Mechanical Properties and Morphology of the Modified HDPE/Starch Reactive Blend

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ABSTRACT: We investigated the effect of reactive blending on the mechanical properties and morphology of high-density polyethylene (HDPE)/plasticized starch blends. HDPE was chemically modified to enhance the compatibility with the plasticized starch. The modified HDPE, HDPE-*g*-glycidyl methacrylate (GMA), was synthesized by melt reaction of HDPE in the presence of dicumyl peroxide (DCP). A finer dispersion of starch in the HDPE matrix was achieved compared to that in the unmodified HDPE. The amount of GMA groups in the modified HDPE enhanced the miscibility of HDPE/starch blends. We also observed that the amount of glycerin improves the mechanical properties of blends. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3313–3320, 2001

Key words: biodegradable; HDPE; starch; reactive blends; mechanical properties; morphology

INTRODUCTION

Considering disposal options, biodegradable polymers that completely mineralize to carbon dioxide, methane, and water, and so forth offer an attractive approach to environmental waste management and contribute to the solution of these disposal problems.

The currently available biodegradable polymers can be divided into three general classes: aliphatic polyesters, plastics based on natural polymers, and biodegradable vinyl polymers. Some commercially available biodegradable polymers are summarized in Table I.[1,2]

Natural polymers such as starch and cellulose are good base materials for rapidly degrading plastics, which are easily digested by microorganisms. Starch contains the polysaccharides amylose [α-(1,4)-linked glucose] and amylopectin [α-(1,4)-linked glucose main chains with α-(1,6)-linked branches of α-(1,4)-linked glucose]. Most cereal and tuber starches contain approximately 30% amylose. Starch is thermally processable when a plasticizer, such as water, is added.[3] The performance of materials blended with starch changes during and after processing as a result of the hydrophilicity of starch. However, starch is a potentially useful polymer as a thermoplastic biodegradable material because of its low cost, availability, and production from annually renewable resources.

A number of studies on the effects of plasticizers on starch have been carried out with the aim of producing thermoplastic materials. However, a drawback of these materials is the loss of mechanical properties with time caused by structural changes attributed to the loss of plasticizer.[4–8]

In the early 1970s, Griffin[9] had the idea to use granular starch as a filler in polyethylene to increase the biodegradability of the resulting material. Most starch applications are focused on polyethylene. Increasing the amount of starch causes

Table I Biodegradable Plastics and Their Potential Applications

Classes	Examples	Characteristics	Potential Applications
Aliphatic Polyesters	Polylactic acid (PLA)	Extrudable, clear, high strength, brittle	Medical uses, packaging
	Polyhydroxybutyrate (PHB), hydroxybutyrate–hydroxyvalerate copolymer (PHBV)	Extrudable, rapid biodegradation, high cost	Packaging, films, coatings
	Polycaprolactone (PCL)	Easily extrudable, water-stable, tough, low melting point	Medical uses, packaging, compost bags
Plastics based on natural polymers	Starch	Extrudable, low cost, rapid biodegradation, water-sensitive	Foam product, packaging
	Cellulose acetate (CA)	Extrudable, high strength, slow biodegradation	Packaging, molded product
Degradable vinyl polymer	Polyvinyl alcohol (PVA)	Extrusion difficult, water-soluble	Detergent, pesticide, fertilizer

a decrease in both tensile strength and elongation at break. To increase the incorporated amount of starch, the latter can be surface-treated with a hydrophobic additive or a compatibilizer.[10]

The ethylene–acrylic acid (EAA) copolymer is known to be the most effective compatibilizer, but it must be used in great quantities to obtain satisfactory mechanical properties.[11–13] It was also reported that EAA inhibits the rate of starch biodegradation.[14]

In the last few years, increased interest has focused on the use of starch together with polymers containing reactive groups. Such polymers are styrene–maleic anhydride (SMA) copolymer and ethylene propylene-*g*-maleic anhydride copolymer (EPMA).[15–17] In this study, we investigated the morphologies and mechanical properties of polyethylene-*g*-maleic anhydride copolymer/starch blends.

EXPERIMENTAL

Materials and Blend Preparation

Commercial-grade HDPE 6010BP was kindly provided by Honam Petrochemical Corp., Korea. The melt flow index of 6010BP was 0.7 g/10 min at 190°C. The modified HDPE, glycidyl methacrylate (GMA, Aldrich, USA) grafted HDPE (HDPE-*g*-GMA, GPE), was prepared by melt reaction in a Brabender mixing head. HDPE (40 g) was hand-mixed with GMA/dicumyl peroxide (DCP, Aldrich)

solution where the DCP content was fixed at 10 wt % relative to the GMA content. The Brabender mixer was maintained at 160°C and 80 rpm during the grafting reaction. The GMA contents of samples were changed to 5, 10, and 15 wt % relative to the HDPE weight, and the samples were named GPE5, GPE10, and GPE15, respectively.

The starch (Aldrich) was plasticized with glycerin (Aldrich) in a Brabender mixing head to destroy the granular structure of starch. The various plasticized starches (PLST) were prepared with changes of glycerin contents of 40, 50, and 60 wt % relative to starch weight, and the samples were named PLST40, PLST50, and PLST60, respectively. These plasticized starches were blended with GPE in a Brabender mixing head. Mixing was performed at 170°C and 80 rpm for 15 min. For GPE/plasticized starch (PLST) blends, we varied starch, glycerin, and grafted GMA contents on the GPE. Melt temperature and torque were recorded during the mixing period. All the blend samples were molded by hot pressing at 200°C to prepare sheets with 1 mm thickness. The actual dimensions of the tensile specimens were the same as those described in the ASTM D1708 method.

FTIR Measurements

FTIR (ThermoMatsson, USA) spectra were acquired to confirm the grafting reaction of HDPE-*g*-GMA, named GPE. For each spectrum, 20 consecutive scans with 4 cm^{-1} resolution were co-
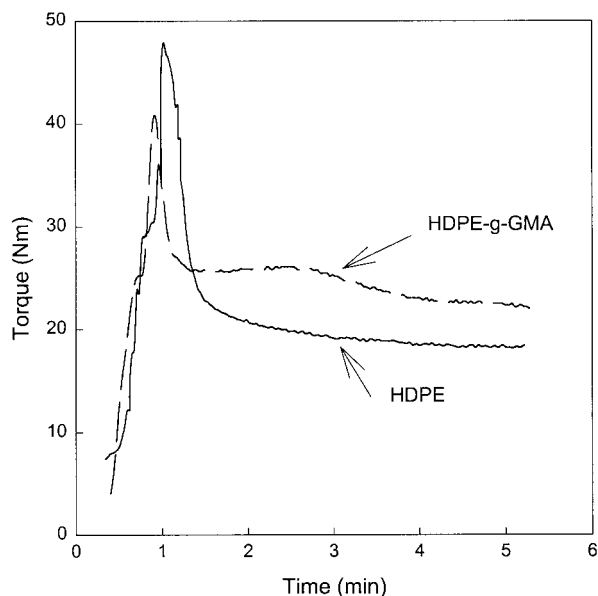
Figure 1 Torque curves of the pure HDPE and HDPE-*g*-GMA.

added. Samples were measured in the form of thin films with about $70 \pm 2 \ \mu$m thickness.

Mechanical Properties of Blends

Mechanical properties such as tensile strength (at break) and elongation at break for all the blend samples were measured with Instron (Model 4204) tensile tester at a crosshead speed of 20 mm/min, and two points of extension for calculating the initial tensile moduli of specimens were selected, 0.1 and 0.3 mm, respectively. Five specimens were tested and results were averaged to obtain a mean value.

Blend Morphology

Morphology of the GPE/PLST blend was investigated by using scanning electron microscopy (Phillips SEM 535M, Holland). To observe the domain structure of the starch phase, the 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. All the SEM micrographs were taken with the electric field strength of 20 kV.

RESULTS AND DISCUSSION

Characterization of HDPE-*g*-GMA (GPE)

Figure 1 shows the torque curves of pure HDPE and HDPE containing GMA/DCP solution. A fixed

amount of DCP was added, which is 10 wt % relative to GMA content. The torque of pure HDPE decreased continuously until it leveled off, whereas for the HDPE containing GMA/DCP, there was a significant torque increase after the initial melting of the HDPE. Such an increase in the torque is expected to be attributable to the grafting reaction of GMA onto HDPE backbone, given that the branched macromolecules, which have a higher melt viscosity than that of linear macromolecules, are produced during the grafting reaction. The steps involved in the grafting reaction are summarized in Figure 2. To investigate the GMA grafting, the FTIR spectrum of HDPE-*g*-GMA was obtained, as shown in Figure 3. The peak corresponding to the vibration of the in-plane deformation of the epoxy ring contained in GMA is about 910 cm^{-1}, whereas there is no such a peak for pure HDPE.

Effect of Starch Content on the Mechanical Property of the Blend

Figure 4 shows the tensile modulus of the GPE10/PLST40 blends. The tensile moduli of the blends containing PLST40 increase with starch content. In general, modulus is closely related to the hard domain of the material. The mechanical properties of PLST40 and GPE10 are listed in Table II. As shown in Table II, the tensile modulus of PLST40 is higher
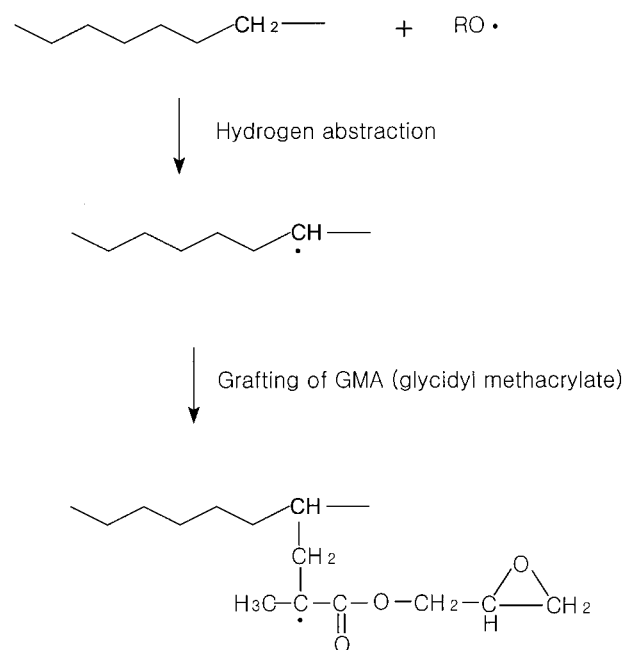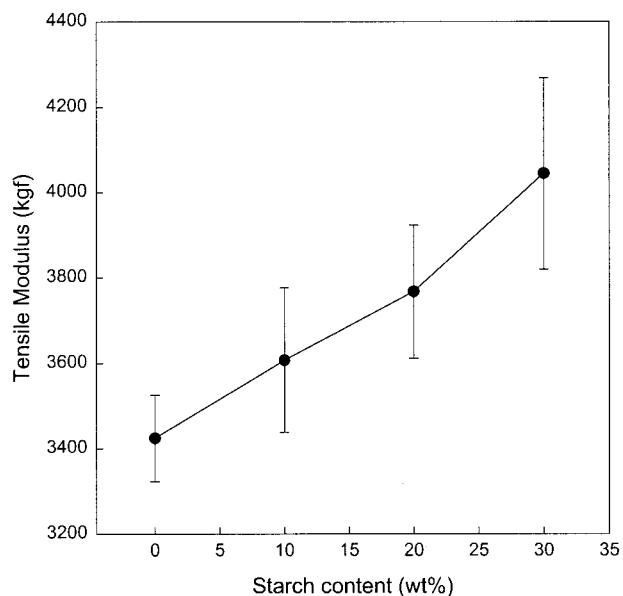

Figure 2 Grafting reaction mechanism of GMA on the HDPE.
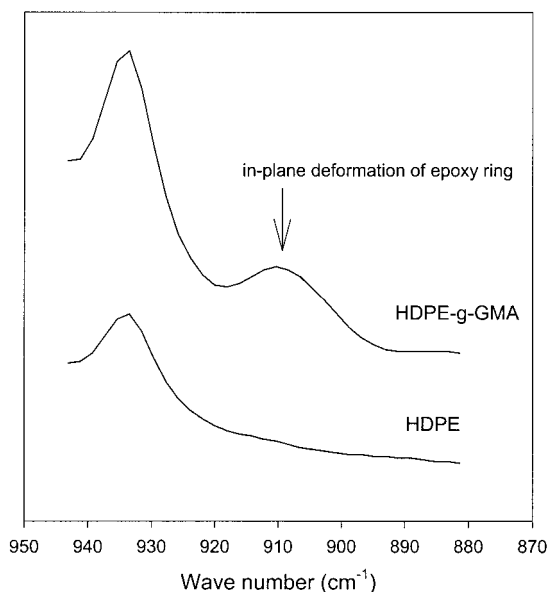
Figure 3 FTIR spectra of pure HDPE and HDPE-*g*-GMA.

Table II   Mechanical Properties of the Plasticized Starch and Pure GPE10

Glycerin Content	Tensile Modulus	Tensile Strength
40 wt% of starch (PLST40)	9408 kgf/cm^2	343 kgf/cm^2
Pure GPE10	3199 kgf/cm^2	225 kgf/cm^2

than that of GPE10. As PLST40 content increases, the hard domain content increases and thus the tensile modulus of the blend increases.

Figures 5 and 6 illustrate the tensile strength and the elongation at break of the GPE10/PLST40 blend with the increase of PLST40 content. As shown in Figure 5, the ten-

sile strength of the blend increases with PLST content. However, elongation at break decreases with increasing PLST40 content, as illustrated in Figure 6. The decrease of elongation at break of the blend is significant. It would be correlated with mechanical properties of the dispersion phase, PLST, and morphology of the PLST40 dispersion phases. As listed in Table II, PLST40 shows a brittle deformation behavior resulting from the low glycerin content. In this reactive blend, the interface between the matrix (GPE10) and the dispersion phase (PLST40) was chemically bounded. Thus, when external stress is applied, the matrix polymer (GPE10) tends to relax and dissipate the external stress. However, because the matrix (GPE10) is bounded with the hard dispersion phase (PLST40), it cannot release the external stress and represents the brittle deformation behav-

Figure 4 Tensile modulus of the GPE10/PLST40 blend with respect to starch content.
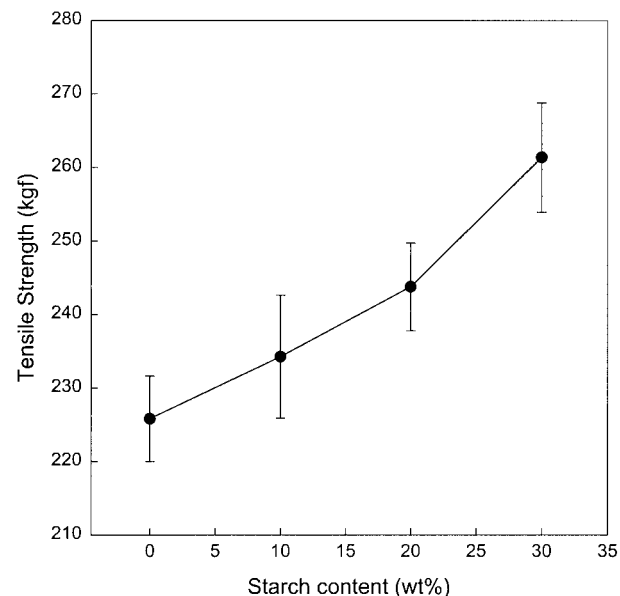
Figure 5 Tensile strength of the GPE10/PLST40 blend with respect to starch content.
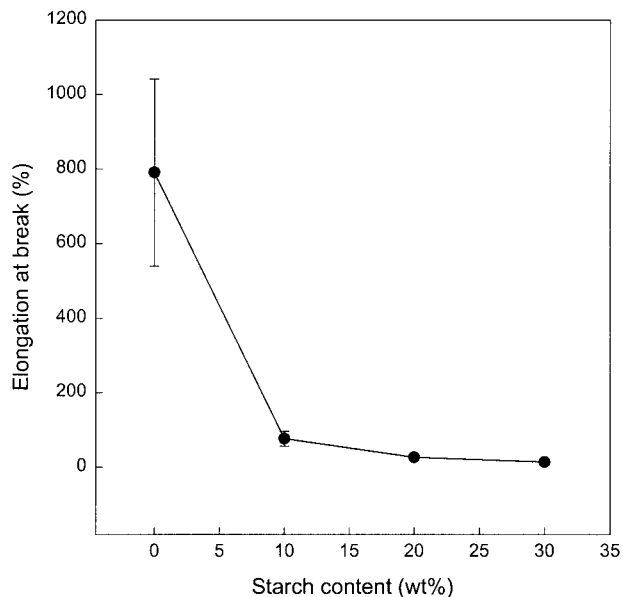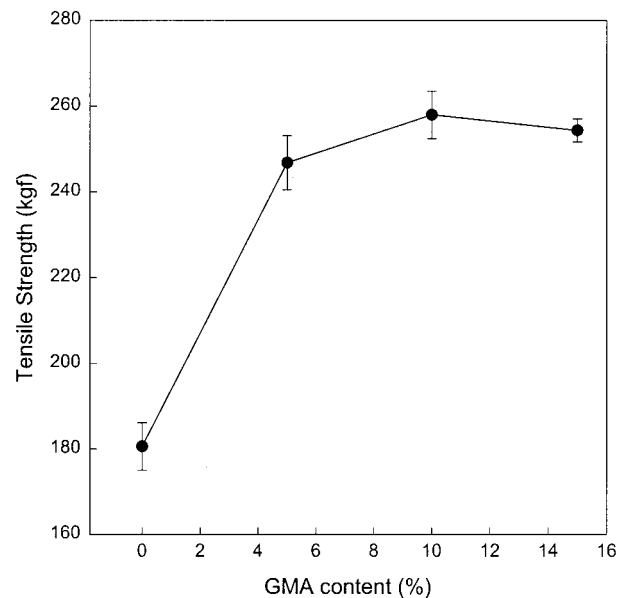
Figure 6 Elongation at break of the GPE10/PLST40 blend with respect to starch content.
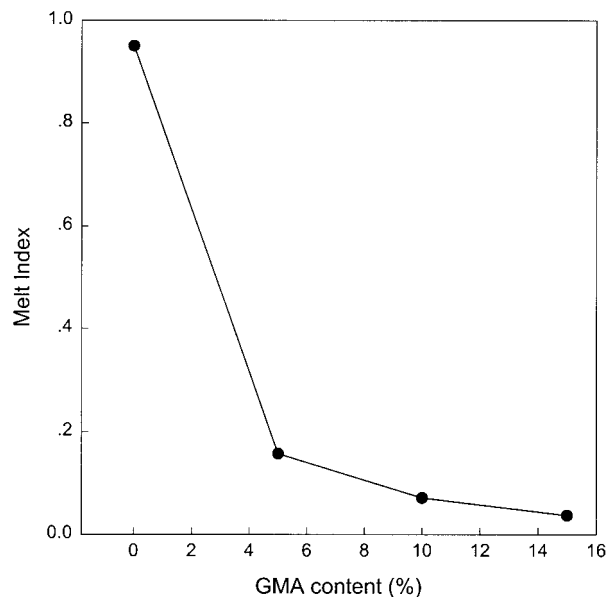
ior. Thus, the abrupt change of elongation at break is observed with the increase of PLST40 content.

Effect of GMA Content of GPE on the Mechanical Property of the Blend

We prepared GPE/PLST50 blend with varying grafted GMA content and investigated the mechanical properties of the given systems. The
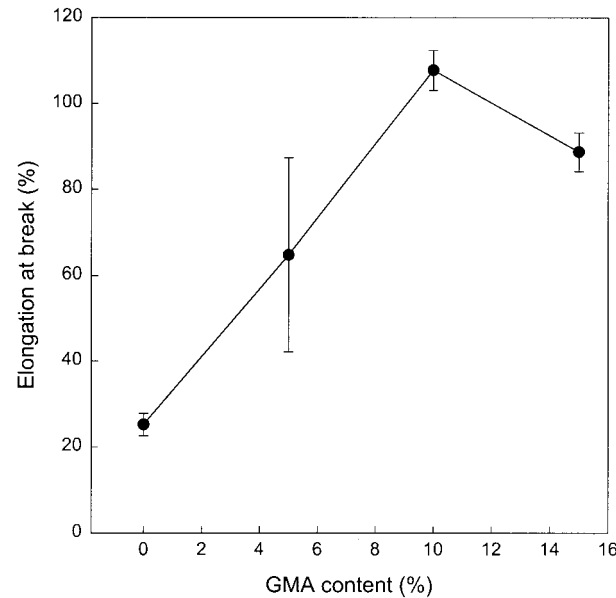

Figure 8 Melt flow index of the GPE/PLST50(70/30) blends with varying GMA content in GPE at 190°C.

weight fraction of each component was fixed at GPE/PLST50 = 70/30.

Figure 7 illustrates the tensile strength change of the blend with varying grafted GMA content. It was found that the tensile strength increased with the grafted GMA content, which induces the network formation by crosslinking reaction with increasing grafted GMA content. The crosslinking reaction results in an increase of the tensile strength of the blend.

Figure 7 Tensile strength of the GPE/PLST50(70/30) blend with respect to GMA content in GPE.

Figure 9 Elongation at break of the GPE/PLST50(70/30) blend with respect to GMA content in GPE.
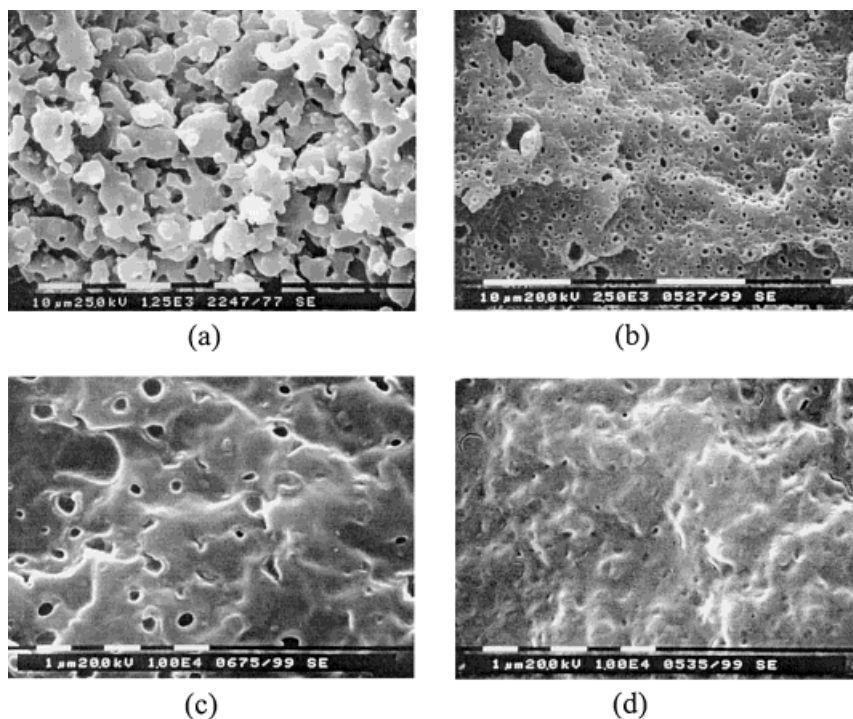
Figure 10   SEM images of the GPE/PLST50(70/30) blends with varying GMA content in GPE.

To investigate the degree of crosslinking, we measured a melt flow index change of the blends, as shown in Figure 8. The melt flow index gives information for the degree of chain entanglement of polymer chains by chemical or physical crosslinking. The melt flow index in the blend decreases with the grafted GMA content, which implies that the crosslinking degree increases with the GMA content.

Figure 9 illustrates the elongation at break of the GPE/PLST50(70/30) blends with the grafted GMA content, where one can observe that as the grafted content increases, the elongation at break increases.

Figure 10 shows SEM images of starch domains dispersed in the HDPE matrix. It is shown that the starch domain size decreases with the grafted GMA content. When the grafted GMA content is higher than 10 wt %, the starch domain size becomes smaller than 1 μm in the range investigated, which is attributed to the higher amount of grafted GMA reacting with hydroxyl groups of starch, thus reducing the starch domain size by the enhancement of interfacial stability between starch and HDPE matrix.

According to the phase morphology, the elongation at break and the tensile toughness must be increased with grafted GMA. The higher grafted

GMA content induces a higher degree of reaction between the starch and the modified HDPE, which enhances the compatibility and also increases the crosslinking degree of the blend. As shown in Figure 8, the melt flow index decreases
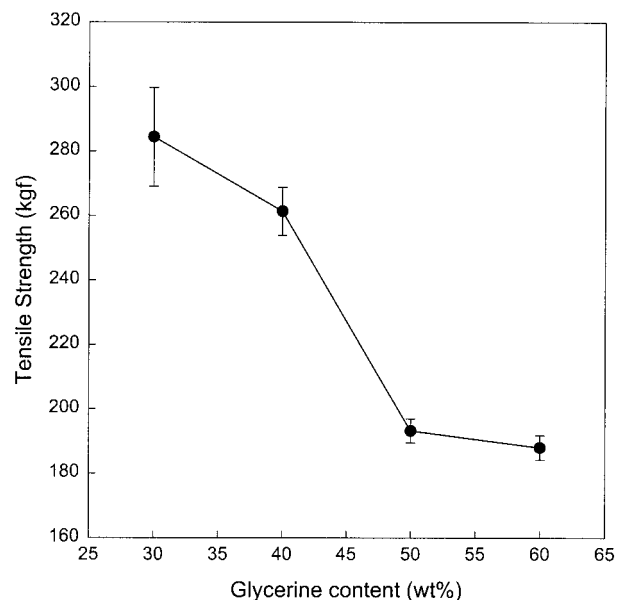
Figure 11   Tensile strength of GPE10/PLST(70/30) blends with respect to the glycerin content.
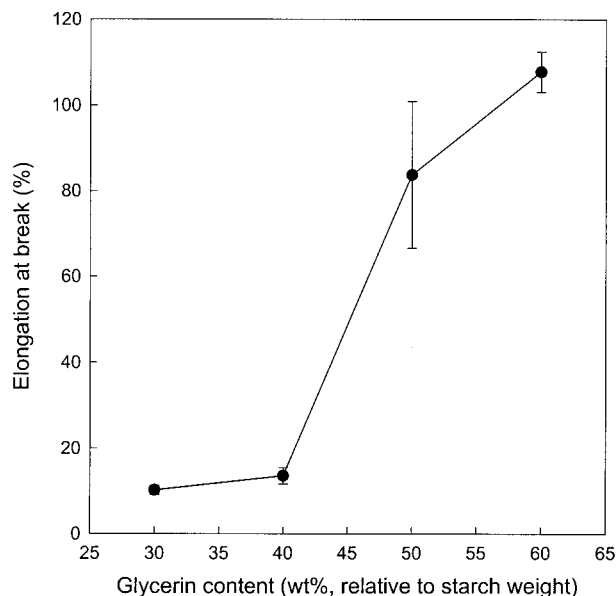
Figure 12 Elongation at break of GPE10/PLST(70/30) blends with respect to the glycerin content.

with the grafted GMA content, which means that the increase of the crosslinking degree reduces the chain relaxation over the external stress and results in the decrease of the elongation at break.

Mechanical Property Change of the GPE/PLST Blend with Varying Glycerin Content

Figures 11 and 12 illustrate the tensile strength and the elongation at break of the GPE10/PLST (70/30) blends with respect to glycerin content. It is clearly observed that the tensile strength and the elongation at break are abruptly changed as the glycerin content varied from 40 to 50 wt % relative to the starch weight.

SEM images of the GPE10/PLST systems containing varying glycerin contents, which are taken for the fracture surfaces etched physically by the ultrasonic treatment, are shown in Figure 13(a)–(d). Figure 13(a) and (b) show larger starch domain sizes than those of Figure 13(c) and (d). As shown in Figure 13(a) and (b), the domain sizes of dispersed starch phases are around 3–5 μm in diameter. In Figure 13(c) and (d), however, the domain size of dispersed starch phases is smaller than 1 μm in diameter. The HDPE blend containing small dispersion phases shows good elongation at break in general. Domain sizes of the dispersed starch in Figure 13(a) and (b) show great differences compared with those shown in Figure 13(c) and (d), which demonstrates their primacy for the significant change of the tensile strength and the elongation at break as the glyc-
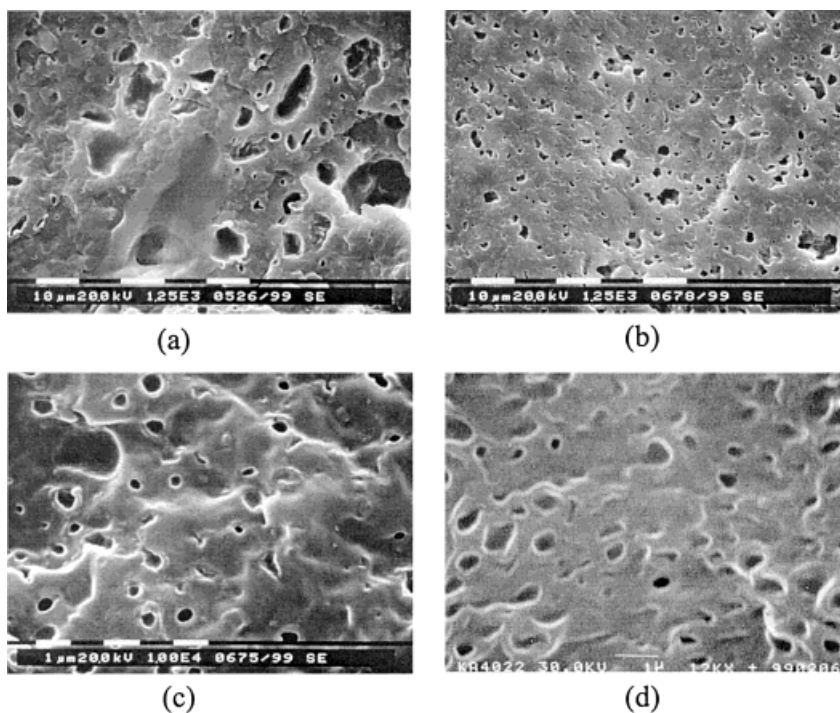
Figure 13 SEM images of the GPE10/PLST(70/30) blends with varying glycerin content.

erin content varies from 40 to 50 wt %. In a previous report,[18] a starch/LDPE blend containing the starch granules, which are characterized by large domain sizes ($\sim$ 15 μm) of dispersed starch, shows high elongation at break over 100%. This implies that the difference of the domain size of dispersed starch alone could not explain the significant change of the tensile strength and the elongation at break of the GPE10/PLST blend.

A previous study[19] reported the mechanical properties of plasticized starch with varying glycerin contents. The tensile strength and the elongation at break of the plasticized starch itself were changed significantly as the glycerin content increased from 40 to 50 wt % relative to the starch weight. This behavior was very similar to the case of the GPE10/PLST blend observed in Figures 11 and 12, which implies that the mechanical properties of the blend are closely related with the mechanical properties of the dispersion phases. The HDPE matrix and the dispersed starch phase are tightly bounded by the reaction of GPE and starch. Thus mechanical properties of the blend strongly depend on the mechanical properties of the dispersed starch phases. When the dispersed starch phases are hard and brittle, the dispersed starch phases restrict the deformation of the matrix HDPE, thus reducing the elongation at break and increasing the tensile strength. However, when the dispersed phases are flexible and mobile to relax the external stresses, the dispersed starch phases deform simultaneously with the matrix HDPE to dissipate the external stresses, thus resulting in the higher elongation at break and a lower tensile strength.

CONCLUSIONS

HDPE-*g*-GMA was prepared by melt reaction of HDPE/GMA in the presence of DCP in the Brabender mixer. The grafting reaction was confirmed from the fact that the in-plane deformation band corresponding to the motion of epoxy group was observed in the range of 920 cm^{-1} in the FTIR spectrum. The morphologies of the given systems were studied using scanning electron microscopy (SEM).

It was observed that a finer dispersion of starch was achieved in the modified HDPE matrix than in the unmodified HDPE, which implies that the HDPE modification by grafting GMA is an effective method for enhancing the compatibility of the blend. As the amount of GMA groups in the modified HDPE increased, the elongation at break showed maximum behavior at certain GMA content, that is, GPE10.

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