Extrusion Processing of Granular Starch-g-Poly(methyl acrylate): Effect of Extrusion Conditions on Morphology and Properties

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SYNOPSIS

Starch-g-poly(methyl acrylate) copolymers (S-g-PMA) containing 10, 30, 46, and 58% PMA, by weight, were prepared by ceric ammonium nitrate-initiated polymerization of methyl acrylate onto granular cornstarch. Graft copolymers were extrusion-processed through a strand die with water contents of 10 and 30% (based on starch) and at temperatures of 140 and 180°C, and the resulting strands were then pelletized. Properties of ribbons prepared from extrusion-processed S-g-PMA depended on the combined effects of processing temperature, PMA level in the graft copolymer, and water content during extrusion. Ribbon formation was poor at the lowest PMA level of 10%, and extruded ribbons did not have sufficient continuity for tensile testing. Ribbons with smooth surfaces were obtained with 10% water in the polymer, whereas a water content of 30% produced extrudates that were rough and pebbly. When processed with 10% water, graft copolymers containing 46 and 58% PMA exhibited the highest values for both ultimate tensile strength (UTS) and % elongation at break (% E) when the extrusion was performed at 180°C. UTS was reduced and % E was increased when the water content during processing was increased to 30%. At the highest grafting level (58%), discrete granules of S-g-PMA were still apparent in scanning electron micrographs of extruded ribbons. More granule disruption occurred when the PMA level was reduced to 46%, and virtually none of the original granule structure remained after extrusion with 30% water. The effect of water content during processing was especially apparent at the grafting level of 30%, and extrudate properties were consistent with the formation of starch as the continuous phase under high moisture conditions. The behavior of S-g-PMA granules during extrusion can be explained by cross-linking within the starch matrix during the graft polymerization reaction. DSC data were consistent with this theory. © 1993 John Wiley & Sons, Inc.*

INTRODUCTION

Use of agriculturally derived products such as starch, as extenders and replacements for totally synthetic polymers, reduces our dependence on petrochemically derived monomers. Also, the starch portion of the polymer can be attacked by microorganisms, leading to environmental breakdown of the material. Graft polymerization of thermoplastic polymers onto starch provides an excellent method for preparing

these starch–polymer composites. 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 separation of polymer phases is less likely to occur.

In the course of our research on starch graft copolymers, the properties of starch-g-poly(methyl acrylate) (S-g-PMA), containing roughly 50–60% PMA, have been especially interesting and have caused us to consider the commercial potential of these materials. In unpublished experiments carried out at our Research Center over two decades ago, Gugliemelli masticated S-g-PMA on the cold rolls

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of a rubber mill and formed tough, flexible films that had some resemblance to polyethylene in their feel and outward appearance. Extrusion processing through a slit die at elevated temperatures yielded similar materials.[1] Dennenberg et al.[2] confirmed that the starch portion of these composites was indeed susceptible to fungal attack.

Graft polymerizations of methyl acrylate (MA) onto starch are conveniently carried out in water using ceric ammonium nitrate as initiator. Ceric ion, a strong oxidant, rapidly complexes with starch and oxidizes the polysaccharide, in a slower secondary reaction, to yield free radicals on the starch backbone.[3] In the presence of monomer, these macroradicals act as polymerization initiators, causing PMA grafts to propagate from the polysaccharide matrix. PMA grafts are typically of high molecular weight (several hundred thousand), and individual grafts may be separated by hundreds or even thousands of glucopyranosyl units. Each starch molecule thus has only a few high molecular weight PMA grafts, even though the final graft copolymer might contain over 60% PMA by weight.

Starch is isolated from plant sources as discrete granules that range in diameter from roughly 5 to 40 μm, depending on the plant variety. Although starch granules are insoluble in water at room temperature, heating results in swelling, disruption, and partial solubility of the granules (i.e., gelatinization). Both granular and gelatinized starches have been used as substrates for graft polymerization. Although the outward appearance of starch granules in scanning electron micrographs is not greatly changed by PMA grafting, a grafting level of 60% PMA by weight increased the mean particle diameter from 8.57 to 13.66 μm.[4] If the behavior of PMA is analogous to that of polyacrylonitrile,[5] grafting most likely takes place throughout the granule interior as well as on the surface.

The extrusion processing of granular S-g-PMA, air-dried to a moisture content of 4–5% (or about 10% based on starch), has been studied by us in some detail. Henderson and Rudin[6,7] also published data on S-g-PMA, but used gelatinized wheat starch for grafting. In our initial publication,[1] we observed that graft copolymer particles in the extruder barrel were poorly fused, whereas material in the high-pressure zone of the extruder die was in the form of a uniform, continuous plastic. Die swell was minimal. The extrusion behavior of S-g-PMA was thus explained as the powder flow of S-g-PMA granules, heat-softened by grafted PMA (T_g, 8°C) and partially fragmented. Photomicrographs of the fused extrudate[4] confirmed the particulate structure. In-

terparticle fusion most likely takes place through grafted PMA on particle surfaces.

The behavior of S-g-PMA ribbon in different solvent systems is in agreement with this picture. Dennenberg et al.[2] observed that prolonged soaking in water lowered the ultimate tensile strength (UTS) of test specimens to 20% of their original value, whereas % elongation at break (% E) increased by a factor of two. Despite these large changes in tensile properties and the observed swelling and whitening of the product, water-soaked samples remained continuous and showed no tendency to disintegrate, apparently because the continuous phase is made up of water-insoluble PMA. Contrary to their behavior in water, tensile specimens disintegrated[8] when placed in solvents that swell and dissolve PMA (e.g., acetone and benzene).

The flow mechanism of heat-softened S-g-PMA particles during extrusion processing was investigated by Swanson et al.,[4] who found that the relationship between die pressure and flow rate was typical of that expected for viscous flow of the particles, as opposed to plug flow. Vacuum-dried graft copolymers (compared to samples containing an ambient water content of about 10%, based on starch) developed higher die pressures during extrusion and continued to exhibit viscous flow, despite the reduced availability of water to function as a plasticizer.

Although S-g-PMA used in previous studies apparently retains much of its granule structure during extrusion, we have not investigated processing conditions that might promote disruption of granules or the changes in extrudate properties that might accompany granule disruption. In this study, we report the preparation and characterization of a series of granular S-g-PMA copolymers containing a range of PMA levels. These graft copolymers were then extruded at different temperatures and moisture contents to determine the combined effects of PMA level, moisture content during extrusion and extrusion temperature on the morphology, tensile properties, and thermal properties of the extrudates.

EXPERIMENTAL

Materials

Cornstarch (Buffalo 3401, containing 10–11% moisture) was obtained from CPC International. Methyl acrylate was obtained from Polysciences, Inc. Except where indicated, methyl acrylate was used as received. Ceric ammonium nitrate was certified ACS grade from Fisher Scientific Co.

Table I Preparation and Characterization of S-g-PMA

Starting Materials			% PMA in S-g-PMA[b]	Conversion of Monomer to PMA (%)	PMA Homopolymer[c]			S-g-PMA after Homopolymer Extraction		Grafted PMA	
Starch (g)	Methyl Acrylate (g)	CAN[a] (g)			% of Total Product	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	% PMA[d]		$M_w \times 10^{-5}$	$M_n \times 10^{-5}$
1250	172	42.5	10	79	0.5	—	—	12		—	—
1250	540	42.5	30	99	2.0	—	—	27		—	—
800	690	27.2	46	98	4.0	2.16	1.01	42		4.02	1.50[e]
800	1255[f]	27.2	58	90	8.0	5.28	2.00	56		5.43	2.05[g]

[a] Ceric ammonium nitrate.
[b] Calculated from weight gain of starch.
[c] Removed by extraction with acetone. PMA was 98–99% soluble in THF for molecular weight determination.
[d] Calculated from weight loss after removal of starch by hydrolysis.
[e] 74% soluble in THF for molecular weight determination.
[f] Distilled before use.
[g] 84% soluble in THF for molecular weight determination.

Graft Polymerization

Starch was dispersed in 10 L of water in a 12 L round-bottomed flask, and the stirred dispersion was sparged with nitrogen for 90 min at 25°C. Methyl acrylate was added, followed after 5 min by a solution of ceric ammonium nitrate in $1N$ nitric acid (0.34 g/mL), and the mixture was stirred for 3 h at 25°C. Quantities used are listed in Table I. The graft copolymer was separated by filtration, washed with water, and neutralized to pH 7 with sodium carbonate. The moist filter cake was screened through a 10 mesh sieve and then allowed to air-dry at room temperature. Moisture content was determined by weight loss on drying over P_2O_5 at 100°C in an Abderhalden drying apparatus. Percent PMA in the graft copolymer was calculated from the weight gain of starch.

Characterization of Graft Copolymers

Percent ungrafted PMA (homopolymer) in graft copolymer preparations was determined by acetone extraction. Five grams of each product was shaken (250 rpm for 24 h) with 100 mL of acetone containing 2% water.[9] The solid was separated by centrifugation and washed three times with fresh portions of acetone. Soluble and insoluble fractions were isolated by allowing the acetone to evaporate.

Grafted PMA was separated from starch for molecular weight determination by first oxidizing starch with periodate and then decomposing the resulting dialdehyde starch with sodium methoxide.[10] Acetone-extracted graft copolymer (1.60 g) was first allowed to swell in acetone and was then washed with water. Water-wet polymer was dispersed in 200 mL of $0.1M$ $NaIO_4$, and the dispersion was allowed to stand in the dark for 1 week with occasional stirring. The polymer was separated by filtration, washed with water and with methanol, and suspended in 20 mL of methanol. Two milliliters of $1N$ sodium methoxide in methanol was added, and the mixture was allowed to stand overnight at 5°C. Supernatant was decanted from settled polymer and the polymer was washed with methanol and dried. Infrared spectroscopy showed no detectable starch. Percent PMA in the graft copolymer was calculated from the loss in weight after $NaIO_4$/sodium methoxide treatment.

Molecular weights were determined with a Spectra-physics GPC system, consisting of a Model SP-8810 pump and an SP-8780 autosampler in combination with a Waters 410 RI detector. The linear Styrogel column (MW range from 2×10^3 to 4×10^6) was calibrated with polystyrene standards.

Molecular weights were multiplied by a correction factor of 0.827, obtained by dividing the molecular weight of methyl acrylate by that of styrene. The mobile phase was HPLC-grade tetrahydrofuran (THF), and the flow rate of the mobile phase was 1 mL/min. PMA samples (30 mg) were stirred with 20 mL of THF for 3 days at room temperature. Insoluble material was separated by centrifugation, dried, and weighed. Solutions were filtered through a 0.5 μm filter before injection.

Extrusion Processing and Tensile Testing

Graft copolymer samples were extruded through a multihole die (17 holes, 1.58 mm diameter) 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 3 : 1. Temperatures in the two heating zones were either 130°C (nearest the feed zone)–140°C (nearest the die) or 170°C (nearest the feed zone)–180°C (nearest the die). Extruded strands were chopped into pellets in a Killion pelletizer. Ribbon was prepared for testing by passing the pellets through the same extruder equipped with a 25.4 × 0.50 mm slit die. Temperatures for ribbon preparation were 140°C (nearest the feed zone), 150°C (nearest the die), and 150°C (at the die). Variations from the set-temperatures during extrusion processing were about ±3°C.

Extruded ribbons were allowed to equilibrate for 7, 28, and 56 days at 23°C and 50% relative humidity before testing. Tensile strips 12.7 mm wide were tested (four replications per sample) on an Instron Universal Testing machine, Model 4201, at a crosshead speed of 5 cm/min. Grip length was 51 mm, and elongation was measured as displacement of the line-contact grips during tensile testing. Sample thickness was measured with a Carson-Dice electronic micrometer. Relative standard deviations averaged 9.86% for UTS and 21.9% for % E.

Electron Microscopy

Samples were mounted on aluminum stubs, coated with a layer of gold–palladium (60–40) alloy, and then examined and photographed in a Hitachi ISI-SS130 scanning electron microscope. Acetone-treated samples were solvent-exchanged with ethanol, and ethanol-wet products were critical-point dried for microscopic examination.

Water Absorption

Accurately weighed samples of extruded ribbon (0.2 g) were placed in 10 mL of water and were allowed to stand at 25°C for about 18 h. Samples were blotted to remove surface water and weighed. Water absorption was calculated as follows:

Water absorption (%)

$$= \frac{\text{Wet wt. of sample} - \text{starting wt.}}{\text{Starting wt.}} \times 100$$

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC7 equipped with the CCA7 liquid nitrogen cooling accessory was used. The thermal cell block was set at −50°C and purged with nitrogen. The instrument was calibrated using the melting temperatures and enthalpies of indium and water. Prior to DSC analysis, extruded S-g-PMA ribbons and mixtures of starch with PMA were pulverized by shaking at liquid nitrogen temperature in a stainless-steel vial with 2 stainless-steel balls. These samples, as well as samples of S-g-PMA before extrusion, were allowed to equilibrate for 1 week in a desiccator containing saturated NaHSO₄ (52% relative humidity). The moisture content of these samples was 12.5 ± 0.6% based on the starch component of the polymer. Approximately 30 mg of each sample was sealed inside a stainless-steel DSC pan (Perkin-Elmer part No. 0319-0218). Samples were heated in the DSC from −20 to 220°C at 10°C/min, rapidly cooled to −20°C, and then reheated to 220°C at 10°C/min. Peak starch melting temperatures and melting enthalpies were determined from the first heating run, whereas starch and PMA glass transitions were measured from the second run. Calculations were performed using DSC7 software.

RESULTS AND DISCUSSION

Graft copolymers shown in Table I were prepared by ceric ammonium nitrate-initiated polymerization of methyl acrylate onto granular corn starch. Percent PMA in starch graft copolymers ranged from 10 to 58%, by weight, and the level of addition was easily varied by adjusting the starch/methyl acrylate ratio. Products contained only small amounts (8% or less) of acetone-extractable PMA homopolymer.

S-g-PMA was extrusion-processed without acetone-extraction of PMA homopolymer, since this step would not be practical in any commercial process. Processing was carried out in two stages: In the first stage, polymers (with water contents equal to either 10 or 30% of the weight of the starch component) were extruded through a strand die at either 140 or 180°C. Water content was based on the starch moiety rather than on the total weight of the graft
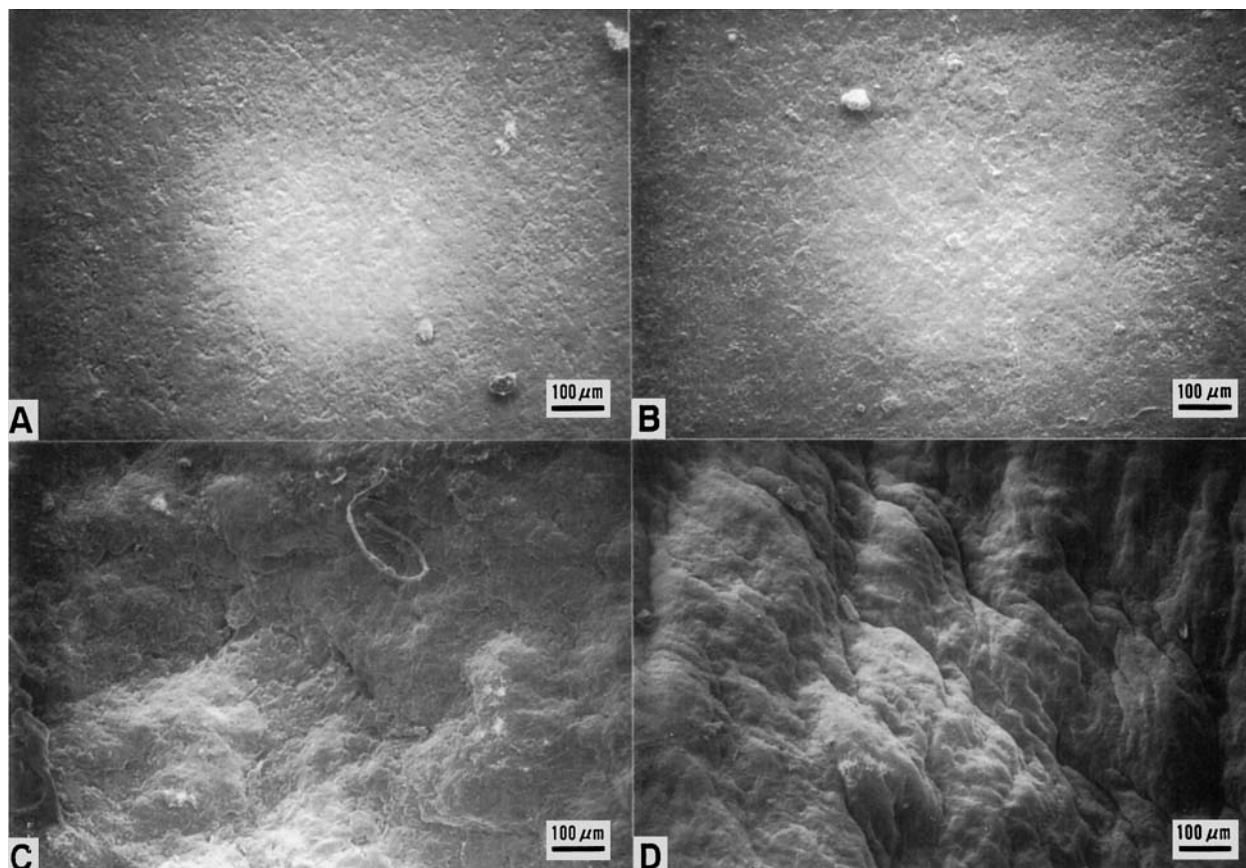
Figure 1 Effect of moisture content of S-*g*-PMA during extrusion of strands on the surfaces of the final extruded ribbons. Extrusion temperature for preparation of strands: 180°C. Samples photographed at 100X. (A) PMA level: 58%; 10% moisture; (B) PMA level: 46%; 10% moisture; (C) PMA level: 58%; 30% moisture; (D) PMA level: 46%; 30% moisture.

copolymer, since PMA is a hydrophobic polymer. In the second stage, strands were chopped into pellets and extruded at 150°C into ribbon for determination of physical properties.

The surface appearance of extruded ribbons varied with the water content during processing. Samples extruded through the strand die with 10% water (which is close to the moisture content obtained after allowing the polymer to air-dry at room temperature) yielded ribbons with smooth surfaces. Chopped strands prepared with an initial water content of 30% yielded ribbons that were rough and pebbly. Scanning electron micrographs of ribbon surfaces (Fig. 1) clearly show these differences in surface morphology. The surface roughness of high-moisture samples could be caused by the escape of water vapor during extrusion or to an enhancement of die swell due to the plasticizing action of water on the starch component. Localized surging of polymer flow in the die could also contribute to surface roughness.

Tensile properties of extruded ribbons obtained from chopped strands processed at 140 and 180°C and with water contents of 10 and 30% are shown in Table II. Properties of the polymer containing only 10% PMA are not included in this table, since formation of ribbon was poor at this low PMA level. Test specimens were equilibrated at 23°C and 50% relative humidity for periods of time ranging from 7 to 56 days, so that moisture levels based on starch would be comparable in all products before testing. In most instances, equilibration for longer than 7 days produced no significant changes in tensile properties. Table II shows that graft copolymers containing high levels of PMA (46 and 58%), processed with only 10% water, exhibited higher values for UTS as well as % *E* when an extrusion temperature of 180°C (as opposed to 140°C) was used. UTS was reduced when the water content was increased to 30%, and this reduction was accompanied by large increases in % *E*. The graft copolymer containing only 30% PMA showed higher values for both UTS

Table II Variations in Tensile Properties and Water Absorption of S-g-PMA Extrudates with Grafting Level, Water Content during Extrusion, and Extrusion Temperature

| % PMA in S-g-PMA | Extrusion Conditions | | Tensile Values, after Aging for 7, 28, and 56 days[b] | | | | | | Water Absorption (%) |
| | H₂O Content (%)[a] | Maximum Temp (°C) | 7 Days | | 28 Days | | 56 Days | | |
			UTS	% E	UTS	% E	UTS	% E	
58	10	180	17	48	16	53	16	60	34
58	30	180	13	118	14	102	12	148	48
58	10	140	15	25	13	24	12	29	28
58	30	140	13	140	—	—	13	133	47
46	10	180	18	32	15	10	14	20	60
46	30	180	10	112	11	108	11	96	67
46	10	140	13	12	12	8	9	5	34
46	30	140	8	84	9	63	8	63	67
30	10	180	12	2.3	11	2.7	10	2.3	95
30	30	180	18	31	24	32	—	—	123

[a] Based on the starch population of S-g-PMA.
[b] Aged at 23°C and 50% relative humidity. UTS = ultimate tensile strength (MN/mm²). % E = Percent elongation at break.

and % E when samples were processed with 30% water, rather than 10%.

The last column of Table II shows the amount of water absorbed by extruded ribbons after prolonged soaking in water at room temperature. As reported by Dennenberg et al.,[2] water-soaked samples become soft and rubbery but remain continuous. In general, the amount of water absorbed increased with the starch content of the graft copolymer, and water absorption was also greater for samples processed with 30% water. Samples extruded with 10% water showed higher water absorption when processing was carried out at 180°C.

A number of factors could be responsible for the observed variations in both tensile properties and water absorption shown in Table II, and more research is obviously needed to completely characterize all variables associated with the extrusion process. One factor of primary importance is the extent to which S-g-PMA granules are deformed and fragmented under the high pressures and temperatures developed during extrusion, since size, shape, and deformability of polymer particles will certainly influence the continuity and thus the physical properties of our tensile specimens. Because of the low T_g of PMA, high PMA levels in the polymer should soften the granule matrix, favor granule fragmentation, and promote interparticle fusion, especially at high temperatures. Addition of water during processing should have a similar effect, because of the plasticizing effect of water on the starch moiety. However, with polymers containing high levels of

grafted PMA, excess water can also be detrimental to interparticle bonding because of the incompatibility of water with PMA. Moreover, the presence of excess water can lead to bubbles and holes in the final product due to steam formation during processing.

Even though PMA is the continuous phase under low moisture conditions (since interparticle fusion takes place through grafted PMA at particle surfaces), phase reversal can take place if the level of PMA in the polymer is sufficiently low and there is sufficient water present to yield a starch melt during extrusion. The behavior of our 30% PMA ribbons, when allowed to imbibe either water or acetone, provides good evidence for such a phase change. PMA is apparently the continuous phase when the polymer is extruded with a water content of only 10%, since soaking this ribbon in water affords a rubbery product that still retains considerable strength. However, gentle agitation in acetone (a good solvent for PMA) causes the ribbon to disintegrate. Contrary to the above behavior, the sample processed with 30% water remains strong and continuous in acetone but can be broken up easily in water, suggesting that the continuous phase is now starch. The effect of solvents on extrudates containing 46% PMA showed no such dependence of properties on water content during extrusion, indicating that this type of phase change does not readily take place at high levels of grafted PMA.

The morphology of extruded ribbons in Table II can be easily observed by scanning electron micros-
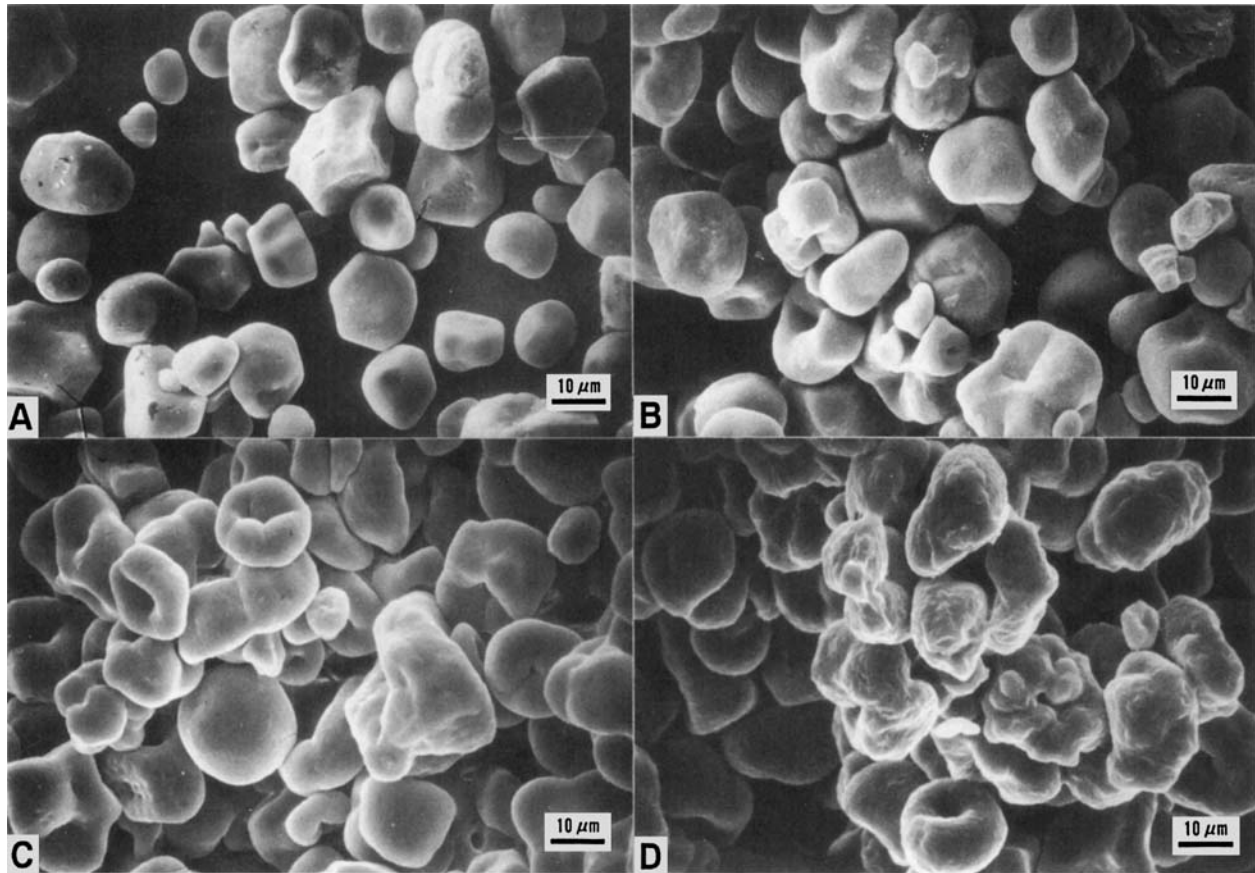
Figure 2 Effect of graft polymerization on the size and shape of cornstarch granules. Samples were extracted with acetone, solvent-exchanged with ethanol, and critical-point dried. Samples photographed at 1K×. (A) Ungrafted cornstarch; (B) PMA level: 30%. (C) PMA level: 46%; (D) PMA level: 58%.

copy, if ribbon samples are first allowed to soak and fragment in acetone to separate the individual particles of S-*g*-PMA. Ungrafted cornstarch and unextruded S-*g*-PMA, prepared at the three different levels of addition, were examined initially to provide references for comparison (Fig. 2). Although graft polymerization leads to an increase in granule size and caused some granule distortion, the outward appearance of cornstarch granules is not greatly changed by the polymerization reaction.

As one might expect, the observed morphology of our extruded ribbons depends upon the combined effects of PMA level, moisture content during extrusion, and extrusion temperature. At the 58% PMA level, remnants of the original granule structure were still visible after extrusion (Fig. 3), even though granules of S-*g*-PMA were increasingly elongated and fragmented as extrusion temperature and moisture level increased. Increased granule disruption was apparent when the PMA level was re-

duced to 46% (Fig. 4), and virtually none of the original granule structure remained after extruding this graft copolymer at a moisture content of 30%. Morphological differences between samples extruded with 10 and 30% water are especially dramatic at the 30% PMA level (Fig. 4) and are consistent with the inversion of phases discussed earlier for this polymer.

Cross-linking within the starch matrix during ceric-initiated grafting provides one explanation for the resistance of S-*g*-PMA granules to stress-induced fragmentation during extrusion processing. Cross-linking can take place not only by a free-radical combination mechanism but also through reaction between starch hydroxyls and carbonyl (e.g., aldehyde) substituents formed on starch by the oxidizing action of ceric ion. Cross-linking during graft polymerization has previously been proposed to explain the physical properties of starch-*g*-polyacrylonitrile and its saponification products.[11] Moreover,
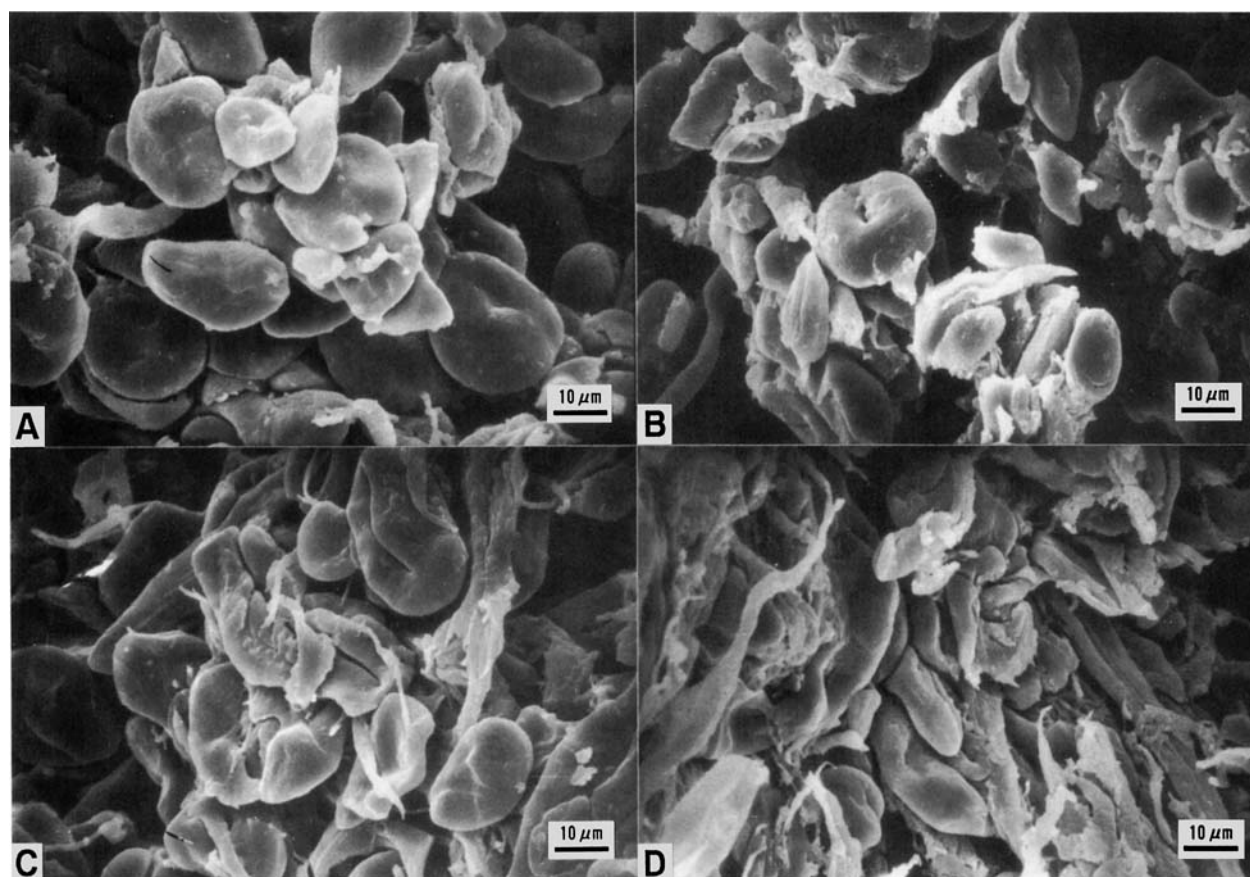
Figure 3 Effect of extrusion temperature and moisture content of S-g-PMA during preparation of strands on the morphology of the final extruded ribbons. PMA level: 58%. Ribbons were soaked in acetone, solvent-exchanged with ethanol, and critical-point dried. Samples photographed at 1K×. (A) Extrusion temperature: 140°C; 10% moisture; (B) extrusion temperature: 180°C, 10% moisture; (C) extrusion temperature: 140°C; 30% moisture; (D) extrusion temperature: 180°C; 30% moisture.

the behavior of starch after treatment with ceric ammonium nitrate in the absence of monomer[12] is consistent with the occurrence of cross-linking through reaction with ceric ion.

Graft copolymers were examined by DSC to obtain information relevant to the question of cross-linking. Results of DSC measurements on S-g-PMA prior to extrusion are shown in Table III. Values for starch melting temperature (T_m) increased with the level of PMA grafting, and a sharp increase in T_m was observed between 46 and 58% PMA. Moreover, the glass transition temperature (T_g) of starch also increased with the level of grafting. Although it was initially thought that these changes were caused by cross-linking within the starch matrix, similar increases in starch T_m and T_g were also observed for a 50 : 50, by weight, physical mixture of starch and PMA. This evidence suggests that increases in T_m and T_g result from absorption of some of the water

in the system by PMA at high temperatures, thus decreasing the amount of water available for plasticizing starch. Also, studies with cross-linked polystyrene[13] have shown that T_g increases only when cross-links occur at intervals of less than 300 monomer units. It is unlikely that the ceric/starch ratio of 1 mol per 100 glucopyranose units used in our experiments is high enough to produce sufficient cross-linking to account for the large variability of T_m and T_g in Table III.

The enthalpy of melting (ΔH) for granular, ungrafted cornstarch equilibrated at 52% relative humidity is 12.6 J/g (Table III), and this value reflects the melting of the crystalline portion of the amylopectin component. Graft copolymers containing 10–46% PMA exhibit about the same ΔH values as does ungrafted cornstarch. Little amylopectin crystallinity has thus been lost through graft polymerization. However, both the 58% PMA graft copol-
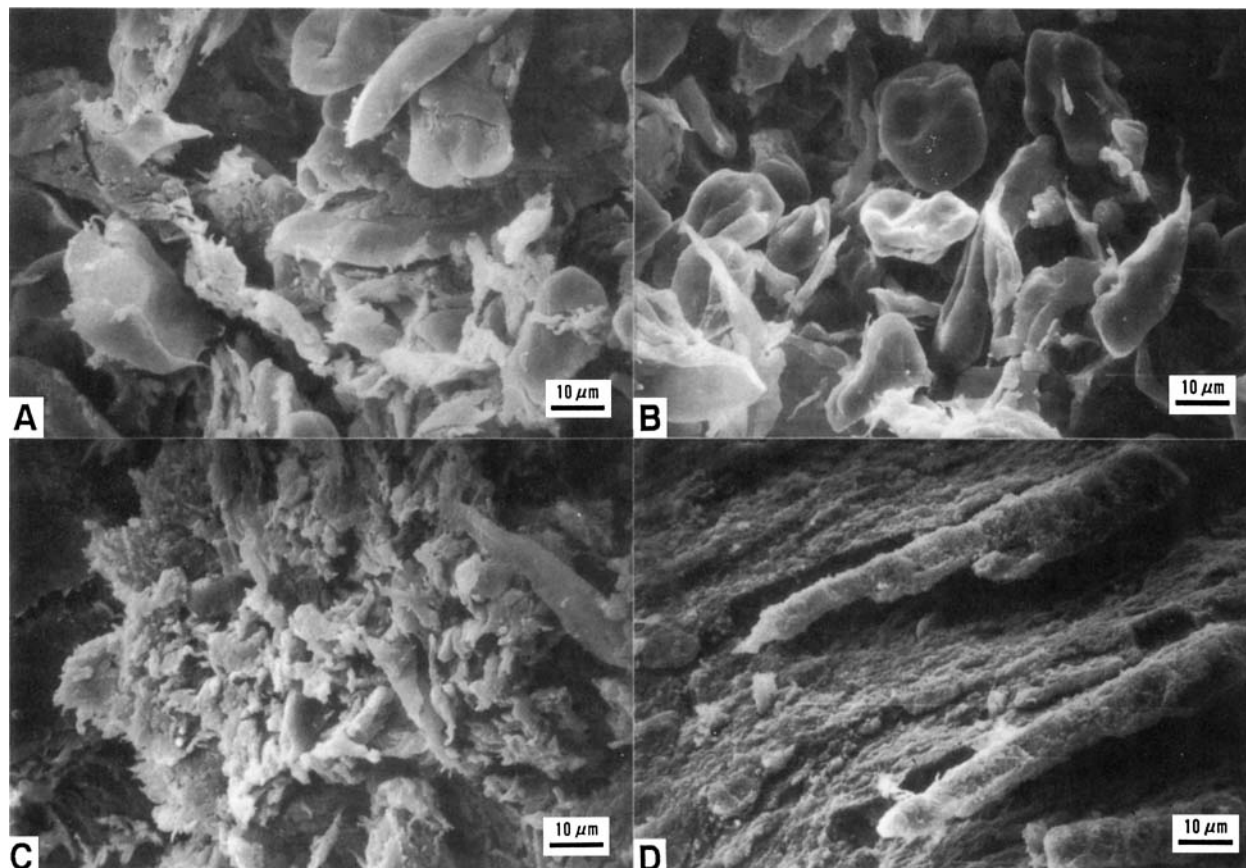
Figure 4 Effect of PMA level and moisture content during extrusion of strands on the morphology of the final extruded ribbons. Extrusion temperature: 180°C. Ribbons were soaked in acetone, solvent-exchanged with ethanol, and critical-point dried. Samples photographed at 1K×. (A) PMA level: 46%, 10% moisture; (B) PMA level: 30%, 10% moisture; (C) PMA level: 46%, 30% moisture; (D) PMA level: 30%; 30% moisture.

ymer and the 50 : 50 starch/PMA blend showed lower ΔH values (7.8–6.0 J/g). Reasons for these changes, as well as the similarity between graft copolymer and physical mixture, are not clear at this time.

Table III also shows that the T_g of the PMA component of our graft copolymers is similar to that of pure PMA and is independent of the level of grafting. It thus appears that starch and PMA occupy separate domains of at least 100 Å in size.[14] These data agree with dynamic mechanical studies of S-*g*-PMA by Henderson and Rudin,[6] who observed sharp loss peaks at about 8°C.

Extruded S-*g*-PMA ribbons showed only small starch melting peaks when examined by DSC (Table IV), and these were only for samples extruded at the lowest moisture content of 10%. Areas of crystallinity in the starch portion of our graft copolymers were thus largely disrupted under the conditions used for extrusion. This is evidence that S-*g*-PMA

granules tend to remain intact during extrusion because of covalent cross-linking and not because of hydrogen bonding through starch. Higher values for starch T_m in Table IV, as compared with Table III, are probably due to the annealing of starch during extrusion. T_g values for the starch and PMA portions of our graft copolymers were the same before and after extrusion (T_g data not shown in Table IV).

CONCLUSIONS

Levels of PMA addition can be easily varied by adjusting starch/methyl acrylate ratios in the polymerization recipe. Conversions of monomer to polymer are high, and ungrafted PMA is produced in only minor amounts. Graft polymerization of PMA does not greatly change the overall appearance of cornstarch granules, even though some increase in

Table III DSC Data for S-g-PMA Copolymers Prior to Extrusion[a]

% PMA in S-g-PMA[b]	Starch Component			T_g of PMA Component (°C)
	T_m^c (°C)	ΔH^d (J/g)	T_g^e (°C)	
0 (starch control)	176	12.6	86	—
10	177	11.2	89	6.2
30	183	11.1	97	8.1
46	190	12.0	108	8.2
58	204	7.8	112	7.9
100 (PMA, control)	—	—	—	7.5
50 (physical mixture, control)	200	6.0	106	6.2

[a] Samples equilibrated at 52% relative humidity.
[b] Calculated from weight gain of starch.
[c] Melting temperature.
[d] Melting enthalpy.
[e] Glass transition temperature.

granule size and some distortion of granule shape are apparent in scanning electron micrographs.

Properties of extruded ribbons prepared from these graft copolymers depend upon the combined effects of the PMA level in the graft copolymer, moisture content of the graft copolymer during extrusion, and the temperature at which samples are processed. Examination of extrusion temperatures of 140 vs. 180°C and water contents during extrusion of 10 vs. 30% (based on the starch component of

Table IV DSC Data for Extruded S-g-PMA Ribbons

% PMA in S-g-PMA[a]	Extrusion Conditions		Starch Component	
	H₂O Content (%)	Maximum Temp (°C)	T_m^b (°C)	ΔH^c (J/g)
10	30	180	—	0.0
30	10	140	191	3.2
30	10	180	—	0.0
30	30	180	—	0.0
46	10	140	196	4.8
46	10	180	—	0.0
46	30	140	—	0.0
46	30	180	—	0.0
58	10	140	208	2.3
58	10	180	211	1.8
58	30	140	—	0.0
58	30	180	—	0.0

[a] Calculated from weight gain of starch.
[b] Melting temperature.
[c] Melting enthalpy.

the graft copolymer) leads to the following conclusions:

1. Under the processing conditions used in this study, extruded ribbons having sufficient continuity for tensile testing are not obtained with PMA levels of 10%.
2. Extruded ribbons with smooth surfaces are produced when graft copolymers contain about 10% water (based on starch) during extrusion. A water content of 30% affords extrudates with rough, pebbly surfaces.
3. When processed with 10% water, graft copolymers containing high levels of grafted PMA (46 and 58%) exhibit higher values for both UTS and % E when the extrusion is performed at 180 rather than at 140°C. UTS is reduced and % E is increased when the water content during processing is increased to 30%. The graft copolymer containing 30% PMA showed the highest values for both UTS and % E when processing was carried out with 30% water in the polymer.
4. Extruded ribbons become soft and rubbery but remain continuous after prolonged soaking in water. Acetone soaking caused extrudates to disintegrate. This behavior is consistent with interparticle bonding through grafted PMA, thus affording PMA as the continuous phase. The amount of absorbed water increases with increasing ratios of starch/PMA in the graft copolymer.
5. When samples are processed with 10% moisture, discrete granules are still apparent in scanning electron micrographs of extruded

ribbons. At the highest PMA level (58%), granules appear increasingly elongated and fragmented, as the moisture level and extrusion temperature are increased. More granule disruption is apparent at the 46% PMA level, and virtually none of the original granule structure remains after extrusion with 30% moisture. Differences between scanning electron micrographs of extrudates processed with 10 and 30% water are especially dramatic at the PMA level of 30%. The behavior of these extrudates in water vs. acetone is consistent with an inversion of the continuous phase, when sufficient water is present during extrusion to produce a fluid starch melt. This type of phase inversion does not occur at the 46 and 58% grafting levels.

Our data are consistent with the occurrence of cross-linking within the starch matrix during the graft polymerization reaction, and DSC shows that areas of starch crystallinity are largely disrupted during extrusion. Even a low degree of cross-linking should stabilize S-g-PMA granules against stress-induced fragmentation during extrusion and would account for the fact that discrete granules remain in many of our samples after processing.

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