

Starch–Poly(ethylene-co-Acrylic Acid) Composite Films. Effect of Processing Conditions on Morphology and Properties

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SYNOPSIS

Formulations containing 4 parts cornstarch, 5 parts poly(ethylene-co-acrylic) (EAA), 1 part urea, and 1.6 parts of either water or aqueous ammonia were extruded at either 110–120°C or 150–160°C; and the resulting extrudates were then extrusion-blown into films. Complex formation between EAA and starch was measured by either X-ray diffraction or by solvent extraction of uncomplexed EAA. Although the processing temperature had only a minor effect on the amount of EAA complexed by starch, use of aqueous ammonia rather than water in these formulations increased the amount of complexed EAA by about a factor of 2. In films prepared with aqueous ammonia, the polysaccharide phase was present as sub-micron-sized domains. When ammonia was omitted from these formulations, the polysaccharide phase was less uniform in size and contained particles that were over an order of magnitude larger than those observed with ammonia.

INTRODUCTION

Composite polymer systems composed of starch and poly(ethylene-co-acrylic acid) (EAA) have been under investigation at our Center by Otey and co-workers^{1–4} for a number of years. Extrusion-blown starch–EAA films are uniform, flexible, and have good physical properties, despite large differences in physical and chemical properties between the two component polymers. The ability of these two polymers to form uniform blends is largely due to formation of helical inclusion complexes between starch and EAA.^{5–7} The complexing ability of starches from different plant sources under various experimental conditions has been compared.⁸ We have been examining the effect of processing conditions on the morphology, extent of complexing, and physical properties of starch–EAA films, since these films are of commercial interest because of the ability of the starch component to biodegrade.

Aqueous ammonia is added to starch–EAA formulations² to increase compatibility between the two component polymers and thus to improve the physical properties of extrusion-blown films. Although EAA is a water-insoluble polymer, it can be dissolved/dispersed in water if carboxylic acid substituents are converted to ammonium carboxylate. Aqueous ammonia, along with urea,⁴ also promotes gelatinization and water solubility of starch. Despite these advantages, evolution of ammonia fumes during film production could be detrimental to a commercial operation. It was thus of interest to investigate the influence of aqueous ammonia on complexing, film morphology, and film quality, and also to determine whether an increase in extrusion processing temperature might compensate for the omission of aqueous ammonia in these formulations.

EXPERIMENTAL

Materials

Starch was Globe 3005 cornstarch from CPC International, Inc. Moisture content was about 10%.

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EAA was Primacor 5981 from Dow Chemical Co. This polymer, which contains 20% copolymerized acrylic acid by weight, has a melt index of 300, M_w of about 18,000, and M_n of about 7000.⁹ Polymer pellets were pulverized by grinding at liquid nitrogen temperature in a Retsch mill equipped with a 0.5 mm screen.

Preparation of Extrusion-Blown Starch-EAA Films

Methods used were similar to the semidry mixing method reported by Otey and co-workers.⁴ Aqueous ammonia-containing formulations were prepared from 155.9 g starch (140.0 g, dry-weight basis), 175.0 g EAA, and 35.0 g urea dissolved in a solution of 28 mL concentrated ammonium hydroxide and 28 mL water. For formulations prepared in the absence of aqueous ammonia, urea was dissolved in 56 mL water. Moist formulations were passed three times through a C. W. Brabender two-zone, single-screw extruder equipped with a strand die having 17 holes, 1.6 mm in diameter. The mixing screw was 1.9 cm in diameter, had a 20 : 1 L/D ratio, and was operated at 60 rpm. For the lower-temperature mixing, the two heating zones of the extruder were maintained at 110°C (closest to addition port) and 120°C (closest to die). For high temperature mixing, 150 and 160°C were used. Strands of extrudate were chopped in a Killion 2-in. pelletizer. Pellets from the third pass were extrusion-blown into film by passing through an extruder with three heating zones maintained at 110, 120, and 130°C and a 25.4 mm diameter blown-film die heated at 130°C.

Testing of Starch-EAA Films

Films were conditioned before testing for 28 days at 50% relative humidity and 23°C. Tensile test specimens 12.7 mm wide were cut parallel to the longitudinal direction of the film. Thickness of each specimen was the average of three measurements with a Carson-Dice electronic micrometer. Tensile strength and elongation values were averages from tests of five samples according to ASTM D 882-83 on an Instron 4201 universal testing machine with a 50.8 mm line-contact grip distance and 50 mm/min crosshead speed.

X-Ray Diffraction of Starch-EAA Films

X-ray powder diffraction experiments were performed by Oneida Research Services, Whitesboro, NY, using a Siemens D500 APD and $\text{CuK}\alpha$ source radiation. Film samples were powdered by shaking

inside a stainless steel vial with two steel balls. Vials were cooled by immersion in liquid nitrogen prior to shaking. Diffraction peaks were cut out and weighed to determine peak areas.

Extraction of Starch-EAA Films

Films to be exhaustively extracted for FTIR analyses (0.5 g) were cut into 5 mm squares and were allowed to soak overnight in 50 mL of 50 : 50 (vol) methanol-water containing 0.1 mL concentrated HCl (to ensure complete conversion of carboxylate substituents in EAA to the carboxylic acid form). Films were separated by filtration, lightly blotted between filter papers, and suspended in about 40 mL of a ternary solvent solution containing 15 : 15 : 70 (by volume) 1,1,2-trichloroethane : isopropanol : toluene.⁸ Suspensions were heated for 1–2 h at 75–80°C, centrifuged, and the clear supernatants decanted. Insoluble polymers were given three more extractions with hot solvent and then washed with ethanol. The films disintegrated during solvent extraction; however, the film processed at 110–120°C in the presence of ammonia produced larger-sized fragments than the other three films. A portion of each ethanol-wet polymer was vacuum-dried, and EAA content was determined by FTIR as previously described.¹⁰

Films were also extracted to determine morphology of the starch-containing phase. These films were not presoaked in methanol-water and were given only a single extraction with hot ternary solvent. The film processed at 150–160°C in the absence of ammonia required centrifugation for separation of solids; for the other films, solids could be separated by decantation. Solids were washed with ethanol; and each ethanol-wet polymer was critical point dried, mounted on an aluminum stub with double-sided tape, and coated with a layer of gold-palladium (60–40) alloy. Samples were then examined and photographed in a Hitachi ISI scanning electron microscope.

RESULTS AND DISCUSSION

The four extrusion-blown films used in this study (prepared with or without aqueous ammonia and at either 110–120 or 150–160°C) were not greatly different in outward appearance. Differences in surface texture can be seen, however, when one examines scanning electron micrographs of film surfaces (Fig. 1). Films prepared in the absence of ammonia appear more heterogeneous than those prepared with

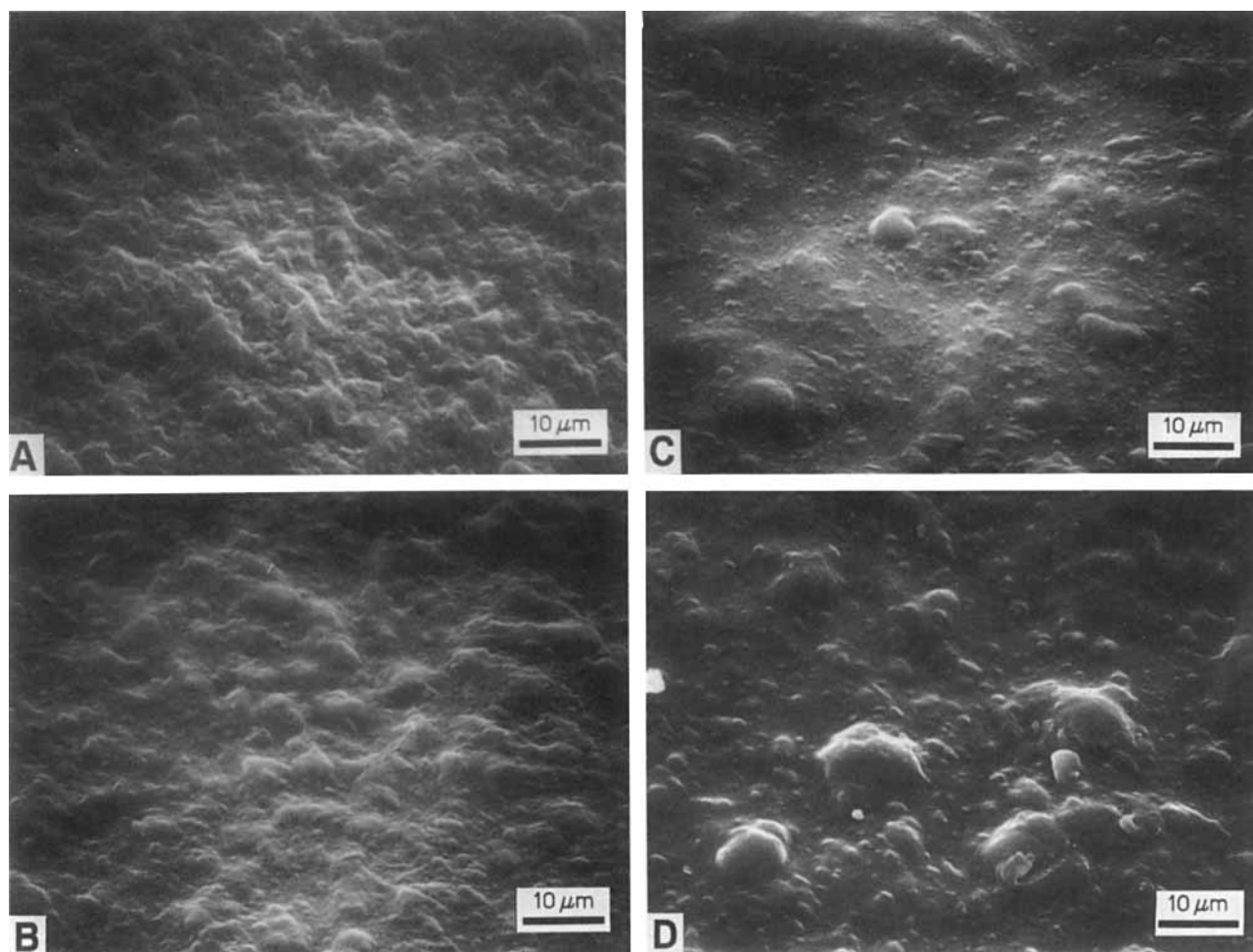


Figure 1 Surfaces of starch-EAA extrusion-blown films: (A) ammonia used; mixing temperature 110–120°C; (B) ammonia used; mixing temperature 150–160°C; (C) no ammonia; mixing temperature 110–120°C; (D) no ammonia; mixing temperature 150–160°C.

ammonia, and this is particularly apparent in films processed at 150–160°C.

The influence of aqueous ammonia and processing temperature on the extractability of EAA from

extrusion-blown films is shown in Table I. EAA remaining in film samples after exhaustive extraction was assumed to be complexed with starch. Films were soaked in methanol-water to maximize ex-

Table I Influence of Ammonium Hydroxide and Processing Temperature on EAA Content after Exhaustive Extraction

NH ₄ OH Used in Formulation	Mixing Temp (°C) ^a	EAA Content after Extraction (%) ^b	Relative Area of 12.6° 2θ Diffraction Peak
Yes	110–120	14	9.8
Yes	150–160	12	8.0
No	110–120	6	3.3
No	150–160	6	3.0

^a Samples were mixed by extrusion through a strand die prior to extrusion-blowing.

^b Determined by FTIR. Films were soaked in 50 : 50 (vol) methanol : water and then extracted four times with 15 : 15 : 70 (vol) 1,1,2-trichloroethane : isopropanol : toluene.

Table II Influence of Ammonium Hydroxide and Processing Temperature on Film Behavior and EAA Content: Single Extraction, No Methanol–Water Pretreatment

NH ₄ OH Used in Formulation	Mixing Temp (°C)	Behavior of Film during Extraction	EAA Content after Extraction (%)
Yes	110–120	Little or no breakup	24.0
Yes	150–160	Fragmented	19.4
No	110–120	Reduced to small particles	19.7
No	150–160	Completely dispersed	15.6

tractability, and the efficiency of this extraction technique for removing uncomplexed EAA was demonstrated in an earlier publication.⁸

Extracted film samples (Table I) contain about twice as much complexed EAA when aqueous ammonia is used in the formulation. This result is not

unexpected, since the solubility of EAA in aqueous ammonia allows the two polymers to be intimately mixed. Although the amount of complexed EAA does not change with processing temperature when aqueous ammonia is absent, there is a small decrease in complexed EAA in the ammonia-containing for-

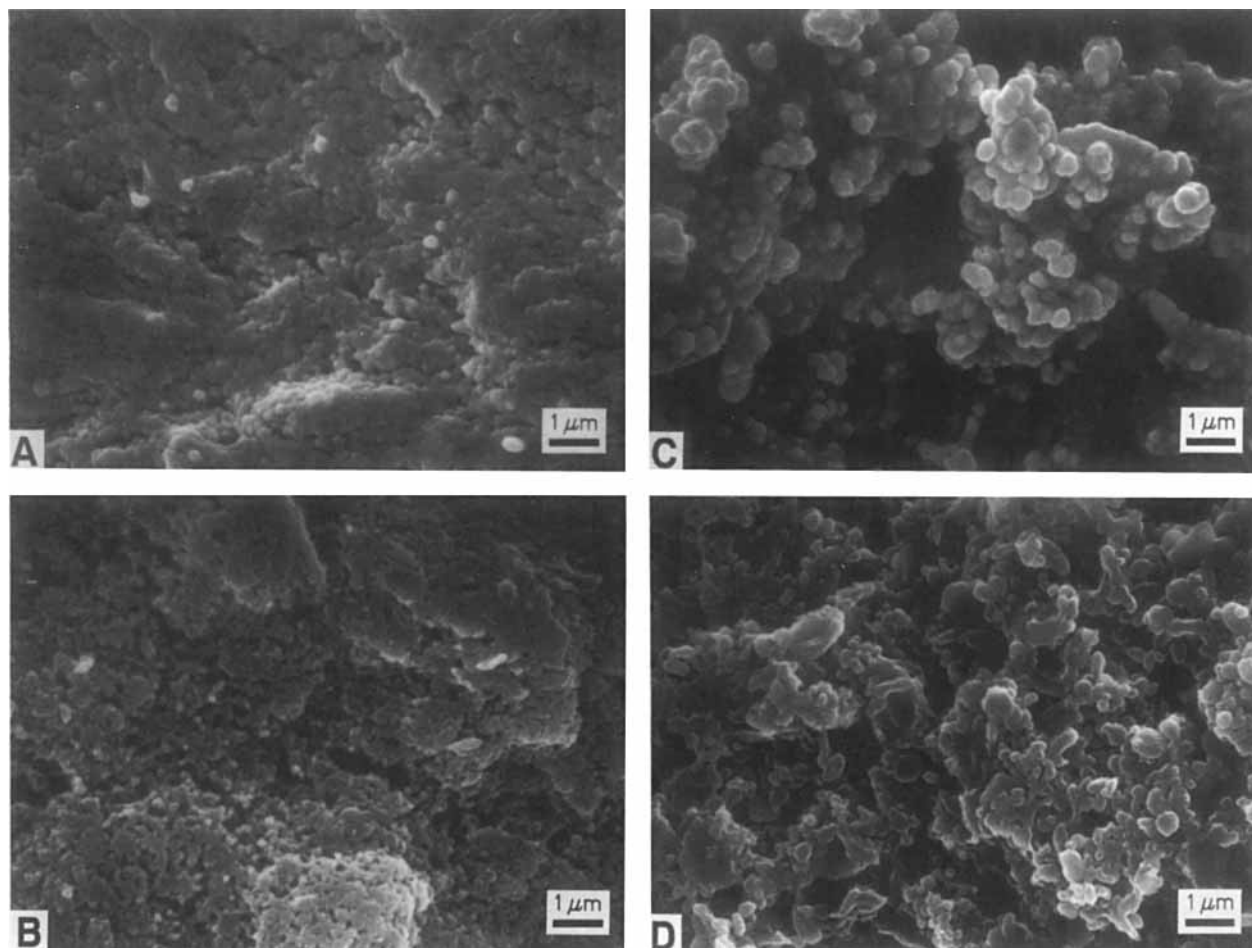


Figure 2 Residues remaining after a single extraction of starch–EAA films with 15 : 15 : 70 (vol) 1,1,2-trichloroethane : isopropanol : toluene: (A) ammonia used; mixing temperature 110–120°C; (B) ammonia used; mixing temperature 150–160°C; (C) no ammonia; mixing temperature 110–120°C; (D) no ammonia; mixing temperature 150–160°C.

mulation when the processing temperature is increased to 150–160°C. High processing temperatures could decrease complexing by driving off ammonia, thereby changing the equilibrium between ammonium carboxylate and carboxylic acid in EAA.

Table I also gives values for the relative areas of the X-ray diffraction peak at $12.6^\circ 2\theta$. This peak is due to the 200 reflection from the crystalline EAA/amylose V-type complex, as shown previously.⁷ These data indicate that two to three times more starch is in the V-complex form when ammonia is included in the formulation, while little change in V-complex content with temperature is noted. Solvent extraction and X-ray measurements, therefore, give similar indications of changes in the extent of starch-EAA complexing with changes in processing conditions.

We next investigated the morphology of the starch-containing phase in these composite films by first subjecting films to a single extraction and then examining the insoluble residues by scanning electron microscopy (Table II). Films were not soaked in methanol-water before extraction to avoid swelling the starch component and to thus preserve as much as possible the original morphology of the polysaccharide. Although most of the uncomplexed EAA was extracted under these conditions, extractability was diminished, as shown by the higher EAA contents in Table II relative to Table I.

The four films behaved differently during solvent extraction. The film prepared in the presence of aqueous ammonia at 110–120°C remained largely intact after extraction, even though about 75% of the EAA originally present had been removed. This observation suggests continuity of the starch-containing phase under these processing conditions. The film prepared with ammonia at 150–160°C broke up during solvent extraction but still remained as millimeter-sized fragments. Unlike the first two films, films prepared in absence of ammonia were reduced to small particles during extraction, and particles from the film prepared at 150–160°C were sufficiently small to require centrifugation to cleanly separate solid from solution.

Scanning electron micrographs of film residues remaining after extraction (Fig. 2) show that use of aqueous ammonia in these formulations has a major effect on morphology. When films are prepared with aqueous ammonia, the polysaccharide phase consists of submicron-sized particles uniformly distributed and in close contact. At a processing temperature of 150–160°C, polysaccharide domains appear to be more separated than at the lower temperature, possibly because water is lost from the formulation, and

Table III Physical Properties of Starch-EAA Composite Films

NH ₄ OH Present during Processing	Mixing Temp (°C)	UTS ^a (MN/m ²)	Elongation ^b (%)
Yes	110–120	15.2	136
Yes	150–160	16.7	108
No	110–120	13.5	180
No	150–160	13.9	107

^a Ultimate tensile strength. Least significant difference = ± 4.34 at a confidence level of 95%.

^b Least significant difference = ± 69.84 at a confidence level of 95%.

interparticle adhesion is thus reduced. The small domain size in the presence of aqueous ammonia is consistent with intimate mixing of starch and EAA. Increased complexing in the presence of ammonia (Table I), the water solubility/dispersability of EAA in aqueous ammonia, and the enhanced disruption and solubility of starch granules under alkaline conditions are all factors responsible for good interpolymer mixing.

When aqueous ammonia is omitted from the formulation, mixing of the two polymer phases is inhibited by the hydrophobic nature of EAA. As a result, the polysaccharide phase is less uniform in size and appears as aggregates of particles ranging in size from submicron to over an order of magnitude larger. The 150–160°C processing temperature appears to give a more uniform particle size distribution; however, the complete disintegration of the sample on solvent extraction (Table II) suggests that any continuity present in the polysaccharide phase is almost totally lost at the higher temperature, and EAA now becomes the continuous phase.

Table III shows some physical properties of the four starch-EAA composite films. Physical property differences between the four samples are not statistically different due to the large margins of error in both UTS and % elongation determinations. Testing variations of this magnitude seem to be common for these starch-containing plastics.¹¹ It is surprising that statistically significant variations in film properties are not observed, if one considers the wide variation in processing conditions used and the resulting morphological differences between the individual films. UTS values in Table III are similar to that of EAA itself (about 13.2 ± 2.3 MN/m²),¹¹ although starch apparently acts as a rigid filler in our films to lower % elongation.

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