

Properties of Starch-*graft*-Poly(glycidyl methacrylate)-PHBV Composites

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ABSTRACT: The use of graft copolymers of starch and glycidyl methacrylate (starch-*g*-PGMA) to improve the mechanical properties of composites with poly(hydroxy butyrate-*co*-valerate) (PHBV) has been investigated. In general, the tensile and flexural strengths of the composites were greater with starch-*g*-PGMA compared to untreated starch and increased with increasing graft content. The modulus and elongation were not significantly changed by grafting. All samples gained weight after immersion in water for 28 days. Tensile strength and modulus decreased with water sorption, while the fracture toughness significantly increased with grafted starch. No differences were observed between properties of grafts prepared with ceric ammonium nitrate or ferrous sulfate-peroxide graft initiators. Scanning electron micrographs of cryogenic fracture surfaces showed improved adhesion between the starch-*g*-PGMA and the PHBV matrix. Although no spectroscopic evidence of reaction between PHBV and the starch-*g*-PGMA was found, the improvement in mechanical properties is consistent with enhanced interactions between the starch-*g*-PGMA and the PHBV matrix compared to ungrafted starch. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1121–1127, 1998

Key words: starch; graft copolymer; PHBV; composite; mechanical properties

INTRODUCTION

Poly(hydroxy alcanoates), or PHAs, have received considerable attention in recent years as biodegradable alternatives to synthetic thermoplastics in disposable applications. Copolymers of hydroxybutyrate and hydroxyvalerate, commonly

referred to as PHBVs, have been produced and marketed by Zeneca Biopolymers. Because of the high cost of PHBV relative to commodity thermoplastics, various attempts have been made to incorporate starch and other low-cost components into PHBV-based composites.^{1–6} Starch is an attractive filler for PHBV because of its low cost and inherent biodegradability.

The use of starch in PHBV composites is hampered by the low degree of adhesion between the starch granules and the polymer matrix. The resulting loss in tensile strength and elongation compared to the unfilled polymer limits the maximum amount of starch which can be incorporated.^{2,5} Shogren has shown that precoating the

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* Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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starch with polyethylene oxide (PEO) improves tensile strength and elongation, presumably due to improved adhesion from PEO-PHBV interactions.³ Kotnis et al. showed that the degree of adhesion between starch granules and PHBV was poor but could be mitigated via appropriate formulation and processing techniques to obtain materials with commercially useful properties.⁴

Another approach to improving adhesion between starch filler and PHBV is by grafting a functional monomer onto the starch. Starch graft copolymers have been extensively studied and are easily prepared by free radical polymerization with unsaturated monomers.⁷ Grafting glycidyl methacrylate (GMA) onto starch provides the potential for chemical bonding between the starch and PHBV through the epoxide functionality of the GMA. The epoxide group can react with either the hydroxyl or the carboxyl endgroups of the PHBV. The resulting covalent bonding between the PHBV matrix and the starch filler should improve the mechanical properties of the composites by increasing the stress transfer across the matrix-granule interface.⁸ The objective of this report is to characterize the effect of graft level and initiator type on the properties of composites of PHBV with graft copolymers of starch and glycidyl methacrylate (starch-*g*-PGMA).

MATERIALS AND METHODS

The starch used was Buffalo 3401, an unmodified corn starch (CPC International, Argo, IL). Two PHBV copolymers were used: D300P (5% HV) and D400P (8% HV), both from Zeneca Biopolymers, Wilmington, DE. Acetyl tributyl citrate was the plasticizer. Glycidyl methacrylate, ceric ammonium nitrate (CAN), ferrous ammonium sulphate (FAS), and hydrogen peroxide were reagent grade and used without further treatment.

Graft Polymerization

A slurry of 125 g of starch (dry basis) in 1 L of distilled water was stirred and sparged with a slow stream of nitrogen gas for 1 h at 25°C. In the CAN-initiated polymerizations, GMA was added, followed after approximately 10 min by a solution prepared by dissolving 8.5 g of CAN in 25 mL of 0.5N nitric acid. The CAN solution was added in 2 equal portions 1.25 h apart. Portion-wise addition of CAN initiator generally leads to higher graft molecular weights and improved properties in

starch-*g*-poly(methyl acrylate) materials.⁹ The amount of GMA monomer added ranged from 4 to 25 g, depending on the desired level of grafting. In FAS-peroxide-initiated polymerizations, 3.026 g of FAS (dissolved in 20 mL of distilled water) was added to the aqueous starch slurry during the nitrogen sparging step. After addition of GMA, the mixture was stirred for 10 min, and a solution of 0.875 g of 30% hydrogen peroxide in 10 mL of water was added. Polymerizations were allowed to proceed for 3 h at 25°C. Graft copolymers were separated by filtration, washed with both ethanol and water, neutralized to pH 7 with NaOH solution, and air-dried.

PGMA add-on of the starch graft copolymers was determined by weight loss on acid hydrolysis. An accurately weighed sample of copolymer (about 5 g) in 450 mL of 0.5N HCl was refluxed for 3 h. PGMA was separated from hydrolyzed starch solution by filtration, followed by drying and weighing. Graft contents in the copolymers ranged from 1.4% to 19% PGMA.

PGMA homopolymer content was determined by extraction with tetrahydrofuran. The graft copolymer with the highest PGMA content (19% by weight) lost only 0.6% upon extraction, suggesting that only low levels of PGMA homopolymer are formed during the polymerization reaction.

Sample Preparation

All formulations were blended to give 25% by weight starch and 5% by weight plasticizer; 1% boron nitride [based on poly(hydroxy butyrate-co-valerate) (PHBV)] was added as a nucleating agent for the PHBV. The graft content was taken into account when determining the amount of starch. Components were blended in a bowl mixer for 15 min. The dry blends were then compounded in a Leistritz 18-mm corotating twin-screw extruder through a single strand die. The temperature profile was 130, 145, 150, 160, 160, and 155°C, from the first heating zone to the die, respectively. The screw speed was 100 rpm. Specimens for tensile and flexural testing were injection molded using conditions reported previously.⁴

Molecular Weight Analysis

Weight-average molecular weights were determined on injection-molded samples, as described previously.⁴

Physical Testing

Molded test specimens were conditioned at 50% relative humidity and 23°C for 28 days prior to testing. Flexural and tensile properties were measured using an Instron model 4201 Universal Tester, with computer control and data acquisition. A minimum of 5 specimens of each formulation were tested. Crosshead speed was 20 mm/min for tensile tests and 12.7 mm/min for flexural tests. Coefficients of variance were 5–10%.

Water Immersion

Prew weighed molded specimens were placed upright in 500 mL of distilled water for 28 days. After removal, they were blotted dry and reweighed to determine weight gain. Sample dimensions were also measured before and after immersion with a micrometer. Flexural and tensile properties were measured as quickly as possible after the reweighing and dimension measurements.

Scanning Electron Microscopy

Samples fractured during tensile or flexural testing were viewed by scanning electron microscopy after sputter coating with Au.

Photoacoustic FTIR Spectroscopy

Photoacoustic Fourier transform infrared (FTIR) spectra were acquired on a Bio-Rad FTS 6000 (Bio-Rad, Cambridge, MA) spectrometer equipped with a dynamically aligned 896 interferometer, a KBr beamsplitter, and a water-cooled globar source. An MTEC Model 2000 photoacoustic cell (MTEC, Ames, IA) with preamplifier and power supply was used to measure the photoacoustic signals. A high-surface-area carbon black sample (MTEC) was used as the reference material. All polymer samples were vacuum dried overnight at 60°C before analysis. Each sample was purged in the photoacoustic cell with dry helium for 30 min to increase the photoacoustic signal and ensure spectra free of water vapor signals.

Phase modulation at 800 Hz was used during step-scan operation of the interferometer at an optical scanning velocity of 0.0032 cm/s (corresponding to a modulation frequency of 50 Hz) to ensure that spectra were measured at a shallow and constant sampling depth across the entire

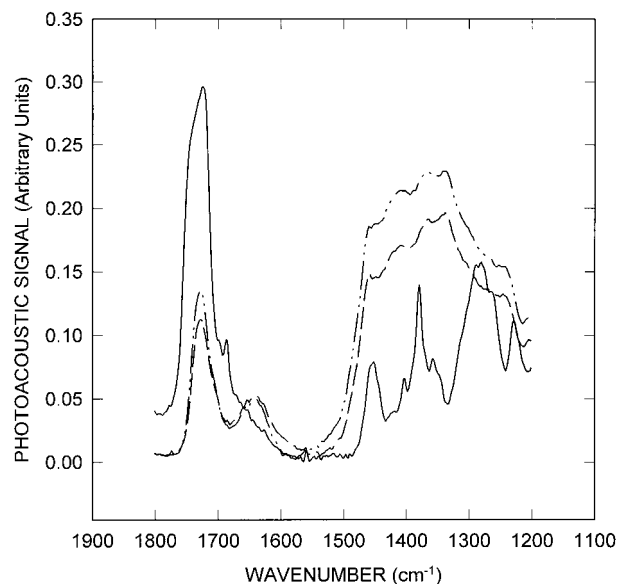


Figure 1 FTIR photoacoustic spectra of PHBV (—), starch-*g*-PGMA before extrusion (---), and starch-*g*-PGMA after extrusion and chloroform extraction of the PHBV (- · -). PGMA content of the graft is 7.4%.

mid-infrared wave number range. A phase modulation amplitude of 1 He-Ne laser fringe was used. In-scan coaddition of 8 scans at 4 cm⁻¹ resolution and medium Norton-Beer apodization was used to maximize the signal-to-noise ratio. The reported spectra are baseline-corrected with no zero filling or smoothing.

RESULTS AND DISCUSSION

Evidence of Grafting Reaction

Figure 1 shows the FTIR photoacoustic spectra of PHBV, starch-*g*-PGMA (7.4% GMA) before extrusion processing, and starch-*g*-PGMA after extrusion followed by extraction of PHBV by chloroform. Both the starch-*g*-PGMA and the PHBV show strong carbonyl absorbances in the range 1700 to 1750 cm⁻¹. While all 3 polymers show absorbance peaks in the range 1200 to 1400 cm⁻¹, there is no significant change in the spectra of the grafted starch before and after extrusion. The spectra in Figure 1 suggest that little, if any, reaction occurred between the PHBV and starch-*g*-PGMA during extrusion; any PHBV residues were below the detection level of the FTIR photoacoustic method.

Table I Mechanical Properties of PHBV-Starch-*g*-PGMA Composites Before Water Immersion (CAN initiator)

% Graft	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (MPa)	Flexural Modulus (GPa)	Flexural Yield Strength (MPa)
0	17.1	15.6	458	1.9	31.0
0 ^a	16.8	15.1	473	1.9	30.5
7.4	22.2	12.5	484	1.9	38.2
13.4	23.6	13	539	1.9	41.8
19.0	24.3	18	—	1.8	43.5

The PHBV used is D400P (8% HV).

^a Treated with CAN initiator, but no GMA was added to reaction mixture.

Extrusion Processing

The graft content had little effect on the extrusion properties of the composites. Neither the torque nor the die pressure showed any dependence on graft content. The initiator type affected the color of the composites. Composites containing Fe-H₂O₂ initiated copolymer were distinctly redder in color, and their extrudates during compounding had a rough surface texture similar to the sharkskin observed in melt fracture. CAN initiated materials were an off-white color, similar to ungrafted controls.

Because transition metals such as iron are known to catalyze oxidative degradation of polymers with hydrocarbon segments in the backbone, molecular weights of the 5% HV composites were measured before and after processing. The weight-average molecular weight of the PHBV with ungrafted starch was 445,000; this decreased to approximately 380,000, regardless of whether Fe or CAN was used as the initiator. These changes are consistent with those observed in processed starch-PHBV composites using unmodified starch.⁴

Mechanical Properties

The tensile and flexural properties of the molded composites (CAN initiator) before water immersion are shown in Table I. Tensile strength and flexural modulus data for the control formulations are in good agreement with the predictive equations of Kotnis et al.,⁴ while the elongation values are somewhat lower. Tensile modulus values are lower than those expected from PHBV product literature, perhaps due to the fact that an extensometer was not used in the tensile measurements. However, since relative changes be-

tween formulations are under consideration, this discrepancy is not serious. The elongation is essentially unchanged by the presence of the graft, while the modulus increases slightly. There is a significant increase in tensile strength when starch-*g*-PGMA is used; the relative increase is greater at low graft levels and diminishes as the graft content increases. The flexural properties show the same behavior as the tensile properties. The flexural yield strength is significantly increased by the graft, while the flexural modulus does not change significantly. Relative increases in both tensile and flexural strength are approximately 40% at the highest PGMA content.

Similar properties are observed when the Fe-H₂O₂ initiator is used instead of CAN, as shown in Table II. There are no significant changes in properties when the graft content is 1.4%. At a graft content of approximately 4%, the tensile strength and flexural yield strength slightly increase, while the modulus and elongation are unaffected. The CAN-initiated graft properties were somewhat lower than those with the Fe-H₂O₂ initiated graft. This result is consistent with the observation that the Fe-H₂O₂ initiator system results in greater levels of ungrafted homopolymer at the granule surface compared to CAN in starch-*g*-poly(methyl acrylate) copolymers.¹⁰

The data in Tables I and II show that the presence of the graft copolymer increases the tensile and flexural strength but not the elongation or modulus. Similar results have been reported for PEO-coated starch in PHBV,³ which is clearly a nonreactive system. It has been pointed out that while perfect adhesion does not always lead to increased stiffening in filled systems, it generally leads to greater strength.⁸ The peak load and the displacement at peak load in tensile mode

Table II Effect of Initiator Type on Mechanical Properties

% Graft	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (MPa)	Flexural Modulus (GPa)	Flexural Yield Strength (MPa)
0 ^a	19.2	16.4	416	2.1	32.7
1.4 ^b	18.6	15.4	373	2.0	32.9
4.4 ^b	23.0	14.7	388	2.0	38.4
4.2 ^c	20.9	14.2	460	1.9	34.8

The PHBV used is D300P (5% HV).

^a No initiator or GMA.

^b FAS-H₂O₂ initiator.

^c CAN initiator.

both increase in the presence of the graft copolymer. Assuming that reduction in effective surface area by debonding is the primary mechanism of tensile strength reduction, then these results suggest improved adhesion (greater debonding stress) between the PHBV matrix and the starch granules grafted with PGMA. Under tensile deformation, composites with grafted fillers are able to bear a greater load before debonding. Once debonding occurs, and the load-bearing area is reduced, the materials then fail.

The data of Tables I and II also indicate that a minimum amount of graft copolymer is required for improved strength. A graft content of 1.4% (Fe-H₂O₂ initiator) has no strengthening effect (Table II), whereas significant improvements are observed at graft contents of approximately 4%. Table I also shows that the relative improvement in strength diminishes as the graft content increases.

Effect of Water Absorption

When immersed in water at room temperature, starch granules swell¹¹ and absorb approximately 0.4 g of water per gram of starch.¹² PHBV itself absorbs approximately 0.9% water (Biopol™ trade literature), corresponding to a water concentration approximately 500 times that of saturated air. Starch granules dispersed in the PHBV matrix are therefore exposed to an “atmosphere” that is supersaturated in water. Since water is an excellent plasticizer for starch, it is expected that water sorption will impact the dimensional and mechanical stability of starch-filled composites.

Weight gain and volume increase data after water immersion (28 days) are given in Table III. The graft content had no significant effect on either the weight gain or the dimensional stability. The differences are not statistically significant at

a confidence level of 95%. Volume increases were on the order of 1.5% in each dimension; weight gains were all approximately 4% of the total sample weight. Correcting for the water sorption by the PHBV matrix, the average water content in the granules is approximately 12%, or about one-third of the equilibrium amount of water expected to be absorbed during immersion. The water distribution will be nonuniform, with granules near the surface having a greater water content compared to those near the center.

Table IV shows the effect of absorbed water on the mechanical properties of the composites. Since the water distribution is nonuniform across the sample, these data reflect the properties of materials with a gradation from edge to center. The tensile strength is essentially unchanged after water immersion, and the elongation increases; this latter effect is consistent with the plasticization of the starch granules by the absorbed moisture. The tensile modulus drops sharply after immersion to values less than half of the original modulus values. Similar results are observed for the flexural properties. The flexural modulus is reduced by about 40%, and the yield strength decreases

Table III Weight Gain and Percent Expansion of PHBV-Starch-g-PGMA Composites After 28 Days of Water Immersion

% Graft	Weight Gain (%)	Volume Increase (%)
0 ^a	4.6	3.7
0 ^b	4.0	4.6
7.4	3.9	5.0
13.4	3.9	5.6

The PHBV used is D400P (8% HV).

^a No initiator treatment.

^b Treated with CAN initiator but no GMA.

Table IV Mechanical Properties of PHBV–Starch-*g*-PGMA Composites After Water Immersion for 28 Days

% Graft	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (MPa)	Flexural Modulus (GPa)	Flexural Yield Strength (MPa)
0	16.8	25.1	168	1.0	26.6
0 ^a	17.7	22.8	185	1.2	28.2
7.4	23.0	31.4	203	1.3	35.7
13.4	22.1	28.6	202	1.2	36.8

The PHBV used is D400P (8% HV).

^a Treated with CAN initiator, but no GMA was added to reaction mixture.

slightly after immersion (compare Tables I and IV). The grafted starch composites retain a greater proportion of their original properties after water absorption than the ungrafted controls. Composites with the highest graft content had modulus values approximately 20% greater than the ungrafted starch controls after immersion.

Water absorption has a significant impact on the toughness, or area under the tensile stress–strain curve, as shown in Figure 2. Before soaking, the toughness increases slowly with graft content. After soaking, the toughness of the control increases slightly but doubles for the graft-

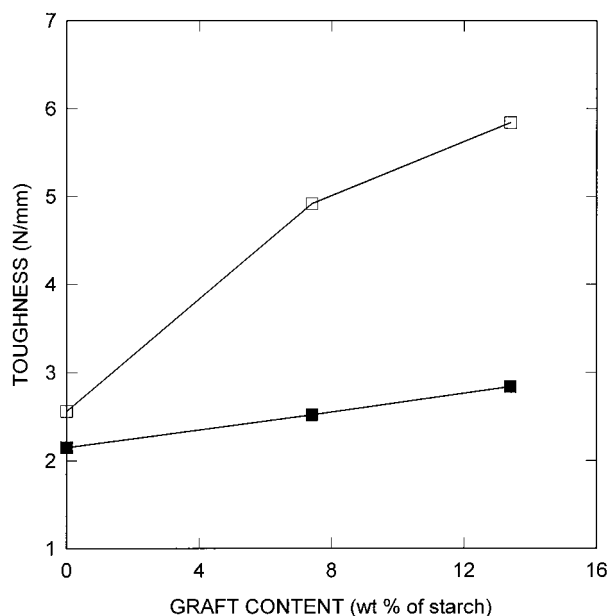


Figure 2 The effect of water absorption on the toughness (area under stress–strain curve) of starch-*g*-PGMA–PHBV composites. PGMA content of the graft is 7.4%. (■) Before soaking. (□) After soaking for 28 days.

containing samples. The enhanced toughness is primarily due to the observed increase in elongation after soaking (compare Tables I and IV). According to data from Biopol™ product literature, 28-day water immersion has no measurable effect on tensile strength or modulus. Since the water absorption of starch–PHBV composites after 28 days is 3–4 times greater than that of pure PHBV, the increase in toughness must reflect starch plasticization by the water. The large increase in toughness observed with the grafted starches is consistent with enhanced adhesion at the starch-*g*-PGMA–PHBV interface compared to ungrafted starch in the presence of water.

Scanning Electron Microscopy

Figure 3 shows the cryogenic fracture surface of an untreated starch. The adhesion between the

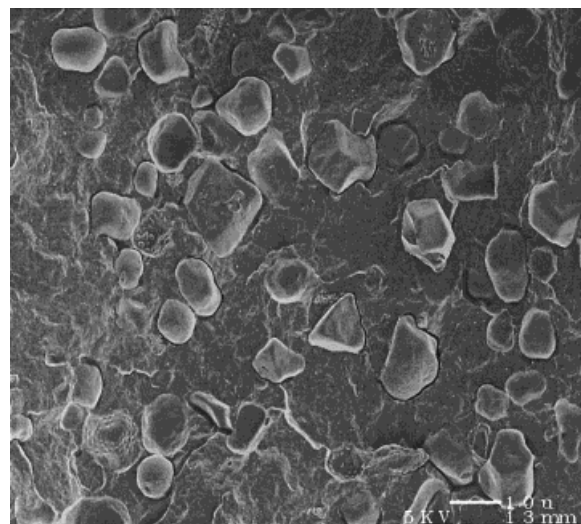


Figure 3 Scanning electron micrograph of cryogenic fracture surface of ungrafted starch–PHBV composite. Scale marker is 10 μ m.

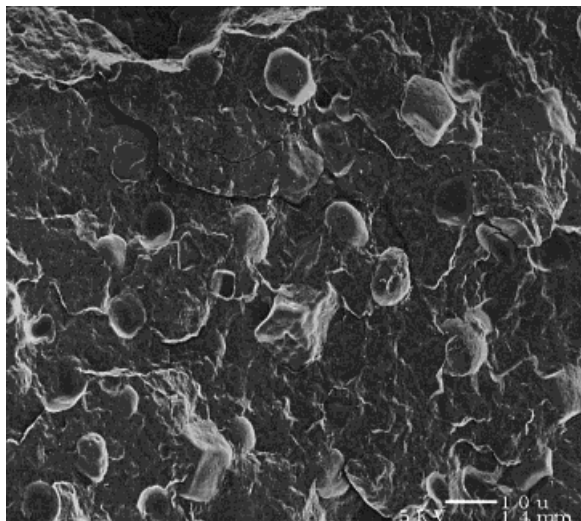


Figure 4 Scanning electron micrograph of cryogenic fracture surface of starch-*g*-PGMA-PHBV composite. PGMA content of the graft is 7.4%. Scale marker is 10 μm .

starch and the PHBV is seen to be poor. In Figure 4, the cryogenic fracture surface of the composite prepared with a graft content of 7.4% (CAN initiator) is shown. There is significantly improved adhesion between the starch and the PHBV matrix, and few voids are observed around the starch granules, as are seen in Figure 3. When fracture surfaces of samples broken in tension at room temperature are examined, considerable debonding is observed in both ungrafted and grafted materials. This result suggests that adhesion at the starch-resin interface breaks down at a critical stress before complete failure; this debonding stress is greater in the starch-graft composites, leading to greater tensile strength.

CONCLUSIONS

Graft copolymers of starch with glycidyl methacrylate were prepared in an effort to improve the mechanical properties of starch-PHBV composite materials. Photoacoustic FTIR analysis provided no evidence of substantial reaction between starch-*g*-PGMA and PHBV during melt processing. The use of starch-*g*-PGMA in composites with PHBV improved the tensile and flexural strength compared to untreated starch controls. The strength increased with increasing PGMA content, although the relative increase diminished above about 7.5% graft. Elongation and modulus

were not significantly affected by the presence of graft copolymer. All formulations had weight gains of approximately 4% after immersion in water for 28 days at room temperature. In all cases, the modulus was considerably reduced by water absorption, but the grafted composites retained a greater proportion of their dry stiffness. The tensile toughness after water absorption was approximately doubled for grafted composites, while ungrafted composites showed little change. Scanning electron microscopy of cryogenic fracture surfaces indicated improved adhesion in the presence of starch-*g*-PGMA. These results suggest that even in the absence of chemical reaction, the presence of grafted poly(glycidyl methacrylate) on starch granules enhances the adhesion with PHBV and leads to improved mechanical properties, particularly after the absorption of water by the starch granules.

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