

Graft Copolymers of Methyl Acrylate onto Bleached Wood Pulp: Preparation and Extrudate Properties

INTRODUCTION

In our continuing study of carbohydrate-containing polymers as extenders and replacements for polymers totally derived from petrochemicals, we have studied the synthesis of starch-*g*-poly(methyl acrylate) (starch-*g*-PMA) and hemicellulose-*g*-PMA and have examined their extrusion processing. These materials form plastics with good tensile properties and with little or no die swell.^{1,2} In this report, we will present a comparable study with bleached wood pulp as the substrate for graft polymerization and will show that cellulose pulp-*g*-PMA has properties different from graft copolymers derived from the other two polysaccharides. Although graft polymerizations of acrylate esters onto cellulose have been reported,³ the extrusion processing of these polymers into continuous plastics is a new area for research.

EXPERIMENTAL

Materials

Bleached softwood pulp (moisture content 7.6%) was Alberta Hi-Brite from St. Regis Paper Co., and analysis showed 0.06% lignin and 85.8% α -cellulose, the remainder being pentosans. Bleached hardwood pulp (moisture content 5.5%) was from Bowater, Inc. and contained 86.3% α -cellulose and 0.13% lignin. Methyl acrylate was obtained from Aldrich Chemical Co., Inc. (monomer A) and from Polysciences (monomer B) and was distilled at atmospheric pressure through a 14-in. Vigreux column. Ceric ammonium nitrate was certified A.C.S. Grade from Fisher Scientific Co.

Pretreatment of Cellulose Pulp

For most graft polymerizations, 75.0 g of cellulose pulp was allowed to soak overnight in 1 L of distilled water. The mixture was stirred in a Waring Blender for about 30 s and was then transferred to the reaction flask.

For the reaction using refined cellulose, 360 g of bleached softwood pulp was first allowed to soak overnight in 6 L of distilled water and was then broken up by stirring. Distilled water was added to give a total weight of 23 kg, and the resulting mixture was refined for 2 h in a Valley Laboratory beater (TAPPI T200 ts-66) to a Schopper-Riegler freeness of 300 mL. Excess water was removed by pressure filtration to give a filter cake (containing 24% solids) that was used without drying in the subsequent graft polymerization.

For the reaction using mercerized cellulose, 100 g of bleached softwood pulp was allowed to soak overnight in 3 L of distilled water. The mixture was stirred, and the cellulose pulp separated by filtration. The wet filter cake (248 g) was then added to a nitrogen-sparged solution of 1500 mL of 25% sodium hydroxide and 335 mL of water. The resulting mixture of cellulose pulp in 18% sodium hydroxide was sparged with nitrogen and allowed to stand with occasional stirring at room temperature for 4 h. The cellulose pulp was separated by filtration and washed repeatedly with water. The pulp (pH 8.9) was then stirred for 2 min in a British disintegrator at a ratio of 80 g wet pulp: 2 L of water. After filtration, the pulp was suspended in water, and the pH was adjusted to 3.5 with a few drops of dilute nitric acid. The pulp was washed again with water, and was used as the wet filter cake (23% solids) in the subsequent graft polymerization.

Graft Polymerization

A stirred slurry of 75.0 g (dry basis) of cellulose pulp in 3 L of water was sparged with nitrogen for 1 h at 22–25°C. Methyl acrylate (93.8 g) was added, followed after 5 min by portionwise addition of 5.00 g of ceric ammonium nitrate dissolved in 45 mL of 1*N* nitric acid. Addition was made in four equal portions at 15-min intervals, and exothermic polymerization occurred within a few seconds

to a few minutes after the first addition. The mixture was stirred for 2 h under nitrogen, while maintaining the temperature below 30°C with an ice bath. The polymer was recovered by filtration, washed with water, and then extracted with acetone to remove homopolymer (8.0–22.6 g, in six separate reactions). The graft copolymer was then dried under vacuum at 60°C.

Weight percent PMA in cellulose pulp-*g*-PMA (% add-on) was calculated from the loss in weight after removal of the polysaccharide component by treatment with sodium periodate and then with sodium methoxide in methanol.² The resulting PMA showed no residual carbohydrate (by infrared). Acetone solubility was determined by stirring an accurately weighed sample of PMA in a known weight of acetone, separating the gel fraction by centrifugation (20 min at 1500 × *g*), and determining the weight of PMA dissolved in a known weight of supernatant.

Molecular weights of acetone-soluble PMA samples were determined by GPC in tetrahydrofuran solution on a Waters Model ALC/GPC 244 Liquid Chromatograph. Tetrahydrofuran solutions were centrifuged before analysis (30 min at 26,000 × *g*) to remove small amounts of gel still present in the sample. Concentration of PMA was about 0.08% (w/v). Four Waters μ -styragel columns were used (10⁵, 10⁴, 10³, and 500 Å) with an injection volume of 200 μ L and a flow rate of 1 mL/min. Polystyrene standards were used.

Averages from four replicate GPC molecular weight determinations are reported for each sample. Standard deviations (56 degrees of freedom) for reported M_w and M_n values are 6800 and 8700, respectively. The greater variability of M_n is a consequence of the difficulty in determining the location of the base line at the end of a GPC run.

Treatment of Cellulose Pulp-*g*-PMA before Extrusion

Zinc Chloride. 95-g of cellulose pulp-*g*-PMA was stirred with water, and the graft copolymer was separated by filtration. The wet polymer (187.4 g) was added to a solution of 1493 g of ZnCl₂ in 547.3 mL of water, and the mixture was stirred thoroughly. The resulting viscous paste (35°C) was allowed to stand at ambient temperature for 30 min and was then diluted with water. The polymer was separated by filtration, washed with water until the pH of the filtrate was 6.5, and finally dried under vacuum at 60°C.

Acetylation.⁴ 75 g of cellulose pulp-*g*-PMA was allowed to stand overnight in a solution of 600 mL of glacial acetic acid and 750 mL of toluene; then 3.8 mL of 60–62% perchloric acid and 188 mL of acetic anhydride were added. After the mixture was stirred for 30 min at room temperature, the solid was removed by filtration and washed first with ethanol and then with water until the pH of the filtrate was 6.0. The yield of polymer, after drying at 60°C under vacuum, was 95.1 g. Acetyl content was calculated from weight gain of the polymer.

Enzyme. About 150 g (dry basis) of cellulose pulp-*g*-PMA (initial add-on 52–53%) was digested for 24 h at 55°C in a solution of 1280 mL of cellulase solution (20 mg/mL) and 1920 mL of pH 4.6 phosphate buffer. The polymer was recovered by filtration, washed with water, and dried under vacuum at 40°C. Graft copolymers with a final add-on of 63% and 70% were prepared from dry cellulose pulp-*g*-PMA after soaking the polymer samples overnight in water. The precursor to the graft copolymer with 81% add-on did not require hydration before treatment, because it had never been dried after washing.

Extrusion and Testing

Samples were extruded through a 0.75-in. C. W. Brabender extruder with an *L/D* ratio of 20:1. The screw had a 2:1 compression ratio and was driven at 40 rpm by a Brabender Plasti-Corder. Temperature of the 1 × 0.020 in. slit die and the end of the barrel was 140°C, whereas the inlet zone was 90°C. With polymers having low PMA content, frictional effects caused the barrel temperature to increase from 140°C to 145–160°C after prolonged extrusion. Pressure, as measured with a transducer mounted just upstream of the die opening, varied from about 2000 psi (for high PMA content polymers) to 4000 psi (for low PMA content polymers). Tensile specimens from leathery extrudates were cut with a dumbbell-shaped die, whereas brittle extrudates were machined on a Tensil Kut Specimen Cutter (Sieburg Industries, Inc.). Specimens were tempered for 4 days at 22.2°C and 50% relative humidity before testing on an Instron testing machine at 5 cm/min crosshead speed.

Microscopy

Samples were examined and photographed in a Hitachi ISI Scanning Electron Microscope. Specimens were cemented onto aluminum stubs and coated with about a 200 Å layer of gold-palladium (60–40) alloy.

RESULTS AND DISCUSSION

Cellulose, like starch and hemicellulose, is a reactive substrate toward ceric ammonium nitrate-initiated graft polymerization, and graft copolymers containing 50–55% grafted PMA were easily prepared in water near room temperature from both bleached softwood and bleached hardwood pulps (Table I). After extraction of ungrafted PMA with acetone, a portion of each graft copolymer was characterized by determining: (1) PMA content, by weight loss after removal of the cellulose component, (2) acetone solubility of the remaining PMA grafts, and (3) molecular weights and molecular weight distributions of soluble PMA grafts. The partial insolubility of grafted PMA in acetone has also been observed when starch¹ and hemicellulose² were used as substrates for graft polymerizations. Moreover, the PMA molecular weights shown in Table I are not greatly different from the molecular weights found in these earlier studies.

Methyl acrylate from two different sources was used for the graft polymerization studies in Table I. Although monomer A, used in the two repeat experiments 1 and 2, and monomer B, used in experiment 3, gave cellulose pulp-*g*-PMA with about the same PMA content, monomer A produced grafted PMA that was less soluble in acetone and that had a higher molecular weight. Graft polymerization onto hardwood pulp (experiment 6) gave results that were similar to those obtained with softwood (experiment 3).

We next investigated the effect on graft polymerization of varying the pretreatment of softwood pulp before graft polymerization. In experiments 1–3, pulp was merely dispersed in water by mechanical stirring, but experiment 4 used pulp that had been refined in a Valley beater to rupture the individual fibers and to provide more surface area. We observed little difference between our PMA graft copolymers as a result of using beaten vs. unbeaten pulp. Mercerization⁵ (swelling the pulp in 18% sodium hydroxide followed by water washing to remove alkali) is perhaps the harshest of the cellulose pulp pretreatments examined, and this treatment should also extract much of the hemicellulose component from the softwood pulp.⁶ Although mercerized pulp (experiment 5) gave higher molecular weight PMA, this increase was not large and was actually less than that caused by simply using methyl acrylate from different manufacturers.

Selected cellulose pulp-*g*-PMA polymers were extrusion-processed under conditions similar to those used previously for starch¹ and hemicellulose² graft copolymers, and tensile properties of extruded ribbons were then determined (Table II). Polysaccharide-*g*-PMA polymers do not melt on extrusion processing because of the rigid, nonmelting nature of the polysaccharide moiety. Continuous extrudates showing little or no die swell are instead produced by fusion of heat-softened particles in the high-pressure zone of the extruder die.

Cellulose pulp-*g*-PMA with no treatment before extrusion (1, Table II) required four passes through the extruder to obtain a completely fused product. The extrudate was also brittle, as compared with those obtained from starch-*g*-PMA (7, Table II) and hemicellulose-*g*-PMA (8, Table II), which were both tough and leathery. This brittleness is reflected in the lower value for % elongation at break. Although an attempt to decrystallize the cellulose portion of the graft copolymer by treatment with 70% zinc chloride⁷ before extrusion (2, Table II) gave a higher tensile strength product that was completely fused in two passes, only a slight increase in % elongation was observed. Acetylation of the cellulose component (3, Table II) did not improve tensile properties, even though the acetylated graft copolymer gave a more translucent extrudate. Tensile properties were best improved by removal of a portion of the cellulose by enzymatic hydrolysis. Cellulase-treated graft copolymers from both softwood (4 and 5, Table II) and hardwood pulps (6, Table II) gave extrudates similar in appearance and properties to those produced from starch and hemicellulose, although % elongation values for cellulosic products were lower, if compared at about the same PMA content.

We next examined the extrudates in Table II by obtaining scanning electron micrographs of fracture surfaces resulting from tensile testing. Although four passes through the extruder destroys the individual fibers of grafted softwood pulp, shown before extrusion in Figure 1(A), fiber fragments

TABLE I
 Synthesis and Properties of Cellulose-g-Poly(methyl Acetate)^a

Experiment number	Cellulose	Methyl acrylate, source ^b	% add-on	Poly(methyl acrylate) grafts		
				Solubility in acetone (%)	\bar{M}_w	\bar{M}_n
1	Softwood	A	52	72	803,000	333,000
2	Softwood	A	54	68	745,000	306,000
3	Softwood	B	53	86	545,000	229,000
4	Softwood (refined)	B	53	82	568,000	251,000
5	Softwood (mercerized)	B	53	83	644,000	280,000
6	Hardwood	B	52	80	556,000	240,000

^a Polymerization recipe: 75 g (dry basis) of cellulose, 93.8 g of methyl acrylate, 3 L of water, 5.00 g of ceric ammonium nitrate.

^b Monomer A obtained from Aldrich Chemical Co., Inc.; monomer B obtained from Polysciences.

TABLE II
Extrusion Processing^a of Cellulose-*g*-Poly(methyl Acrylate)

Experiment number	Graft copolymer	Treatment before extrusion	UTS ^b	Elongation at break (%)
1	1, Table I	None	2.8 ^c	2.5
2	3, Table I	70% ZnCl ₂	3.3	7.5
3	2, Table I	Acetylate (2,2 acetyl groups per glucose unit)	2.7	1.5
4	Prepared like 3, Table I	Cellulase (to give 63% add-on)	2.8	47
5	Prepared like 3, Table I	Cellulase (to give 81% add-on)	2.2	250
6	6, Table I	Cellulase (to give 70% add-on)	2.1	54
7	Starch- <i>g</i> -poly(methyl acrylate); 47%, 64%, 77% add-on ^d	None	3.0, 2.0, 1.9	48, 140, 340
8	Larchwood hemicellulose- <i>g</i> -poly(methyl acrylate); 55% add-on ^e	None	2.2 ^f	150

^a Except where indicated, samples were given two passes through the extruder.

^b Ultimate tensile strength, kg/mm². Except where indicated, crosshead speed = 5 cm/min.

^c Sample given four passes through the extruder.

^d Ref. 1.

^e Ref. 2.

^f Crosshead speed = 50 cm/min.

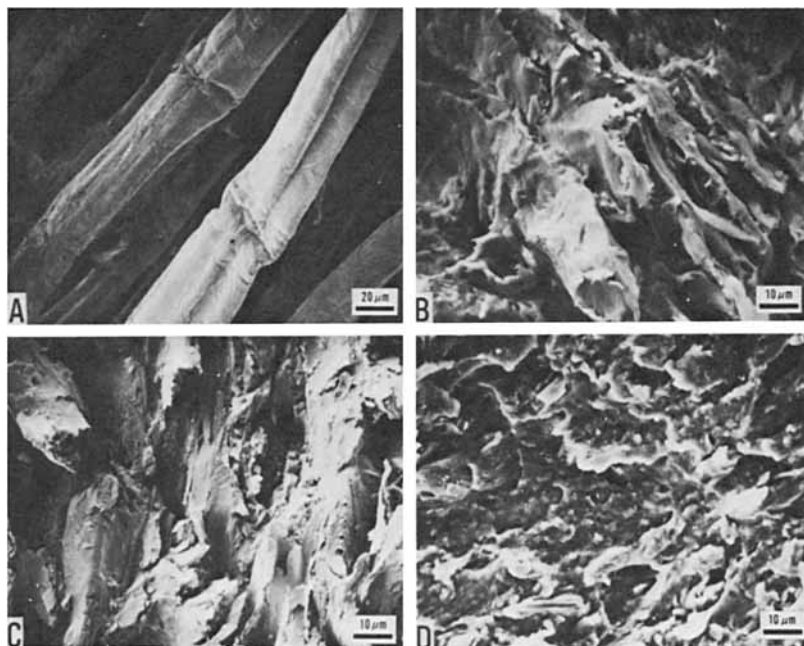


Fig. 1. Scanning electron micrographs. (A) Graft copolymer 1, Table I, before extrusion. (B) Fracture surface of extrudate 1, Table II (graft copolymer 1, Table I after four passes through extruder). (C) Fracture surface of extrudate 3, Table II (acetylated graft copolymer after two passes through extruder). (D) Fracture surface of extrudate 5, Table II (enzyme-treated graft copolymer after two passes through extruder).

are still clearly present in the extrudate [Fig. 1(B)]. Note that Figure 1(B) is at twice the magnification of Figure 1(A). Acetylation of the cellulose component before extrusion also results in a fibrous extrudate [Fig. 1(C)], even though the extrudate has a highly translucent appearance. The fracture surface of the zinc chloride-treated graft copolymer (not shown) resembled those shown in (B) and (C) of Figure 1. As might be expected from the tensile properties, removal of a portion of the cellulose with enzyme results in an extrudate that is more homogeneous and less fibrous in appearance [Fig. 1(D)].

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References

1. C. L. Swanson, G. F. Fanta, R. G. Fecht, and R. C. Burr, in *Polymer Applications of Renewable Resource Materials*, C. E. Carraher, Jr. and L. H. Sperling, Eds., Plenum, New York, 1983, p. 59.
2. G. F. Fanta, R. C. Burr, and W. M. Doane, *J. Appl. Polym. Sci.*, **27**, 4239 (1982).
3. J. C. Arthur, Jr., in *Advances in Macromolecular Chemistry*, W. M. Pasika, Ed., Academic, New York, 1970, Vol. II, p. 1.
4. L. J. Tanghe, L. B. Genung, and J. W. Mench, in *Methods in Carbohydrate Chemistry*, R. L. Whistler, Ed., Academic, New York, 1963, Vol. III, p. 196.
5. W. D. Nicoll, N. L. Cox, and R. F. Conaway, in *Cellulose and Cellulose Derivatives*, E. Ott and H. M. Spurlin, Eds., Interscience, New York, 1954, Part 2, p. 825.

6. R. L. Whistler and M. S. Feather, *Methods Carbohydr. Chem.*, **5**, 144 (1965).
7. J. L. Williams, V. Stannett, L. G. Roldan, S. B. Sello, and C. V. Stevens, *Int. J. Appl. Radiat. Isot.*, **26**, 169 (1975).

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