

Physical Properties of Extruded Strands of Hydroxypropylated Normal and High-Amylose Corn Starch¹

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ABSTRACT

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Normal (25% amylose) and high-amylose (70% amylose) corn starches (CS and HA) were hydroxypropylated to 0.1 degree of molar substitution (MS) with propylene oxide in an alkaline-ethanol medium (70% ethanol). CS and hydroxypropylated corn starch (HPCS) were mixed on dry basis with water and glycerol at a weight ratio of 7:2:1, and HA and hydroxypropylated high amylose corn starch (HPHA) were mixed at 7:3:1. Stearic acid, glycerol monostearate, or lecithin (3%, based on starch) was added to each mixture to examine the effects on the physical properties of the extrudate. The starch mixtures were extruded at high shear (100 rpm) to nonexpanded strands using a corotating twin-screw extruder in a temperature range of 75–90°C. HA, alone and with all additives, showed lower die swelling in extrusion than did CS, whereas HPCS and HPHA showed higher die swelling than the corresponding unmodified starches. Water absorption of all HA extrudates was lower than those of all CS

extrudates (22–35% and 68–97%, respectively, at 25°C). Hydroxypropylation increased the absorption for both starches. All extruded starches, regardless of additives, showed low solubility in water (0.1–1.0% for 2 hr at 25°C). Differential scanning calorimetry indicated that during extrusion, the lipid additives formed a helical complex with amylose in CS and HA, but weakly with HPCS and HPHA. The extruded strands of HA, alone and with additives, exhibited higher tensile and bending strengths (37.1–58.4 and 2.16–5.07 MPa, respectively), compared to the CS strands (12.5–59.3 and 1.06–4.10 MPa, respectively) at the same moisture content (7.5–8.5%). Both tensile strength and percent of elongation of the starch strands were reduced by the presence of a lipid additive. Hydroxypropylation increased elongation and flexibility of the extrudates. HPHA exhibited the greatest mechanical strength and flexibility among the tested starches.

Utilization of starch as a degradable plastic material has been reported in numerous publications during the recent years. Applicable products include various plastic items such as polyethylene films, injection-molded plastics, thermoformed containers, and expanded foams. In plastics where starch is used as the major component, starch usually exists in its molecularly dispersed state. The plastic films and articles containing gelatinized starch are susceptible to direct water contact or moisture uptake from the atmosphere. Various techniques have been introduced to improve the water resistance of the starch-based products. For example, blending starch with water-resistant synthetic polymers is commonly practiced to improve the water resistance of the plastics (Otey et al 1974, 1977; Fanta and Doane 1986; Wiedmann 1987). In blends or composites, however, the inherent incompatibility between starch and hydrophobic polymers often resulted in the loss of original mechanical properties. In addition, the incorporation of a non-degradable polymer will reduce the degradability of the starch-based product.

Hydrophobic cereal proteins that are relatively compatible with starch, such as corn zein and wheat gluten, have been blended with starch to improve water resistance and strength of molded plastics (Cole and Daumesnil 1989, Lim and Jane 1993). Recently, degradable polyesters produced from microbial fermentation or chemical synthesis have been blended with starch to produce molded disposable plastics. By using proper compatibilizers or blending techniques, the composites displayed relatively good mechanical properties and water resistance (Shogren 1993, Chapman 1996, Shogren and Lawton 1996). However, high unit price of degradable polyesters remains an obstacle.

Films and coatings made solely from starch have lower oxygen permeability when compared to many synthetic polymer films (Swanson 1992). This barrier property allows starch to be used as a protective material for oxygen-susceptible items. Another commercially available plastic made almost entirely from starch is biodegradable loose fill packaging. Currently, the patented tech-

nology using extruded hydroxypropylated amylose has been used to replace expanded polystyrene (Altieri and Lacourse 1991). Amylose was reportedly superior to amylopectin in the physical properties of cast films and extruded foams because of its structural linearity (Wolff et al 1951, Muetgeert and Hiemstra 1958, Lloyd and Kirst 1963, Jokay et al 1967, Altieri and Lacourse 1991, Swanson 1992, Louridin et al 1995).

Hydroxypropylation was used to improve mechanical properties of starch-based films and expanded loose fill (Roth and Mehlretter 1967, Altieri and Lacourse 1991). Roth and Mehlretter (1967) reported that tensile strength of amylo maize starch film was reduced by hydroxypropylation, but elongation and burst strength were increased. Hydroxypropylated amylo maize starch had higher resilience than the unmodified starch when used for expanded loose fill packaging (Altieri and Lacourse 1991). In addition, this modification technique is currently used in altering the pasting properties of starch for food use.

In this study, normal and high-amylose corn starches (CS and HA) were hydroxypropylated to 0.1 degree of molar substitution (MS). The parent and modified starches were then extruded with a lipid additives, including stearic acid, glycerol monoester of stearic acid, or lecithin. The mechanical and water-resistance properties of the extruded strands were measured to determine the effects of hydroxypropylation and the lipid additives.

MATERIALS AND METHODS

Materials

Normal corn starch (25% amylose) and HA (70% amylose) were provided by Samyang Genex (Seoul, Korea) and Cerestar Inc. USA (Hammond, IN). Lecithin, as a lipid additive, was provided by America Lecithin Co. (Danbury, CT). Stearic acid and glycerol monostearate were purchased from Kokusan Chemicals Works Ltd. (Tokyo, Japan) and Ilsin Chemicals (Seoul, Korea).

Starch Hydroxypropylation

Normal and HA corn starches were hydroxypropylated according to the method reported by Choi et al (1997). To obtain a high degree of molar substitution (MS) of the hydroxypropyl group while maintaining granular structure, starch was modified in an aqueous ethanol (70%) medium at 33% of starch (dry basis). The MS was measured using a spectrophotometric method reported

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by Johnson (1969). Starch was mixed with 10% propylene oxide (v/w, based on starch dry weight) in the presence of 2.4% NaOH (w/w, based on starch dry weight) for 18 hr at 60°C. The MS values of the hydroxypropylated normal (HPCS) and high-amylose corn starches (HPHA) were 0.096 and 0.098, respectively.

Extrusion of Starch

The CS or HPCS (210 g, dry weight) was mixed with a glycerol solution in water (30 g in 60 mL) using a Hobart mixer. The HA or HPHA was mixed with 90 mL of water and 30 g of glycerol. More water was required for the HA to be extruded at the same temperature range as that for CS. Stearic acid, glycerol monostearate, or lecithin (6.3 g, equivalent to 3% starch basis) was added to the mixture. Using a corotating twin-screw extruder (Baek Sang Instruments, Umsung, Korea), the mixtures were extruded into nonexpanded strands through an opening 3.6 mm in diameter. Screw speed was a 100 rpm and barrel temperatures were 75, 85, 95, and 90°C from the feeding zone to the die. The feeding rate was 30 g/min, and the screw was configured without kneading or reverse flight in a L/D ratio of 24 with a screw diameter of 31 mm. The strands were allowed to extrude through the die without any force of pulling.

Die Swelling

Cross-sectional area of extruded strand was measured after 5 min of cooling after extrusion. Its ratio to the die hole area was calculated as the die swelling value. Die swelling has been called sectional expansion index by some authors (Alvarez-Martinez et al 1988).

Thermal Analysis

The extrudates were thermally analyzed using differential scanning calorimetry (DSC) (6100, Seiko Instruments, Japan) calibrated

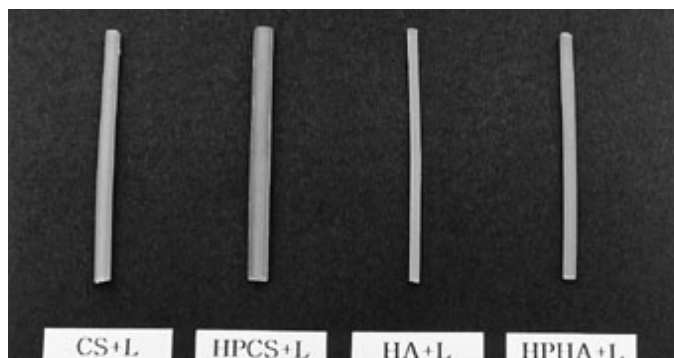


Fig. 1. Extruded strands of normal corn starch (CS), high-amylose corn starch (HA), hydroxypropyl corn starch (HPCS), and hydroxypropyl high-amylose corn starch (HPHA) containing 3% lecithin (L) (w/w, based on starch). CS and HPCS were extruded with water and glycerol at 7:2:1; HA and HPHA were extruded at 7:3:1.

by indium. The extruded strands were dried at 40°C overnight, then ground and sieved to collect the particles passing through a 50-mesh sieve. Ground sample (1.5–2.0 mg) was weighed in an aluminum pan, and distilled water (4× starch weight) was added. DSC analysis was performed from 25 to 140°C at a heating rate of 10°C/min under nitrogen flow. Rescanned thermograms were obtained under the same conditions immediately after cooling a scanned sample with an ice bath.

Tensile Properties

The extruded strands were cut into pieces 30 cm long and dried at 40°C until the moisture content reached a range of 7.5–8.5%. Moisture contents of the strands were measured after drying the crushed pieces of the strands at 105°C for 4 hr.

Tensile strength and percent of elongation of the moisture-adjusted strands were measured with a texture analyzer (Instron 1011, UK). Gauge length was 80 mm, and the testing speed was 50 mm/min. To prevent the slippage of a specimen at the grips, thin rubber layers were glued on both sides of the grip surface, and sandpaper was glued on top of the rubber layers.

Bending Strength

Bending tests of extruded strands was performed using a texture analyzer (TX-XT2, Stable Microsystem, UK). A moisture-adjusted (7.5–8.5%) strand was placed on a plate with a cutting slot 45 mm wide, and a V-shaped dull knife was moved down perpendicularly to the strand at a speed of 3.0 mm/sec. The stress and strain at the breaking point were measured.

Water Resistance

A moisture-adjusted strand was cut into 1-cm pieces, and the pieces (≈1.0 g) were immersed in 30 mL of water for 2 hr at room temperature without stirring. The strand pieces were carefully taken from water, and water was gently removed from the surface with a paper towel. Percentage of the weight gain from the water immersion to the original weight of the pieces was calculated as percent of water absorption. The aqueous solution was filtered (Whatman No. 41), and the filtrate was tested to determine the total soluble starch content using the phenol-sulfuric acid method (Dubois et al 1956). Glycerol can leach from the extrudate during the test. In a preliminary test, glycerol also formed a pale orange color with phenol and sulfuric acid. But this effect was ignored because the color intensity was insignificant when compared to that of starch at the same concentration.

Statistical Analysis

The data were analyzed with a statistical analysis system (SAS Institute, Cary, NC). Mean differences were calculated using a least significant difference (LSD) test at $P < 0.05$.

TABLE I
Die Pressure and Die Swelling During Extrusion of Normal and High-Amylose (70%) Corn Starches with Additives^a

Additives ^b	CS		HPCS		HA		HPHA	
	Pressure (MPa)	Die Swelling ^c	Pressure (MPa)	Die Swelling	Pressure (MPa)	Die Swelling	Pressure (MPa)	Die Swelling
W	0.49	1.10	0.30	1.35	1.96	0.67	0.30	0.87
WG	0.98	1.80	0.98	2.09	2.94	0.71	0.98	0.95
WGS	2.45	1.01	1.47	2.48	3.43	0.69	1.47	1.34
WGM	2.94	1.04	2.45	2.00	2.94	0.74	0.98	1.36
WGL	1.47	2.03	0.98	3.09	2.94	0.69	0.98	1.21
LSD ^d	0.15	0.17	0.20	0.24	0.11	0.03	0.10	0.11

^a Extrusion temperatures 75–85–95–90°C (feeding zone to die). Screw speed 100 rpm. Normal corn starch (CS) was mixed with water and glycerol at 7:2:1. High-amylose corn starch (HA) was mixed at 7:3:1. HPCS = hydroxypropylated corn starch. Degree of molar substitution (MS 0.1). HPHA = hydroxypropylated high-amylose corn starch (MS 0.1). Three replicates for each starch.

^b W = water, G = glycerol, S = stearic acid, M = glycerol monostearate, L = 3% lecithin (w/w, based on starch).

^c Die swelling is the ratio of extruded strand measurement to the die hole area.

^d Least significant difference ($P < 0.05$).

RESULTS AND DISCUSSION

Die Swelling

HA showed a relatively lower degree of die swelling (0.67–0.74) than did CS (1.01–2.03) (Fig. 1 and Table I). And HA extruded with more water built greater die pressure than CS (Table I). HPCS and HPHA, however, showed higher die swelling than did the corresponding unmodified starches. The reason for the shrinkage in cross-sectional area of the HA extrudates, with or without an additive, is unknown. The extrudate underwent linear expansion rather than radial expansion at the die. One possible explanation is that the amylose molecules become aligned with the direction of the flow through the die, and the flow in the linear direction upon leaving the die meets less resistance than it does in the radial direction. This molecular alignment led to the shrinkage of the strands, and the temperature drop while the extrudate exited the die might have accelerated this shrinkage.

Hydroxypropylation and glycerol addition increased die swelling of both CS and HA (Table I). Hydroxypropylation generally facilitates starch gelatinization and inhibits the molecular reassociation between starch chains (Tuschhoff 1986). Therefore, the decreased degree of intermolecular reassociation resulted in the high degree of die swelling. Glycerol behaves as a plasticizer for starch providing free molecular volume and mobility of the starch chains. Therefore, the molecular association between aligned starch chains might be hindered by the presence of glycerol, so the die swelling increased.

During the dehydration for moisture adjustment, CS and HPCS strands occasionally showed wrinkles on the surface of the strands, whereas HA and HPHA retained their initial appearance and shape. This indicates that the HA, regardless of the modification, forms a more stable matrix of starch molecules than CS does. The hydroxypropylated starch strands required longer periods of drying to reach the desired moisture range than the native starch strands, indicating the imparted hygroscopic property of the hydroxypropyl groups (Wootton and Manatsathit 1983).

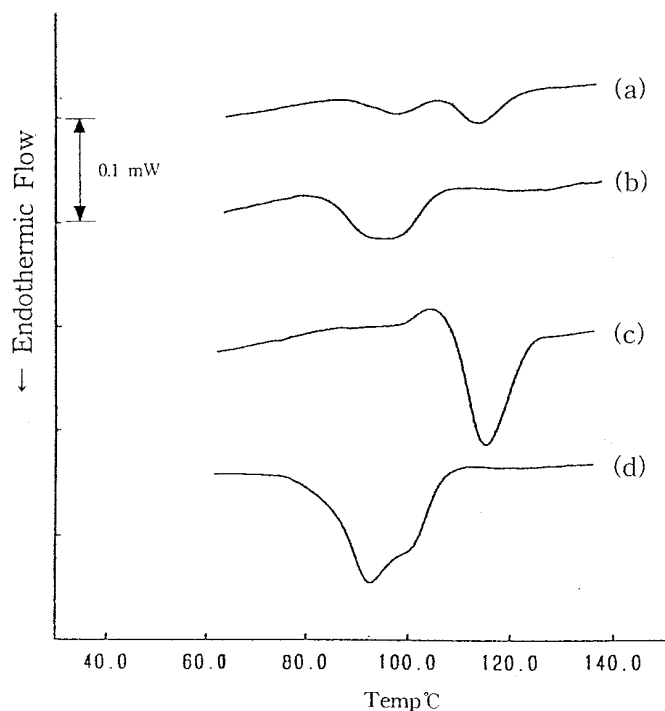


Fig. 2. Differential scanning calorimetry thermograms of extruded strands of normal corn (a) and high-amylose corn starch (c) containing 3% stearic acid (w/w, based on starch). Thermograms b and d were rescans of a and c, respectively.

The strands without lipid additive or glycerol (W in Table I) occasionally showed bubbles inside the strands during extrusion. Changes on the surface were also frequently observed during drying. Addition of glycerol (WG) caused the strands to have a smooth surface appearance.

Thermal Transitions

The extrudates of native and hydroxypropylated starches showed no endothermic peaks for starch melting on DSC thermograms, indicating that starch had been fully gelatinized by the extrusion (data not shown). Thermograms of the CS and HA starch extrudates containing stearic acid (3% based on starch), however, showed transitions over a wide temperature range (85–125°C) with melting enthalpies of 3–5 J/g (Fig. 2a and c). This transition (85–125°C) is typical for a lipid complex with amylose. The endogenous lipids (<1.0%) in the corn starches apparently formed no detectable complex in the relatively dry (20–30% moisture) and rapid extrusion procedure.

Melting of the complex in extrudates of unmodified starches (Fig. 2a and c) appeared to be biphasic, and the remelting (Fig. 2b and d) appeared at reduced temperature ranges (75–110°C). This change in the melting temperature of V-complex upon rescanning has been reported by Galloway et al (1989). The bimodal phasic profiles in the melting of the complex might have resulted from the structural heterogeneity and metastable behavior of an amylose-lipid complex (Biliaderis et al 1985, Galloway et al 1989). The melting enthalpy of the stearate complex in the rescanned thermograms appeared higher than that in the initial thermograms (Fig. 2). Possibly, some uncomplexed stearic acid remaining in the strands interacted with amylose during the second heating in the DSC analysis, causing the increased melting enthalpy.

The HPCS extruded with stearic acid gave a melting transition with a much lower enthalpy of melting (≈ 0.5 J/g) at a lower temperature range of 55–60°C when compared to the unmodified starches (Fig. 3). From the rescanned thermograms (Fig. 3b and d), this transition was reversible, which is typical for V-complex melting. HPHA extrudate with stearic acid gave two endothermic

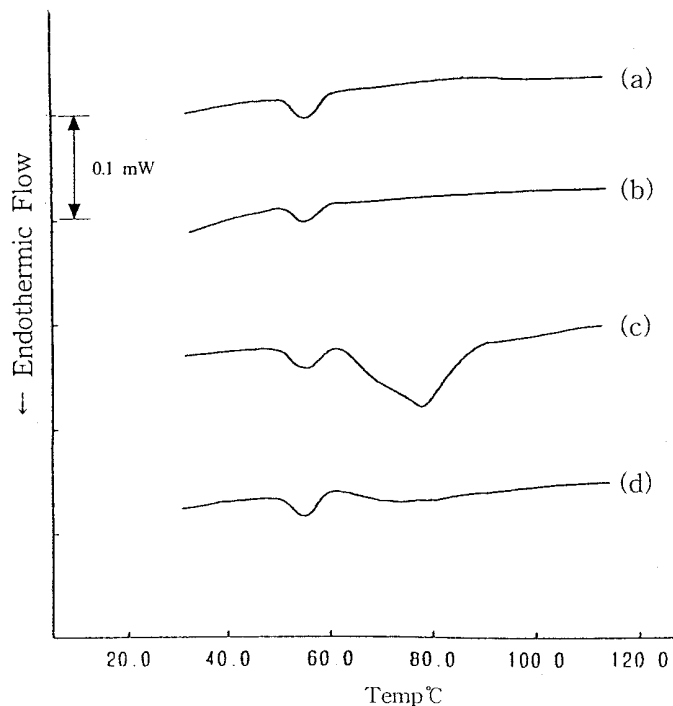


Fig. 3. Differential scanning calorimetry thermograms of extruded strands of hydroxypropyl corn starch (a) and hydroxypropyl high-amylose corn starch (c) containing 3% stearic acid (w/w, based on starch). Thermograms b and d were rescans of a and c, respectively.

peaks: a low enthalpy peak at 50–60°C and a high enthalpy peak at 60–90°C. The low temperature peak is likely caused by hydroxypropylated amylose, whereas the high temperature transition is assignable to amylose in HA that was not substituted. The high-temperature transition was not observed on rescanning, probably because the unmodified amylose had less mobility than the hydroxypropylated amylose.

The low melting temperature and low enthalpy of the HPCS and HPHA indicate a weak lipid complex formation of the hydroxypropylated amylose molecules, which agrees with previous results on acetylated high-amylose corn starch and hydroxypropylated potato starch (Eliasson et al 1988, Kim et al 1992). Chemical modifications of granular starch occur mainly on the starch molecules residing in the amorphous regions. Amylose is believed to exist mainly in the amorphous region, and the hydroxypropyl groups on amylose may inhibit the single helix formations by complexing with lipids because of increased steric hindrance.

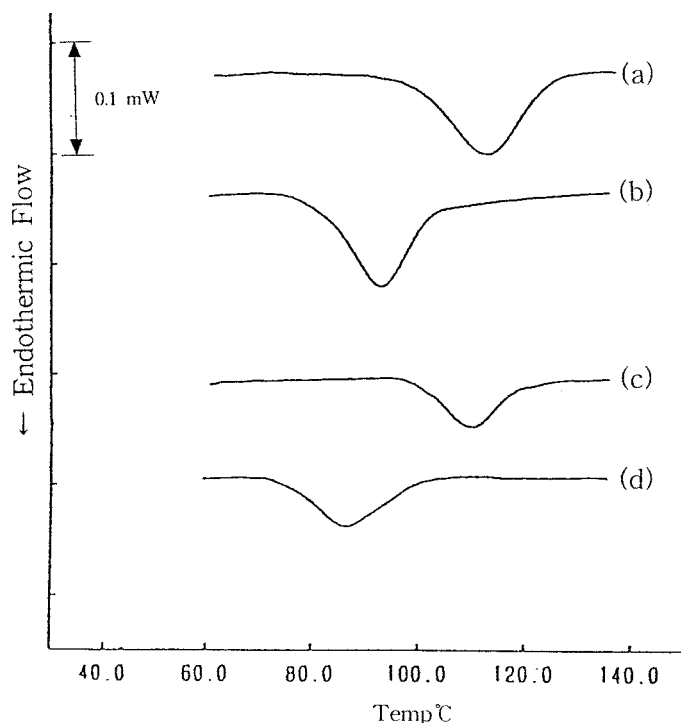


Fig. 4. Differential scanning calorimetry thermograms of extruded strands of normal corn starch (a) and high-amylose corn starch (c) containing lecithin (3% w/w based on starch). Thermograms b and d were rescans of a and c, respectively.

TABLE II
Tensile Strength of Extruded Starch Strands from Normal and High-Amylose (70%) Corn Starches with Additives^a

Additives ^b	Tensile Strength (MPa)			
	CS	HPCS	HA	HPHA
W	59.3	63.0	58.4	57.6
WG	29.6	29.6	44.0	56.3
WGS	12.5	15.4	38.9	42.6
WGM	15.5	24.8	42.1	44.9
WGL	28.3	26.0	37.1	40.1
LSD ^c	7.4	5.5	4.6	4.2

^a Strands were dried to 7.5–8.5% moisture before testing. CS = normal corn starch, HA = high-amylose corn starch, HPCS = hydroxypropylated corn starch, HPHA = hydroxypropylated high-amylose corn starch. Five replicates for each starch.

^b W = water, G = glycerol, S = stearic acid, M = glycerol monostearate, L = 3% lecithin (w/w, based on starch).

^c Least significant difference ($P < 0.05$).

Glycerol monostearate, a monoglyceride, showed melting patterns similar to those of stearic acid on DSC thermograms (data not shown). Lecithin, a diglyceride, which was reportedly difficult to complex with amylose because of its two hydrocarbon chains (Osman et al 1961), also showed complex melting peaks similar to those of stearic acid on DSC thermograms (Fig. 4). But the DSC peaks of lecithin-amylose complex appeared monophasic. Unlike stearic acid, the hydroxypropylated starches (HPCS and HPHA) showed no amylose complex peak on the thermograms when lecithin was added (data not shown). This also indicates that lecithin is more difficult to complex with amylose when compared to stearic acid.

Tensile Strength and Elongation

The HA extrudates, with or without lipid additive, showed relatively higher tensile strength value (37.1–44.0 MPa) than the CS extrudates (12.5–29.6 MPa) when glycerol was added (Table II). It has been reported by many researchers that HA or amylose has superior mechanical properties over CS in plastic products such as films and foam articles (Wolff et al 1951, Muetgeert and Hiemstra

TABLE III
Elongation at the Break of Extruded Starch Strands from Normal and High-Amylose (70%) Corn Starches with Additives^a

Additives ^b	Elongation (%)			
	CS	HPCS	HA	HPHA
W	3.45	5.03	3.44	8.35
WG	2.33	4.00	3.43	6.70
WGS	1.43	3.47	2.75	4.80
WGM	1.99	2.40	2.15	3.80
WGL	2.13	4.93	3.21	7.19
LSD ^c	1.22	0.97	0.80	1.05

^a Strands were dried to 7.5–8.5% moisture before testing. CS = normal corn starch, HA = high-amylose corn starch, HPCS = hydroxypropylated corn starch, HPHA = hydroxypropylated high-amylose corn starch. Five replicates for each starch.

^b W = water, G = glycerol, S = stearic acid, M = glycerol monostearate, L = 3% lecithin (w/w, based on starch).

^c Least significant difference ($P < 0.05$).

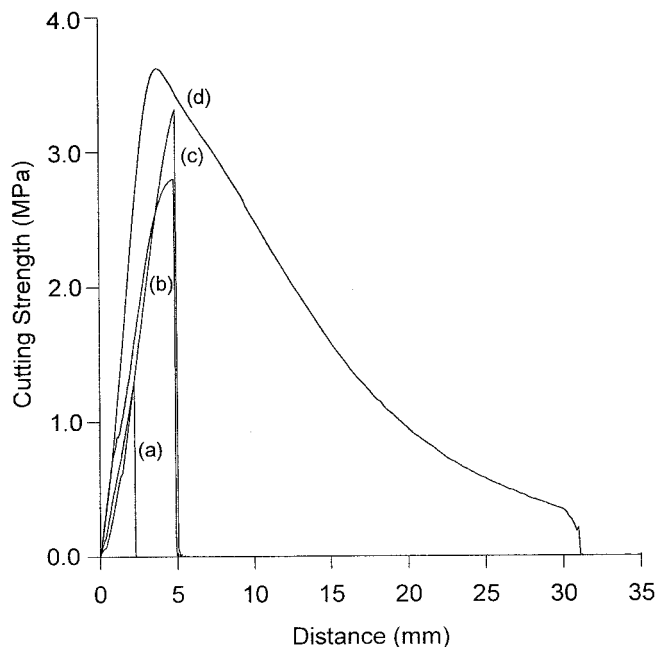


Fig. 5. Stress-strain curves from the bending test on extruded strands of normal corn starch (a), high-amylose corn starch (b), hydroxypropyl corn starch (c), and hydroxypropyl high-amylose corn starch (d) in the presence of 3% lecithin (w/w, based on starch).

1958, Lloyd and Kirst 1963, Jokay et al 1967, Altieri and Lacourse 1991, Swanson 1992, Lourdin et al 1995).

The presence of glycerol and the lipid additive decreased the tensile strength and elongation values regardless of amylose content and hydroxypropylation (Tables II and III). There was a large difference (29.6 vs. 44.0 MPa) between the tensile strengths of CS and HA strands that contained glycerol, whereas the same strands without glycerol had similar strength values (59.3 vs. 58.4 MPa). Plasticizer increases the free volume of polymer molecules and thus decreases the intermolecular interactions between polymer chains. These effects often impart flexibility to plastics but reduce the mechanical strength (Wolff et al 1951, Banker 1966). Assuming that the added glycerol remained in the matrix while the water was evaporated during the moisture adjustment, the residual glycerol content in the moisture-adjusted strands would be ≈12%. This amount might be excessive, beyond the optimum range to give proper flexibility and strength to the extruded starch strands.

According to Bader and Goritz (1994), fatty acids and amylose complexes in films made from 55% amylose starch did not alter their stress behavior but decreased the maximum elongation of the film. If the added lipids were not completely complexed with starch, the residual free lipids may cause inhomogeneity in the matrix and reduce the mechanical strength of the film. Kakalas and Raphaelides (1986) found that ≈9.5 g of stearic acid was required for maximum complex formation with 100 g of amylose in an alkaline solution (pH 12). Based on the approximate amylose contents in CS and HA starches (25 and 70%, respectively), 2.4 and 6.7 g of stearic acid could saturate the amylose in 100 g of CS and HA, respectively. Theoretically, the stearic acid added at 3% (w/w based on starch) would be mostly complexed with amylose in CS and HA. But in the extrusion with limited moisture contents (20–30%), amylose-lipid complexing was significantly less than in the crystallization optimized in a solution (Galloway et al 1989). The increased melting enthalpy of the complex in the rescanned DSC thermograms was in accord with the presence of some free lipids in the

extrudates of both CS and HA with stearic acid (Fig. 2) that subsequently complexed with amylose while reheating.

Hydroxypropylation resulted in the slight increase in the tensile strength (Table II) and elongation (Table III) of the extrudates. Elongation is proportionally related to the mobility of the amorphous starch molecules (Bader and Goritz 1994). It was suggested that hydroxypropyl groups functioned as an internal plasticizer, which increased the free volume and mobility of starch chains (Seow and Thevamaralar 1993). These covalently linked hydroxypropyl groups may be advantageous as plasticizers because unlike added plasticizer, the hydroxypropyl groups do not migrate or evaporate during processing and storage.

Bending Properties

Figure 5 shows the stress and strain curves from the bending test with extruded strands of the various starches all containing glycerol and lecithin. HPHA strands (Fig. 5d) were stretched over the yield point (maximum stress) without breakage, indicating that the plasticizer content might exceed the optimum range for proper rigidity. But the maximum stress value for HPHA was still higher than that of the unmodified HA (Fig. 5b). Therefore, it was assumed that the breaking strength of HPHA would increase if the plasticizer content was optimally fixed. Overall, the strands prepared with HA and hydroxypropylated starch had higher bending and breaking strength than those prepared with CS (Table IV).

Strains at breakage with hydroxypropylated starch increased significantly because of the increased flexibility of polymer chains caused by the hydroxypropyl groups. Like the tensile testing results, the additions of glycerol or the lipids did not improve the breaking properties except for the HPCS containing glycerol.

Water Resistance

Water absorption of the extruded strands with different formulations are given in Table V. All extruded samples showed <1% soluble starch. No test was done to determine glycerol leached

TABLE IV
Bending Stress and Strain of Extruded Starch Strands from Normal and High-Amylose (70%) Corn Starches with Additives^a

Additives ^b	CS		HPCS		HA		HPHA	
	Stress (MPa)	Strain (mm)	Stress (MPa)	Strain (mm)	Stress (MPa)	Strain (mm)	Stress (MPa)	Strain (mm)
W	4.10	6.16	3.73	5.78	5.07	6.78	4.35	7.74
WG	3.67	3.92	5.30	8.98	3.28	3.96	3.81	...
WGS	1.06	1.52	2.54	4.06	2.46	5.18	3.10	...
WGM	1.40	1.81	2.08	2.83	2.16	3.26	3.09	...
WGL	1.34	2.19	3.11	4.98	2.80	4.88	3.64	...
LSD ^d	0.30	0.62	0.61	0.71	0.29	1.37	0.20	...

^a Strands were dried to 7.5–8.5% moisture before testing. CS = normal corn starch, HA = high-amylose corn starch, HPCS = hydroxypropylated corn starch, HPHA = hydroxypropylated high-amylose corn starch. Five replicates for each starch.

^b W = water, G = glycerol, S = stearic acid, M = glycerol monostearate, L = 3% lecithin (w/w, based on starch).

^c Strands containing glycerol were not broken at the maximum stress point.

^d Least significant difference ($P < 0.05$).

TABLE V
Water Absorption (%) and Solubility (%) of Extruded Starch Strands from Normal and High-Amylose (70%) Corn Starches with Additives^a

Additives ^b	CS		HPCS		HA		HPHA	
	Water Absorption	Starch Solubility	Water Absorption	Starch Solubility	Water Absorption	Starch Solubility	Water Absorption	Starch Solubility
W	80.3	0.89	93.6	0.84	21.9	0.08	55.6	0.53
WG	96.9	1.03	75.9	0.50	23.8	0.04	45.7	0.18
WGS	69.7	0.53	115.5	0.61	35.5	0.09	44.7	0.16
WGM	67.6	0.19	94.6	0.37	29.1	0.09	47.2	0.24
WGL	70.4	0.14	75.6	0.19	30.3	0.10	40.7	0.14
LSD ^c	13.5	0.09	18.0	0.21	5.97	0.06	16.0	0.12

^a Strand pieces (1.0 g) were placed in water for 2 hr and weight gain was measured as water absorption. CS = normal corn starch, HA = high-amylose corn starch, HPCS = hydroxypropylated corn starch, HPHA = hydroxypropylated high-amylose corn starch. Three replicates for each starch.

^b W = water, G = glycerol, S = stearic acid, M = glycerol monostearate, L = 3% lecithin (w/w, based on starch).

^c Least significant difference ($P < 0.05$).

from the extrudates. Hydroxypropylation generally increased the water absorption of the extruded strands, but HA and HPHA, extruded alone or with additives, absorbed less water than did the CS and HPCS extrudates. Both HPHA and HPCS showed slight disintegration at the surface of the starch strands during water immersion.

Several researchers reported that amylose-lipid complexing decreased water solubility of starch (Mercier et al 1980, Schweizer et al 1986, Bhatnagar and Hanna 1994). Among the four starches tested, only CS extruded with lipids showed a significant decrease in the water absorption values. HA extruded with lipids showed a more pronounced lipid complex formation on DSC thermograms than CS did, yet those did not show significant improvement in water resistance when compared to HA extruded without lipids (Table V).

CONCLUSIONS

Extruded (<95°C) strands of HA showed lower die swelling and greater water resistance than did normal CS. Hydroxypropylated HA extruded with glycerol and mono- or diacyl lipids displayed significantly improved mechanical strength and elongation when compared to native or hydroxypropylated CS. The lipid additives (3% based on starch) that complexed with unmodified starches during extrusion had little effect on water absorbed by the extruded strands.

ACKNOWLEDGMENTS

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