

Graft Polymerization of Methyl Acrylate onto Granular Starch: Comparison of the $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ and Ceric Initiating Systems

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SYNOPSIS

Graft polymerizations of methyl acrylate (MA) onto granular cornstarch were carried out in water with both ferrous ammonium sulfate/hydrogen peroxide (FAS/ H_2O_2) and ceric ammonium nitrate (CAN) initiation. Starch concentrations were 10, 20, and 30% in water, and the amount of MA used was either 0.5, 1, or 2 mol per AGU of starch. Two concentrations of FAS/ H_2O_2 were used: 1 mol each of FAS and H_2O_2 per 100 AGU of starch, and 1 mol per 1000 AGU. Significant amounts of acetone-extractable PMA homopolymer were produced, and homopolymer formation was especially high at the 1 : 100 ratio. Sharp exotherms were observed, and reaction mixtures reached maximum temperature within 2 min or less. Total conversions of MA to PMA were higher at the 1 : 100 ratio, and conversions in some polymerizations were nearly quantitative. CAN-initiated polymerizations were run under the same conditions used for FAS/ H_2O_2 ; however, the amount of CAN used was limited to 1 mol per 100 AGU because of low conversions at the 1 : 1000 ratio. Compared with FAS/ H_2O_2 , CAN gave more moderate exotherms; and longer time periods were required for reaction mixtures to reach maximum temperature. CAN gave quantitative conversions of MA to PMA, but only low percentages of PMA homopolymer were observed. Differences between FAS/ H_2O_2 and CAN initiation are consistent with differences in the two initiation mechanisms. High levels of homopolymer produced on starch granule surfaces with FAS/ H_2O_2 could be seen in scanning electron micrographs and were also apparent in infrared spectra obtained with an attenuated total reflectance (ATR) cell. ATR spectra of acetone-extracted products indicated that the amount of PMA actually grafted to starch granule surfaces was similar with both initiating systems. Tensile properties of extruded ribbons prepared from these polymers did not vary greatly with the initiator used. © 1996 John Wiley & Sons, Inc.†

INTRODUCTION

Use of annually renewable products such as starch as extenders and replacements for petrochemical-based polymers is currently an active research area, largely because of the biodegradability of these plant-derived materials. Graft polymerization of vinyl and acrylic monomers onto starch is an excellent method for preparing composites of starch with

synthetic polymers, and numerous monomers and free radical initiating systems have been investigated.¹

In the course of our research, the properties of starch-*g*-poly(methyl acrylate) (*S-g*-PMA) have proven to be especially interesting. Graft polymerization of methyl acrylate (MA) onto starch takes place readily in water with ceric ammonium nitrate (CAN) initiation. Moreover, the formation of PMA grafts ($T_g = 8^\circ\text{C}$) onto the rigid starch matrix produces graft copolymers that yield leathery plastics on extrusion processing.^{2,3} Dennenberg and co-workers⁴ have shown that the starch portion of these extrudates is susceptible to fungal attack.

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The excellent physical properties of S-*g*-PMA extrudates have caused us to study these materials in more detail and to consider their commercial potential. In an effort to reduce production costs, we have examined the initiation of graft polymerizations with the ferrous ammonium sulfate (FAS)-hydrogen peroxide redox system, which is a less expensive initiator than CAN. This report will discuss some of the important differences in the structures and properties of polymers prepared with these two initiating systems.

EXPERIMENTAL

Materials

Starch was unmodified Globe 3005 cornstarch (13.6% moisture) from CPC International. All weights of starch were corrected for moisture and are given on a dry-weight basis. MA, containing 15–20 ppm MEHQ inhibitor, was a product of Hoechst-Celanese and was used as received. FAS (99+% certified A.C.S. grade) was purchased as the hexahydrate from Aldrich Chemical Co. CAN and 30% hydrogen peroxide were obtained from Fisher Chemical Co. and were both certified A.C.S. grade. Deionized water was used for all graft polymerization reactions.

Preparation and Characterization of Polymers

Cornstarch (84.0 g) was dispersed in either 743, 323, or 183 mL of water to give slurries containing 10, 20, or 30% starch solids, respectively. Reactions were carried out in glass resin kettles (either 500 or 1000 mL) equipped with stainless-steel paddle stirrers. Flasks were immersed in a water bath, which was maintained at 25°C. Starch slurries were stirred and sparged for 1 h with a slow stream of nitrogen and were maintained under a nitrogen atmosphere throughout the reaction. In polymerizations initiated by FAS/H₂O₂, FAS was added in an amount equal to either 1 mol per 100 anhydroglucose units (AGU) of starch (2.033 g) or 1 mol per 1000 AGU (0.2033 g). An AGU molecular weight of 162 was used for these calculations. MA was then added in amounts equal to either 0.5 mol (22.5 g), 1 mol (45.0 g), or 2 mol (90.0 g) per AGU. Hydrogen peroxide was then added as a dilute water solution (3 mL total volume) in amounts equivalent to the number of moles of FAS used. In polymerizations initiated by CAN, a 1N nitric acid solution (3 mL total volume) containing 2.843 g of CAN (1 mol per 100 AGU of

starch) was added to the aqueous dispersion of starch and MA.

After addition of initiator, reaction mixtures were stirred for 30 min. The maximum temperature of the reaction mass was recorded as well as the time required to attain this temperature maximum. Unreacted MA in the reaction mixture was determined by gas chromatography. A Chrompack Model 437 gas chromatograph equipped with 6 ft capillary Carbowax 20 M column was used. Retention time of MA at 50°C was 0.5 min.

Reaction products were isolated by filtration, washed with water, and allowed to air-dry. Moisture contents were then determined by vacuum drying for 4 h at 100°C. PMA content of reaction products and percent conversion of MA to PMA were calculated from the gain in weight of starch after polymerization. Acetone-extractable PMA homopolymer in each air-dried polymer was determined by shaking 10 g of polymer in 100 mL of acetone, containing 2% water,⁵ for 16 h at room temperature. Insoluble polymer was separated by filtration, washed with fresh acetone, and dried. Acetone solutions were evaporated to dryness, and weights of acetone-soluble PMA were determined. Infrared analysis showed that acetone-soluble PMA fractions contained little or no carbohydrate.

PMA grafts were separated from acetone-extracted graft copolymers by acid hydrolysis of starch. Graft copolymer (3.00 g) was suspended in 300 mL of 0.5N HCl, and the mixture was heated under reflux for 2 h. Insoluble PMA was separated by filtration, washed with water and with 0.5% sodium bicarbonate solution, vacuum-dried (2 h at 100°C), and accurately weighed. PMA content of the graft copolymer was then calculated from weight loss on acid hydrolysis.

Grafting efficiency was calculated from the following equation:

$$\begin{aligned} \% \text{ Grafting efficiency} \\ = \frac{100 \times \text{grafted PMA (g)}}{\text{Grafted PMA (g)} + \text{PMA homopolymer (g)}} \end{aligned}$$

PMA samples for molecular weight determination were freed of small amounts (<5%) of insolubles by dissolving the polymers in tetrahydrofuran (THF) and centrifuging the resulting solutions. Molecular weights were determined in THF solution by gel permeation chromatography. Calibration was carried out with polystyrene standards. Determinations were carried out by Arro Laboratory, Inc., Joliet, IL.

Infrared Analysis

Spectra were obtained with a Mattson Polaris FTIR equipped with He-Ne laser and DTGS detector. Mattson FIRST analytical software was used for spectral manipulation. A ZnSe horizontal attenuated total reflectance (ATR) cell was used (Spectra Tech, Inc., Model OO1L-371; 45° incidence). Polymer samples were agitated gently in 95% ethanol, and the suspension was allowed to stand for about 1 h. The resulting paste was applied to the surface of the ATR cell, and ethanol was allowed to evaporate. The resulting polymer cake adhered sufficiently to the ATR cell to provide good contact between the cell surface and the surfaces of individual polymer granules. After the spectrum was obtained, the polymer was resuspended in 95% ethanol and was applied again the ATR cell for a replicate determination. Spectra were baselined at 1763, 1483, 1182, 1066.7, and 947 cm^{-1} for determination of absorbance.

Scanning Electron Microscopy

A Hitachi ISI scanning electron microscope was used to examine and photograph caked polymer samples that had been in contact with the surface of the ATR cell. Flakes of dried polymer were removed from the ATR cell surface, mounted onto aluminum stubs with double-sided tape, and coated with 60–40 gold-palladium alloy. Samples were photographed at a magnification of 1000 \times .

Extrusion Processing and Tensile Testing

Polymers used for extrusion processing were air-dried to a moisture content of 5.9–6.3% and were not extracted with acetone.

The extrusion process used to prepare ribbon samples for testing was similar to that previously described.⁶ For the extrusion of strands (to be chopped into pellets), extruder temperatures were 170°C nearest the feed zone and 180°C nearest the die. Ribbons were extruded at the same temperatures through a 25.4 \times 0.50-mm slit die. The die temperature was 180°C.

Extruded ribbons were allowed to equilibrate for 7 days at 23°C and 50% relative humidity before testing. Dog-bone tensile specimens (width: 6.35 mm; gauge length: 25.4 mm) were tested (five replications per sample) as described previously.⁶

RESULTS AND DISCUSSION

Graft polymerizations were carried out in water dispersions with starch concentrations of 10, 20, and

30%. Concentrations were varied by adjusting water volume, and the same weight of starch (84 g) was used in all polymerizations. The weights of monomer used (22.5, 45.0, or 90.0 g) correspond to 0.5, 1, and 2 mol of MA per AGU of starch, respectively.

PMA contents of graft polymerization products were calculated from the gain in weight of starch due to polymer formation. Portions of each product were then extracted with acetone to remove soluble PMA homopolymer. Any unextractable PMA remaining in the starch-containing product was assumed to be grafted. PMA contents of acetone-insoluble graft copolymers were then calculated from the loss in weight after removal of the starch by acid hydrolysis. Grafting efficiency, i.e., the percentage of total PMA that was grafted to starch, was calculated from the amount of grafted PMA and PMA homopolymer present in a given weight of product.

Two initiator concentrations were used with the FAS/H₂O₂ initiating system: 1 mol each of FAS and H₂O₂ per 100 AGU of starch, and 1 mol of FAS and H₂O₂ per 1000 AGU. Results are shown in Table I. Significant amounts of acetone-extractable PMA homopolymer were produced in each of these reactions, and homopolymer formation was especially high at FAS/H₂O₂ : AGU ratios of 1 : 100. Both levels of initiation produced sharp exotherms, and reaction mixtures reached their maximum temperatures within 2 min or less. As expected, higher exotherms were observed at the higher MA and starch concentrations. Total conversions of MA to PMA were higher at FAS/H₂O₂ : AGU ratios of 1 : 100; and in some polymerizations, conversions were nearly quantitative. The difficulties encountered in stirring some of these reaction mixtures at high reactant concentrations are reflected in the relatively low conversions observed in Reactions 3 and 7 (see column 5). In most instances, percent conversion values calculated from gain in weight of starch agreed with those determined by gas chromatographic analysis for unreacted MA. Molecular weights of PMA grafts, separated by acid hydrolysis of starch, were determined for two of the products prepared at different FAS/H₂O₂ concentrations. Weight average and number average molecular weights were higher and \bar{M}_w/\bar{M}_n was lower at the 1 : 1000 ratio of initiator : AGU.

Results observed with FAS/H₂O₂ initiation are consistent with the mechanism of initiation. Hydroxyl radicals, produced by the redox reaction between Fe²⁺ and H₂O₂, abstract hydrogen atoms from starch to produce starch macroradicals.⁷ These free radicals then react with MA to initiate polymerization of PMA grafts. In addition to entering into

Table I Graft Polymerization of Methyl Acrylate onto Cornstarch: FAS/H₂O₂ Initiation

Polymerization Conditions				Properties of Product					
No.	Starch Conc. (% in H ₂ O) ^a	MA (g)	Max. Temp. (°C) (min, after initiator addn.)	% Conversion, MA to PMA		PMA Content (%) ^b	% Extractable with Acetone	PMA Content after Acetone Extraction (%) ^c (\bar{M}_w ; \bar{M}_n of PMA)	Grafting Efficiency (%) ^d
				Cald. from Wt Gain	Cald. from GLC				
FAS/H ₂ O ₂ : AGU = 1 : 100									
1	10	22.5	30 (2)	94	97	20.2	14.1	5.0	23.2
2	10	45.0	34 (1)	93	96	33.2	20.4	— ^e	—
3	10	90.0	40 (1)	76	81	44.8	22.1	21.7	43.3
4	20	22.5	35 (0.5)	99	98	21.0	11.8	8.7 (265,000; 16,000)	39.6
5	20	45.0	40 (0.5)	81	85	30.2	14.1	17.3	51.3
6	30	22.5	39 (1)	94	96	20.0	9.0	11.3	53.4
7	30	45.0	43 (1.5)	71	84	27.5	10.0	— ^e	—
FAS/H ₂ O ₂ : AGU = 1 : 1000									
8	10	22.5	29 (2)	82	84	18.0	5.3	12.7	69.2
9	10	45.0	31 (2)	66	72	26.1	5.0	— ^e	—
10	20	22.5	34 (2)	87	89	18.9	3.1	16.7 (393,000; 54,000)	83.9
11	20	45.0	38 (1)	71	81	27.5	5.1	23.3	81.2
12	30	22.5	38 (1)	92	93	19.7	3.0	17.3	84.8
13	30	45.0	43 (1.5)	68	89	26.6	4.3	— ^e	—

^a All reactions were carried out with 84.0 g (dry basis) of starch. Water volume was varied to give the desired starch concentration.

^b Calculated from weight gain of starch.

^c Calculated from weight loss after removal of starch by acid hydrolysis.

^d Percent of total PMA in reaction product that was grafted to starch (i.e., unextractable with acetone).

^e Not determined.

chain transfer reactions with starch, hydroxyl radicals also react with MA (largely in the aqueous solution surrounding starch granules) to initiate formation of PMA homopolymer, which is deposited largely on starch granule surfaces. Lower yields of homopolymer and higher grafting efficiencies would, therefore, be expected as the concentration of starch in water is increased (compare reactions 1, 4, and 6 of Table I). Chain transfer reactions of hydroxyl radicals with starch appear to be favored at low initiator concentrations, since higher grafting efficiencies were observed at FAS/H₂O₂ : AGU ratios of 1 : 1000.

CAN-initiated polymerizations (Table II) were run under the same conditions as polymerizations initiated by FAS/H₂O₂; however, the amount of CAN used was limited to 1 mol per 100 AGU. Only a 13% conversion of MA to PMA was observed when

the first reaction in Table II was repeated with a CAN : AGU ratio of 1 : 1000. Compared with FAS/H₂O₂, more moderate exotherms were observed with CAN, and longer time periods were required for reaction mixtures to reach maximum temperature. CAN also gave quantitative conversions of MA to PMA and yielded relatively low percentages of acetone-soluble PMA homopolymer. The molecular weight of grafted PMA for the one sample examined was about midway between the molecular weights determined for the two FAS/H₂O₂-initiated samples in Table I.

The mechanism of initiation with CAN⁸ is different than the FAS/H₂O₂ mechanism and provides an explanation for the differences in polymerization products. CAN is not only a strong oxidizing agent but complexes rapidly with starch. A slower redox reaction then takes place to produce cerous ion and

starch macroradicals, which can then initiate graft polymerization. The relatively slow rate of free radical formation from the redox reaction between CAN and starch accounts for the moderate exotherms observed. Homopolymer is produced in low yield because starch macroradicals are formed through a direct reaction between CAN and starch and not through a chain transfer reaction between starch and initially formed hydroxyl radicals. Unlike the FAS/H₂O₂ system, reaction between initiator and MA to form PMA homopolymer occurs to only a minor extent.

ATR infrared spectroscopy was used to estimate the amount of PMA formed on the surfaces of starch granules with the two initiator systems. Scanning electron micrographs (Fig. 2) of polymer samples that were carefully removed from the surface of the ATR cell show that individual granules of starch remain largely intact during the polymerization process and during ATR spectroscopy. Surface PMA in FAS/H₂O₂ initiated products is easily seen as a polymer matrix that surrounds and agglomerates individual granules of grafted starch (see A, B, C, and E of Fig. 2). Surface PMA is not apparent with CAN initiation. As an example of the spectra obtained by ATR, Figure 1 shows the ATR spectrum of product 1, Table I, as compared with a conventional FTIR spectrum of the same product run as a KBr pellet. It is easily seen that the ATR spectrum

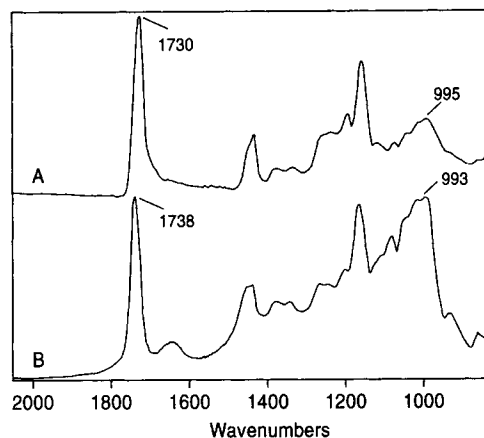


Figure 1 FTIR spectra of product 1, Table I; PMA content: 20.2%. (A) ATR spectrum; first application of the product to the ATR cell; absorbance ratio (Table III): 5.87. (B) Transmission spectrum, run as a KBr pellet.

of the sample surface shows higher PMA absorbance relative to starch than the KBr spectrum of the whole polymer sample.

Although relative amounts of PMA and starch could not be quantitatively determined by ATR spectroscopy due to the lack of suitable standards, the ratio of PMA carbonyl absorbance at 1732 cm⁻¹ to starch C—O absorbance at about 995 cm⁻¹ could be used for the qualitative comparison of individual products. Results are shown in Table III. As a check

Table II Graft Polymerization of Methyl Acrylate onto Cornstarch: Ceric Ammonium Nitrate Initiation

Polymerization Conditions				Properties of Product					
No.	Starch Conc. (% in H ₂ O) ^a	MA (g)	Max. Temp. (°C) (min, after initiator addn.)	% Conversion, MA to PMA		PMA Content (%) ^b	% Extractable with Acetone	PMA Content after Acetone Extraction (%) ^c (\bar{M}_w ; \bar{M}_n of PMA)	Grafting Efficiency (%) ^d
				Cald. from Wt Gain	Cald. from GLC				
1	10	22.5	29 (10)	100	99	21.3	1.4	21.0	93.9
2	10	45.0	31 (10)	100	99	35.0	3.3	— ^e	—
3	10	90.0	35 (20)	100	99	52.0	6.0	48.7	88.4
4	20	22.5	31 (5)	100	100	21.8	3.0	19.3	86.3
								(311,000; 31,000)	
5	20	45.0	36 (7)	100	100	35.6	3.7	32.7	89.4
6	30	22.5	34 (4)	99	100	21.6	3.5	19.0	83.8
7	30	45.0	36 (6)	99	98	35.1	4.1	— ^e	—

^a All reactions were carried out with 84.0 g (dry basis) of starch and a 1 : 100 molar ratio of Ce⁴⁺ : AGU. Water volume was varied to give the desired starch concentration.

^b Calculated from weight gain of starch.

^c Calculated from weight loss after removal of starch by acid hydrolysis.

^d Percent of total PMA in reaction product that was grafted to starch (i.e., unextractable with acetone).

^e Not determined.

Table III Results of ATR Infrared Spectroscopy

Polymerization Product	Initiator	Absorbance Ratio, PMA Carbonyl, 1732 cm ⁻¹ /Starch C—O Stretch, 995 cm ⁻¹				
		Unextracted Polymer		Acetone-Extracted Polymer		
		Sample A	Sample B	Sample A	Sample B	
No. 1, Table II	CAN	0.550	0.548	—	—	
		0.535	0.539			
			0.514			
No. 4, Table II	CAN	0.634	0.737	0.382	0.341	
		0.618	0.613	0.405	0.337	
				0.419	0.419	
No. 1, Table I	FAS/H ₂ O ₂	6.34	5.87	—	—	
		4.40	3.75			
			3.21			
			2.58			
			2.33			
			2.35			
			2.09			
			2.02			
			3.17	3.10	—	—
			2.75	2.81		
No. 4, Table I	FAS/H ₂ O ₂	2.41	2.52			
			2.39			
			2.39			
No. 5, Table I	FAS/H ₂ O ₂	2.54	2.64	0.232	0.265	
		2.36	2.46	0.228	0.299	
		2.23	2.26		0.247	
		2.23	2.10		0.227	
		1.92	2.04			
		1.88				

on reproducibility, ATR analyses were performed on two samples of each polymer product (designated A and B in Table III). After the initial spectrum was obtained, samples were washed off the ATR cell with 95% ethanol and were then reapplied to the cell for a repeat determination. This process was repeated several times. Absorption ratios were highest for products prepared with FAS/H₂O₂ initiation, indicating that this initiating system yields more PMA on starch granule surfaces than CAN. This is the same conclusion reached earlier on the basis of scanning electron micrographs in Figure 2. The decrease in absorbance ratio observed for Fe²⁺/H₂O₂ initiated products with each reapplication to the ATR cell can be explained by micrographs A, B, and C of Figure 2, which show the break-up of polymer aggregates with each succeeding spectral determination. Since the freshly exposed aggregate interiors are composed primarily of starch, the starch moiety makes a greater contribution to the overall ATR spectrum with each repetitive analysis. Repeat de-

terminations show much less variation with ceric initiated products.

To estimate the amount of PMA actually graft polymerized to starch granule surfaces with the two initiating systems, ATR spectra were also run on products that were extracted with acetone. The two products chosen for comparison (No. 5 of Table I and No. 4 of Table II) contained roughly the same amount of grafted PMA after acetone extraction (17.3 and 19.3%, respectively). Comparison of E and F of Figure 2 shows that acetone effectively removes surface homopolymer from the FAS/H₂O₂ initiated product. Absorbance ratios for these two extracted polymers were not greatly different, suggesting that FAS/H₂O₂ and CAN both give similar amounts of surface grafting. Also, repetitive ATR analyses of these acetone-extracted products gave absorbance ratios that were relatively constant.

To determine the effect of initiator on the tensile properties of starch-PMA extrudates,

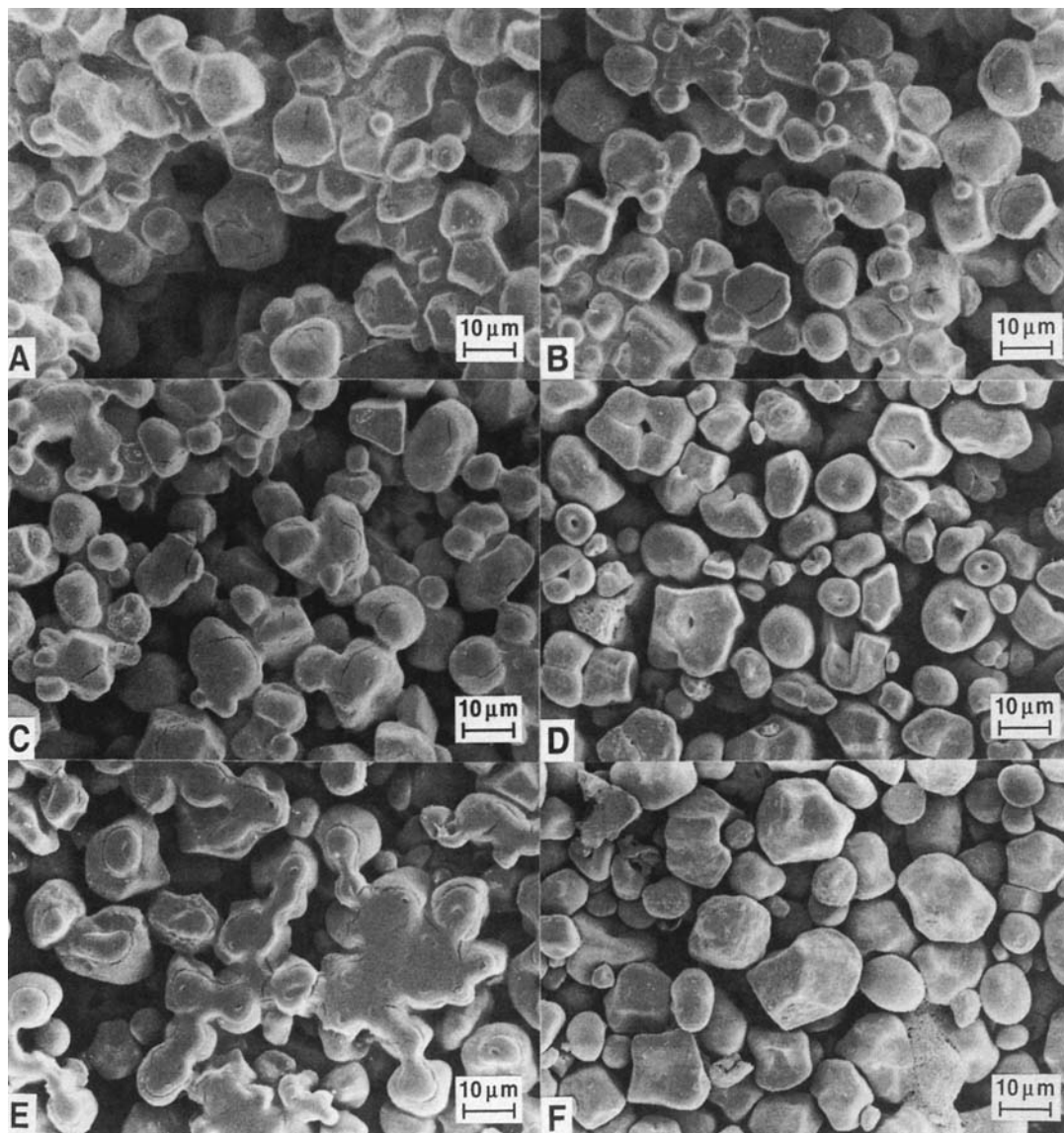


Figure 2 Scanning electron micrographs of polymer samples removed from the ATR cell surface. (A) Product 1, Table I; FAS/H₂O₂; PMA content 20.2%; first application to the ATR cell; absorbance ratio (Table III): 5.87. (B) Same as A, except third application to the ATR cell; absorbance ratio: 3.21. (C) Same as A, except eighth application to the ATR cell; absorbance ratio: 2.02. (D) Product 1, Table II; CAN; PMA content: 21.3%; third application to the ATR cell; absorbance ratio: 0.514. (E) Product 5, Table I; FAS/H₂O₂; PMA content: 30.2%; first application to the ATR cell; absorbance ratio: 2.64. (F) Product 5, Table I, after acetone extraction; PMA content: 17.3%; absorbance ratio: 0.232.

products prepared with FAS/H₂O₂ and with CAN were extruded into ribbons, and the tensile properties of extruded products were compared (Table IV). Although CAN initiation gave extrudates with somewhat better properties, differences between products prepared with the two initiating systems were minor and might simply be a result of the higher PMA content of the CAN-initiated product.

CONCLUSIONS

Different products are obtained when FAS/H₂O₂ and CAN are used to initiate graft polymerizations of MA onto granular cornstarch. Although CAN initiation yielded relatively small amounts of acetone-soluble PMA homopolymer, significant quantities of homopolymer were produced with FAS/H₂O₂. Homopolymer formation was especially high

Table IV Tensile Properties of Extruded Ribbons

Polymerization Product	Initiator	PMA Content (%)	Tensile Strength (MPa) (SD)	Elongation at Break (%) (SD)	Tensile Energy Absorption (N/mm) (SD)
No. 3, Table I	FAS/H ₂ O ₂	44.8	9.3 (1.7)	17.6 (7.0)	0.6 (0.3)
No. 3, Table II	CAN	52.0	12.4 0.3	36.8 (6.7)	1.5 (0.3)

at FAS/H₂O₂:AGU ratios of 1:100, as opposed to 1:1000. Sharp exotherms were observed with FAS/H₂O₂ initiation, and reaction mixtures reached maximum temperature within 2 min or less. More moderate exotherms were observed with CAN, and longer time periods were required to attain maximum temperature. These observations are consistent with differences between the two initiation mechanisms.

High levels of homopolymer produced on starch granule surfaces with FAS/H₂O₂ initiation could be seen in scanning electron micrographs as well as in ATR infrared spectra. Relative amounts of PMA and starch could be estimated from the ratio of the PMA carbonyl absorbance at 1732 cm⁻¹ to the starch C—O absorbance at about 995 cm⁻¹. ATR spectra of products that were extracted with acetone to remove homopolymer suggest that the two initiating systems produce similar amounts of surface grafted PMA.

Despite major differences in the products produced by FAS/H₂O₂ and CAN initiation, tensile properties of extruded ribbons prepared from these products did not vary greatly with the initiating system used.

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