NOTE

Graft Polymerization of Methyl Acrylate–Vinyl Acetate Mixtures onto Starch

INTRODUCTION

Use of natural polymers such as starch as extenders and replacements for totally synthetic polymers reduces our dependence on petrochemically derived monomers; moreover, attack by microorganisms on the starch moiety can lead to polymer degradation. The ability of a polymer to degrade in the environment is currently a desirable property, when polymers are to be processed into plastics for single-use applications.

In preparing starch–synthetic polymer composites, graft polymerization is in many respects preferred over physical blending, since chemical bonding provides the most intimate association possible between starch and synthetic polymer. Graft polymerizations are, moreover, easily carried out in aqueous media.

In the course of our research on starch graft copolymers, the properties and possible commercial applications of starch-*g*-poly(methyl acrylate) have attracted our attention because of the tough, flexible plastics obtained from these materials.[1,2] Although Dennenberg et al.[3] confirmed that the starch portion of these graft copolymers is indeed susceptible to fungal attack, poly(methyl acrylate) is resistant to biodegradation. Enzymes produced by microorganisms can theoretically hydrolyze ester linkages to yield poly(acrylic acid); however, the biodegradation of poly(acrylic acid) is molecular weight-dependent,[4] and high molecular weight polymer apparently remains resistant to microbial attack despite its water solubility.

To enhance biodegradability of the poly(methyl acrylate) portion of our graft copolymers, we are exploring the introduction of poly(vinyl acetate) segments into polymer grafts by copolymerizing vinyl acetate with methyl acrylate during the grafting reaction. We expect that esterases produced by microorganisms will convert poly(vinyl acetate) to poly(vinyl alcohol). Poly(vinyl alcohol) can then undergo further microbial attack to cleave the polymer chain,[4,5] thus yielding fragments of poly(methyl acrylate) that might be susceptible to further degradation in the environment because of their low molecular weight. Bailey and Kuruganti[6,7] enhanced the biodegradation of synthetic polymers by a similar approach, in which degradable polyester segments were introduced into polymer chains by free-radical ring-opening polymerization of cyclic ketene acetal comonomers.

In this report, we show that starch-*g*-poly(methyl acrylate-*co*-vinyl acetate) polymers, having a range of poly(vinyl acetate) contents, can be prepared by a ceric-initiated grafting procedure identical to that used to prepare starch-*g*-poly(methyl acrylate).[1] Graft copolymers have been completely characterized, and a rapid analytical method using Fourier transform infrared spectroscopy (FTIR) has been developed to determine the poly(vinyl acetate) content of polymer grafts as well as ungrafted homopolymer. Selected polymers have been extrusion-processed to yield continuous plastic ribbons, and a preliminary examination of physical properties has been carried out.

EXPERIMENTAL

Materials

The starch used was Buffalo 3401 cornstarch from CPC International. Moisture content was 10–11%. Weights have been corrected for moisture and are given on a dry weight basis. Methyl acrylate (from Polysciences) and vinyl acetate (from Aldrich Chemical Co.) were distilled at atmospheric pressure through a 45 cm Vigreaux column. Ceric ammonium nitrate was certified ACS grade from Fisher Scientific and was used as received.

Graft Polymerization

A stirred suspension of 20.0 g of starch in 400 mL of water was sparged with a slow stream of nitrogen for 1 h at 25°C. Monomer (30.0 g) was added, followed after 5 min by a solution of 0.676 g of ceric ammonium nitrate in 6 mL of 0.1*N* nitric acid. The mixture was then stirred for 3 h at 25°C. The graft copolymer was separated by filtration, resuspended in water, and neutralized with 0.1*N* sodium hydroxide to pH 7. Graft copolymer was again separated by filtration, washed with methanol, and allowed to air-dry to a moisture content of about 5%. The methanol wash solution was evaporated to dryness and the weight of dissolved solids determined. These methanol-soluble fractions were not examined further.

Homopolymer was extracted from the air-dried polymer

Journal of Applied Polymer Science, Vol. 49, 1679–1682 (1993)

CCC 0021-8995/93/091679-04

by shaking 5 g of polymer with 100 mL of acetone containing 2% water to facilitate solvent penetration into the starch matrix.[8] The solid was separated by centrifugation, washed with pure acetone, and vacuum-dried. Supernatants were evaporated to dryness and the weight of soluble polymer determined.

Isolation of Grafted Polymer by Starch Hydrolysis

One gram of acetone-extracted, vacuum-dried graft copolymer was heated under reflux for 2 h with 100 mL of 0.5*N* HCl. The polymer was separated by filtration and washed first with 0.5% sodium bicarbonate and then with water. The isolated polymer was dried under vacuum and weighed. Infrared analysis showed no detectable polysaccharide. Weight percent grafted polymer in the starting graft copolymer was calculated from weight loss on acid hydrolysis. With this low HCl concentration and short reflux time, infrared spectra showed no evidence of poly(vinyl acetate) hydrolysis to poly(vinyl alcohol). This observation is in agreement with results published for poly(vinyl acetate) grafted to poly(ethylene terephthalate) fibers.[9]

Molecular Weight of Polymer Grafts

Grafted polymer isolated after removal of starch by acid hydrolysis (30 mg) was stirred with 20 mL of tetrahydrofuran (THF) for 3 days at room temperature. Insoluble polymer was separated by centrifugation, dried, and weighed. The molecular weight of polymer in THF solution was determined by GPC as described earlier.[2] The linear Styrogel column with a MW range of 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 86 (molecular weights of methyl acrylate and vinyl acetate) by 104 (molecular weight of styrene).

Determination of Copolymerized Vinyl Acetate

Infrared spectra were recorded on a Mattson Polaris FTIR spectrometer equipped with a He–Ne laser and a DTGS detector. Mattson ICON analytical software was used for spectral manipulation and subtraction. Polymers were not fractionated by THF extraction prior to FTIR analyses.

Polymer samples were formed into KBr pellets for analysis. Approximately 10 mg of polymer and 350 mg of KBr were covered with 2 mL of toluene in a 4 in. agate mortar. The mortar was covered with a watchglass to retard evaporation of toluene and was placed in a 75°C oven for 1 h. The hot mixture was then ground vigorously with an agate pestle until the KBr appeared visually dry. Mortar and pestle were then allowed to cool in a desiccator, and the sample was once again ground to yield a smooth powder. Sufficient powder to give 1.0 mg of polymer was then combined with enough KBr to give a total mass of 301.0

Table I Preparation and Characterization of Starch Graft Copolymers[a]

			Acetone-insoluble Fraction									
			Acetone-soluble Fraction				Grafted Polymer					
VAc : MA[b]	Polymer Yield (g)	Methanol-soluble Fraction (g)	% of Total Polymer	PVAc[b] Content (%)	% of Total Polymer	Grafted Polymer Content (%)	PVAc[b] Content (%)	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	Insoluble in THF (%)
0 : 100	48.8	—	7.4	0	92.6	55.1	0	4.71	1.72	2.74	2
5 : 95	48.5	0.5	14.1	4	85.9	50.9	3	5.35	2.01	2.66	8
10 : 90	47.9	0.4	23.5	7	76.5	44.6	7	6.20	2.40	2.58	22
15 : 85	46.0	0.7	19.6	9	80.4	46.9	10	5.39	2.06	2.62	20
20 : 80	45.0	0.7	26.8	14	73.2	41.7	12	5.90	2.30	2.57	35
30 : 70	43.2	1.1	26.9	20	73.1	39.9	20	5.28	2.07	2.55	35
50 : 50	39.8	2.8	28.5	25	71.5	33.3	35	5.09	1.89	2.69	41
100 : 0	22.8	8.4	1.9	100	98.1	15.3	100	2.89	1.14	2.54	46

[a] Polymerizations were carried out with 20.0 g of starch and 30.0 g of total monomer in 400 mL of water. Products were washed with methanol, air-dried, and extracted with acetone.
[b] Abbreviations: VAc = vinyl acetate; MA = methyl acrylate: PVAc = poly(vinyl acetate).

mg. The sample was mixed thoroughly and pressed into a 13 mm-diameter pellet using a Perkin-Elmer evacuable KBr die (186-0025). A Carver press was used to attain 22,000 lb on the plunger (100,000 psi).

Most FTIR spectra were arbitrarily base-lined using the following three points: (1) 1600 cm^{-1}; (2) the valley between the 1440 and 1375 cm^{-1} peaks (about 1413 cm^{-1}); and (3) the valley between the 1243 and 1338 cm^{-1} peaks (1319–1325 cm^{-1}). However, for polymers prepared from monomer mixtures containing greater than 30% vinyl acetate, this last base-line point was arbitrarily set at 1325 cm^{-1}, since the 1243 cm^{-1} peak overwhelms the valley. Absorbances of the 1375 cm^{-1} peak of the vinyl acetate repeating unit and the 1439 cm^{-1} peak of the methyl acrylate repeating unit were measured, and the 1375 cm^{-1}/1439 cm^{-1} absorbance ratio was calculated. Weight percent poly(vinyl acetate) in the copolymer was then determined from an empirical curve of absorbance ratio vs. weight percent poly(vinyl acetate). Repeat determinations of unknown polymer samples generally agreed to within ±10% of the measured value. To construct the empirical curve, spectra were obtained and absorbance ratios determined for 11 polymer mixtures of known composition containing 2–51% poly(vinyl acetate). These polymer mixtures were prepared by first combining 5% solutions of poly(vinyl acetate) in acetone and poly(methyl acrylate) in benzene and then drying the mixed solutions.

The FTIR method of analysis was compared with the analysis of these polymer systems by proton nuclear magnetic resonance spectroscopy (NMR). NMR was performed on a 400 MHz Bruker WM-300 WB spectrometer. The 4.8 ppm multiplet from the methine proton of poly(vinyl acetate) and the 2.4 ppm multiplet from the methine proton of poly(methyl acrylate) were integrated for these determinations. Two unknown samples of acetone-soluble homopolymer were used for the comparison of analytical methods. Poly(vinyl acetate) contents by FTIR vs. NMR were 9.0 vs. 9.1 for the first sample and 21.7 vs. 18.2 for the second.

Extrusion Processing and Tensile Testing

Graft copolymer samples were extruded through a 25.4 × 0.50 mm slit die attached to a 19.5 mm-diameter, 20 : 1 L/D single-screw extruder driven at 20 rpm by a C.W. Brabender Plasticorder Torque rheometer. Temperatures were 90°C (nearest the feed zone), 140°C (nearest the die), and 140°C (at the die). Variations from the set temperatures during extrusion processing were about ±3°C. Although a single pass yielded a well-formed ribbon, extrudates were passed a second time through the extruder and slit die to provide ribbon samples for testing.

Extruded ribbons were allowed to equilibrate for 7 days at 23°C and 50% relative humidity before testing. Dogbone tensile strips 6.35 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 50.8 mm, and elongation was measured as displacement of the line-contact grips during tensile testing. Sample thickness was measured with an Electro-Physik electronic micrometer.

RESULTS AND DISCUSSION

Preparation and characterization of starch graft copolymers are summarized in Table I. Conversion of monomer to polymer, as estimated from the weight of polymer isolated, decreased with increasing vinyl acetate : methyl acrylate ratios, while at the same time, an increase in acetone-soluble homopolymer was observed. Although only small amounts of methanol-soluble polymer were isolated with monomer mixtures containing 20% vinyl acetate or less, higher percentages of vinyl acetate increased the yield of this fraction, presumably due to the methanol solubility of poly(vinyl acetate).[10]

Molecular weights of the THF-soluble portions of polymer grafts (isolated by removal of starch by acid hydrolysis) did not change greatly when ratios of methyl acrylate : vinyl acetate were varied between 0 : 100 and 50 : 50; however, graft polymerization of pure vinyl acetate resulted in a sharp lowering of graft molecular weight. Values for $\bar{M}_w/\bar{M}_n$ varied little with the ratio of the two monomers. The magnitude of the THF-insoluble fraction in polymer grafts increased with increasing percentages of vinyl acetate in the monomer mixture. This observation suggests that free radicals formed on methyl groups of vinyl acetate (e.g., by chain transfer or through oxidation by ceric ion) can lead to cross-linking during graft polymerization.

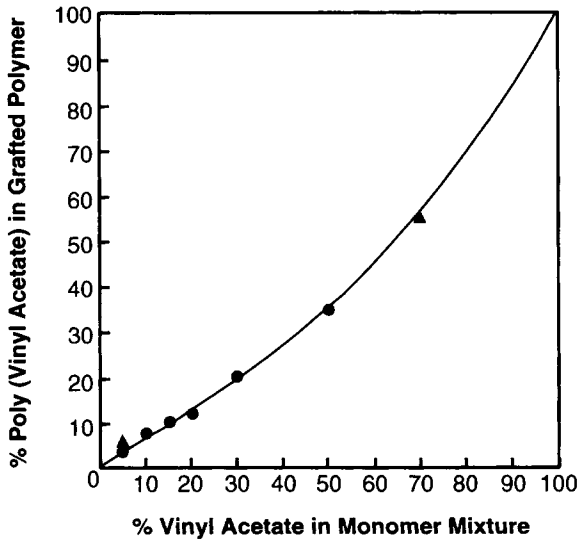

Figure 1 Poly(vinyl acetate) content of grafted polymer vs. % vinyl acetate in initial monomer mixture: (●) data from Table I; (▲) data from graft polymerizations onto cellulose, Fernandez et al.[12]

Table II Tensile Properties of Starch Graft Copolymers

VAc : MA	Synthetic Polymer Content (%)	H_2O Content (%) Based on Total Polymer	H_2O Content (%) Based on Starch Portion	Tensile Values after Aging for 7 Days[a] UTS	Tensile Values after Aging for 7 Days[a] %E
0 : 100[b]	58	4.5	10.0	15	25
5 : 95	59	4.2	9.7	13	32
15 : 85	58	4.3	9.7	14	25
30 : 70	57	4.4	9.7	15	13

[a] Aged at 23°C and 50% relative humidity. UTS = ultimate tensile strength (MN/mm^2). %E = percent elongation.
[b] Data from previous study (Ref. 2).

Poly(vinyl acetate) contents of grafted polymers, as well as those of acetone-soluble homopolymers, were lower than vinyl acetate percentages in starting monomer mixtures. This is the expected result, based on published reactivity ratios for the two monomers. Casinos[11] determined reactivity ratios of 0.020 for vinyl acetate and 6.750 for methyl acrylate in the graft polymerization of this monomer system at high conversion onto cellulose. Poly(vinyl acetate) percentages in grafted polymers were similar to those in the corresponding homopolymers, with the exception of the polymerization run with equal amounts of the two monomers. Reasons for the difference in poly(vinyl acetate) content between homopolymer and polymer grafts in this particular reaction are at this time unknown. A plot of grafted polymer composition vs. monomer composition is shown in Figure 1. Data published by Fernandez and co-workers[12] on graft polymerizations of methyl acrylate–vinyl acetate mixtures onto cellulose fall on about the same curve as our data for starch.

Graft polymerizations run with vinyl acetate : methyl acrylate ratios of 5 : 95, 15 : 85, and 30 : 70 were scaled-up by a factor of 10 to provide products for extrusion processing (Table II). Products were not extracted with methanol or acetone to remove homopolymer, since such extractions would not be practical in a commercial process. Air-dried graft copolymers with water contents of 4.2–4.4% (9.7% based on the starch component of the polymer) were extruded into ribbons for physical testing. Moistures were calculated on the basis of the starch component, since water is a plasticizer for starch but not for the hydrophobic synthetic polymer. Increasing amounts of poly(vinyl acetate) in the starch graft copolymer did not adversely affect extrudate formation, and continuous ribbons containing no unfluxed polymer were obtained from all products. Tensile values in Table II did not show large variations with vinyl acetate content. All samples were flexible but could be fractured if bent over double. Ribbon prepared from the 30 : 70 vinyl acetate–methyl acrylate graft copolymer appeared to be somewhat more brittle than was ribbon prepared earlier[2] from starch-*g*-poly(methyl acrylate) containing no copolymerized vinyl acetate. This increased brittleness is reflected in the lower %E value for the vinyl acetate-containing product.

We are currently examining the biodegradation of extruded ribbons prepared from starch-*g*-poly(methyl acrylate) and starch-*g*-poly(methyl acrylate-*co*-vinyl acetate). Results of these investigations will be reported separately.

We are indebted to Dr. D. R. Patil for molecular weight determinations, to Dr. D. Weisleder for NMR spectra, to C. L. Swanson and R. P. Westhoff for extrusion processing, and to G. D. Grose for physical property determinations. The mention of firm names and trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

References

1. E. B. Bagley, G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *Polym. Eng. Sci.*, **17**, 311 (1977).
2. D. Trimnell, C. L. Swanson, R. L. Shogren, and G. F. Fanta, *J. Appl. Polym. Sci.*, to appear.
3. R. J. Dennenberg, R. J. Bothast, and T. P. Abbott, *J. Appl. Polym. Sci.*, **22**, 459 (1978).
4. G. Swift, *Polym. Mater. Sci. Eng.*, **63**, 846 (1990).
5. P. J. Hocking, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C32**, 35 (1992).
6. W. J. Bailey, *Prog. Pac. Polym. Sci. Proc. Pac. Polym. Conf.* **1**, 105 (1989).
7. W. J. Bailey and V. K. Kuruganti, *Polym. Mater. Sci. Eng.*, **62**, 971 (1990).
8. C. E. Brockway, *J. Polym. Sci. A*, **2**, 3733 (1964).
9. S. A. Faterpeker and S. P. Potnis, *Angew. Makromol. Chem.*, **93**, 111 (1981).
10. M. K. Lindemann, *Encycl. Polym. Sci. Technol.*, **15**, 625 (1971).
11. I. Casinos, *Makromol. Chem.*, **192**, 1091 (1991).
12. M. J. Fernandez, I. Casinos, and G. M. Guzman, *J. Macromol. Sci.-Chem.*, **A27**, 969 (1990).

G. F. FANTA
D. TRIMNELL
J. H. SALCH

Plant Polymer Research
USDA-ARS-NCAUR
1815 N. University St.
Peoria, Illinois 61604

Received December 7, 1992
Accepted December 31, 1992