibrated at a lower relative humidity level.

4. Discussion

The various additives affected the potato starch formulations in different ways. Nexton and Triton X-100 had little or no impact on the performance of the product and were able to prevent latex coagulation at low overall concentrations (≤0.25%). The appearance of the panels made with these additives is more homogeneous. The consumer may feel that the panel with an additive is cleaner than the one without. Furthermore, the ‘cleaner’ appearance of a product may also present a ‘cleaner’ appearance of a product may also present a cleaner appearance of a product may also present a cleaner appearance of a product. Generally, CaCO₃ does not affect the flexural properties in formulations with wheat and waxy corn starch more than with potato starch (Tables 1 and 2). The added Triton X-100 appears to affect the flexural properties in formulations with wheat and waxy corn starch more than with potato starch (Tables 1 and 2). This could be due to the potato starch having more of a lubricating effect that prevents the latex from coagulating unlike the wheat or waxy corn starch. One possibility is the larger starch granules in potato starch compared with the other starches (Shannon and Garwood, 1984). The larger granule sizes would result in a smaller surface area for interaction with the latex particles. Thus, the added stabilizer has a smaller effect on potato starch formulations than wheat or waxy corn.

The utilization of latex in the baked foam panels is expected to have another advantage. Latex is inherently hydrophobic and its addition to the batter clearly lowers the equilibrium MC of the foam products. Latex also reduces the effect that relative humidity has on the flexural properties of the starch foam when potato and waxy corn are used. Unfortunately, coating the product with a thin plastic layer is still required because a majority of the dried product is still starch. However, the integrity of the baked product when contacted with water will likely improve because of the latex.

In summary, latex can be added to the batter of baked starch foams to increase their flexibility and moisture resistance. Stabilization of the latex by using an additive improves the aesthetic qualities of the baked starch product. Generally, CaCO₃ does not affect the flexural properties of the baked product. Finally, using different starches along with latex allows the tuning of the mechanical properties of the products to match or surpass that of commercial products.

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References


