

Formation of Hydrophilic Starch Coatings on Polyethylene Films

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ABSTRACT: Thin starch coatings were deposited onto polyethylene (PE) film surfaces when PE films were immersed in 1% jet cooked starch solutions and the hot solutions were allowed to cool. Normal cornstarch, waxy cornstarch, high amylose cornstarch, and solvent-extracted normal cornstarch (to remove native lipid) were used in these experiments. Amounts of adsorbed starch varied from about 0.03–0.05 mg per cm² of PE, and these starch coatings imparted hydrophilic properties to film surfaces, as evidenced by contact angle measurements. Although starch could be removed by gently rubbing water-wet PE surfaces, air-dried coatings were more firmly attached, and did not separate from the PE surface when films were bent or flexed. SEM images of starch-coated film surfaces showed that starch was deposited as particles less than 1 μm in diameter, and also as aggregates of these submicron particles. Despite the fact that some starch samples contained only very small amounts of amylose and native lipid, surface-deposited starch in all experiments contained 90–100% amylose; and exhibited the same V_h X-ray diffraction pattern, indicative of helical inclusion complex formation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1781–1788, 2002; DOI 10.1002/app.10589

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INTRODUCTION

Starch is produced in the United States in amounts that greatly exceed market needs, and the conversion of this surplus starch to new value-added products is an active area of research.

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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 on the plant source. Commercial starch samples contain both linear and branched components (i.e., amylose and amylopectin) in varying amounts. For example, normal food grade cornstarch has an amylose to amylopectin ratio of about 25 : 75. Waxy cornstarch, however, is composed of almost pure amylopectin; and high amylose cornstarch has an amylose to amylopectin ratio of about 70 : 30. Cereal starch granules, such as cornstarch, also contain minor amounts of native lipid

material. Although lipids on the granule surface are easily extracted with cold solvents, internal lipids are more tightly bound, and can only be extracted with hot polar solvents such as aqueous alcohols at reflux temperature. The internal lipid material in normal cornstarch is comprised of about 62% fatty acids and about 38% lysophospholipids, with the predominant species being the nitrogen-containing lysophosphatidylcholine.¹ Lipid amounts increase with the amylose content of the starch granule; and waxy, normal, and high amylose cornstarches typically contain about 0.1, 0.7, and 1% native lipid, by weight, respectively.²

Starch granules do not dissolve in water at room temperature. Although some solubility is observed at higher temperatures (largely the amylose component of the granule), solubility is not complete, even at 100°C; and a major portion of the starch still remains in the form of highly swollen granules and granule fragments. Although starch may be dissolved by heating water slurries in an autoclave at temperatures greater than 100°C, solutions of starch for commercial applications are generally prepared by a continuous steam jet cooking process, in which a water slurry of granular starch is pumped through a hydroheater, where it is instantly heated with high-pressure steam under high-temperature, high shear conditions.³

As part of our research program on starch utilization, we are studying the jet cooking of aqueous mixtures of starch and water-immiscible oils and lipids and have used this technique to prepare new starch-lipid compositions. Previous work^{4,5} has shown that the high temperature and intense mechanical shear of the steam jet cooking process not only dissolves starch, but also converts the lipid component to micrometer-sized droplets that do not phase separate or coalesce, even when aqueous dispersions are dried. The preparation, properties, and commercial applications of these starch/lipid compositions have been summarized in a recent review.⁶ Our previous studies⁷ have shown that individual lipid droplets do not coalesce because of a thin film of adsorbed starch that forms at the lipid-water interface after the jet cooking process. This spontaneous formation of interfacial starch is best explained by a process referred to as *prewetting*. Prewetting occurs when starch is dissolved in a thermodynamically poor solvent (i.e., water), and when the accumulation of starch at the lipid/water interface leads to a reduction in interfacial tension. Literature related to prewetting has been summarized

in our earlier publication.⁷ We have isolated these thin films of interfacial starch from jet cooked starch/lipid systems, and their structures have been observed using both light- and scanning electron microscopy (SEM).^{7,8}

Because dissolved starch separates from aqueous solution and accumulates at the oil/water interface of micrometer-sized oil droplets, we wished to determine whether starch might similarly be deposited onto other hydrophobic surfaces, such as polyethylene (PE) films, and might thus impart hydrophilic properties to film surfaces. Methods for altering the surfaces of hydrophobic polymers to make them more hydrophilic have been the subject of numerous investigations, because increased hydrophilicity should reduce static buildup, alter friction and adhesion properties, improve the absorption of dyes and inks, and enhance the compatibility of polymer surfaces with aqueous systems. Examples of techniques that have been used to carry out these surface modifications include oxidation,⁹ treatment with ozone,¹⁰ fixation of poly(ethylene glycol),¹¹ plasma treatment,¹² and graft polymerization.¹³⁻¹⁵

In this study, we have shown that starch is indeed deposited onto PE film surfaces when these films are immersed in hot, jet-cooked solutions of starch, and that the resulting starch coatings impart hydrophilic properties to film surfaces. We have characterized these starch coatings by SEM, X-ray diffraction, and amylose content, and these results are also described in this report.

EXPERIMENTAL

Materials

Normal, unmodified food grade dent cornstarch and waxy cornstarch (Waxy No.1) were obtained from A. E. Staley Mfg. Co., Decatur, IL. High amylose cornstarch, containing about 70% amylose (AmyloGel 03003), was obtained from CereStar, Hammond, IN. Percent moisture was determined by vacuum drying starch samples at 100°C, and all weights are given on a dry weight basis. Native lipid was extracted by heating starch under reflux in 85% methanol/water followed by 75% *n*-propanol/water.⁸ The solvent-extracted starch was allowed to air dry, and was further dried under vacuum at 55°C. The dried starch was then allowed to air equilibrate at room temperature and ambient relative humidity.

PE films were clear, 6×6 inch (15.2×15.2 cm) interlocking seal bags purchased from Envision, Wichita, KS (A-A-1799B 6×6). Bags were washed in a solution of 11 g of Alconox detergent (Alconox, Inc., NY) in 1 liter of deionized water at 55°C and were then rinsed in deionized water and stored under water until used. Brass weights (about 15 g) were sealed inside each bag, so they would remain submerged when placed in aqueous starch solutions. ATR and transmission FTIR spectra of washed and dried PE bags were identical to a standard spectrum of low density PE.

Preparation of Starch-Coated PE Films

A stirred mixture of 50.0 g of starch in 4 liters of water was passed through a Penick & Ford Laboratory Model steam jet cooker operating under excess steam conditions.³ Cooking temperature was 140°C (back pressure: 40 psig steam), and steam line pressure was 70 psig. Pumping rate through the cooker was about 1 liter/min. Cooked starch solutions were collected in preheated Dewar flasks and contained $1.14 \pm 0.03\%$ starch, by weight (determined by freeze drying). The difference in solids content from the calculated amount in the uncooked slurry is caused by dilution of cooked solutions with condensed steam.

About 3700 mL of hot, jet-cooked starch solution was transferred to a 4-L beaker, and two PE bags were suspended in the solution. The beaker was covered with plastic wrap, and the mixture was stirred magnetically at about 150 rpm and allowed to cool to room temperature over a 24-h period. An OMB TempBook/66 thermocouple data acquisition system (purchased from Omega, Stamford, CT) was used to continuously monitor temperature. A typical plot of time vs. temperature is shown in Figure 1. Initial and final temperatures averaged $78.2 \pm 2.3^\circ$ and $23.2 \pm 2.0^\circ\text{C}$, respectively, in 16 experiments. The PE bags were removed from the cooled starch solution and allowed to stand for 1 h in a 4-L beaker containing about 3700 mL of distilled water to remove loosely bound starch. Two additional washings were carried out in a similar manner, and the bags were allowed to air dry. Experiments with each corn-starch sample were repeated three to five times.

Determination of Starch on PE Film Surfaces

Three samples of starch-coated PE (each having an area of 10 sq. cm) were cut from three different sides of the two washed and dried PE bags. Samples were then transferred to three separate

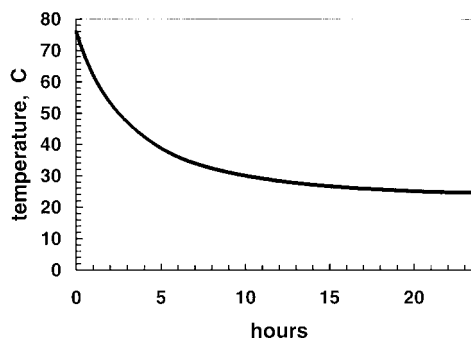


Figure 1 Typical plot of time vs. temperature for a stirred, jet-cooked starch solution containing two immersed PE bags (approx. 3700 mL in a 4-L glass beaker).

10-mL volumetric flasks after cutting them into roughly 5-mm squares. Starch was dissolved from PE surfaces by adding 7 mL of a solution prepared from 9 volumes of dimethylsulfoxide (DMSO) and 1 volume of 6-M urea¹⁶ and then heating the mixture for 2 h in a boiling water bath. The flasks were cooled, diluted to 10 mL with urea–DMSO solution, and analyzed for starch using the phenol–sulfuric acid method of Dubois et al.¹⁷ A standard curve of absorbance vs. mg starch per mL was prepared by analyzing solutions containing known concentrations of corn amylose (same amylose sample used by Knutson¹⁸). Amount of adsorbed starch was calculated as mg per cm^2 of PE (adsorption onto a single side). Values for adsorbed starch from the three analyses were averaged, and standard deviations were calculated from the averages obtained from three to five repetitive experiments.

Scanning Electron Microscopy

Samples, cut from water-wet, starch-coated PE films, were placed in absolute ethanol, washed with ethanol, and critical point dried using supercritical carbon dioxide. Dried specimens were sputter coated with gold-palladium and were examined and photographed with a JEOL 6400 V scanning electron microscope.

X-Ray Diffraction of Surface-Deposited Starch

Starch was removed from PE films by placing the films in excess water and gently rubbing the water-wet surfaces. Starch was isolated from water extracts by freeze drying. X-ray diffraction patterns of freeze dried starch samples were obtained as described previously.¹⁹ Samples were

equilibrated at 23°C and 45% relative humidity for 2 days prior to analysis.

Amylose Analysis of Surface-Deposited Starch

Percent amylose in surface starch was determined by using the method of Morrison and Laignelet¹⁶ to measure the absorbance of the blue amylose–iodine complex in urea–DMSO solution. A standard curve of absorbance vs. % amylose was obtained by analyzing known mixtures of waxy cornstarch and the corn amylose described by Knutson.¹⁸ Prior to analysis, residual lipid was extracted by heating 20–30 mg of freeze dried surface starch under reflux with 50 mL of 75% *n*-propanol–water for 2 h. Starch was separated by filtration, and the extraction procedure was repeated two additional times. The extracted starch was washed with methanol, vacuum dried at 50°C for 2–3 h, allowed to air equilibrate overnight, and then vacuum dried again at 50°C for 5–6 h. Four repeat analyses were carried out on each starch/urea–DMSO solution, the analyses were averaged, and standard deviations were calculated from averages obtained from three to four repetitive experiments.

Contact Angle Measurements

Water drops were placed on dry film surfaces, and contact angles were immediately measured with a Tante Contact Angle Meter, Model CAM-MICRO, manufactured by Tante, Schaumburg, IL. Five replicate determinations were carried out for each film sample, and the results were averaged.

Infrared Spectra

Spectra (in KBr) were obtained with a Nicolet Impact 410 Midrange FTIR spectrometer, using

Omic software to isolate the lipid spectrum by subtracting the spectrum of starch. Percent native lipid in surface starch was estimated by comparing the CH₂ absorbance at 2852 cm⁻¹ with the 2852 cm⁻¹ absorbance of a series of products prepared by blending starch with varying amounts of paraffin wax. Although absorbance in the carbonyl region was also observed, lipid could not be reproducibly estimated from the intensities of these carbonyl bands.

RESULTS

Deposition of thin starch coatings onto PE film surfaces was achieved by first jet cooking aqueous starch dispersions to yield hot solutions containing about 1% starch solids. PE films were then immersed in these hot solutions, and the mixtures were slowly stirred and allowed to cool over a period of 24 h. Loosely bound starch was removed from film surfaces by washing with water at room temperature, and the films were allowed to air dry. The hydrophilic surface coating was identified as starch by its FTIR spectrum.

Amounts of starch deposited onto PE film surfaces are summarized in Table I. With normal cornstarch, the amount of starch adsorbed was 0.056 ± 0.013 mg per cm² of PE. When native lipid was extracted from the starting starch, adsorbed starch amounted to 0.031 ± 0.003 mg per cm². Adsorption of waxy cornstarch was about the same as that observed with defatted normal cornstarch. Finally, when high amylose cornstarch was used, 0.052 ± 0.003 mg of surface starch per cm² was adsorbed. Although these low levels of surface starch imparted only a slight hazy appearance to dry film surfaces, surface wetting

Table I Deposition of Cornstarch onto Polyethylene Film Surfaces^a

Cornstarch	Surface Starch	
	mg per cm of PE ^b	Percent Amylose
Normal	0.056 ± 0.013 ^c	96.5 ± 2.8 ^d
Normal (solvent extracted)	0.031 ± 0.003 ^c	91.7 ± 4.0 ^e
Waxy	0.030 ± 0.003 ^e	91.4 ± 2.0 ^e
High amylose	0.052 ± 0.003 ^e	95.6 ± 5.5 ^e

^a Concentration of starch in water solution: 1.14 ± 0.03%. Contact time: 24 h.

^b Adsorbed onto one side of PE film.

^c Average value ± standard deviation of five replicate experiments.

^d Average value ± standard deviation of four replicate experiments.

^e Average value ± standard deviation of three replicate experiments.

could be clearly seen when films were placed in water. Hydrophilic surface properties were verified by contact angle measurements of water droplets placed on dry film surfaces. The contact angle for PE film coated with normal cornstarch was 44°; whereas a contact angle of 72° was observed for uncoated PE.

Although starch coatings could be removed from PE films by placing them in water and gently rubbing the water-wet surfaces, air-dried coatings were not as easily removed and could withstand considerable bending and manipulation of the PE substrate without separating from the surface. There appears to be little or no chemical association between starch and PE; and Instron peel tests carried out on PE coated with normal cornstarch gave peeling load values too low for accurate measurement (data not shown). The amount of adsorbed starch increased with the concentration of starch in water solution, and the thinner coatings obtained with 1% starch solutions adhered more strongly than heavier coatings obtained under the same conditions from 4% solutions. These heavier coatings exhibited non-uniform areas of light and heavy coverage, and starch in the more heavily coated areas separated readily from the PE surface when dried. SEM images of these heavier coatings showed the presence of spherocrystals, similar in appearance to those formed from amylose/native lipid complexes, when jet cooked starch solutions were slowly cooled.^{20,21} The amount of surface-adsorbed starch and the uniformity of coverage also depends upon the contact time between starch solution and PE film. In a single experiment, reducing this time from 24 to 4 h with a 4% solution of normal cornstarch resulted in more uniform surface coverage and the deposition of 0.082 mg of starch per cm².

SEM images of starch-coated films obtained from the four starch samples (Table I) are shown in Figure 2. Although the four samples exhibit subtle differences in morphology, starch coatings all seem to be comprised of submicron particles of starch, many of which seem to have aggregated to form larger particles. The strong adherence of these starch coatings to PE surfaces is probably related to the particulate and partially discontinuous nature of these coatings. This morphology allows the PE substrate to be bent or otherwise manipulated without applying excessive stress to the dry starch coating.

Starch coatings, removed from water-wet PE surfaces and then isolated by freeze drying, were

analyzed for % amylose; and these results are also shown in Table I. Despite the large differences in the amounts of amylose and native lipid present in the four starting cornstarch samples, the amylose content of adsorbed surface starch remained relatively constant at 90–100%.

X-ray diffraction patterns of freeze dried samples of surface starch are shown in Figure 3. These samples all exhibited the same V_h pattern, indicative of helical inclusion complex formation between amylose and native lipid. Absorption bands that could be attributed to native lipid were also seen in FTIR spectra. For example, spectra of surface starch obtained from normal cornstarch and solvent-extracted normal cornstarch showed weak carbonyl absorption as well as weak CH₂ absorption at 2924 and 2852 cm⁻¹, after the spectrum of amylose was subtracted. Estimates based upon the intensity of the 2852 cm⁻¹ band suggested a lipid content of about 5–8%.

DISCUSSION

Because the four starch samples in Table I varied in amylose content from approximately 0 to 70%, it was unexpected that all of these starch coatings would be comprised almost exclusively of amylose. Observation of the same V_h X-ray diffraction pattern for these four starch coatings was also unexpected; because the V_h pattern is indicative of helical inclusion complex formation between amylose and native lipid,²² and the starch samples in Table I contain widely different lipid amounts. In fact, in one series of experiments, cornstarch was solvent extracted under conditions shown by Morrison and Coventry²³ to remove nearly all native lipid from the cornstarch granule.

The above results differ from those obtained in our previous investigation of jet-cooked starch/paraffin wax mixtures.⁸ When normal cornstarch was used in this earlier study, adsorbed starch isolated from wax droplet surfaces contained less than 50% amylose, the remainder being amylopectin. Also, experiments carried out with lipid-extracted normal starch yielded surface-adsorbed starch that contained less amylose than the surface-adsorbed starch obtained when native lipid was still present. Finally, with paraffin wax as the substrate, X-ray diffraction patterns of surface starch varied with both the amylose and native lipid content of the starting starch. The V_h pattern was most intense with high amylose

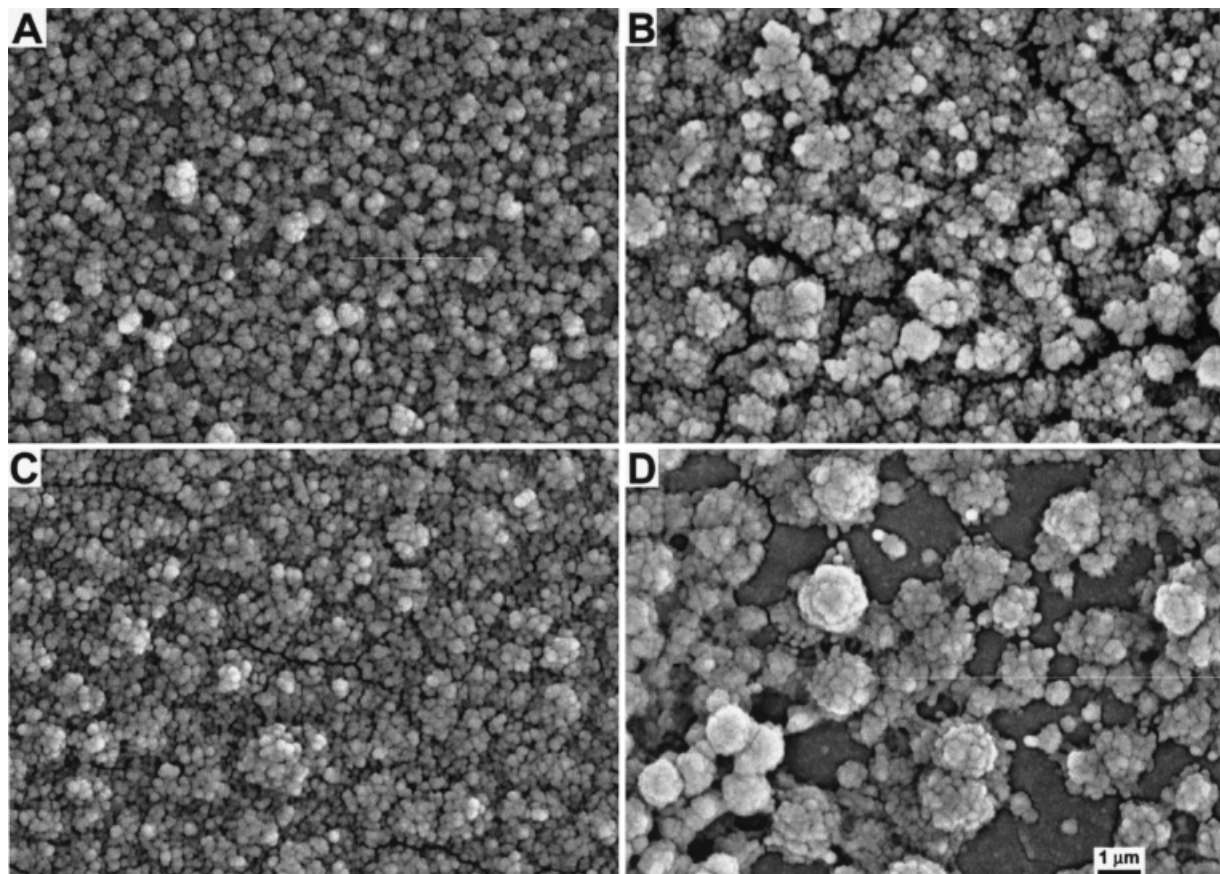


Figure 2 SEM images of starch-coated PE surfaces. Samples of water-wet, coated films were placed in excess ethanol; and the ethanol-wet films were critical point dried using supercritical CO₂. (A) PE film coated with normal cornstarch. (B) PE film coated with waxy cornstarch. (C) PE film coated with solvent extracted (i.e., defatted) normal cornstarch. (D) PE film coated with high amylose cornstarch.

starch, whereas the V_h pattern was not observed when native lipid was extracted from normal cornstarch and when waxy starch was used.

Although additional studies are needed to fully explain the different results obtained with paraffin wax vs. PE film, the difference in starch concentrations in these two investigations and the large difference in surface area between dispersed wax droplets and PE film are important factors. In the paraffin wax study,⁸ total solids (starch plus paraffin wax) in jet-cooked dispersions was about 11%, by weight, and about 75% of this material was dissolved starch (i.e., solutions contained about 8.2% dissolved starch). Based on a nominal wax droplet diameter of 10 μm and an approximate density of 0.85 for paraffin wax, the calculated surface area of wax droplets was about 2×10^5 cm² per liter of dispersion. In contrast, the starch concentration used in the present

study was about 1%; and the surface area of PE film was only about 250 cm² per liter of dispersion. Although amylose/native lipid complexes are probably adsorbed at the interface more rapidly than uncomplexed starch because of their higher degree of hydrophobicity, amylopectin, and uncomplexed amylose are also adsorbed in the paraffin wax experiments because of their relatively high concentration in water solution. Entanglements between amylose and amylopectin molecules may also play a role in the coadsorption of these two starch polymers. In the present study, the concentration of starch in water is relatively low; and after rapid adsorption of the starch/lipid complex, uncomplexed starch is adsorbed at a much slower rate.

Amylose/lipid complex is adsorbed in all of our experiments because all starches (including waxy cornstarch) contain at least a small amount of

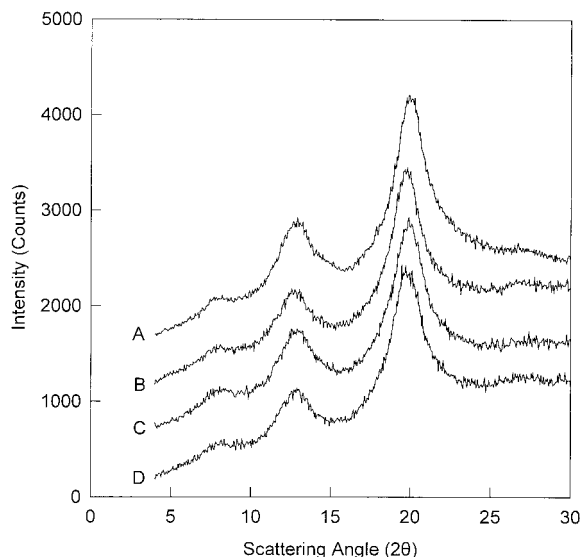


Figure 3 X-ray powder diffraction scans of starch coatings. Starch was removed from PE surfaces by placing films in excess water and gently rubbing water-wet surfaces. Starch was isolated from water extracts by freeze drying. (A) Coating obtained from normal cornstarch. (B) Coating obtained from solvent extracted (i.e., defatted) normal cornstarch. (C) Coating obtained from waxy cornstarch. (D) Coating obtained from high amylose cornstarch.

amylose that can complex with native lipid. Waxy cornstarch may also contain amylopectin fractions having outer branches sufficiently long to form helical inclusion complexes having properties similar to those formed from amylose. Research related to complex formation between polar lipids and the outer branches of amylopectin has been summarized by Eliasson.²⁴ All starches (including solvent-extracted normal cornstarch) also contain native lipid, because even the most efficient extraction techniques do not remove 100% of the lipid component. Despite the very small amount of amylose/lipid complex produced in some experiments, this amount is apparently sufficient to coat the surface of immersed PE film because of its small surface area.

Although high amylose cornstarch might be expected to produce a heavier coating of adsorbed starch than normal cornstarch because it contains the highest percentages of both amylose and native lipid, this result was not observed. Apparently, once the hydrophobic PE surface is covered with a thin coating of starch/lipid complex, only a minor amount of additional adsorption takes place.

SUMMARY AND CONCLUSIONS

Thin starch coatings were adsorbed onto PE film surfaces when films were immersed in hot, jet-cooked solutions of normal cornstarch, solvent-extracted normal cornstarch (to remove native lipid), waxy cornstarch, and high amylose cornstarch. Amounts of adsorbed starch varied from about 0.03–0.05 mg per cm² of PE, when 1% starch solutions were used. These thin coatings of adsorbed starch imparted hydrophilic properties to the PE surface. Although starch coatings could be removed by gently rubbing water-wet PE surfaces, air-dried coatings were more firmly attached and were not as easily removed. SEM images of starch-coated film surfaces showed that starch was deposited as particles less than 1 μm in diameter and also as larger aggregates of these submicron particles. The adherence of dry starch coatings to hydrophobic film surfaces is probably caused by the particulate nature of adsorbed starch. Although cornstarch samples varied widely in both percent amylose and percent native lipid, the amylose content of surface starch was 90–100% in all experiments; and surface starches all exhibited similar V_h X-ray diffraction patterns, indicative of helical inclusion complexes formed between amylose and native lipid.

The spontaneous deposition of starch onto hydrophobic surfaces is best explained by a process known as prewetting, which takes place when starch is dissolved in a thermodynamically poor solvent (i.e., water), and when the accumulation of adsorbed starch at the hydrophobic/hydrophilic interface leads to a reduction in interfacial tension. When starch is dissolved by steam jet cooking, amylose forms helical inclusion complexes with native lipid; and these complexes are adsorbed rapidly onto PE surfaces due to their enhanced hydrophobicity relative to uncomplexed starch. All starches used in this study, including waxy cornstarch and solvent-extracted normal cornstarch, contain at least small amounts of amylose and native lipid. Although the amount of amylose/lipid complex formed in some experiments is extremely small, this amount is sufficient to uniformly coat the small surface area of PE film immersed in these hot starch solutions.

Methods for altering hydrophobic plastic surfaces to make them more hydrophilic have been described in numerous publications, and there are many practical uses for these surface-modified polymers. We are investigating end-use applications for starch-coated PE films.

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