

Effects of Water on Starch-*g*-Polystyrene and Starch-*g*-Poly(methyl Acrylate) Extrudates

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Synopsis

Polystyrene and poly(methyl acrylate) were grafted onto wheat starch by gamma radiation and chemical initiation, respectively. The respective percent add-on values were 46 and 45; 68% of the polystyrene formed was grafted to starch, and the corresponding proportion of poly(methyl acrylate) was 41%. The molecular weight distributions of the homopolymer and graft portions were characterized, and extrusion conditions were established for production of ribbon samples of starch-*g*-PS and starch-*g*-PMA. Both copolymer types were considerably weakened by soaking in water, and this effect was more immediate and drastic for starch-*g*-poly(methyl acrylate). Both graft copolymers regained their original tensile strengths on drying, but the poly(methyl acrylate) specimens did not recover their original unswollen dimensions and retained high breaking elongations characteristic of soaked specimens. Tensile and dynamic mechanical properties of extruded and molded samples of both graft polymers are reported, and the plasticizing effects of water are summarized.

INTRODUCTION

There are numerous publications on the syntheses of thermoplastic graft copolymers of starch and cellulose, as summarized in recent review articles on the subject.¹⁻⁴ Comparatively little has appeared, however, on the processing of such materials and their physical properties.⁵⁻⁹ This article reports reaction conditions for the synthesis of starch-*g*-polystyrene and starch-*g*-poly(methyl acrylate) copolymers which produce good-quality extrudates. These materials were characterized with respect to the amount and molecular weight distributions of the thermoplastic portions that were grafted. Extrusion conditions for production of apparently homogeneous specimens are reported, and some mechanical and dynamic mechanical properties of the extrudates are reviewed. These copolymers contain large proportions of starch, and it was of interest to determine the effect of water on the properties of such materials. These observations are reported here.

EXPERIMENTAL

Supergel 1201C wheat starch (International Grain Products, Montreal, Canada) supplied with nominal 11.8 wt % moisture was used throughout this work. Styrene and methyl acrylate were washed with 10% sodium hydroxide to extract phenolic inhibitors, distilled under reduced pressure, and freeze-thawed to remove oxygen before polymerization.

Cobalt-60 radiation was used in the synthesis of starch-*g*-polystyrene.¹⁰ Starch, 100 g, 30 mL distilled H₂O, and 150 g styrene were trituated in a glass

jar with a screw-top lid. A vertical copper tube was soldered to the steel jar top, and a rubber septum was wired onto the tube. The jar and contents were flushed with N_2 and evacuated to a pressure of 120 torr three times, using a syringe needle inserted through the septum. The jar and contents were then irradiated in a Gammacell (Atomic Energy of Canada, Limited) ^{60}Co source to 1.7 Mrad. The strength of the ^{60}Co source decayed through the course of this work from 1.47×10^5 rad/h to 1.2×10^5 rad/h. This was determined by Fricke dosimetry¹¹ with $G(Fe^{3+}) = 15.6$ and from the natural decay of ^{60}Co given by

$$A_t/A_0 = e^{-(0.693/5.27)t} \quad (1)$$

where t is the time in years, A_0 is the initial source intensity, A_t is the intensity after time t , and 5.27 is the ^{60}Co half-life in years. After the reaction, the jar was broken away from the solid white copolymer mass, and the product was dried for several hours in a vacuum oven at $60^\circ C$ and 30 torr pressure and then crushed into a powder.

The homopolymer and graft copolymer composition of the product was analyzed as follows. Ungrafted polystyrene (PS) was extracted from a small portion of the product polymer by Soxhlet extraction with 1,2-dichloroethane followed by benzene for a total extraction time of at least one week. No water was added to the copolymer to increase extraction efficiency,¹² but the long extraction times utilized in this work achieved the complete removal of homopolymer.¹³ Grafted polystyrene was isolated from the purified copolymer by hydrolyzing the starch with refluxing 1.5 N HCl for 5 h.

The initiator for the graft polymerization of methyl acrylate on starch was $Ce(NH_4)_2(NO_3)_6$.¹⁷ Starch, 80 g, was gelatinized by stirring in 2 L boiled, distilled water in a round-bottom flask under N_2 atmosphere for 30 min at $85^\circ C$. The flask was cooled to $30^\circ C$ in a water bath and 160 g methyl acrylate and then 25 mL of a solution of $Ce(NH_4)_2(NO_3)_6$ (3.39 g) in 1 N HNO_3 were added. The reaction mixture was stirred for 5 h under N_2 . To ensure maximum conversion of methyl acrylate to polymer, the flask was then placed in a water bath at $65^\circ C$ and 1 g initiator azodiisobutyronitrile was added. The reaction mixture was stirred for a further 2 h. A white curdlike suspension was obtained. Methanol, 1 L, was added to coagulate the polymer, which was then filtered through Whatman #41 filter paper. The spongy mass was broken into small lumps and dried in a vacuum oven for 24 h at $60^\circ C$ and 30 torr pressure.

The product was characterized as follows. Ungrafted poly(methyl acrylate) was removed from a portion of the material by Soxhlet extraction, first with acetone and then with benzene for at least one week total extraction time. Addition of 20 wt % water to the copolymer 12 h before Soxhlet extraction was started¹² did not have a significant effect on the amount extracted. The technique of stirring the moistened copolymer in refluxing acetone for 24 h, filtering, and then repeating this procedure with refluxing benzene as an alternate means of ungrafted homopolymer separation¹² yielded the same results as Soxhlet extraction. Grafted poly(methyl acrylate) was isolated from the purified copolymer using glacial acetic acid and perchloric acid.¹⁴ First, 4 g purified copolymer was swollen by mixing for 8 h in 100 mL refluxing 80/20 (v/v) benzene/dimethyl sulfoxide mixture. This mixture was frozen, and the benzene was removed by freeze drying to leave a jellylike mass which was refluxed for 1.5 h in 200 mL glacial acetic acid before adding 12 mL 72% $HClO_4$. When the resulting sus-

pension became clear, it was poured onto 1 L cold H₂O to precipitate the poly-(methyl acrylate) (PMA). This mixture was stirred for 0.5 h and the PMA was collected. To remove trapped acid, the PMA was dissolved in approximately 50 mL acetone, reprecipitated with 1 L H₂O, and dried under vacuum.

Quantities used to characterize the copolymers were

$$\% \text{ Conversion} = \frac{\text{weight product} - \text{weight starch}}{\text{weight monomer}} \times 100$$

$$\% \text{ Add-on} = \frac{\text{weight pure copolymer} - \text{weight starch}}{\text{weight pure copolymer}} \times 100$$

% Polymer grafted

$$= \frac{\text{weight grafted polymer}}{\text{weight grafted polymer} + \text{weight ungrafted polymer}} \times 100$$

$$\text{Grafting frequency (AGU/graft)} = \frac{(100 - \% \text{ add-on})/162}{\% \text{ add-on}/\bar{M}_w \text{ graft}}$$

where AGU/graft is the number of anhydroglucose (formula weight 162) units per grafting point.

Average molecular weights and molecular weight distributions of the grafted polymers and homopolymers were determined by gel permeation chromatography (GPC) using a calibration method which takes account of the effects of concentration on hydrodynamic volume.^{15,16} The GPC calibration employed anionic polystyrene standards in tetrahydrofuran (THF) solvent. Analyses were carried out with commercially available columns packed with styrene-divinyl benzene gels. Column lengths were 2 × 61 cm, nominal pore sizes were 10⁶, 10⁵, 10⁴, and 10³ Å, and the solvent flow rate was 2.5 mL/min. This arrangement produced a linear calibration curve from polystyrenes with molecular weights between 10³ and 2 × 10⁷ amu. Molecular weight distributions were characterized by \bar{M}_n , \bar{M}_w , standard deviation, and skewness parameters. A measure of the skewness of the number distribution, (skew)_n, is given by¹⁷

$$(\text{skew})_n = (\bar{M}_z \bar{M}_w \bar{M}_n - 3\bar{M}_n^2 \bar{M}_w + 2\bar{M}_n^3) / (\text{Sd})_n^3 \quad (2)$$

where (Sd)_n is the standard deviation of the number distribution:

$$(\text{Sd})_n = \bar{M}_w \bar{M}_n - \bar{M}_n^2 \quad (3)$$

The corresponding terms for the weight distribution are

$$(\text{skew})_w = (\bar{M}_{z+1} \bar{M}_z \bar{M}_w - 3\bar{M}_w^2 \bar{M}_z + 3\bar{M}_w^3) / (\text{Sd})_w^3 \quad (4)$$

and

$$(\text{Sd})_w = \bar{M}_z \bar{M}_w - \bar{M}_w^2 \quad (5)$$

Extrusions were carried out with a 1/2-in. extruder, designed in our laboratory, with a 27:1 length-to-diameter barrel. Drive was provided by a 1/2-hp shunt-wound motor and a 30:1 worm gear reducer. The extruder barrel had three temperature-controlled zones, and the interchangeable head and die were also independently controlled. A pressure transducer was mounted in the die head. The screw had a 4:1 compression ratio. Crude starch-*g*-PS and starch-*g*-PMA (containing homopolymers) were extruded in continuous ribbon shapes.

The starch-*g*-PS was extruded with the first (feed) zone heater set at 135°C and the two subsequent barrel zones set at 135°C and 140°C, respectively. The die zone heater was set at a surface temperature reading of 140°C; the die face had a temperature of 152°C as measured by a surface thermometer. The 1-in.-long die contained a $\frac{1}{16}$ -in. \times $\frac{1}{4}$ -in. slit opening which was $\frac{1}{4}$ in. long. The die tapered from the $\frac{1}{2}$ -in. barrel diameter to the slit through a $\frac{3}{4}$ -in. channel at approximately a 20° angle. During steady operation, the melt pressure in the extruder head was about 700 psi, as measured by a pressure transducer $1\frac{1}{4}$ in. from the die exit. The starch-*g*-PS was extruded at 20 rpm and produced a smooth off-white product.

The starch-*g*-PMA was extruded with the first barrel zone at 115°C surface temperature and the two remaining barrel zones at 130°C. The die zone heater was set at a surface temperature reading of 125°C, and the die face had a temperature of 143°C. The 2-in.-long die had a $\frac{1}{100}$ -in. \times $\frac{1}{4}$ in. slit opening which was 1 in. long. The die tapered from the $\frac{1}{2}$ -in. barrel diameter to the slit through an approximately 20° angle. The longer die land and narrower slit in this case produced smoother starch-*g*-PMA extrudates than those obtained with the shorter die employed for starch-*g*-polystyrene extrusions. Steady extrusion was at 4 rpm and 2500 psi pressure. The extrudate surface was matte at 20 rpm and smooth and glossy at 4 rpm.

Tensile strengths of the extruded ribbons were measured with an Instron tensile tester with hydraulic jaws. Starch-*g*-PS samples were tested with rubber-covered jaws, a crosshead speed of 0.3 cm/min, and 80 psi jaw pressure; the more ductile starch-*g*-PMA samples were tested with steel jaws, a crosshead speed of 10 cm/min, and 20 psi jaw pressure. Breaking elongations were measured using a hand-held ruler to measure the progressive separation of gauge lines marked on the samples. The initial gauge length was 2 mm. Starch-*g*-polystyrene ribbon samples tended to break at the clamps, rendering the measured tensile strengths at break doubtful. The starch-*g*-PMA ribbon samples had higher elongations and broke between the gauge marks.

ASTM D-638 Type I tensile test specimens¹⁸ were injection molded from graft copolymer samples. The molding machine was a plunger model designed and built in our laboratory.

Starch-*g*-PS injection moldings were made with 165°C cylinder temperature and 140°C mold temperature. The mold was cooled to room temperature before the moldings were removed. Graft copolymers tended to discolor when residence times in the cylinder approached 15 min. There was no visual evidence of degradation with shorter residence times. Molding conditions for the starch-*g*-PMA samples were 150°C cylinder temperature and 95°C mold temperature. Molded samples of this polymer warped upon ejection at 95°C, so the mold was cooled to room temperature before sample removal.

Dynamic mechanical measurements on the copolymers were carried out using a Rheovibron (model DDV-II) with oscillator frequency set at 3.5 Hz. Isolated grafts (after hydrolysis of the starch) and extruded graft copolymer were compression molded into thin strips for testing and comparison. Data were handled by the method of Massa.¹⁹

Scanning electron microscope photographs of extruded starch-*g*-PS and starch-*g*-PMA samples were taken using an ISI microscope. The extruded ribbons were frozen in liquid N₂ and snapped cleanly to expose a cross section.

The same technique was applied to as-extruded specimens and to samples which had been soaked in water and then dried under ambient conditions. The specimens were sputtered with a thin layer of gold.

RESULTS AND DISCUSSION

The quantities which characterize the starch-*g*-PS and starch-*g*-PMA copolymers are listed in Table I. The Mark-Houwink constants,²⁰ $K = 6.82 \times 10^{-3}$ and $a = 0.766$ for polystyrene in THF, were used to calculate PS molecular weights from GPC data.

Characterization of PMA and starch-*g*-PMA required knowledge of the Mark-Houwink constants for this polymer in the GPC solvent, tetrahydrofuran. This information was not found in the literature, and these values were deter-

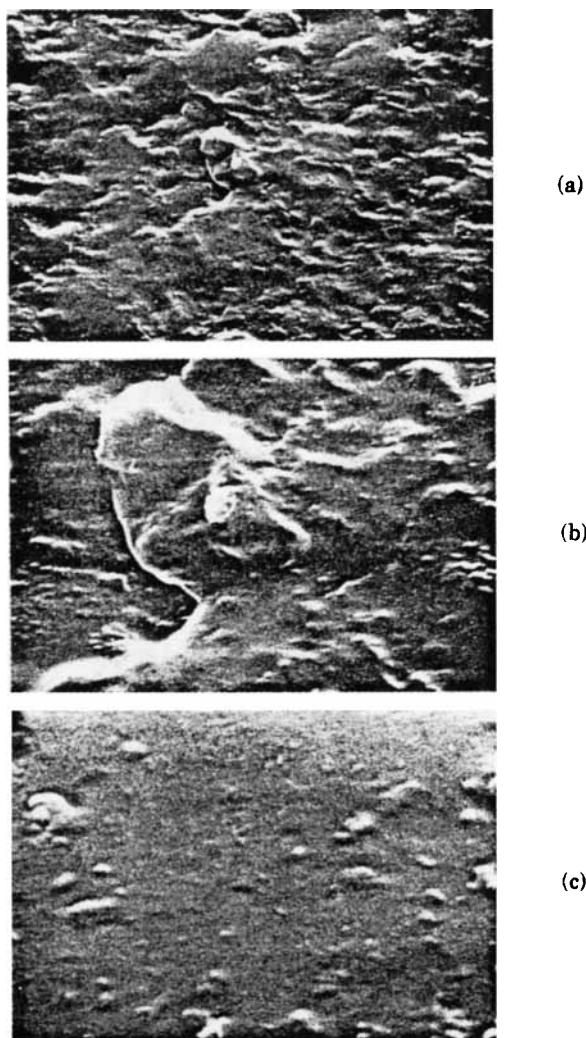


Fig. 1. Scanning electron microscope photograph of extruded starch-*g*-PMA cross section: (a) 2000 \times ; (b) 7000 \times ; (c) 15000 \times .

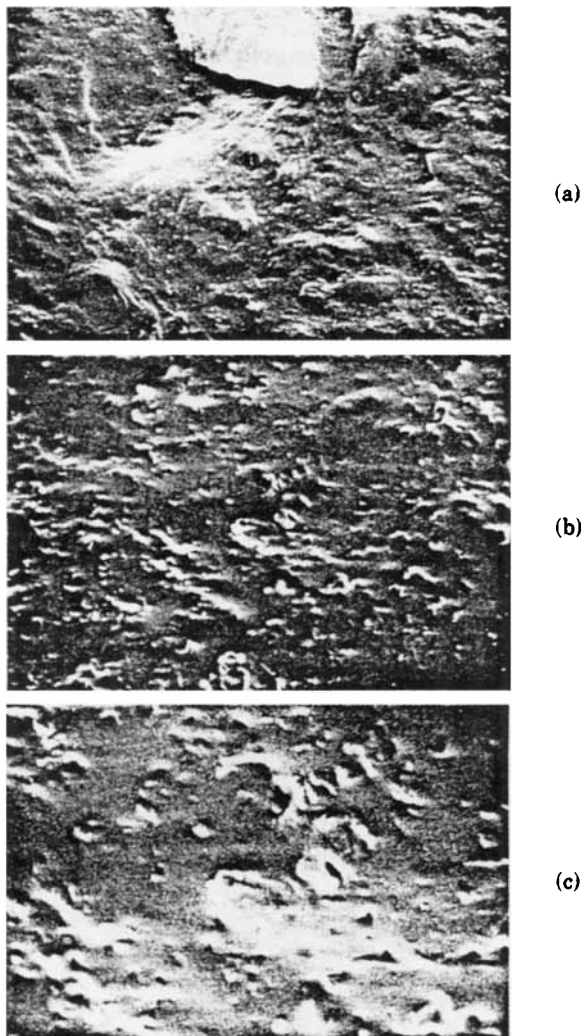


Fig. 2. Scanning electron microscope photograph of extruded starch-g-PMA cross section, soaked 24 h in water, then dried: (a) 2000X; (b) 7000X; (c) 15000X.

mined by two methods using GPC data. One method employed \bar{M}_n and intrinsic viscosity data from a single polymer,²¹ while the second procedure used intrinsic viscosities of two different polymer samples in the GPC solvent.²² The second method was tried with intrinsic viscosity ratios from four different high-molecular-weight samples and one low-molecular-weight specimen. Not all the combinations produced viscosity ratios for which the GPC data calculations converged. This is probably so because these samples contained a small high-molecular-weight shoulder that was outside the resolution range of the GPC columns. The high-molecular-weight species are suspected to be gel resulting from incomplete hydrolysis of starch. The samples reported in Table I were isolated under optimum conditions and did not appear to contain unresolved high-molecular-weight species. The values taken to characterize PMA in tetrahydrofuran were $K = 0.0094 \text{ cm}^3/\text{g}$ and $a = 0.72$. These constants do not agree

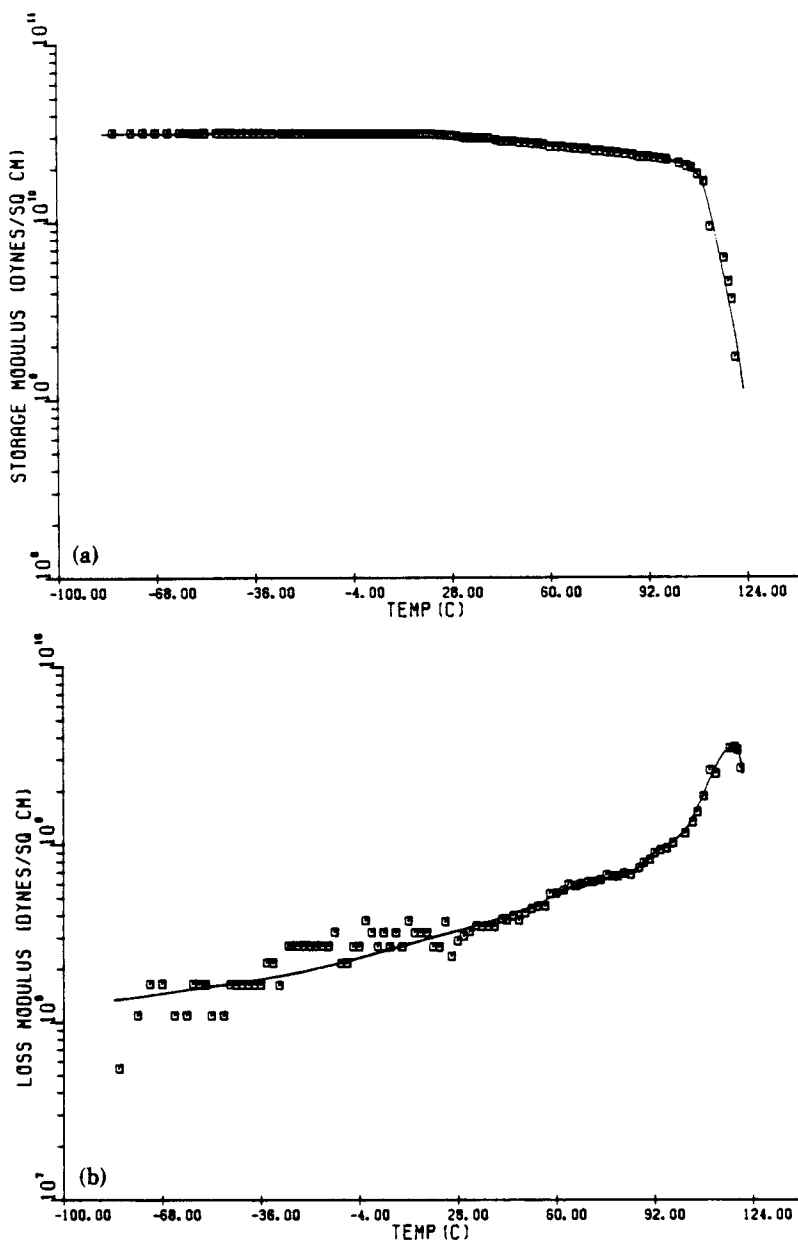


Fig. 3. Dynamic mechanical spectra of grafted PS after removal of attached starch; 3.5 Hz: (a) storage modulus; (b) loss modulus.

with those from the \bar{M}_n -intrinsic viscosity technique, which is believed to be less reliable for reasons discussed elsewhere.²² The choice of the former set of Mark-Houwink constants was supported by comparison with those for PMA in acetone.²³ The intrinsic viscosity of a sample of PMA was measured in both solvents, and the \bar{M}_v values calculated were found to be comparable. Acetone and tetrahydrofuran have similar solubility parameters,²⁴ and this coincidence of dilute solution properties should therefore be expected.

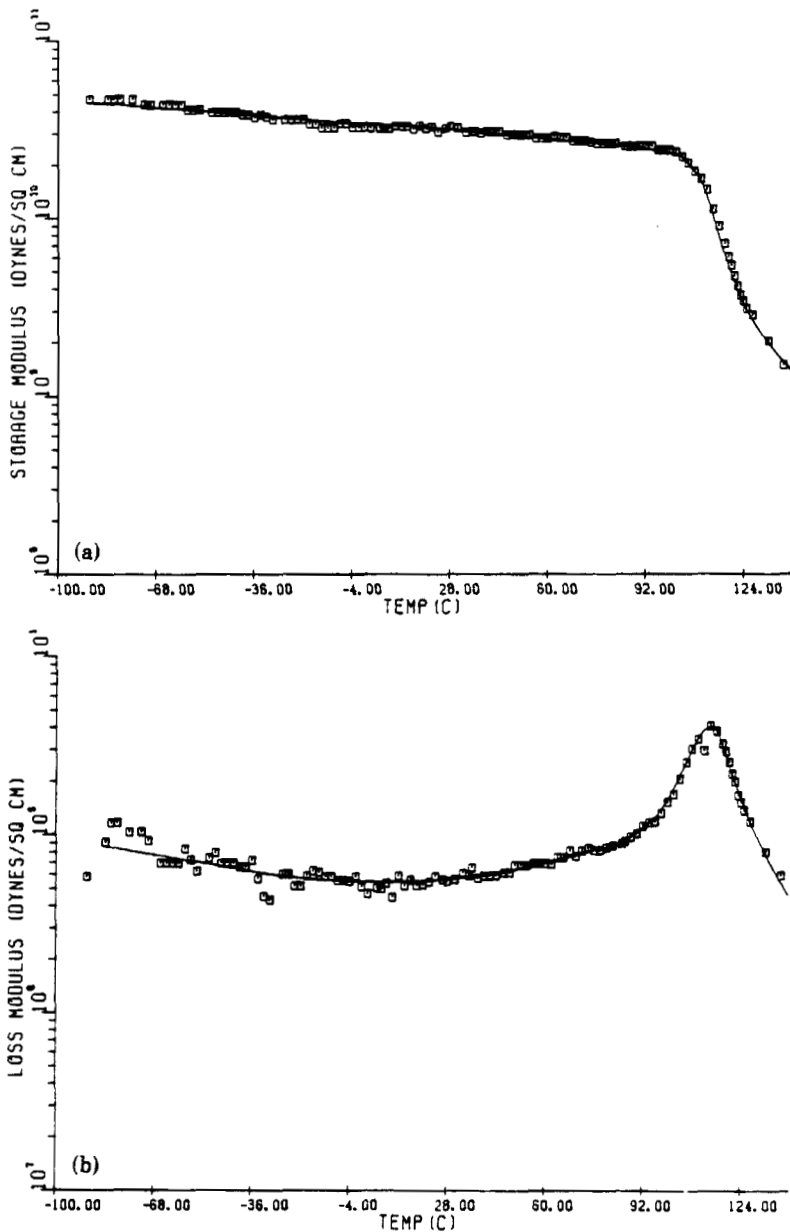


Fig. 4. Dynamic mechanical spectra of starch-*g*-PS as made, containing homopolymer PS; 3.5 Hz: (a) storage modulus; (b) loss modulus.

The molecular weights of the graft and homopolymer PS and PMA materials are comparable to those obtained by others under similar synthesis conditions.^{6,7}

More homopolymer (30–40% of the crude copolymer) could be extracted from the starch-*g*-PMA prepared here than in another study⁷ in which approximately the same starch/PMA ratio was used. This difference may be attributed to the

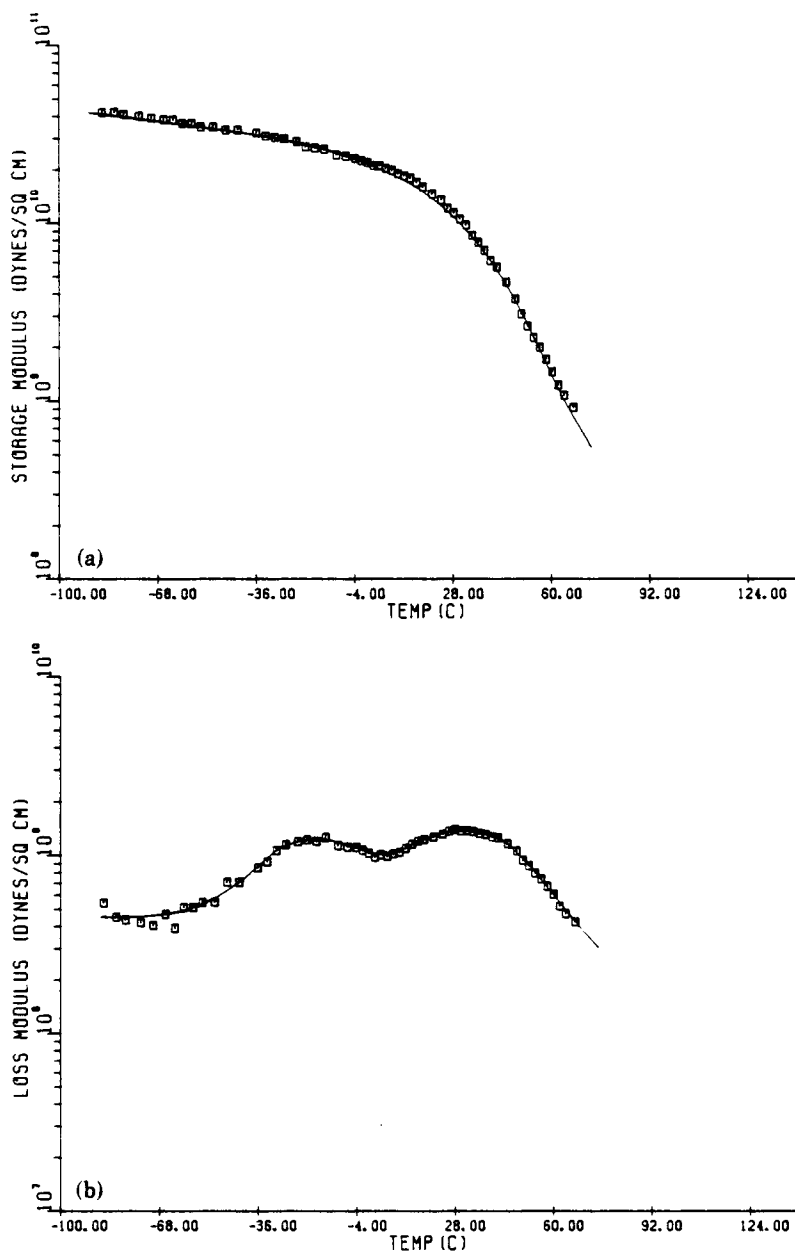


Fig. 5. Dynamic mechanical spectra of starch-*g*-PS plasticized with about 20 wt % butyl benzyl phthalate; 3.5 Hz: (a) storage modulus; (b) loss modulus.

lower ratio of starch to water used in the present work. Such variations have been shown to reduce the percent add-on of acrylonitrile to starch in Ce(IV)- and Fe(II)-H₂O₂-initiated systems.^{25,26} Another possible reason for the difference could be that the excess methyl acrylate was homopolymerized by initiation with azodiisobutyronitrile, and this initiating system gives little or no grafting onto starch.

TABLE I
 Characteristics of Graft Copolymers^a

Copolymer	% Conversion	% Add-on	% Polymer grafted	Grafting frequency, AGU/graft	Graft polymer		Homopolymer	
					Molecular weights ($\times 10^6$)	(skew) _n	Molecular weights ($\times 10^5$)	(skew) _n
Starch-g-PS	97.5 ± 0.5	46.5 ± 6	67.0 ± 7.0	6800	$M_n = 2.7 \pm 0.46$	3.7 ± 0.15	$M_n = 1.2 \pm 0.02$	4.6 ± 0.05
					$M_o = 8.7 \pm 0.38$		$M_o = 4.6 \pm 0.19$	
					$M_w = 9.6 \pm 0.39$		$M_w = 5.1 \pm 0.22$	
					$M_n = 4.5 \pm 1.4$		$M_n = 1.3$	
Starch-g-PMA	95.8 ± 1.5	45.5 ± 1.4	41.0 ± 3.9	15000	$M_o = 17.6 \pm 3.6$	5.1 ± 0.7	$M_o = 7.4$	6.7
					$M_w = 20.3 \pm 3.9$		$M_w = 8.7$	

^a Values reported are the means of two replicate experiments ± standard deviation.

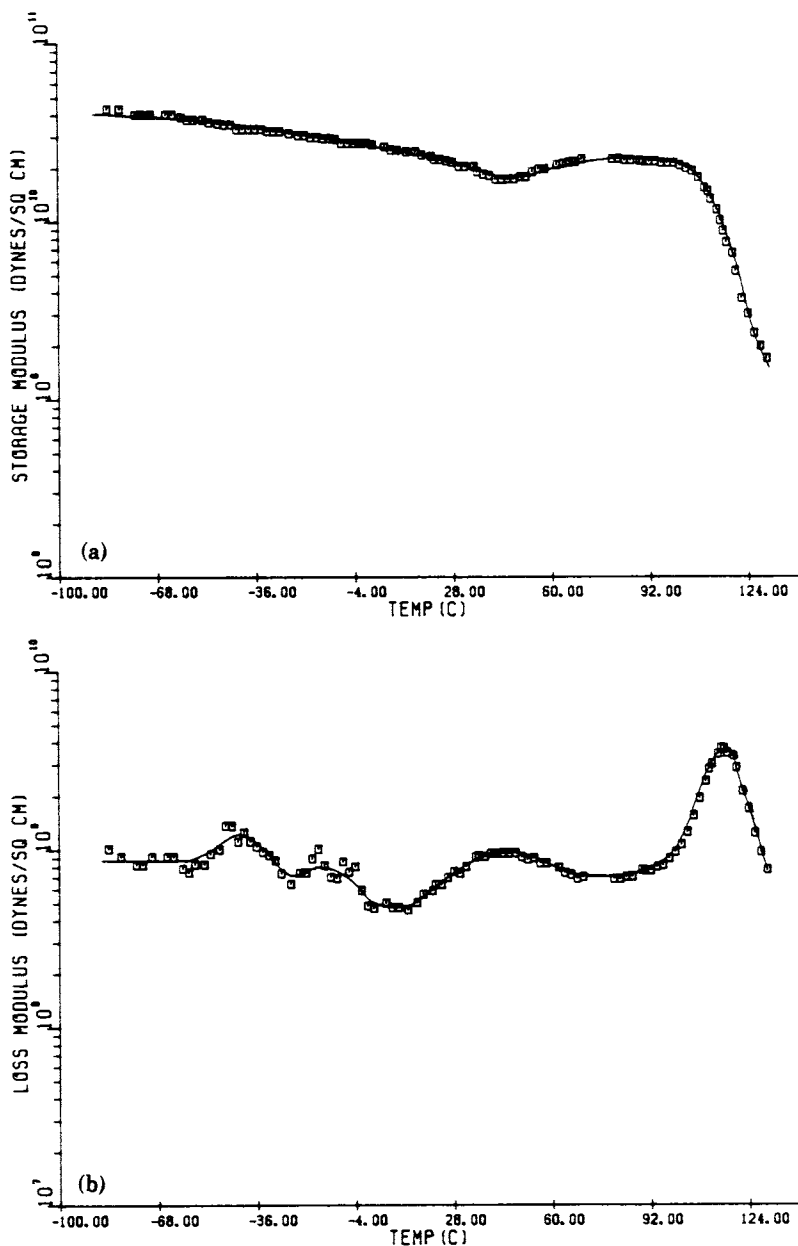


Fig. 6. Storage and loss moduli of extruded starch-*g*-PS which has been soaked 12 h in water (water content about 2.5% w/w); 3.5 Hz: (a) storage modulus; (b) loss modulus.

A single pass through the extruder produced starch-*g*-PS and starch-*g*-PMA ribbons which appeared to be homogeneous and well fused. Extrudates were classified as good if examination under 80 \times magnification with a binocular light microscope revealed a translucent structure without opaque white specks of unfluxed polymer. The ribbon surface was also required to be smooth and unblemished to the naked eye. The starch-*g*-PMA ribbons could be folded back on themselves without stress whitening.

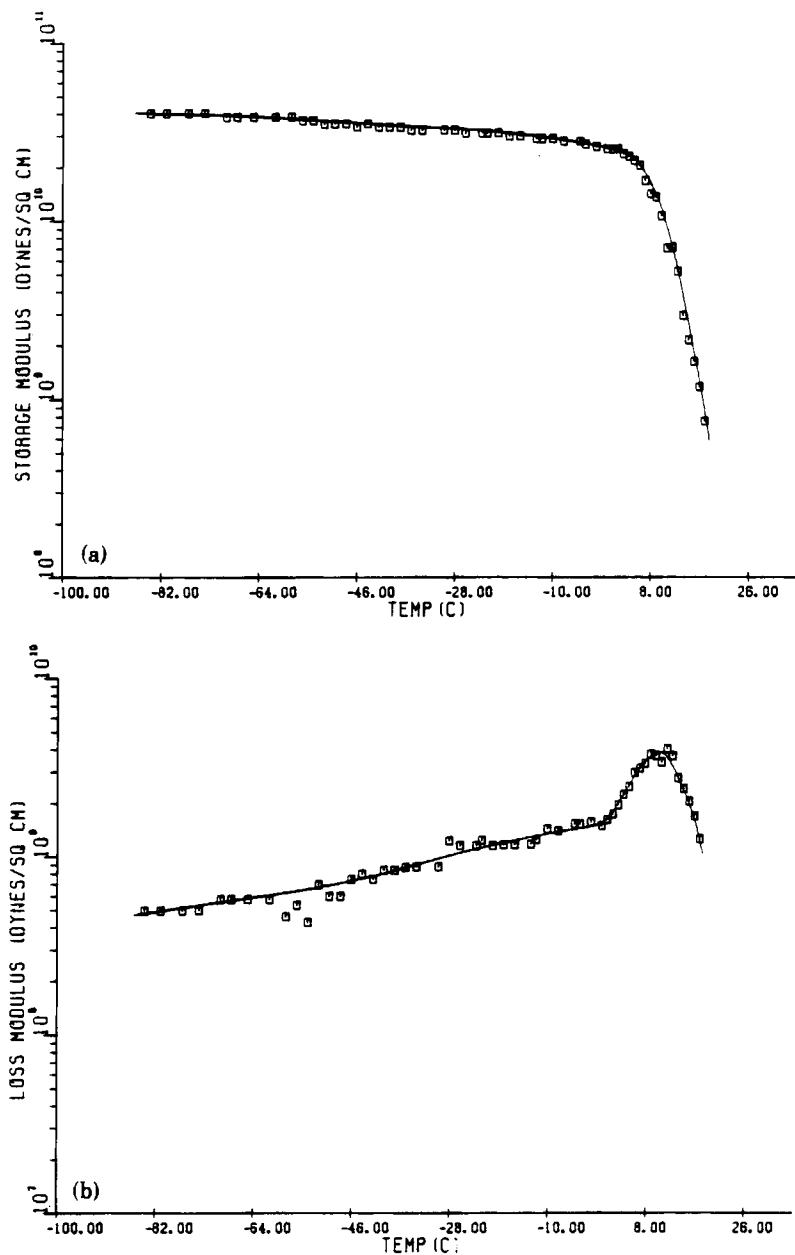


Fig. 7. Storage and loss moduli of grafted poly(methyl acrylate) after removal of attached starch; 3.5 Hz: (a) storage modulus; (b) loss modulus.

Dull spots and die scratches were detectable under magnification, especially with the starch-*g*-PS copolymer, which was extruded fairly close to the glass transition temperature of the thermoplastic portion of the copolymer. The number-average molecular weight of the polystyrene homopolymer and grafted polymer are higher than those in conventional "crystal" extrusion grades of this material, and the extruder temperature settings for the starch graft copolymer

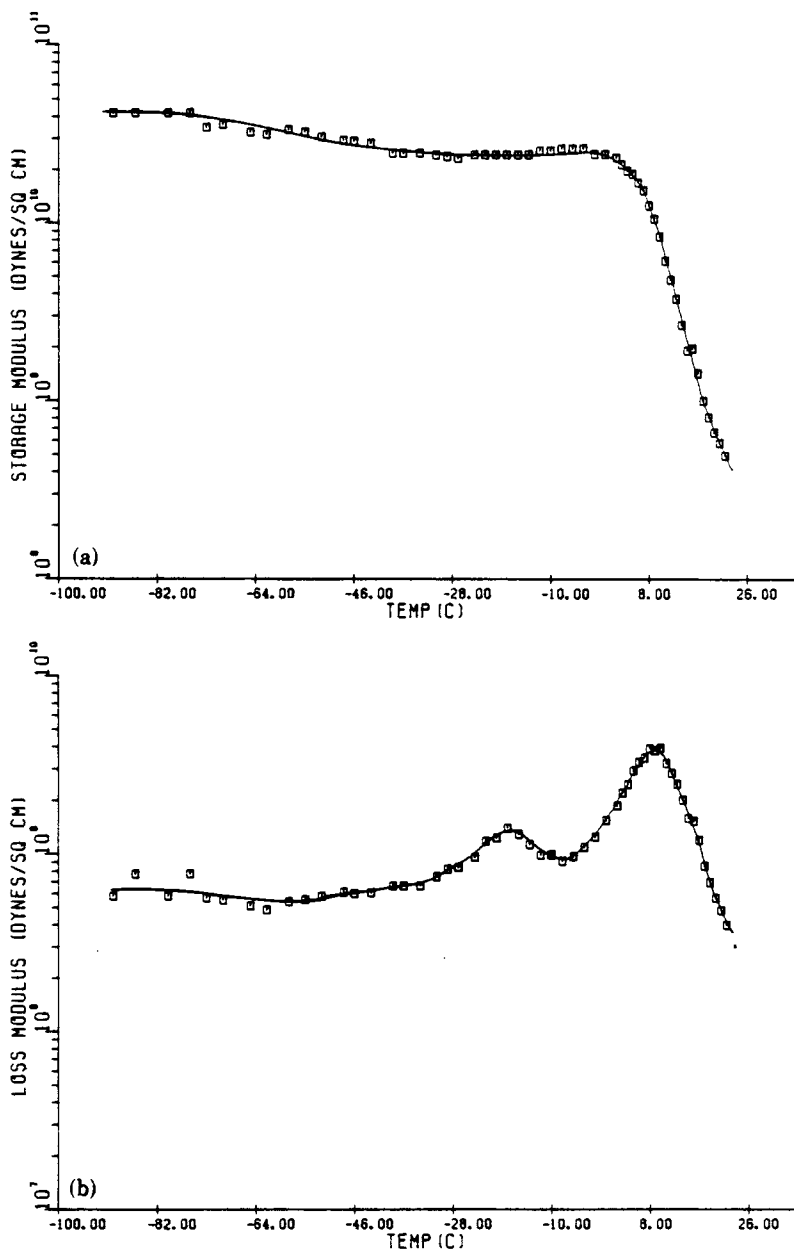


Fig. 8. Dynamic mechanical spectra of starch-*g*-PMA as made, containing homopolymer PMA; 3.5 Hz: (a) storage modulus; (b) loss modulus.

were substantially cooler than normal. It seems likely, then, that the forming process here involves a substantial sintering component. We do not believe, however, that the extrusion process is accomplished entirely by sintering of thermoplastic regions of the starch graft copolymers. Occasionally, the crude mixture of PMA homopolymer and graft copolymer would exhibit a rough, sharkskin²⁷ surface which is characteristic of the flow behavior of continuum

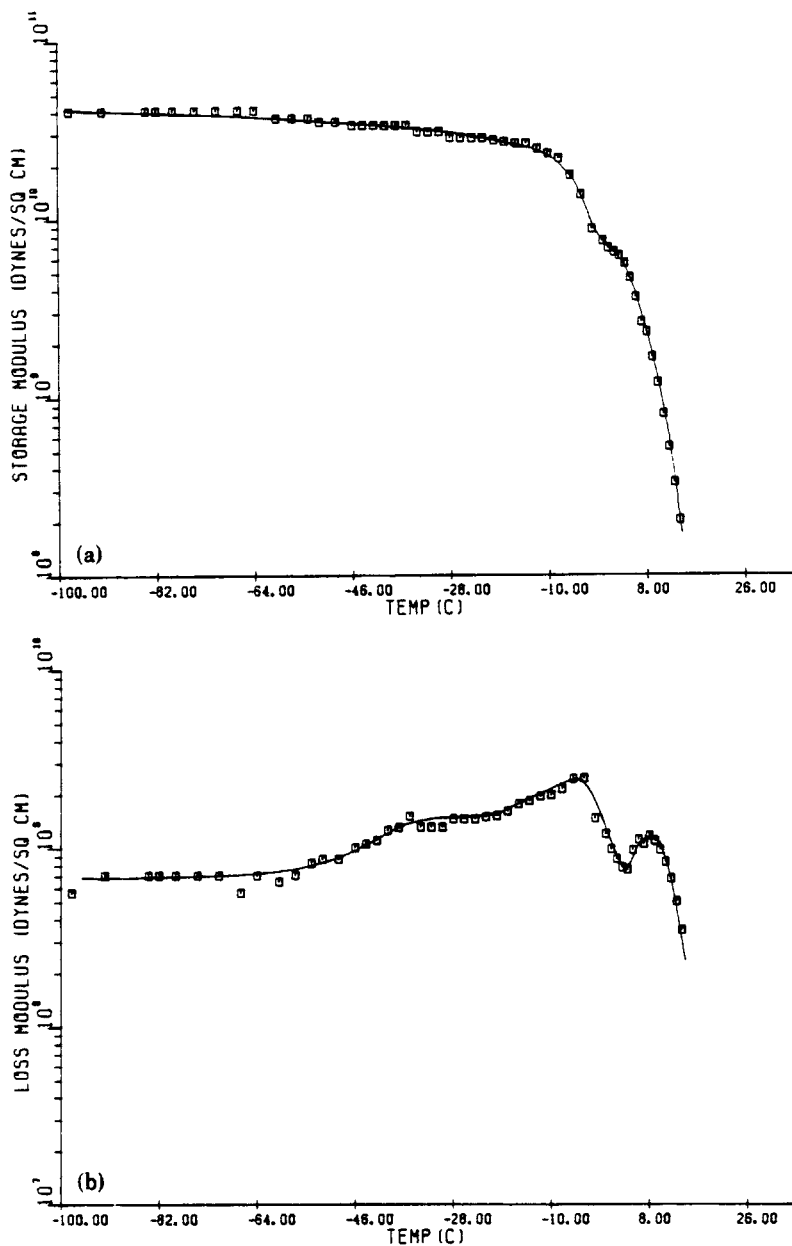


Fig. 9. Dynamic mechanical spectra of starch-*g*-PMA which had been soaked 6 h in water (water content about 33% w/w); 3.5 Hz: (a) storage modulus; (b) loss modulus.

melts of polymers. This extrusion defect could be cured, as usual, by decreasing the extruder screw speed slightly or increasing the die temperature.

The effects of soaking in water on the strengths of extruded graft copolymer ribbons are summarized in Tables II, III, and IV. The samples were soaked in deionized water in tared beakers at room temperature for the indicated periods

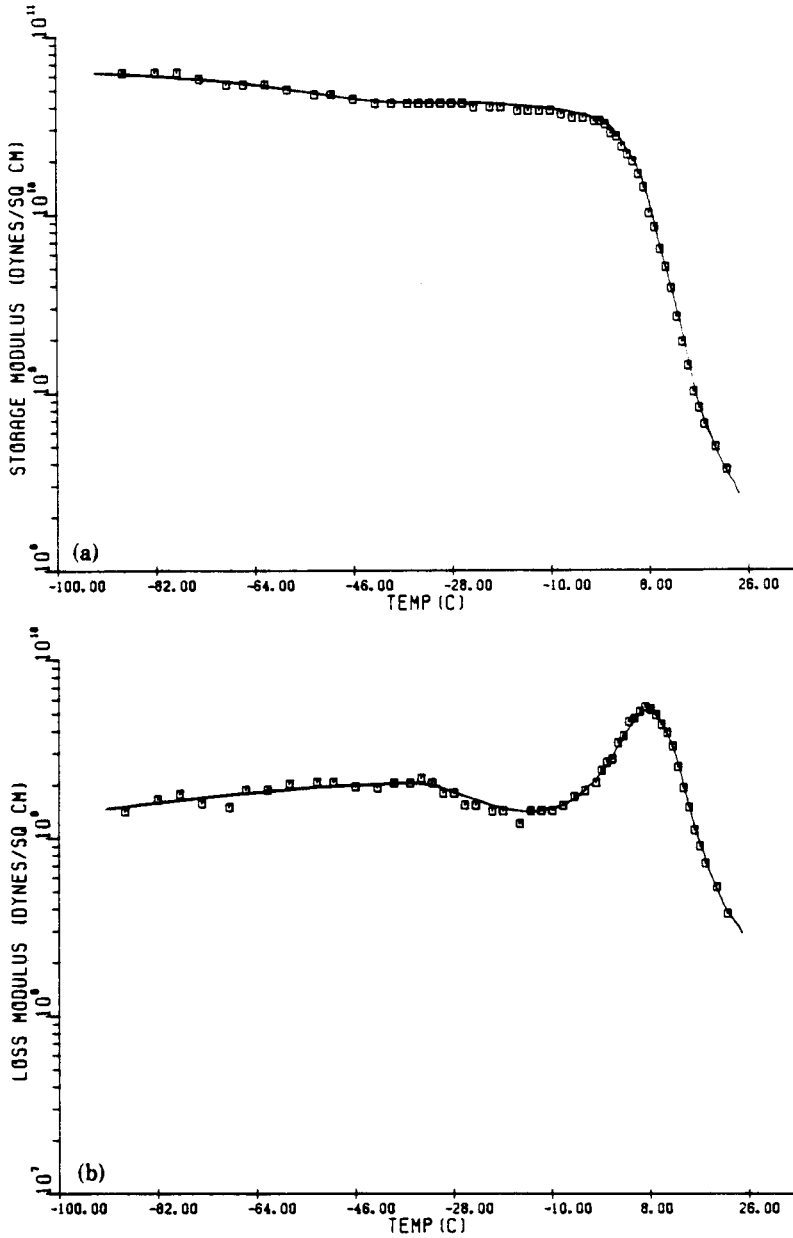


Fig. 10. Dynamic mechanical spectra of starch-*g*-PMA which had been soaked for 24 h in water and then dried at room temperature; 3.5 Hz: (a) storage modulus; (b) loss modulus.

and then dried with absorbent towelling. The parameters tabulated are

$$\% \text{ Weight gain} = \frac{\text{weight soaked sample} - \text{initial sample weight}}{\text{initial sample weight}} \times 100$$

$$\% \text{ Extractables} = \frac{\text{weight material recovered from H}_2\text{O}}{\text{initial sample weight}} \times 100$$

TABLE II
 Extruded Starch-*g*-PS: Effect of Water Absorption^a

No. of samples tested	Time in H ₂ O, h	Cross-sectional area, m ² (× 10 ⁻⁶)	Weight gain, %	Extractables, wt %	Ultimate tensile strength, MN/m ²
8	0	10.42 ± 0.04	—	—	35.3 ± 3.2
1	1	10.68	0.6	—	38.0
4	6	10.62 ± 0.04	1.4 ± 0.2	—	29.9 ± 1.2
2	12	10.75 ± 0.05	2.5 ± 0.1	~0.3 ± 0.2	28.7 ± 0.8
4	24	10.78 ± 0.09	3.4 ± 0.4	—	27.9 ± 2.3
4	48	10.82 ± 0.09	5.6 ± 0.2	~0.2 ± 0.1	23.9 ± 1.8
4	240	11.08 ± 0.15	8.9 ± 0.9	—	19.3 ± 0.9
6 ^b	0				27.5 ± 2.3
3 ^c	0				29.9 ± 2.5

^a Values reported are means ± standard deviations.

^b Injection molded specimens from extruded sample.

^c Injection molded specimens from powder sample.

% H₂O retention

$$\begin{aligned}
 & \text{weight dried soaked sample} - (\text{initial sample weight} \\
 & \quad - \text{weight material recovered from H}_2\text{O}) \\
 = & \frac{\quad}{\text{initial sample weight}} \times 100
 \end{aligned}$$

The weight of material recovered from the water was taken to be the weight increase of the respective containers after removal of the polymer samples and evaporation of the water. The data in the tables are average values plus or minus the standard deviation of the indicated number of replicate trials.

The tensile strength of extruded dry starch-*g*-PS samples is in the lower range characteristic of general-purpose polystyrene, while that of starch-*g*-PMA ribbons is comparable to that of commercial acrylate elastomers. The last entries in Tables II and III record tensile strengths of graft copolymers which had been injection molded as described in the experimental section.

It has been noted^{6,8} that strengths of starch graft copolymers reflect the influence of processing history on the degree of fusion of the specimens. Flow lines were visible in the PS graft copolymer moldings but not in the PMA specimens,

 TABLE III
 Extruded Starch-*g*-PMA: Effect of Water Absorption^a

No. of samples tested	Time in H ₂ O, h	Cross-sectional area, m ² (× 10 ⁻⁶)	Weight gain, (%)	Extractables, wt %	Ultimate tensile strength, MN/m ²	Ultimate elongation, %
4	0	2.24	—	—	14.3 ± 1.9	70 ± 25
3	1	2.63 ± 0.03	19 ± 1.7	2.3 ± 0.7	3.8 ± 0.5	330 ± 115
3	6	2.97 ± 0.09	33 ± 3.2	3.6 ± 1.1	3.0 ± 0.3	275 ± 66
3	12	3.07 ± 0.12	38 ± 4	4.8 ± 2.1	3.0 ± 0.4	316 ± 80
3	24	3.08 ± 0.12	38 ± 6	6.0 ± 3.2	3.1 ± 0.5	330 ± 104
3	48	3.04 ± 0.25	29 ± 8	10.1 ± 4.1	3.0 ± 0.4	350 ± 108
3	240	3.02 ± 0.22	25 ± 10	12.4 ± 5.1	2.4 ± 0.2	290 ± 120
5 ^b	0				12.5 ± 1.2	150 ± 20
5 ^c	0				10.6 ± 0.28	140 ± 40

^a Values reported are means ± standard deviations.

^b Injection molded specimens from extruded sample.

^c Injection molded specimens from powder sample.

which were formed at temperatures relatively higher than the glass transition temperature of the thermoplastic component. Frozen-in stresses are more likely, therefore, in the PS graft copolymer samples, and this may be evidenced in the slightly lower strength of molded PS samples compared to extruded materials.

Injection-molded starch-*g*-PS specimens exhibited essentially the same strengths whether or not the material had been extruded previously (Table II). This is not the case for injection-molded starch-*g*-PMA, where prior extrusion produced somewhat stronger specimens (Table III). This difference probably reflects the quality of dispersion of starch in the two graft copolymers. The PMA graft was noticed to have more starch or starch-*g*-PMA agglomerates than the PS graft. Such agglomerates were apparently better dispersed in the screw extruder than in the ram injection molder. PMA graft copolymer specimens molded from powder were observed to contain opaque specks which were not present in the test pieces molded from extruded ribbons.

The starch graft copolymers swelled in water as evidenced in the increases in cross-sectional areas and weight gains recorded in Tables II and III. A negligible amount of material was extracted from the PS copolymers, which continued to absorb increasing amounts of water during the entire 10-dry soaking period.

Starch-*g*-PMA samples swelled proportionately more than the PS copolymers and gained more weight. More material was also extracted from the PMA specimens into the water medium.

Three different extrusion batches of starch-*g*-PMA were tested. One of these was browner than the other two because of greater degradation of starch in the extruder. The mechanical properties of this batch were the same as those of the other two trials, but the darker product lost more extractable material after 24 h of water soaking. As a consequence, its degree of swelling and net weight gain were diminished. This difference probably reflects a greater water solubility of starch degradation products. Some extruded starch-*g*-PMA samples which were much darker than the samples reported in Table III developed surface blisters after immersion for several days in water. Starch-*g*-PS ribbons that were extruded before processing conditions were optimized were browner than the samples of Table II and cracked after water soaking for several days. The off-white ribbons of Table II did not exhibit this behavior. These observations emphasize the importance of avoiding starch degradation in the processing of these graft copolymers.

Both copolymer types were weakened considerably by soaking in water. The effect was more immediate and drastic for starch-*g*-PMA, where the tensile strength decreased very rapidly after 1 h of immersion to a value which changed relatively little thereafter. The elongation of this graft copolymer increased fourfold concurrently and became similar to that of acrylate elastomers. The very low strength of wet starch-*g*-PMA products precludes their use for many applications but may be an advantage for end uses such as agricultural mulch film.⁷

Polystyrene is more hydrophobic than poly(methyl acrylate), but even the starch-*g*-PS copolymers were plasticized by water. Dry samples of this material tended to break near the clamps in tensile tests, showing evidence of the notch sensitivity characteristic of polystyrene. Thoroughly wetted specimens generally broke between the clamps, however, although their breaking elongation was not measurably increased over that of dry products.

TABLE IV
Properties of Soaked, Extruded Copolymers after Drying^a

Copolymer	No. of samples tested	Time in H ₂ O, h	Extractables, wt %	H ₂ O retention, wt %	Ultimate tensile strength, MN/m ²	Increase in cross-sectional area, %	Elongation, %
Starch-g-PS	6	240	~0.2 ± 0.1	—	35.2 ± 4.0	~0.4 ± 0.2	— ^b
Starch-g-PMA	6	24	4.8 ± 2.0	0.4 ± 0.2	16.5 ± 2.5	14.0 ± 3.6	250 ± 60
Starch-g-PMA	6	240	8.1 ± 5.0	0.3 ± 0.07	13.0 ± 2.0	12.0 ± 6.4	295 ± 90

^a Values reported are averages ± standard deviations.

^b Starch-g-PS samples broke with very low elongations (<3%) which could not be measured accurately.

Table IV records the results of tensile tests on extruded copolymer ribbons which had been soaked and then dried at room temperature. Both copolymers regained their original tensile strengths during the drying process. The cross-sectional areas of starch-*g*-PMA samples remained significantly higher than their initial dimensions before exposure to water. It is also remarkable that the breaking elongations of these products remained nearly as high as in the water-soaked condition. This could result from the plasticizing effect of slight amounts of water retained in the graft copolymer after two weeks of drying under ambient conditions (Table IV). It should also be noted that 10–35% of the starch had been extracted from the crude copolymer samples by soaking in water. This process would produce an expanded structure which may facilitate the motion of segments of PMA and contribute to the enhanced ductility of the material.

Scanning electron micrographs of cross sections of starch-*g*-PMA as extruded and after soaking 24 h in water and subsequent drying are shown in Figures 1 and 2, respectively. The material which had been soaked appears to be more pitted than the unsoaked material. The size of the large pit near the center of Figure 2(c) measures 0.4 cm in diameter under 15000 \times magnification, indicating that its actual diameter is approximately 0.3×10^{-4} cm. This is much smaller than the granule size of wheat starch, which has two populations, 2–10 $\times 10^{-4}$ and 20–35 $\times 10^{-4}$ cm.²⁸ The granules were gelatinized during the copolymer synthesis, which causes some breakdown in granule structure.²⁹ Shearing during extrusion would also tend to break down the granules. Therefore, the observed pits in the SEM photographs of the soaked extruded starch-*g*-PMA could result from the leaching out of starch from the copolymer.

Photographs of the cross sections of extruded starch-*g*-PS and copolymer which had been soaked for 24 h in water and then dried were indistinguishable. An insignificant amount of material was leached out of this copolymer.

Figures 3 and 4 contain dynamic mechanical results for grafted PS isolated by starch hydrolysis and crude starch-*g*-PS, respectively. Both materials have identical storage moduli in the glassy state, but the stiffness of the grafted material decays less rapidly in the glass–rubber transition region. This is presumably so because attachments to starch entities hinder the motions of polystyrene segments. The only transition evident in Figures 3 and 4 is the main glass transition of polystyrene.

The dynamic mechanical properties of starch-*g*-PS plasticized with about 20 wt % butyl benzyl phthalate are summarized in Figure 5. The plasticizer was mixed with the preextruded copolymer on a two-roll mill at 165°C. Butyl benzyl phthalate is a plasticizer for the polystyrene portion of the graft copolymer, and the transitions have been moved to lower temperatures and spread over a wide temperature range. This is as expected since motion of polystyrene segments is facilitated by the plasticizer and restricted by the anchored starch component. The loss modulus exhibits two broad maxima centered at about 36 and -18°C . The authenticity and cause of the latter transition are not clear.

The storage and loss modulus curves of extruded starch-*g*-PS which had been soaked in water for 12 h are shown in Figure 6. The main damping peak at about 120°C (at the experimental frequency) is the T_g of high-molecular-weight polystyrene, as in Figure 4. A secondary peak seems to occur around 48°C, and a third transition may be present in the neighborhood of -40°C . The storage modulus curve also dips in the temperature region near 48°C. These observa-

tions seem to be evidence for plasticization of the graft copolymer by water. This action presumably occurs preferentially in the starch-rich regions. The behavior of the material at the higher-temperature secondary transition may be complicated by the effects of a simultaneous evaporation of water from the specimen. The low-temperature secondary transition ($\sim -40^{\circ}\text{C}$) is likely due to water itself.³⁰

Figures 7 and 8 compare the dynamic mechanical responses of PMA isolated by starch hydrolysis and starch-*g*-PMA, respectively. The main glass-rubber transition of poly(methyl acrylate) is not significantly broadened to higher temperatures by the effects of attached starch moieties in this case. This difference from the polystyrene grafts mentioned above is probably due to the inherent greater flexibility of poly(methyl acrylate) tie molecules between starch fragments as well as the high average molecular weight of the grafted poly(methyl acrylate). Anchorages on starch will have less effect on the mobility of intervening thermoplastic molecules the more widely spaced the attachments and the shorter the natural segment length for motion in these tie molecules are.

The graft copolymer exhibits two transitions, as opposed to only one in the detached poly(methyl acrylate). The main transition at about 8°C is the T_g of PMA, while the secondary transition centered near -18°C may be due to water.

The dynamic mechanical spectrum of a sample of starch-*g*-PMA which had been soaked in water for 6 h is shown in Figure 9. The effect of water here is that of a typical plasticizer, as can be seen by comparing Figures 7(a) and 9(a). The "water" peak in the loss modulus of Figure 8(b) is much broader in the corresponding spectrum of the wet graft copolymer in Figure 9(b).

Figure 10 shows the spectra of starch-*g*-PMA which had been soaked 24 h in water and then allowed to dry at room temperature. The storage modulus curve [Figure 10(a)] is not significantly different from that of as-extruded material in Figure 8(a). It will be remembered that the dried material had a much higher elongation at break than the initial as-extruded material and had lost about 10–20% of its starch during its exposure to water. This loss could explain the absence of a significant secondary damping peak in this copolymer sample.

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