

Adsorption of Polyethylene from Solution onto Starch Film Surfaces

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ABSTRACT: We prepared starch films by jet-cooking aqueous dispersions of high-amylose starch and then allowing the jet-cooked dispersions to air-dry on Teflon surfaces. When the starch films were immersed in 1% solutions of polyethylene (PE) in 1-dodecanol, dodecane, and xylene at 120°C and the solutions were allowed to slowly cool, PE precipitated from the solutions and adsorbed onto the starch film surfaces. Fourier transform infrared spectroscopy was used to estimate the micrograms of PE adsorbed per square centimeter of starch film. PE was preferentially adsorbed onto the film side that was in contact with the Teflon surface during drying. The amount of PE adsorbed ranged from about 8 to 45 µg/cm² and depended upon the

solvent used and the final temperature of the cooled solution. Scanning electron microscopy of the starch film surfaces showed discontinuous networks of adsorbed PE on the Teflon side and widely spaced nodules of adsorbed PE on the air side. NMR analysis showed that the PE adsorbed onto the starch surface was more linear and/or had a higher molecular weight than the starting PE. Possible reasons for the selective adsorption of PE onto the Teflon side of the starch film surface are discussed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1840–1847, 2009

Key words: adsorption; coatings; FTIR; polyethylene (PE); polysaccharides

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 to 40 µm, depending on the plant source. Commercial cornstarch samples contain both linear and branched components (amylose and amylopectin) in weight ratios of about 0 : 100 for waxy cornstarch, 25 : 75 for normal dent cornstarch, and 70 : 30 for high-amylose cornstarch. Cornstarch granules also contain small amounts of tightly bound native lipids.¹ Unmodified cornstarch does not dissolve completely when heated in water, and aqueous dispersions for commercial applications are usually prepared by a continuous steam-jet-cooking process, in which a

starch–water slurry is pumped through a hydro-heater, where it is mixed with high-temperature, high-pressure steam under high-shear conditions.²

When aqueous, two-phase mixtures of starch and lipid are jet-cooked, the high temperature and high-shear conditions of the steam-jet-cooking process not only dissolves starch but also converts the lipid phase into micrometer-sized droplets that do not coalesce after cooling because of a thin layer of adsorbed starch that forms at the lipid–water interface.³ The adsorption of complexes formed from amylose and native lipids can also occur. A reduction in the interfacial tension of these oil–water dispersions, coupled with the well-known tendency of starch to hydrogen-bond and precipitate from a water solution (i.e., retrograde), appear to be major factors responsible for the observed adsorption of starch at the lipid–water interface. The adsorption of starch onto the hydrophobic surfaces of polyethylene (PE) films has similarly been observed.⁴

Because starch adsorbs onto PE surfaces from cooled solutions of jet-cooked starch, this study was carried out to determine whether the adsorption of PE onto hydrophilic starch film surfaces would also take place if the starch films were placed in hot solutions of PE in organic solvents and the solutions were allowed to cool. In this report, we show that this phenomenon indeed takes place. Methods such

Names are necessary to factually report on available data; however, the U.S. Department of Agriculture neither guarantees nor warrants the standard of the product, and the use of the name by the U.S. Department of Agriculture implies no approval of the product to the exclusion of others that may also be suitable.

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as this for reducing the water sensitivity of starch films through the application of hydrophobic coatings will expand the range of applications for starch films as alternatives to plastic films. In contrast with petrochemical-based film materials, starch is biodegradable, annually renewable, and environmentally friendly.

EXPERIMENTAL

Materials

High-amylose cornstarch (AmyloGel 03003, containing approximately 70% amylose) was obtained from Cargill, Inc. (Minneapolis, MN). Percentage moisture was calculated from weight loss on drying at 100°C *in vacuo*, and all weights of starch are given on a dry-weight basis. We defatted the starch by extraction by refluxing with 85% methanol–water followed by refluxing with 85% *n*-propanol–water.^{5,6} Dodecane (anhydrous, 99+ %), 1-dodecanol (98+ %, American Chemical Society), and xylene (xylenes, isomers plus ethylbenzene, 98.5+%, American Chemical Society reagent) were purchased from Sigma-Aldrich (Milwaukee, WI) and were used as received.

PE (ca. number-average molecular weight = 6500) was purchased in pellet form from Scientific Polymer Products, Inc. (Ontario, NY). The polydispersity index (weight-average molecular weight/number-average molecular weight) was not available from the supplier; however, a polydispersity index of approximately 5 for commercially prepared LDPE was reported.⁷ The pellets were cooled in liquid nitrogen and ground into a fine powder. To remove any insoluble PE, 10 g of powdered PE was dispersed in 200 mL of 1-dodecanol, and the dispersion was heated to 115°C. The hot, clear solution was then vacuum-filtered through a 1.0- μm , 47-mm (diameter) Advantec glass fiber filter (Toyo Roshi, Ltd., Tokyo, Japan). The filtration assembly was heated in a forced-air oven to 120°C before filtration. Weighing the glass filter before and after filtration indicated that only about 0.3% of the original 10 g of PE was removed by this procedure. The cooled filtrate was diluted with excess ethanol, and the precipitated PE was isolated by filtration, washed with ethanol, and dried.

Preparation of the starch films

A dispersion of 30 g of starch in 1 L of water was passed through a Penick and Ford laboratory model steam-jet cooker operating under excess steam conditions.² The temperature in the hydroheater was 140°C, the steam back pressure was 380 kPa (40 lb/in.²), and the steam line pressure from the boiler

was 550 kPa (65 lb/in.²). The pumping rate of the starch slurry through the jet cooker was about 1 L/min. The hot, jet-cooked dispersion was poured into Teflon-lined pans and allowed to air-dry at 22°C and 50% relative humidity. The thickness of the resulting film was approximately 0.0075 cm. The film was cut into strips (ca. 1 \times 6 cm²) and stored at room temperature and 52% relative humidity.

Deposition of PE onto the starch films

The experiments were carried out in 20-mL, 2.5-cm diameter scintillation vials that were placed in a temperature-controlled copper block that was part of a custom-built turbidometer previously described by Kim and Xu.⁸ The copper block had openings to allow visual observation of the sample and to allow a beam from a He–Ne laser to pass through the sample. Dispersions of PE at concentrations of 1 wt % were prepared in 1-dodecanol, dodecane, and xylene, and the dispersions were heated to dissolve the PE. About 20 mL of hot solution was placed in the scintillation vial, and the vial was placed in the copper block, stirred magnetically, and heated to 120°C. A starch strip (ca. 1 \times 6 cm²) was immersed in the hot solution and secured by a clamp mounted above the vial. The stirred PE solution was then allowed to cool, and the slow precipitation of PE from the solution during the cooling cycle was monitored by the reduction in the intensity of the transmitted laser beam, as detected by a laser power meter. The strip was removed and rinsed three times at room temperature with hexane and allowed to air-dry.

Determination of the adsorbed PE by Fourier transform infrared (FTIR) spectroscopy

Because the amounts of PE that adsorbed onto the starch films were too small to be determined gravimetrically, a new FTIR technique for quantitative analysis was devised, with both midrange FTIR and near infrared (NIR) instruments. Essentially, the PE-coated starch film samples were analyzed by the more sensitive FTIR instrument with a standard curve based on the extrapolation of PE mass values obtained by NIR on a different instrument. The validity of this method was verified experimentally as described later.

Midrange FTIR spectra were obtained with a Nicolet Avatar (Thermo Fisher Scientific, Inc., Waltham, MA) 370 spectrometer equipped with a SensIR DuraScope with a single-bounce diamond stage. The PE peak at 2852 cm⁻¹ was used for midrange attenuated total reflection (ATR) analyses. The pressure on the diamond anvil was slowly increased until additional pressure did not increase the absorbance of PE at 2852 cm⁻¹. A spectrum of uncoated starch film

was used to manually subtract the interfering starch peaks from the PE–starch spectra. NIR spectra were obtained with a PerkinElmer 100N spectrometer equipped with a Spectrum One NTS NIR reflectance accessory. Spectra were gathered with the use of a Spectralon, which was a NIR mirror used to close the port to obtain the background spectra. The Spectralon was placed on top of the sample to reflect the transmitted beam back through the sample and into the detector. The portion of the beam reflected off of the surface of the sample was insignificant compared to the transmitted portion, and the absorbance of the beam was dependent only on the mass of PE in the beam. Peaks attributable to PE were found with absorbance values of 5776, 5665, 4323, and 4253 cm^{-1} . The height and area of the peak at 4323 cm^{-1} had the least interference from the starch film, and it was, therefore, used for the analyses.

We obtained a calibration curve for the NIR spectrometer by plotting the absorbance values at 4323 cm^{-1} against the mass of commercially purchased PE films placed in the beam path. To vary the amount of PE in the beam path, we used either uniform films of various thicknesses or smaller fragments of the thinnest film that could be handled. A straight-line plot with a range of about 220 to 2500 $\mu\text{g}/\text{cm}^2$ and a correlation coefficient (R^2) of 0.987 was obtained.

To establish the relationship between the calibration data for PE obtained by NIR and the mass dependence of absorbance values observed by midrange ATR, the heaviest PE coatings on the starch films were used, which yielded valid PE spectra on both the midrange ATR and NIR spectrometers. The NIR calibration curve described previously was used to calculate the micrograms of adsorbed PE per square centimeter on these heavily coated films. These values for adsorbed PE (which were on the order of 220 $\mu\text{g}/\text{cm}^2$) were then used with their corresponding ATR absorbance values at 2852 cm^{-1} to construct a second straight-line calibration plot. This ATR plot was extrapolated through the origin, with zero absorbance assumed at 2852 cm^{-1} in the absence of adsorbed PE.

The use of this extrapolated plot to determine the small amounts of adsorbed PE observed in our experiments was validated by the following two methods:

1. Several starch films that were coated with PE (to obtain a sufficient amount of adsorbed PE for the NMR analyses described later) were extracted with *o*-xylene- d_{10} to dissolve the adsorbed PE from the film surfaces. The evaporation of the *o*-xylene- d_{10} yielded 1.87 mg of recovered PE. This weight of recovered PE was 83% of the weight estimated from the extrapolated calibration plot.
2. A microliter syringe was used to deposit accurately weighed 0.1 and 1.0% solutions of PE in hot dodecane onto pieces of Teflon that were $2 \times 2 \times 0.762 \text{ mm}^3$. Shallow depressions were pressed into the Teflon surfaces to confine the dodecane solutions to an area approximating the area of the diamond surface of the ATR. The dodecane was then allowed to evaporate at 60°C, and the micrograms of PE applied were calculated from the weight of dodecane solution applied and the concentration of PE in the applied solution. The micrograms of PE applied were also determined by measurement of the absorbance at 2852 cm^{-1} (with midrange diamond ATR) and then by the use of the extrapolated calibration plot to calculate μg of PE applied. When the mass values estimated from the extrapolated calibration plot were plotted against the mass values applied from dodecane solution, the slope of the resulting straight line was 0.98 with an R^2 of 0.93 over a range of 0.04–2.8 μg of applied PE (or 2–158 $\mu\text{g}/\text{cm}^2$).

Scanning electron microscopy (SEM)

PE-coated starch films were mounted on aluminum stubs with double-sided conductive tape and sputter-coated with gold. SEM images were obtained with a JEOL (Tokyo, Japan) 6400 V scanning electron microscope.

NMR spectroscopy

We obtained the sample of adsorbed PE for NMR analysis by carrying out eight replicate experiments, in which PE was adsorbed onto starch films from a 1% solution in dodecane, while cooling the dodecane solution from 120 to 50°C. The coated strips were cut below the solvent line to ensure that only the coating adsorbed from dodecane solution, and not the coating resulting from solvent evaporation, was analyzed. The coated strips were combined and extracted with two 1-mL portions of *o*-xylene- d_{10} at 100°C. The *o*-xylene- d_{10} was then evaporated at 100°C under a stream of nitrogen. Spectra were obtained on a Bruker Avance 500 spectrometer (500-MHz ^1H) with a 5-mm broadband observed (BBO) probe (Bruker Biospin Corp., Billerica, MA). Samples were dissolved in *o*-xylene- d_{10} , and spectra were acquired at 80°C. The chemical shifts are reported as parts per million from tetramethylsilane, calculated from the lock signal. Sixteen thousand scans were acquired for the carbon 13 spectra, and the data were then processed with Bruker Topspin version 1.3 software.

Contact-angle measurement

Contact angles on a PE-coated starch film and a commercial PE film were measured visually with a

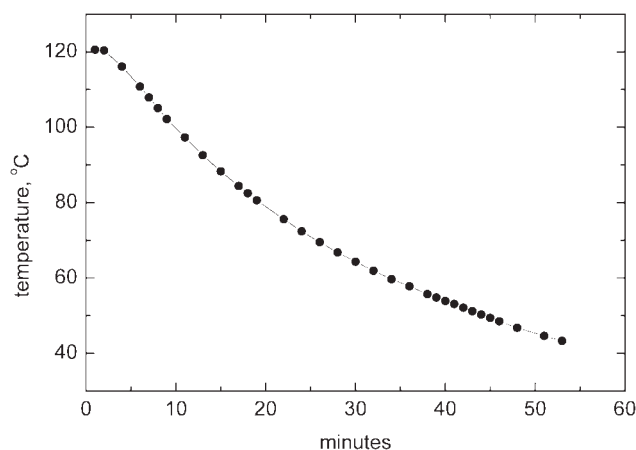


Figure 1 Rate of cooling of 1% solutions of PE in 1-dodecanol, dodecane, and xylene. Similar cooling rates were observed with each of the three solvents.

Tantec contact angle meter (model CAM-Micro, Tantec, Schaumburg, IL).

RESULTS AND DISCUSSION

We prepared starch films by jet-cooking aqueous dispersions of high-amylose cornstarch and then allowing the jet-cooked solutions to air-dry in Teflon-lined pans. High-amylose cornstarch was used in this study because the high-amylose content yielded starch films that were more resistant to cracking when they were immersed in hot organic solvents. Native lipids (normally present in small amounts in cereal starch granules) were extracted from the high-amylose cornstarch to avoid any effects of these lipids on the surface properties of the films.

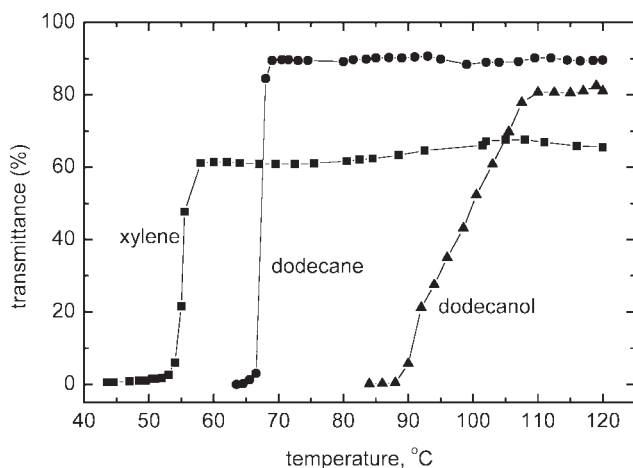


Figure 2 Effect of temperature on the transmittance (%) of a laser beam through 1% solutions of PE in 1-dodecanol, dodecane, and xylene.

TABLE I
Deposition of PE on the Starch Film Surfaces

Solvent for PE	Temperature range during cooling (°C)	Cooling time (min)	Amount of adsorbed PE (µg/cm ²)	
			Teflon surface	Upper surface
1-Dodecanol	120-80	19	9.3	— ^a
	120-80	21	8.2	— ^a
	120-80	21	8.0	— ^a
	120-44	56	21.4	— ^a
	120-50	47	19.6	— ^a
	120-50	47	22.0	— ^a
Dodecane	120-80	21	11.9	7.9
	120-80	20	9.1	10.7
	120-80	19	7.8	9.3
	120-40	61	30.2	21.5
	120-50	43	33.8	18.9
	120-50	51	32.0	18.8
Xylene	120-80	19	9.4	8.2
	120-80	20	10.0	12.2
	120-50	47	45.8	16.7
	120-48	44	41.6	20.9

^a There was only a trace of adsorbed PE, which was not large enough for accurate measurement.

Solutions of PE were prepared in 1-dodecanol, dodecane, and xylene at concentrations of 1%. The PE dissolved readily when the solvents were heated but precipitated when the solutions were cooled. The PE solutions were heated to 120°C, the starch films were suspended in the hot solutions, and the stirred solutions were allowed to slowly cool. The temperatures were monitored during cooling, and a typical plot of temperature versus time is shown in Figure 1. Similar cooling rates were observed with the three solvents used. The precipitation of PE was monitored by observation of the reduction in percentage transmittance of a laser beam passing through the solutions. Plots of percentage transmittance versus temperature for 1% solutions of PE in the three different solvents are shown in Figure 2. PE precipitated from 1-dodecanol between about 110 and 90°C, whereas precipitation from dodecane and xylene occurred more sharply at about 65 and 55°C, respectively.

Because the weights of PE adsorbed onto the starch film surfaces were too small to be determined gravimetrically, FTIR spectroscopy was used to estimate the amount of PE adsorbed. Although microgram quantities of PE on starch film surfaces are easily detected by midrange ATR, calibration standards for the accurate determination of these small amounts are difficult to prepare. In contrast, we could easily prepare accurate calibration standards for NIR by placing PE films of known mass in the IR beam because the NIR beam is more penetrating than midrange ATR. For both techniques, the

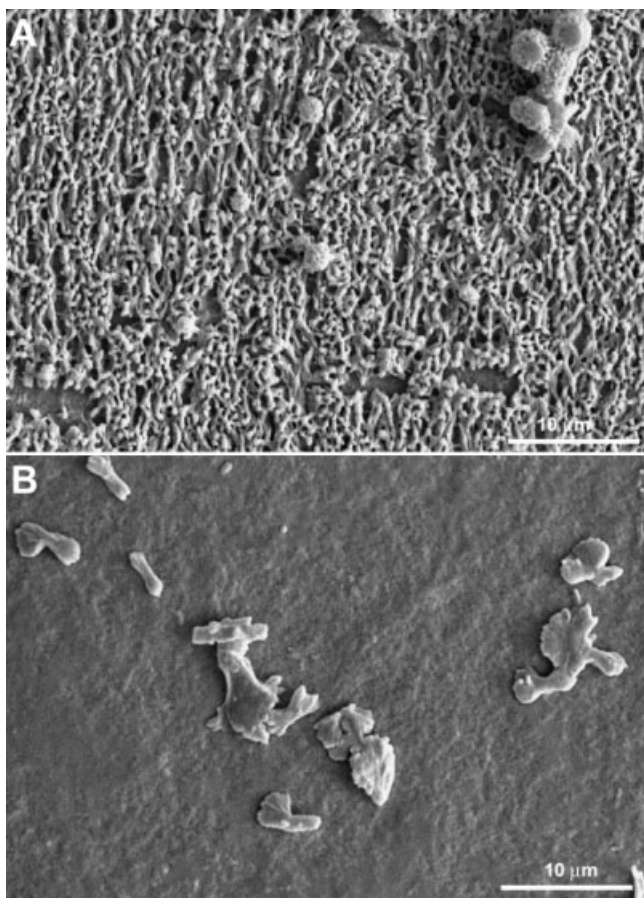


Figure 3 SEM images of PE adsorbed onto starch film surfaces from 1-dodecanol: (A) Teflon side ($19.6 \mu\text{g}$ of PE/ cm^2) and (B) upper side (or air side; the amount of PE was too small for accurate measurement). The temperature range during cooling was $120\text{--}50^\circ\text{C}$.

absorbance at a given wavelength obeys Beer's law and is directly proportional to the mass of PE in the IR beam. NIR, however, is not as sensitive as mid-range ATR and, therefore, could not detect the extremely small quantities of adsorbed PE observed in this study. An analytical method with the advantages of both of NIR and midrange ATR spectroscopy was, therefore, developed for these determinations. The details of this method are given in the Experimental section.

The amounts of PE adsorbed onto the starch surfaces from the three solvents under different cooling conditions are shown in Table I. As expected, larger amounts of PE were adsorbed when the solutions were cooled to $40\text{--}50^\circ\text{C}$, as compared to 80°C . The amount of PE adsorbed at $40\text{--}50^\circ\text{C}$ varied with the solvent and was lowest with 1-dodecanol and highest with xylene. These differences were related to the differences in temperature at which PE precipitated from these solutions (see Fig. 2). PE remained in solution at the lowest temperature when xylene was used and precipitated at higher

temperatures when solutions were prepared in dodecane and 1-dodecanol. More PE was, thus, available in solution for adsorption onto starch when xylene and dodecane were used as opposed to when 1-dodecanol was used. We also observed that, in most experiments, particularly those in which the PE solutions were cooled to $40\text{--}50^\circ\text{C}$, larger amounts of PE were adsorbed onto the sides of the starch films that were in contact with the Teflon surface during drying (designated as the Teflon surfaces in Table I), as compared to the upper surfaces, or air sides, of the films. Differences in adsorption between the two film surfaces were greatest when 1-dodecanol was used. Although quantitative measurements of adhesion were not carried out as part of this study, preliminary examination showed that the PE coatings exhibited some adhesion to the starch surface and were not removed with gentle rubbing.

Figures 3, 4, and 5 show SEM images of the PE adsorbed from 1-dodecanol, dodecane, and xylene, respectively, onto the Teflon sides and air sides of

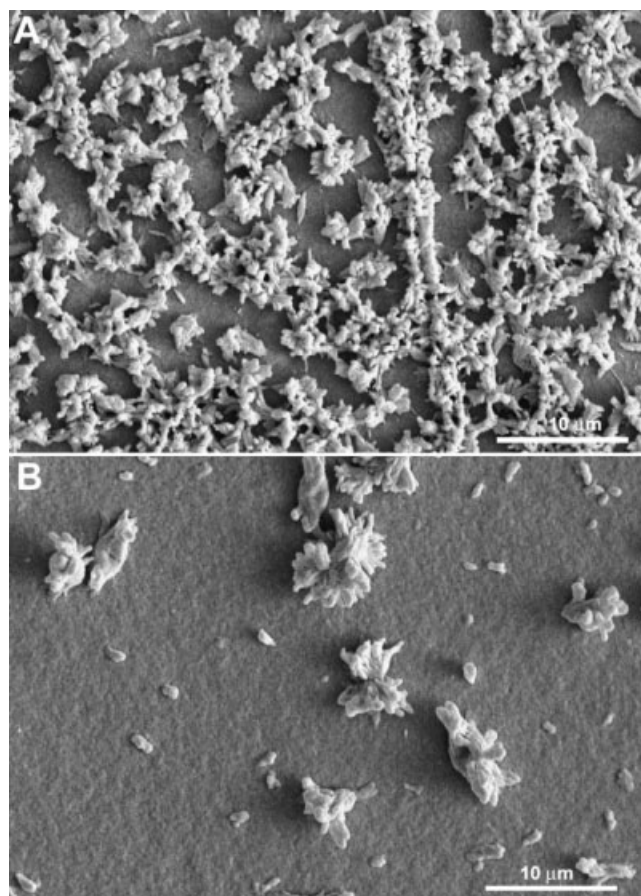


Figure 4 SEM images of PE adsorbed onto the starch film surfaces from dodecane: (A) Teflon side ($33.8 \mu\text{g}$ of PE/ cm^2) and (B) upper side (or air side; $18.9 \mu\text{g}$ of PE/ cm^2). The temperature range during cooling was $120\text{--}50^\circ\text{C}$.

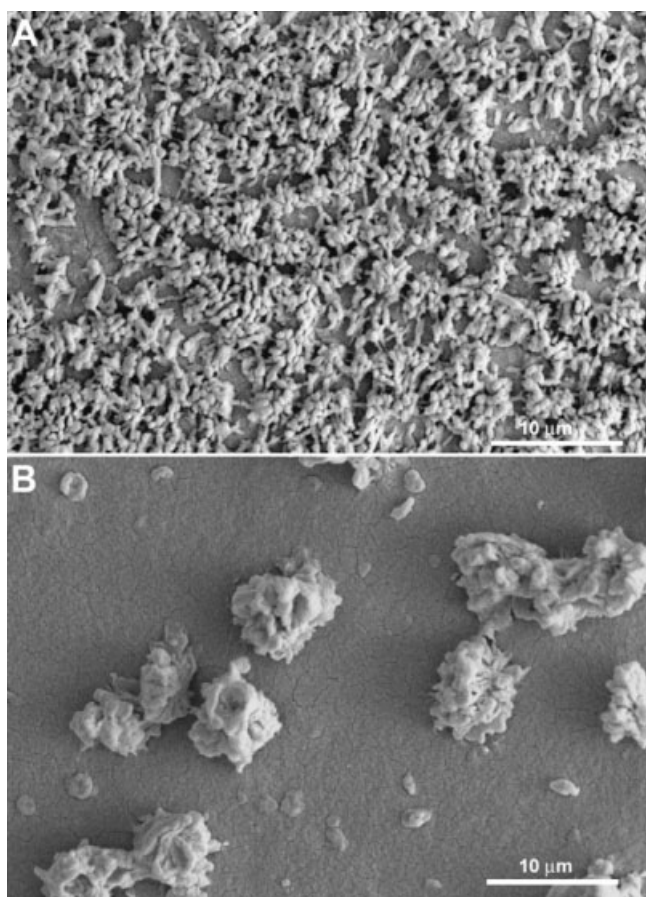


Figure 5 SEM images of PE adsorbed onto the starch film surfaces from xylene: (A) Teflon side ($41.6 \mu\text{g}$ of PE/ cm^2) and (B) upper side (or air side; $20.9 \mu\text{g}$ of PE/ cm^2). The temperature range during cooling was $120\text{--}48^\circ\text{C}$.

the starch film surfaces under the cooling conditions that led to maximum adsorption. Discontinuous networks of adsorbed PE with similar morphology

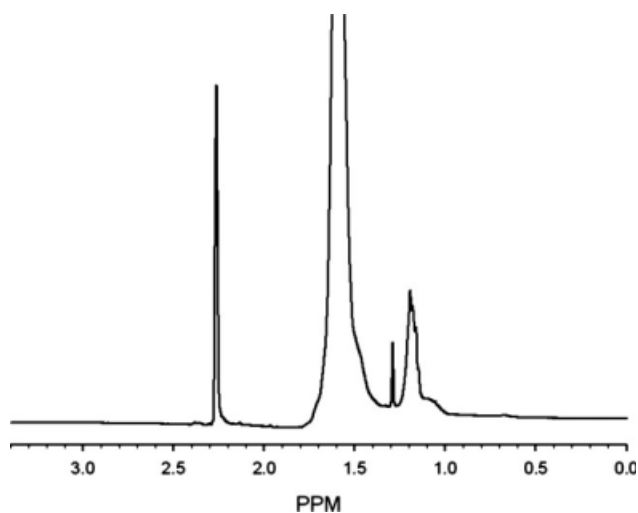


Figure 6 ^1H -NMR spectrum of starting PE.

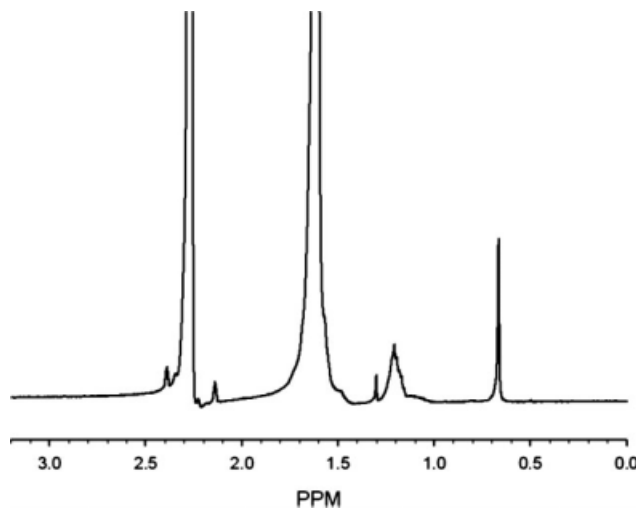


Figure 7 ^1H -NMR spectrum of PE adsorbed onto the starch films from a dodecane solution and then desorbed by dissolution in hot *o*-xylene- d_{10} .

were observed on the Teflon sides with all three solvents, although a coarser network with larger areas of uncoated starch was observed with dodecane. In contrast to the Teflon sides, the air sides of the starch films showed widely spaced nodules of adsorbed PE. Despite the coarse network of adsorbed PE, a contact angle of 115° was observed for a water droplet on the PE-coated Teflon side of the film obtained in dodecane. In contrast, a contact angle of 90° was measured for a water droplet on the surface of a commercial PE film, which indicated that the PE-coated starch surface exhibited more hydrophobic surface properties.

We obtained a quantity of adsorbed PE sufficient for NMR analysis by carrying out replicate adsorption experiments with dodecane solutions of PE that

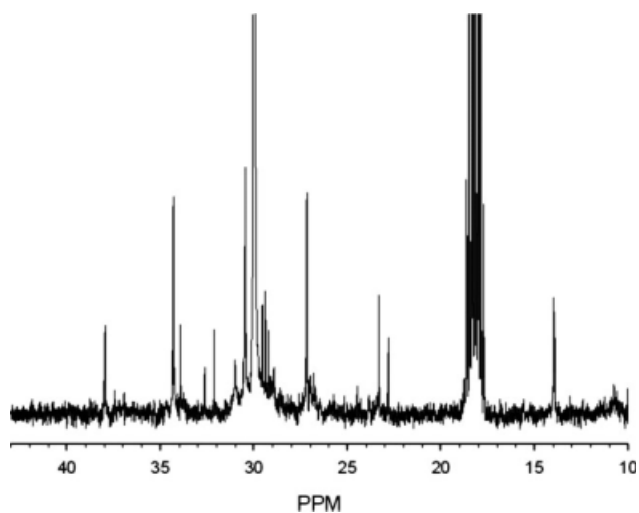


Figure 8 ^{13}C -NMR spectrum of starting PE.

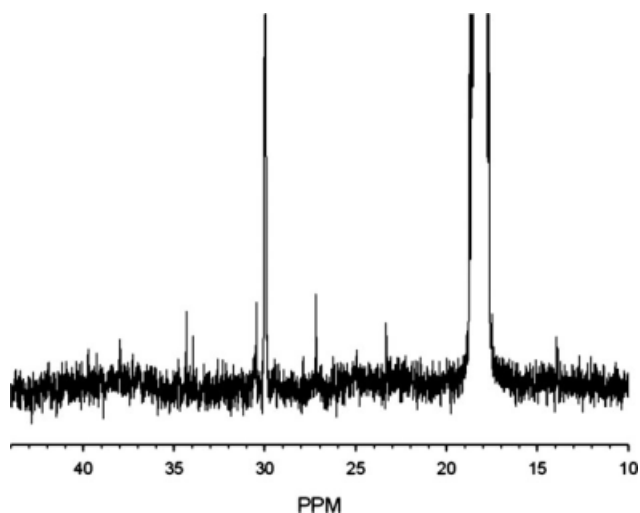


Figure 9 ^{13}C -NMR spectrum of PE adsorbed onto the starch films from a dodecane solution and then desorbed by dissolution in hot *o*-xylene- d_{10} .

were cooled from 120 to 50°C. The adsorbed PE was then dissolved from the starch surfaces with hot *o*-xylene- d_{10} . ^1H -NMR and ^{13}C -NMR spectra for the starting PE compared with the PE adsorbed onto the starch surface are shown in Figures 6–9. The ^1H spectrum of the starting PE (Fig. 6) showed major resonances at 1.6 and 1.2 ppm, which corresponded to main-chain CH_2 and end CH_3 groups, respectively. The resonance at approximately 2.3 was from the xylene solvent. A similar spectrum (Fig. 7) was obtained for the PE that was dissolved from the starch surface. The extra peak in Figure 5 at 0.7 ppm was likely due to water. The ratios of the areas under the peaks at 1.2 and 1.6 ppm were 0.079 for the starting PE and 0.043 for the PE adsorbed on starch, which suggested that the adsorbed PE was more linear (less branched) and/or had a higher molecular weight than the starting PE. PE fractions that were more linear and higher in molecular weight would be expected to be less soluble in dodecane and would precipitate more readily from solution and thus adsorb onto starch surfaces. The ^{13}C -NMR spectra for the starting PE (Fig. 8) and the adsorbed PE (Fig. 9) were also similar. In addition to the main-chain CH_2 resonance at 30 ppm, a number of minor peaks were observed, which corresponded to carbons near branch points and end groups, as described by Randall et al.⁹ Although it was more difficult to obtain accurate quantitative data from the ^{13}C spectra, many of the minor peaks were smaller for the adsorbed PE than for the starting PE, which suggested more linearity and a higher molecular weight, in agreement with the conclusions based on the ^1H spectra. The spectra of adsorbed PE obtained with the other two solvents were not determined because of the number of replicate

experiments needed to obtain sufficient quantities of PE for NMR analysis.

Although factors responsible for the differences in PE adsorption between the Teflon sides and air sides of the starch film surfaces were not determined, several possibilities can be suggested. The air side of the film may have had more surface imperfections than the Teflon side and, therefore, may have been less receptive to the adsorption of PE. Although SEM images of the two surfaces (images not shown) showed only minor differences in morphology, differences too small to be detected by SEM could have had a significant effect on PE deposition. Consistent with this theory, Rindlav-Westling and Gatenholm¹⁰ used atomic force microscopy to examine the air-side surfaces of solution-cast starch films and observed nanometer-sized surface protrusions, which they ascribed to crystalline and phase-separated structures that formed as water diffused through the film and evaporated from the surface. These workers¹⁰ also found that the small amount of protein normally present in native starch granules migrated to the film surface during air-drying. The presence of a higher concentration of protein on the air-side surface might have altered the surface properties and adversely influenced the adsorption of PE. Another possibility is that hydroxyl groups in the starch molecules closest to the hydrophobic Teflon surface became oriented away from the Teflon surface during drying to improve the compatibility between the two dissimilar surfaces. The Teflon side of the starch film would have thus been less hydrophilic than the air side, which would have made it more receptive to the adsorption of PE. This theory has been used to explain the results of contact angle measurements on starch films cast from water solution onto different substrates.¹¹ Finally, hydrogen-bonded water will vaporize and escape from the starch films when they are placed in hot organic solvents, and the preferential loss of water vapor from the air side of the film could affect the surface properties and inhibit PE adsorption. Small bubbles (presumably water vapor) were indeed observed when the starch films were immersed in hot PE solutions. The relative abilities of the different solvents to form azeotropic mixtures with water released from the film surfaces could have also affected PE adsorption. Regardless of the reasons for the observed differences in adsorption, our results indicate that PE adsorption was quite sensitive to the surface characteristics of the starch films and that small variations in the surface properties resulted in large changes in the amount of PE adsorbed.

SEM images were obtained by Arthur Thompson. NMR spectra were obtained by Karl Vermillion.

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