

# Grafting of Glycidyl Methacrylate onto Ethylene–Propylene Copolymer: Preparation and Characterization

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## SYNOPSIS

Ethylene–propylene copolymer (EP) was functionalized with glycidyl methacrylate (GMA) by means of a radical-initiated melt grafting reaction. FTIR and ESCA were used to characterize the formation of EP-*g*-GMA copolymers. The content of GMA in EP-*g*-GMA was determined by using hydrochloric acid/xylene titration. Effects of concentrations of GMA and dicumyl peroxide on grafting rate were studied. It was found that contact angles of the water on surfaces of EP-*g*-GMA samples increased with increasing content of GMA in EP-*g*-GMA. The influence of the content of GMA on the crystallization structure of EP-*g*-GMA was investigated by DSC and WAXD. Compared with the plain EP, the crystallization temperature of propylene blocks of EP-*g*-GMA increased over 10 K, and the melting temperature and crystallinity decreased somewhat. Functionalization of EP led to the change of the crystal form of propylene blocks from the mixed form of  $\alpha$  and  $\beta$  into the  $\alpha$  form.

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## INTRODUCTION

Due to their versatile properties and low price, polypropylene and propylene–ethylene copolymers have become some of the largest and fastest growing resins in use. However, lack of reactive sites, difficulty in dyeing, and poor hydrophilicity limit their further development. Chemical modification has been carried out in the past 20 years to give additional properties by means of grafting unsaturated polar groups onto the backbone of these polymers.<sup>1–10</sup> Maleic anhydride (MAH), maleic acid (MA), dibutyl maleate (DBM), and acrylic acid (AA) and its esters are the main grafting monomers adopted in the chemical modification. Several commercial products have been reported in the literature.<sup>11,12</sup>

In recent years glycidyl methacrylate (GMA) has been utilized as the grafting monomer of polyolefins that can be functionalized as *in situ* compatibilizers of polymer alloys such as polyolefins/polyamides, polyesters,<sup>13–17</sup> etc., because epoxy groups of GMA are able to react with —OH, —COOH, and

—NH<sub>2</sub>. GMA was also grafted on the surface of ultrahigh modulus polyethylene (UHMPE) fiber to improve the wettability and adhesion.<sup>18</sup> Chang et al. reported on polymer blends of phenoxy/acrylonitrile–butadiene–styrene employing styrene–acrylonitrile–GMA copolymer as an *in situ* compatibilizer and polystyrene/nylon blends having styrene–GMA copolymer as an *in situ* compatibilizer.<sup>19</sup>

In the present study, modification of ethylene–propylene (EP) copolymer was attempted by grafting with GMA. The purpose was to use the modified EP as an effective toughening agent for nylon 1010 and an *in situ* compatibilizer of polypropylene–nylon 1010 blends. The influence of concentrations of the GMA and initiator on the grafting degree and the characterization of the crystal structure of EP-*g*-GMA are reported.

## EXPERIMENTAL

### Materials

EP copolymer used in this work was kindly supplied by Liaoning Panjin Natural Gas Co. (China). The C<sub>2</sub> content is about 10% and the melting index is 2

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**Table I** Effect of Concentrations of DCP and GMA on Content of GMA in EP-*g*-GMA

EP (g)	DCP (wt %)	GMA (wt %)	Content of GMA in EP- <i>g</i> -GMA (mol %)
100	0.05	2	0.29
100	0.10	2	0.26
100	0.15	2	0.51
100	0.20	2	0.29
100	0.25	2	0.26
100	0.20	1	0.06
100	0.20	2	0.29
100	0.20	4	0.54
100	0.20	5	0.51
100	0.20	6	0.77

g/min (230°C). Reagent grade GMA was purchased from Suzhou Anli Chemical Co. (China) and used without purification.

#### Preparation of EP-*g*-GMA

A Brabender-like apparatus was used to prepare EP-*g*-GMA. EP was introduced into its mixing chamber at 190°C. After EP was melted, a solution consisting of different amounts of GMA and dicumyl peroxide (DCP) was added. Mixing was continued for another 5 min at a roller speed of 32 rpm. Concentrations of GMA and DCP are shown in Table I.

#### Purification and Characterization of EP-*g*-GMA

To remove residual GMA, and possible homopolymer of GMA, the following purification procedure was adopted. The grafted EP samples were pressed into films with thickness about 0.2 mm. Then the films were extracted by using boiling benzene for at least 12 h.

An FTS-7 Fourier-transform infrared spectrophotometer (Bio Rad Co.) and ESCA CAB MK-II electron spectrometer (VG Co.) were used to qualitatively characterize the formation of EP-*g*-GMA copolymers.

Evaluation of the content of GMA in the copolymers was carried out by using a hydrochloric acid/xylene titration method. A copolymer sample (about 2 g) was added to 100 mL of xylene. After the sample was completely dissolved, 0.5 mL of concentrated hydrochloric acid (1.2N) were added to open the epoxide rings of GMA. Then, the solution was titrated with 0.05N methanolic sodium hydroxide solution to the first red color of the end point. Phenolphthalein/ethanol was used as the red indicator.

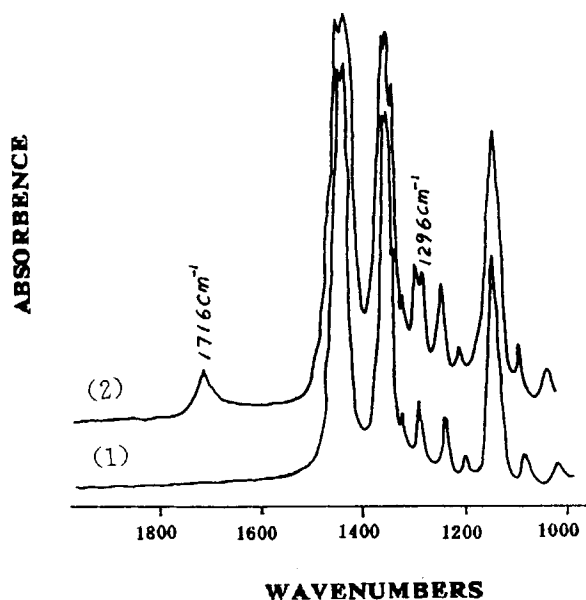
Contact angles ( $\theta$ ) of a water drop on the plain EP and EP-*g*-GMA samples were measured at 20°C by using a home-made apparatus.

A Perkin-Elmer 7 differential scanning calorimeter was used to investigate thermal behaviour of EP-*g*-GMA. Heating and cooling rates were 10°C/min and the quantity of specimens was about 10 mg.

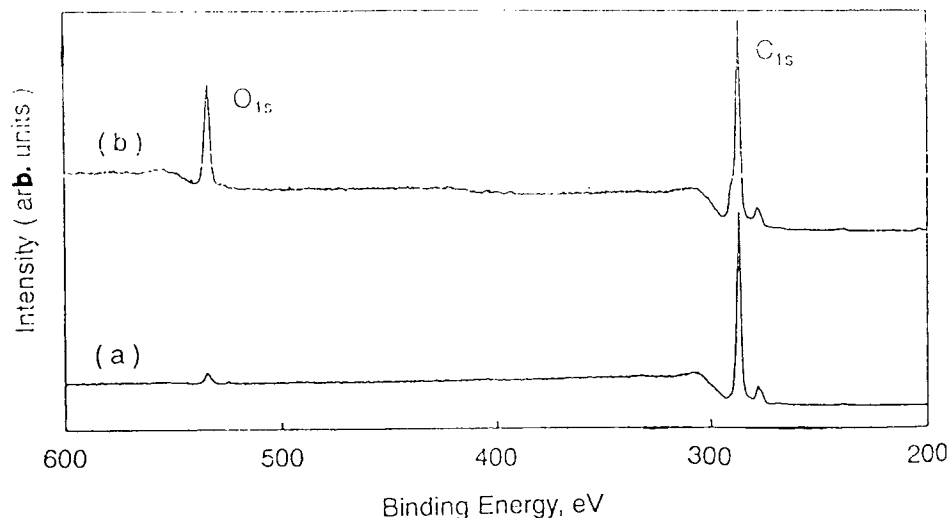
Wide angle X-ray diffraction profiles of EP-*g*-GMA and the plain EP were obtained by using a PW 1700 Philips diffractometer with Cu K $\alpha$ , Ni-filtered radiation, 40 kV of tube electric pressure, and 30 mA of tube electric current.

## RESULTS AND DISCUSSION

FTIR spectra of the plain EP and EP-*g*-GMA are shown in Figure 1. It is clearly seen that new absorptions at 1716 and 1296 cm<sup>-1</sup>, which are attributed to contributions of carbonyl and epoxy groups of GMA, respectively, appear for the EP-*g*-GMA sample. This result verifies that GMA has been grafted onto the EP molecular chains. Figure 2 shows XPS spectra of the plain EP and EP-*g*-GMA. The intensity of the oxygen peak of EP-*g*-GMA is significantly larger than the value of the plain EP. This can be tentatively explained as follows. The small O<sub>1s</sub> peak of the plain EP originates from the absorbed oxygen of the air on the surface of the EP sample. The O<sub>1s</sub> peak of the EP-*g*-GMA sample comes from two contributions: one is from the ab-



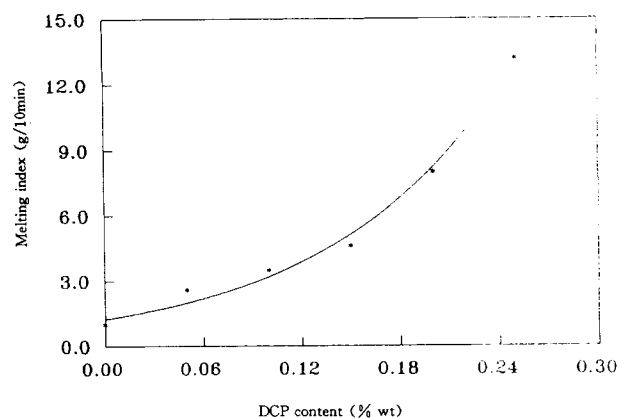
**Figure 1** FTIR spectra of (1) plain EP and (2) EP-*g*-GMA.



**Figure 2** XPS spectra of (a) plain EP and (b) EP-*g*-GMA.

sorbed free oxygen in the air, and the other is from the oxygen element of the carbonyl and epoxy groups of the grafted GMA.

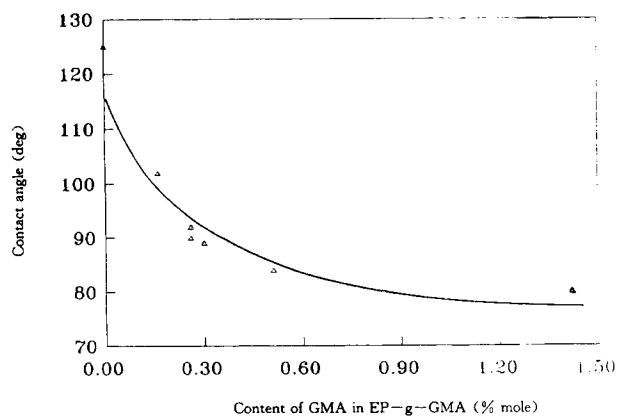
The content of GMA in EP-*g*-GMA copolymers is dependent upon concentrations of the initiator and monomer in the melt grafting reaction. As shown in Table I, when the monomer concentration was kept at 2%, a maximum GMA content occurred at the DCP concentration of 0.15%. This feature can be attributed to the competition between the initiated grafting reaction of EP-*g*-GMA and degradation of the propylene blocks of EP. In fact, with increasing DCP concentrations, the melt index of EP-*g*-GMA increased dramatically as shown in Figure 3. When the initiator concentration was fixed at 0.20%, the GMA content in EP-*g*-GMA increased with increasing monomer concentrations.



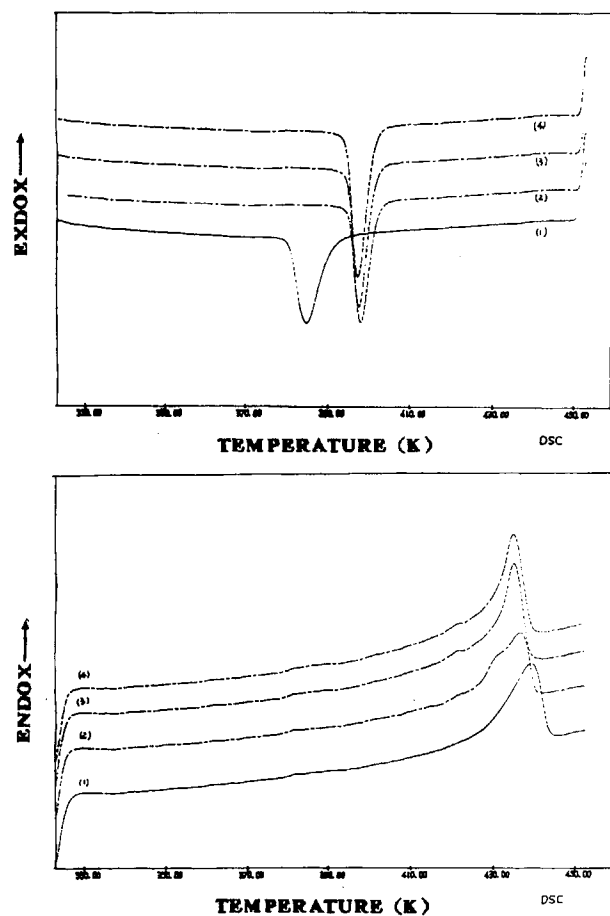
**Figure 3** Melt index of EP-*g*-GMA as a function of DCP concentrations.

Contact angles of a water drop on surfaces of the plain EP and EP-*g*-GMA samples are reported in Figure 4. It is observed that with an increasing percentage of grafted GMA, contact angles increased monotonically. This result suggests that the surface polarity of grafted copolymer is augmented by an increase of the content of GMA in EP-*g*-GMA samples.

Thermograms of the plain EP and EP-*g*-GMA samples are shown in Figure 5. The melting temperature of propylene blocks of the plain EP is about 438 K, and that of EP-*g*-GMA is 432–435 K. Compared with the plain EP, melting peaks of propylene blocks of EP-*g*-GMA shift about 3–6 K toward lower temperature. The crystallization temperature of propylene blocks of EP-*g*-GMA samples is about 10 K higher than that of the plain EP, and the crys-



**Figure 4** Contact angles ( $\theta$ ) of water drop on surfaces of EP-*g*-GMA as a function of the content of GMA in EP-*g*-GMA.



**Figure 5** Thermograms of plain EP and EP-*g*-GMA samples. Content of GMA in EP-*g*-GMA (mol %): (1) 0, (2) 0.26, (3) 0.51, and (4) 0.77.

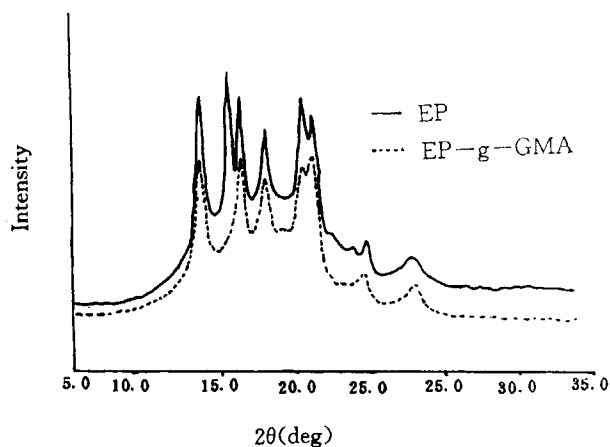
tallinity of EP-*g*-GMA is a little lower than the plain EP. These features can be tentatively explained as follows. Introducing grafted GMA monomers into EP molecular chains results in the reduction of the regularity of EP molecular chains and the enhancement of steric hinderance for folding of propylene sequences. Perfection of crystals of propylene blocks is decreased. Therefore, melting temperatures and crystallinities of propylene blocks of EP-*g*-GMA are lower than those of the plain EP. However, grafted GMA can act as a nucleating agent for the crystallization of propylene sequences. The capability of crystallization of propylene sequences increases and the supercooling ( $\cdot T_m - T_c$ ) drops. This bring about an increase in crystallization temperature of the propylene sequences.

WAXD patterns of EP and EP-*g*-GMA are shown in Figure 6. As indicated by the patterns, grafting of GMA leads to some change in the crystallization structure of EP crystals. The peak at  $2\theta$  is  $12.9^\circ$ ,

corresponding to the 300 diffraction peak of the  $\beta$  form (hexagonal phase), which disappeared after GMA was grafted onto EP molecular chains. It suggests that the mixture of the  $\alpha$  and  $\beta$  form of crystals of the propylene sequences is replaced by the pure  $\alpha$ -form crystals. The proportion of these two forms of crystals usually depends on preparation conditions of the samples and the nucleating process. In our work preparation conditions were the same for all samples. Therefore, it can be concluded that the change of the crystallization structure of EP-*g*-GMA originated from a different nucleating process.

## CONCLUSIONS

The results of FTIR and ESCA confirmed that GMA was grafted onto molecular chains of the EP copolymer. The content of GMA in EP-*g*-GMA changed with the concentrations of the initiator and monomer. Using an appropriate concentration of initiator, high functionalization levels with small amounts of chain degradation were obtained. Measurements of contact angles of water drops on EP and EP-*g*-GMA surfaces showed that they increased with an increasing percentage of grafted GMA. This result suggested that the surface polarity of grafted copolymer was augmented with an increase of the content of GMA in EP-*g*-GMA. Functionalization of EP led to an increase of crystallization temperature and a decrease of melting temperature and crystallinity, which was attributed to the modification of the structure of EP copolymer. Furthermore, grafted GMA could act as a nucleating agent for crystallization of propylene sequences. This brought about an increase in crystallization tem-



**Figure 6** WAXD patterns of EP and EP-*g*-GMA.

perature of propylene sequences, and a change of the crystal form of EP-*g*-GMA.

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