Synthesis of Starch-*g*-Poly(glycidyl methacrylate) and Its Blending with Poly(ε-caprolactone) and Nylon 610

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Summary: Different amounts of glycidyl methacrylate (GMA) were grafted onto corn starch dispersed in water or dimethyl sulfoxide (DMSO) to yield starch-*graft*-poly(glycidyl methacrylate) (ST-*g*-PGMA). ST-*g*-PGMAW, obtained by grafting PGMA onto corn starch that was dispersed in water, showed a higher PGMA grafting content and a lower content of the homopolymerized PGMA than ST-*g*-PGMAD, which was prepared in DMSO. The modified starches were blended with poly(ε-caprolactone) (PCL) and nylon 610, respectively, and the tensile properties of the blends were measured by UTM. Mechanical properties of the biodegradable ST-*g*-PGMA/PCL blends were dependent on the PGMAD content grafted on starch. Without dramatic loss of the tensile properties of PCL, ST-*g*-PGMAW was melt blended with PCL. Meanwhile, an increase in the tensile modulus was observed in the ST-*g*-PGMAW/nylon 610 blend. When nylon 610 was reacted with ST-*g*-PGMAW in DMSO in the presence of triethylamine, the tensile modulus and strength were much higher than those of the pure nylon 610, and phase-separated domains of starch were not observed microscopically.

Keywords: nylon 610; phase-separation; poly(ε-caprolactone); starch-*g*-poly(glycidyl methacrylate); tensile properties

Introduction

Starch is a biodegradable polymer and it is abundant in nature. However, it is insoluble in most solvents and its processibility and mechanical properties are rather poor. In order to improve its processibility and physical properties, chemical and/or physical modification of starch has been extensively studied.[1-7] In particular, the hydroxyl group of the glucose unit in starch has been utilized for the chemical modification of starch. For example, acetylized starch displays better solubility and fiber forming ability than unmodified starch.[8] Moreover, the hydroxyl groups of starch can easily react with isocyanates and the starch/polyurethane blend enhances the solvent resistance and the tensile properties. Dosmann and Steel added starch to polyurethane to yield shock-absorbing elastomeric foams,[9] and Bennett and coworkers reported enhanced chemical resistance and

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biodegradability of rigid urethane foam when 10-40% starch was added. [10] Starch can also act as an additive for commodity plastics and films to impart biodegradability. Biodegradable agricultural mulching films usually contain varying amounts of starch. However, the mechanical properties of the starch containing blends drastically decrease with an increase in the starch content, thus either an adequate compatibilizer should be used or starch should be modified properly. The introduction of an epoxide group such as glycidyl methacrylate (GMA) to starch can suppress the reduction of the mechanical properties of the blends resulting from the increase in the interaction between GMA grafted starch and the polymer containing either a hydroxyl group or carboxyl group.

In this study, starch-*g*-poly(glycidyl methacylate)s (ST-*g*-PGMAs) having various amounts of GMA grafted onto starch were synthesized and they were blended with poly(ε-caprolactone) (PCL) and nylon 610, respectively, in both solution and melt. Tensile properties and morphology of the various blends were investigated. In addition to the physical blending, a chemical reaction between nylon 610 and ST-*g*-PGMA was induced by blending them in the presence of triethylamine (TEA) at 170 °C in dimethyl sulfoxide (DMSO) and the change in the tensile properties was closely monitored.

Experimental

Materials. GMA, ceric ammonium nitrate (CAN), DMSO, and deuterated dimethyl sulfoxide (DMSO-d_6) were purchased from Aldrich and used without further purification. Corn starch (ST, Samyang Co., Korea, average particle size = 10 μm), PCL (Union Carbide, Tone® Polymer P-787, M_w=117,000), and nylon 610 (RTP200B, RTP Co., MN, USA, M_w=205,000) were vacuum dried at 30 °C for three days to eliminate residual water.

Characterization. The chemical structure of ST-*g*-PGMA was analyzed by ^{1}H-NMR (Bruker AC-250) in DMSO-d_6 (20wt/vol%) as a solvent at 60 °C. Thermal properties of the graft copolymer were determined by DSC (Perkin Elmer, DSC 7). Samples were heated to 200 °C at 20 °C/min, slowly cooled to 30 °C at 5 °C/min, and then heated to 200 °C at 20 °C/min to obtain the second scan curves. Tensile properties of the blends were measured by UTM (Instron 4200) at a crosshead speed of 50 mm/min using a 10 kN load cell. Tensile specimens were prepared according to the ASTM D638 and were conditioned for a week at 20°C and 65% relative humidity prior to the tensile test. In order to investigate the fracture morphology, the blend films were cleaved in liquid nitrogen,

coated with gold, and examined by a scanning electron microscope (Hitachi S-4200).

Grafting of starch. An initiator solution was prepared by dissolving CAN (0.85 g) in 2.5 mL nitric acid aqueous solution (0.5 N). Corn starch (12.5 g) was dispersed in distilled water (100 mL) at 25°C for one hour. GMA (10 mL) was added to the reactor and dispersed for 10 min. Then, the initiator solution was introduced to the reactor and the polymerization continued for 5 h. The reaction product was filtered, washed with distilled water and ethanol, respectively, and dried in vacuum at 40°C. PGMA, a byproduct of the copolymerization, was removed by extracting the product in hot THF for 24 h. Finally, the ST-*g*-PGMA copolymer was dried in vacuum at 40°C until a constant weight was attained. Grafting was also carried out in DMSO using the same procedure, and ST-*g*-PGMAD was obtained. Graft copolymers prepared in water are denoted by ST-*g*-PGMAW, whereas those prepared in DMSO are denoted by ST-*g*-PGMAD.

Blending of ST-*g*–PGMA. ST-*g*-PGMA was blended with PCL and nylon 610, respectively, in a Brabender (Duisburg, Type 810602) extruder at 180 °C for 20 min at 60 rpm. In order to prevent thermal degradation during melt blending, an antioxidant (Irganox B 225, Ciba-Geigy Corp.) was introduced to the blends. Starch-*g*-PGMA was also blended with nylon 610 in solution to compare with the blends prepared in the melt. Five grams of the ST-*g*-PGMA/nylon 610 (10:90 by weight) mixture was dissolved in DMSO (40 mL) at 160°C to form a homogeneous solution, which was then reacted with 1 mL of TEA for 1 h. The blend was re-crystallized in excess methanol, filtered and dried in vacuum at 40°C. Blends were pressed into sheets using a Carver lab press, after preheating at 200°C for 5 min.

Results and Discussion

Synthesis of ST-*g*-PGMA. Graft copolymers are denoted by ST-*g*-PGMA, followed by the number which is ten times the weight percent of GMA in the copolymer. For example, ST-*g*-PGMAD287 means that the PGMA-starch graft copolymer was prepared in DMSO in which the GMA content in the copolymer was 28.7% by weight. The characteristic chemical shifts in the ^{1}H-NMR spectra of both ST-*g*-PGMAW and ST-*g*-PGMAD were identical, indicating that they had the same chemical structures. Table 1 shows the reaction conditions and the results of the graft copolymerization. The amount of the byproduct, PGMA homopolymer, per 1 g of ST-*g*-PGMA was dramatically increased

when water (0.007～0.019 g) was replaced by DMSO (0.078～3.75 g) as a dispersion medium for starch. Similarly, Willet et al.[2] reported that the yield of PGMA homopolymers during the grafting copolymerization of GMA with corn starch in water was only 0.6%, whereas the PGMA content in the ST-g-PGMA was 19 wt%. The amount of grafted PGMA in the copolymer prepared in water increased with the GMA concentration in the feed, whereas the amount of grafted PGMA for ST-*g*-PGMAD did not increase significantly. It is believed that the initiator can hardly partition into the droplets of the GMA monomer in water and radicals were predominantly formed in the corn starch particles. Therefore, GMA monomers could be grafted onto starch particles rather effectively. However, when DMSO was used as the medium, not only corn starch but also the initiator and the monomer formed a homogeneous solution. Since the GMA monomer contains a double bond, it may react with the initiator radicals more easily than the starch does. Thus, with increasing the GMA concentration in the reactant, the amount of the PGMA homopolymer increased, whereas the amount of the PGMA grafted onto starch did not increase significantly.

Table 1. Characteristics of ST-*g*-PGMA.

Sample code	Dispersion medium	GMA ([M] $\times 10^{-1}$)	Reaction temp. (°C)	Copolymer yield (g)	GMA content (wt%)	Grafted PGMA conversion (%)	Homo PGMA per Grafted PGMA
ST-*g*-PGMAW146	Water	1.83	25	14.64	14.6	82.1	0.007
ST-*g*-PGMAW231		3.66	25	16.25	23.1	72.0	0.019
ST-*g*-PGMAW433		5.49	25	22.06	43.3	91.7	0.012
ST-*g*-PGMAW539		7.32	25	27.11	53.9	93.5	0.019
ST-*g*-PGMAD126	DMSO	3.66	30	14.30	12.6	34.5	0.078
ST-*g*-PGMAD287		5.49	30	17.54	28.7	48.4	0.558
ST-*g*-PGMAD188		7.32	30	15.40	18.8	18.6	3.748

Properties of ST-*g*-PGMA containing blends. Table 2 shows the tensile properties of the various PCL/ST-*g*-PGMA (90/10 by weight) blends. When ST-*g*-PGMAW was blended with PCL, the ultimate strength of the blends slightly decreased in comparison with that of

PCL, but both the tensile modulus and elongation at break did not change much except for the blend containing the starch with high PGMA grafting density (i.e., ST-*g*-PGMAW539). Meanwhile, the tensile properties of the PCL/ST-*g*-PGMAD blends were inferior to those containing ST-*g*-PGMAW with similar compositions, and reduction in the elongation at break, in particular, was noticeable.

Table 2. Tensile Properties of PCL/Starch-*g*-PGMA 90/10 Blends.

Sample code	Tensile modulus (MPa)	Ultimate strength (MPa)	Elongation at break (%)
PCL	130.4 ± 21.0	24.5 ± 6.1	1229.0 ± 226.9
PCL/ST-*g*-PGMAW146	150.7 ± 12.7	16.1 ± 1.3	1127.9 ± 36.4
PCL/ST-*g*-PGMAW231	137.3 ± 15.3	18.7 ± 4.5	1124.9 ± 189.2
PCL/ST-*g*-PGMAW433	154.7 ± 18.3	21.1 ± 4.6	1237.2 ± 478.2
PCL/ST-*g*-PGMAW539	143.6 ± 30.6	13.2 ± 0.6	733.5 ± 179.0
PCL/ST-*g*-PGMAD126	108.2 ± 10.7	7.58 ± 1.0	115.8 ± 47.6
PCL/ST-*g*-PGMAD287	110.2 ± 28.3	8.43 ± 3.1	82.4 ± 20.4
PCL/ST-*g*-PGMAD188	137.1 ± 11.4	9.33 ± 1.4	64.2 ± 4.1

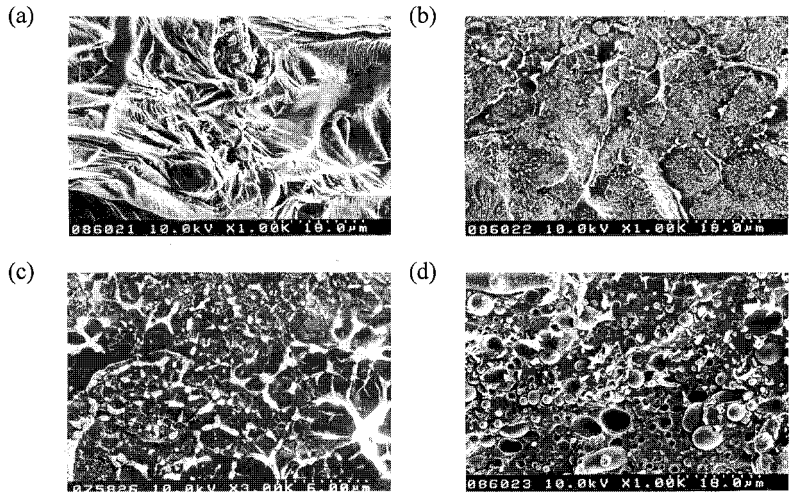

Figure 1. Scanning electron micrographs of the fractured surfaces: (a) PCL/ST-*g*-PGMAW433 90/10, (b) PCL/ST-*g*-PGMAD 287 90/10, (c) nylon610/ST-*g*-PGMAW433 90/10, (d) nylon 610/ST-*g*-PGMAD287 90/10.

Table 3. Tensile Properties of Nylon 610/ST-*g*-PGMA 90/10 Melt Blends.

Sample code	Tensile modulus (MPa)	Ultimate strength (MPa)	Elongation at break (%)
Nylon 610	141.3 ± 34.4	27.6 ± 5.7	598.9 ± 48.2
Nylon 610/ST-*g*-PGMAW146	180.4 ± 26.4	23.8 ± 5.0	319.8 ± 59.0
Nylon 610/ST-*g*-PGMAW231	173.7 ± 20.7	14.2 ± 1.8	100.9 ± 19.8
Nylon 610/ST-*g*-PGMAW433	158.3 ± 34.4	17.7 ± 3.7	112.6 ± 42.5
Nylon 610/ST-*g*-PGMAW539	187.1 ± 30.6	20.4 ± 1.8	111.9 ± 53.9
Nylon 610/ST-*g*-PGMAD126	133.7 ± 27.2	13.7 ± 3.6	33.2 ± 5.7
Nylon 610/ST-*g*-PGMAD287	222.6 ± 112.5	19.8 ± 9.6	31.4 ± 3.1
Nylon 610/ST-*g*-PGMAD188	126.0 ± 32.9	12.8 ± 3.1	33.9 ± 6.6

Table 4. Tensile Properties of Nylon 610/ST-*g*-PGMA Solution Blends.

Sample code	Blend composition	Tensile modulus (MPa)	Ultimate strength (MPa)	Elongation at break (%)
Nylon 610	100/0	141.3 ± 34.4	27.6 ± 5.7	598.9 ± 48.2
Nylon 610/ST-*g*-PGMA-W433[a]	90/10	158.3 ± 34.4	17.7 ± 3.7	112.6 ± 42.5
Nylon 610/ST-*g*-PGMA-W433[b]	90/10	498.7 ± 34.4	37.3 ± 3.7	29.9 ± 11.0
Nylon 610/ST-*g*-PGMA-W433[a]	80/20	205.3 ± 45.9	21.0 ± 3.7	54.5 ± 17.6
Nylon 610/ST-*g*-PGMA-W433[b]	80/20	481.2 ± 66.2	34.0 ± 5.9	24.4 ± 16.2
Nylon 610/ST-*g*-PGMA-W433[a]	70/30	231.9 ± 8.57	21.1 ± 1.2	44.2 ± 22.9
Nylon 610/ST-*g*-PGMA-W433[b]	70/30	531.2 ± 28.2	32.7 ± 6.7	11.2 ± 3.82

[a] Melt blended at 180°C.

[b] Solution blended in DMSO at 170 °C in the presence of TEA.

Tensile properties of the nylon 610/ST-*g*-PGMA melt and solution blends are shown in Table 3 and 4. As a rigid ST-*g*-PGMA was blended with nylon, it was expected that the tensile modulus of the nylon 610/ST-*g*-PGMA blend would increase, whereas the elongation at break would decrease. The tensile modulus of the nylon 610/ST-*g*-PGMAW433 melt blend was slightly higher than that of nylon 610, while the ultimate strength and the elongation at break of the melt blend were lower than those of nylon 610. Especially, a dramatic decrease in the elongation at break was observed in the nylon

610/ST-*g*-PGMAD blends, which may be caused by the poor distribution of ST-*g*-PGMAD with a low content of GMA in the matrix of nylon 610 (Figure 1). However, it is interesting to observe in Table 4 that the tensile modulus and the ultimate strength of the solution blends were significantly higher than that of the melt blend. Even the tensile modulus of the nylon 610/ST-*g*-PGMAW433 solution blend was more than three times higher than that of nylon 610. This can be explained by the SEM photographs shown in Figure 2. The size of the dispersed domains of the nylon 610/ST-g-PGMA melt blends ranges between 1 and 3 μm, whereas in the nylon 610/ST-*g*-PGMA solution blends, the dispersed domains were absent. This is a clear indication that in the solution blends there is a strong interaction between the amide group in nylon 610 and the epoxide group in PGMA or a covalent bond between nylon 610 and PGMA due to the nucleophilic addition reaction.

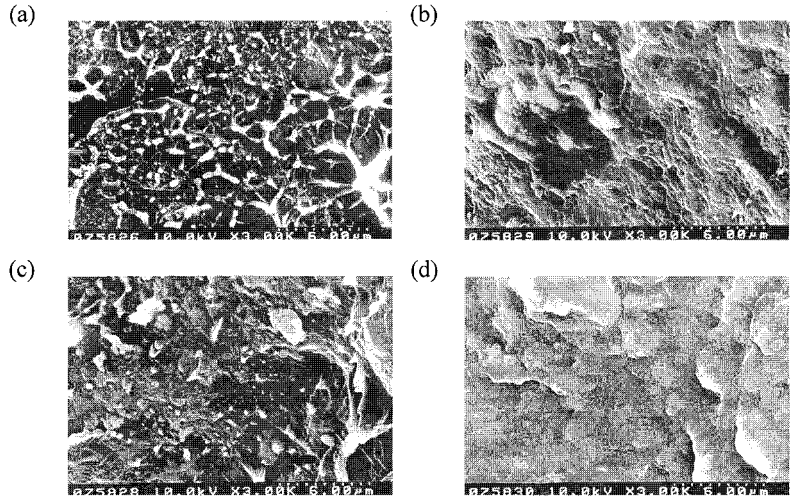

Figure 2. Scanning electron micrographs of the fractured surfaces: (a) melt blended nylon 610/ST-*g*-PGMAW433 90/10, (b) solution blended nylon 610/ST-*g*-PGMAW433 90/10, (c) melt blended nylon 610/ST-*g*-PGMAW433 80/20, (d) solution blended nylon 610/ST-*g*-PGMAW433 80/20.

Thermogravimetric analyses of the nylon 610/ST-*g*-PGMAW433 blends in Figure 3 showed consistent results. The melt blends containing 10 wt% of ST-*g*-PGMA and 20 wt% of ST-*g*-PGMA, respectively, began to lose weight at a lower temperature than nylon

610 did. However, the weight of the solution blends remained constant up to higher temperatures than that of nylon 610.

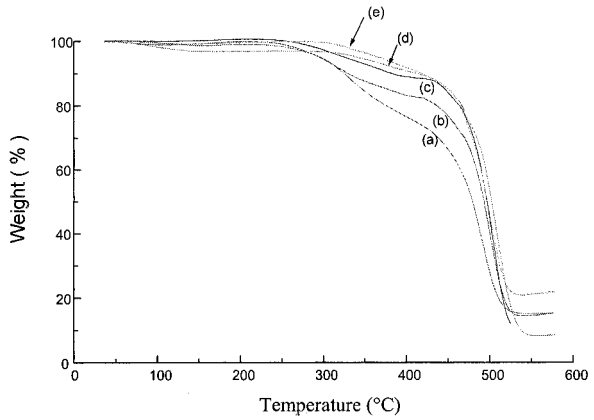

Figure 3. Thermogravity analysis (TGA) of nylon 610/ST-*g*-PGMA blends: (a) melt blended nylon 610/ST-*g*-PGMAW433 80/20, (b) melt blended nylon 610/ST-*g*-PGMAW433 90/10, (c) nylon 610, (d) solution blended nylon 610/ST-*g*-PGMAW433 80/20, (e) solution blended nylon 610/ST-*g*-PGMAW433 90/10.

Conclusion

Varying amounts of GMA were grafted onto starch in water and in DMSO, respectively, to yield ST-*g*-PGMA copolymers, which were then blended with PCL or nylon 610. ST-*g*-PGMA prepared in water contained a higher amount of grafted PGMA than that prepared in DMSO under the same condition. When ST-*g*-PGMAW was blended with PCL or nylon 610, the tensile properties of the blend were better than those of the blend of ST-*g*-PGMAD with PCL or nylon 610. This is partly because homopolymerization of GMA became very prominent in DMSO and the amount of the graft copolymers (ST-*g*-PGMAD) was reduced. In the case of the completely biodegradable PCL/ST-*g*-PGMAW blend, the tensile modulus and the tensile strength were not significantly lower than those of PCL itself, although the elongation at break was greatly reduced. When nylon 610 was chemically reacted with ST-*g*-PGMAW during the blending, the tensile modulus and the strength of the blend were much higher than those of nylon 610, and the phase-separated domains of starch were not observed microscopically.

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