Effect of starch type on the properties of starch containing films

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Ultimate tensile strength (UTS), percent elongations at break (%E), tear resistance, and impact strength were investigated for starch–poly(vinyl alcohol) (PVA) cast films. Films contained 41% starch, 41% PVA, 15% glycerol and 3% poly(ethylene-co-acrylic acid) (EAA). Films were made with each of the following starch types: normal cornstarch, waxy cornstarch, high amylose cornstarch (50% amylose and 70% amylose), wheat starch, potato starch, and tapioca starch. Films were aged before testing from 7 to 168days, or stored at 15 to 93% relative humidity (RH) for 7days prior to testing. All films showed an increase in %E and a decrease in UTS as RH increased. The high amylose films showed the greatest stability over the RH range for %E. The largest decrease in UTS of the films occurred between 15 and 33% RH, followed by a linear decrease in UTS as RH increased. The large decrease in UTS was thought to be due to the T_g of the films. Tear resistance of the films was effected by RH. Films stored at high RH (93%) absorbed so much water that they became weak and had very little tear resistance. Film stored at low RHs (15 and 33%) also had low tear resistance. Films stored at intermediate RHs had high tear resistance. The difference in tear resistance is thought to be due to chain mobility. At low RH the polymer chains in the films have less mobility to absorb the stress associated with tearing. Impact strengths of the films were about the same. except films made with waxy cornstarch, which were significantly lower. Aging the films for 28days did not significantly effect the impact strength of the films. All films, except films containing high amylose cornstarch, showed a large decrease in %E after aging for 168days. Films made with waxy cornstarch showed the greatest loss in %E after aging, going from 144% after 7days to 34% after 168days. UTS of the films increased with aging, except films made with waxy cornstarch. Films other than those containing waxy cornstarch showed no %E less than 100% or an UTS of greater than 35MPa, even after aging for 168days. Films containing high amylose cornstarch had the most consistent properties over the entire range of test conditions.

INTRODUCTION

Over the last few years, there has been a renewed interest in biodegradable plastic and plastics made from annually renewable, natural polymers such as starch. Numerous studies have been done which study the properties of starch-based films (Otey et al., 1980; Fanta et al., 1990, 1992; Stenhouse et al., 1992; Evangelista et al., 1993; Lawton & Fanta, 1994; Bastioli et al., 1994), but only the last study reported investigating the effects of different types of starch on the properties of films. Reports do show that films made only of starch from different starch sources have different properties (Neale, 1924; Wolff et al., 1951; Lloyd & Kirst, 1963). Some of these differences have been attributed to the amylose content of the starch (Lloyd & Kirst, 1963).

This work will investigate the properties of starch–PVA films. PVA and starch are not compatible when each is added in high concentration (Okaya et al., 1992). Lawton and Fanta (1994) showed that cast films containing PVA and starch could be produced if a small amount of EAA was added to the formulation. Starch–PVA films cast without EAA will phase separate during drying. For this reason EAA will be added to the cast film formulations.

MATERIALS AND METHODS

Materials

Normal commercial grade cornstarch (Buffalo 3401) was purchased from CPC International Inc. (Argo, IL).
Waxy cornstarch (Amioca) and high amylose corn-starch (Hylon V and VII) were purchased from National Starch (Bridgewater, NJ). potato starch was purchased from Avebe (Veendam Holland), tapioca came from A. E. Staley Manufacturing Co. (Decatur, IL), and wheat starch came from Midwest Grain Products (Atchinson, KS). All starch samples were unmodified and used as purchased. Poly(vinyl alcohol) (PVA) was obtained from Air Products and Chemicals Inc. (Allentown, PA) under the trade name Airvol 325. Airvol 325 is 98–98.8% hydrolyzed with a molecular weight average of 85,000–146,000. Poly(ethylene-co-acrylic acid) (EAA) was obtained from Dow Chemical Co. (Midland, MI) under the trade name Primacor 5981. This EAA had a $M_w$ of about 18,000 and $M_n$ of about 7000, and contained about 20% acrylic acid. Reagent grade glycerol was from Fisher Scientific. All salts used to make saturated solutions for the constant relative humidity chambers were from Sigma.

A 10% (w/w) solution/dispersion of EAA in aqueous ammonium hydroxide was prepared as described by Fanta et al. (1992). A 10% (w/v) solution of PVA was prepared as described by Lawton and Fanta (1994).

Methods

Cast films were prepared by the method previously described by Lawton and Fanta (1994). The generic film formulation was constant for all the films produced and contained 41% starch, 41% PVA, 3% EAA, and 15% glycerol on a dry basis. Glycerol, EAA, and PVA were weighed out into flasks, and enough water was added to the ingredients to make a final solids content after jet cooking of approximately 10%. The liquids were then mixed with the pre-weighed starch in large beakers. The dispersion was cooked using a laboratory model continuous jet cooker (Penick and Ford Ltd, Cedar Rapid, IA). The cooked solutions were collected in Dewar flasks to maintain the temperature of the solutions at approximately 90°C until the films were cast. The jet-cooked solutions were cast at 50-ml (1.25mm) wet thickness onto preheated glass plates (95°C). To prevent the film from sticking to the glass plate, a release paper (S.D. Warren Co. South Portland, Maine) was glued to the plate with a silicon adhesive. After the films had been cast, they were placed in a humidity cabinet and dried overnight at 50°C and 50% relative humidity. After drying overnight the films were stored at 23°C and 50% RH in a constant temperature and humidity room until needed.

Mechanical testing

UTS and %E were evaluated for each film using an Instron universal testing machine. Four “dog bone” shaped specimens (ASTM D412-68, Type C) were cut from each film. Specimens had a width of 6.35mm. Each piece was measured for thickness in three places along the test length using a Mini Test 3000 (Elektro-Physik, Koln, Germany). The specimens’ averaged thickness was about 0.1mm. The gauge length and grip distance were both 50.8mm. Crosshead speed of the Instron was 50mm/min, with a data collection rate of 20pts/s. The tests were carried out at 23°C and 50% RH in a constant temperature and humidity room.

UTS, %E and tear resistance of each film were evaluated after storage in different RHs for 7 days. Constant RHs were obtained by using saturated salt solutions of Na$_2$SO$_4$ (~93% RH), NaCl (~76% RH), Ca(NO$_3$)$_2$·4H$_2$O (~51% RH), CaCl$_2$ (~33% RH), and LiCl (~15% RH). Films were stored in desiccator chambers over the salt solutions at 23°C. UTS and %E were done as described above. Tear resistance of the films was evaluated using a modified ASTM D-1938 (trouser) method. Four samples of each cast film were cut into 50mm x 50mm squares and were about 0.1 mm thick. A 12.5mm slit was cut in the sample, giving the sample an appearance of a pair of trousers. The samples were pulled apart at the slit by an Instron testing machine. The test was performed at 200mm/min. Care was taken to remove the specimens just before they were tested to minimize the chance of samples drying out or picking up moisture due to the change in humidity from the desiccator to the testing room.

Impact tests were done on a Dynatup impact testing machine (General Research Corp., Santa Barbara, CA). The film tup and a 2.02kg mass were used for testing, and were dropped from a height of 35cm. generating a velocity of 1.86m/s. Films tested were cut into 100mm x 75mm pieces and were about 0.1mm thick. Samples were aged 7 or 28 days at 23°C and 50% RH prior to testing. Four films were impact tested for each starch type. Tests were run in duplicate giving a total of eight impact tests for each starch-based film. Mean values of the impact test were analyzed for differences using Duncan’s multiple range test for the mean of SAS (SAS, 1992).

RESULTS AND DISCUSSION

Figure 1 shows the effect of percent relative humidity on starch-based films containing different starch types. Percent elongation of the films increases as %RH increases for all films tested. Starch is hygroscopic and will gain or lose water to achieve equilibrium with the ambient air (Christensen et al., 1982). Water is also a plasticizer for starches (Hoseney, 1994). By placing the starch-based films in different RHs, the films will either lose or gain water to be in equilibrium with the air in the humidity chamber. Since water is a plasticizer, changing the water content in the film will change the properties of the films. Increasing plasticizer levels in synthetic plastic has been shown to increase %E (Sears &
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containing normal levels of amylose or no amylose. This property of the high amylose containing starch is an improvement over the other starches, due to the stability of the high amylose starch when exposed to different humidity. Shogren and Jasberg (1994) got similar results for extruded ribbons. Ideally, films with good properties should not change with humidity or change very little.

Tensile strength of the films decreased as relative humidity increases, which is consistent for polymers that contain increasing amounts of plasticizer (Sears & Touchette, 1989). Figure 2 shows that there is a large decrease in UTS for all films tested as the storage rela-

Touët, 1989). This is consistent with other work done with starch-based films (Bader & Göritz, 1994) and is consistent with systems where the plasticizer is increasing.

The slopes of the regression line for the two high amylose containing films seem parallel to each other and different from the other films tested. The slopes for the High Amylose V and High Amylose VII are 3.61 and 3.40 respectively, while the slope for the other starch containing films varied from 4.68 to 5.04. The percent elongation of the films that contain more amylose does not vary as much over the different relative humidity ranges as do films made with starch containing normal levels of amylose or no amylose. This property of the high amylose containing starch is an improvement over the other starches, due to the stability of the high amylose starch when exposed to different humidity. Shogren and Jasberg (1994) got similar results for extruded ribbons. Ideally, films with good properties should not change with humidity or change very little.

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Table I. Tear resistance of starch containing films, stored for 7 days at 50% relative humidity and 23°C

<table>
<thead>
<tr>
<th>Starch type</th>
<th>Relative humidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Tear resistance (N/mm)</td>
<td></td>
</tr>
<tr>
<td>Normal corn</td>
<td>8.96</td>
</tr>
<tr>
<td>Amylose VII corn</td>
<td>10.15</td>
</tr>
<tr>
<td>Waxy corn</td>
<td>12.78</td>
</tr>
<tr>
<td>Amylose V corn</td>
<td>8.12</td>
</tr>
<tr>
<td>Potato</td>
<td>8.44</td>
</tr>
<tr>
<td>Tapioca</td>
<td>8.80</td>
</tr>
<tr>
<td>Wheat</td>
<td>11.17</td>
</tr>
</tbody>
</table>

Tear resistance of the films was also affected by the relative humidity in which they were stored (Table I). The films were easily torn when stored at low relative humidities or when stored at high relative humidities. At high RH the films absorbed more water. One of the effects of a plasticizer is the lowered strength of the substrate (Bernard & Burrell, 1972). This was seen in the UTS data where the films stored at high RH had the lowest UTS. Here, so much water is absorbed by the films stored at high RH, that the strength of the films becomes low and has very little resistance to tearing. The tear resistance of films stored at 51 and 76% RH was very high. In fact, films stored at these conditions did not really tear, but were pulled apart more like a tensile test. This is probably due to these films being above their glass transition temperature ($T_g$). The tear resistance of films stored at low RH (15 and 33) is also low (Table 1). A possible reason for the low tear resistance at 15% RH is that the materials in the films are below their glass transition temperature. Being below $T_g$, the films do not have much motion in their chains to absorb the stress of being torn. The same phenomenon could also be occurring with films stored at 33% RH. Although the UTS data suggest that films stored at 33% RH are above their $T_g$, there could still be little motion in the chains in the time frame needed to absorb the stress from tearing.

Figure 3 shows the results of impact testing on films aged 7 and 28 days. Films aged 7 days showed no significant difference in impact strength, except for films made with waxy cornstarch which had significantly (0.05) lower impact strength. Films aged for 28 days followed the same pattern as films aged for 7 days. Films made from waxy cornstarch had significantly lower impact strengths. Films made with potato starch and aged for 28 days had lower impact strengths when compared with films made with other starch types, but were only significantly lower in impact strength than films made with high amylose cornstarch. These films were not significantly different from the films made with waxy cornstarch. There was no significant difference (0.05) in impact strength due to aging within a starch type.

Percent elongation of all films declined after aging (Fig. 4). Films made with waxy cornstarch had the lowest %E after aging for 168 days. Films made with normal cornstarch also had a large decrease in their elongation after aging for 168 days. Films made with the remaining starches also showed decreases in %E, but still had %E values well over 100% even after aging for 168 days. The films made with high amylose cornstarch and potato starch were the most stable during aging and

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**Fig. 3. Impact strength of starch containing films, aged for 7 and 28 days at 50% relative humidity and 23°C.**
lost little of their elongation. Tensile strength increased or remained approximately the same for all films after aging for 168 days, except those made with waxy cornstarch which showed a slight decrease in UTS (Fig. 5). Decreases in %E and a constant UTS with aging have been reported in the past for starch-containing materials (Shogren & Jasberg, 1994).

The fact that films made with waxy cornstarch performed poorly when compared with other films may be attributed to its structure. Waxy cornstarch contains almost 100% amylopectin. EAA has been shown not to complex as well with amylopectin as it does with amylose (Shogren et al., 1991a, b). Perhaps EAA and the amylopectin are not complexing to the degree necessary to make waxy cornstarch and PVA truly compatible. Blends of incompatible synthetic polymers have been shown to produce weaker materials than either polymer alone (Paul, 1978). Amylopectin structure could also affect the elongation of the films during aging. The amylopectin content of the starch could be crystallizing during storage. This would give films that have lower free volume and less molecular movement for the chains to move during the elongation test. Films containing waxy cornstarch did show acceptable elongation initially (144%), but had %E of only 34% after aging. Films containing normal cornstarch showed a similar trend by having %E of 288% after 7 days and 97% after 168 days. Only films containing high amylose starch did not show large decreases in %E after aging for 168 days.

Fig. 4. Elongation at break of starch containing films, aged 7, 28, 84, and 168 days at 50% relative humidity and 23°C.

Fig. 5. Ultimate tensile strength of starch containing films, aged 7, 28, 84, and 168 days at 50% relative humidity and 23°C.
CONCLUSIONS

Excellent films can be made containing starch, PVA and EAA. The starch type used does make a difference in the properties of the films. Films that contain high amylose cornstarch and PVA have good elongations, tensile strength, tear resistance and impact strength. Films containing high amylose cornstarch are also more stable at different RHs than films containing other starches. The properties of the films containing high amylose cornstarch are also more stable over time than films made with other starches. Films containing starch other than high amylose starch had decreased with time or showed far more variation with humidity than did films containing high amylose starch. These properties not only are the properties initially better than films made with high amylose cornstarch, but starches containing normal levels of amylose are less expensive.

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REFERENCES


