

Reactive Blends of Gelatinized Starch and Polycaprolactone-*g*-Glycidyl Methacrylate

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ABSTRACT: Blends of the modified polycaprolactone (PCL) and the gelatinized starch with glycerin were prepared. The modified PCL, PCL-*g*-glycidyl methacrylate (GPCL), was synthesized by melt reaction of PCL and glycidyl methacrylate (GMA) in the presence of benzoyl peroxide (BPO) in a Brabender mixer. The size of the dispersed starch in the GPCL matrix was found to be smaller than that in the PCL matrix. As the relative content of the GMA groups in the GPCL increases, the elongation at break of the blend showed the highest value at a grafted GMA content of 4.2 wt %. With the increase of the glycerin content in the starch, an abrupt change of the mechanical properties of the blend were observed between 40 and 50 wt % glycerin content based on the starch weight. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1507–1516, 2001

Key words: polycaprolactone-*g*-glycidyl methacrylate; gelatinized starch; size of dispersed starch; grafted GMA content; glycerin content

INTRODUCTION

Many research and industrial attempts have been focused on the use of natural biopolymers such as starch, cellulose, lignin, chitin, and chitosan. These materials are fully biodegradable and also quite cheap. Despite these advantages, they have some drawbacks such as poor long-term stability caused by the water absorption, poor mechanical properties, and processability. To overcome these problems, the various physical or chemical modifications including blending,^{1–6} chemical derivations,^{7–9} and graft copolymerization^{10,11} have thus been considered.

The blends of starch and aliphatic polyester, especially polycaprolactone (PCL), are known to be completely biodegradable plastics.^{12–18} The

previous studies have shown that the mechanical properties of the starch/PCL blends become poorer with increase of the starch content in the blend.^{12,13,15} This may be attributed to the incompatibility between the hydrophobic PCL and the hydrophilic starch. It is thus necessary to use a proper method to enhance the compatibility of PCL with starch in the blend.

In the present study, polycaprolactone-*g*-glycidyl methacrylate (GPCL), which can act as a matrix material as well as a compatibilizer, was newly synthesized for the reactive blend with starch plasticized with glycerin, and the effect of the amount of the grafted glycidyl methacrylate (GMA) and the glycerin content on the mechanical properties of the blends were also investigated.

EXPERIMENTAL

Blend Preparation

Commercial-grade PCL TONE787 was purchased from Union Carbide. The unmodified granular

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Table I The Grafted GMA Content of Various GPCLs

Sample	GPCL1	GPCL4	GPCL7	GPCL13
GMA content in the feed	5 wt %	10 wt %	15 wt %	20 wt %
Grafted GMA content	1.4 wt %	4.2 wt %	7.2 wt %	13.2 wt %

corn starch with 30 wt % amylose and 70 wt % amylopectin, which was purchased from Sigma Chemical Co., was used in this work. Because the starch is very sensitive to moisture, it was used after drying in vacuum at 100°C for 24 h. The glycidyl methacrylate grafted PCL (GPCL) was prepared by melt reaction of GMA and PCL with a Brabender mixing head. The 40 g of PCL was hand mixed with GMA/benzoyl peroxide (BPO) solution where the BPO content was fixed at 10 wt % of the GMA amount. The GMA content in the blend was varied from 5 to 20 wt % of the PCL amount. This mixture of PCL and GMA in the presence of BPO was introduced into the chamber of the Brabender mixer. Mixing speed was kept constant at 80 rpm. The grafting reaction was carried out at 130°C for about 8 min. After completion of the grafting reaction, the reaction product was dissolved in tetrahydrofuran. The solution was poured into a large excess of methanol and the white precipitate, GPCL, was obtained and dried in vacuum. The grafted GMA content of the resulting GPCL could be calculated by using ¹H-NMR spectra. The methylene proton peaks of PCL appeared at the chemical shifts completely separated from those of the proton peaks of the grafted GMA unit. From the relative peak area of the methylene proton of PCL and the methine proton of GMA, the content of GMA grafted onto PCL could be calculated, and the results are summarized in Table I.

The GPCL/gelatinized starch blends were prepared by melt mixing with a Brabender mixing head as follows: the starch was gelatinized with glycerin in a Brabender mixer to disrupt the granular structure of starch and then blended with GPCL. The purity of the glycerin is 99%, and was purchased from Samchun Pure Chemical Corp. Mixing was performed at 170°C and 80 rpm for about 15 min. The melt temperature and torque of the reacting mixture were recorded during the mixing period. All the blend samples were molded by hot pressing at 150°C to make sheets with 1-mm thickness and then the specimens for tensile measurements were cut from the sheets and shaped into dog bone-type bars using a cutter.

The actual dimensions of tensile specimen were the same as the ones described in the ASTM-D1708 method.

Mechanical Properties

The mechanical properties of all the blend samples were measured with an Instron (Model-4204) tensile tester at a crosshead speed of 10 mm/min, and the two points of extension for calculating the initial tensile moduli of the specimens were selected at 0.1 mm and 0.3 mm, respectively. A minimum of five specimens were tested and the results were averaged.

Scanning Electron Microscopy

The morphology of the GPCL/gelatinized starch blend was investigated by using scanning electron microscopy (Phillips SEM 535M). To observe the domain structure of the starch phase, the fracture surface of the compression-molded blend specimen was etched physically in water medium by applying the ultrasonic wave (Branson 2210). The ultrasonication was performed at 40°C for 1 h for all the specimens. The SEM micrographs were taken with the electric field strength of 20–30 kV.

NMR Spectroscopy

The ¹H-NMR spectra and proton decoupled ¹³C-NMR spectra were recorded on a Bruker AMX500 operating at 500 MHz for the proton. The solvent used for the sample preparation was DMSO-d₆ in the NMR measurements. The chemical shifts for resonance peaks are reported in parts per million (ppm) using tetramethyl silane as a reference.

Melt Shear Viscosity

The melt shear viscosity of the blend was measured at 170°C with an Instron 3213 Capillary Rheometer with a die orifice radius of 0.03 inch and a die length of 1.0 inch.

RESULTS AND DISCUSSION

Reaction of Melt Blend

Figure 1 shows a change in torques of the GPCL/gelatinized starch blend and the PCL/gelatinized

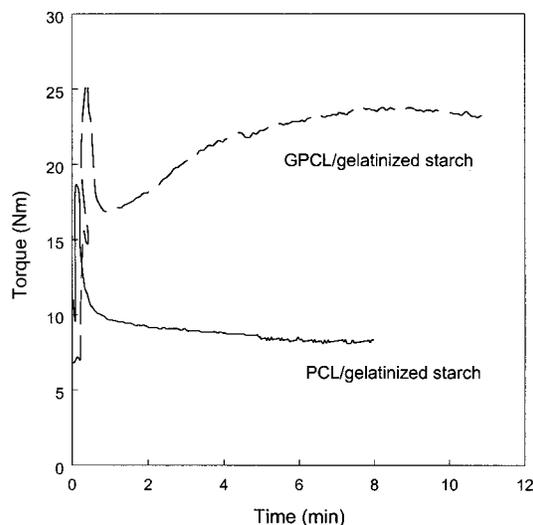


Figure 1 Torque vs. reaction time for the GPCL/gelatinized starch and the PCL/gelatinized starch blends.

starch blend during mixing in a Brabender mixer. For the PCL/gelatinized starch blends, the torque is found to decrease continuously until it becomes stable. However in the blend with GPCL, there is a significant increase in the torque after the initial melting of the blend. Such an increase in the torque is often observed in reactive blends, and is normally understood to be due to the reaction between the chemically reactive groups in the blend. The epoxide groups of the grafted GMA and the hydroxyl groups of either the starch or glycerin are expected to induce a chemical reaction, resulting in the formation of the ether linkage, as shown in Figure 2.

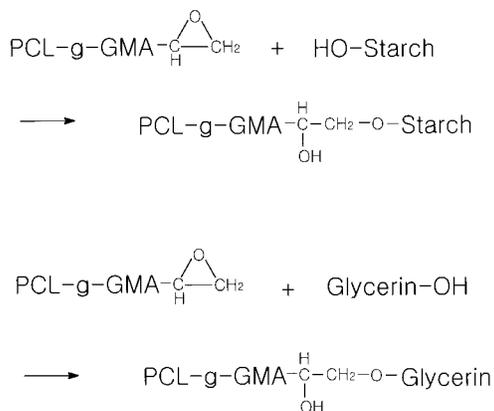


Figure 2 Reaction scheme between epoxide group of PCL-g-GMA and the hydroxyl end group of starch or glycerin.

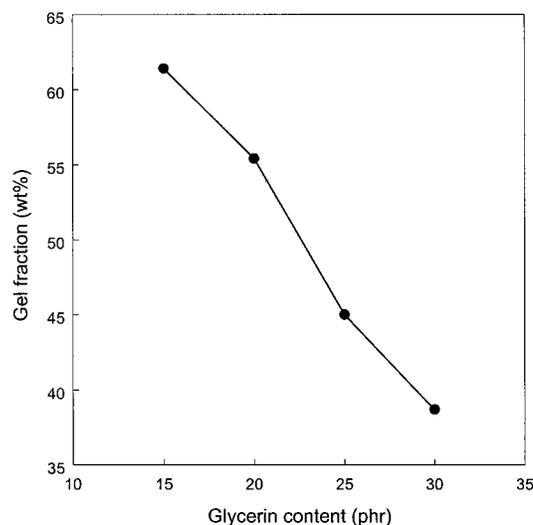


Figure 3 Gel content of the GPCL4/gelatinized starch blend as a function of the glycerin content.

During the reactive blending, gel can be formed by the reaction between GPCL4 and starch. After extracting the soluble fraction from the reacted blend with dimethyl sulfoxide (DMSO), the gel fraction could be obtained. Figure 3 illustrates the gel fraction of the reacted GPCL4/starch blend as a function of glycerin content in the blend. It is found that the gel fraction decreases with increase of the glycerin content in the blend. This would be because the glycerin hinders the reaction between GPCL4 and starch.

Figure 4(a) and 4(b) illustrate the ^1H - and ^{13}C -NMR spectra of the soluble fraction in the GPCL4/gelatinized blend. The soluble fraction is composed of GPCL4, starch, and glycerin. The peaks are assigned on the basis of chemical shift of each component reported by the previous studies.^{16,19} To compare the reactivity of starch and glycerin, the weight ratio of glycerin to starch in the soluble fractions of the reacted blend was determined from the ratio of the NMR peak areas corresponding to glycerin and starch, and the results are summarized in Table II. It is found that the glycerin/starch weight ratios in the soluble fraction of the reacted blend are much higher than those in the unreacted blend. It implies that the starch participates more favorably in the network formation by the reaction with the GPCL4 than the glycerin. Starch is a high molecular weight polymer containing three hydroxyl groups in a monomeric unit. Thus, it has a high possibility to react with the GPCL and a small number of reaction can more easily form a crosslinked network.

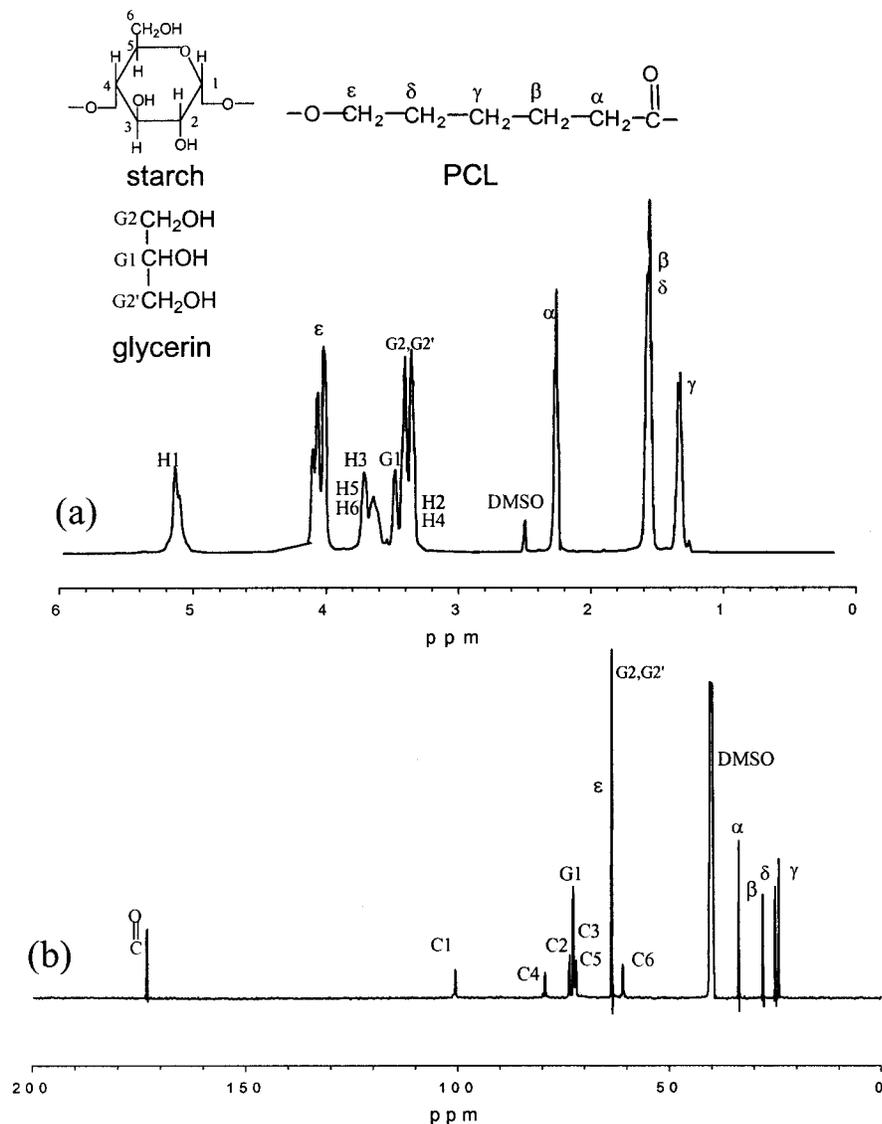


Figure 4 NMR spectra of the soluble fraction in the GPCL4/gelatinized blend: (a) ¹H-NMR, and (b) ¹³C-NMR.

Effect of Starch Content on Mechanical Properties of the GPCL/Gelatinized Starch Blends

Figure 5 shows the tensile modulus of the GPCL4/gelatinized starch blend as a function of starch

Table II The Change of Glycerin/Starch (w/w) Ratio after Reactive Blending

		Glycerin/Starch (w/w) Ratio			
		0.3	0.4	0.5	0.6
Before Blending					
After blending	¹ H-NMR	0.45	0.51	0.70	0.97
	¹³ C-NMR	0.45	0.58	0.83	1.05

content in the blend. The tensile moduli of the blends based on the starch gelatinized with 40 wt % of glycerin (with respect to starch) are found to increase with the increase of the starch content in the blend. As the relative content of the gelatinized starch itself containing 40 wt % glycerin in the blend increases, the hard domain fraction in the blend increases, and thus the tensile modulus of the blend increases. Table III shows the mechanical properties of the gelatinized starch and GPCL4. As shown in Table III, the modulus of the gelatinized starch itself containing 40 wt % glycerin is much higher than that of GPCL4. It implies that the gelatinized starch containing 40 wt % glycerin is harder than GPCL4.

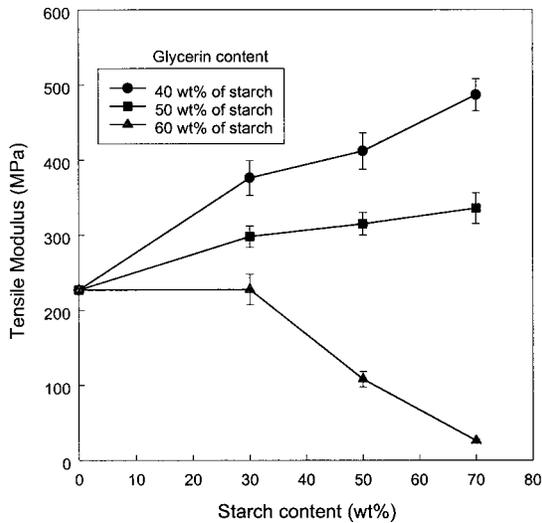


Figure 5 The tensile modulus of the GPCL4/gelatinized starch blends with different glycerin content.

For the blends based on the gelatinized starch containing 50 wt % glycerin, the modulus of the gelatinized starch is only a little higher than that of GPCL4, and thus the modulus increase of the blend with the starch content becomes less significant than that of the blend based on the gelatinized starch containing 40 wt % glycerin. However, in the case of the blend based on the gelatinized starch containing 60 wt % glycerin, the tensile modulus of the blend is shown to decrease with the increase of the starch content, as shown in Figure 5. When the glycerin content is high, the modulus of the gelatinized starch becomes much lower than that of GPCL, and thus the modulus of the blend would decrease with increase of the starch content.

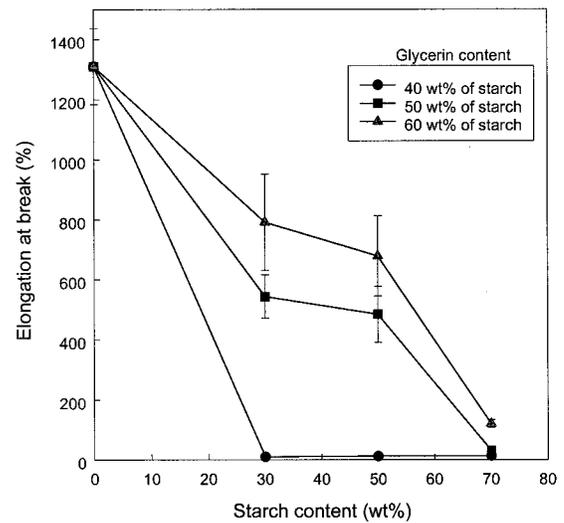
Figure 6(a) and (b) illustrates the elongation at break and tensile toughness of the GPCL4/gelatinized starch blend with different glycerin content. As expected, the elongation at break and tensile toughness of the blend decrease with increasing the gelatinized starch content. The decrease of elongation at break with the starch content is more significant in the blends based on the gelatinized starch containing 40 wt % glycerin compared to those containing 50 wt % and 60 wt % glycerin. This would be associated with the mechanical properties of the gelatinized starch and morphology of the blend. The detailed discussion is given in the following section.

Effect of Glycerin Content on the Mechanical Property of the GPCL/Gelatinized Starch Blend

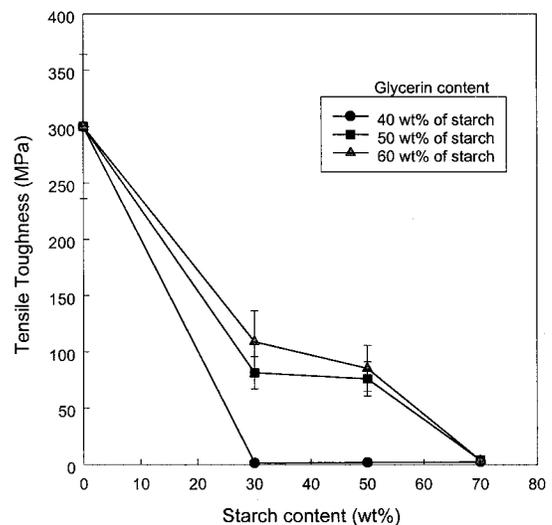
Figures 7 and 8 show the tensile strength and elongation at break of the GPCL4/gelatinized

starch (50/50) blend as a function of glycerin content. It is observed that the tensile strength and elongation at break abruptly change as the glycerin content changes from 40 to 50 wt % of the starch in the blend. To understand this phenomenon, the blend morphology and the mechanical properties of the dispersion phase, gelatinized starch, was investigated.

Figure 9(a)–(d) shows the SEM images of the GPCL4/gelatinized starch blends containing different amount of glycerin. The images were taken for the fracture surfaces etched physically by the



(a)



(b)

Figure 6 Tensile properties of the GPCL4/gelatinized starch blends with various glycerin content: (a) Elongation at break, and (b) tensile toughness.

Table III The Mechanical Properties of GPCL4 and the Gelatinized Starch Containing Various Amounts of Glycerin

Samples	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
GPCL4	227	34.3	1300
Gelatinized starch containing glycerin (40 wt % of starch) ^a	960	35	6
Gelatinized starch containing glycerin (50 wt % of starch)	321	19	30
Gelatinized starch containing glycerin (60 wt % of starch)	20	5.5	109

^a 40 wt % of starch: 40 parts of glycerin was used for gelatinization of 100 parts of starch.

ultrasonic treatment. The resulting morphologies were significantly different among each other. The starch domain sizes in Figure 9(a) and (b) are larger than those in Figure 9(c) and (d): the domain size of the dispersed starch phases shown in Figure 9(a) and (b) is found to be around 2–3 μm in diameter, while the domain size of the dispersed starch phases shown in Figure 9(c) and (d) is less than 1 μm in diameter. This difference in the domain size could lead to a significant change in the tensile strength and elongation at break as the glycerin content changes from 40 to 50 wt % of the starch in the blend. In a previous report,^{15,18} however, the starch/PCL blend exhibiting a large domain size (about 15 μm) of the dispersed starch showed a high elongation at break. Therefore, a

significant change of the tensile strength and the elongation at break of the GPCL4/gelatinized starch blend cannot be explained only by the difference of the domain size of dispersed starch. It is thus necessary to additionally consider the effect of the mechanical properties of the dispersed starch itself on the mechanical properties of the blend.

Figure 10 illustrates the tensile strength and elongation at break of the gelatinized starch with the glycerin content ranged from 30 to 60 wt % of the starch. It is found that the tensile strength and elongation at break change very significantly as the glycerin content increases from 40 to 50 wt % of the starch. The gelatinized starch containing glycerin lower than 40 wt % of the starch showed

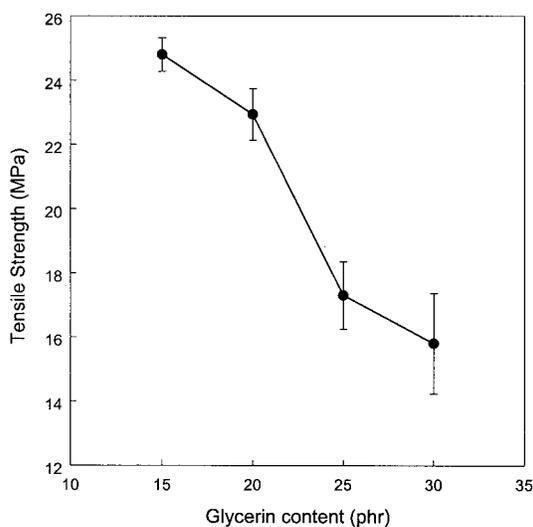


Figure 7 Tensile strength of the GPCL4/gelatinized starch (50/50) blend as a function of the glycerin content.

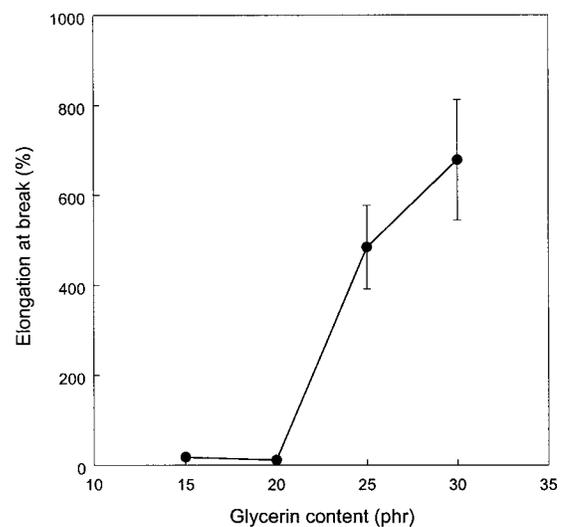


Figure 8 Elongation at break of the GPCL4/gelatinized starch (50/50) blend as a function of the glycerin content.

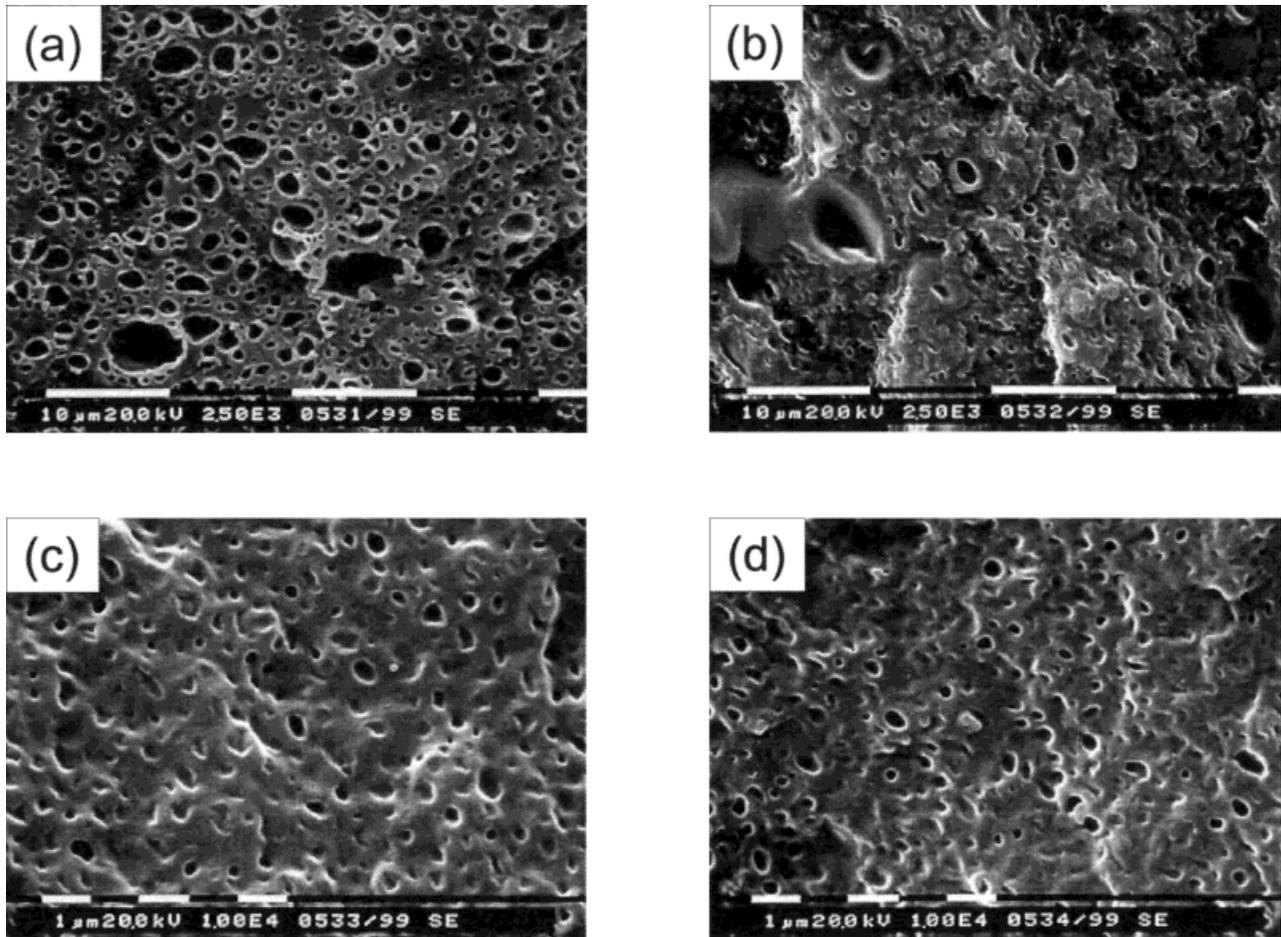


Figure 9 SEM micrographs of the GPCL4/gelatinized starch (50/50) blend containing different amounts of glycerin: (a) 30 wt % ($\times 2500$), (b) 40 wt % ($\times 2500$), (c) 50 wt % ($\times 10,000$), and (d) 60 wt % ($\times 10,000$) of starch content.

a brittle behavior, while the gelatinized starch containing glycerin greater than 50 wt % was rather ductile. This behavior is sometimes referred in the literature,^{20,21} but has not been studied in detail. It is conjectured that the complicate glycerin–starch interactions would be involved in this behavior, and thus further study should be performed to clarify this behavior.

As is shown in Figures 7, 8, and 10, the change of mechanical properties of the gelatinized starch with glycerin content is very similar to that of the blends. It implies that the mechanical properties of the blends are closely related to the mechanical properties of the dispersion phases. In a previous study on filled polymers,²² the enhanced interfacial adhesion results in a reduction of the elongation at break and an increase in the tensile strength. In this case, the dispersed phase of the filler is hard to deform, and thus it cannot relax

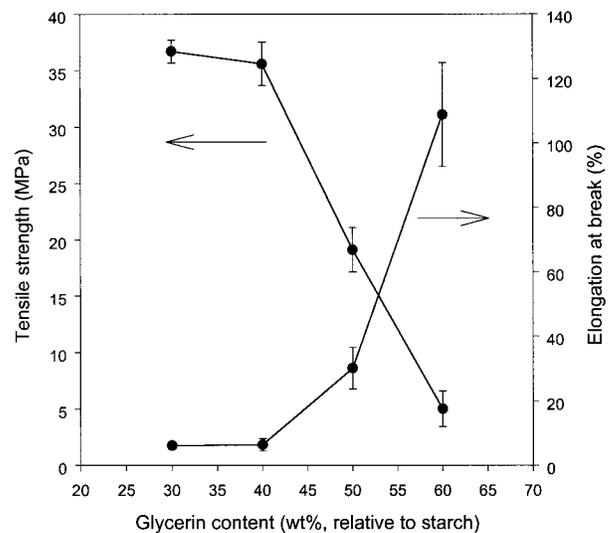


Figure 10 Tensile strength and elongation at break of the gelatinized starch as a function of the glycerin content.

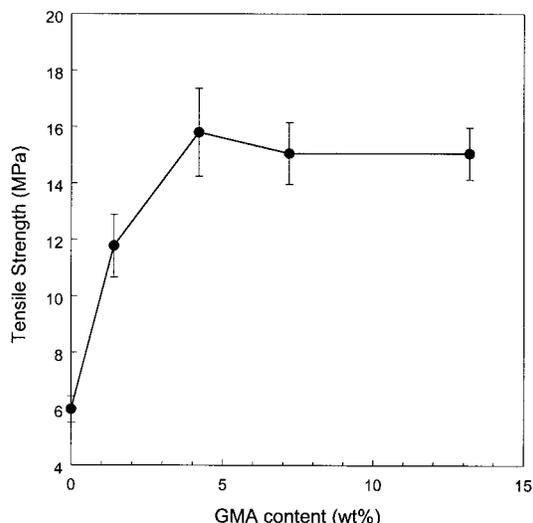


Figure 11 Tensile strength of the GPCL/glycerin/starch (50/30/50) blend as a function of the grafted GMA content.

the external stress and restrict the deformation of ductile matrix caused by the good interfacial adhesion. The increase of the interface adhesion could thus reduce the elongation at break and increase the tensile strength of the blend.

In the GPCL4/gelatinized starch blend, the interfacial adhesion between the matrix PCL and the dispersed starch phase can be enhanced by the reaction of GPCL and starch. Because the matrix PCL is tightly bound to the dispersed starch phase, the mechanical properties of the blend are influenced by the mechanical properties of the dispersed starch phase. When the dispersed starch phase is hard and brittle, the dispersed starch phase will restrict the deformation of the matrix PCL. It can lead to a reduction of the elongation at break and an increase in the tensile strength of the blend. When the dispersed starch phase is flexible and mobile enough to relax the external stresses, however, the dispersed starch phase can induce the subsequent deformation of the matrix PCL and dissipate the external stresses. It may result in a higher elongation at break and a lower tensile strength of the blend.

Mechanical Properties of the GPCL/Gelatinized Starch Blends with Grafted GMA Content

In preparing GPCL, the GMA content grafted on the PCL was varied by changing the feed ratio of GMA and PCL for the reaction and the results are summarized in Table I. The weight ratio of each

component in the blend was fixed at GPCL/glycerin/starch = 50/30/50.

Figure 11 illustrates the tensile strength of the blend as a function of the grafted GMA content. It is found that the tensile strength increases as the grafted GMA content increases. With the increase in the amount of GMA grafted on PCL, the reaction between GPCL and starch becomes more probable, and it induces the network formation by crosslinking reaction. The crosslinking reaction can lead to an increase of the tensile strength of the blend. To have some idea on the degree of crosslinking, a gel content in the blend and melt shear viscosity of the blend were measured. The gel fraction with the GMA content in the blend and the melt shear viscosity of the blend are plotted in Figures 12 and 13, respectively. It is found that the gel content in the blend increases with the increase of the grafted GMA content. The melt shear viscosity also increases as the grafted GMA content increases because the degree of crosslinking increases with the increase of the grafted GMA content.

Figure 14(a) and (b) illustrates the change of the elongation at break and the tensile toughness of the GPCL/glycerin/starch (50/30/50) blends with the grafted GMA content. When the pure PCL was used in the blend, the elongation at break and tensile toughness are very low. As the grafted GMA content increases, the elongation at break and the tensile toughness increase and show the highest value at a certain grafted GMA content.

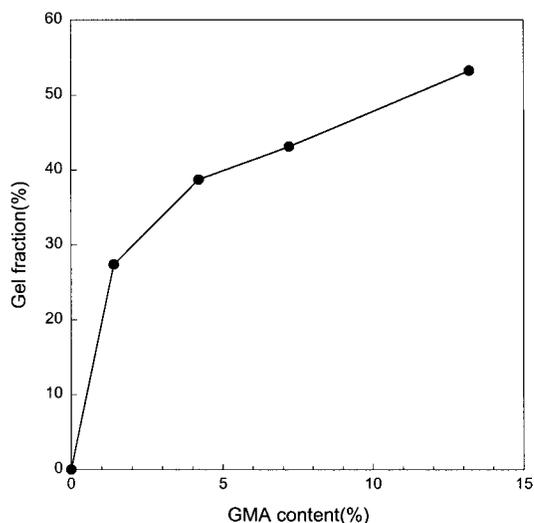


Figure 12 Gel content of the GPCL/glycerin/starch (50/30/50) blend as a function of the grafted GMA content.

C. B. Bucknall²³ reported that in polycarbonate (PC), which is relatively resistant to crazing, and shows shear yield deformation, the smaller dispersion phase could lead to a higher tensile toughness. The smaller dispersed domain size ensures that both cavitation and debonding at interfaces are postponed until they can initiate immediate dilatational shear yielding. PCL is a typical polymeric material that exhibits shear yield deformation. In the previous study on the PCL/starch blend,¹⁵ the blend with a smaller starch domain size showed a higher tensile toughness than that with a larger starch domain size. Figure 15 shows the SEM images of the starch domains dispersed in PCL or GPCL matrix in the blends. It is found that the starch domain size of the blend decreases as the grafted GMA content in the blend increases. When the grafted GMA content is higher than 4 wt %, the starch domain size in the blend is smaller than 1 μm . It is because the reaction between the grafted GMA and starch is much more probable at the higher content of the grafted GMA and it can reduce the starch domain size by enhancement of interfacial stability between the starch and the matrix.

According to the phase morphology shown in Figure 15, the domain size of the dispersion phase decreases with increase in the grafted GMA content. It was thus expected that the elongation at break and the tensile toughness increase with the increase of the grafted GMA content. However, the elongation at break and the tensile toughness showed a highest value at a certain amount of the

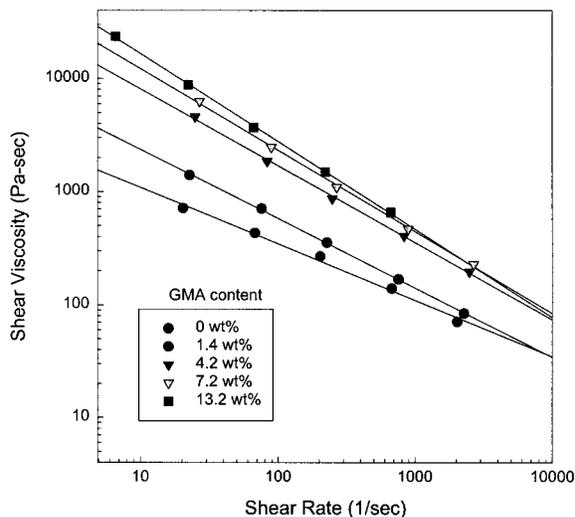
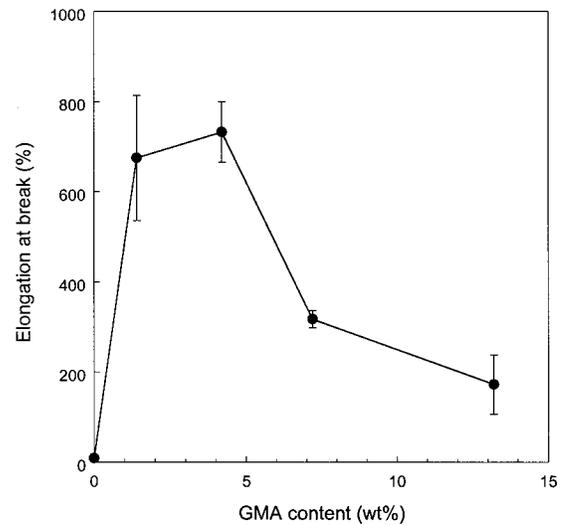
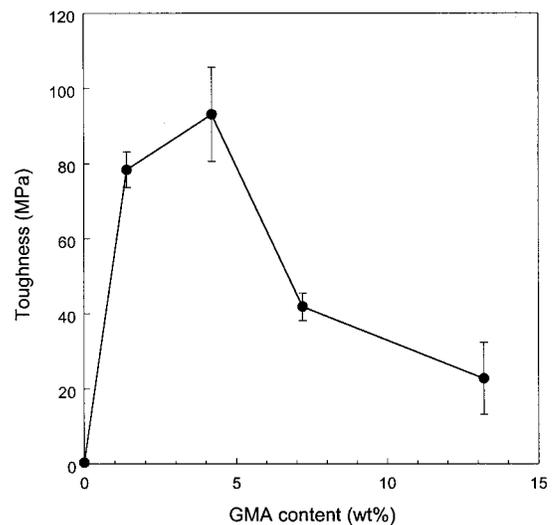


Figure 13 Melt shear viscosity vs. shear rate of the GPCL/glycerin/starch (50/30/50) blend.



(a)



(b)

Figure 14 Tensile properties of the GPCL/glycerin/starch (50/30/50) blend as a function of the grafted GMA content: (a) elongation at break, and (b) tensile toughness.

grafted GMA. With the increase in the grafted GMA content, the crosslinking degree of the blend is also expected to increase. This is already shown in Figures 12 and 13. The gel fraction and melt viscosity increase as the grafted GMA content increases. The increase of the crosslinking degree may reduce the chain relaxation over the external stress and lead to a decrease of the elongation at break. The elongation at break and the tensile toughness could show a highest value at a certain grafted GMA content due to these two opposite effects.

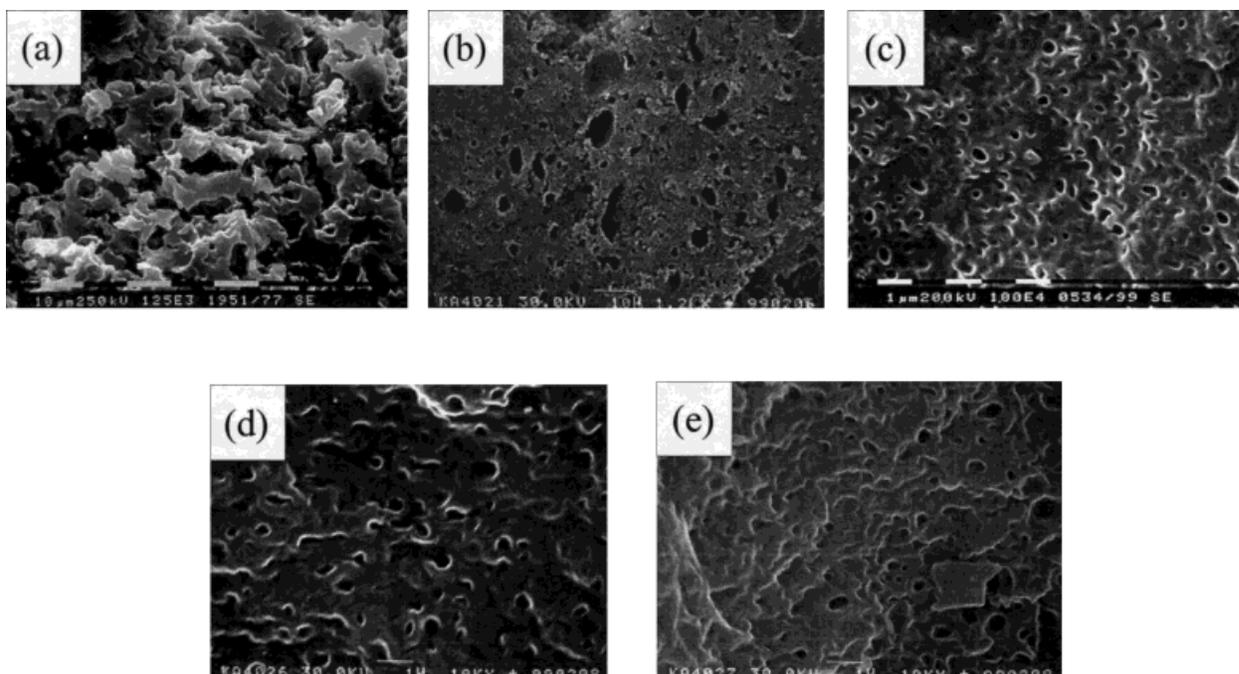


Figure 15 SEM micrographs of the GPCL/glycerin/starch (50/30/50) blend containing different amount of the grafted GMA: (a) pure PCL ($\times 1000$), (b) GPCL1 ($\times 1000$), (c) GPCL4 ($\times 8000$), (d) GPCL7 ($\times 8000$), and (e) GPCL13 ($\times 8000$).

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REFERENCES

- Hocking, P. J. *J Macromol Sci Rev Macromol Chem Phys* 1992, C32, 35.
- Otey, F. H.; Westhoff, R. P.; Russell, C. R. *Ind Eng Chem Prod Res Dev* 1977, 16, 305.
- Otey, F. H.; Westhoff, R. P.; Doane, W. M. *Ind Eng Chem Prod Res Dev* 1980, 19, 592.
- Otey, F. H.; Westhoff, R. P.; Doane, W. M. *Ind Eng Chem Res* 1987, 26, 1659.
- Fanta, G. F.; Bargley, E. B. In *Encyclopedia of Polymer Science and Technology*, Suppl. 2; Interscience: New York, 1977, p. 665.
- Stenhouse, P. J.; Mayer, J. M.; Hepfinger, M. J.; Costa, E. A.; Dell, P. A.; Kaplan, D. L. In *Biodegradable Polymers and Packaging*; Technomic Publishers: Lancaster, PA, 1993, p. 151.
- Wolff, I. A.; Olds, D. W.; Hilbert, G. E. *J Am Chem Soc* 1951, 73, 346.
- Wolff, I. A.; Olds, D. W.; Hilbert, G. E. *Ind Eng Chem* 1951, 43, 911.
- Sagar, A. D.; Merrill, E. W. *J Appl Polym Sci* 1995, 58, 1647.
- Bargley, E. B.; Fanta, G. F.; Burr, R. C.; Doane, W. M.; Russell, C. R. *Polym Eng Sci* 1977, 17, 311.
- Fanta, G. F.; Burr, R. C.; Doane, W. M.; Russell, C. R. *J Appl Polym Sci* 1977, 21, 425.
- Koenig, M. F.; Huang, S. J. *Polym Mater Sci Eng* 1992, 67, 290.
- Tokiwa, Y.; Iwamoto, A.; Koyama, M. *Polym Mater Sci Eng* 1990, 63, 742.
- Bastioli, C.; Cerutti, A.; Guanella, I.; Romano, G. C.; Tosin, M. *J Environ Polym Deg* 1995, 3, 81.
- Koenig, M. F.; Huang, S. J. *Polymer* 1995, 36, 1877.
- Choi, E. J.; Kim, C. H.; Park, J. K. *Macromolecules* 1999, 32, 7401.
- Choi, E. J.; Kim, C. H.; Park, J. K. *J Polym Sci Polym Phys Ed* 1999, 37, 2430.
- Kim, C. H.; Choi, E. J.; Park, J. K. *J Appl Polym Sci* 2000, 77, 2049.
- Zhao, W. B. In *Polymer Data Handbook*; Mark, J. E., Ed.; Oxford Univ. Press: New York, 1999, p. 14.
- Shogren, R. L.; Swanson, C. L.; Thompson, A. R. *Starch* 1992, 9, 335.
- Lourdin, D.; Bizot, H.; Colonna, P. *J Appl Polym Sci* 1997, 63, 1047.
- Utracki, L. A.; Khanh, T. V. In *Multicomponent Polymer Systems*; Miles, I. S.; Rostami, S., Ed.; John Wiley & Sons: New York, 1992, p. 207.
- Bucknall, C. B. In *The Physics of Glassy Polymers*; Haward, R. N.; Young, R. J., Ed.; Chapman & Hall: London, 1997, p. 363.