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### Effects of Poly(Ethylene Glycol) on the Physical Properties of Blended Molecules of Starch and Poly(Ethylene-co-Acrylate, Ammonium Salt)

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## EFFECTS OF POLY(ETHYLENE GLYCOL) ON THE PHYSICAL PROPERTIES OF BLENDED MOLECULES OF STARCH AND POLY(ETHYLENE-*co*-ACRYLATE, AMMONIUM SALT)<sup>†</sup>

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### ABSTRACT

A mixture of starch (36%) poly(ethylene-*co*-acrylate, ammonium salt) (41%), water (12.5%), urea (8.4%), and poly(ethylene glycol) ( $M_n$  4600) (2.1%) were converted to plastic test pieces by extruding (130°C), drying and grinding (25°C), and hot pressing (175°C). After equilibration at ~50% relative humidity and 25°C, the test pieces contained 3.5–4.6% moisture and 2.3% poly(ethylene glycol) (PEG). Among wheat, corn, potato, and rice starches, the wheat starch (WS) blend showed the highest Young's modulus (181.3 MPa), whereas the corn starch (CS) blend had a modulus and elongation that almost matched those of low-density polyethylene. When PEG was eliminated from the WS formulation, tensile strength remained constant, but Young's modulus doubled. The modulus decreased continually as test pieces absorbed water up to 27% moisture, but elongation and argon laser light transmittance were optimum at ~12% moisture. Differential scanning calorimetry indicated that PEG formed a solid inclusion complex with amylose upon drying at 60°C, but no complex was detected in dilute alkali by optical rotation.

<sup>†</sup>Contribution 95-571-J from the Kansas Agricultural Experiment Station, Manhattan, KS 66502.

## INTRODUCTION

Interest has increased in developing plastics containing starch, an abundant and low-cost natural polymer [1-4]. Compositions containing starch and poly(ethylene-co-acrylic acid) (EAA) were investigated originally at the National Center for Agricultural Utilization Research, Peoria, IL. Starch-EAA blends containing urea were extrusion-processed into blown films having satisfactory mechanical properties for agricultural mulch applications [5-7]. Other investigators (8, 9) used the same basic blend to produce injection-molded plastics.

Poly(ethylene glycol) (PEG) was found to increase the linear and radial expansion of extruded starch and to reduce brittleness in the resulting loose-fill packaging material [10]. In the present investigation, selected starches from different sources were compounded by extrusion with 41% EAA (ammonium salt), 36% starch (dry solids), 12.5% water, 8.4% urea, and 2.1% PEG of  $M_n$  4600. In addition, the ratio of starch/EAA, the molecular weight of PEG, and the level of PEG with  $M_n$  4600 were varied in EAA-wheat starch blends. Physical properties of molded test bars were compared after they were equilibrated to room conditions or to various relative humidities at 25°C. Evidence is presented indicating that amylose forms a weak inclusion complex with PEG in the solid state.

## MATERIALS AND METHODS

### Materials

Wheat starch (WS, Midsol 50) was obtained from Midwest Grain Products, Inc. (Atchison, KS); normal corn and rice starches (CS and RS) from Sigma Chemical Co. (St. Louis, MO); and potato starch (PS) from Avebe America Inc. (Princeton, NJ). The RS bound 4.35% of iodine [11], which is equal to 21.2% amylose assuming that rice amylopectin bound no iodine and amylose bound 20.5% [12]. EAA was Primacor 5980 from Dow Chemical Co. (Midland, MI) containing 20 wt% copolymerized acrylic acid. The copolymer had a melt index of 300 g/10 min and  $M_w$  of 18,000 ( $M_n$  7000). PEGs with  $M_n$  2000, 4600, 8000, and 10,000 were from Aldrich Chemical Company, Inc. (Milwaukee, WI). Low density (LDPE resin 722M) and high density polyethylene (HDPE resin 12350N) were from Dow Chemical Co.

Amylose was leached from WS as described by Shi et al. [13]. Lipids were removed [14] from WS by three extractions with hot (100°C) *n*-propanol/water 3:1 (v/v), and the starch (0.9 g) was added to water (30 minutes) in a plastic centrifuge tube (25 × 100 mm). The tube was heated at 95°C for 30 minutes in a water bath with gentle shaking, and the thin paste was immediately centrifuged at 1000g for 15 minutes. The sediment was discarded, and the supernatant was slowly added to four volumes of 95% ethanol with stirring. The precipitate was collected by centrifugation, washed with absolute ethanol three times, and dried under vacuum overnight. The dry solid amylose (170 mg) gave an iodine binding capacity of 19.0% compared to the reported value [12] of 19.5% for pure wheat amylose.

## General Methods

All tests were replicated at least twice unless otherwise specified, and results were reported as means. Moisture was determined by loss of weight upon drying a sample to constant weight at 95°C. Relative humidities (RH) of 23, 57, 75, 83, and 90% at 25°C were established in desiccators with saturated salt solutions [15]. Optical rotations were measured at 589 nm and room temperature on a Perkin-Elmer 241 (Norwalk, CT) polarimeter. The cell path length was 1 dm, and specific rotation was calculated from  $[\alpha] = 100\alpha/lc$ , where  $\alpha$  is the rotation in degrees,  $l = 1$  dm, and  $c$  is concentration in g/dL. Turbidity measurements were made at 490 nm in a 1-cm path cell using a Milton Roy Spectronic 601 spectrophotometer (Rochester, NY).

Tensile properties of polymers were measured on an Instron 4202 Universal Testing Machine (Instron, Canton, MA) according to ASTM Method D638-91 [16]. The instrument was operated at a speed of 5 cm/min and a grip-length of 64 cm on a test piece. Measurements were replicated 4 or 5 times. Transmittance of argon laser light (3 W,  $\lambda$  488 nm, Model No. 165, Spectra Physics, Mountain View, CA) through a plastic test piece was measured with a Quantum Photometer (Princeton Applied Research, Model 1140A, Princeton, NJ).

Differential scanning calorimetry (DSC) measurements were made using a Perkin-Elmer DSC-2 (Norwalk, CT) equipped with a mechanical cooler. A sample (~3 mg) was weighed into an aluminum pan with or without water (~9 mg); the pan was sealed, held overnight, and then cooled to 7°C and heated to 157°C at 10°C/min. Peak onset temperatures ( $T_i$ ) and ending temperatures ( $T_f$ ) were determined by the intercepts of the extrapolated baseline and the leading and trailing edges of a peak. Enthalpy ( $\Delta H$ ) was calculated from the area of a peak.

Water solubility of the WS/EAA blend containing 2.3% PEG ( $M_n$  4600) was determined on pellets ( $d = 1$ –3 mm) of the blend (1 g) in water (100 mL). After the mixture was stirred for 30 minutes in a constant temperature bath, insoluble material was removed on a 60-mesh screen and dried to constant weight at 95°C.

## Complex of Amylose and Poly(Ethylene Glycol)

Amylose (600 mg) was added slowly to 0.5 M sodium hydroxide (10 mL) with rapid stirring. After being stirred for 1–1.5 hours, the mixture was centrifuged at 15,000g for 1 hour to remove a low level of insoluble particles, and the supernatant made to volume (100 mL) with water. Total carbohydrate analysis [17] on an aliquot (1 mL) of the solution indicated an amylose concentration of 5.5 mg/mL. The mixture was neutralized with 1 M hydrochloric acid (5.0 mL) and warmed to 50°C; then PEG ( $M_n$  4600) (850 mg) was added with gentle stirring. The clear solution was stirred for 30 minutes, cooled, and kept at room temperature for 2 days, at which time the aqueous mixture was cloudy. The mixture was dried at 60°C for 2 days to give a thin film on the drying dish. The film was scraped off and ground to a powder with a mortar and pestle; the ground solid was sifted on a Ro-Tap Testing Sieve Shaker (W.S. Tyler Co., Cleveland, OH) through a U.S. Standard wire screen No. 70 ( $< 213 \mu\text{m}$ ). DSC measurements were made on the neat powder, which contained amylose/PEG/sodium chloride at a weight ratio of 0.65/

1.0/0.35, as well as on the neat physical mixture of those three substances at the same weight ratio. Other DSC measurements were made after adding 3 parts water to 1 part powder and sealing and holding the mixture for 8–12 hours at 25°C.

### Blended Polymers

The procedure of Otey et al. [7] was followed with modification of the formula and the process. Wheat, rice, corn, or potato starch (203 g, d.s.) was held in a 100% RH cabinet at 37°C until the starch contained 17.4% moisture (43 g). Then, the humidified starch, EAA (222 g, 0.6 eq.), urea (48 g), and PEG ( $M_n$  4600) (12 g) were mixed by a paddle mixer (Hobart, Model N-50, Troy, OH) while a solution of concentrated ammonium hydroxide (40.8 mL, 0.6 eq.) in water (24 mL) was added slowly. The mixture of components, which contained 12.5% moisture and 2.1 wt% PEG on a wet basis with 526 g of dry solids, was passed through a 1.9-cm ( $\frac{3}{4}$  in.) Brabender (Hackensack, NJ) single-screw extruder (Model 2503) equipped with a 3.2-mm ( $\frac{1}{8}$  in.) rod die and a screw with a 5:1 compression ratio. The inlet, middle, and final zones were maintained at 25, 130, and 110°C, respectively, and the screw speed was 90 rpm. The shear rate at the inlet and outlet ends of the screw were 24 and 133  $s^{-1}$ , respectively. The extruded rods were cut into pellets that were dried at 30°C to ~3% moisture. The dried pellets were ground to a powder in a Wiley mill through a 1.0-mm opening, and the powder was equilibrated at ambient conditions for several weeks. The powder then was compression-molded (1380 kPa, 5 minutes) at 175°C into test specimens 3.0 mm thick using a Wabash (Wabash, IN) hydraulic press (Model V50-18-2TRW). The test piece was equilibrated at ambient conditions for several weeks prior to measuring tensile properties and moisture content. Wheat starch/EAA blends containing 2.1% PEG going into the extruder were also prepared with PEGs having  $M_n$  2000, 8000, and 10,000.

Wheat starch was also blended with the other components to produce mixtures (PEG 0 through PEG 3) with 1.0, 2.1, 2.5, and 3.1% PEG ( $M_n$  4600). To prepare those mixtures, the levels of urea, WS, and moisture were kept at 8.4%, 36.0%, and 12.5%, respectively, while the levels of EAA were decreased from 41.0 to 38.0% as the levels of PEG were increased from 0 to 3.0%. Ammonium hydroxide varied (40.2–41.4 mL) according to the amount of EAA. In another experiment the weight ratio of dry WS to EAA was increased from 36/39 (WS) to 39/39 (WS-MID) and 45/30 (WS-HI). The weight of urea (8.4%) remained constant, whereas the ammonia (1.9 and 1.5%) and the moisture (12.5 and 13.0%) varied in the new mixtures.

## RESULTS AND DISCUSSION

The components in the starch/EAA plastics were compounded under high shear at 130°C and 12–13% moisture content (Table 1). After the test pieces were prepared and equilibrated at room conditions (~50% RH), those labeled 2% PEG actually contained 2.3% PEG and 3.4–4.6% moisture (Table 1). The PEG and moisture levels of other test pieces are given in Table 1.

TABLE 1. Compositions Fed into Extruder and of the Test Pieces after Equilibrium under Room Conditions

Sample label	Starch source	Mixed components <sup>a</sup>	Test piece	
		ST/EAA/Urea/NH <sub>3</sub> /PEG/H <sub>2</sub> O, %	PEG, %	MC, %
OLD <sup>b</sup>	Corn	34/39/12.9/2.0/0/12.1	0	5.0
CS	Corn	36/39/8.4/2.0/2.1/12.5	2.3	3.9
PS	Potato	36/39/8.4/2.0/2.1/12.5	2.3	3.9
RS	Rice	36/39/8.4/2.0/2.1/12.5	2.3	4.6
WS	Wheat	36/39/8.4/2.0/2.1/12.5	2.3	4.5
WS-MID	Wheat	39/39/8.4/1.9/2.1/12.6	2.3	3.4
WS-HI	Wheat	45/30/8.4/1.5/2.1/13.0	2.3	3.8
PEG0	Wheat	36/41/8.4/2.1/0/12.5	0	4.0
PEG1	Wheat	36/40/8.4/2.1/1.0/12.5	1.1	—
PEG2	Wheat	36/39/8.4/2.0/2.1/12.5	2.3	4.5
PEG2.5	Wheat	36/38.5/8.4/2.0/2.5/12.5	2.7	—
PEG3	Wheat	36/38/8.4/2.0/3.1/12.5	3.3	4.6

<sup>a</sup>Abbreviations: ST, starch (d.b.); EAA, poly(ethylene-*co*-acrylic acid); PEG, poly(ethylene glycol).

<sup>b</sup>Original formulation of Otey et al. [7].

### Blends of EAA and Various Starches

Young's modulus of the EAA-CS plastic containing 2.3% PEG ( $M_n$  4600), 8.4% urea, and 3.9% moisture was 3 times higher (Fig. 1) than that of plastic made from Otey's original formula (OLD) containing no PEG, 12.9% urea, and 5.0% moisture (Table 1). The elongations of the two test pieces were only slightly different. Prior work [18] showed that test ribbons extruded from CS/urea/water (1/0.6/0.2, w/w) and aged for 1 week at 50% RH and 23°C had reduced (50%) tensile strength and elongation (25%) compared to strips made from CS/urea/water (1/0.2/0.2, w/w). In addition, increasing the level of urea caused a test piece to be more hygroscopic above 60% RH. Reducing the urea level in the new CS plastic (CS, Fig. 1) from 12.9 to 8.4% apparently increased the tensile strength by increasing the interaction between polymer molecules. Also, some of the increase in tensile strength may be attributed to formation of an inclusion complex between amylose and PEG (see discussion below). It is well established that EAA complexes with amylose [19–22] and weakly with AP [21], and that such complexes promote compatibility in a multipolymer system [23]. PEG at 2.1% in WS blend test bars increased equilibrium moisture content by less than 1% at 75% RH and 25°C compared to a control sample with no PEG and 2.1% more EAA.

Among the blended polymers containing ~40% starch, ~43% EAA, and 2.3% PEG, the WS blend gave the highest Young's modulus and the CS blend the

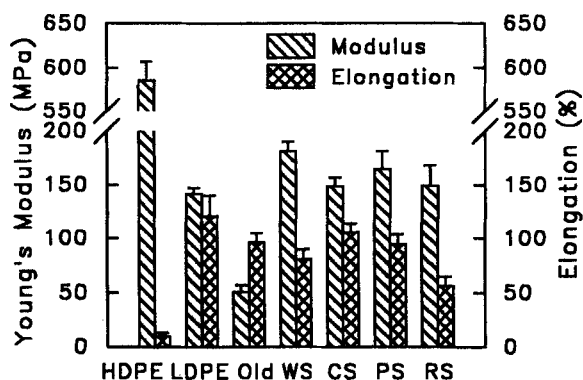


FIG. 1. Young's modulus and percent elongation of starch/EAA (36/39, w/w) blends containing 2.3% PEG ( $M_n$  4600), ~9.2% urea, and 3.9–5.0% moisture. The OLD blend was prepared from Otey's original formula with CS [7], and high-density (HDPE) and low-density polyethylenes (LDPE) were the control plastics. WS = wheat starch, CS = corn starch, PS = potato starch, and RS = rice starch.

highest elongation (Fig. 1). The modulus and elongation of the CS sample almost matched those of low-density polyethylene (LDPE). The tensile strengths (MPa) of the control samples and blended polymers were as follows: HDPE (22.8), LDPE (7.7), OLD (4.95), WS (9.8), CS (10.1), PS (10.3), and RS (7.6).

### Tensile Properties of EAA–WS Blends with PEG

Changing the weight ratio of WS/EAA from 36/39 (WS) to 45/30 (WS-HI, Table 1), while maintaining a moisture level of 12.5–13.0% and PEG level of 2.1% into the extruder, gave an extrudate with polymer incompatibility. The extrudate contained tiny opaque zones caused by incomplete dispersion of starch granules, which were observed by scanning electron microscopy. At an intermediate ratio (WS-MID) of WS/EAA, few granules were observed in the extrudate and opaque specks were not visible. Nevertheless, the WS-MID blend gave tensile properties approaching those of the WS-HI blend, and both were much stiffer than the WS blend (Fig. 2). Apparently the moisture level of 13% in the formulation with 45% starch was insufficient at 130°C to disperse all the starch granules in one pass through the extruder. A second pass was not attempted. However, two passes of the WS formulation with 36% starch and 39% EAA gave only a slight reduction in modulus for the RE plastic (Fig. 2).

PEG ( $M_n$  4600) levels of 1–2% (PEG1 and PEG2) in WS/EAA blends (Table 1) doubled elongation compared to the blend with no PEG (PEG0), whereas those levels reduced the modulus by 30% (Fig. 3). Increasing the PEG level above 2% decreased the modulus of the starch-EAA plastic, whereas elongation did not change (Fig. 3). A PEG level of 3.3% in the polymer blend (PEG3) did not cause extra moisture absorption at 50% RH (Table 1). Those results (Fig. 3) are in agreement with the hypotheses (see below) that PEG may complex with amylose

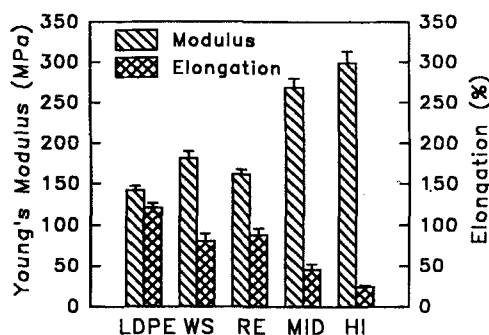


FIG. 2. Tensile properties of different WS/EAA blends all containing 2.3% PEG ( $M_n$  4600), ~9.2% urea, and 3.4–4.5% moisture. Weight ratios of starch/EAA were: WS, 36/39; MID, 39/39; HI 45/30. RE is reextruded WS, and low-density polyethylene (LDPE) was the control plastic.

and that the PEG-amylose complex may occur together with the EAA-amylose complex. The extent of complexing of starch with EAA (ammonium salt) or with PEG in any of the polymer blends is not known. The almost 1/1 weight ratio of EAA to starch exceeds the saturation level of 0.6/1 for amylose and 0.9/1 for amylopectin [21]. However, some starch molecules may be available to PEG for complexing because EAA salts exist as micelles in water with their hydrophobic methylene chains in the interior of a micelle. Moreover, the high viscosity of the molten mixture in the extruder limits the mobility of the polymer molecules so that complexing by EAA is incomplete.

Increasing PEG levels in the EAA/WS blend above 2.3% decreased Young's modulus, possibly because a high percentage of the PEG was not complexed with starch but acted as a plasticizer to reduce starch interactions. However, at concentrations between 2.3 and 1.1%, a higher proportion of the PEG molecules may have complexed with two starch molecules, which effectively increased the interaction between polymer molecules and countered the plasticizing effect.

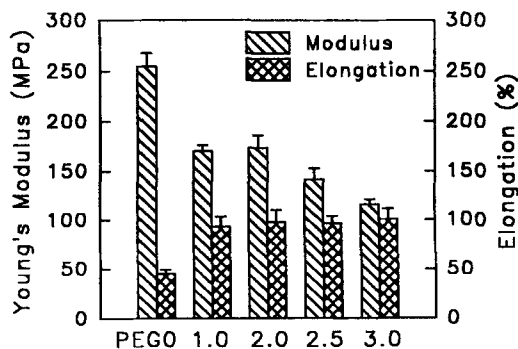


FIG. 3. Tensile properties of WS/EAA (36/39, w/w) blends containing 0–3.3% PEG ( $M_n$  4600), ~9.2% urea, and 4.0–4.6% moisture.



At a constant level of 2% PEG in a 36/39 (w/w) WS/EAA formula, increasing the molecular size of PEG in the formula from  $M_n$  2000 to 10,000 gradually decreased elongation at  $M_n$  8000, at which point elongation remained constant. However, Young's modulus gave a maximum value at  $M_n$  4600 (Fig. 4). The reduction in elongation for the high molecular weight PEG might be caused by fewer PEG molecules and, therefore, less free volume for movement of the large starch molecules. The optimum value of tensile strength at  $M_n$  4600 could result from two opposing forces. PEG molecules should be of sufficient length to enable both ends to form helical complexes with starch molecules, thereby strengthening the blend. However, excessively long PEG molecules would have less mobility during compounding of the polymer mixture and would be ineffective at complexing.

### Tensile Properties and Light Transmittance; Change with Humidity

Figure 5 shows the moisture gained by the WS test bars at RH 23–90% and 20°C. As the WS plastic gained moisture from 2 to 27%, its modulus decreased continuously, whereas elongation proceeded through a maximum at ~12% moisture content (Fig. 6). Light transmittance was also optimum at ~12% moisture (75% RH, Fig. 7), and that phenomenon was reversible. The light transmittance data suggest incomplete blending of the polymer components, possibly due to the micellar structure of EAA salts and the viscosity of the molten mixture in the extruder. The starch domains apparently had a different refractive index than EAA at high and low moisture levels. The moisture sensitivity of starch-containing plastics is well known [4, 7, 18].

### Inclusion Complex of PEG with Amylose

The formation of inclusion complexes of amylose with hydrophobic guests is one of that molecule's distinguishing features. The guest molecule, which may be iodine [24], a polar lipid [25–28], alcohol [29, 30], polyolefin [19–22], or polycar-

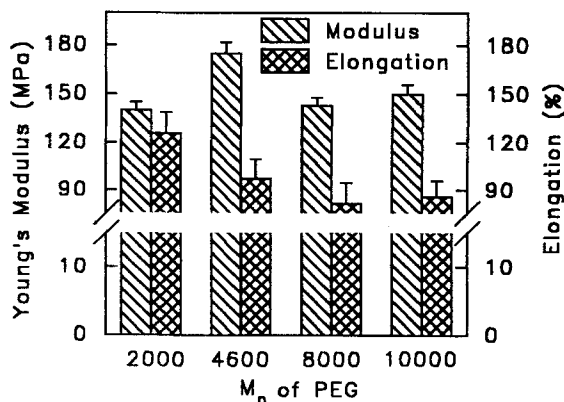


FIG. 4. Tensile properties of WS/EAA (36/39, w/w) blends with ~9.2% urea and 2.3% PEGs of various molecular sizes.

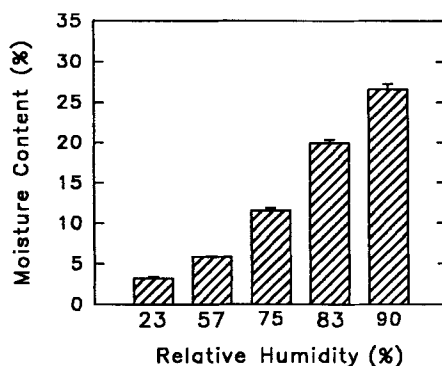


FIG. 5. Moisture content of the WS/EAA (36/39, w/w) blend after equilibration at different relative humidities and 25°C. The test pieces containing 2.4% PEG ( $M_n$  4600) and 9.6% urea on a dry basis were held at least 4 weeks in desiccators.

bonate [31], induces the amylose molecules in aqueous solution (usually hot) to form a helical complex, which often precipitates from the medium and gives a V-type x-ray diffraction pattern [32]. Amylopectin also appears to form inclusion complexes, but they are weak [21, 33–35].

PEG with  $M_n$  4000 failed to decrease the iodine-binding capacity of tapioca starch, which indicated that iodine either displaced PEG from an inclusion complex in water or that no complex formed. However, drying a 20/1 (w/w) mixture of gelatinized tapioca starch and PEG at 100°C did produce a solid complex as evidenced by a V-type x-ray diffraction pattern [36]. Crystalline complexes of PEG

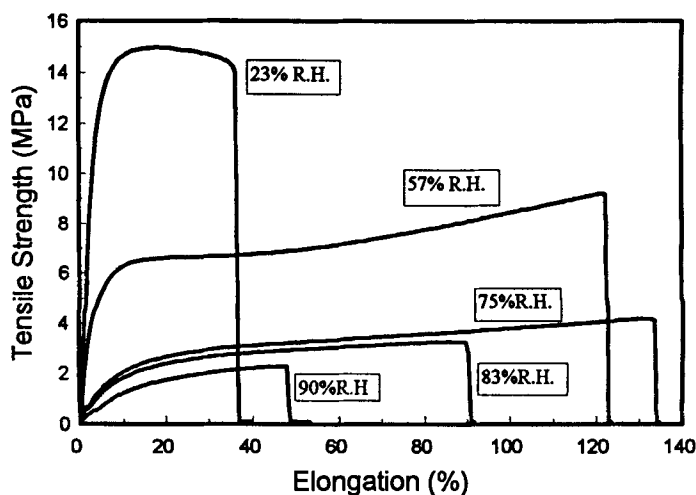


FIG. 6. Tensile strength and elongation of the WS/EAA (36/39, w/w) blend after equilibration at various relative humidities and 25°C. The blend contained 2.4% PEG ( $M_n$  4600) and 9.6% urea on a dry basis.

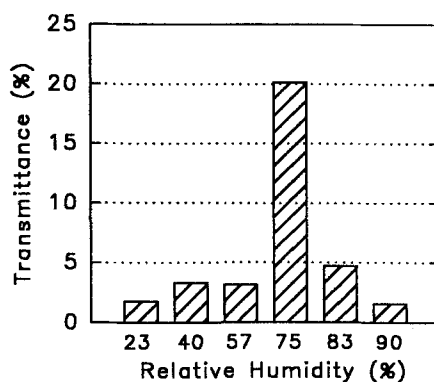


FIG. 7. Light transmittance of the WS/EAA (36/39, w/w) blend at various relative humidities and 25°C. The blend contained 2.4% PEG ( $M_n$  4600) and 9.6% urea on a dry basis.

with  $\alpha$ -cyclodextrin have been isolated [37]. Solid-state  $^{13}\text{C}$ -NMR data indicated that a complex may have formed when a mixture of water/triethyleneglycol/CS (0.2/0.4/1.0, w/w) was extruded at 175°C, and the extrudate equilibrated at 20% RH and 25°C [18].

In the present investigation, no complex was detected by a change in optical rotation of amylose in 10 mM sodium hydroxide when up to 3 parts by weight of

TABLE 2. Stoichiometry of Amylose Inclusion Complexes with Fatty Acids and EAA

Guest	Methylene, <sup>b</sup> wt%	Saturated inclusion complex <sup>a</sup>	
		Guest per 100 g amylose, g	Mole ratio of methylene to anhydroglucose unit
Myristic acid	80	8.5	0.79
Palmitic acid	82	8.7	0.83
Stearic acid	84	8.1	0.79
EAA	84	60	5.83
PEG <sup>c</sup>	64	9.1	0.67

<sup>a</sup>Saturation of amylose by fatty acid determined by change in viscosity number at pH 12 [27]. Saturation by poly(ethylene-co-acrylate, sodium salt) was determined by the change in optical rotation in 10 mM sodium hydroxide [21].

<sup>b</sup>Methyl group in fatty acid counted with methylene groups.

<sup>c</sup>PEG complex with  $\alpha$ -cyclodextrin with 2 ethylene glycol units per cyclodextrin molecule [37]. Complex crystallizes from aqueous solution at a fast rate when PEG has  $M_n$  1000.

PEG ( $M_n$  4600) were added, whereas a control sample of sodium palmitate reduced the specific rotation from  $+200^\circ$  to  $+140^\circ$  ( $\lambda = 589$  nm) at saturation. Shogren et al. [21] previously demonstrated complexing of EAA with amylose using optical rotation in 10 mM sodium hydroxide. The mole ratio of methylene units of a fatty acid per anhydroglucose unit in a saturated amylose complex was  $\sim 0.8$  compared to a mole ratio of 5.8 for EAA (Table 2). The relatively inefficient complexing of EAA with amylose was explained by the inaccessibility of the polymethylene chains inside the micelles [21].

The scheme shown in Fig. 8 appeared to produce a solid complex of PEG with amylose. The solid complex contained a weight ratio of 2.9/2.1/1.0 of PEG/amylose/sodium chloride. Heating the neat solid, which contained  $\sim 7\%$  moisture, in the DSC gave thermogram D in Fig. 9, showing an endotherm centered at 330 K ( $57^\circ\text{C}$ ) (Peak 1). Peak 1 matched the peak in thermogram E (Fig. 10) of pure PEG. Moreover, the enthalpy of peak 1 in the complex (thermogram D), which was not normalized for PEG content, was 45% of that of pure PEG (Table 3), in near agreement with the 48.3% of PEG in the complex. The small exotherm peaking at  $\sim 390$  K ( $117^\circ\text{C}$ ) in thermogram D was unexplained. Thermogram D was similar to thermogram G of a physical mixture (2.9/2.1/1.0, w/w) of PEG, amylose, and

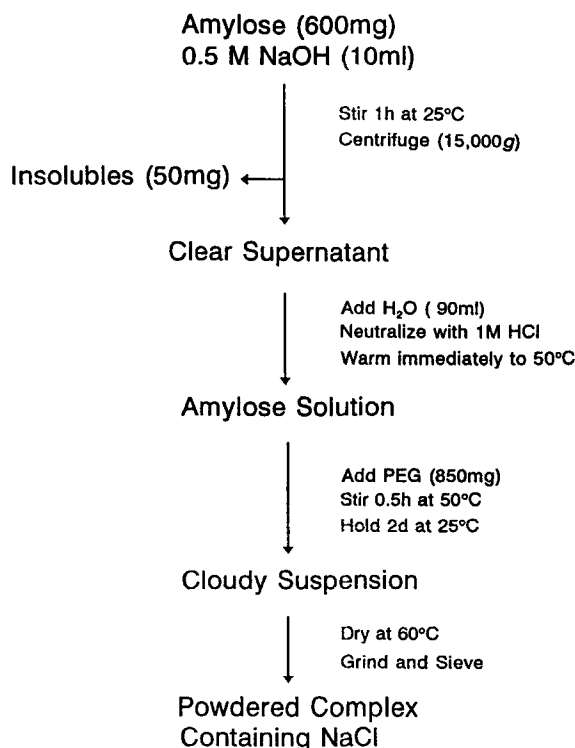


FIG. 8. Preparation of solid-state complex of amylose and PEG ( $M_n$  4600) containing sodium chloride.

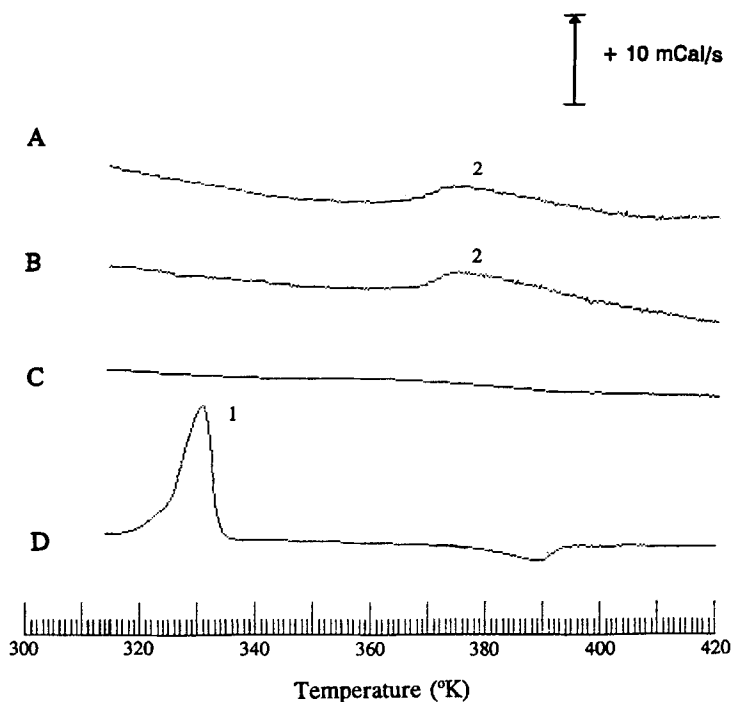


FIG. 9. Differential scanning calorimetry heating curves of; A. PEG-amylose complex (1 part) and water (3 parts); B. Rescan of A; C. complex (1 part) and water (1.5 parts); and D. complex, neat.

sodium chloride, except that the small exotherm in thermogram G was shifted to 415 K (142°C).

Heating PEG in 3 parts water (thermogram F, Fig. 10) showed that it dissolved in the water before its melting temperature was reached. In a similar manner, all thermal transitions were eliminated when excess water was added to the physical mixture of PEG/amylose/sodium chloride and the mixture heated in the DSC (thermogram H, Fig. 10). On the other hand, heating the PEG/amylose/sodium chloride complex in 3 parts water gave a new broad endotherm at  $T_i$  367 K (94°C) and  $T_f$  397 K (124°C), which was attributed to dissociation of a PEG/amylose complex (thermogram A, Fig. 9). The complex re-formed upon cooling as shown by the rescan (thermogram B). Adding 1.5 parts water to the complex and heating the mixture gave no peaks (thermogram C). Apparently that proportion of water was sufficient to dissolve the PEG and sodium chloride, but the melting temperature of the complex remained above 420 K (147°C).

Thermogram D of the neat complex failed to show an endotherm for the PEG/amylose complex, probably because the complex melted above 420 K (147°C) in the absence of added water, especially because sodium chloride was also present with the complex. Biliaderis et al. [38] showed that the melting temperature of amylose inclusion complexes with myristic and palmitic acids and lysophospholipid

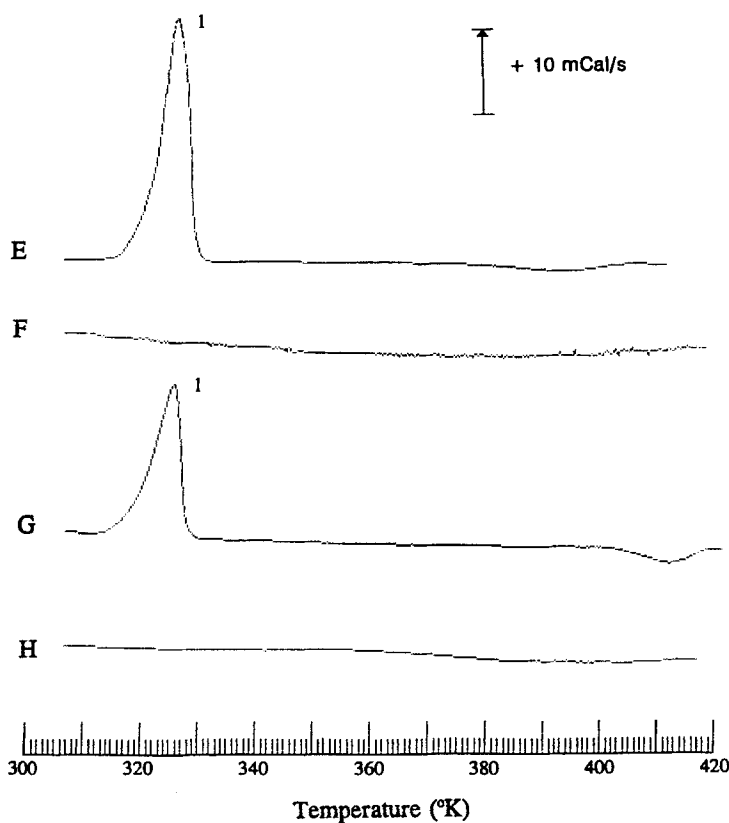


FIG. 10. Differential scanning calorimetry heating curves of; E. PEG; F. PEG (1 part) and water (3 parts); G. physical mixture of PEG/amylose/sodium chloride (2.9/2.1/1.0, w/w); and H, mixture of PEG/amylose/sodium chloride (2.9/2.1/1.0, w/w) (1 part) and water (3 parts).

rose from 368–378 K (95–105°C) to 390–416 K (117–143°C) as the weight ratio of the water/complex was decreased from 4/1 to 1/4. The neat melting temperatures of those complexes were not reported, but extrapolation of the authors' data gave 408–438 K (135–165°C). Biliaderis et al. [38] also observed broadening of the DSC endotherm for the amylose/palmitic acid complex and a reduced enthalpy of melting when the water concentration was decreased in the DSC experiment. Shifting and broadening of an endotherm peak for the PEG/amylose complex may have obscured its observation at  $T < 420$  K (147°C) in thermogram D.

The enthalpy of melting of the purported PEG/amylose complex in excess water was 2.64 cal/g when the experimentally observed value was adjusted for dilution by the sodium chloride present. The enthalpy of melting of a lipid/amylose complex (5–8 cal/g) in excess water was at least twice as high [28, 38]. This low enthalpy of melting is consistent with weak complexing of the polyoxyethylene chains in the helical cavity of amylose or a low extent of complexing.

TABLE 3. DSC Data on PEG ( $M_n$  4600) and Its Inclusion Complex with Amylose (AM)

Sample	Moisture, %	Water added, parts	Peak 1				Peak 2			
			$\Delta H_m$ (Cal/g)	$T_i$ (°C)	$T_p$ (°C)	$T_f$ (°C)	$\Delta H$ (Cal/g)	$T_i$ (°C)	$T_p$ (°C)	$T_f$ (°C)
A. PEG·AM (NaCl)	7	3.0	—	—	—	—	2.2	94	106	124
B. PEG·AM (NaCl) <sup>a</sup>	7	3.0	—	—	—	—	1.3	95	104	127
D. PEG·AM (NaCl)	7	0	24.6	42	56	61	—	—	—	—
E. PEG	7	0	55.0	48	60	66	—	—	—	—
G. PEG/AM/NaCl <sup>b</sup>	7	0	21.8	43	55	60	—	—	—	—

<sup>a</sup>After heating, sample A was cooled and rescanned immediately.

<sup>b</sup>Poly(ethylene glycol), amylose (AM), and NaCl (2.9/2.1/1.0, w/w) were mixed, water was added, and then the pan was sealed and heated 12 hours later.

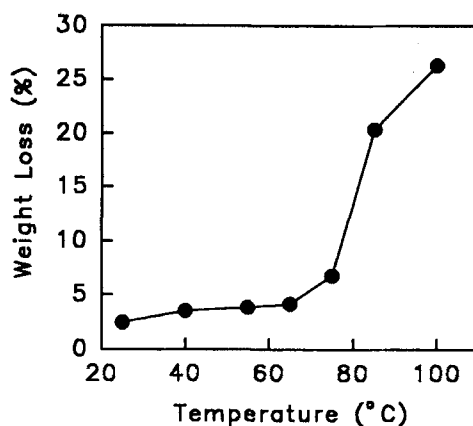


FIG. 11. Solubility of WS/EAA (36/39, w/w) plastic containing 2.3% PEG ( $M_n$  4600) and ~9.2% urea in excess water.

An x-ray diffractogram of the PEG/AM complex containing sodium chloride, after equilibrating for several days at 57% RH and 25°C, showed that the complex was an amorphous solid. In contrast, drying a 19/1 (w/w) mixture of gelatinized tapioca starch and PEG ( $M = 4000$ ) at 100°C gave a solid with a V-type x-ray pattern [36]. Perhaps the drying temperature of 60°C used in the present work and the presence of sodium chloride imparted insufficient mobility to the helical complexes and they remained amorphous. Amorphous V-type complexes of amylose with long acyl chains of lipids are known [39, 40].

### Dissolution of the WS Blend in Hot Water

The dissolution of pellets of the WS/EAA plastic (WS in Table 1) in a large excess of water rapidly increased above ~75°C (Fig. 11). Most of the weight lost from the pellets up to 75°C was urea, which constituted 9.2% of the pellets (data not given). The sharp rise in water solubility above 75°C is consistent with the melting of a complex of amylose with EAA at those temperatures [21] and perhaps melting of a PEG/amylose complex in the absence of sodium chloride (Table 3).

### CONCLUSIONS

Low levels (1-2%) of poly(ethylene glycol) ( $M_n$  2000-4600) maintain the strength of a starch/urea/poly(ethylene-co-acrylate, ammonium salt) (1/1, w/w) blend without diminishing elongation. Poly(ethylene glycol) appears to form inclusion complexes with starch molecules in the solid state, which may account for its improving action in the polymer blend. The complex of amylose with a polyoxyethylene chain apparently is weaker than the complex with a polymethylene chain, as



evidenced by its low enthalpy of melting and by a lack of complexing at pH 12 or in the presence of iodine near neutral pH.

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