

Modification of Starch–Poly(methyl acrylate) Graft Copolymers by Steam Jet Cooking

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ABSTRACT: Starch-*g*-poly(methyl acrylate) containing 12.3, 31.9, 51.7, and 58.3% PMA, by weight, were prepared by ceric ammonium nitrate-initiated polymerization of methyl acrylate onto granular cornstarch. The granular structures of these graft copolymers were not disrupted by steam jet cooking at 140°C. At most, only 13% of the polymer was dissolved, and this soluble fraction was comprised largely of starch. The probability of crosslinking within these graft copolymer granules was considered. Physical properties of extruded ribbons depended upon whether or not granular graft copolymers were jet cooked prior to extrusion. Although tensile strengths were not greatly affected by steam jet cooking, cooked samples showed significant increases in both percent elongation and tear resistance. The effects of jet cooking upon the properties of extruded ribbons can be explained by gelatinization of starch within the grafted starch granules. Although jet-cooked granules still remain intact, gelatinization of the starch moiety causes these granules to be less rigid, more deformable, and more easily plasticized by small amounts of water. Loss of starch crystallinity after steam jet cooking was proved by both differential scanning calorimetry and X-ray diffraction. © 1997 John Wiley & Sons, Inc.* *J Appl Polym Sci* **65**: 1021–1029, 1997

Key words: starch; poly(methyl acrylate); graft copolymer; steam jet cooking

INTRODUCTION

Use of annually renewable, plant-derived polymers as extenders and replacements for petrochemical-based polymers is currently an active area for research. Agricultural polymers are not only biodegradable, but their widespread use would also help conserve valuable petrochemical resources. Graft polymerization of vinyl and acrylic monomers onto starch is an excellent

method for preparing starch–synthetic polymer composites, and numerous monomers and initiating systems have been investigated.¹ Since starch and synthetic polymer are held together by chemical bonding, as opposed to merely existing as a physical mixture, the two dissimilar polymers are intimately associated, and thus have physical properties that cannot be obtained by standard blending techniques.

In the course of our research, the properties of starch-*g*-poly(methyl acrylate) (*S-g*-PMA), containing 50–60% PMA, have proven to be especially interesting and have caused us to study these materials in more detail. Graft polymerization takes place readily in water at room temperature with ceric ammonium nitrate (CAN) initiation, and the grafting of PMA ($T_g = 8^\circ\text{C}$) onto the rigid starch matrix yields copolymers that produce tough, leathery plastics on extrusion pro-

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

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cessing.^{2,3} Dennenberg, Bothast, and Abbott⁴ have shown that the starch portion of these extrudates is susceptible to fungal attack.

Starch is isolated from plant sources as discrete granules that range in diameter from roughly 5 to 50 μm , depending upon the particular plant variety. Although starch granules swell and partially dissolve (i.e., gelatinize) when heated in water, they are insoluble and unswollen at room temperature. Graft polymerization onto granular starch most likely takes place throughout the granule matrix as well as on the surface; scanning electron microscopy (SEM) has shown that polymerization does not greatly change the outward appearance of starch granules, even though an increase in mean particle diameter has been observed.⁵ Gelatinized starch has also been used in graft polymerizations⁶; however, starch in this form yields viscous pastes after graft polymerization, in contrast to the particulate products obtained from granular starch. Graft copolymers are therefore not easily isolated by filtration or centrifugation, and must be coagulated and precipitated with a nonsolvent such as methanol.

The formation of continuous extruded plastics from PMA-grafted starch granules takes place by fusion of heat-softened granules under the high pressures and temperatures encountered in the extruder die. Granule melting is inhibited by the starch matrix, which remains rigid at low moisture contents. SEM confirms the fused granule structure of these extrudates, and the absence of significant die swell in graft copolymer extrudates is also consistent with this mode of formation. Interparticle fusion most likely takes place through grafted PMA on granule surfaces, and the behavior of S-*g*-PMA extrudates in different solvent systems is in agreement with this theory. Although prolonged soaking of extrudates in water lowers the ultimate tensile strength (UTS) and increases percent elongation at break (%*E*), water-soaked samples remain continuous and do not disintegrate, apparently because the continuous phase is comprised of water-insoluble PMA.^{4,7} Extrudates disintegrate, however, when they are placed in good solvents for PMA (e.g., acetone and benzene).

Jet cooking^{8,9} has been used commercially for decades to prepare starch solutions and involves pumping an aqueous starch slurry through a narrow orifice, where it is contacted with steam at high temperature and pressure and under conditions of high mechanical shear. Under these rigorous conditions, starch granules are totally dis-

rupted and dissolved, and little or no insoluble starch remains in the cooked dispersion/solution. When large amounts of excess steam are allowed to pass through the jet cooker along with the starch-water slurry (i.e., steam pressure at the entrance to the cooker exceeds the steam pressure within the cooker itself), turbulence and mechanical shear are maximized, and a significant lowering of starch molecular weight is observed.¹⁰ As part of our research program on starch utilization, we have studied the jet cooking of mixtures of starch with a number of other components, such as poly(ethylene-co-acrylic acid),¹¹ hydrocolloid gums,¹² and lipid-like materials.¹³

In this article we describe the results observed when water-insoluble granules of S-*g*-PMA are passed through a steam jet cooker. Although we suspected that these granular products might be disrupted by the high temperature and turbulence of the cooking process, this was not the case. Not only was the outward appearance of grafted starch granules retained after cooking, but extrusion processing of these jet-cooked materials yielded extrudates having properties significantly different from those of extrudates obtained from uncooked polymer.

EXPERIMENTAL

Materials

Unmodified cornstarch (Globe 3005, containing ~ 13% moisture) was obtained from CPC International. All weights of starch were corrected for moisture and are given on a dry weight basis. Methyl acrylate (MA, containing 15–20 ppm MEHQ inhibitor) was a product of Hoechst-Celaneso and was used as received. CAN was Certified A.C.S. Grade and was obtained from Fisher Chemical Co. Distilled water was used for all graft polymerization reactions.

Moisture contents of starch and starch graft copolymers were calculated from weight loss on drying at 100°C under vacuum over P₂O₅. Moisture contents of graft copolymer samples were adjusted to desired levels by either air equilibration, equilibration at 100% relative humidity, or vacuum drying. Moisture values are based on total polymer (i.e., not on just the starch component).

Graft Polymerization

An aqueous starch slurry containing 100 g starch per liter of water was stirred and sparged with a

slow stream of nitrogen for 1 h at 25°C. MA (in varying amounts, depending upon the desired PMA content of the final polymer) was added, followed after 10 min by a solution of CAN in 1*N* nitric acid (0.34 g/mL). The amount of CAN used was equivalent to 1 mol/100 anhydroglucose repeating units (AGU) of starch (M_w of AGU = 162). The mixture was then stirred for 3 h at 25 ± 3°C. The graft copolymer was separated by filtration, washed with water, and neutralized in an aqueous slurry to pH 6.5–7. The final filter cake had a water content of ~ 50% and was stored at 5–10°C. A portion of the graft copolymer was also allowed to air dry.

Percent PMA in graft copolymer products was determined from the loss in weight after removal of starch from air-dried polymers by hydrolysis in refluxing 0.5*N* HCl (reflux time: 3 h). Infrared spectra of isolated PMA showed little or no residual carbohydrate after acid hydrolysis.

Percent ungrafted PMA (homopolymer) was determined by extracting air-dried products with acetone. Ten grams of graft copolymer was stirred overnight with 100 mL acetone containing 2% water.¹⁴ The solid was separated by centrifugation and washed twice with fresh portions of acetone. Soluble and insoluble fractions were isolated and weighed.

Steam Jet Cooking

Jet cooking was carried out with a Penick & Ford laboratory model continuous steam jet cooker, operated with 65 psig line pressure steam. Cooking was carried out at 140°C (40 psig steam) with a pumping rate of ~ 1.4 L polymer slurry per minute through the cooker. Products used in jet cooking experiments were not extracted with acetone.

Undried samples of starch graft copolymer were combined with water to give 10% solids dispersions, and any lumps were removed by brief stirring in a Waring blender. The resulting dispersions were passed through the steam jet cooker, and cooked dispersions were then cooled in ice-water to ~ 30°C. Dispersions obtained from graft copolymers prepared with starch/MA ratios of 100 : 150, 100 : 125, and 100 : 50 could be filtered through Whatman 54 paper. Solid polymers separated by filtration were allowed to air dry, and were then coarsely ground. Water-dispersible polymer fractions were isolated from the turbid filtrates by freeze-drying. The jet-cooked dispersion obtained from the 100 : 15 graft copolymer

was highly viscous and could not be filtered. It was therefore diluted 10-fold with water, and the solid polymer was separated by centrifugation. Soluble and insoluble fractions were isolated by freeze-drying. Weights of soluble and insoluble fractions were used to calculate the percentage of the original polymer solubilized by jet cooking.

Extrusion Processing and Tensile Testing

Graft copolymers were given two passes through a 25.4 × 0.5 mm ribbon die attached to a 19.5-mm diameter, 20 : 1 L/D, single-screw extruder driven by a C. W. Brabender Plasticorder Torque Rheometer. Compression ratio of the screw was 2 : 1. Temperatures in the two heating zones were 140°C (nearest the feed zone) and 150°C (nearest the die). Die temperature was 150°C. Extruded ribbon from the first pass was chopped in a Killion pelletizer before passing a second time through the extruder.

Extruded ribbons were allowed to equilibrate for 7, 14, or 28 days at 23°C and 50% relative humidity before testing. Dog bone tensile specimens (ASTM, D 412-68, Type C) were tested (4–5 replications per sample) on an Instron Universal Testing Machine, Model 4201, at a crosshead speed of 5 cm/min. Grip length was 63.5 mm, and %*E* was measured as displacement of the line-contact grips during tensile testing. Sample thickness was measured with a Minitest 3001 electronic micrometer (Elektro-Physik). Longitudinal tear strengths (trouser) were determined at a crosshead speed of 20 cm/min and a grip distance of 12.7 mm.

Microscopy

Water-wet graft copolymer samples were solvent-exchanged with ethanol, and the ethanol-wet products were critical-point dried. Samples were mounted on aluminum stubs, coated with gold-palladium (60–40) alloy, and examined in a Hitachi ISI-SS130 scanning electron microscope. Samples were photographed at a magnification of 1000×.

Samples of extruded ribbon were allowed to soak in excess acetone to separate the individual particles of heat-fused polymer, and the acetone solution was then removed. Acetone-swollen products were solvent-exchanged with ethanol and critical-point dried.

Table 1 Synthesis, Characterization, and Jet Cooking of Starch Graft Copolymers

Product No.	Wt. Ratio, Starch/MA ^a	Uncooked Polymer			Jet-Cooked Polymer		
		PMA Content (%) ^b	% of Polymer Extractable with Acetone	SEM, Fig. No.	Water Solubles, (% of Total)	Water-Insoluble Fraction	
						PMA Content (%) ^b	SEM, Fig. No.
1	100 : 150	58.3	10.4	1(A)	4.6	60.8	1(B)
2	100 : 125	51.7	13.8	1(C)	7.1	55.9	1(D)
3	100 : 50	31.9	3.8	1(E)	10.8	34.2	1(F)
4	100 : 15	12.3	0.9	1(G)	13.0	14.2	1(H)
5	100 : 0 ^c	0	—	1(I)	87.2	—	1(J)

^a Polymerizations were carried out with 100 g starch per liter of water and 1 mol CAN/100 AGU.

^b Calculated from weight loss on acid hydrolysis.

^c Control reaction. Starch allowed to react with CAN in the absence of MA.

Infrared Spectroscopy

Samples for transmission FTIR were blended with potassium bromide and pressed into discs. Spectra were recorded on a Mattson Polaris FTIR equipped with a He–Ne laser and DTGS detector to provide a resolution of 4.0 cm⁻¹. Mattson FIRST analytical software was used for spectral manipulation.

Attenuated total reflectance (ATR) spectra were obtained on graft copolymer samples that had been solvent-exchanged with 95% ethanol and then allowed to air dry. A Spectra Tech ZnSe horizontal ATR cell (Model 001L-371; 45° incidence) was used.

Differential Scanning Calorimetry (DSC)

Approximately 35 mg of undried starch graft copolymer (containing 50–54% water) was placed in stainless steel, high-pressure DSC pans (Perkin–Elmer No. 0319) and sealed. DSC was performed with a Perkin–Elmer DSC7 equipped with a CCA7 cooling accessory. The instrument was calibrated using the melting temperatures and enthalpies of water and indium. Samples were heated from 5 to 160°C at 10°C/min. Starch melting temperatures and enthalpies were calculated using DSC7 software.

X-ray Diffraction

Samples of untreated Globe 3005 cornstarch and undried graft copolymer were equilibrated at 23°C and 50% relative humidity, and were then spread onto a zero-background sample holder. Jet-cooked

samples were chopped with a razor blade to reduce the large particle size to a coarse powder. X-ray powder diffraction analyses were performed with a Phillips 1820 diffractometer operated at 40 kV, 30 mA, with graphite-filtered CuK α radiation and a theta compensating slit. Data were acquired in 0.05 degree two-theta, 4-s steps.

RESULTS

Graft copolymers shown in Table I were prepared by CAN-initiated polymerization of MA onto granular cornstarch. Percent PMA in starch graft copolymer products ranged from 58.3 to 12.3%, and the level of addition was varied by adjusting the starch/MA ratio. Percent PMA homopolymer was determined by extraction of air-dried products with acetone, and the PMA content of unextracted graft copolymer products was calculated from the loss in weight after acid hydrolysis. SEM (Fig. 1A, C, E, and G) showed that the granular structure of cornstarch is maintained after grafting, even after incorporation of high levels of PMA.

Jet cooking experiments were carried out with undried graft copolymer products and yielded aqueous dispersions that were comprised largely of insoluble polymer, easily separable from the water phase by filtration or centrifugation. Soluble polymer isolated from filtrates and supernatants exhibited only weak carbonyl absorption in FTIR spectra and thus contained only small amounts of PMA. SEM of water-insoluble polymer fractions (Fig. 1B, D, F, and H) showed that the starch granule structure had not been disrupted

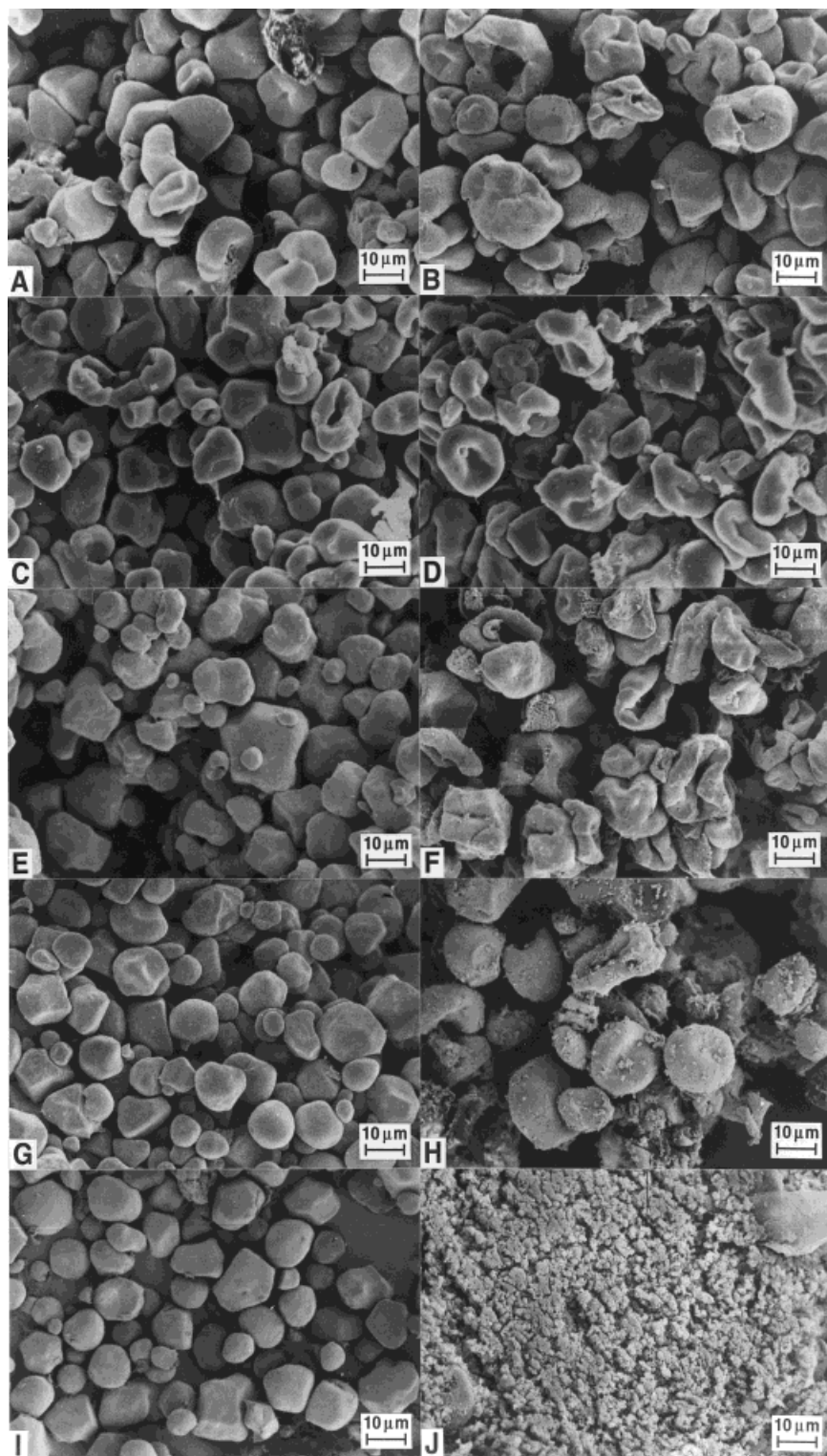


Figure 1 Scanning electron micrographs of uncooked and jet-cooked graft copolymer samples described in Table I. (A) Product 1, 58.3% PMA, uncooked. (B) Product 1, after jet cooking. (C) Product 2, 51.7% PMA, uncooked. (D) Product 2, after jet cooking. (E) Product 3, 31.9% PMA, uncooked. (F) Product 3, after jet cooking. (G) Product 4, 12.3% PMA, uncooked. (H) Product 4, after jet cooking. (I) Product 5, 0% PMA, uncooked. (J) Product 5, after jet cooking.

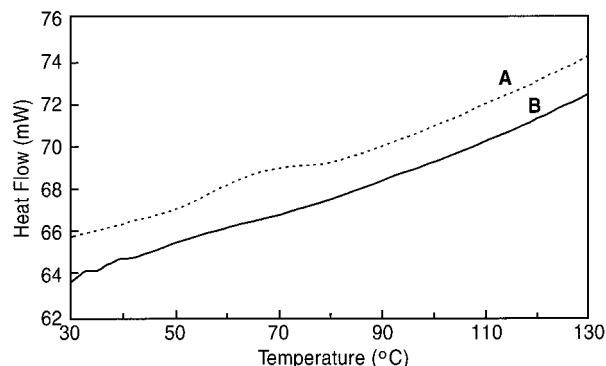


Figure 2 DSC thermograms for Product 1, Table I, 58.3% PMA. (A) Uncooked sample, 50.4% water. (B) Jet-cooked sample, 53.8% water.

by the jet-cooking process, even when the PMA content was as low as 12.3%. Also, the amount of water-soluble polymer in jet-cooked dispersions was at most only 13% of the total cooked sample (Table I). PMA contents of graft copolymers after jet cooking were somewhat higher than the PMA contents of uncooked polymers, since soluble material removed from grafted starch granules was comprised largely of polysaccharide. In contrast to S-g-PMA, a control product (No. 5, Table I), prepared by reacting starch with CAN in the absence of MA, was 87% soluble when jet-cooked under the same conditions.

Granules of S-g-PMA were examined by FTIR using an ATR cell to compare the relative amounts of PMA and starch on granule surfaces, before and after jet cooking. Although the ATR spectra did not yield quantitative results, spectra of uncooked and jet-cooked samples showed similar PMA/starch ratios. Samples were also examined by DSC (Fig. 2) and by X-ray diffraction (Fig. 3). Both of these techniques showed that starch crystallinity was absent in jet-cooked samples.

Graft copolymers containing 58.3 and 51.7% PMA (Products 1 and 2, Table I) were extrusion-processed into ribbons, along with their jet-cooked counterparts. The physical properties of these extrudates were then compared (Table II). Polymers containing 58.3% and 51.7% PMA were chosen since they are easily extruded at low moisture contents without the development of excessive torque and pressure. Products with 58.3% PMA were adjusted to two different moisture contents (~ 3 and 7%) prior to extrusion, whereas the products with lower PMA levels were extruded at 7% moisture only (Table II). The effects of both water and PMA content upon the formation and proper-

ties of extrudates have been reported,⁷ and we have observed that both torque and pressure are reduced when PMA and water content are increased.

Some areas of the extruded ribbon obtained from the jet-cooked polymer with 51.7% PMA exhibited a rough, pebbly surface, in contrast to the smooth surfaces usually observed. These rough-surfaced sections were more tear-resistant and had higher %E values than the smoother sections of ribbon. Although the cause of this surface roughness was not investigated further, it might result from uneven distribution of moisture along the extruder barrel during processing. Rough-surfaced extrudates were observed previously, when S-g-PMA samples were extruded at high moisture.⁷

Table II shows that physical properties of extruded ribbons depend upon whether or not granular S-g-PMA is jet-cooked before extrusion processing. Although tensile strengths were not significantly affected by jet cooking, cooked samples showed increases in both %E and tear resistance. Jet cooking also reduced torque and pressure in the extruder by $\sim 10\%$, when the 58.3% PMA product was processed at 3% moisture. Torque and pressure differences between cooked and uncooked samples were not as pronounced at 7% moisture. To compare the effects of jet cooking prior to extrusion with the effects of extrusion processing at high water content, the 58.3% PMA polymer was moistened to a water content of 30% and was then extruded under the same conditions used for the other samples. The wet extrudate was dried to a moisture content of 6.93% and was

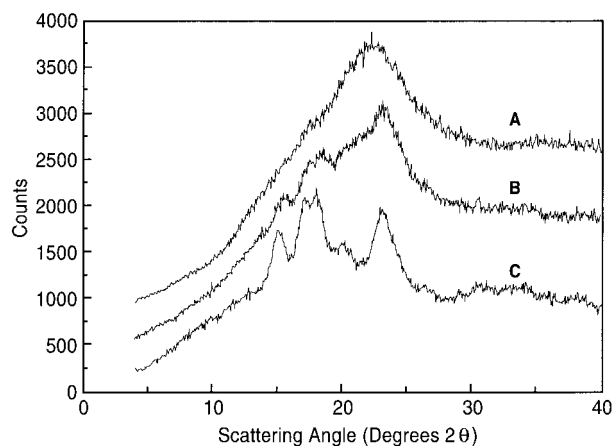


Figure 3 X-ray diffractometer scans. (A) Product 1, Table I, 58.3% PMA, jet-cooked. (B) Product 1, Table I, 58.3% PMA, uncooked. (C) Untreated cornstarch.

Table II Physical Properties of Extruded Ribbons

Product	Moisture Content (%) ^a	Equilibration Time (Days)	Tensile Strength (MPa) ^b	% Elongation ^b	Tear Resistance (N/mm) ^b	SEM Fig. No.
No. 1, Table I, untreated	2.84	7	10.3 (0.7)	21.8 (2.2)	3.3 (0.2)	4(A)
		28	10.9 (0.4)	20.2 (1.4)	3.0 (0.1)	
	7.32	7	13.3 (0.4)	89.4 (13.9)	6.9 (0.6)	4(B)
		28	12.2 (0.6)	49.6 (11.7)	3.3 (0.1)	
No. 1, Table I, jet-cooked	3.15	7	11.6 (0.6)	76.8 (15.3)	7.4 (0.4)	4(C)
		28	11.7 (0.4)	63.2 (6.2)	7.4 (0.4)	
	7.02	7	14.5 (0.5)	153.0 (18.5)	10.2 (1.3)	4(D)
		28	12.9 (0.7)	134.2 (18.9)	10.3 (0.3)	
No 1, Table I, extruded with 30% H ₂ O	6.93	7	12.6 (0.5)	148.0 (8.9)	9.8 (0.4)	4(E)
		28	11.9 (1.1)	145.1 (24.4)	11.2 (0.4)	
No. 2, Table I, untreated	7.02	14	14.7 (0.2)	24.4 (1.8)	2.7 (0.3)	
		28	14.5 (0.8)	23.0 (4.9)	2.6 (0.2)	
No. 2, Table I, jet-cooked	6.94	14	13.6 (0.4)	40.5 (2.4)	4.3 (0.2)	
		14 ^c	13.4 (0.3)	79.1 (8.9)	9.1 (0.9)	
		28	13.4 (0.4)	47.2 (4.5)	6.7 (0.7)	
		28 ^c	14.0 (0.2)	68.5 (12.6)	7.7 (0.9)	

^a Prior to extrusion.

^b Standard deviations are given in parentheses.

^c Ribbon section having a pebbly, rather than smooth surface.

passed a second time through the extruder to obtain a continuous ribbon for testing. Physical properties of this extrudate were not greatly different from those of the jet-cooked sample. SEM of extruded ribbons (Fig. 4) showed that individual granules of S-*g*-PMA were still present and had not been destroyed by processing. Granule disruption was most evident in the sample pre-extruded with 30% water, suggesting that S-*g*-PMA granules are more intensely sheared by extrusion processing than by jet cooking. Also consistent with this idea is our previous observation that complete granule disruption and phase inversion took place when a graft copolymer containing 30% PMA was extruded at high water content.⁷

DISCUSSION

Conversions of MA to PMA were nearly quantitative in these graft polymerizations, and only minor amounts of ungrafted homopolymer could be extracted from reaction products with acetone. Figure 1 shows that the outward appearance of cornstarch granules was not greatly altered by graft polymerization, even after incorporation of large amounts of PMA within the granule matrix.

Since unreacted starch is totally disrupted and

dissolved by jet cooking, we suspected that jet cooking might also disrupt granules of S-*g*-PMA; since the cooking temperature of 140°C is far above the 8°C T_g of the water-insoluble PMA grafts. The resistance of graft copolymer granules to disruption, even under the high temperature, high shear conditions of the jet cooking process, suggests that crosslinking may have occurred during graft polymerization. Free radical combination of growing PMA chains is a logical explanation for crosslinking and has been considered by us previously.⁷ Evidence for crosslinking in CAN-initiated graft polymerizations of acrylonitrile onto starch has also been cited.¹⁵ Although there is evidence to support crosslinking of starch when it is treated with CAN,¹⁶ these crosslinks apparently do not survive hot water treatment, and granules of CAN-treated starch are disrupted and dissolved by jet cooking. Product 5, Table I, was 87% soluble when it was jet-cooked under the same conditions as S-*g*-PMA; the small fraction of insoluble starch (13%) isolated from the cooled solution probably resulted from retrogradation of amylose.

Various explanations were considered to account for the increases in both %*E* and tear strength, brought about by jet-cooking S-*g*-PMA granules prior to extrusion. The possibility that

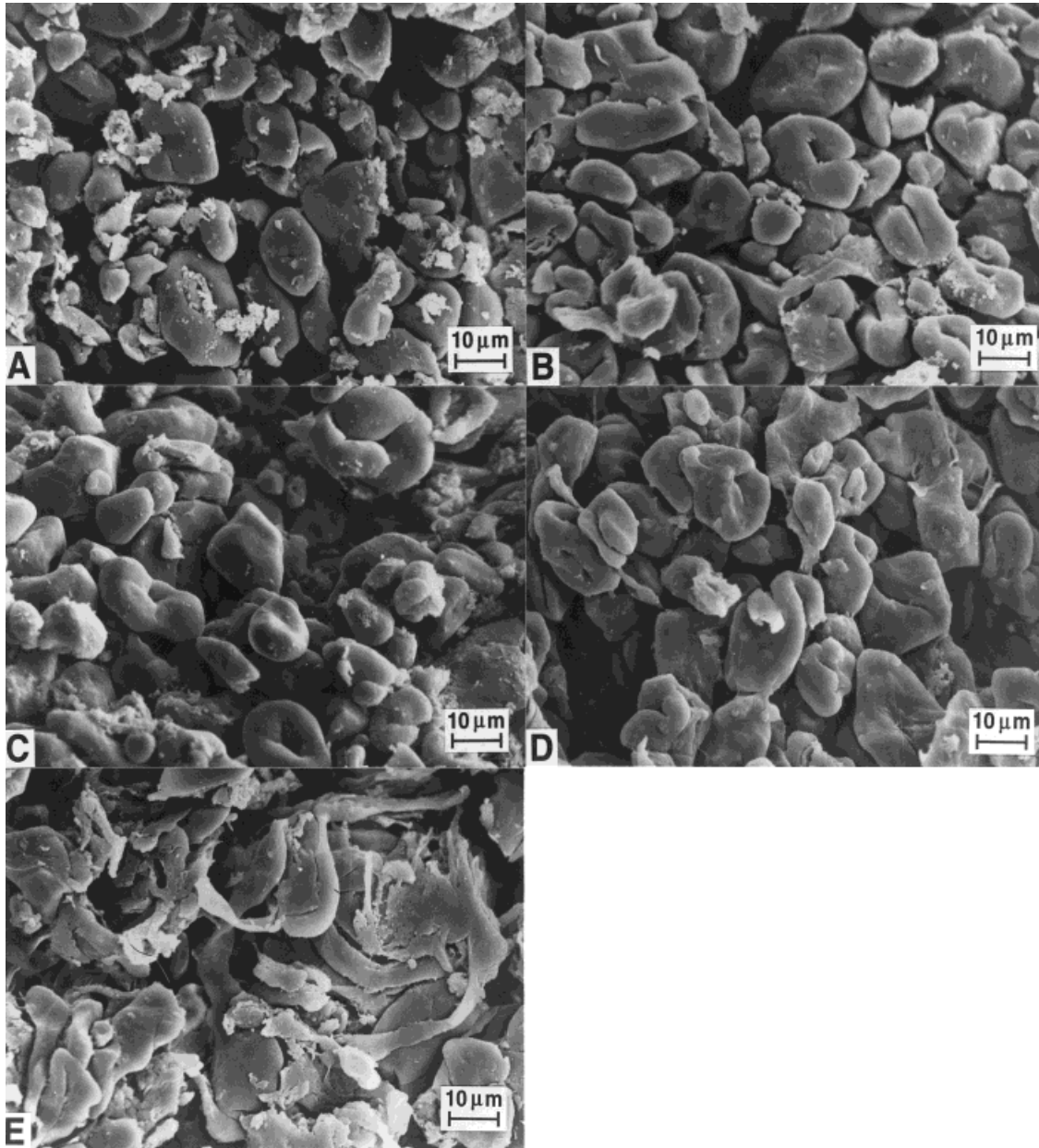


Figure 4 Scanning electron micrographs of extruded ribbons described in Table II. Extruded ribbons were prepared from Product 1, Table I, 58.3% PMA. (A) Uncooked polymer, 2.84% moisture. (B) Uncooked polymer, 7.32% moisture. (C) Jet-cooked polymer, 3.15% moisture. (D) Jet-cooked polymer, 7.02% moisture. (E) Polymer pre-extruded with 30% water, 6.93% moisture.

property differences are caused by jet-cooked granules becoming more fragmented during the process of extrusion was disproved by SEM of ribbon samples (Fig. 4). These micrographs show that individual granules still remain in extruded samples, and that there is little difference between the morphology of ribbons prepared from cooked and uncooked S-*g*-PMA. We also consid-

ered the possibility that minor amounts of starch dissolved during the jet-cooking process might have been removed from near the granule surface, yielding S-*g*-PMA granules having high surface concentrations of PMA. The individual fused granules that comprise the extruded ribbon might thus be separated by a softer and more flexible layer of polymer. Evidence against this theory

was obtained from ATR-FTIR spectra, which showed that relative absorbencies of starch and PMA were similar in jet-cooked versus uncooked samples.

Perhaps the most reasonable explanation for the observed differences in ribbon properties is that jet cooking disrupts the crystallinity and hydrogen bonding of starch (i.e., gelatinizes the starch portion of the graft copolymer). Even though starch is gelatinized, granules of S-g-PMA remain intact because of the water-insolubility of PMA and the crosslinking that has taken place between PMA grafts. Gelatinization of the starch moiety produces S-g-PMA granules that are less rigid, more deformable, and more readily plasticized by small amounts of water.

Evidence for starch gelatinization was provided by both DSC and X-ray diffraction. DSC thermograms for Product No. 1, Table I, before and after jet cooking are shown in Figure 2. A starch-melting endotherm having $T_m = 65^\circ\text{C}$ and $\Delta H = 8 \text{ J/g}$ of dry starch was obtained for the uncooked sample. This melting enthalpy is somewhat smaller than the value of 13 J/g obtained for granular, untreated cornstarch.⁷ After jet cooking, no melting endotherm was observed, suggesting that all of the crystalline structure of starch was disrupted by the cooking process. X-ray diffractometer scans for the same sample pair, as well as for untreated cornstarch, are shown in Figure 3. Both cornstarch and S-g-PMA have diffraction patterns characteristic of the A-type crystal structure found in cereal starches.¹⁷ The crystalline scattering intensity is smaller for uncooked S-g-PMA, probably because of the lower percentage of starch in the sample as well as the possibility that some disruption of the starch moiety has occurred during graft polymerization. In contrast to the uncooked sample, jet-cooked S-g-PMA exhibited only an amorphous scattering curve, supporting the conclusion that jet cooking has caused complete melting of the starch portion of the polymer.

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