A New Biodegradable Plastic Made from Starch Graft Poly(methyl Acrylate) Copolymer

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Synopsis

A starch graft poly(methyl acrylate) copolymer was developed having grafted side chains with molecular weight of less than 500,000. This material can be easily extruded into a film which shows excellent initial tensile strength and elongation. Tensile strength, however, falls off rapidly after 70 hr of water immersion at 25°C. Starch graft poly(methyl acrylate) films show excellent susceptibility to fungal growth, some samples losing more than 40% of their weight after 22 days of incubation with *Aspergillus niger*. Tensile tests and scanning electron micrographs of the incubated samples, after being freed of mycelium, indicate substantial biodegradation of the starch portion of the copolymer. This material may have application as a biodegradable plastic mulch.

INTRODUCTION

Plastic films for agricultural mulching have become increasingly important in recent years. They are used to control weeds, to conserve soil moisture and heat for early cropping, and to reduce nutrient leaching. These films are used most often for the production of truck crops such as tomatoes, strawberries, peppers, and okra where increases in yield provide a large monetary advantage. Plastic mulch has found widespread use in Florida[1] because weeds and nutrient leaching are major problems for many truck crops.

Plastic mulch is applied to the field after the soil is prepared, and then plants are set through holes punched in the plastic. Polyethylene film is the most common plastic, but its use presents a disposal problem. Since it does not decompose during the growing season, it must be removed from the field in the fall at a cost of $70–100/acre. It is either buried, burned, or dumped after removal from the field. Vegetable growers would like to be able to use a plastic mulch that would degrade between growing seasons in order to eliminate mulch removal expenses.

Several workers have been active in pursuing this goal. Griffin[2] reports that a starch-filled polyethylene film becomes porous after starch extraction. This porous film is readily invaded by microorganisms and rapidly saturated with oxygen, thereby increasing degradation by biologic and oxidative pathways.

Otey et al.,[3] in a study on starch-based films, found that a starch–poly(vinyl alcohol) film could be coated with a thin layer of water-resistant polymer to give a degradable agricultural mulching film.

In this study, we found that starch graft poly(methyl acrylate) (S–*g*–PMA), which can be extruded to give a film, shows excellent susceptibility to fungal attack in a moist environment. In preliminary work, Gugliemelli[4] prepared S–*g*–PMA at 1:1 and 1:2 starch:poly(methyl acrylate) levels and masticated it

Journal of Applied Polymer Science, Vol. 22, 459–465 (1978)

0021-8995/78/0022-0459$01.00

on cold rolls of a rubber mill to form films resembling polyethylene in appearance, feel, flexibility, and toughness. However, no quantitative physical properties or biodegradation rates were determined.

EXPERIMENTAL

Preparation of Starch Graft Poly(methyl Acrylate)

Pearl corn starch (58 g) was added to 750 ml water and heated to 40°C under nitrogen. Distilled methyl acrylate (133 g) was added to the starch slurry. Grafting sites were initiated on the starch by the addition of ceric ammonium nitrate dissolved in 1*N* HNO_3 (2.5 ml 1*N* HNO_3 per gram of $Ce(NH_4)_2(NO_3)_6$). Equal portions of the initiator solution were added over a period of 1 hr at 15-min intervals. This mixture was allowed to react for 2 hr after the final initiator addition. The product was collected by filtration, washed several times in water, and air dried. Samples typically contained 5–10% homopolymer as determined by extraction with toluene.

Film Preparation

The dry powdery S–*g*–PMA was fed into a ¾-in. Brabender Plasticorder extruder equipped with a 15:1 length-to-diameter barrel which had two independent temperature-controlled zones. A temperature-controlled slit die with an opening of 0.5 mm was fitted to the barrel. The screw had a compression ratio of 3:1 and was operated at 50 rpm. The temperature of the barrel was maintained at 115°C and 140°C for zones 1 and 2, respectively. The die was maintained at 140°C. The extruded film was cut into dumbbell-shaped tensile pieces (4 mm × 8 cm) and physical properties were determined on an Instron testing machine at a cross-head speed of 5 cm/min.

Biological Testing

Replicate tensile strips of each formulation were placed on the surface of nutrient-salts agar [KH_2PO_4, 0.7 g; K_2HPO_4, 0.7 g; $MgSO_4 \cdot 7H_2O$, 0.7 g; NH_4NO_3, 1.0 g; NaCl, 0.005 g; $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 0.003 g; $ZnSO_4 \cdot 7H_2O$, 0.002 g; $MnSO_4 \cdot H_2O$, 0.0006 g; and agar 15.0 g per liter of distilled H_2O with pH adjusted to 6.0] in Petri dishes and inoculated on the surface with 0.1-ml spore suspensions of the standard test organisms[5] *Aspergillus niger,* NRRL 3536; *Penicillium funiculosum,* NRRL 3503; and *Trichoderma viride,* NRRL 2314. Spore suspensions (about 10^6/ml) were prepared by washing conidia from 2-week old Czapek's agar ($NaNO_3$, 3.0 g; K_2HPO_4, 1.0 g; $MgSO_4 \cdot 7H_2O$, 0.5 g; KCl, 0.5 g; $FeSO_4 \cdot 7H_2O$, 0.01 g; sucrose, 30 g; agar, 15 g per liter distilled H_2O) slants with distilled H_2O containing 0.005% Triton X-100 Appropriate controls were also included, e.g., uninoculated strips on agar plates and agar alone. All plates were incubated at 25°C for 22 days and growth was evaluated visually throughout incubation. After incubation, the strips were washed free of spores and mycelium with a dilute (1/100 v/v) Lysol solution and air dried. The degree of degradation or starch utilization was determined via tensile test and scanning electron micrographs.

TABLE I
Effect of Ceric Ion Concentration on Side-Chain Molecular Weight and Copolymer Physical Properties

Sample no.	Moles Ce(IV) $\times 10^3$	% PMA[a]	Mol. wt. of PMA $\times 10^{-5}$	S–g–PMA[b] UTS,[c] MN/m^2	Elongation, %
1	3.28	58.8	9.36	9.27	30
2	8.89	62.5	6.35	15.62	55
3	13.68	65.6	4.65	22.06	200
4	17.79	67.5	5.44	24.31	265
5	26.64	65.2	3.47	22.02	225
6	35.58	64.8	2.73	22.37	255
7	43.79	64.9	3.58	18.96	240
8	71.17	66.1	2.52	22.69	255

[a] PMA = Poly(methyl acrylate).
[b] S–g–PMA = Starch graft poly(methyl acrylate).
[c] UTS = Ultimate tensile strength.

Side-Chain Separation and Viscosity Measurements

Grafted side chains were removed from the starch backbone by the procedure of Dennenberg and Abbott.[6] Approximately 2 g of S–g–PMA were weighed accurately and added to 100 ml glacial acetic acid; the mixture was stirred for 1 hr at 90°–100°C to swell the grafted side chains. Two milliliters perchloric acid (60%) then were added dropwise, and within 1–2 min the mixture became a clear solution. The reaction products were immediately poured into ice water to precipitate the poly(methyl acrylate) (PMA) side chains. The polymer was washed in water and dried in a vacuum oven, and weight per cent PMA in the original sample was calculated.

The recovered PMA side chains were dissolved in acetone in preparation for intrinsic viscosity measurements. Viscosity measurements were run in a constant temperature bath (±0.1°C) at 20°C with Cannon No. 75 viscometers. Each viscosity was determined at four different dilutions. Molecular weights were calculated by using the Mark–Houwink equation $[\eta] = KM^a$ for PMA determined by Staudinger,[7] where $K = 7.4 \times 10^{-5}$ dl/g and $a = 0.76$.

TABLE II
Effect of 70 Hours of H_2O Immersion on Physical Properties of S–g–PMA

			70 hr H_2O immersion	
Sample no.	UTS, MN/m^2	Elongation, %	UTS, MN/m^2	Elongation, %
2	15.62	55	5.10	310
4	24.31	270	4.41	535
5	22.02	225	4.00	520
6	22.37	255	4.58	535

RESULTS AND DISCUSSION

S–*g*–PMA samples were prepared using various amounts of $Ce(NH_4)_2(NO_3)_6$ as the free-radical initiator on the starch backbone. All other reaction variables were held constant. Results of a somewhat similar experiment reported by Burr et al.[8] for starch graft polyacrylonitrile show no change in the number of chains grafted with a 25-fold increase in ceric ion concentration. However, in our study with approximately a 25-fold increase in ceric ion concentration, we observed a four-fold increase in the number of grafted chains. Table I shows the calculated molecular weight of the isolated PMA side chains as a function of ceric ion concentration. The molecular weight of the grafted side chains varied from nearly $\overline{M}_v$ = 1,000,000 with 0.00328 moles of Ce(IV) ion initiator down to $\overline{M}_v$ = 250,000 with 0.07117 moles of Ce(IV) ion. Molecular weight is seen to decrease with increasing Ce(IV) ion concentration. It is reasonable to expect greater Ce(IV) ion concentration to initiate greater numbers of free-radical grafting sites on the

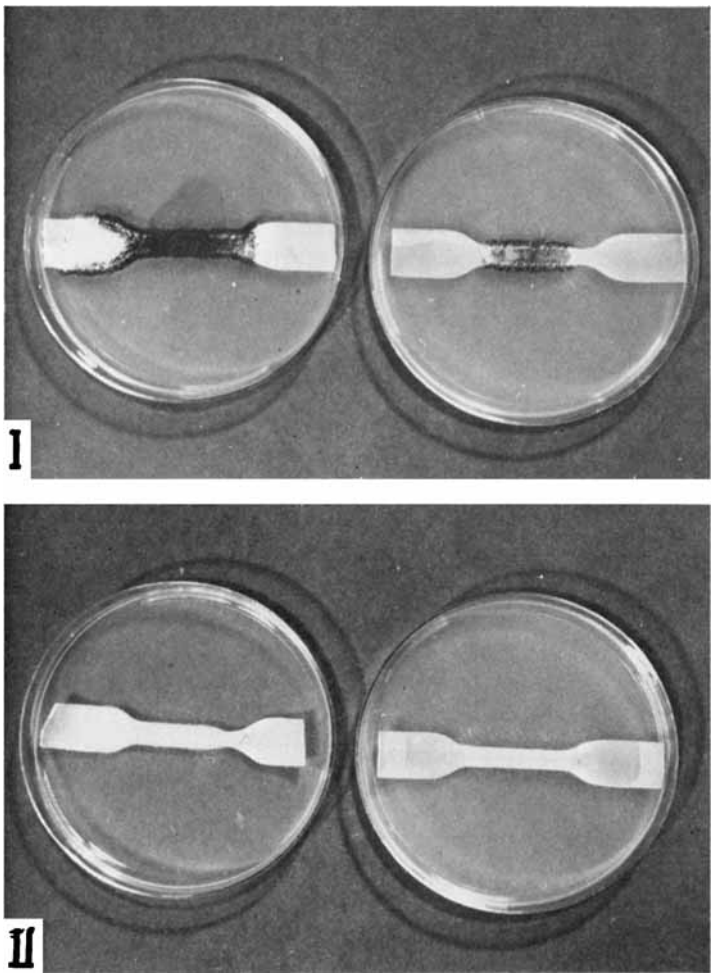

Fig. 1. Biodegradation of starch graft poly(methyl acrylate) after five days: (I) *Aspergillus niger* on copolymer A containing 50% starch (left) and on copolymer B containing 40% starch (right); (II) *Penicillium funiculosum* on copolymer A (left) and on copolymer B (right).

starch backbone. Increases in Ce(IV) concentration in solution can also cause chain termination of polymer radicals which would yield lower molecular weight products.

Table I also reports the ultimate tensile strength and the elongation at break of S–*g*–PMA as a function of Ce(IV) ion concentration. All samples, except the one prepared with 0.00328 mole Ce(IV) ion, have nearly the same composition as indicated by the per cent PMA reported in column 3. The data indicate that the physical properties of the S–*g*–PMA increase significantly with increasing Ce(IV) ion initiator. Hence, as the molecular weight of the grafted side chain decreases, the UTS and per cent elongation at break increase. The trend, however, is not constant and appears to reach a plateau. The best physical properties were obtained when the PMA grafts had a molecular weight of $\overline{M}_v$ = 500,000 or less.

Physical properties of S–*g*–PMA compare favorably with the plastic films already in use in the agricultural field. Low-density polyethylene with UTS of

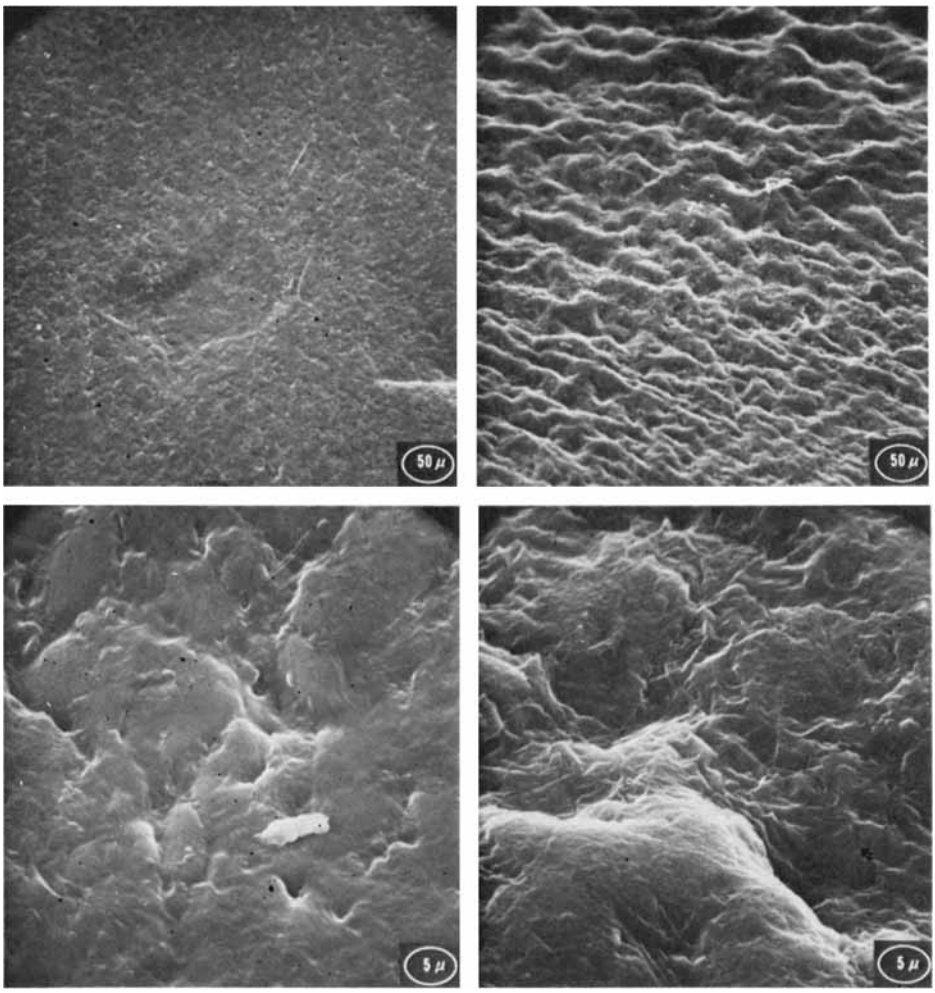

Fig. 2. Scanning electron micrographs of copolymer A before inoculation (left) with *Penicillium funiculosum* and after incubation for 22 days (right). Top micrographs are enlarged 200×; bottom micrographs are enlarged 2000×.

TABLE III
Weight Loss and Tensile Properties of Biodegraded S–*g*–PMA

Copolymer[a]	Inoculum[b]	Weight loss, %	UTS,[c] MN/m^2	Elongation, %
A	NRRL 3503	37.5	4.14	195
A	NRRL 3536	40.0	8.41	40
A	NRRL 2314	16.9	7.52	500
A	none[d]	10.2[e]	10.10	25
A	control	—	20.44	35
B	NRRL 3503	12.9	5.93	170
B	NRRL 3536	16.0	5.34	95
B	NRRL 2314	12.4	5.65	215
B	none[d]	0.0	8.03	55
B	control	—	11.82	50

[a] Copolymer A contains 50% starch and copolymer B 40% starch.
[b] *Aspergillus niger,* NRRL 3536; *Penicillium funiculosum,* NRRL 3503; *Trichoderma viride,* NRRL 2314.
[c] Specimens were washed and air-dried before testing.
[d] Incubated for 22 days at 25°C without inoculum.
[e] Specimens were naturally contaminated with mold.

13.79 MN/m^2 and 500% elongation at break is commonly used as a mulch.[9] Also these films are little affected by biodegradation during soil burial as determined by per cent weight loss.[10] S–*g*–PMA films exhibit these high initial strengths and elongations necessary for field applications when dry; however, their strength decreases rapidly on exposure to moisture. Samples with dry strengths of 20.68 MN/m^2 or more lost 80% of their strength after 70 hr of water immersion at room temperature. Elongation increased by a factor of 2. Some typical values are given in Table II.

Biologic degradation was observed during the following series of experiments. Two S–*g*–PMA films were cut into tensile strips and inoculated with *Aspergillus niger, Penicillium funiculosum,* and *Trichoderma viride.* The two samples differed by their starch content; copolymer A contained 50% starch while copolymer B was 40% starch by weight.

With only the starch as a readily available carbon source, excellent growth and sporulation was observed in five days on copolymer A with *A. niger,* whereas good growth but less sporulation was noted with *P. funiculosum* and *T. viride.* Copolymer B produced less growth and sporulation than did copolymer A in all cases. These results are illustrated in Figure 1 for *A. niger* and *P. funiculosum.*

Values of weight loss, ultimate tensile strength, and elongation were observed for copolymers A and B after 22 days of incubation at 25°C for the organisms mentioned above. These values are tabulated and compared to controls in Table III. Weight loss was assumed to be due to utilization of the starch portion of the copolymer because of the relatively short incubation period used in this study and the well-known ability of starch to biodegrade.

The data for per cent weight loss indicate excellent utilization of the starch portion of the copolymer by *P. funiculosum* and *A. niger* for copolymer A (50% starch). Moderate utilization was observed for copolymer A by *T. viride* and

for copolymer B (40% starch) by all three organisms. Tensile strength showed substantial decreases from the controls of both copolymers with all organisms tested. No major trends were observed for per cent elongation-at-break measurements.

Scanning electron micrographs were taken of copolymer A before and after incubation for 22 days with *P. funiculosum*. Figure 2 shows the degraded sample and the control at 200× and 2000×. The incubated sample shows extensive pitting and erosion of material. Presumably, these pits are caused by the utilization of the starch portion of the copolymer as a carbon source by the microorganism.

CONCLUSIONS

A S–*g*–PMA copolymer with grafted side chains of $\overline{M}_v$ = 500,000 or less exhibits excellent initial physical properties suitable for mechanized application to vegetable fields. Strength decreases rapidly on exposure to moisture and common test molds. This rapid decrease in strength should not adversely affect a mulch film, since high strength is important only during application. Utilization of the starch portion of the copolymer by the fungi increases the surface area of the PMA, which should increase its susceptibility to microbial and oxidative degradation.

The authors are indebted to F. L. Baker for scanning electron micrographs.

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Received November 1, 1976
Revised December 13, 1976