Skin and Layer Formation in Films Prepared from Carbohydrates, Poly(ethylene-co-acrylic acid), and Polyethylene*

C. L. SWANSON,[†] G. F. FANTA, and J. H. SALCH

Plant Polymer Laboratory, National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture, 1815 N. University, Peoria, Illinois 61604

SYNOPSIS

Cornstarch, a canary dextrin, and a maltodextrin were compared in films blown from carbohydrates compounded with poly(ethylene-co-acrylic acid) (EAA), low-density polyethylene (LDPE), and aqueous ammonium hydroxide plasticizer. Dextrins or maltodextrins having dextrose equivalent values of one and greater caused dark-colored films with caramel odors, probably due to Maillard reactions. Blown films with hydrophobic skins and water-sensitive cores were produced with the dextrinized carbohydrates, but not from natural cornstarch. Water sensitivity of films containing the dextrinized carbohydrate was reduced by recycling the films through the blown film die. A mechanism for development of the skins is proposed, as is a method for preparing thin semipermeable membranes. © 1993 John Wiley & Sons, Inc.[‡]

INTRODUCTION

Cornstarch and poly(ethylene-co-acrylic acid) (EAA) were extrusion-compounded and blown into flexible and water-resistant films by Otey et al.[1,2] These films were proposed for use as biodegradable agricultural mulch films that would become friable as the starch component was consumed by microorganisms. The friable film residues might be left on the fields to be tilled into the soil when preparing for a new crop, rather than being burned in the field or removed for disposal. It is customary to dispose of conventional polyethylene (PE) agricultural mulch films rather than to try to till them into the soil, since they tend to entangle tillage equipment. Despite the low cost of starch (< $0.10/lb), starch–EAA film that contains sufficient EAA (> 40%) to provide useful properties is more expensive than PE

film, since polyethylene's cost is about one-fourth that of EAA ($0.45 vs. $2.00/lb). This fact led Otey et al. to replace a portion of the EAA in the formulations with low-density polyethylene (LDPE) to produce material that might be marketed at a more competitive price.[3] Gould et al. showed that bacteria can metabolize most of the starch in these films and thus significantly decrease tensile strength.[4] However, films containing LDPE were inferior to those prepared from only starch and EAA, especially at higher (40%) starch levels.[5] Percent elongations of 4–37% and tear strengths (resistance to propagation) of 69–89 kN/m, observed after 4 weeks at 50% relative humidity and 23°C, were unsatisfactory for most mulch or packaging film applications.

One approach to improving the film properties was replacement of normal cornstarch in the plastics with starches modified to have different viscoelastic properties. Unmodified normal cornstarch is composed of about 27% linear amylose (molecular weight 4×10^4–10^6) and 73% highly branched amylopectin (molecular weight 2×10^5–10^9 and an average of about 26 monomer units between branch points). These molecules may be envisioned as condensation polymers of glucose. They become highly

swollen in hot water and can form helical inclusion complexes with lipidlike materials[6-10] and an intensely blue–purple-colored iodine complex. Each helix in the complexes is composed of about 6 glucose units oriented with hydroxyl groups primarily directed toward the outside of the helix, so that the core of the helix is hydrophobic. Hydrophobic molecules of proper size may enter the helix to form complexes with lower energy than that of separate solvated molecules. A linear carbohydrate chain with a minimum of about 9 glucose monomer units is required for helical complex formation. EAA that has been dispersed in ammonium hydroxide or other alkaline aqueous solution mimics natural lipids and forms inclusion complexes with amylose and with the longer outer branches of amylopectin molecules.[11-15] Formation of helical complexes renders starch and EAA compatible up to an EAA/starch ratio of about 0.5/1.[16] EAA in excess of this ratio may form separate domains. LDPE does not enter into these complexes to any appreciable extent and is incompatible with starch–EAA complexes as well as with starch.

The molecular structures of the amylose and amylopectin components of starch contribute to the shortcomings of starch for some applications. In addition to the high viscosity of aqueous starch dispersions, the linear amylose polymer tends to crystallize and separate from aqueous dispersions, i.e., retrograde. Also, the branching in amylopectin is detrimental to film properties. Dextrins, i.e., starches of lower molecular weight produced by heating starch, often in the presence of acids or enzymes, provide superior performance in many applications. Because they are usually lower in molecular weight than is native corn starch, dextrins are typically easier to disperse, form more stable gels, and have lower paste viscosities than that of unmodified starch. The color of dextrins varies from off-white to deep yellow. Yellow (canary) dextrins are produced by using lower acid levels, higher temperatures, and longer heating times than are used in producing white dextrins. Canary dextrins are cold water soluble, highly branched, and produce pastes with better clarity than those prepared from white dextrins or starch. Dextrins are preferred over starch because of their viscosity stability and clarity in some foods and because of their superior film-forming characteristics in adhesives and paper coatings.

Starch may also be converted into maltodextrins and corn syrup solids by acid or enzyme treatments at temperatures below those used for dextrinization. These products provide good film formation, good oxygen barrier properties, and high solubility. Their primary use is in foods where they provide chewiness, binding, surface sheen, protective coating, and nutritive value. Their degree of conversion is defined by their dextrose equivalent (DE) value, which indicates the number of reducing end groups per 100 monomer units. Average degree of polymerization of a maltodextrin with a DE of 1 would be 100. Carbohydrates from low-temperature conversion that have DE values of 1–20 are designated maltodextrins and those with DE values of 20–28 are called corn syrup solids.

Among the variables investigated in attempts to improve physical properties of starch–EAA–PE films was replacement of normal cornstarch with more fluid-modified cornstarches such as dextrins or maltodextrins. Although films with the desired film strength properties were not achieved, we did obtain films that exhibit unusual properties when placed in water. In this article, we compare effects of water on films blown from EAA–LDPE formulations containing starch, a canary dextrin, and a maltodextrin with a DE of 1. We also attempt to explain the unusual behavior of this polymer composite system.

EXPERIMENTAL

Materials

Unmodified cornstarch was Globe 3005 from CPC International. Canary dextrin was Stadex-132 from A.E. Staley Manufacturing Co. It has a cold-water solubility range of 94–99% and a Brookfield viscosity of 1750 cp at 77°C and 58% solids. Maltodextrin was Star-Dri 1 from A.E. Staley Manufacturing Co. It is produced from high amylopectin starch and has a nominal saccharide distribution of 0.3% mono-, 0.1% di-, 0.2% tri-, and 99.4% higher-saccharides. Brookfield viscosity at 48% solids is about 10,000 cp at 100°C and 48% solids. Gel permeation chromatography (GPC) analyses suggested that the molecular weight of Star-Dri 1 was about 10 times that of Stadex 132, assuming equal degrees of branching. EAA was Primacore 5981 from Dow Chemical Co. It contained about 20% acrylic acid and had a melt index of 300, a weight-average molecular weight of 18,000, and a polydispersity index of 2.6. LDPE was Norchem 3404B from USI, a division of Quantum Chemical Corp. EAA and LDPE pellets, cooled in liquid nitrogen, were ground to pass through a 0.5 mm screen in a Retsch centrifugal grinder. Concentrated ammonium hydroxide was ACS grade (EM Science). Urea was prilled ACS grade (EM Science).

Film Preparation

Two basic formulations were prepared: One contained 44.4 parts carbohydrate, 27.8 parts EAA, 27.8 parts LDPE, 8.2 parts concentrated NH_4OH, and 13.7 parts water, by weight. The other contained 61.6 parts carbohydrate, 38.4 parts EAA, 15.3 parts urea, 12.4 parts concentrated NH_4OH, and 19.3 parts water. The carbohydrate : EAA ratio in each formulation was 1.6. The ratio of the sum of the weights of carbohydrate and EAA to water was 5.2 or 5.3, and to concentrated NH_4OH, 8.9 or 8.0. For each formulation, water and concentrated NH_4OH were weighed into a beaker. If urea was included in the formulation, it was weighed into a beaker, the ammonium hydroxide solution was added, and the solution was heated, with stirring, to dissolve the urea. The carbohydrate, EAA, and LDPE (if used in the formulation) were weighed into a beaker and the ammonium hydroxide solution was added while stirring. The moist, powdered formulations were compounded by passing four times through a C.W. Brabender extruder (diameter, 19 mm; length/diameter ratio, 25 : 1; hopper end temperature, 95°C; discharge end temperature, 120°C; standard two-zone mixing screw; die, 17–1.7 mm diameter strand). Strands were chopped with a Killion pelletizer. Films were blown with the same extruder using a 3 : 1 compression ratio screw and a 25 mm-diameter blown-film die (die temperature, 120°C). The bubble was blown to about 7.5 cm diameter. The film was recycled through the extruder up to 12 times, and samples from each pass were reserved for examination. Moisture levels were determined by drying film samples for 8 h under vacuum (< 100 mm Hg) at 100°C.

Scanning Electron Microscopy

Samples of blown films were fractured while immersed in liquid nitrogen, warmed to room temperature, and glued onto aluminum sample supports with cross sections facing the microscope's field of view. The exposed cross sections were soaked in water (approx. 24°C) for either 5 s (water-sensitive films) or 30 min (water-resistant films). Water-wet samples were solvent-exchanged with ethanol (by brief immersion in successively higher concentrations of ethanol in water) and were then critical point dried from absolute ethanol. Samples were coated with a layer of gold–palladium (60–40) alloy and were examined and photographed with a Hitachi ISI electron microscope.

Analysis of Films

Levels of carbohydrate, EAA, and LDPE in the various film fractions were determined by FTIR spectroscopy. This is a purely empirical method based on the comparison of absorption ratios in FTIR spectra of unknown films with absorption ratios in spectra of composite films of known composition. Average errors [calculated as 100 × (actual percentage − experimental percentage)/(actual percentage) in standard samples], standard deviation of average errors, and degrees of freedom for the method were, respectively, for LDPE, −1.8, 18.5, and 10; for EAA, −3.0, 12.3, and 10; and for carbohydrate, −7.5, 20.5, and 6. Negative values for the average error indicate overestimation of the amount present. Samples of film weighing 9–10 mg, 300–330 mg potassium bromide powder (Spectra-Tech), and 2 mL toluene (Baker analyzed reagent grade) were placed in a 4 in.-diameter agate mortar, covered with a watch glass, and allowed to stand at 75°C for 60 min. Hot dispersions were then ground with the pestle until they appeared to be dry. After cooling for 1 h in a desiccator, samples were reground to form smooth powders. A weighed portion of this powder containing 1 mg of the original film sample was diluted with additional anhydrous KBr to bring the final weight to 301.0 mg. The resulting mixture was stirred thoroughly and pelletized at 100,000 psi in a Carver hydraulic press using a Perkin-Elmer evacuable KBr die (cat. no. 186-0025). Spectra were obtained with a Mattson Polaris Fourier transform infrared spectrometer, equipped with a He—Ne laser and DTGS detector to provide a resolution of 0.5 cm^{-1}. Mattson ICON analytical software was used for spectral manipulation and subtraction.

The importance of grinding with a mortar and pestle rather than intimate grinding in a reciprocating ball-mill, such as a Wig-L-Bug amalgamator, must be stressed. In the Wig-L-Bug, moisture in varying amounts was absorbed by the KBr, producing poorly defined FTIR spectra with a water peak overlapping the region where the major EAA peak appears. Attempts to subtract this water peak from the spectra produced a scatter in the EAA absorbance measurements that proved to be unsuitable for concentration determination. The dispersion procedure described above successfully circumvented this complication.

Carbohydrate/EAA and LDPE/EAA ratios were determined from intensities of absorption at 1026 cm^{-1} (C—O stretch, carbohydrate, which overlies a tail from EAA absorption), 1705 cm^{-1} (carbonyl, EAA), and the overlapping C—H deformation

bands at 1472 cm^{-1} (LDPE, with underlying carbohydrate contribution) and 1466 cm^{-1} (EAA). Subtraction of the spectrum of pure carbohydrate provided the EAA–LDPE spectrum (1026 cm^{-1} absorption = 0) and subtraction of the spectrum of pure EAA provided the carbohydrate–LDPE spectrum (1705 cm^{-1} absorption = 0) for each specimen. Base lines were set from 1806 to 1500 cm^{-1} for EAA peaks and from 1500 to 1390 cm^{-1} for EAA/LDPE peaks in the EAA–LDPE spectra. Base lines were set from 1185 to 965 cm^{-1} for carbohydrate peaks in the carbohydrate–LDPE spectra. The ratio of absorbance of the 1472–1466 cm^{-1} peak to the absorbance of the 1705 cm^{-1} peak in a spectrum of EAA–LDPE obtained by spectral subtraction is proportional to the ratio of LDPE to EAA in the specimen. Likewise, the ratio of the absorption of the 1026 cm^{-1} peak in a carbohydrate–LDPE spectrum obtained by spectral subtraction to that of the 1705 cm^{-1} peak in the difference spectrum of EAA–LDPE is proportional to the ratio of carbohydrate to EAA for the specimen. Percentages of the components in each specimen were computed as follows:

Percentage EAA = 100/(1 + LDPE/EAA + carbohydrate/EAA)

Percentage LDPE = percentage EAA (LDPE/EAA)

Percentage carbohydrate = percentage EAA (carbohydrate/EAA)

Physical Testing

Specimens were equilibrated 28–34 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. The 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.

Tear-resistance specimens were 50.8 mm squares that were slit 12.7 mm from the center of one edge toward the center of the specimen. Slits were transverse (five specimens) or parallel (five specimens) to the direction of extrusion. Film thickness was the weighted average of five measurements, three (weight 1) along the path of tear and two (weight 0.5) along the perpendicular at the midpoint of the projected tear line. Samples oriented in the trouser position (one flap up and one down) were torn at 200 mm/min in the Instron. Initial grip distance was 19 mm. Tear resistance was the average for the 10 specimens of the integrated tearing load divided by the product of travel distance and film thickness.

RESULTS

Experiments in which dextrins were substituted for starch in polysaccharide–EAA–LDPE formulations produced brown films with strong caramel odors. In contrast, films containing unmodified starch were whitish and almost odor free. The difference is believed to result from Maillard reactions initiated by heating low molecular weight carbohydrates with ammonium hydroxide and urea. These complex reactions, which usually involve condensation of amino acids in proteins with aldehyde groups in carbohydrates, are partially responsible for browning of bread during baking.[17,18] We verified that lower DE (lower aldehyde) dextrins produced lighter-colored films than did more highly converted dextrins. For example, the lower molecular weight Stadex 132 canary dextrin produced darker products than did Star-Dri 1 maltodextrin.

Films containing 40% unmodified starch were water-resistant with the appearance of uniformly distributed materials after one pass through the film die. They became more papery and difficult to blow when recycled through the extruder and die, but their water resistance did not change. We observed, however, that repeated extrusion of films containing unmodified starch was very detrimental to the physical properties of the films. Ultimate tensile strength, measured 28 days after film preparation, decreased from 16.2 MPa at pass 1 to 3.06 MPa at pass 7. Percentage elongation decreased from 7.4 to 4.1, and tear resistance decreased from 1.8 N/mm to 0.75 N/mm between passes 1 and 7. The moisture content of blown films decreased from 10.4 to 7.0% between passes 1 and 6. Scanning electron micrographs of exterior and cross-sectional surfaces of 2 and 6 pass specimens of starch–EAA–LDPE films showed no swelling, cracking, or separation of surface skin after soaking in water for 30 min (Fig. 1). Surface skins rich in EAA and LDPE may be present, however, since films made from this formulation stained with iodine along cut edges, but stained little on the original surface. Also, Shogren et al. showed the presence of carbohydrate-rich layers and EAA–LDPE-rich surfaces.[16]

Water resistance of films containing canary dextrin and maltodextrin was inferior to that of films
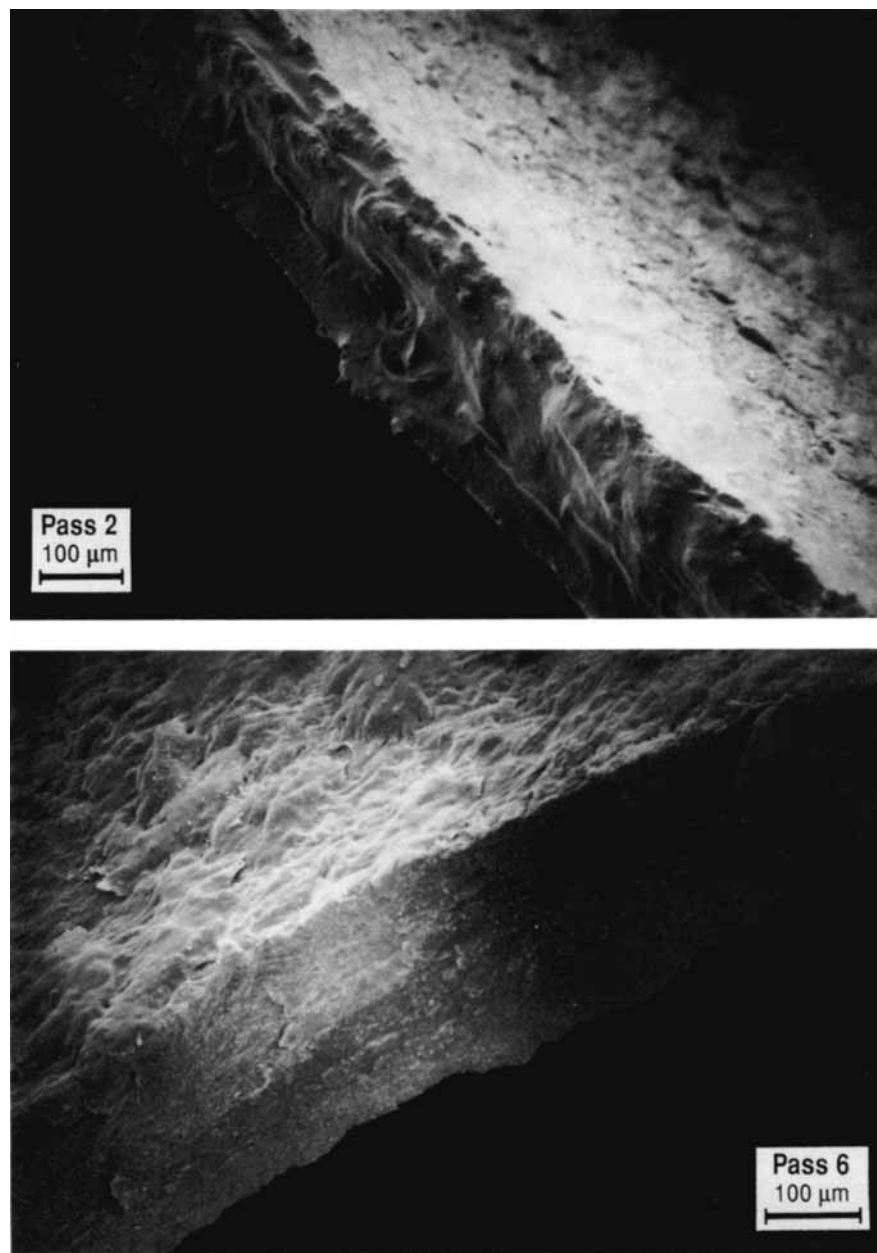
Figure 1   Scanning electron micrographs of starch-based film after soaking in water for 30 min (passes 2 and 6). Composition was starch, 44.4 parts; EAA, 27.8 parts; and LDPE, 27.8 parts.

containing unmodified starch. Films prepared from canary dextrin–EAA–LDPE (44.4 : 27.8 : 27.8), with 1–5 passes through the extruder, disintegrated in water to produce milky dispersions and very thin water-insoluble exterior-surface skins. However, water resistance improved dramatically between the fifth and eighth pass through the extruder and die (Fig. 2). After six or seven passes, the surface skins thickened and the films became very water-resistant.

Scanning electron micrographs of canary dextrin–EAA–LDPE films (Fig. 3), after soaking in water for either 5 s (passes 2 and 5) or 30 min (passes 7 and 9), clearly show the dramatic difference in water resistance produced by recycling through the extruder and die. After two passes, most of the interior of the film appeared as particles, perhaps released from a water-soluble continuum. The exterior surfaces appeared to be thin porous membranes or
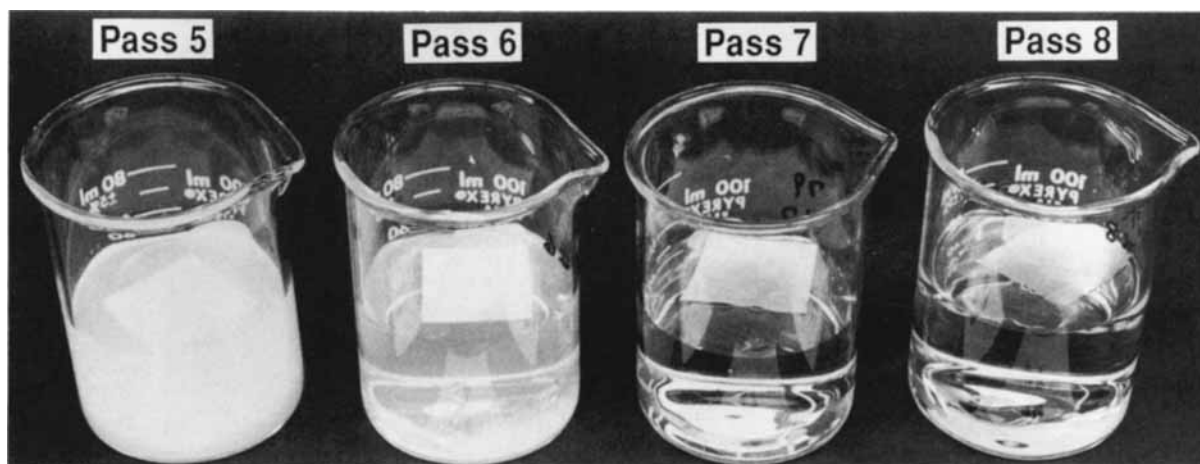
Figure 2   Sections of canary dextrin-based film extruded 5–8 times and floated on water overnight. Composition was Stadex 132, 44.4 parts; EAA, 27.8 parts; and LDPE, 27.8 parts.

skins. After five passes, the exterior skins appeared thicker and less porous and other membranes were observed in the center of the film. After seven passes, the film was water-resistant and appeared to consist of several laminae. No particles were visible in the interior of the film. After 10 passes, the film re-
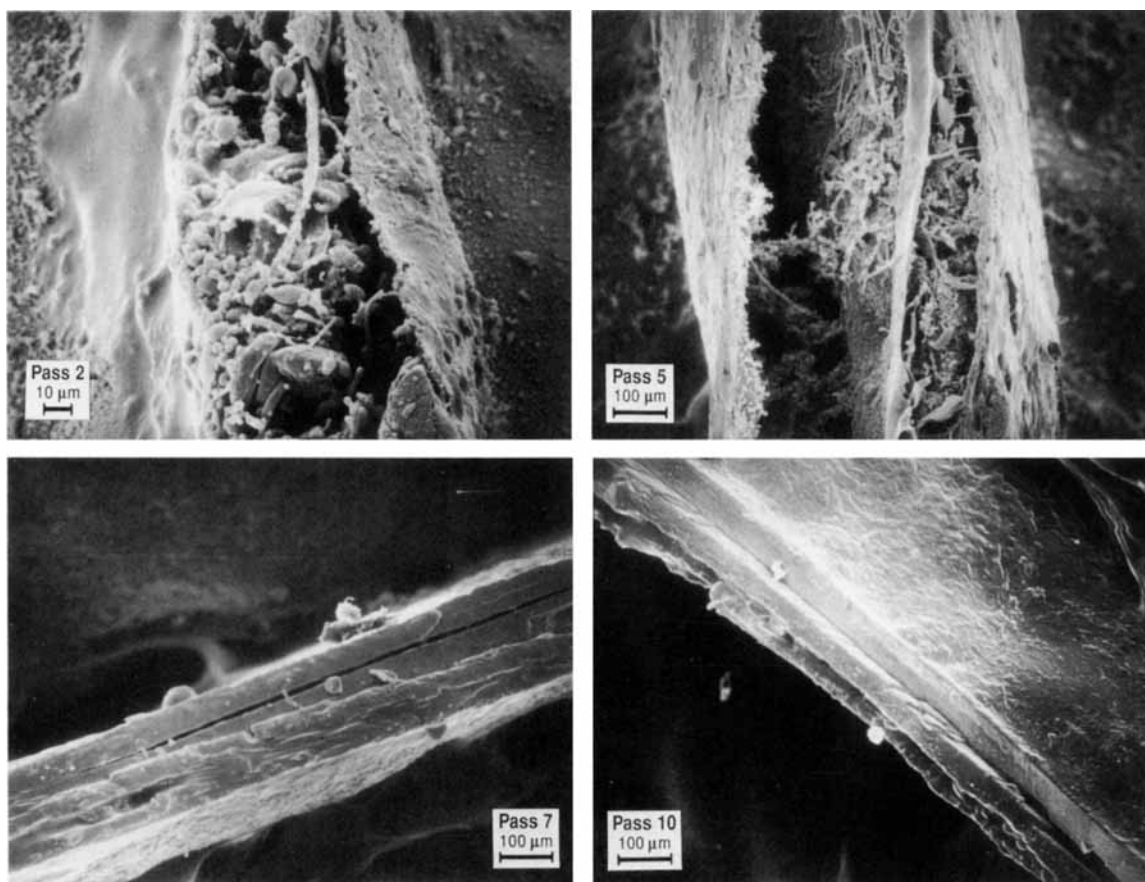

Figure 3   Scanning electron micrographs of canary dextrin-based film after soaking in water for 5 s (passes 2 and 5) or 30 min (passes 7 and 10). Composition was Stadex 132, 44.4 parts; EAA, 27.8 parts; and LDPE, 27.8 parts.

mained water-resistant and had fewer, but thicker, laminae. Before treatment with water, all films appeared continuous and almost void-free.

In another experiment, samples of film from passes 2 and 5 were soaked in water until they disintegrated to form surface skins plus a milky dispersion of particles from the films interior. The top and bottom skins were then lifted from the dispersion. Particles from the interior of the film greater than about 1 μm in size could be separated from smaller particles by centrifugation or by filtration through a 1 μm Millipore filter. The larger particles were less dense than water and tended to float to the surface, while the smaller particles were denser than water and precipitated. Uncomplexed canary dextrin is water-soluble and was thus largely discarded with the supernatant liquid.

FTIR analysis of skins from the second-pass film showed more than 82% LDPE, 10–17% EAA, and no more than 1% carbohydrate (Table I). Larger interior particles were also primarily LDPE but contained 7% carbohydrate and 16% EAA. This EAA:carbohydrate ratio is far in excess of that expected for complex formation with canary dextrin. The small particles from the center of the film contained less than 4% LDPE and were primarily carbohydrate. The EAA/carbohydrate ratio of the small particles was between 0.5 and 0.25 and was within the range expected to complex with unmodified starch. However, this amount of EAA may exceed the maximum that can be complexed by a canary dextrin, due to shorter chain lengths and increased branching relative to starch.

Physical properties of the film changed significantly with succeeding passes through the extruder and die. Ultimate tensile strength averaged 1.74 MPa for passes 2–4 and 13.3 MPa for passes 8–11. Average percentage elongation at break increased from 11.4 (passes 2–4) to 19.3 (passes 8–11) and average tear resistance increased from 0.17 N/mm (passes 2–4) to 0.41 (passes 8–11). No trends were apparent in either the 2–4 pass or the 8–11 pass values.

Films prepared from 44.4 parts maltodextrin (Star-Dri 1), 27.8 parts EAA, and 27.8 parts LDPE were far more water-resistant than those prepared from canary dextrin and they did not disintegrate in water after a few seconds soaking. Scanning electron microscopy of film from pass 2 (Fig. 4) revealed pitting after soaking 30 min in water that might result from removal of water solubles. Water-resistant skins apparently cover the exterior of the films. Films produced with five passes appear as multilamina sheets after soaking in water. The number of laminae decreased with continued recycling through the die (pass 7), and only one or two layers were evident after 10 passes.

In contrast to the canary dextrin, skins and interior layers obtained by extended soaking of early passes of the maltodextrin film varied little in composition (Table I). EAA level was about 36–38% in all fractions. LDPE composed 37–45% of the skins and was 36–37% of the interior fractions. Maltodextrin composed 19–25% of the skins and was about 25–26% of the interior portions of the film. Ultimate tensile strength, percentage elongation, and tear re-

Table I   Composition of Fractions from Water-soaked Films[a]

Carbohydrate Used	Pass	Fraction	Percentage of Total	EAA (%)	LDPE (%)	Carbohydrate (%)
Canary dextrin	2	Skin	8	10	90	< 1
	2	Skin	3	17	82	1
	2	Interior (> 1 μm)	—	16	78	7
	2	Interior (< 1 μm)	—	20–33	0–4	66–78
	5	Skin	4	36	48	16
	5	Skin	4	36	45	19
	5	Interior (> 1 μm)	—	31	49	20
	5	Interior (< 1 μm)	—	9–23	0	77–91
Maltodextrin	2	Skin	5	38	40	22
	2	Skin	9	36	45	19
	5	Skin	—	37	38	25
	5	Skin	—	38	37	25
	5	Interior	—	38	37	25
	5	Skin	—	38	36	26

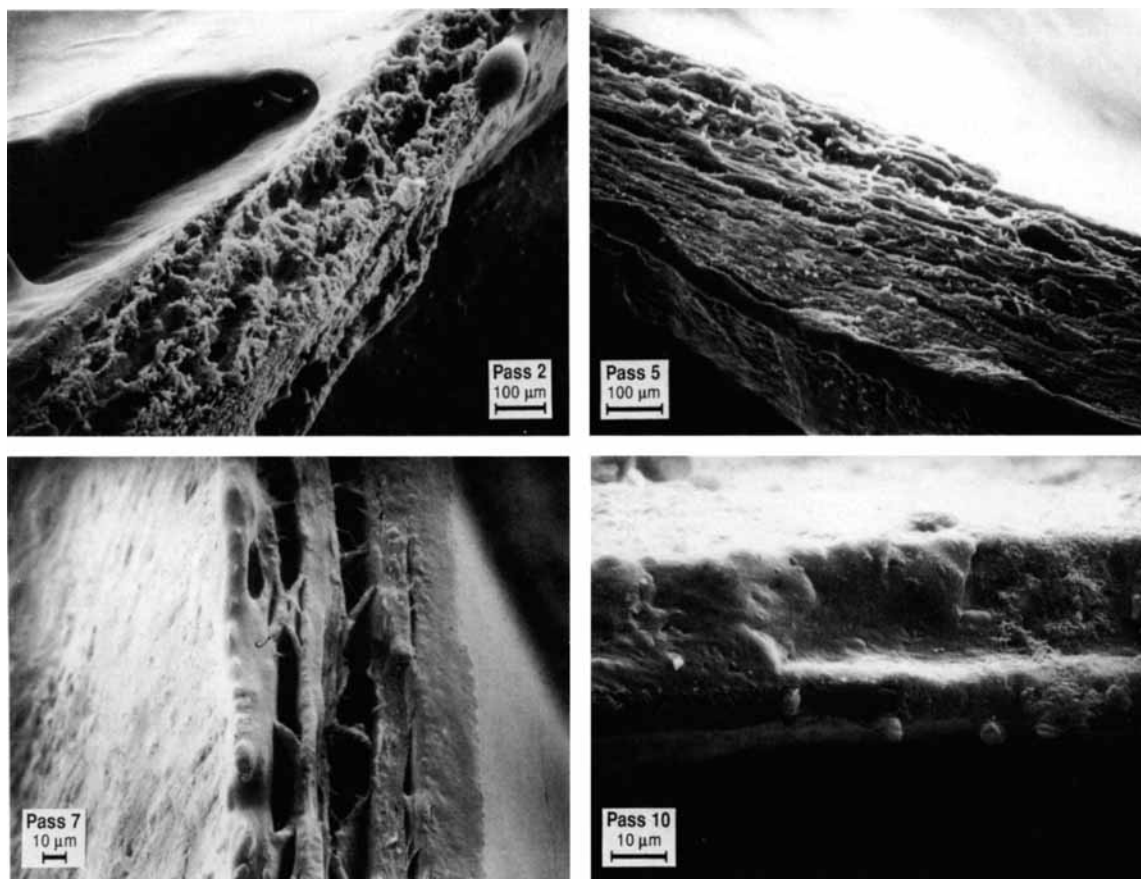[a] The films contained 44.4 parts carbohydrate, 27.8 parts EAA, and 27.8 parts LDPE.

Figure 4 Scanning electron micrographs of maltodextrin-based film after soaking in water for 30 min (passes 2, 5, 7, and 10). Composition was Star-Dri 1, 44.4 parts; EAA, 27.8 parts; and LDPE, 27.8 parts.

sistance of films did not change significantly with the number of passes through the extruder and die. Moisture contents of the films immediately after extrusion were 9.7% (pass 1), 6.5% (pass 6), and 6.2% (pass 11).

LDPE was next eliminated from the formulation, and urea was added as a polysaccharide plasticizer to give a formulation containing 53.3 parts maltodextrin, 13.3 parts urea, and 33.3 parts EAA. Elimination of LDPE and addition of urea to the maltodextrin film greatly increased its water sensitivity. In fact, these films were so water-sensitive that 5 s soaking was sufficient to reveal the morphology even after 10 passes through the extruder and die (Fig. 5). Microscopy revealed the presence of skins on all fractions. The center of pass 2 film appeared particulate. On each pass, the weights of skins recovered from each side of the film were about equal. However, the percentage of the total film recovered as skin increased from 0.630 at pass 2 to 3.6 at pass

10. Succeeding passes through the extruder and die caused the particulate interior seen after the second passage to coalesce into extremely thin laminae. These laminae were discontinuous, however, and unlike the surface skins, they dispersed in water to form a milky suspension. The behavior of these films is quite different from that of comparable films prepared with unmodified cornstarch in the formulation instead of dextrin. Cornstarch-containing films were water-resistant, and urea could, in fact, be leached from these films with water without affecting film integrity.[19]

DISCUSSION

A number of factors are responsible for the behavior of these films when they are placed in water. These factors include extent of depolymerization of the carbohydrate, degree of complexing of carbohydrate
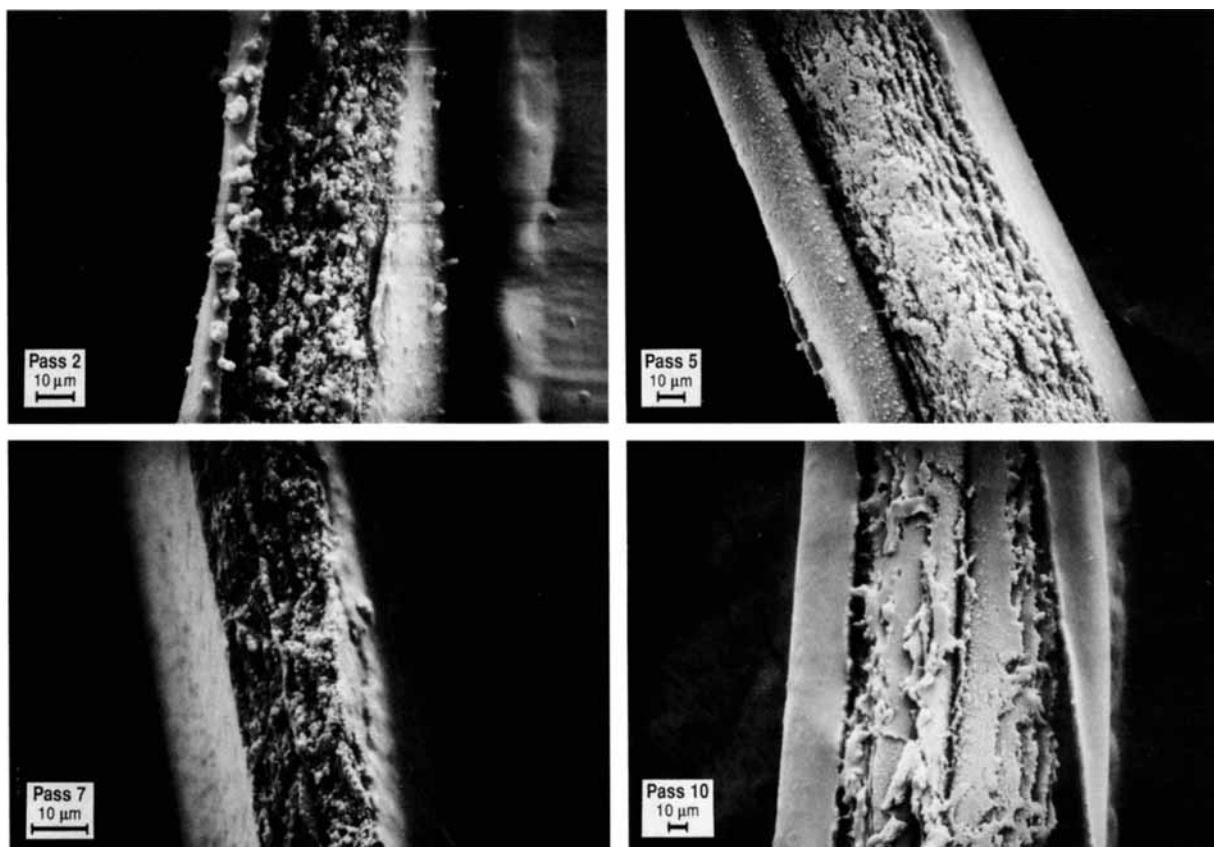
Figure 5   Scanning electron micrographs of maltodextrin-based film after soaking in water for 30 min (passes 2, 5, 7, and 10). Composition was Star-Dri 1, 53.3 parts; EAA, 33.3 parts; and urea, 13.3 parts.

with EAA, the moisture content of the formulation (which influences the relative viscosities of the hydrophilic and hydrophobic phases), differences in shear rate at the surface and the interior of the die, and chopping of recycled film by the screw as it enters the extruder. All these factors are further influenced by the structure of the polysaccharide used in the formulation and the number of passes through the extruder and die.

Tensile strength of films containing unmodified starch decreased with repeated passage through the extruder and die, probably due largely to continued depolymerization of amylopectin. EAA is probably changed little, since its temperature–time history is well below the recommended pot conditions for its use as a melt adhesive. The starch–EAA complex may be protected somewhat from shear effects, since water resistance of films was unaffected. To a point, drying during recycling should increase viscosity of the carbohydrate-rich phase and, therefore, the shear applied to the carbohydrate molecules. How-

ever, at very low moisture levels, carbohydrate molecules will probably behave as particulate fillers in the polymer system and will thus be unaffected by shear stress. Tensile properties of films containing the intermediate molecular weight maltodextrin were unchanged by successive passes through the extruder and die. Films containing canary dextrin, the lowest molecular weight carbohydrate, actually improved in tensile strength with recycling until they reached the water-resistant stage. Thereafter, their tensile strength remained constant, probably because the continuous hydrophobic phase carried the test loads.

Complexing between starch molecules and EAA could distribute the EAA widely throughout the film and also provide cross-linking that would impede swelling at room temperature. Both effects should enhance water resistance. The starch–EAA complex should occupy the largest volume fraction in the polymer matrix and should tend to become the continuous phase. It is widely accepted that the polymer

in the largest volume fraction will become the continuous phase unless its viscosity is substantially lower than that of the minor polymer.[20] As predicted by this theory, we have seen examples of LDPE globules in some examples of starch–EAA–PE films that were fractured in liquid nitrogen. Starch modifications that reduce levels of complexing and crosslinking (i.e., conversion of starch to dextrin and maltodextrin) should allow more carbohydrate to dissolve and allow greater segregation of carbohydrate and EAA. These effects should be reflected in lower moisture resistance of films in which the modified starch–EAA domain constitutes the continuous phase. Cores of films that contain unmodified starch complexed with EAA should not disintegrate, whereas those of less complexed carbohydrates might be expected to behave in a manner similar to canary dextrin and maltodextrin.

Formation of skins suggests an effect of higher shear, higher temperatures, or a combination of the two at the die surface. Thermal effects alone are an unlikely cause of skinning, since skins of about equal thickness occur at both the unheated mandrel (which was cooled somewhat by movement of air through its core to maintain inflation of the plastic bubble) and the heated body of the die. It is well known that extrudate velocity increases from the die surface to the center of the die opening and that the shear rate is greatest near the die surface. Also, a series of papers by Mason et al. (e.g., Ref. 21) and Segré et al. (e.g., Ref. 22) showed the tendency of deformable particles suspended in sheared fluids to migrate to the region of minimum shear. Brandt and Bugliarello demonstrated the same behavior in suspensions of nearly nondeformable spherical particles,[23] whereas Schreiber et al. demonstrated shear-induced fractionation according to the molecular weight of polymer molecules.[24] Skin formation may thus be a manifestation of this phenomenon, wherein a phase inversion occurs, and the major carbohydrate–EAA phase then becomes dispersed in the minor hydrophobic LDPE phase in the high shear area at the die surface. Material in the center of the die might move as a plug because of the low shear field and would thus not be driven to invert. As the carbohydrate becomes more viscous, the shear effects may extend further into the opening to create thicker films. Viscosity of the carbohydrate-containing phase appears to be the most important factor controlling skin formation in our equipment. Doubling or halving the extruder speed when blowing films containing canary dextrin, EAA, and LDPE changed by no more than one pass the recycling required for development of water resistance.

However, a water-sensitive film produced in the first pass through the extruder and die was oven-dried overnight and produced a highly water resistant film on the subsequent pass.

Multiple laminae in the films probably result from successive passes through the extruder and die. If film that was returned to the extruder was partially melted, compressed, and moved through the extruder largely by plug flow, it might retain its identity, at least in part, when it appeared in a subsequent film. In agreement with this theory, the number of layers that could be observed on water soaking of films seemed to increase with the number of passes. However, the number of laminae varied from area to area within a film. Also, when the skin thickness became a significant fraction of the film thickness, the number of lamina decreased on subsequent passes. Although the skins were continuous, the inner laminae were discontinuous, as one might expect as a result of chopping of films between the screw and barrel of the extruder.

Dependency of skin formation on shear rate suggests that formation of skins on films blown with a given formulation probably depends on the type of equipment used for preparing the film. For example, a formulation with moderate moisture content should be less likely to form skins if compounded under high-shear conditions in a twin-screw extruder than if compounded in a low-shear single-screw extruder.

Multilayer films or sheets consisting of a largely carbohydrate core sandwiched between layers of a water-impervious polymer might be envisioned as degradable packaging materials meeting MARPOL treaty requirements for disposal at sea. The observed water sensitivity of multilayer films composed of dextrin or maltodextrin–EAA cores inside skins of water-resistant polymer suggests that incidental abrasive damage to such films could cause catastrophic failure of the film on exposure to water. The starch–EAA complex, however, is water-resistant and survives immersion. Similar complexes between unmodified starch and a totally biodegradable polymer might provide highly water-resistant and biodegradable core films for multilayer containers or packaging films. Dextrins or maltodextrins, however, are unlikely to develop adequate water resistance for this application without additional crosslinking.

The Star Dri-EAA film skins may have potential as ultrathin semipermeable membranes. Otey and Westhoff showed that urea diffused 32 times faster than did sucrose through starch–EAA films prepared from formulations in which NaOH replaced

NH$_4$OH.[25,26] Ultrathin films with like permeability properties might prove useful as reverse osmosis membranes.

CONCLUSIONS

Replacement of starch by dextrins or maltodextrins in starch–EAA–LDPE formulations resulted in dark-colored malodorous films. The color and odor problem was probably due to Maillard reactions and was reduced by use of carbohydrates with fewer reducing end groups.

Thin water-resistant skins observed on films blown from carbohydrate–EAA and carbohydrate–EAA–LDPE formulations may form through phase inversion due to high shear in the die throat. Thickness of the layers was controlled by the structure of the carbohydrate, moisture content, amount of EAA or EAA/LDPE in the formulation, and, possibly, the level of urea in the formulation. Drying of the formulation by recycling the film through the extruder a number of times probably increased the viscosity of the carbohydrate–EAA phase and resulted in more water-resistant films and thicker skins. Partial drying of the film in an oven can replace recycling as a means of increasing skin thickness. Skins from these films might be formulated to possess semipermeable membrane properties.

Sensitivity to water of these carbohydrate-based films coated with a thin waterproof skin suggests that coating of starch films with hydrophobic layers may not, in itself, provide sufficient water protection to allow their use as packaging films. The starch layer may also require formulating so as to provide water resistance.

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