Graft Copolymerization of Starch with Methyl Acrylate: An Examination of Reaction Variables

DAMODAR R. PATIL[1,*] and GEORGE F. FANTA[2]

[1]Agricultural Utilization Research Institute, Crookston, Minnesota 56716; and [2]Plant Polymer Research, National Center for Agricultural Utilization Research, Agricultural Research Service, U.S. Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604

SYNOPSIS

Starch-g-poly(methyl acrylate) (S-g-PMA) copolymers containing 55–60% PMA were prepared from cornstarch, high amylose cornstarch, and waxy cornstarch with ceric ammonium nitrate initiation. Graft copolymers were characterized with respect to % PMA homopolymer, % conversion of monomer to polymer, grafted PMA content, grafting frequency, and the molecular weight and molecular weight distributions of PMA grafts. Variables investigated in the graft copolymerization reaction were nitric acid concentration, ceric ion-to-starch ratio, reaction time, gelatinization of the starch, and reactant concentration in water. At high reactant concentrations, high conversions of methyl acrylate to grafted PMA could be obtained in less than 0.5 h at 25°C. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Starch, a high polymer composed of repeating 1,4-α-D-glucopyranosyl units (anhydroglucose units [AGU]) is generally a mixture of linear and branched components. The linear component, amylose, has a molecular weight of several hundred thousand, whereas the molecular weight of the branched amylopectin is on the order of several million. Although normal cornstarch contains about 20–25% amylose, cornstarch varieties are available commercially that range in amylose content from 0% (waxy cornstarch) to about 70% (high-amylose cornstarch).

Starch occurs in living plants in the form of discrete granules ranging from about 5–40 microns in diameter, depending on the plant source. When starch is slurried in water at room temperature, granule swelling and solubility are minimal; however, when a water slurry of starch is heated, hydrogen bonds between starch molecules are broken and granules swell and lose their birefringence. Starch in this form is referred to as being gelatinized. Although corn starch typically loses its birefringence at 62–72°C,[1] granules remain largely undissolved. Even at 95°C, only about 25% of the starch actually dissolves in water, the remainder being present as highly swollen granules and granule fragments. Starch solutions can be readily prepared by passing starch–water slurries through a steam jet cooker. Jet-cooking[2] has been used commercially for decades to prepare starch solutions. The method involves pumping an aqueous starch slurry through an orifice where it contacts a jet of high-pressure steam. In this study, graft copolymers were prepared from unswollen, gelatinized, and jet-cooked cornstarch varieties containing a range of amylose contents.

Use of annually renewable, agriculturally derived products such as starch as extenders and replacements for synthetic, petroleum-based polymers is currently an active area of research. Use of polysaccharides in plastics not only reduces our dependence on petrochemical-derived monomers, but the polysaccharide portion will also biodegrade, causing the finished plastic article to lose its integrity and be reduced to particles small enough to be of minimal damage to the environment.

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* To whom correspondence should be addressed at 1815 N. University St., Peoria, IL 61604.

A number of researchers have studied the incorporation of starch into plastics. For example, Griffin[3] successfully incorporated starch into polyethylene film, and films of this type are now being marketed. Otey and co-workers[4-7] prepared composite films from starch and poly(ethylene-co-acrylic acid) and considered their use as biodegradable agricultural mulches. Mulches of this type are used to control weeds, to conserve soil moisture, to reduce heat loss during early cropping, and to reduce nutrient leaching for high-value crops. Vegetable growers would profit from a plastic mulch that would break up in the soil between growing seasons and thus eliminate the expenses associated with mulch removal. Otey et al.[8] also studied starch–poly(vinyl alcohol) films coated with a thin layer of water-resistant polymer.

Graft copolymerization of thermoplastic polymers onto starch provides another method for preparing starch–polymer composites. An important advantage of graft copolymerization is the fact that starch and synthetic polymer are held together by chemical bonding rather than existing merely as a physical mixture. The two dissimilar polymers therefore tend to be more intimately associated, and separation of the two polymer phases is less likely to occur.

We have made an extensive study of the synthesis and properties of starch graft copolymers[9]; and in the course of this research, the properties of starch-g-poly(methyl acrylate) (S-g-PMA) have proven to be especially interesting. Graft polymerization of methyl acrylate onto either granular or gelatinized starch takes place readily in water with ceric ammonium nitrate initiation, and graft copolymers containing about 50–60% PMA can be easily prepared with minimal formation of ungrafted homopolymer. The combined properties of the rigid starch matrix and PMA (T_g 8°C) result in the formation of a tough leathery plastic on extrusion processing.[10] Dennenberg and co-workers[11] showed that the starch portion of these S-g-PMA extrudates is susceptible to fungal attack.

The excellent physical properties of articles fabricated from S-g-PMA have caused us to consider the commercial potential of these materials. Although preparative methods have been described in previous publications, no systematic study of graft polymerization parameters has been made. We have therefore examined some of the more important variables in the graft polymerization reaction and their effects on graft copolymer structure. This study should serve as a first step in the design of a commercially viable process for the preparation of these polymers.

EXPERIMENTAL

Materials

Cornstarch (Buffalo 3401) was obtained from CPC International. Cornstarch with 70% amylose (Amylomaize VII) and waxy cornstarch (Amioca) were purchased from American Maize Products and National Starch and Chemical Corp., respectively. Methyl acrylate (MA) (15–20 ppm MEHQ) was purchased from Hoechst Celanese and was used without further purification. Conversion of this low-inhibitor grade of monomer to grafted polymer was as high as that of distilled methyl acrylate. Ceric ammonium nitrate (ACS) was from Fisher Scientific Co. Polystyrene standards for molecular weight determination were purchased from Polysciences. Deionized water was used for the grafting reactions.

Measurements

Infrared spectra were run on a Mattson Polaris FTIR equipped with a He—Ne laser and DTGS detector.

Molecular weights were determined with a Spectra-physics GPC system, consisting of a model SP-8810 pump and a SP-8780 autosampler in combination with a Waters 410 RI detector. A linear Styrogel column with MW range from 2000 to 4×10^6 was used. The mobile phase was HPLC-grade tetrahydrofuran (THF), and the velocity of the mobile phase was 1 mL/min. Polymer concentration in the sample solution was 0.1%, and solutions were filtered (0.5 μm filter) before injection. Calibration was carried out 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.

Moisture contents in graft copolymers were measured by vacuum drying known amounts of copolymer at 100°C in an Abderhalden drying apparatus over P_2O_5. Moisture content was calculated from weight loss on drying.

Graft Copolymerization

In a typical graft copolymerization reaction, starch (20 g) was stirred in water (400 mL) and sparged with a slow stream of nitrogen for 1 h at 25°C. For reactions with gelatinized starch, starch slurries were nitrogen-sparged for 1 h at either 85 or 95°C. A water solution of starch was prepared by passing a starch–water slurry through a Penick & Ford laboratory

model steam jet-cooker[2] operated with 65 psig line pressure steam. Cooking was carried out at 140°C (40 psig steam) with a pumping rate of about 1.1 L/min. Solutions/dispersions of starch were then cooled to 25°C. Methyl acrylate (30 g) was added, followed after 5 min by a solution of ceric ammonium nitrate in dilute nitric acid. After the mixture had stirred for a specific period of time, the graft copolymer was isolated by filtration, washed with water and methanol, and dried under vacuum at 50°C to a constant weight.

Purification of Graft Copolymer

Ungrafted PMA was extracted by dispersing the graft copolymer in acetone that contained sufficient water to impart 25% moisture to the polymer.[12] This mixture was stirred for 24 h and was then centrifuged to separate insoluble graft copolymer from acetone-soluble homopolymer. Two more extractions with acetone were then carried out. Supernatant and acetone-washed graft copolymer were dried, and the weights of these fractions were used to calculate weight percent homopolymer in the graft copolymer.

Isolation of Grafted PMA by Hydrolysis of Starch

Grafted PMA was separated from starch by heating 4 g of S-g-PMA in 200 mL of 0.5N HCl for 2 h under reflux. Grafted PMA was isolated by filtration, washed with water, and dried under vacuum at 50°C to a constant weight. Infrared spectra, run as KBr pellets, showed no detectable carbohydrate.

The gel content of grafted PMA was determined by stirring 30 mg of PMA for 2 days at room temperature in 20 mL of THF. The gel fraction was separated by centrifugation at 0°C, washed with THF, and dried at 50°C to a constant weight. Insoluble gel amounted to less than 10% of the grafted PMA sample.

Parameters

The meaning of graft polymerization parameters and the methods used to calculate their values are given below:

$$\% \text{ add-on} = \text{wt. of PMA in 100 g of S-}g\text{-PMA}$$

$$\% \text{ Conversion} = \frac{\begin{array}{c}\text{total wt. of PMA produced}\\\text{(i.e., grafted plus ungrafted)}\end{array}}{\text{wt. of monomer used}}$$

$$\% \text{ Homopolymer} = \text{wt. of acetone extractable}$$
$$\text{polymer in 100 g of S-}g\text{-PMA}$$

$$\text{AGU/graft} = M_n \text{ of grafted PMA}$$
$$\times \frac{\text{wt. \% starch in graft copolymer}}{\text{wt. \% PMA in graft copolymer}} \times \frac{1}{162}$$

$$\text{Wt. \% starch + wt. \% PMA} = 100$$

$$162 = \text{MW of the AGU repeating unit}$$

RESULTS AND DISCUSSION

The method used to prepare S-g-PMA was essentially that reported by Mino and Kaizerman in 1958.[13] Starch was slurried in water, the system was sparged with nitrogen to remove dissolved oxygen, and MA was then added followed by ceric ammonium nitrate dissolved in dilute nitric acid. Nitric acid was used, since ceric salts precipitate from water solution unless an acidic pH is maintained during the polymerization. Under these conditions, ceric ion rapidly complexes with starch and then oxidizes the polysaccharide to form free radicals.[9] Polymerization can then take place because MA is sufficiently water-soluble to diffuse rapidly to free radical sites onto and within the starch granule. In most experiments, MA-to-starch ratios of 3 : 2 were used to give graft copolymers containing 55–60% PMA by weight (i.e., 55–60% add-on). Our previous experiences with the extrusion processing of these materials at low moisture contents showed that this level of PMA addition was necessary to get good formation and throughput without the development of excessive torque and die pressure.

Values for % add-on were calculated from the weight gain of starch due to graft polymerization. Calculations were made before removal of ungrafted PMA by acetone extraction, since homopolymer would, of course, not be separated from graft copolymer in any commercial process. After extraction of homopolymer, selected graft copolymers were subjected to further treatment to more fully characterize the products. Starch was removed by acid hydrolysis, % add-on was calculated from the loss in weight of S-g-PMA, and molecular weights of PMA grafts were determined by gel permeation chromatography. Grafting frequency (average number of AGU separating grafted PMA branches) was then calculated from experimentally determined values for % add-on and M_n.

Table I Effect of Nitric Acid Concentration on Graft Polymerization[a]

HNO₃ (Mol/L × 10²)	Conversion (%)	% Add-On (Wt. Gain)	Homo-polymer (%)	Acetone-Extracted Starch-g-PMA % Add-On (Wt. Loss)	Grafted PMA $M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	AGU/ Graft
3.0	93	58	7.5	—	—	—	—	—
1.5	93	58	7.8	54.4	7.89	3.67	2.15	1900
0.75	92	58	7.7	—	—	—	—	—
0.15	92	58	7.0	—	—	—	—	—

[a] Reaction carried out with 20 g normal cornstarch (granular) and 30 g MA in 400 mL water. Starch: 0.309 mol AGU/L; MA: 0.87 mol/L; Ce⁺⁴: 3.08 × 10⁻³ mol/L (100 AGU per Ce⁺⁴); time: 3 h; temp: 25°C.

There is ample evidence that PMA formed in these polymerizations is indeed grafted to the starch backbone, as opposed to being simply formed within the starch matrix without chemical attachment. Physical mixtures prepared from starch and PMA can be readily separated by acetone extraction. Moreover, under our reaction conditions, conversion of MA to polymer by ceric ammonium nitrate initiation is less than 5% in the absence of polysaccharide.

A number of reaction variables influence both the conversion of MA to grafted polymer and the structure of S-g-PMA. As shown in Table I, however, there was no significant effect on either % add-on, homopolymer content, or % conversion when the concentration of nitric acid was varied from 0.030 to 0.0015 M. A nitric acid concentration of 0.015 M was thus used in most polymerizations. PMA grafts of high molecular weight are formed under these conditions, and grafted branches are separated by almost 2000 AGU.

The amount of ceric ammonium nitrate used in these polymerizations is examined in Table II, and

it is apparent from these results that once a certain ceric ion concentration is reached higher levels of initiator do not increase either the conversion to grafted PMA or the number of grafted branches. Values for % conversion and % add-on were about as high with 1 mol of ceric ion per 200 AGU (1.54 × 10⁻³ mol/L) as they were with twice this concentration of initiator; and the number of AGU separating grafted branches was actually larger at the higher initiator concentration. When the ceric ammonium nitrate concentration was lowered to 0.77 × 10⁻³ mol/L (1 mol per 400 AGU), conversion and % add-on were lowered significantly.

The influence of reaction time on graft polymerization is shown at two different initiator levels in Table III. Although % add-on and % conversion decreased with shorter reaction times, the molecular weight of grafted PMA actually showed a small increase when the reaction time was reduced from 3 to 1 h. Apparently, depletion of monomer in the latter stages of the polymerization results in PMA grafts of lower molecular weight, thus lowering the overall molecular weight average. As expected, re-

Table II Effect of Ceric Ion Concentration on Graft Polymerization[a]

Ce⁺⁴ (mol/L × 10²) (AGU/Ce⁺⁴)	Conversion (%)	% Add-On (Wt. Gain)	Homo-polymer, (%)	Acetone-Extracted Starch-g-PMA % Add-On (Wt. Loss)	Grafted PMA $M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	AGU/ Graft
3.08 (100)	93	58	7.8	54.4	7.89	3.67	2.15	1900
1.54 (200)	91	58	8.4	53.8	6.05	2.77	2.18	1470
0.77 (400)	31	32	7.5	—	—	—	—	—

[a] Reaction carried out with 20 g normal cornstarch (granular) and 30 g MA in 400 mL water. Starch: 0.309 mol AGU/L; MA: 0.87 mol/L; HNO₃: 1.5 × 10⁻² mol/L; time: 3 h; temp: 25°C.

Table III   Effect of Reaction Time on Graft Polymerization[a]

Reaction Time (h)	Conversion (%)	% Add-On (Wt. Gain)	Homo-polymer (%)	Acetone-Extracted Starch-g-PMA				
				% Add-On (Wt. Loss)	Grafted PMA			AGU/ Graft
					$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	
Ce^{+4}: 1.54 $\times$ 10^{-3} mol/L (200 AGU/Ce^{+4}								
3.0	91	58	8.4	53.8	6.05	2.77	2.18	1470
2.0	87	57	8.6	—	—	—	—	—
1.0	79	54	8.4	49.9	7.23	3.71	1.95	2300
0.5	61	48	6.6	—	—	—	—	—
Ce^{+4}: 3.08 $\times$ 10^{-3} mol/L (100 AGU/Ce^{+4})								
3.0	93	58	7.8	54.4	7.89	3.67	2.15	1900
1.0	87	57	8.3	—	—	—	—	—

[a] Reaction carried out with 20 g normal cornstarch (granular) and 30 g MA in 400 mL water. Starch: 0.309 mol AGU/L; MA: 0.87 mol/L; HNO_3: 1.5 $\times$ 10^{-2} mol/L; temp: 25°C.

ducing the reaction time from 3 to 1 h had less effect at the higher initiator level.

With a reaction time of 3 h, slight decreases in % add-on and % conversion were observed when the reaction temperature was increased from 25 to 40°C (Table IV). A variety of factors could be responsible for this temperature effect, e.g., starch hydrolysis in the acidic reaction medium, an increase in termination rate, and an increase in the rate of oxidation of starch by ceric ion at the higher temperature.

Table IV also shows results obtained with starch gelatinized at 85°C and at 95°C prior to graft polymerization. Although gelatinization did not greatly change % add-on and % conversion, higher molecular weight PMA grafts were obtained with gelatinized starch than with granular starch. These results are analogous to those obtained earlier in the graft polymerization of acrylonitrile[14]; however, the magnitude of these differences is not as large with PMA. Interestingly, the graft molecular weight obtained from starch that was dissolved by steam jet-cooking was not greatly different than the graft molecular weight obtained with granular starch.

Graft polymerizations onto high-amylose cornstarch (70% amylose) are shown in Table V. If these results are compared with earlier tables, it appears

Table IV   Effect of Reaction Temperature and Gelatinization Conditions[a]

Temp (°C)	Granule State	Conversion (%)	% Add-On (Wt. Gain)	Homo-polymer (%)	Acetone-Extracted Starch-g-PMA				
					% Add-On (Wt. Loss)	Grafted PMA			AGU/ Graft
						$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	
25	Granular	91	58	8.4	53.8	6.05	2.77	2.18	1470
40	Granular	84	56	9.1	—	—	—	—	—
25	Gelatinized (85°C)	93	58	12.3	53.9	8.89	4.33	2.05	2290
25	Gelatinized (95°C)	96	59	13.9	54.6	9.17	4.52	2.03	2320
25	Jet-cooked	91	56	11.4	47.5	6.47	3.03	2.13	2070

[a] Reaction carried out with 20 g normal cornstarch and 30 g MA in 400 mL water. Starch: 0.309 mol AGU/L; MA: 0.87 mol/L; HNO_3: 1.5 $\times$ 10^{-2} mol/L; Ce^{+4}: 1.54 $\times$ 10^{-3} mol/L (100 AGU per Ce^{+4}); time: 3 h.

Table V Graft Polymerizations onto High-Amylose Cornstarch (HA) and Waxy Cornstarch[a]

Starch	Granule State	Time (h)	Ce^{+4} (mol/L $\times 10^3$) (AGU/Ce^{+4})	MA (mol/L) (g)	Conversion (%)	% Add-On (Wt. Gain)	Homopolymer (%)	% Add-On (Wt. Loss)	Acetone-Extracted Starch-g-PMA			
									Grafted PMA			AGU/ Graft
									$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	
HA	Granular	3	3.08 (100)	0.87 (30)	93	58	6.6	57.8	6.18	2.80	2.20	1260
HA	Granular	1	3.08 (100)	0.87 (30)	95	59	5.0	58.7	6.20	2.84	2.18	1230
HA	Granular	1	1.54 (200)	0.87 (30)	69	51	6.3	50.1	5.48	2.32	2.36	1430
HA	Granular	1	3.08 (100)	0.58 (20)	90	47	4.0	49.0	5.08	2.29	2.21	1470
HA	Granular	1	3.08 (100)	0.38 (13.1)	89	37	2.5	37.8	3.70	1.72	2.15	1750
HA	Gelatinized (85°C)	3	3.08 (100)	0.87 (30)	92	58	7.4	59.5	7.09	3.27	2.16	1370
HA	Gelatinized (95°C)	3	3.08 (100)	0.87 (30)	92	58	6.2	59.4	6.87	3.15	2.18	1330
Waxy	Granular	3	3.08 (100)	0.87 (30)	93	58	15.0	—	—	—	—	—

[a] Reaction carried out with 20 g starch in 400 mL water. Starch: 0.309 mol AGU/L, HNO_3: 1.5 $\times$ 10^{-2} mol/L; temp: 25°C.

that substitution of high amylose cornstarch for normal cornstarch leads to grafts of somewhat lower molecular weight as well as to more frequent grafting. This suggests that amylose might complex more efficiently with ceric ion than with amylopectin; however, further research on this question is needed. With 1 mol of ceric ion per 100 AGU (3.08×10^{-3} mol/L), conversions to grafted PMA were comparable (93–95%) after reaction times of 1 and 3 h; however, with half this amount of initiator, conversion after 1 h was only 69%. Polymerization with reduced amounts of MA showed that lower levels of monomer led to lower graft molecular weights and less frequent grafting, as well as to a reduction in % add-on. As observed with normal cornstarch, gelatinization of high amylose starch led to increases in both graft molecular weight and the number of AGU per graft, although the effect of gelatinization with high amylose starch was not as large. A high conversion of MA to polymer was observed in the single experiment run with waxy cornstarch; however, more acetone-extractable homopolymer was produced than with the normal- or high-amylose cornstarch varieties.

Since the concentrations of starch, MA, and ceric ion could be progressively increased by simply decreasing the amount of water used in the polymerization recipe, we examined the effect of increased reactant concentration on both polymerization rate and graft copolymer structure (Table VI). With 20 g of granular cornstarch, 30 g of methyl acrylate, 1 mol of ceric ion per 100 AGU, and a reaction time of 1 h, conversion of monomer to polymer increased from 87 to 94% when the water volume was reduced from 400 to 200 mL. With only 100 mL of water, 94% conversion was obtained in as little as 0.5 h. Although conversion was also high with 50 mL of

water, the reaction mass coagulated with this low volume of water and was difficult to stir in conventional glassware.

CONCLUSIONS

We have studied some of the more important variables in the ceric-initiated graft polymerization of MA onto starch and have determined their effects on % conversion of MA to polymer, % add-on, graft molecular weight, and grafting frequency. Graft copolymers containing 55–60% PMA can be easily obtained from normal cornstarch, high amylose cornstarch, and waxy cornstarch, with 90–95% conversion of monomer to polymer. Only minor amounts of ungrafted PMA are formed. Removal of inhibitor from MA is not required, provided that a low-inhibitor grade of monomer is used. Typically, about 1 mol of ceric ion per 100–200 AGU is required to give high conversions to grafted polymer. The concentration of nitric acid in the reaction mixture does not affect graft copolymer structure. Although graft molecular weights are high (several hundred thousand), PMA grafts onto high amylose cornstarch tend to have somewhat lower molecular weights than those obtained with a normal cornstarch variety containing 20–25% amylose. As observed previously with acrylonitrile, use of gelatinized starch in graft polymerizations produces higher molecular weight grafts and less frequent grafting than does granular starch; however, the changes in polymer structure due to gelatinization are not as large with methyl acrylate. PMA grafts have molecular weight distributions (M_w/M_n) of approximately 2. By reducing the amount of water in the polymerization recipe, and thus increasing the concentrations of reactants,

Table VI Effect of Reactant Concentration and Reaction Time[a]

| | | | | | Acetone-Extracted Starch-g-PMA | | | | |
| | | | | | | Grafted PMA | | | |
Water (mL)	Time (h)	Conversion (%)	% Add-On (Wt. Gain)	Homo-polymer (%)	% Add-On (Wt. Loss)	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	M_w/M_n	AGU/ Graft
400	1.0	87	57	8.3	—	—	—	—	—
200	1.0	94	59	6.9	55.3	7.48	3.53	2.12	1760
100	1.0	96	59	6.1	58.1	6.06	2.81	2.16	1250
50	1.0	96	59	7.6	—	—	—	—	—
100	0.5	94	58	5.7	56.9	6.62	3.04	2.18	1420

[a] Reaction carried out with 20 g normal cornstarch (granular) and 30 g MA. Ce^{+4}: 100 AGU per Ce^{+4}; $HNO_3 = 1.5 \times 10^{-2}$ mol/L with 400 mL water; temp: 25°C.

the time required to obtain over 90% conversion of MA to grafted polymer can be reduced to as little as 0.5 h.

The results of this research will enable us to design a practical process for the preparation of kilogram quantities of S-*g*-PMA, so that variables involved in extrusion processing and injection molding of these polymers into continuous plastics can be studied.

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