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Preparation, thermal properties, and extrusion of high-amylose starch acetates

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Starch acetates having degrees of substitution (DS) 1.5, 2.0 and 2.5 were prepared by the reaction of high-amylose cornstarch with acetic anhydride and aqueous sodium hydroxide. Differential scanning calorimetry studies revealed that water was an effective plasticizer for the starch acetates. Glass transition temperatures (T_g) of dry starch acetates (165–185°C) were lowered to 95–35°C in the presence of excess moisture. Extrusion of DS 2.5 starch acetate containing 15% moisture at 150°C gave an expanded, water-resistant foam. The foam had a higher bulk density, higher compressive strength and lower resiliency than polystyrene foam. Little degradation of the starch acetate occurred during extrusion. Possible uses for starch acetate foam include seedling containers, soil drainage aids and food packaging/serving. Published by Elsevier Science Ltd

INTRODUCTION

There has been much recent interest in the utilization of starch as a biodegradable plastic material (Swanson *et al.*, 1993; Narayan, 1994; Mayer & Kaplan, 1994; Tiefenbacher, 1993; Bastioli *et al.*, 1992; Koch *et al.*, 1993). Starch-based films, foams and molded articles have been commercialized for use as disposable garbage bags, food packaging, cutlery, plates, and cushioning. These single-use items can then be disposed of by composting rather than accumulating in landfills. Starch, however, suffers from a lack of moisture resistance and brittleness (Zobel, 1988; Shogren, 1992). Acetylation of the hydroxyl groups of starch to increase hydrophobicity is one approach toward increasing the water resistance of starch. Derivatization of starch hydroxyl groups may also reduce the tendency of starch to form strongly hydrogen-bonded networks and increase film flexibility.

There is little literature available on the preparation, properties, and utilization of starch acetate of intermediate degree of substitution (DS 1.0–2.5). Whistler and Hilbert (1944) described the preparation and mechanical properties of films cast from fully acetylated (DS 3) starch acetate. Recently, Borchers *et al.* (1993) found that starch esters (DS 1.5–2.5) could be plasticized with low molecular weight organic compounds and injection molded. Granular, intermediate DS starch esters have been prepared in aqueous suspension (Billmers & Tessler, 1993).

This paper describes a rapid method for preparing starch acetates of intermediate DS, the plasticization of starch acetates by water, and the extrusion of hydrated starch acetate into foam.

EXPERIMENTAL

Materials

High (70%) amylose starch was amylomaize VII from American Maize-Products, Hammond, IN. It had a moisture content of 13.5%. High-amylose starch was chosen for this study because previous work (Whistler & Hilbert, 1944) had demonstrated that films cast from fully acetylated normal starch (27% amylose) were very brittle, while acetylated amylose films were more flexible. Acetic anhydride, 98%, was from Aldrich and Eastman. 2,6-Di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT), glyoxal and silica gel (2–400 mesh, 60 Å) were from Aldrich. Polyoxyethylene (20) sorbitan monostearate (Polycon T60K) was obtained from Witco, Newark, NJ. Other chemicals were reagent grade.

[1]Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

Preparation of starch acetates

Starch acetates of DS 1.5, 2.0 and 2.5 were prepared by a modification of the procedure of Mark and Mehltretter (1972). Reactions were performed in a 3 liter resin flask equipped with an air stirrer, thermometer, condenser and heating mantle. Starch (~500 g) was added to the flask followed by the required quantity of acetic anhydride (Table 1). For the DS level of 2.5, acetic anhydride was added in excess of the amount required to react with all the hydroxyl groups of starch as well as with the water and NaOH added. To prepare starch acetates having DS 1.5 and 2.0, only enough acetic anhydride was added to react with the water and NaOH and 1/2 and 2/3 of the hydroxyl groups of the starch, respectively. To begin the reaction, 50% aqueous NaOH (0.14 g/g starch) was added slowly while stirring the mixture. Only a small amount of current was supplied to the heating mantle. Within 5–10 min the reaction reached reflux temperature (120–128°C) and power to the heater was terminated. Heat generated by the reaction was sufficient to maintain reflux. Glacial acetic acid was added to reactions 1 and 2 to reduce the viscosity enough to allow stirring. After approximately 50 min, reactions were terminated by pouring the mixtures into cold distilled water in a blender and blending for 1 min. The white starch acetate precipitates were separated from the supernatant by filtration or decantation, resuspended in water and adjusted to pH 7, washed several times with water and dried in an oven at 40°C. Dried precipitates were ground in a Retsch mill using a 1 mm screen.

Assay of acetyl content

Acetyl contents were determined by titrations of samples hydrolyzed in sodium hydroxide solution (Mullen & Pascu, 1942).

Intrinsic viscosity

Intrinsic viscosities of starches regenerated from the acetates were determined by the procedure of Mark and Mehltretter (1970). Briefly, starch acetates were hydrolyzed in 1 M KOH for 3 days at 3°C. Viscosites were measured in the same solvent at 25°C using a Cannon-Ubbelohde #75 viscometer. Flow times were measured in duplicate and had a repeatability of <0.5 s. Care was taken to perform the measurements within 1–2 h after warming to avoid degradation due to the basic conditions. Intrinsic viscosities were determined from the intercepts of plots of $(\eta_r-1)/c$ vs. c.

Differential scanning calorimetry (DSC)

Approximately 20 mg of dry (3–5% moisture) starch acetates were placed in stainless steel DSC pans (Perkin-Elmer #0319) and then these were placed in a desiccator containing water to gain moisture to the desired level. Pans were then sealed and left to equilibrate for 1 day. Differential scanning calorimetry was performed with a Perkin-Elmer DSC7 equipped with a CCA7 cooling accessory. The instrument was calibrated using the melting temperatures and enthalpies of water and indium. Samples were heated from 5 to 160°C at 10°C/min then cooled at 200°C/min to 5°C, and reheated. Glass transition temperatures were calculated using DSC7 software.

X-ray diffraction

X-ray powder diffraction analysis was performed with a Philips 1820 diffractometer operated at 40 kV, 30 mA with graphite filtered CuK_α radiation and a theta compensating slit. Data were acquired in 0.05 degree two theta, 4 s steps.

Extrusion of starch acetate foams

Samples of starch acetate (DS 2.5) were mixed with water and other reagents (Table 2) and left to set overnight to equilibrate. These mixtures were then extruded into foam using a Brabender PL2000 3/4 inch single screw extruder. The screw had a 30/1 L/D and 3/1 compression ratio, screw speed was 30 rpm, temperatures were 100, 150, 150 and 155°C (die end) and die diameter was 2.4 mm. The torque was 3–15 Nm and the die pressure 5–20 bar (0.5–2 MPa).

Mechanical testing of foams

Foam samples were equilibrated at 23°C and 50% relative humidity for 45 days prior to testing. Testing was carried out using a method similar to that described by Lacourse and Altieri (1989). A 1/4 inch diameter steel probe was attached to the crosshead of an Instron model 4201 Universal Testing Machine. A piece of foam was placed on the base and the probe was lowered until contact was made and the load reached 0.5 N. The probe was then lowered at 30 mm/min for a distance of 3 mm, held for 60 s and then raised. Compressive strength was calculated as the maximum load/cross-sectional area of the probe while resiliency was the load at the end of the 60 s relaxation period/maximum load.

RESULTS AND DISCUSSION

Preparation of starch acetates

Under the reaction conditions given in Table 1, the solvent for the reaction is essentially acetic anhydride and acetic acid. Initially, residual water and sodium

Table 1. Preparation of starch acetates

Reaction	Acetic anhydride[1]	50% NaOH[1]	Acetic acid[1]	Reaction time (min)[2]	DS[3]
1	2.2	0.14	0.95	50 (10)	1.55
2	2.5	0.14	0.42	50 (20)	2.00
3	3.4	0.15	0	50	2.50

[1] Ratio of reagent weight to starch weight.
[2] Parentheses indicate reaction was completed (evolution of heat ceased) in approximately this amount of time.
[3] Degree of substitution; reproducibility ± 0.05.

Table 2. Composition of starch acetate (DS 2.5) formulations for extrusion into foam

Sample	Water (%)	Additive (%, type)[1]	Silica (%)[1]
A	15	none	0
B	15	3% sodium citrate	0.5
C	15	0.1% BHT[2], 0.3% POESMS[3]	0.5
D	15	0.5% glyoxal	0.5

[1] Percentage of additive based on starch acetate weight.
[2] Butylated hydroxytoluene.
[3] Polyoxyethylene sorbitan monostearate.

hydroxide probably act to swell the starch and make it more reactive with the anhydride. As water and NaOH react with anhydride, the temperature rapidly rises. The starch then begins to react and dissolve, forming a viscous solution.

Reaction 1 in Table 1 was very rapid, being essentially complete within a few minutes after reaching reflux temperature (based on observation of decreasing reaction temperature and bubbling). Reaction 2 was somewhat slower, reaching completion 5–10 min after reflux. Reaction 3 was the slowest, with reflux still continuing without added heat after 50 min. Since the volume of acetic anhydride increases from reaction 1 to 3, the concentration of catalyst (NaOH) is reduced and may cause slowing of the reaction. The rate of acetylation may also decrease with increasing DS of the starch.

Interestingly, starch acetate of DS 2.5 was obtained from reaction 3 in 50 min compared to 3 h obtained by Mark and Mehltretter (1972) using a similar procedure. One possible reason for the difference is that they preheated the starch and anhydride before adding NaOH, while in the present work, the former were cool when NaOH was added. The starch may have had more time to be swollen by water and NaOH when heating was gradual. Billmers and Tessler (1993) have recently prepared DS 0.5–1.8 granular starch esters by reaction of starch with anhydrides and NaOH in aqueous suspension. Reaction times were rather long (2–8 h), probably because of the need to hold reaction temperatures at less than 40°C to avoid gelatinization and dilution of the reaction with large amounts of water.

Structural and thermal properties

Table 3 shows intrinsic viscosity data for starch acetates and native starch. The acetylation procedure apparently causes little reduction in the molecular weight of the starch. This is in agreement with the data of Mark and Mehltretter (1972) for DS 3 starch acetates.

X-ray diffraction scans of starch acetate samples are shown in Fig. 1. The native B-type crystalline structure of the high amylose starch is lost after acetylation. It is well known (Jarowenko, 1986) that chemical modification of starch, even at low DS levels, will slow or suppress recrystallization of gelatinized starch. Therefore, it is understandable that no A- or V-type X-ray patterns, commonly observed after retrogradation of starch, are observed for the more highly substituted starch acetates. Fully substituted (DS 3) amylose acetates were found to partially crystallize after annealing or orientation (Wolff *et al.*, 1951).

Water vapor sorption isotherms for starch acetates are shown in Fig. 2. As expected, water absorption decreases as the DS increases.

Table 3. Intrinsic viscosity of starch acetates and native starch

Degree of substitution	Intrinsic viscosity (dl/g)[1]
0	1.28
1.55	1.24
2.00	1.22
2.50	1.18

[1] Samples were treated with 1 M KOH for 3 days at 3°C to remove acetate groups; intrinsic viscosities were then measured at 25 °C in the same solvent.

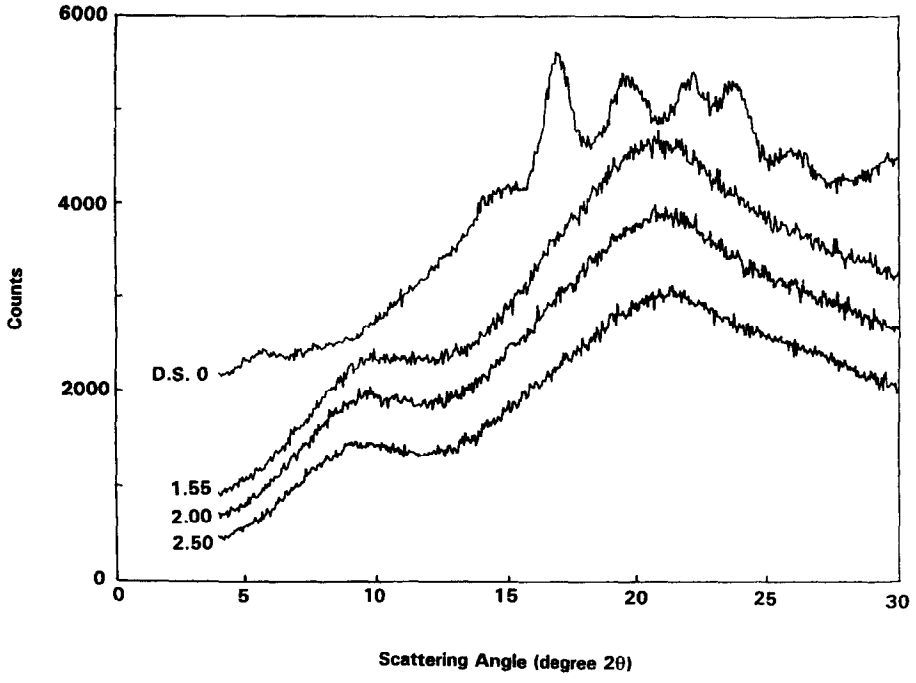

Fig. 1. X-ray powder diffraction scans of native high-amylose starch (DS 0) and starch acetates having DS 1.55, 2.0 and 2.5.

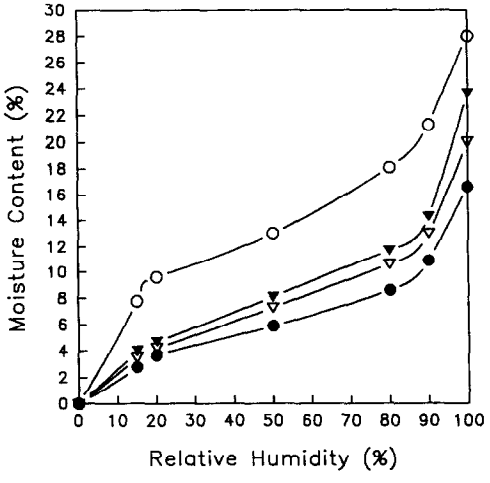

Fig. 2. Moisture absorption isotherms for native high-amylose starch (○) and starch acetates having DS 1.55 (▼), 2.0 (▽) and 2.5 (●).

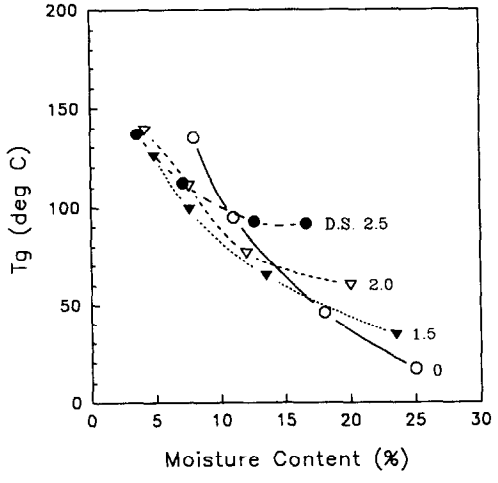

Fig. 3. Plots of glass transition temperature vs. moisture content for native high-amylose starch (○) and starch acetates having DS 1.55 (▼), 2.0 (▽) and 2.5 (●).

Plots of glass transition temperature (T_g) vs. moisture content for starch acetates are presented in Fig. 3. Data for unmodified high-amylose cornstarch are also shown for comparison (Shogren, 1994). Values of T_g for dry starch acetates obtained by extrapolation of $1/T_g$ vs. moisture content are given in Table 4. Values of T_g for samples equilibrated to 100% r.h. at 23°C are also shown in Table 4.

Glass transition temperatures decrease with increasing DS for dry starch acetates. Replacement of hydroxyl by acetyl groups probably decreases the extent of intermolecular hydrogen bonding and allows more molecular mobility in the dry state. Values of T_g decrease with increasing moisture content for all samples, indicating that water interacts with the starch acetates to increase free volume. The glass transition temperature for starch acetate of DS 2.5 is decreased the least by water. Addition of water above approximately 12% causes no further decrease in T_g below 93°C for this sample. It is likely that the hydroxyl and acetate groups have bound as much water as possible at this stage and that any additional water forms a separate phase. Samples having DS 2.0 and 1.5 have lower values of T_g (60 and 35°C) when equilibrated to 100% r.h. since the greater number of hydroxyl groups causes more water absorption and an increase in free volume.

Table 4. Effect of moisture on the glass transition temperature (T_g) of starch acetates

Degree of substitution	T_g (°C, dry)[1]	T_g (°C, wet)[2]
0	230	~0
1.55	185	35
2.00	175	60
2.50	165	93

[1] Values of T_g at 0% moisture determined by extrapolation of $1/T_g$ vs. moisture content.
[2] Values of T_g determined after exposure of samples to 100% relative humidity at 23°C.

These glass transition data are important since they define temperatures where extrusion processing is possible and useful temperature ranges for practical applications. For applications involving exposure to water, a starch acetate could be selected having a T_g higher than the expected use temperature. Processing temperatures would need to be greater than the experimental value of T_g.

Properties of extruded starch acetate foams

To test the ease of extrusion processing of starch acetates, a sample having a DS of 2.5 and moisture content of 15% was selected (Sample A, Table 2). Sample B was identical except that sodium citrate was added to maintain a neutral pH and protect against possible acidic degradation of the starch acetates. Butylated hydroxytoluene (BHT) was added to sample C to lessen oxidative degradation. A surfactant was also added to C to help disperse the BHT and to reduce surface tension and bubble size of the extrudate. Sample D contained glyoxal which could cross-link the starch acetate and increase strength. Samples B–D also contained silica which is thought to act as a bubble nucleating agent (Neumann & Seib, 1993).

Table 5 shows the effects of extrusion at 150°C on the intrinsic viscosity and pH of starch acetate DS 2.5. Intrinsic viscosities decrease only slightly after extrusion, indicating that little degradation of the starch backbone occurs during extrusion. pH values for the starch acetates declined from about 5 before to 4 after extrusion, indicating that few of the acetate groups were hydrolyzed during extrusion. (A pH of 4 corresponds to an acetic acid concentration of 4×10^{-4} M.) The pH of the sample buffered with citrate remained at 6.6. These data suggest that extrusion at 150°C for several minutes in the presence of water does not cause significant degradation of starch acetate.

Physical and mechanical properties of extruded starch acetate foams are presented in Table 6. The expansion ratio was largest and bulk density lowest for sample B. The sodium citrate in B may act to bind water in the system, thus increasing rigidity and expansion. Sample C had the lowest expansion ratio due to collapse of the foam soon after exiting the extruder. The presence of surfactant (polyoxyethylene sorbitan monostearate) probably acted as a plasticizer for the starch acetate causing the softer foam to collapse on cooling. Sample D which contained glyoxal was brown and suffered more degradation than the other samples (Table 5). All starch acetate foams were 10 or more times more dense than commercial expanded polystyrene foam. As a result, compressive strengths for starch acetate foams were also much higher than for polystyrene foam. The resiliency or degree of volume recovery after compression was less for starch acetate foam than for polystyrene foam. Pore sizes for the starch acetate foams were quite large (1–3 mm) compared to those for polystyrene foam (0.05–0.2 mm) (Shutov, 1991).

The properties of extruded starch acetate foams could probably be improved by changing formulations and extrusion conditions. Expansion ratios might be

Table 5. Effect of extrusion on intrinsic viscosity and pH of DS 2.5 starch acetate

Sample	Intrinsic viscosity (dl/g)[2]	pH[1]
before extrusion	1.18	4.9
A	1.15	4.0
B	1.13	6.6
C	1.15	4.5
D	1.09	4.2

[1] pH of a suspension of 1 g sample in 4 ml distilled water
[2] In 1 M KOH (see Table 3).

Table 6. Properties of extruded starch acetate (DS 2.5) foams

Sample	Expansion ratio[1]	Bulk density (g/l)	Compressive strength (Pa)[2]	Resiliency (%)[3]
A	16	43	460	61
B	21	37	520	64
C	10	62	540	65
D	14	54	550	63
polystyrene foam	—	4	51	78

[1] Extrudate area/die area.
[2] Maximum load/area of 6.3 mm diameter probe at 3 mm insertion depth.
[3] Load after 1 min delay/maximum load.

increased by lowering the moisture content during extrusion so as to increase melt elasticity and die pressure. A higher compression ratio screw could also be helpful in increasing die pressure given the difficulty of filling the screw with fluffy starch acetate powder. Melt elasticity needs to be high to prevent bubble rupture and collapse (Kim & Kim, 1991). Higher flow rates or die pressures give a more rapid and extensive foam expansion (Kim & Kim, 1991). Melt viscosities and die pressures were both rather low in the experiments described above (see Experimental section). Pore size and wall thickness could be reduced by appropriate selection of a hydrophobic additive to reduce surface tension and a nucleating agent. Bubble size also generally decreases with lower blowing agent content (Kim & Kim, 1991).

Interestingly, attempts to prepare extruded foams from cellulose acetate, DS 2.5, and water were unsuccessful due to very high melt viscosites (the screw locked up). Higher melt viscosites for cellulose acetate than starch acetate probably result from the more highly extended nature of the cellulose backbone (Brant & Christ, 1990). This is supported by preliminary DSC experiments on cellulose acetate, DS 2.5, which gave higher glass transition temperatures (T_g = 200°C (dry), 105°C (wet)) than starch acetate. The more highly extended cellulose acetate molecules probably pack together more efficiently giving a system with a lower free volume and greater crystallinity than starch acetates.

In conclusion, a rapid method for the preparation of starch acetates of intermediate DS has been developed and the effect of water on the thermal and extrusion properties has been characterized. Although many compounds such as triacetin and acetyl triethyl citrate are known to plasticize starch acetates, use of water as a plasticizer or co-plasticizer may be advantageous in cases when a foamed structure is desired or when leaching of plasticizer may be a problem. The latter may be important in applications such as foamed packaging for food. Other possible applications are biodegradable soil drainage aids, seed propagation blocks, and replacements for polystyrene foam and vermiculite/perlite.

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