Starch esterification by reactive extrusion

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Abstract

The objectives of this study were to synthesize starch-fatty acid esters via a reactive extrusion process and to determine the effects of level and chain length of the anhydrides used on the physical properties of the extrudates. Starch esters were synthesized by extruding 70% amylose starch with fatty acid anhydrides and sodium hydroxide (catalyst) in a single screw extruder. Acetic, propionic, heptanoic, and palmitic anhydrides were used at 0.01, 0.02, and 0.03 mol levels to obtain different degrees of substitution (DS) in the starch. Physical properties of the extrudates such as unit and solid density, specific mechanical energy, water absorption, and water solubility indices as well as molecular degradation and DS of the starch were measured. DS increased as the level of anhydride increased. Lower molecular weights and higher levels of anhydride resulted in the greatest reduction in starch molecular weight. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Starch is used extensively in the production of both food and industrial products. Chemical modification of the starch is often required to better suit its properties to specific applications. Traditionally, starch esters with low degrees of substitution (DS) have been prepared in aqueous media by batch methods (Jarowenko, 1986). Extruders have been used as chemical reactors for polymerization of plastics (Wielgolinski and Nangeroni, 1982) and graft polymerization of plastics onto starch (Chinnaswamy and Hanna, 1991). Although extrusion is not used widely for starch modifications, it has great potential. Extruders have been used to manufacture carboxymethylated and cationic potato starch (Gimmler et al., 1994), starch phosphates (Chang and Lii, 1992), anionic starch (esters of various dicarboxylic acids) (Tomasik et al., 1995) and oxidized starches (Wing and Willett, 1997). The reactions are carried out continuously and quickly in the extruder. Extruders can handle viscous liquids, and gelling of the starch is not a problem.
Starch is plasticized in the extruder with very small amounts of water (16–20%), thus reducing subsequent drying requirements.

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2. Materials and methods

2.1. Materials

Amylomaize VII (70% amylose corn starch) was procured from American Maize Products Co. (Hammond, IN). Chemicals used for starch modification (acetic anhydride, propionic anhydride, heptanoic anhydride, palmitic anhydride, and sodium hydroxide) were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI).

2.2. Extrusion

Extrusion processing was carried out in a single screw C.W. Brabender (Model 2003 GR-8) laboratory extruder. The drive system was a Plasticorder with controlling units type FE-2000 and FE-2000A. This system automatically controlled and recorded torque, barrel temperature, and pressure in the barrel. Temperatures of the feeding, metering, and die sections were maintained at 50, 140, and 140°C, respectively. Die nozzle diameter was 3 mm. The screw had a compression ratio of 3:1 and its rotational speed was maintained at 140 rpm. The feed moisture content was 20% on a dry basis (db). Starch was modified in the extruder using acetic, propionic, heptanoic and palmitic anhydrides at levels of 0.00, 0.01, 0.02, and 0.03 mols of anhydride per mol of anhydroglucose unit of starch. To the above levels of anhydride, 0.00, 0.02, 0.03, 0.04 mols of catalyst (sodium hydroxide) were added per mol anhydroglucose unit of starch. The sodium hydroxide also neutralizes the organic acids released in the course of the reaction. The respective amount of sodium hydroxide was dissolved in water and added to the starch. The samples were conditioned for 12 h in a sealed plastic container at 25°C. The anhydrides were added to the samples immediately before extrusion.

2.3. Moisture content

Moisture content of native starch was determined by an oven drying method (Chinnaswamy and Hanna, 1988). Approximately 10 g of sample were placed in a tarred aluminum dish and weighed on a Mettler PJ 3000 balance (Mettler Instrument Corp., Hightstown, NJ) with accuracy of ± 0.01 g. The samples were dried in a Precision Mechanical Convection Oven (GCA Corp., Chicago IL) at 105°C for 24 h, and then cooled to ambient temperature (25°C) in a desiccator for 60 min. Moisture content of samples before extrusion did not deviate more than 0.5% db.

2.4. Specific mechanical energy

Specific mechanical energy (SME) is defined as a total input of mechanical energy per unit dry weight of extrudate. It was determined as described by Bhatnagar and Hanna (1994). Extrudate was collected for 30 s and dried. SME was calculated as:

$$\text{SME} = \frac{2 \times \pi (n/60) \times \tau)}{MFR}$$

where $n$ = screw speed (rev/min), $\tau$ = torque (N-m), and $MFR$ = mass flow rate (kg/h).

2.5. Solid and unit densities

Extrudate solid density is the density of the solid material only. The void volumes are not included in this measurement. The solid density was measured using a Multivolume Pycnometer 1305 (Micromeritics, Norcross, GA). Unit density is the density of the foam and includes all the void volumes. The diameters of the extrudates were measured along a 30 cm-long section. An average of ten diameters was used. A circular cross-sectional area of the extrudate was assumed and calculated from the average diameter. The volume of the extrudate was calculated as the product of the cross sectional area and length. The weight of the extrudate was measured and the unit density
was calculated by dividing the extrudate mass by extrudate volume. Knowing both densities describes the extent to which the extrudate expands. Overall expansion is a ratio of solid density to density unit.

2.6. Spring index

Spring index refers to the ability of a material to recover its original shape after it has been deformed. The samples were conditioned for 72 h at room temperature (25°C) and 80% relative humidity and tested at the same conditions. Spring index was determined using an Instron Universal Testing Machine (Model 5566) described by Altieri and Lacourse (1990). A flat plate was used to compress five 5-cm long pieces of extrudate at once to deform them to 80% of their original diameter at a loading rate of 1 mm/min. After releasing from the first compression, the sample was recompressed after 1 min. The recovery of the sample was determined by dividing the recompression force after 1 min by the original force of compression and was reported as a coefficient from 0 to 1. Each sample's spring index was measured three times and reported as an average of the three readings.

2.7. Degree of substitution

Degree of substitution (DS) indicates the average number of substitutions per anhydroglucose unit in starch. The highest possible DS is 3 since there are three OH groups available per anhydroglucose unit. The DS of esterified starch can be determined by hydrolyzing substituted groups with 0.1 N NaOH and then titrating back with 0.1 N HCl to the original pH prior to the NaOH addition. The ground sample was rinsed twice with acetone and then twice with water to extract the free fatty acids and sodium salts and dried. Ten grams of sample were put in a 250 ml conical flask covered with 25 ml of distilled water. The mixture was conditioned in a Tecator 1024 shaking water bath (Höganäs, Sweden) for 1 h at 30°C and then the pH of the mixture was measured. The pH of the samples was from 6 to 7. To each flask, 150 ml of 0.1 N NaOH were added. The sample was then conditioned for 48 h at 50°C to hydrolyze the fatty acids substitutes. The excess NaOH of the samples was titrated with HCl back to the original pH. DS was calculated as:

\[
DS = \frac{M_{FA} \times MW_{AN}}{W - M_{FA}(MW_{FA} - MW_{H2O})}
\]

where DS = degree of substitution; \( W \) = weight of the sample (g); \( M_{FA} \) = mols of titrated fatty acid; \( MW_{FA} \) = molecular weight of the fatty acid; \( MW_{H2O} \) = molecular weight of water (18); and \( MW_{AN} \) = molecular weight of an anhydroglucose unit (162).

2.8. Size exclusion chromatography

Molecular degradation was monitored by size exclusion chromatography. The sample (0.0300 g) was dissolved in 3 ml of a 90% (v:v) solution of dimethyl sulfoxide (DMSO) in water and then filtered through a 5 μm membrane (Alttech, Deerfield, IL). Then 20 μl of the solution were injected into a Shodex KS-806 HPLC column. A refractive index detector was used. The mobile phase was water and the flow rate was 1 ml/min. Markers with molecular weights of 180, 38 900, 485 000, and 2 000 000 were used.

2.9. Water absorption index and water solubility index

Water absorption index (WAI) is the weight of gel obtained per g of dry sample. It was determined by the method of Anderson et al. (1969). Water solubility index (WSI) is the amount of soluble carbohydrate that stays permanently in the water phase when starch is submerged in water. It was measured as total carbohydrate in solution using the phenol sulphuric acid method of Dubois et al. (1956).

2.10. Statistical analysis

A completely randomized experimental design with full factorial treatment design was used. The experiment was replicated three times with a different day of extrusion representing a replicate. Independent variables were type and level of
3. Results and discussion

3.1. Specific mechanical energy

SME requirements (Table 1) are an indicator of the relative ease with which a material can be extruded and the relative cost of the extrusion operation. Acetic anhydride and propionic anhydride treatments did not significantly influence SME. Higher concentrations of heptanoic (0.03 mol) and palmitic anhydride (0.02 and 0.03 mol) significantly reduced the SME requirements. No changes in the amount of SME were required when the levels of acetic, propionic, and heptanoic anhydrides were varied. A statistically significant difference between the 0.01 and 0.03 mol treatments of palmitic acid was established. The SME in the single screw extruder depends on the barrel friction and the viscosity of the material (Harper, 1989). The longer chain fatty acids were less soluble in water, tended to form separate phases, and may have acted as a lubricant between the extruder barrel and the viscous gelatinized starch. On the other hand, the long chain fatty acids that esterified the starch reduced the intermolecular interactions between the starch molecules by sterically hindering hydrogen bonding. Less intermolecular interactions resulted in lower viscosity of the extrudate. Both effects could be expected to accumulate with an increase in the anhydride concentration. The net effect was a reduced SME for higher concentrations of the long-chain fatty acid anhydride treatments.

3.2. Solid and unit densities

Extrudate densities give indications of the porosity and expansion characteristics. The addition of acetic anhydride to the starch did not significantly affect the unit density of the extrudates (Table 1). Propionic anhydride added at 0.01 mol per anhydroglucose unit, as well as heptanoic and palmitic anhydrides, when added at any level, resulted in unit densities higher than the control. Higher molecular weight fatty acids, such as heptanoic and palmitic, have higher boiling points. Most likely, significant amounts of fatty acids remained in the extrudate and increased the unit density. Lipid addition to starch prior to extrusion has been shown to increase the unit density (Bhatnagar and Hanna, 1994). Therefore, the high molecular weight fatty acids were expected to have similar behaviors. A statistically significant difference in unit density was detected only between 0.01 and 0.03 mol levels for propionic and palmitic anhydrides. In all other cases, the level of the anhydrides did not cause statistically significant differences in the unit density.

The acetic anhydride treatment did not influence the solid density of the extrudates. However, the other acid anhydrides significantly lowered the solid density of the extrudates. No change in the solid density was registered when the level of anhydride was changed.

3.3. Spring index

The spring index is an indirect measure of a material’s ability to absorb energy. There was no change in the spring index of the extrudate when either acetic or propionic anhydride was added (Table 1). The three levels of heptanoic anhydride and the 0.01 mol level of palmitic anhydride treatments had spring indices lower than the control treatment. The level of the treatment influenced significantly the spring indices of the extrudates only when the level of palmitic acid was changed from 0.01 to 0.02 M.

3.4. Degree of substitution

Adding organic acid anhydrides and sodium hydroxide, as a catalyst, to starch and extruding the mixtures resulted in chemical modifications of the starch. Chemical modifications to starch were observed for all levels and types of acid anhydrides. No significant differences in DS between the different acid anhydrides applied at the same
Table 1
Physical and chemical properties of starch extruded with acid anhydrides and sodium hydroxide a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit density (g/cm³)</th>
<th>Degree of substitution (Macid/AgU)</th>
<th>Spring index</th>
<th>SME (W·h/kg)</th>
<th>Solid density (g/cm³)</th>
<th>WAI (g gel/g starch)</th>
<th>WSI (g soluble starch/g starch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (no anhydride, no NaOH)</td>
<td>0.128 ± 0.019 de</td>
<td>–</td>
<td>0.902 ± 0.008 a</td>
<td>342 ± 50 a</td>
<td>1.59 ± 0.06 a</td>
<td>3.48 ± 0.24 a</td>
<td>0.082 ± 0.029 abc</td>
</tr>
<tr>
<td>0.01 mol AA, 0.02 mol NaOH</td>
<td>0.237 ± 0.005 de</td>
<td>0.0085 ± 0.0003 c</td>
<td>0.904 ± 0.007 a</td>
<td>342 ± 68 a</td>
<td>1.58 ± 0.05 ab</td>
<td>3.24 ± 0.04 bc</td>
<td>0.080 ± 0.033 abc</td>
</tr>
<tr>
<td>0.02 mol AA, 0.03 mol NaOH</td>
<td>0.257 ± 0.062 de</td>
<td>0.0164 ± 0.0013 b</td>
<td>0.931 ± 0.020 a</td>
<td>338 ± 35 ab</td>
<td>1.58 ± 0.05 ab</td>
<td>3.27 ± 0.03 bc</td>
<td>0.088 ± 0.036 abc</td>
</tr>
<tr>
<td>0.03 mol AA, 0.04 mol NaOH</td>
<td>0.190 ± 0.061 de</td>
<td>0.0237 ± 0.0011 a</td>
<td>0.885 ± 0.037 a</td>
<td>297 ± 27 ab</td>
<td>1.57 ± 0.05 ab</td>
<td>3.20 ± 0.05 bc</td>
<td>0.109 ± 0.055 ab</td>
</tr>
<tr>
<td>0.01 mol PrA, 0.02 mol NaOH</td>
<td>0.404 ± 0.203 cd</td>
<td>0.0075 ± 0.0011 c</td>
<td>0.933 ± 0.014 a</td>
<td>318 ± 36 ab</td>
<td>1.56 ± 0.04 bc</td>
<td>3.29 ± 0.10 b</td>
<td>0.071 ± 0.025 abcd</td>
</tr>
<tr>
<td>0.02 mol PrA, 0.03 mol NaOH</td>
<td>0.238 ± 0.028 de</td>
<td>0.0157 ± 0.0006 b</td>
<td>0.895 ± 0.050 a</td>
<td>302 ± 57 ab</td>
<td>1.56 ± 0.07 bc</td>
<td>3.28 ± 0.14 b</td>
<td>0.088 ± 0.027 abc</td>
</tr>
<tr>
<td>0.03 mol PrA, 0.04 mol NaOH</td>
<td>0.147 ± 0.027 e</td>
<td>0.0230 ± 0.0009 a</td>
<td>0.857 ± 0.056 ab</td>
<td>289 ± 6.7 ab</td>
<td>1.56 ± 0.04 bc</td>
<td>3.23 ± 0.28 bc</td>
<td>0.119 ± 0.053 a</td>
</tr>
<tr>
<td>0.01 mol HA, 0.02 mol NaOH</td>
<td>0.708 ± 0.265 ab</td>
<td>0.0076 ± 0.0001 c</td>
<td>0.753 ± 0.069 cd</td>
<td>305 ± 18 ab</td>
<td>1.55 ± 0.07 cd</td>
<td>2.88 ± 0.11 c</td>
<td>0.069 ± 0.040 bcd</td>
</tr>
<tr>
<td>0.02 mol HA, 0.03 mol NaOH</td>
<td>0.575 ± 0.086 bc</td>
<td>0.0158 ± 0.0001 b</td>
<td>0.746 ± 0.037 d</td>
<td>274 ± 14 ab</td>
<td>1.55 ± 0.08 cd</td>
<td>2.94 ± 0.08 de</td>
<td>0.064 ± 0.020 bcd</td>
</tr>
<tr>
<td>0.03 mol HA, 0.04 mol NaOH</td>
<td>0.828 ± 0.182 ab</td>
<td>0.0230 ± 0.0004 a</td>
<td>0.736 ± 0.031 d</td>
<td>214 ± 9 b</td>
<td>1.53 ± 0.04 de</td>
<td>3.09 ± 0.08 cd</td>
<td>0.058 ± 0.018 cd</td>
</tr>
<tr>
<td>0.01 mol PA, 0.02 mol NaOH</td>
<td>0.620 ± 0.098 bc</td>
<td>0.0071 ± 0.0005 c</td>
<td>0.773 ± 0.100 dc</td>
<td>302 ± 73 ab</td>
<td>1.55 ± 0.07 cd</td>
<td>3.18 ± 0.07 bc</td>
<td>0.031 ± 0.027 d</td>
</tr>
<tr>
<td>0.02 mol PA, 0.03 mol NaOH</td>
<td>0.753 ± 0.206 ab</td>
<td>0.0162 ± 0.0010 b</td>
<td>0.909 ± 0.044 a</td>
<td>208 ± 106 b</td>
<td>1.52 ± 0.05 e</td>
<td>3.58 ± 0.02 a</td>
<td>0.050 ± 0.014 cd</td>
</tr>
<tr>
<td>0.03 mol PA, 0.04 mol NaOH</td>
<td>0.880 ± 0.095 a</td>
<td>0.0230 ± 0.0005 a</td>
<td>0.845 ± 0.030 abc</td>
<td>99 ± 23 c</td>
<td>1.50 ± 0.05 f</td>
<td>3.66 ± 0.10 a</td>
<td>0.045 ± 0.005 cd</td>
</tr>
</tbody>
</table>

a AA, Acetic anhydride; PrA, propanoic anhydride; HA, heptanoic anhydride; PA, palmitic anhydride, NaOH, sodium hydroxide; mol, molar ratio per anhydroglucose unit. Macid/AgU-relative amount of mols of acid esterifying one anhydroglucose unit. Means followed by the same letter in a column are not significantly different at 0.05 probability level according to LSD multiple range test.
level were present (Table 1). However, the level of chemical application had a statistically significant effect on the DS for all acid anhydrides used. The lowest degree of substitution was obtained with 0.01 M of acid anhydrides, and the highest was recorded with 0.03 M.

3.5. Size exclusion chromatography

The molecular weight (MW) distribution pattern of the extruded samples is illustrated in Fig. 1. A slight decrease in the amylopectin portion at about 6 min approximately corresponding to the elution time of blue dextran with average MW of 2,000,000 was observed for the acetic anhydride treatment. This was most likely attributable to the fact that acetic anhydride was the most active anhydride occurring the greatest hydrolysis of starch. The hypothesis of the increased rate of the hydrolysis was supported by the slight increase in the amount of the amyllose fraction at about 9 min (MW 200,000). This was most observable with the acetic anhydride, less noticeable for propionic anhydride and only for the 0.03 mol level of heptanoic acid. The amount of the amyllose fraction at 9 min increased with increases in the level of acetic anhydride. This increase was less with the propionic acid, was difficult to determine with the heptanoic acid, and was not apparent with the palmitic acid.

3.6. WAI and WSI

All acid anhydride treated samples, except for two palmitic anhydride (0.02 and 0.03 mol treated samples, had lower WAI than the control. No differences in the WAIs among the different levels of acetic and propionic anhydride treated samples were observed. The 0.03 mol level of heptanoic anhydride treated sample had a higher WAI than the 0.01 mol level. A similar trend was observed for the palmitic anhydride. The 0.02 and 0.03 mol levels had higher WAIs than the 0.01 mol level. Apparently, the acid esters decreased the hydrophilic character of the starch. The hydrophilic OH group of the starch was replaced with a more hydrophobic organic acid substitute, which reduced the ability of the starch to interact with water via hydrogen bonding. The higher WAI of the heptanoic and palmitic anhydrides were explained by the disruption of the crystalline structure of the starch. The bulkier heptanoic and palmitic acid residues provided more significant steric hindrance for starch crystal formation than the smaller acetic and propionic acid residues. By disrupting the crystalline structure of the starch, the opportunity for hydrogen bonding between starch and water was increased. The 0.01 mol level of palmitic anhydride was the only acid anhydride treated sample with significantly lower WSI than the control sample. No significant differences between the WSI of the...
control and any of the other anhydride treated samples were present. No significant differences were detected when the levels of the treatments were varied.

4. Conclusions

Reactive extrusion produced starch esters by co-extruding starch and organic acid anhydrides in the presence of a sodium hydroxide catalyst. Some molecular weight reduction of the amylopectin fraction was detected. The effect was diminished when the level of anhydride was reduced or when higher molecular weight anhydrides were used. An increase in extrudate unit density and a decrease in extrudate solid density were present with an increase in the molecular weight of the anhydride. Specific mechanical energy decreased with the addition of heptanoic and palmitic anhydrides. The higher levels of anhydride lowered the specific mechanical energy. The water absorption index of acetic, propionic, and heptanoic anhydrides treatments decreased compared to the control and did not change with 0.02 and 0.03 mol levels of palmitic anhydride. A decrease in the water solubility index occurred with 0.01 mol level of palmitic anhydride treatments.

References