

Application of Hydrophilic Starch-Based Coatings on Polyethylene Surfaces

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ABSTRACT: Coatings were applied to polyethylene (PE) film surfaces by spraying formulations prepared from a jet cooked dispersion of waxy cornstarch, a water-born epoxy resin, a wax emulsion, and a fluorinated surfactant. The air-dried coatings were comprised of discontinuous areas of polymer that adhered tightly to the PE surface. Although the starch component separated rapidly from the coating when the film was placed in water at room temperature, heating the coated film for 24 h at 80°C increased the adhesion of starch and produced a surface coating that remained uniformly wet when the film was placed in water. Most of the starch, however, could be still be

removed by gently rubbing the wet surface. If melamine-formaldehyde resin was added to the formulation as a crosslinking agent for starch, and the coated film was then heated for 24 h at 80°C, most of the starch remained bonded to the wet coating, even after the surface was gently rubbed. Identification of successful spray application techniques and formulations will allow the development of commercial production methods for starch-coated PE films and similar products. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2749–2755, 2008

Key words: coatings; composites; polysaccharides; surfaces

INTRODUCTION

Starch is a polysaccharide composed of repeating α -D-glucopyranose units and is produced by living plants as discrete granules that range in diameter from about 5–40 μm , depending upon the plant source. Commercial starch samples contain both linear and branched components (i.e., amylose and amylopectin) in varying amounts. Normal food grade cornstarch has an amylose to amylopectin ratio of about 25 : 75, by weight; waxy cornstarch is composed of almost pure amylopectin; and high amylose cornstarch has an amylose to amylopectin ratio of about 70 : 30. Native starch granules do not swell or dissolve in water at room temperature. Although amylose is preferentially dissolved at elevated temperatures, solubility of starch granules is incomplete even at temperatures approaching 100°C; and a major portion of the starch still remains as highly swollen granules and granule fragments. Although

starch can be dissolved in water in an autoclave at temperatures greater than 100°C, solutions of starch for commercial applications can be conveniently prepared by a continuous steam jet cooking process, in which an aqueous starch slurry is pumped through a hydroheater where it is heated with steam at high temperature and pressure.¹

As part of an on-going research program on starch utilization, we are examining steam jet cooking as a processing method for producing new starch composites and derivatives. As part of this research effort, we have studied the adsorption of starch onto polyethylene (PE) film surfaces by immersing PE films into hot, jet cooked starch dispersions and then allowing the mixtures to slowly cool.² The dried coatings of adsorbed starch adhered to the PE surface and imparted hydrophilic surface properties to the PE films. The coatings adhered more tightly to the PE surface when the adsorbed starch was graft polymerized with acrylonitrile.³

Methods for imparting hydrophilic surface properties to hydrophobic plastics are of interest because of the ability of hydrophilic surfaces to retard the build-up of static electricity, to alter friction and adhesion properties between surfaces, to allow surfaces to be printed with water-based dyes and inks, and to improve the compatibility of surfaces with biological fluids. Since our earlier method for depositing starch onto PE films by slow adsorption from jet cooked dispersions would be difficult to carry out under large scale production conditions, we are

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currently examining other methods of application. This study describes the application by spraying of aqueous formulations prepared from jet cooked cornstarch, a water-based epoxy resin, a wax emulsion, a fluorinated surfactant, and a melamine/formaldehyde resin that was added in some experiments as a crosslinking agent for starch.

EXPERIMENTAL

Materials

Normal, unmodified food grade cornstarch, and waxy cornstarch (Waxy No. 1) were obtained from A. E. Staley Mfg., Co., Decatur, IL.

PE films were cut from 6 × 6 inch (15.2 cm × 15.2 cm) clear interlocking seal closure bags produced from a blend of linear low density PE and low density PE. The bags (Skilcraft) were purchased from Envision, Wichita, KS, and were manufactured according to Commercial Item Description A-A-1799B. The bags were used as received. To minimize surface contamination, the inside surfaces were used for spraying.

The epoxy resin was Epi-Rez[®] 3510-W-60 Waterborne Resin, manufactured by Shell Chemical, Houston, TX, and was obtained from Resolution Performance Products, Pueblo, CO. This product is an aqueous dispersion of bisphenol A-epichlorohydrin epoxy resin⁴ containing 60–62% nonvolatile resin with an average particle size of less than 2 μm (reported by the manufacturer). The reported weight per epoxide, based on nonvolatile resin, was 199. Although a number of water-based resins were screened for their ability to promote adhesion between the hydrophilic coating and the hydrophobic PE surface, coating formulations prepared with water-based epoxy resin were superior to all others examined.

The fluorinated alkyl surfactant was Zonyl[®] FSA from Dupont Chemical Solutions Enterprise, Wilmington, DE. This surfactant has the general structure: $RfCH_2CH_2SCH_2CH_2CO_2Li$, where $Rf = F(CF_2CF_2)_x$ and $x = 1$ to about 9. The reported surface tension in deionized water (for 0.01% active ingredient at 25°C) was 22 dyn/cm. A variety of other surfactants were also tested, but the fluorinated surfactant gave the best results.

The nonionic/anionic wax emulsion was Aqua-bead[®] 270E from Micro Powders Inc., Tarrytown, NY. This product had a reported solids content of 40.0% ± 1.0%, a viscosity of 200–500 cps, and a pH of 9.5–10.3.

The melamine-formaldehyde resin was Cymel 323 from Cytec Industries Inc., West Paterson, NJ. This material is a methylated high imino (—NH) melamine/formaldehyde resin in isobutanol. Percent non-

volatiles was 80 ± 2, degree of polymerization was 1.8, and water dilutibility (cc to haze/10 g resin) was 100+, as reported by the manufacturer.

Steam jet cooking of starch, and preparation of coating formulations

Jet cooked dispersions of waxy cornstarch were prepared by passing a dispersion of 700 g of starch in 3500 mL of water through a Penick & Ford Laboratory Model steam jet cooker operating under excess steam conditions.¹ Cooking temperature was 140°C, back pressure was 40 psig (380 kPa), and steam line pressure was 70 psig (580 kPa). Pumping rate through the cooker was about 1-L/min. Jet cooked dispersions of normal dent cornstarch were similarly prepared from 150 g of starch in 1000 mL of water. Jet cooked dispersions of starches with intermediate amylose contents were prepared from mixtures of waxy cornstarch and normal dent cornstarch. Percent starch solids in jet cooked dispersions were determined by freeze drying weighed portions of jet cooked dispersions. Values for percent solids were lower than the calculated amounts due to dilution of the dispersions with condensed steam.

Weighed amounts of the different components of the formulation were added to the starch dispersion in a beaker, and enough water was then added to give the required concentration of total solids. The mixture was then stirred for about 30 min. Stirring speed was adjusted to produce a vortex in the stirred dispersion; however, excessive stirring speed was avoided to inhibit the formation of air bubbles. Viscosities were measured at room temperature with a Brookfield Synchro-Lectric viscometer, Model LVT (Brookfield Engineering, Middleboro, MA) using a No. 2 spindle at 60 rpm.

Formulations were sprayed onto PE film surfaces (about 14 cm × 14 cm) with a Badger Model 400 Detail/Touch-Up Gun (Badger Spray Supply, Madison, WI). Films were mounted on a solid backing at an angle of about 45° and were sprayed from a distance of about 15 cm. To minimize the coalescence of aqueous droplets on the PE surface, the film surface was dried for about 5 s with a hot-air gun between each back-and-forth pass. The thickness of the applied coating varied with the number of passes, and 10–20 back-and-forth passes of the sprayer were typically used. The amount of coating applied (μg/cm²) was determined gravimetrically after the applied coatings were allowed to air-dry overnight. The amount of coating that separated from the surface when the films were placed in water was determined by weighing sections of film (about 1.5 cm × 4 cm) before and after water treatment.

TABLE I
Basic Coating Formulation

Component	Weight (g)	Weight (%)
Waxy starch dispersion (13.1% solids)	91.6	6.0
Epoxy resin dispersion (62% solids)	6.4	2.0
Wax emulsion (40% solids)	6.0	1.2
Fluorinated surfactant (25% solids)	2.0	0.25
Water	94.0	90.55
Total	200.0	100.0

Microscopy

Coated film surfaces were sputter coated with gold, and SEM images were obtained with a JEOL 6400 V scanning electron microscope. Phase contrast images were obtained with a Zeiss Axioskop light microscope (Carl Zeiss, Thornwood, NY), and representative fields were photographed using a Kodak DCS 460 digital camera (Eastman Kodak, Rochester, NY).

FTIR spectroscopy

Spectra were obtained with a single bounce 1.5 mm diameter Diamond midrange Attenuated Total Reflectance (DATR) DuraScope from SensIR. The DuraScope was mounted in a Thermo Nicolet Avatar 370 FTIR, and spectra were collected using high pressure on the diamond platform. The spectra were analyzed with Nicolet Omnic software.

RESULTS

Initial experiments were carried out with the spray-coating formulation shown in Table I. Waxy cornstarch, which is comprised of about 100% amylopectin, was used to avoid viscosity increases due to the formation of amylose gel when the jet cooked dispersion was cooled. The total solids content of the aqueous formulation was 9.45%, the pH was 9, and the Brookfield viscosity was 140 mPa s (or cP). Reducing the total solids content to 8.0% and 6.0% (while maintaining the same relative amounts of each of the individual components) reduced Brookfield viscosities to 90 and 55 mPa s, respectively; however, the adhesion of the air-dried coating to the PE film surface was not affected. Formulations with waxy cornstarch concentrations greater than about 6% solids had Brookfield viscosities greater than 200 mPa s and were generally too viscous for spray application. When starches with amylose contents less than about 20–25% were used, the gels that formed in cooled dispersions could be redispersed by high-shear stirring. Gel formation could also be reduced by rapidly cooling the jet cooked dispersions in ice. The viscosities of these formulations, however, were still higher than those of comparable formulations prepared from waxy cornstarch; and it was often necessary to reduce the starch concentration to obtain efficient spraying. For example, when the concentration of normal, dent cornstarch was

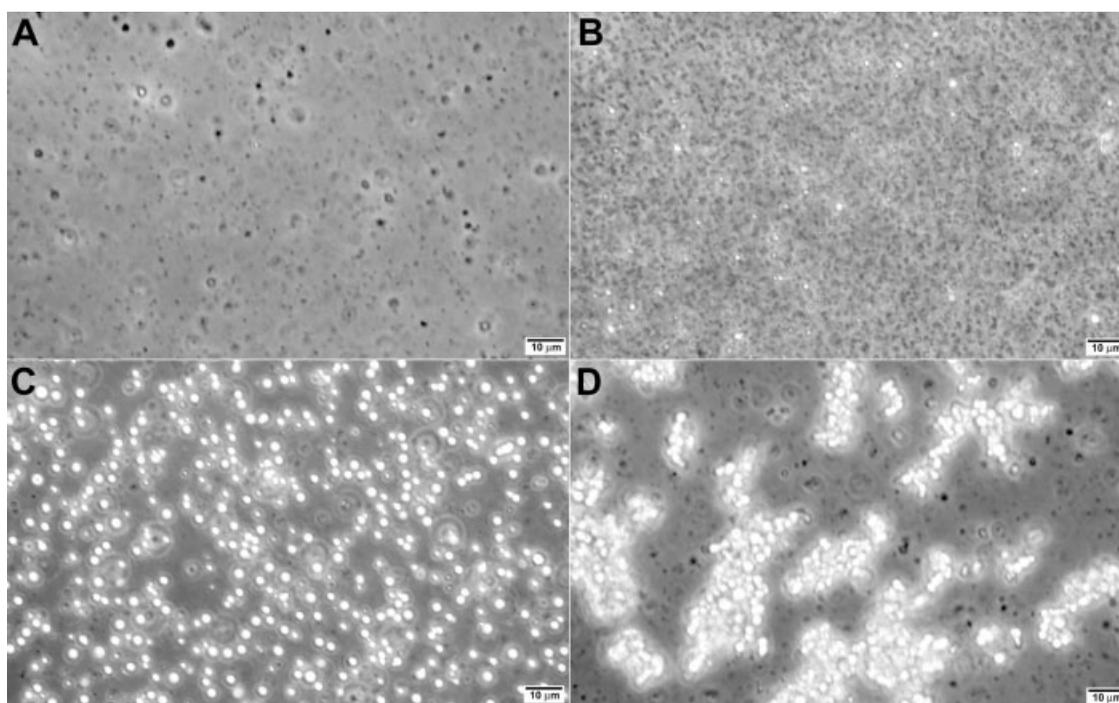


Figure 1 Phase contrast images of the components of the coating formulation shown in Table I. (A) Jet cooked dispersion of waxy cornstarch, (B) Wax emulsion, (C) Aqueous epoxy resin dispersion, and (D) Combined components of the formulation.

reduced from 6 to 4% (with the same epoxy resin concentration of 2%), the Brookfield viscosity was less than 200 mPa s; and good adhesion of the air-dried coating was observed. At starch concentrations of both 6 and 4%, reducing the epoxy resin concentration from 2 to 1% resulted in poorer adhesion to the PE surface.

Phase contrast images of the individual components of the coating formulation are shown in Figure 1. The waxy cornstarch granules were completely dispersed by steam jet cooking, and the dispersion showed only a few insoluble fragments [Fig. 1(A)]. The insoluble wax particles in the aqueous emulsion were sub-micron in size [Fig. 1(B)]; whereas the droplets of epoxy resin in the aqueous dispersion [Fig. 1(C)] were about 1–2 μm in diameter. The fluorinated surfactant was a clear dispersion and showed no discrete particles. Aggregation of epoxy resin droplets was observed when the components of the formulation were combined [Fig. 1(D)]. These aggregates formed a precipitate if the formulation was allowed to stand for several hours at room temperature; however, the precipitate could be re-dispersed by rapid stirring.

The amount of coating applied could be easily varied by varying the number of passes of the sprayer across the film surface, and coating amounts typically ranged from about 100–500 $\mu\text{g}/\text{cm}^2$. The film surface was briefly heated with a hot-air stream between passes to increase the rate of evaporation of water from the sprayed droplets and inhibit their coalescence into larger drops. SEM images of a 188 $\mu\text{g}/\text{cm}^2$ coating (Fig. 2) showed that the air-dried coating was comprised of discontinuous areas of adsorbed solid. The coating adhered tightly to the PE surface and did not separate from the surface when the film was creased or rubbed.

The properties of the coating when the film was placed in water depended upon whether or not the coated film was heated after air drying. When an unheated film, with 188 μg of coating per cm^2 , was placed in water at room temperature, about 90% of the coating separated from the surface and dispersed in water within about 1–2 min. FTIR spectra of (A) the air-dried coating before water treatment, (B) the portion of coating that separated from the surface in water, and (C) the coating that remained on the surface after the film was allowed to stand in water for 10 min are shown in Figure 3 (A–C), respectively. Spectra of the four components of the coating formulation [Fig. 3(D–G)] are also shown for comparison. As expected, comparison of these spectra showed that the water dispersible portion of the coating was comprised mostly of starch (major absorptions at 1022, 1075, and 1149 cm^{-1}), with lesser amounts of epoxy resin (absorption at 1510 and 1240 cm^{-1}). The coating that remained on the PE surface after water

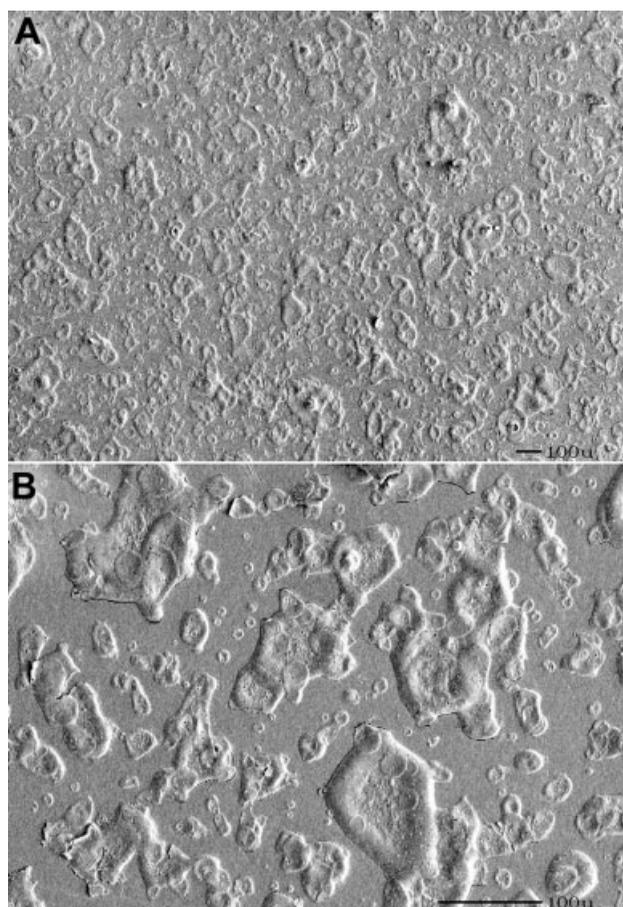


Figure 2 SEM images of air-dried coating sprayed onto a PE film surface. Coating formulation is shown in Table I. Surface coverage: 188 $\mu\text{g}/\text{cm}^2$. Images A and B are at two different magnifications.

treatment contained a higher percentage of epoxy resin relative to starch. The C–H absorption of the wax emulsion at 1462 cm^{-1} was in the same region as PE and therefore could not be differentiated from the PE film. Because of the small amount of surfactant used in the formulation, absorption bands for the fluorinated surfactant were difficult to identify in the spectra of the applied coatings.

Adhesion of starch to the wet film surface was improved when the air-dried film was heated in an oven for 24 h at 80°C, presumably because of reaction between starch and epoxy resin at the elevated temperature. SEM showed that heating did not change the morphology of the coated film surface, and images of the heated surface (not shown) resembled the images in Figure 2. The surface of the heated film was rapidly and uniformly wet when the film was placed in water, and only about 25% of the coating was lost when the film was allowed to stand in water for 10 min at room temperature. When the wet surface was gently rubbed, about 75% of the coating was removed; and the surface lost

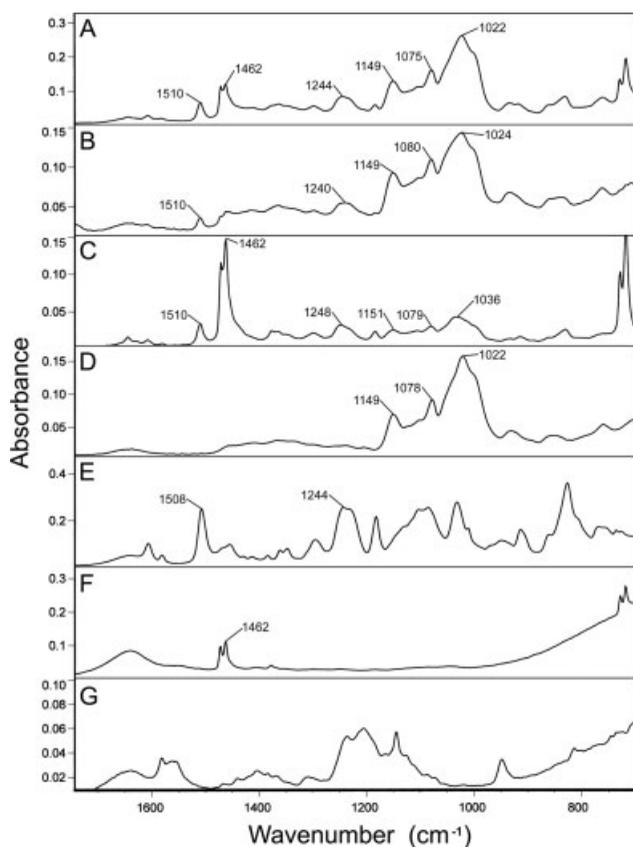


Figure 3 FTIR spectra. (A) Coating on PE surface from formulation shown in Table I. Coating not heated. Surface coverage: $188 \mu\text{g}/\text{cm}^2$, (B) The portion of the coating that separated from the PE surface when the film was placed in water, (C) Coating remaining on the PE surface after water treatment, (D) Cornstarch, (E) Epoxy resin, (F) Wax emulsion, and (G) Fluorinated surfactant.

most of its hydrophilic properties, as indicated by beads of water that formed on the rubbed surface. Figure 4 shows FTIR spectra of (A) the heated coating before water treatment, (B) the coating that remained on the surface after immersion of the film in water for 10 min, (C) the coating remaining after gently rubbing the wet surface, and (D) the portion of the coating removed from the wet surface by rubbing. These spectra showed that a high concentration of starch still remained on the surface after the film was allowed to stand in water at room temperature; however, most of the starch component was removed when the wet surface was rubbed.

We next examined the effect of adding melamine/formaldehyde resin to the formulation as a crosslinking agent for starch. In addition to its ability to crosslink polyols,⁵ melamine-formaldehyde can also react with epoxy resin.⁴ The total solids concentration of the new formulation (shown in Table II) was 11.45%, the Brookfield viscosity was 150 mPa s, and the pH was 9. Spraying this formulation onto PE films, gave surface coverages of $260 \mu\text{g}/\text{cm}^2$ (Film A)

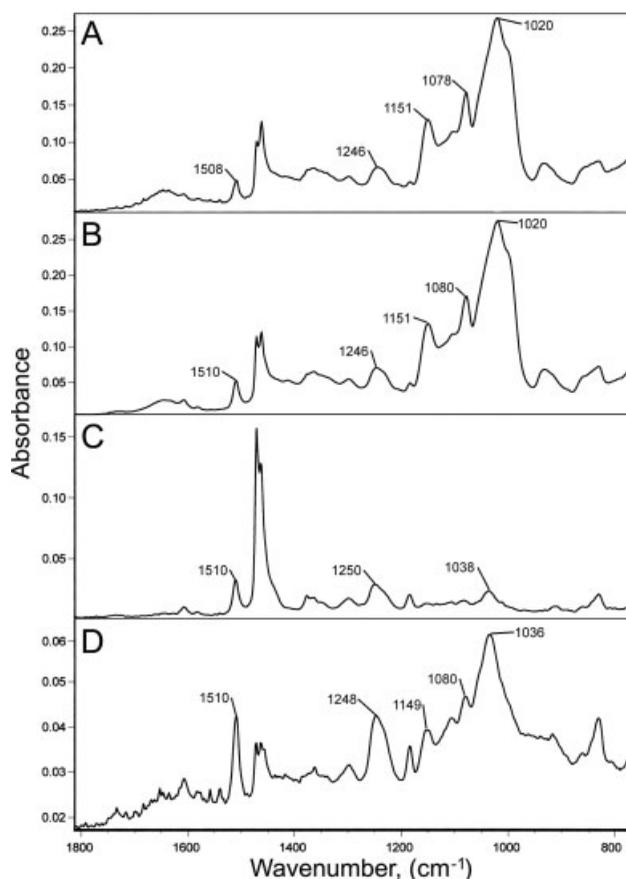


Figure 4 FTIR spectra. (A) Coating on PE surface from formulation shown in Table I. Coating heated for 24 h at 80°C . Surface coverage: $188 \mu\text{g}/\text{cm}^2$, (B) Coating remaining on the PE surface after water treatment, (C) Coating remaining on PE after gently rubbing the water-wet surface, and (D) The portion of the coating removed by gently rubbing the wet surface.

and $310 \mu\text{g}/\text{cm}^2$ (Film B) in two replicate experiments. The films were then heated for 24 h at 80°C to initiate reactions between starch, melamine-formaldehyde, and epoxy resin. An SEM image of the coated surface [Fig. 5(A)] was similar to the image shown in Figure 2. Curling of the film after heating [shown in Fig. 5(B)] was also observed. Curling of starch-coated PE films was observed previously

TABLE II
Coating Formulation with Added Crosslinker for Starch

Component	Weight (g)	Weight (%)
Waxy starch dispersion (12.7% solids)	94.4	6.0
Epoxy resin dispersion (62% solids)	6.4	2.0
Wax emulsion (40% solids)	6.0	1.2
Fluorinated surfactant (25% solids)	2.0	0.25
Melamine/formaldehyde resin (80% solids)	5.0	2.0
Water	86.2	88.55
Total	200.0	100.0

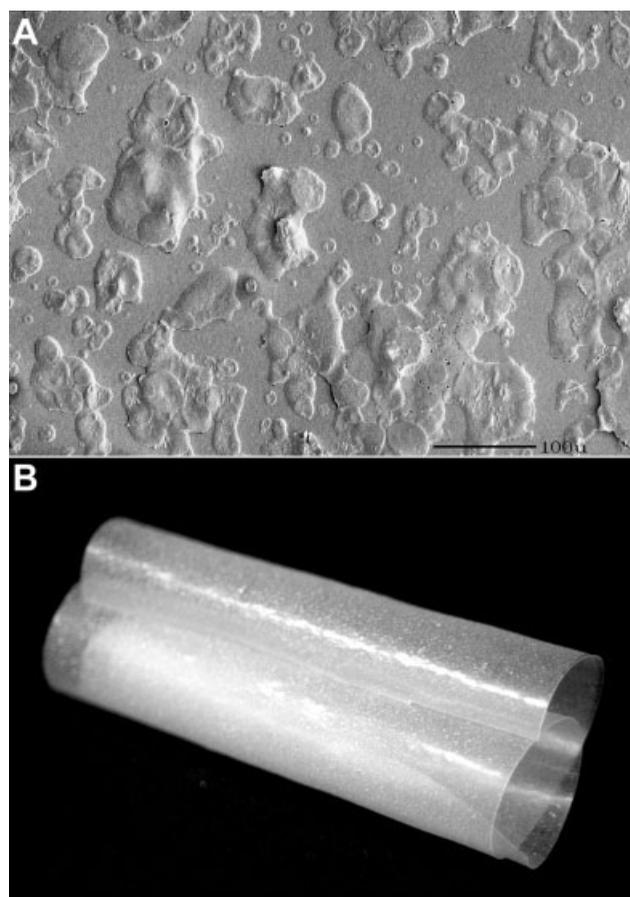


Figure 5 (A) SEM image of coating sprayed onto PE film surface. The coating formulation (containing melamine-formaldehyde resin) is shown in Table II. Surface coverage was $260 \mu\text{g}/\text{cm}^2$. The coating was heated for 24 h at 80°C and (B) Photograph of the heated film to show curling.

when starch coatings adsorbed from jet cooked dispersions were graft polymerized with acrylonitrile.³

Addition of melamine-formaldehyde resin to the formulation followed by heating at 80°C increased the adhesion of the coating to the wet film surface. When the heated films were placed in water and the surfaces were gently rubbed, only about 30% of the coating was removed from Film A, and 45% was removed from Film B. The surfaces remained uniformly wet after rubbing. Figure 6 shows FTIR spectra of (A) Film A, after heating for 24 h at 80°C , (B) the heated film after rubbing the wet surface, (C) the particles of coating removed from the surface by rubbing, and (D) the melamine-formaldehyde resin used in the formulation shown in Table II. These spectra suggested that the particles of coating that were removed from the surface were probably reaction products of starch, melamine-formaldehyde resin, and epoxy resin, and that starch was not selectively removed by water treatment. Therefore, despite the removal of a significant percentage of the coating, a high concentration of starch still remained

on the film surface; and the surface thus retained its hydrophilic properties.

DISCUSSION AND CONCLUSIONS

Coatings were applied to PE surfaces by spraying formulations prepared from a jet cooked dispersion of cornstarch, a water-born epoxy resin, a wax emulsion, and a fluorinated surfactant. The air-dried coatings were comprised of discontinuous areas of polymer that adhered tightly to the PE surface. Although the starch component separated rapidly from the coating when the film was placed in water at room temperature, heating the coated film for 24 h at 80°C increased the adhesion of starch and produced a surface coating that remained uniformly wet after standing in water for about 10 min. Most of the starch component, however, could be still be removed by gently rubbing the wet surface. If melamine-formaldehyde resin was added to the formulation, and the

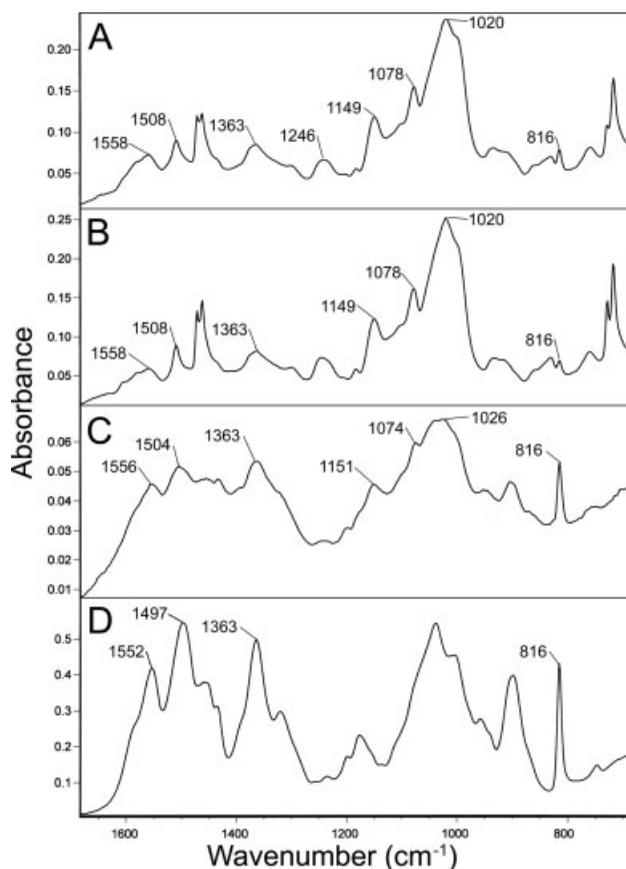


Figure 6 FTIR spectra. (A) Coating on PE surface from the formulation (containing melamine-formaldehyde resin) shown in Table II. Surface coverage was $260 \mu\text{g}/\text{cm}^2$. The coating was heated for 24 h at 80°C , (B) Coating remaining on the PE surface after placing the film in water and gently rubbing the wet surface, (C) The particles of coating removed by gently rubbing the wet surface, and (D) Melamine-formaldehyde resin.

coated film was heated for 24 h at 80°C to crosslink the starch, a high percentage of the starch remained bonded to the wet coating, even after gentle rubbing.

Several factors are probably responsible for the adherence of these starch-containing formulations to hydrophobic PE surfaces. Heating the air-dried coating to 80°C initiates reaction between starch and epoxy resin and also reduces the viscosity of the resin droplets, enabling them to diffuse rapidly through the dry coating and migrate to the PE/coating interface, where the resin can function as an adhesive for the starch-based coating. Alcohols are known to react with epoxy resin,⁴ and there are also references in the literature to support the reaction of epoxy resin with polysaccharides.^{6,7} Crosslinking starch with melamine-formaldehyde resin reduces its solubility in water and thus inhibits its separation from the applied coating. Although epoxy resin does not bind as tightly to untreated PE as some other adhesive systems,⁸⁻¹⁰ the level of adhesion is apparently sufficient to bond a thin coating of starch to the film surface. Also, stresses on the applied coating when the film is bent or creased would be minimized by the discontinuous nature of the sprayed coating. The fluorinated surfactant facilitates adhesion by reducing the interfacial free energy between the aqueous sprayed droplets and the PE surface. Fluorinated surfactants appear to work particularly well for this application, since inferior results were obtained with some of the more common surface active agents. The wax emulsion provides an additional hydrophobic component that is similar in structure to the PE surface, and the emulsion also contains additional surfactant that enhances the surface active properties of the aqueous formulation.

In summary, aqueous starch-containing formulations have been developed that can be applied to PE

films to impart hydrophilic surface properties. The properties of these coatings are governed by interactions between the various components of the coating formulation, and are influenced by variations in experimental conditions and procedure. Although additional research is needed to fully understand the many factors that influence the adhesion of these coatings, this initial study will provide a basis for further research on other starch-based formulations.

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