

Properties of Extruded Starch–Poly(methyl acrylate) Graft Copolymers Prepared from Spherulites Formed from Amylose–Oleic Acid Inclusion Complexes

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ABSTRACT: Mixtures of high-amylose corn starch and oleic acid were processed by steam jet cooking, and the dispersions were rapidly cooled to yield amylose–oleic acid inclusion complexes as micron- and submicron-sized spherulites and spherulite aggregates. Dispersions of these spherulite particles were then graft polymerized with methyl acrylate, both before and after removal of uncomplexed amylopectin by water washing. For comparison, granular, uncooked high-amylose corn starch was also graft polymerized in a similar manner. Graft copolymers with similar percentages of grafted and ungrafted poly(methyl acrylate) (PMA) were obtained from these polymerizations. The graft copolymers were then processed by extrusion through a ribbon die, and the tensile properties of the extruded ribbons were determined. Although extruded ribbons with similar tensile strengths were obtained from the three starch–PMA graft copolymers, much higher values for % elongation were obtained from the spherulite-containing systems. Also, the tensile properties were not significantly affected by removal of soluble, uncomplexed amylopectin by water washing before graft polymerization. These results are consistent with the observation that these PMA-grafted starch particles did not melt during extrusion, and that continuous plastic ribbons were formed by fusing these particles together in the presence of small amounts of thermoplastic PMA matrix. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40381.

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INTRODUCTION

The preparation and properties of starch–poly(methyl acrylate) graft copolymers (S-g-PMA) have been the subject of a number of investigations. These graft copolymers are of interest because chemically combining starch (a rigid nonmelting polysaccharide) with PMA (a soft, flexible polymer with T_g of about 10°C) produces composites that are tough, leathery, and partially biodegradable. Ceric ammonium nitrate (CAN) is a commonly used initiator in these graft polymerizations and rapidly forms a complex with the glucose repeating units of starch. Oxidation of starch then takes place to generate free radicals on the starch backbone, which then initiate graft polymerization. Ungrafted PMA homopolymer formed in these polymerizations can be removed by extraction with acetone, which is a good

solvent for PMA. The inability to remove PMA by acetone extraction is considered to be definitive evidence that PMA is chemically bonded to acetone-insoluble starch. Grafted PMA can be separated from starch by hydrolysis of the starch moiety with dilute HCl at reflux temperature. The hydrolysis of starch has also been carried out by dissolving the graft copolymer in hot, glacial acetic acid and then adding 60% perchloric acid,¹ and also by oxidation of starch with periodic acid followed by addition of sodium methoxide in methanol.²

Bagley et al. were the first to study the extrusion processing of S-g-PMA, and continuous extrudates with good tensile properties were observed with little or no die swell.³ Although the extruded ribbons swelled on prolonged soaking in water, they remained strong and continuous. As die swell, which commonly

occurs during the extrusion of thermoplastic polymer melts, was not observed, it was proposed that continuous extrudates were formed by the powder flow of heat-softened particles of S-g-PMA coupled with fusion of these nonmelting, starch-containing particles under the high pressures encountered in the extrude die. Although starch does not melt at the temperatures used for extrusion, the thermoplastic PMA portion softens sufficiently to allow the graft copolymer particles to fuse together; die swell is minimal because the starch graft copolymer is never in a molten state.

The preparation and characterization of S-g-PMA and the properties of extruded plastics prepared from these materials have been an active area for research. Dennenberg et al.⁴ prepared S-g-PMA from normal pearl cornstarch and observed that extruded samples showed excellent susceptibility to fungal growth. Henderson and Rudin^{5,6} prepared S-g-PMA from gelatinized wheat starch and determined the effects of water soaking on the properties of extruded ribbons. Swanson et al.⁷ prepared S-g-PMA from granular corn starch and examined the effects of polymerization temperature, % PMA in the graft copolymer, homopolymer content, molecular weight of PMA, and the strain rate used for tensile testing on the properties of extruded specimens. In a later publication,⁸ the flow mechanism of particulate polymers during extrusion was reviewed. Trimnell et al.⁹ prepared S-g-PMA from granular corn starch and observed that the properties of extruded samples depended on the combined effects of processing temperature, % PMA in the graft copolymer, and water content of S-g-PMA during extrusion. S-g-PMA was also prepared from normal, high-amylose, and waxy corn starches with CAN initiation, and the graft copolymers were characterized with respect to % grafted PMA, amount of PMA homopolymer, conversion of monomer to polymer, and the molecular weight and molecular weight distributions of the PMA grafts.¹⁰ Granular and gelatinized starches were used as well as starch samples that were dissolved by steam jet cooking. Larger quantities of graft copolymers were also prepared in a 2 gallon reactor from normal, waxy, and high-amylose corn starch,¹¹ and tensile properties of extruded specimens were determined. Trimnell et al.¹² prepared S-g-PMA from granular corn starch, and polymerizations initiated with CAN and the $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ redox system were compared. Fanta and Shogren¹³ prepared S-g-PMA with PMA contents of 12.3, 31.9, 51.7, and 58.3% and then processed these graft copolymers by steam jet cooking at 140°C. Despite the high temperature and intense mechanical shear in the steam jet-cooking process, at most only 13% of the polymer was dissolved, and this soluble fraction was comprised largely of starch. Although tensile strengths were not greatly affected by steam jet cooking, jet-cooked samples showed significant increases in both % elongation and tear resistance. Liu et al.¹⁴ prepared S-g-PMA from potato starch gelatinized at 90°C, and Rahman et al.¹⁵ grafted methyl acrylate onto sago starch gelatinized at 80°C. Mr et al.¹⁶ also prepared S-g-PMA from sago starch and examined the kinetics and mechanism of the grafting reaction.

End-use applications for S-g-PMA, other than those related to extruded plastics, have also been investigated. Latex-like dispersions were prepared from cationic S-g-PMA copolymers

by sonication, and the ability of these polymer dispersions to stabilize soil to water erosion was studied.¹⁷ Extrusion-blown films could also be prepared if the graft copolymers were plasticized with urea and water.^{18,19} These films exhibited the interesting property of shrinking in size when placed in an atmosphere of high humidity.

Although graft polymerization onto starch has been carried out under a variety of different reaction conditions, grafting of methyl acrylate onto the particulate spherulites that form from amylose–fatty acid inclusion complexes has not been reported. Amylose inclusion complexes obtained from fatty acids such as oleic acid form insoluble, micron- and submicron-sized spherulites when hot, jet-cooked dispersions are rapidly cooled.²⁰ Because these spherulites are smaller than starch granules, we were interested in determining whether graft polymerization of PMA onto these insoluble spherulites would take place in a manner similar to the graft polymerizations previously observed with granular starch, and if so, how the presence of these small PMA-grafted spherulites would influence the tensile properties of extruded ribbons prepared from these graft copolymers. Graft polymerization of PMA onto these spherulites should increase their compatibility with the PMA matrix, and the small size of these PMA-grafted particles should enhance their ability to function as reinforcing agents in extruded plastics.

In this report, we will describe the graft polymerization of PMA onto spherulite-containing mixtures prepared by steam jet cooking high-amylose corn starch with oleic acid to form the amylose–oleic acid inclusion complex and then rapidly cooling the resulting dispersions. The properties of extruded ribbons prepared from these graft copolymers will then be compared with those of extrudates obtained under similar conditions from (1) S-g-PMA prepared from granular, unprocessed high-amylose corn starch and (2) S-g-PMA prepared from the amylose–oleic acid spherulites after extraction of soluble amylopectin with water. This information will allow us to better understand the effects of starch particle size and morphology on the tensile properties of these extruded graft copolymers.

EXPERIMENTAL

Materials

High-amylose corn starch (AmyloGel 03003) containing 70% apparent amylose was a product of Cargill, Minneapolis, MN. Percent moisture in starch samples was calculated from weight loss after drying at 100°C under vacuum, and all starch weights are given on a dry weight basis. Oleic acid (NF/FCC) was purchased from Fisher Scientific, Pittsburgh, PA. Methyl acrylate, containing 15 ppm MEHQ was purchased from Scientific Polymer Products, Ontario, NY. Inhibitor was removed by passing the methyl acrylate through a DHR-4 column (Scientific Polymer Products). CAN, Certified A.C.S., was purchased from Fisher Scientific.

Preparation of Amylose–Oleic Acid Spherulites by Steam Jet Cooking

Oleic acid (6.14 g) was blended with 175.0 g of dry, high-amylose corn starch to give a mixture containing 5% oleic acid, based on the apparent amylose content of 70%. The mixture

was then dispersed in 1750 mL of water, and the resulting dispersion was passed through a Penick & Ford (Penford Corp., Englewood, CO) laboratory model steam jet cooker operating under excess steam conditions.²¹ Temperature in the hydroheater was 140°C, the steam back pressure was 380 kPa (40 psig), and the steam line pressure from the boiler was 550 kPa (65 psig). Pumping rate through the jet cooker was 1 L/min. The hot, jet-cooked starch dispersion was collected in a Dewar flask that was previously heated with 100°C water from the jet cooker, and the jet cooker was flushed with excess water to maximize the amount of starch–oleic acid collected. The hot dispersion was then transferred to a 4-L beaker and cooled in an ice water bath to 25°C. Percent solids in these cooled, spherulite-containing dispersions were determined by freeze-drying weighed amounts of dispersion, and varied from 7 to 8%. These dispersions were then diluted to a solid content of 5% for graft polymerization.

Water-insoluble spherulites were separated from water-soluble amylopectin by centrifuging the cooled, jet-cooked dispersions at 3000 rpm (2000 × *g*) for 45 min (Sorvall Legend centrifuge equipped with Fiberlite F14-6X250 rotor, Thermo Fisher Scientific, Hanover Park, IL). The spherulites were then washed thrice by dispersing in fresh water followed by centrifugation. The water-washed spherulites were then dispersed in water at 5% solids for graft polymerization. The yield of spherulites was 67–68%, based on the starting weight of 175 g of high-amylose starch.

Graft Polymerization

Graft polymerization of methyl acrylate onto granular, high-amylose corn starch was carried out by dispersing 150 g of starch in 3 L of nitrogen-sparged water in a 5-L, three-necked round-bottomed flask equipped with mechanical stirrer. Methyl acrylate (225 g) was then added, and the mixture was stirred at room temperature for 10 min. A solution of 5.076 g of CAN in 45 mL of 1*N* nitric acid was then added. The mixture was stirred for 30 min, and a second solution of 5.076 g of CAN in 45 mL of 1*N* nitric acid was added. The total amount of CAN added was equivalent to 1 mol of Ce⁺⁴ per 50 glucopyranose units of starch. The mixture was then allowed to stir for an additional 1.5 h. The solution of CAN was added at 25°C, and the exotherm was allowed to peak to 35°C during the polymerization without external cooling. After the reaction was complete, 1*N* sodium hydroxide solution was added to adjust the pH to 6.5, and 1 L of ethanol was added to coagulate and precipitate the polymer. The aqueous ethanol supernatant was decanted from the settled graft copolymer, and fresh ethanol was then added. The graft copolymer was isolated by vacuum-filtration through Whatman 54 filter paper, and the filter cake was allowed to air-dry overnight at room temperature.

Jet-cooked dispersions of amylose–oleic acid spherulites (in both presence and absence of water-soluble amylopectin) were diluted with water to give 3 L of dispersion with a solid concentration of 5% by weight. Graft polymerizations were then carried out under the same conditions used for granular, high-amylose starch.

Acetone Extraction of PMA Homopolymer

A 10.0 g sample of air-dried graft copolymer of known moisture content was weighed into a 500-mL beaker, and 4 mL of water

was blended into the sample. Acetone (400 mL) was added, and the dispersion was stirred at room temperature for 24 h, and the insoluble solid was separated by centrifugation for 1 h at 3000 rpm (RCF: 1800). The clear acetone supernatant was decanted, and the settled solid was extracted two additional times with acetone in a similar manner. The acetone-extracted polymer was dispersed in 50 mL of ethanol, and the graft copolymer was isolated by vacuum-filtration through an accurately weighed, medium porosity sintered glass filter funnel. The funnel containing the acetone-extracted solid was then dried in a vacuum oven at 60°C, and the weight of dry, extracted S-g-PMA was determined. To determine the weight of acetone-extracted PMA homopolymer, the acetone extracts were concentrated on a rotary evaporator and then dried in a vacuum oven at 60°C.

Separation of Starch from S-g-PMA by Acid Hydrolysis

A 4.00 g sample of acetone-extracted, oven-dried graft copolymer was placed in a round-bottomed flask, 200 mL of 0.5*N* HCl was added, and the mixture was heated under reflux for 2 h. The water-insoluble grafted PMA, after removal of starch by acid hydrolysis, was isolated by vacuum-filtration of the cooled dispersion through a dried, preweighed circle of Whatman 54 filter paper. The solid was washed with deionized water, and the filter paper containing the isolated PMA was dried to a constant weight in a vacuum oven at 60°C. The weight of PMA was then determined by subtracting the weight of the filter paper from the total dry weight.

Extrusion Processing of S-g-PMA

Graft copolymers were reduced in particle size using a Thomas-Wiley mill (Thomas Scientific, Swedesboro, NJ) equipped with a 6-mm screen. Milled samples were stored at 23°C and 50% relative humidity for a minimum of 3 days before extrusion. The conditioned material was starvation-fed through a 19-mm-diameter single-screw extruder driven by an Intelli-Torque Plasti-Corder Torque Rheometer (CW Brabender, South Hackensack, NJ) at a screw speed of 25 rpm. The temperature profile was 80/130/140/145°C, and a 3 : 1 compression screw and a 5.5-mm rod die were used. The extrudate was pelletized with a Killion Laboratory pelletizer and stored at 23°C and 50% relative humidity for 24 h before the second extrusion. Pellets were then processed into ribbon using the same extruder and screw with a 1 × 0.06 in. ribbon die (CW Brabender). The temperature profile during ribbon extrusion was 80/130/140/145°C at a screw speed of 25 rpm.

Tensile Testing of Extruded S-g-PMA

Tensile specimens 3.18 mm wide were cut from extruded ribbons immediately after extrusion and were allowed to equilibrate for 3 days at 23°C and 50% relative humidity before testing. Tensile specimens were tested (five replications per sample) in accordance with ASTM D 638 Type V on an Instron Universal Testing Machine, Model 4201 (Instron, Canton, MA) at a crosshead speed of 10 mm/min. Gauge length was 7.62 mm, and elongation was measured as displacement of the line-contact grips during tensile testing. Sample thickness was measured with a TMI model 49–63 Precision Micrometer (Testing Machines, Amityville, NY).

Table I. Analysis of Graft Polymerization Products

Polysaccharide	PMA homopolymer removed (wt %) ^a	Grafted PMA (wt %) ^b	% Conversion of MA to PMA ^c
Granular starch	12.6 (2.2)	47.0 (1.5)	89.4 (0.7)
Jet-cooked starch-oleic acid	14.9 (2.1)	46.5 (1.8)	90.8 (1.6)
Amylose-oleic acid spherulites (washed)	10.9 (1.8)	49.9 (1.6)	92.3 (1.4)

^aPercentage of product extracted with acetone, mean (SD) of three experiments.

^bPercentage in acetone-extracted product, mean (SD) of three experiments.

^cHomopolymer + graft, mean (SD) of three experiments.

Moisture Analysis

Samples of S-g-PMA were analyzed for percent moisture by heating 1 g of sample for 20 min at 105°C using an Ohaus MB45 moisture meter (Ohaus, Pine Brook, NJ).

Disintegration of Extruded Ribbon into Particles by Stirring in Acetone

Samples of extruded ribbon were cut into 1-mm squares, placed in 100 mL of acetone, slowly stirred with a magnetic stir bar overnight at room temperature, and then allowed to stand overnight at room temperature. The acetone supernatant was decanted and the extraction procedure was repeated a second time. The settled solid was suspended in 25 mL of fresh acetone, and 100 μ L of the dispersion was added to ethanol for critical point drying and scanning electron microscopy (SEM).

Critical Point Drying and SEM

Samples in ethanol were dried onto aluminum SEM stubs in a Tousimis Samdri-PVT-3D critical point drier (Tousimis Research Corp., Rockville, MD), coated with Au-Pd, and examined with a JSM-6010LA SEM (JEOL USA, Peabody, MD).

RESULTS AND DISCUSSION

Table I shows the results of replicate CAN-initiated graft polymerizations of methyl acrylate that were carried out under identical conditions with (1) water dispersions of granular uncooked high-amylose corn starch; (2) aqueous dispersions of high-amylose corn starch that were steam jet-cooked with oleic acid and then rapidly cooled to precipitate the water-insoluble, micrometer-sized spherulites formed from the amylose-oleic acid complex; and (3) aqueous dispersions of amylose-oleic acid spherulites, prepared as in (2), but water-washed to remove soluble amylopectin. Conversion of high-amylose corn starch to water-insoluble spherulites was 68% based on the starting weight of starch, the remainder being uncomplexed amylopectin. An SEM image showing the micron and aggregated submicron structure of these spherulites is shown in Figure 1.

The water-insoluble products formed in these graft polymerizations were isolated by filtration, and the percent ungrafted PMA homopolymer was then determined by extracting the products with acetone, which is a good solvent for PMA. The weight % grafted PMA in the acetone-insoluble graft copolymers was calculated from the loss in weight after removal of the starch moiety by acid hydrolysis, and the total conversion of methyl acrylate to grafted PMA plus PMA homopolymer was then determined. Table I shows that the products formed in these

three different graft polymerizations contained 10.9–14.9% ungrafted homopolymer, the graft copolymers after acetone extraction contained 46.5–49.9% grafted PMA, and the total conversion of methyl acrylate to PMA was 89.4–92.3%. These graft polymerizations therefore take place in a similar manner despite the differences in composition between the three starch substrates, and graft polymerization is apparently not inhibited by the oleic acid complexed within the amylose helix.

The S-g-PMA products described in Table I were extrusion-processed to yield continuous plastic ribbons, and the tensile properties of the extruded ribbons were determined. PMA homopolymer was not extracted before extrusion, because this step would not be practical in a commercial process. The tensile properties of these extruded ribbons are shown in Table II. Although the tensile strengths and values for Young's modulus were similar for the three different graft copolymers, the values for % elongation and tensile energy absorbed were considerably higher for the graft copolymers prepared from the starch-oleic acid spherulites. Also, removal of residual amylopectin from the starch-oleic acid spherulites before graft polymerization did not greatly affect the tensile properties of the extruded ribbons.

These tensile properties are consistent with the formation of these extrudates by the fusion of rigid particles of S-g-PMA at the high temperature and pressure encountered in the extruder die. As the starch portion of these graft copolymers does not melt, the granules of high-amylose corn starch and the micrometer-size spherulites formed from the amylose-oleic acid

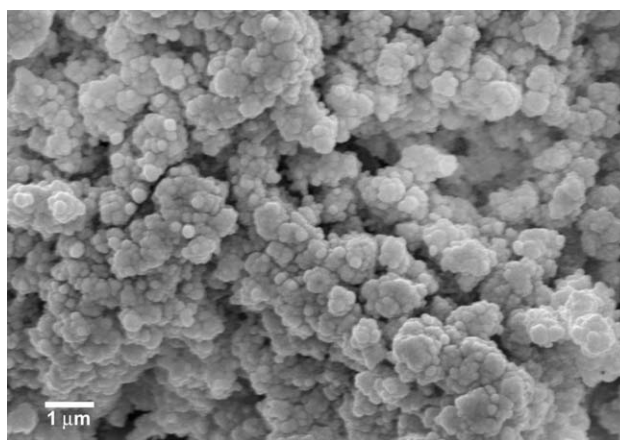


Figure 1. Scanning electron micrograph of spherulites used for graft polymerization.

Table II. Tensile Properties of Extruded Ribbons^a

Polysaccharide	Young's modulus (MPa)	Tensile energy absorbed (N/mm)	% Elongation	Tensile strength (MPa)
Granular starch	34.1 (2.2)	42.3 (5.4)	218.1 (7.3)	16.4 (1.5)
Jet-cooked starch-oleic acid	28.7 (2.9)	94.8 (26.8)	448.5 (98.4)	17.4 (1.7)
Amylose-oleic acid spherulites (washed)	27.5 (3.4)	109.7 (16.2)	532.4 (58.6)	17.3 (1.1)

^aMean (SD) of three experiments.

inclusion complex remain largely intact after graft polymerization and extrusion. Only minor amounts of ungrafted PMA are formed, and this homopolymer, together with the PMA grafted onto the particle surfaces, forms the continuous thermoplastic matrix that binds the individual particles of S-g-PMA together. This fact is substantiated by the behavior of our extruded ribbons when they are placed in acetone, which is a good solvent for PMA homopolymer. Within a short period of time at room temperature, the PMA homopolymer dissolves, causing the ribbons to disintegrate into the individual particles that were fused together during the extrusion process. An SEM image of the particulate material obtained from an extruded ribbon prepared from PMA-grafted granular high-amylose corn starch (Figure 2A) shows that most of the starch granules have retained their original structure, even after graft polymerization and extrusion processing. SEM images of the particulate materials obtained from extruded ribbons prepared from amylose-oleic acid spherulites, in both the presence and absence of uncomplexed amylopectin [Figure 2(B,C), respectively], show that the spherulites have also retained most of their original structure after PMA grafting and extrusion; and some of the micrometer-sized aggregates may have separated into smaller particles during processing. Comparison of the X-ray scattering patterns of the water-washed, ungrafted spherulites (Figure 3A), the same spherulites after PMA grafting (Figure 3B), and the PMA-grafted particles isolated from the extruded ribbon by disintegration in acetone (Figure 3C) shows that the 6₁V scattering pattern, indicative of the complexed amylose helix, is retained after graft polymerization and extrusion. The broader reflections observed in Figure 3(B,C) may be due to a reduction in crystallite size owing to graft polymerization and extrusion processing.

Filled polymer systems of this type, where the granular filler comprises more than 60% of the total product, have been referred to in the literature as particulate composite systems.^{22,23} The properties of these composites are influenced by factors such as the ratio of filler to matrix polymer, the size of the filler particles, adhesion between the filler and the thermoplastic matrix, and the porosity of the composite. Even though the PMA-grafted granules of native high-amylose starch can deform somewhat as they fuse together during extrusion, the minor amount of PMA homopolymer formed in these polymerizations is not sufficient to completely fill the voids between the large individual granules of S-g-PMA. These voids produce weak points in the extruded ribbon that reduce the elasticity necessary for high % elongation. The tensile strength remains high, however, because there is strong adhesion between the grafted granules and the PMA matrix, owing to graft polymerization of

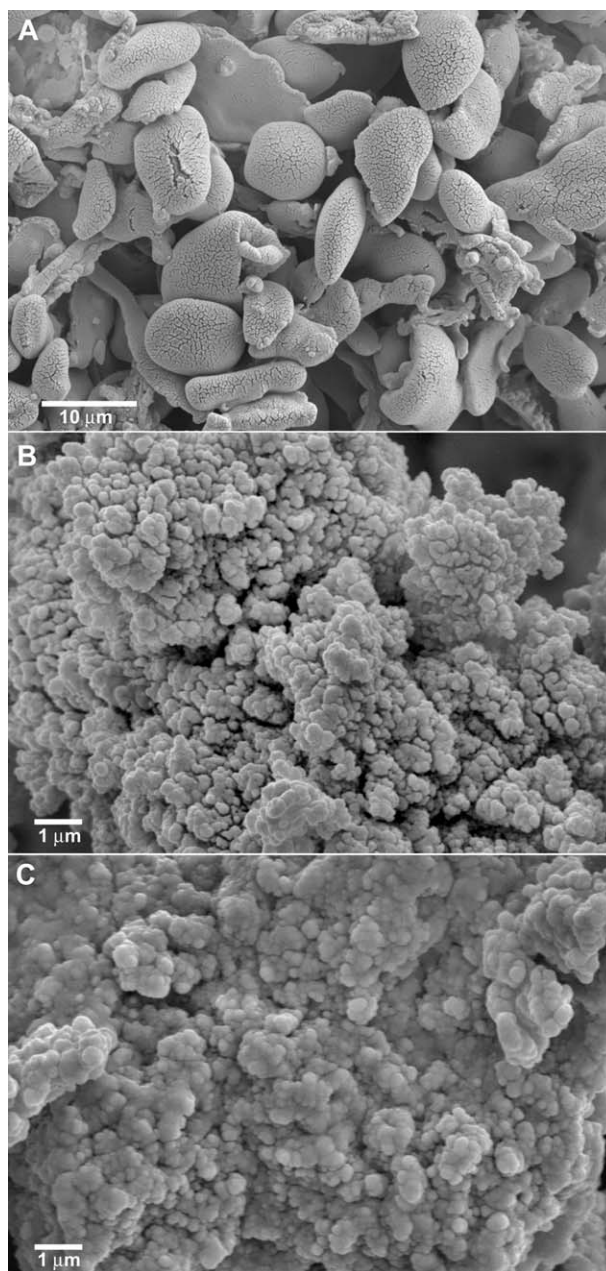


Figure 2. Scanning electron micrographs of particulate materials isolated by disintegration of S-g-PMA ribbons by stirring in acetone. S-g-PMA was prepared from (A) granular, high-amylose corn starch; (B) spherulites containing residual amylopectin; and (C) spherulites washed with water to remove amylopectin.

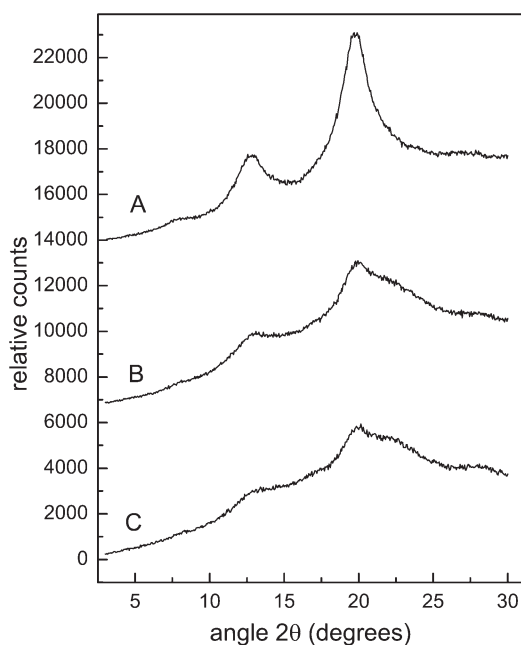


Figure 3. X-ray diffraction patterns of (A) water-washed, ungrafted spherulites, (B) water-washed spherulites after PMA grafting, and (C) PMA-grafted particles isolated from the extruded ribbon by disintegration in acetone.

PMA onto the starch granule surfaces and the fact that the thermoplastic matrix and the surface-grafted polymer are both composed of the same PMA polymer.

The higher % elongation values observed for extruded ribbons prepared from the spherulite-containing dispersions can be explained by considering the compositions of the different graft copolymers. In the graft copolymers prepared from spherulite dispersions that also contain soluble, uncomplexed amylopectin, the insoluble spherulites comprise 68% of the total starch used for graft polymerization, the rest being water-soluble amylopectin. As graft polymerization of PMA onto water-soluble amylopectin also takes place, this nonparticulate amylopectin–PMA graft copolymer can combine with PMA homopolymer to increase the amount of thermoplastic polymer that comprises the matrix that surrounds and binds the PMA-grafted spherulites together. The small size of these spherulites, compared to the relatively large size of the grafted, native high-amylose starch granules, provides more efficient packing of the filler particles with fewer voids, which leads to higher values for % elongation at low concentrations of the PMA-containing matrix. As observed for the grafted granules of native high-amylose corn starch, tensile strengths are high because of the strong adhesion between the PMA-containing matrix and the PMA grafted onto the spherulite surfaces. Similar high values for tensile strength and % elongation were observed for extruded ribbons prepared from the PMA-grafted spherulites in the absence of water-soluble amylopectin. Because of the small size of these spherulites, low levels of the thermoplastic PMA matrix are apparently sufficient to bind these grafted spherulites together without the formation of voids.

CONCLUSIONS

Mixtures of high-amylose corn starch and oleic acid were processed by steam jet cooking, and the dispersions were rapidly cooled to yield amylose–oleic acid inclusion complexes as sub-micron spherulites and spherulite aggregates. Graft polymerization of PMA onto these spherulites was not inhibited by the complexed oleic acid within the amylose helix, and the conversion of methyl acrylate to grafted PMA was similar to that obtained with granular, high-amylose corn starch. Although values for tensile strength and Young's modulus were similar for the extruded ribbons prepared from these graft copolymers, higher values for % elongation and tensile energy absorbed were obtained for the graft copolymers prepared from PMA-grafted spherulites. These results are consistent with the formation of continuous extrudates by fusing together the nonmelting particles of S-g-PMA at the high temperatures and pressures encountered during the extrusion process. The small amount of PMA homopolymer formed during these graft polymerizations, together with the PMA grafted onto the starch particle surfaces, forms the continuous matrix that binds these S-g-PMA particles together. When graft copolymers are prepared from native high-amylose corn starch, the amount of homopolymer formed is not sufficient to completely fill the voids between the large granules of PMA-grafted starch. These voids produce weak points in the extruded ribbon that reduce the % elongation. The tensile strength, however, remains high owing to the strong adhesion between the PMA-grafted granules and the PMA thermoplastic matrix. As the PMA-grafted spherulites are considerably smaller in size, they pack together more efficiently with fewer voids. Therefore, low levels of PMA homopolymer are sufficient to fill the voids and give the good interparticle adhesion necessary to obtain the higher % elongation values needed for many practical applications.

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