

Graft Polymerization of Acrylonitrile onto Starch-Coated Polyethylene Film Surfaces

George F. Fanta,¹ Frederick C. Felker,² John H. Salch¹

¹Plant Polymer Research, National Center for Agricultural Utilization Research, United States Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604-3999

²Cereal Products and Food Science Research, National Center for Agricultural Utilization Research, United States Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604-3999

Received 8 October 2002; accepted 17 December 2002

ABSTRACT: Starch-coated polyethylene (PE) films were prepared by immersing PE in a hot, jet cooked solution of starch. They were allowed to react with acrylonitrile (AN) in the presence of ceric ammonium nitrate initiator, and the graft polymerization that occurred produced starch-g-polyacrylonitrile (PAN) coatings that contained about 25 wt % grafted PAN. The starch-g-PAN coatings tightly adhered to the PE film surfaces. When grafted starch coatings were wetted with water and the surfaces vigorously rubbed, less than 20% of the coating was removed. The fact that PAN-grafted coatings were not removed with boiling water provided further evidence for their strong adherence. When starch was removed from the coating by acid hydrolysis, the residual grafted PAN still remained adsorbed on the PE surface. Because the grafted coating was completely removed by treatment with refluxing 0.7N sodium hydroxide,

there is apparently no chemical bonding between starch-g-PAN and PE. The dimensional changes associated with the evaporation of water from these PAN-grafted coatings caused the films to curl during drying. Because the final shape of these coated films depends upon the presence or absence of water in the surrounding environment, these films may be considered to be a type of stimulus-responsive polymer. Attempts to graft polymerize methyl methacrylate and methyl acrylate onto starch-coated PE surfaces, under conditions similar to those used with AN, were unsuccessful. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3323–3328, 2003

Key words: starch; polyethylene; acrylonitrile; polyacrylonitrile; graft copolymer

INTRODUCTION

Starch is a polysaccharide composed of repeating α -D-glucopyranose units. It is produced by living plants as discrete granules that range in diameter from about 5 to 40 μm , depending on the plant source. Commercial starch samples contain both linear and branched components (i.e., amylose and amylopectin, respectively) in varying amounts. Normal dent cornstarch has an amylose/amylopectin ratio of about 25:75 and contains about 0.7 wt % native lipid that is tightly bound within the granule. This native lipid material can be removed only by extraction with hot, polar solvents.

Starch granules are only partially soluble in water at 100°C, and a major portion still remains as highly swollen granules and granule fragments after heating. Although starch may be dissolved by heating in an

autoclave at temperatures in excess of 100°C, solutions of starch for industrial applications are usually 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 shear conditions.¹

As part of our research on starch utilization, we have studied the jet cooking of aqueous mixtures of starch and water-immiscible oils and lipids.^{2,3} We have shown that this process not only dissolves starch but also converts the lipid component to micron-sized droplets that do not phase separate or coalesce, even when aqueous dispersions are dried. The preparation, properties, and applications of these starch–lipid compositions have been summarized.⁴ Previous studies⁵ have shown that individual lipid droplets do not coalesce because of a thin layer of starch that spontaneously forms at the lipid–water interface during the jet cooking process. The formation of this layer of interfacial starch is best explained by a process referred to in the literature as *prewetting*. Prewetting takes place when starch is dissolved in a thermodynamically poor solvent such as water and when the formation of a thin film of starch at the lipid–water interface leads to a reduction in interfacial tension.⁵ We have isolated

Mention of a trademark, proprietary product, or vendor does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products or vendors that may also be suitable.

Correspondence to: G. Fanta (fantagf@ncaur.usda.gov).

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).^{5,6}

We have shown that starch is similarly deposited onto the surfaces of polyethylene (PE) films, when these films are placed in hot, jet cooked solutions of starch and the mixtures are then allowed to slowly cool.⁷ With normal dent cornstarch, the amount of adsorbed starch is about 0.05 mg/cm² PE. This thin coating of starch imparts hydrophilic properties to the PE film surface, and the dry starch coating does not readily separate from the film surface when coated films are bent or flexed.

In this report, we show that these coatings of adsorbed starch may be modified by graft polymerization of acrylonitrile (AN) and that grafted polyacrylonitrile (PAN) greatly enhances the adhesion of these coatings to the PE film surface. Moreover, the dimensional changes associated with the evaporation of water from these tightly adhering starch-g-PAN coatings cause the coated films to curl when they are dried, thus making the final shape of the coated film dependent upon the presence or absence of water in the surrounding environment.

EXPERIMENTAL

Materials

Unmodified food-grade dent cornstarch was obtained from A. E. Staley Mfg. Co. (Decatur, IL). The moisture content was calculated from the weight loss of the starch after drying at 100°C under a vacuum. All starch weights are given on a dry weight basis.

Jet cooked and drum dried cornstarch was used for the preparation of starch-g-PAN standards; it was obtained by passing a dispersion of 1 kg of cornstarch in 3 L of water through a Penick & Ford laboratory model steam jet cooker under conditions similar to those described earlier.⁷ The hot starch solution was dried on a 24 × 18 in. (61 × 45.7 cm) double-drum drier heated with 40 psi (2.81 kg/cm²) steam.

The AN in the study (99+%, inhibited with 35–45 ppm hydroquinone monomethyl ether) was purchased from Aldrich Chemical Co. (Milwaukee, WI) and was used as received. Ceric ammonium nitrate (ACS certified) was purchased from Fisher Scientific (Chicago) and was used as received. Methyl methacrylate (MMA, inhibited with 25 ppm hydroquinone) was obtained from Eastman Chemical Co. (Rochester, NY) and was distilled before use. Methyl acrylate (MA, inhibited with 15–20 ppm hydroquinone monomethyl ether) was a product of Hoechst Celanese (Charlotte, NC) and was used as received.

The preparation of the starch-coated PE film and the determination of the surface-deposited starch were

carried out as described previously.⁷ The amount of surface-deposited starch was 0.053 mg/cm² PE (single side coverage).

Graft polymerization of AN onto starch-coated PE film

Water (100 mL) was placed in a 125-mL Erlenmeyer flask and purged for 1 h with a slow stream of nitrogen at 25°C to remove dissolved oxygen. Then AN (5.0 g) was added, and the mixture was stirred for 30 min to dissolve the monomer. A 2 × 5 cm strip of starch-coated PE film was placed in the solution, and the solution was gently mixed for 5 min to thoroughly wet the starch coating. A solution of 0.33 g of ceric ammonium nitrate in 3 mL of 1N nitric acid was added, and the mixture was gently stirred for 20 min. At the end of this time, the yellow solution remained clear and showed no opalescence due to precipitation of ungrafted PAN. The PE strip was washed with water and allowed to air dry. The reaction conditions were similar for polymerizations carried out with different amounts of AN and different reaction times.

Ungrafted PAN was extracted by placing a 1 × 5 cm portion of the grafted strip in 20 mL of dimethylformamide (DMF) and allowing the mixture to stand overnight with occasional stirring. The strip was transferred to fresh DMF; after 1 h, the strip was washed with water and allowed to air dry. Ungrafted PAN was not recovered from the DMF extract.

To remove loosely bound starch-g-PAN from PE film surfaces, a 1 × 5 cm grafted strip was covered with 1 mL of water in a glass Petri dish. The dish was covered and placed in an oven at 100°C for 5 min. The wet surface of the strip was vigorously rubbed with a latex gloved fingertip (about 15–20 strokes using an applied pressure of roughly 100 g/cm²), and the water extract was then removed. The wet surface was rubbed twice more with fresh water at room temperature, and the strip was allowed to air dry. The starch-g-PAN fraction removed with water was isolated from the combined water extracts by freeze-drying. The IR absorbance of the nitrile band at 2243 cm⁻¹ and the weight percentage of PAN in this fraction (calculated from the PAN/starch absorbance ratio as described in succeeding paragraphs) were used to calculate the weight of this small amount of separated material. In some samples, the starch peaks in the 1026 cm⁻¹ region were severely distorted, which was possibly due to oxidation and degradation of the starch by the strongly oxidizing ceric ammonium nitrate initiating system.

Preparation of starch-g-PAN standards for fourier transform IR (FTIR) spectroscopy

A stirred mixture of 10.0 g of jet cooked and drum dried cornstarch in 200 mL of water was purged for

1 h with a slow stream of nitrogen. Then AN (10.0, 8.0, 6.0, or 4.0 g) was added, and the mixture was stirred for 5 min at 25°C. A solution of 0.336 g of ceric ammonium nitrate in 3 mL of 1N nitric acid was subsequently added, and the mixture was allowed to react for 1.5 h at 25°C. The swollen precipitate of starch-g-PAN was isolated by centrifugation, neutralized with dilute NaOH solution to pH 6.0–6.5, and washed thoroughly with water. The precipitated graft copolymer was finally diluted with water to about 300 mL and stirred for 1 min in a Waring blender at high speed. These undried dispersions were used as standards for the analysis of film surfaces by attenuated total reflectance (ATR) FTIR spectroscopy. The graft copolymers isolated from these dispersions by freeze-drying were used as standards for KBr transmission spectra.

To determine the weight percentage of PAN in these polymers, 5.00 g (dry basis) of freeze-dried graft copolymer was heated for 3 h under reflux in 500 mL of 0.5N HCl. The insoluble PAN remaining after hydrolysis of the starch was isolated by filtration, washed with water and ethanol, and dried at 60°C under a vacuum. The weight percentages of PAN, which were calculated from the weight loss after acid hydrolysis, were 47.6, 40.4, 33.1, and 24.1 wt %.

FTIR analyses of starch-g-PAN coatings

The FTIR spectra were obtained on a Nicolet Impact 410 spectrometer using Omnic software from Nicolet. Starch-g-PAN standards were applied to the surface of an ATR crystal as aqueous dispersions, and the dispersions were allowed to dry under ambient conditions. The absorbances of the PAN peak at 2243 cm^{-1} and the starch peak at 1026 cm^{-1} were then determined, and percentage of PAN in each graft copolymer standard was plotted against the 2243/1026 absorbance ratio. Four replicate determinations were made on each graft copolymer standard. A formula derived from this plot by regression analysis was then used to determine the percentage of PAN in unknown graft copolymer coatings. Coated PE films were pressed onto the ATR crystal using the same pressure for each film sample.

The same graft copolymer standards were used to prepare KBr pellets for transmission spectroscopy. For these analyses, aqueous dispersions of each polymer were diluted with water and freeze-dried. The particle size of these freeze-dried polymers was sufficiently small that further grinding of the samples had no effect on the absorbance per milligram of sample. Four replicates analyses were carried out for each polymer standard, and regression analysis of a plot of the percentage of PAN versus the 2243/1026 absorbance ratio was used to analyze unknown samples.

The absorbances at 2243 and 1026 cm^{-1} in the transmission FTIR spectra were also used to estimate the milligrams of PAN and starch in KBr pellets prepared from freeze-dried samples. Pellets used to obtain standard curves of absorbance versus milligrams of PAN and starch in the pellets were prepared from the four graft copolymer standards using sample sizes ranging from 0.050 to 1.0 mg. The ratio of the absorbance to the weight was constant throughout the entire range.

SEM study

Samples cut from the wet films after graft polymerization were placed in excess absolute ethanol and critical point dried from ethanol using supercritical carbon dioxide. The dried specimens were sputter coated with gold and palladium and then examined and photographed with a Jeol 6400 V scanning electron microscope.

Resistance of PAN-grafted coated films to refluxing aqueous solvents

Sections of PAN-grafted film, which were graft polymerized with 5 g of AN in 100 mL of water, were treated as follows: 3-h reflux in 50 mL of water, 3-h reflux in 50 mL of 0.5N hydrochloric acid, and 1-h reflux in 50 mL of 0.7N sodium hydroxide. The films were washed with water and allowed to air dry. Then their surfaces were analyzed by FTIR spectroscopy.

Attempted graft polymerization of MMA onto starch-coated PE film

The procedure was similar to that used for AN, except that the polymerization was carried out with 2.5 g of MMA and the reaction time was 30 min. The polymerization was stopped when the aqueous solution became opalescent because of precipitation of poly(MMA) (PMMA). An analysis of the starch coating by FTIR showed no grafted PMMA.

Attempted graft polymerization of MA onto starch-coated PE film

The procedure was similar to that used for AN, except that the polymerization was carried out with 5.0 g of MA and the reaction time was 1 h. No opalescence of the aqueous solution due to precipitation of poly(MA) (PMA) was observed. An analysis of the starch coating by FTIR showed no grafted PMA.

RESULTS AND DISCUSSION

A low density PE film, coated with 0.053 mg starch/ cm^2 , was prepared as described earlier⁷ by immersing PE in a hot 1% solution of jet cooked cornstarch and

TABLE I
PAN Content (wt %) of PAN-Grafted Starch Coatings on PE Films

Grafted Film No.	Polymerization Conditions	Coating Not Extracted with DMF			DMF-Extracted Coating		
		Initial Coating	Fraction Removed with Water	Coating Remaining on PE	Initial Coating	Fraction Removed with Water	Coating Remaining on PE
1	5 g AN/100 mL, 20-min reaction ^a	25 ± 2	19 ± 5 ^b	34 ± 4	23 ± 1	20 ± 6 ^c	33 ± 1
2	3.75 g AN/100 mL, 20-min reaction	6	ND	ND	ND	ND	ND
3	2.5 g AN/100 mL, 20 min reaction	0	0	—	—	—	—
4	2.5 g AN/100 mL, 55 min reaction	23	7 ^d	29	24	9 ^e	28

ND, not determined.

^a Values are the mean of 4-5 replicate experiments ± standard deviation.

^b 15 ± 5% of the coating was removed with water.

^c 31 ± 3% of the coating was removed with water.

^d 19% of the coating was removed with water.

^e 20% of the coating was removed with water.

then allowing the solution to slowly cool. Graft polymerization of AN onto the starch coating was then initiated with ceric ammonium nitrate using published polymerization procedures.⁸

The weight percentages of PAN in the grafted starch coatings were estimated from FTIR spectra (see Experimental section), and the results are summarized in Table I. With an AN concentration of 5 g in 100 mL of water and a polymerization time of 20 min (film no. 1, Table I), grafted starch coatings contained 25 ± 2 wt % PAN (average of five replicate experiments ± standard deviation). A reaction time of only 20 min was used to avoid formation and precipitation of PAN homopolymer during the reaction. Under the same conditions, 3.75 g of AN in 100 mL of water yielded a grafted starch coating containing only 6% PAN (film no. 2, Table I). Although no detectable grafting was observed after a 20-min reaction with 2.5 g of AN in 100 mL of water (film no. 3, Table I), increasing the polymerization time to 55 min yielded a grafted starch coating containing 23% PAN (film no. 4, Table I). Some precipitation of PAN homopolymer was observed with this longer polymerization time.

DMF was used to extract PAN homopolymer from the grafted starch coatings. However, similarities in the PAN contents of the film coatings before and after DMF extraction indicated that the grafted coatings contained only minor amounts of ungrafted PAN. No attempt was made to isolate PAN homopolymer from the DMF extracts.

Figure 1(A) shows a scanning electron micrograph of the surface of PAN-grafted film number 1 (Table I) that is not extracted with DMF. The film after DMF

extraction is shown in Figure 1(B). To minimize the effects of drying on the morphology, the wet films were dehydrated with ethanol and then critical point dried using supercritical carbon dioxide. Figure 1(C) shows the surface of the ungrafted starch-coated PE. To provide the best comparison with Figure 1(A,B), the dry film was first placed in water and then dried by the same procedure. These figures show that the graft polymerized surface that is not extracted with DMF is rougher and more particulate in appearance than the starch surface prior to grafting. Much of the surface roughness is lost, however, when the film is extracted with DMF. If Figure 1(C) is compared with our earlier published micrographs of starch-coated film surfaces,⁷ it is seen that the film used in the current study does not show the same clear definition of adsorbed starch particles, probably because the film was allowed to air dry after the coating process. In our earlier study, the wet films were dehydrated with ethanol and critical point dried immediately after coating. To rule out the possibility that the particulate appearance of the surface in Figure 1(A) might not be due to deposited PAN but might result from starch degradation attributable to the reaction with ceric ammonium nitrate, the coated film was allowed to react with ceric ammonium nitrate under the same conditions used for graft polymerization, but in the absence of AN. The surface of this ceric-treated film [Fig. 1(D)] was similar to that of the untreated film shown in Figure 1(C).

In contrast to ungrafted coatings of starch, which were easily removed by gently rubbing the wet films,⁷ starch-g-PAN coatings tightly adhered to the PE sur-

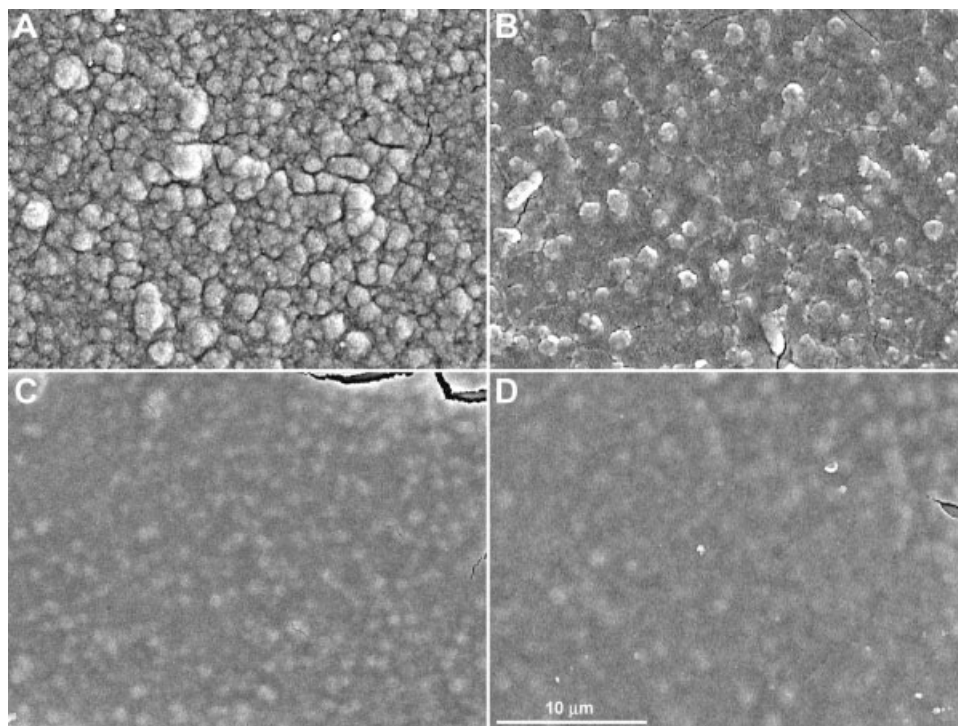


Figure 1 SEM images of PE film surfaces. Water-wet films were placed in excess ethanol and the ethanol-wet films were critical point dried using supercritical CO₂. (A) PAN-grafted film no. 1 (Table I) not extracted with DMF, (B) PAN-grafted film no. 1 (Table I) extracted with DMF, (C) ungrafted starch-coated PE film, and (D) starch-coated PE film treated with ceric ammonium nitrate in the absence of AN.

face. When PAN-grafted surfaces were wetted with water and then vigorously rubbed, less than 20% of the coating was removed (Table I). A higher percentage of the coating could be removed if the films were first extracted with DMF. The fraction removable with water generally contained a smaller percentage of PAN than the original starch-g-PAN coating.

The resistance of starch-g-PAN coatings to boiling water provides further evidence for their strong adherence to PE surfaces. When grafted film number 1 (Table I) was boiled for 3 h in water, an FTIR examination still showed the presence of starch-g-PAN, although selective removal of starch increased the PAN content of the coating from 23 to about 58%. In comparison, treatment of the ungrafted film with boiling water for 5 min completely removed the starch coating from the surface. Treatment of the PAN-grafted film with refluxing 0.5N hydrochloric acid for 3 h hydrolyzed and selectively removed the starch component from the coating; however, grafted PAN was not removed and remained clearly visible in the FTIR spectrum. In contrast to the effects of boiling water and refluxing mineral acid, the grafted coating was completely removed when the film was refluxed for 1 h in 0.7N sodium hydroxide, indicating that no carbon-carbon bonds were formed between starch-g-PAN and PE during graft polymerization.

An interesting property of these starch-g-PAN coated films is their tendency to curl when the wet

films are allowed to air dry. Although the dry, curled films relax immediately when they are again placed in water, they recur when dried. Curling is apparently caused by dimensional changes in the starch-g-PAN coatings during the drying process, coupled with the strong adherence of these coatings to the PE surface. The extent to which these films curl seems to depend upon a number of factors, such as the AN concentration during grafting, the conditions used for graft polymerization, and the size and dimensions of the grafted film sample. For example, a curled 2 × 5 cm sample of grafted film number 1 (Table I) is shown in Figure 2(A) whereas Figure 2(B) shows a more tightly curled sample obtained by graft polymerizing a 1 × 5 cm film sample under similar conditions, but with a polymerization time of 30 min. The coating on the latter sample contained 21% grafted PAN. The curling phenomenon is not completely understood, and further work is needed to define the parameters involved. Because the final shape of these coated films depends upon the presence or absence of water in the surrounding environment, these films may be considered to be a type of stimulus-responsive polymer. Studies are in progress to further investigate their properties and possible end use applications.

Finally, we attempted to graft polymerize MMA and MA onto starch-coated PE under conditions similar to those used with AN (see Experimental section). Despite the fact that both of these monomers graft

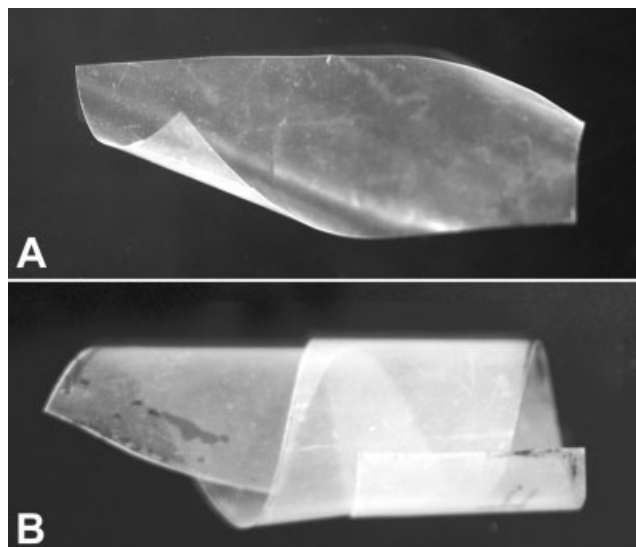


Figure 2 PAN-grafted PE films photographed to show varying amounts of curl after drying. (A) 2×5 cm sample of PAN-grafted film no. 1 (Table I) and (B) 1×5 cm sample of PAN-grafted film prepared under similar conditions but with a polymerization time of 30 min. The coating contains 21% grafted PAN.

polymerize efficiently onto unmodified cornstarch when initiated with ceric ammonium nitrate,⁸ the FTIR spectra of film surfaces showed no evidence of graft polymerization. Its absence could be due to the fact that starch coatings consist of helical inclusion complexes formed from amylose and the small amount of native lipid normally present in cornstarch granules.⁷ Compared to cornstarch itself, starch complexes of this type might exhibit a reduced level of reactivity with some monomer systems.

CONCLUSIONS

When starch-coated PE films (prepared by immersing PE in hot, jet cooked solutions of starch) were allowed to react with AN in the presence of ceric ammonium nitrate initiator, graft polymerization occurred to produce starch-g-PAN coatings that contained about 25 wt % grafted PAN. The PAN content of grafted starch coatings was estimated by FTIR spectroscopy. Although DMF was used to extract the PAN homopolymer from grafted starch coatings, similarities in the PAN contents of the coatings before and after DMF extraction indicated that only minor amounts of ungrafted PAN were produced.

Coatings of starch-g-PAN adhered tightly to PE film surfaces. When grafted starch coatings were wetted with water and the surfaces vigorously rubbed, less than 20% of the coating was removed. The fraction

removed contained more starch and less PAN than the original starch-g-PAN coating. A greater percentage of the coating was removed from films previously extracted with DMF. Another indication of the strong adherence of the coating was its resistance to removal with boiling water. Furthermore, when starch was completely removed from the grafted coating by acid hydrolysis, the residual PAN remained firmly attached to the PE film surface. There is apparently no carbon-carbon bonding between grafted PAN and PE, because the coating was completely removed by treatment with hot sodium hydroxide solution.

Another interesting property of these films is their tendency to curl when the wet films are allowed to air dry. Curling is apparently caused by dimensional changes in the starch-g-PAN coating during the drying process, coupled with the strong adherence of the coating to the film surface. Varying amounts of curl were observed in our experiments. The amount of curl seemed to be influenced by factors such as the polymerization conditions, the PAN content of the coating, and the size and dimensions of the grafted film sample. Because the shape of these coated films depends upon the presence or absence of water in the surrounding environment, these films may be considered to be a type of stimulus-responsive polymer. Further studies of their properties and applications are in progress.

Attempts to graft polymerize MMA and MA onto starch-coated PE under conditions similar to those used with AN were unsuccessful, despite the fact that both monomers are known to be efficiently graft polymerized onto unmodified cornstarch with ceric ammonium nitrate initiation.

We are grateful to Janet Lingenfelter for technical assistance and Arthur R. Thompson for SEM.

References

1. Klem, R. E.; Brogly, D. A. *Pulp Paper* 1981, 55, 98.
2. Fanta, G. F.; Eskins, K. *Carbohydr Polym* 1995, 28, 171.
3. Eskins, K.; Fanta, G. F.; Felker, F. C.; Baker, F. L. *Carbohydr Polym* 1996, 29, 233.
4. Fanta, G. F.; Eskins, K. In *Paradigm for Successful Utilization of Renewable Resources*; Sessa, D. J., Willett, J. L., Eds.; AOCS Press: Champaign, IL, 1998; p 266.
5. Fanta, G. F.; Felker, F. C.; Eskins, K.; Baker, F. L. *Carbohydr Polym* 1999, 39, 25.
6. Fanta, G. F.; Felker, F. C.; Shogren, R. L.; Knutson, C. A. *Carbohydr Polym* 2001, 46, 29.
7. Fanta, G. F.; Felker, F. C.; Shogren, R. L.; Salch, J. H. *J Appl Polym Sci* 2002, 84, 1781.
8. Fanta, G. F.; Doane, W. M. In *Modified Starches: Properties and Uses*; Wurzburg, O. B., Ed.; CRC Press: Boca Raton, FL, 1986; p 149.