Grafting of Glycidyl Methacrylate onto High-Density Polyethylene with Reaction Time in the Batch Mixer

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ABSTRACT: The melt grafting of glycidyl methacrylate (GMA) onto high-density polyethylene (HDPE) in the presence of free radical initiators was investigated in the batch mixer. The graft content was determined with the titration and FTIR spectroscopy. The graft content increased with the increase of peroxide and initially introduced GMA concentration. Increase of the grafted GMA content resulted in decrease of the melt index. Interestingly, there was a sudden drop of GMA grafting content with the reaction time. It is assumed that depolymerization of GMA have taken place over the ceiling temperature. The crystallinity of the prepared glycidyl methacrylate grafted high density polyethylene (HDPE-*g*-GMA) was determined by the measurement of the heat of fusion. GMA grafted site acted as defect and crystallinity of the HDPE-*g*-GMA decreased with the increase of grafting reaction. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1093–1099, 2008

Key words: graft copolymer; functionalization of polymers; polyethylene; melt; initiators

INTRODUCTION

Free radical grafting of polyolefin with monomers containing potentially reactive group is one of the attracting methods to modify basic properties of the pristine polymer.[1] Especially, it is powerful method to produce compatibilizer for the blends of polar and nonpolar polymer pair. It is because that chemical reaction between functional groups in the modified nonpolar and polar polymer during mixing procedure gives good miscibility of the blend.[2]

Vinyl monomers such as, maleic anhydride, dibutyl maleate, maleic acid, dimethyl aminoethyl methacrylate, and glycidyl methacrylate (GMA) are widely adopted as grafting monomer[3–7] using various grafting method, which is radical reaction using chemical initiator,[8–10] high energy irradiation,[11] plasma,[12] UV photografting,[13] and solvothermal process.[14]

In recent years, studies of the grafting GMA onto various polymer species such as polycaprolactone,[15] polypropylene,[16] low and high density polyethylene,[8,9] are highlighted owing to its epoxy group, which is capable of reacting with various other groups like hydroxyl, amine, and anhydride.[17,18]

Related with GMA grafting, previous works on the mechanism of grafting, graft yield of GMA, and side reactions are reported from other researchers.[19–21]

It is reported that the grafting mechanism differs from the selected polymer used for modification. Grafting yield of GMA was influenced by the species or amount of initiator used, concentration of GMA, and reaction temperature. However, the grafting yield was unsatisfactory compared with the amount introduced. Thus monomer with electron donating character, styrene, was used to enhance graft yield.[9,19–21]

Although radical grafting of GMA onto polymer has been extensively reported, a few work is focused on the grafting with the reaction time. Thus in this work, we report on the GMA grafting onto high-density polyethylene (HDPE) with the mixing time using two different initiators in the internal batch mixer using without any solvent or comonomer.

METHODS

Materials

High density polyethylene grade 2700J in pellet form was kindly supplied by Honam PetroChemical in Korea. Melt index (ASTM 1238, 190°C and 2160 g) of this resin is 7.0 g/10 min. Reagent grade GMA (97% pure) was purchased from Aldrich and used as received. Two peroxide initiators, benzoyl peroxide (BPO) and dicumylperoxide (DCP), were purchased from Fluka and used as received. Dichlorobenzene (DCB) and acetone, which are solvent and nonsolvent for the prepared samples were purchased from Merck and Samchun Chemical (Korea) and distilled before
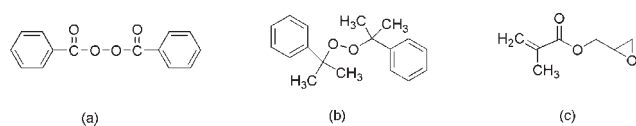
Figure 1 The chemical structures of used peroxides and GMA (a) benzoyl peroxide (b) dicumylperoxide and (c) glycidyl methacrylate.

use. The structure of BPO, DCP, and GMA are shown in Figure 1.

Preparation of HDPE-*g*-GMA

Glycidyl methacrylate grafted high density polyethylene (HDPE-*g*-GMA) were prepared by an internal mixer (Brabender Plasticorder, capacity of 300 cm³) equipped with two roller blades rotating in opposite directions to ensure complete mixing. The speed of the rotor was held constant operating at a speed of 60 rpm. Determined amounts of polymers, monomer and initiator were premixed, by hand in a small container, before being charged into the mixing chamber. After the addition of the mixture, the plunger, which is pressed by the five-bar air pressure, was lowered immediately to minimize the loss of GMA due to vaporization. The wall temperature inside mixer was set to 160°C and air cooling device were connected to prevent overheating induced by the heat in mixing procedure. The reaction product was removed from mixing chamber and quenched to stop any further reaction. The feed compositions of prepared HDPE-*g*-GMA samples are shown in Table I.

Purification of HDPE-*g*-GMA from batch mixer

To remove unreacted GMA, and possible homopolymer of GMA, following two different purification procedures were performed.

1. Crude grafted samples were hot pressed into films with thickness about 0.2 mm at 160°C and cut into small pieces. Then the films were extracted by using boiling benzene for 12 h[22] followed by vacuum drying for 24 h at 80°C.
2. Crude grafted samples were dissolved in DCB (5 wt % solution) at 120°C. After complete dissolution, solutions were washed in the cold acetone for several times[23] followed by vacuum drying for 24 h at 80°C.

From the procedures above, pellet and powder type samples can be obtained, respectively. Several repetition of the purification were made for same samples and showed no weight change of the HDPE-*g*-GMA after first purification, which ensures the removal of the GMA mononer and homopolymer.

Characterization of HDPE-*g*-GMA

The quantification of GMA grafted onto HDPE was performed by using titration method.[16] The purified sample (2 g) was added to 100 mL DCB at 120°C. After the sample was completely dissolved, 0.6 mL of hydrogen chloride in diethyl ether (1.0M) was added to open the epoxide rings of GMA grafted. Then, the excess of HCl was titrated with 0.05M methanolic sodium hydroxide solution by using ethanolic phenolphthalein as a red indicator. The grafting yield was determined by using the following relationship:

$$\text{Grafting yield (wt \%)} = \big[(0.6 \times 10^{-3} - 0.05 \\ \times 10^{-3}V_t)\,\text{mol} \times 142.15\,\text{g/mol}\big] \times 100/2\,\text{g}$$

where V_t is the volume of NaOH solution for titration (mL) and molecular weight of GMA is 142.15 g/mol.

TABLE I
The Feed Compositions of HDPE-*g*-GMA Samples

Sample	HDPE content (%)	Initiator	Initiator content (phr)[a]	GMA content (phr)[a]	Reaction time (min)
2700 J	100	–	0	0	0
A1	100	BPO	0.15	5.0	5
A2	100	BPO	0.25	5.0	5
A3	100	BPO	0.40	5.0	5
A4	100	BPO	0.50	5.0	5
A5	100	BPO	0.50	3.0	5
A6	100	BPO	0.50	8.0	5
A7	100	BPO	0.50	5.0	2
A8	100	BPO	0.50	5.0	8
A9	100	BPO	0.50	5.0	12
B1	100	DCP	0.25	5.0	15
B2	100	DCP	0.40	5.0	15
B3	100	DCP	0.50	5.0	15
B4	100	DCP	0.25	5.0	10
B5	100	DCP	0.25	5.0	20
B6	100	DCP	0.25	5.0	30

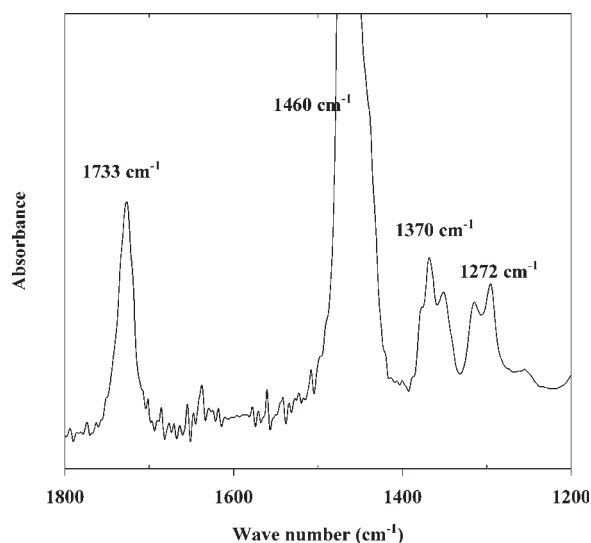^a ''phr'' stands for parts per hundred parts of resin.

Figure 2 FTIR spectrum of HDPE-*g*-GMA.

FTIR was used to confirm grafting reaction and evaluation of relative amount of GMA grafted onto HDPE. To that end, purified samples were hot pressed into thin film (about 10 μm) at 160°C under 220 bar between two copper sheets. The FTIR spectra were recorded in the absorption mode on Bomem MB 102 FTIR spectrometer at a resolution of 4 cm^{-1}. Minimums of 40 scans were signal-averaged and the spectra were stored for further analysis. Figure 2 shows the representative FTIR spectrum of HDPE-*g*-GMA with peak assignment. The peak at 1370 cm^{-1} corresponding to the bending of methyl group in the PE was chosen as the reference and that at 1733 cm^{-1} to stretching of the carbonyl group of GMA were used to determine the grafted amount of GMA.

Melt flow index measurements were performed on all pelletized samples according to ASTM D1238-E ($T = 190°C$ and 2160 g) in a Multi Indexer T-001 (Toyoseki Company). The results are reported in terms of the weight of the extrudate in gram per 10 min.

The crystallinity of HDPE-*g*-GMA was evaluated with differential scanning calorimetry (DSC). The DSC measurements were conducted with a Thermal Analyzer 2000 (Du pont) in a hermetically-sealed cell and taken over a temperature range for −30 to 220°C at a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

HDPE-*g*-GMA was prepared with the introduction of HDPE/GMA/initiator in the internal mixer. Torque of the mixture shows small peak slightly after the initial melting of HDPE and stabilizes with reaction time. This was obvious with the increase of BPO content as shown in Figure 3. Torque increase is due to the rapid decomposition of peroxides and decreases with the consumption of peroxides. Since the torque is related with the melt viscosity of the mixture, branched and crosslinked macromolecules shows higher torque value compared with linear macromolecules at the end of reaction. From the figure, product of higher BPO content showed slightly higher torque at the end of reaction compared with that of smaller BPO content sample, which implies extent of chemical reaction such as grafting of GMA onto HDPE backbone and chain extension or crosslinking of HDPE[15] increased with the BPO introduced. Graft copolymers were analyzed to determine if any gel was formed due to the crosslinking. Purified HDPE-*g*-GMA were dissolved in DCB at 120°C and verified the absence of crosslinked material by visual examination.[4,24]

Effect of initiator concentration on GMA grafting

Samples of HDPE-*g*-GMA with various grafting yields were prepared by varying the amount of peroxide used in the preparation. Reaction time was set to 5 and 15 min for BPO and DCP initiators, respectively. This is five times longer than that of peroxide's half-life time at 160°C and it is enough for the exhaustion of the free radical generator at this reaction time. The effect of initiator concentration on the graft level is illustrated in Figure 4. GMAs grafting yield increased with increasing peroxide concentration for BPO. Same trend was observed for the results obtained by FTIR experiment (GMA graft ratio) as shown in Figure 5. It is clearly shown that the new absorbance peak at 1733 cm^{-1}, which represents carbonyl group of GMA, appeared for HDPE-*g*-GMA samples and peak intensity increased with the increase of BPO concentrations. It is interesting to note that BPO was more effective than the DCP in grafting GMA at 160°C. Also the grafting yield by
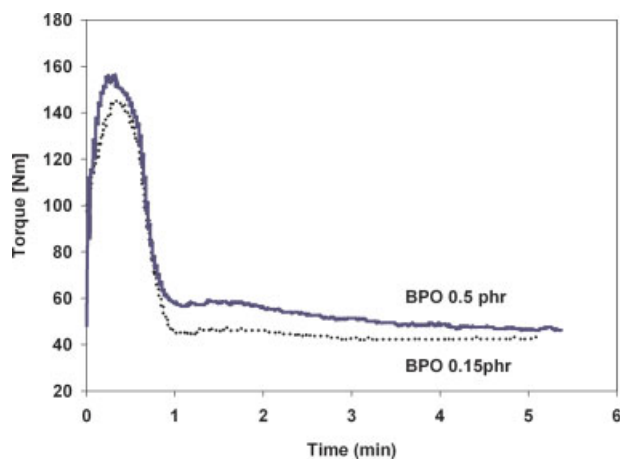

Figure 3 Plot of processing torque versus reaction time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
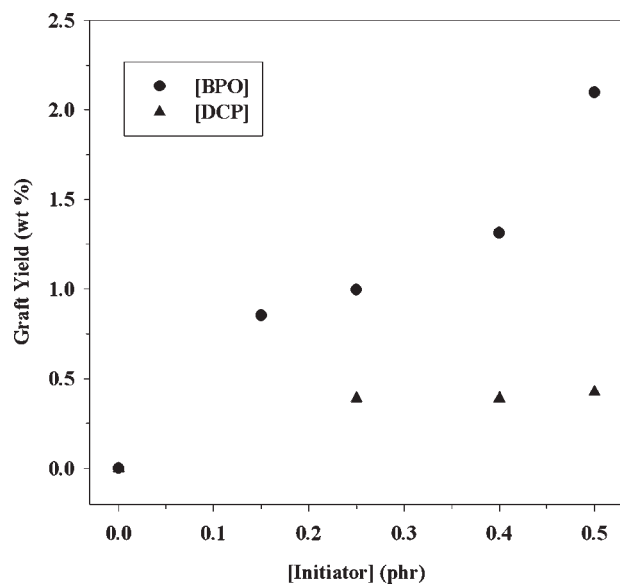
Figure 4 Effect of peroxide concentration on GMA graft yield measured by titration method. $[GMA]_i$ = 5 phr, temperature = 160°C, reaction time = 5 min (BPO), 15 min (DCP).

DCP initiation initially increased with the increase of peroxide concentration and then saturated earlier than that by BPO at 160°C. This is rather different result compared with previous workers at high temperature. Catier and Hu[21] reported that BPO had weak free radical grafting efficiency due to its short half-lifetime (1.2 s at 180°C) at high temperatures. Our result shows that when the BPO has sufficient half-life for the grafting reaction, BPO was more effective for the graft reaction compared with DCP.
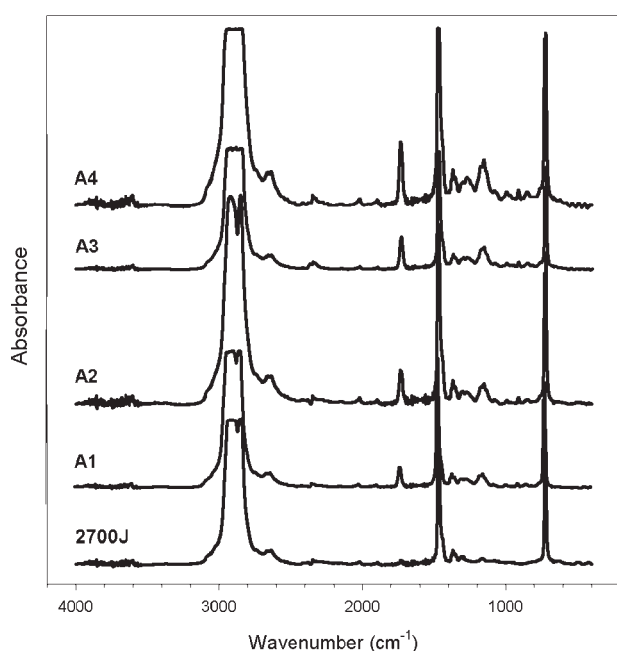

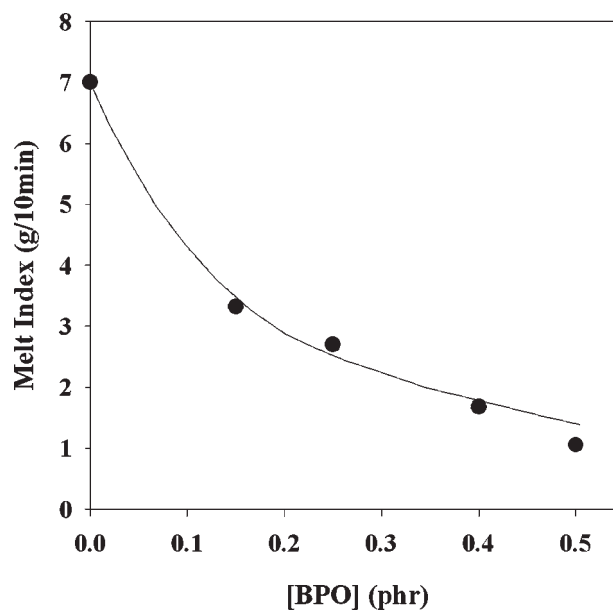**Figure 5** FTIR spectra of the HDPE/GMA/BPO system with the increase of BPO concentration.

Figure 6 Melt index of HDPE-*g*-GMA as a function of peroxide concentration.

It is also found that the degree of grafting was strongly influenced by the type of initiator used (from Fig. 4, maximum GMA graft efficiency per added GMA monomers [5 phr] are 0.44 for BPO and 0.09 for DCP) and effect of initiator species were more obvious in the low reaction temperature.

Melt index of HDPE-*g*-GMA was measured and shown in Figure 6. From the figure, the melt index of HDPE-*g*-GMA decreased with increasing peroxide concentrations. This is attributed to the increase of the grafting of GMA and chain extension between HDPE main chains.

Effect of glycidyl methacrylate concentration

The effect of monomer concentration on the grafting yield measured by titration method is shown in Figure 7. It is evident that the grafting level increases with increase in monomer concentrations. However, GMA grafting efficiency, which is defined as graft GMA divided by initial GMA concentration, gradually decreases. It is thought that GMA homopolymerization exceed GMA grafting in rate with the increase of monomer concentration. As a result, the efficiency of grafted GMA based on initial GMA concentration decreases. Similar result was found elsewhere.[18]

Effect of reaction time on GMA grafting

Figure 8 illustrates the effect of reaction time on the GMA grafting amount. It was expected that GMA grafting would increase initially and reach a plateau with reaction time. The result, however, shows drop of GMA graft level at a certain mixing time. This
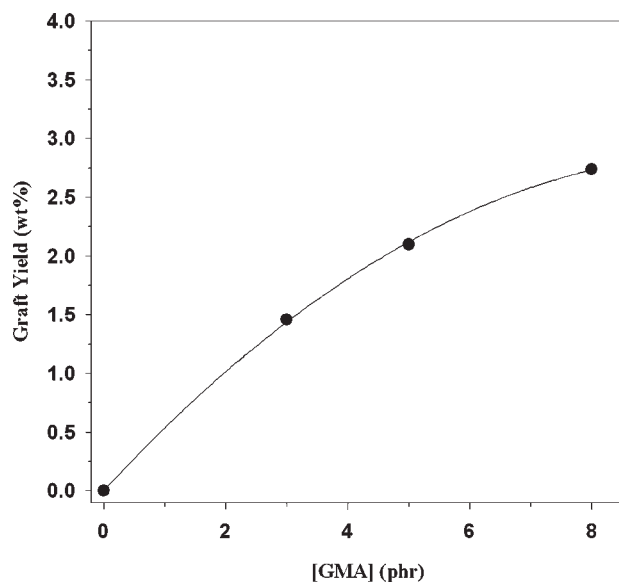
Figure 7 Effect of GMA monomer concentration on GMA graft yield. [BPO] = 0.5 phr, temperature = 160°C, reaction time = 5 min.
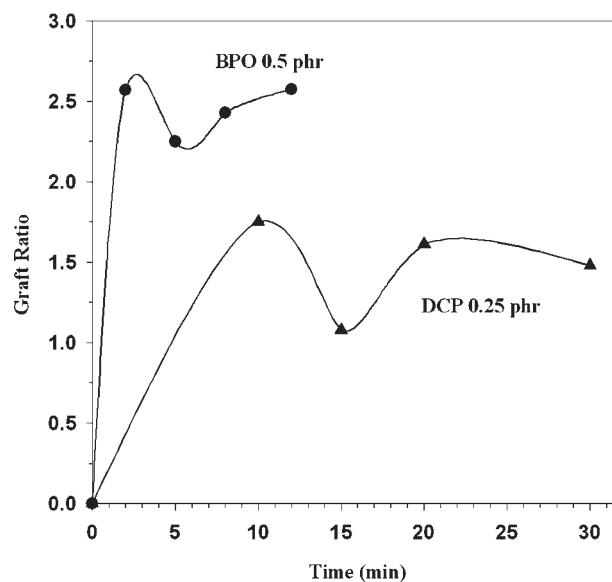

Figure 9 Effect of reaction time on GMA graft ratio measured by FTIR spectra. [GMA]$_i$ = 5 phr, temperature = 160°C.

trend was observed from the both of initiator used. The reason for this may be attributed to the breakage of the epoxide ring in GMA unit. To verify this, FTIR spectra of HDPE-*g*-GMA with different reaction time were obtained. Since FTIR experiment is based on the carbonyl peak at the GMA, actual graft ratio can be obtained whether epoxide ring has opened or not. Figure 9 shows the GMA grafting ratio with the reaction time measured by FTIR. By contraries, the trend obtained by FTIR is similar to that obtained by titration method, which means appreci-
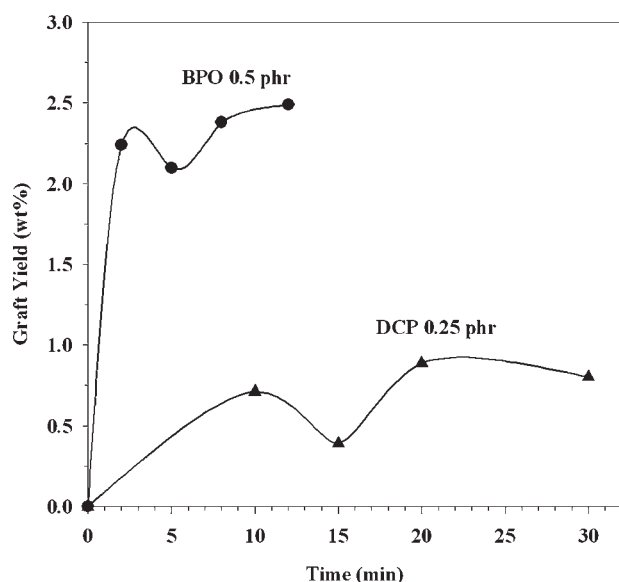
able epoxide breakage did not occur. From the GMA grafting result measured by titration and FTIR, it is clear that absolute amount of GMA in graft site changes with reaction time. In lieu of a knowledge of the influence of the epoxide breakage with the reaction time, we may assume that depolymerization of GMA has taken place over the ceiling temperature in the mixing procedure. Some works have reported that the ceiling temperature of GMA is expected to be between 150 and 220°C, like other methacrylates.[20,21] In our system, though reaction temperature is fixed to 160°C and air cooling device is equipped to the batch mixer, there are overheat generated by the mixing heat from shear force and reaction heat. Thus the reaction temperature is saturated around 170–176°C (in 5–8 min from the start of reaction), which is expected to be over ceiling temperature. Figure 10 shows the proposed mechanism of GMA grafting with reaction time. When the GMA is grafted onto HDPE, it can be suggested that two different graft reactions occur. One is extension of GMA side chain (Rxn-1) and the other is grafting of single GMA unit onto HDPE (Rxn-2).[15] Both Rxn-1 and 2 take place in the reaction medium at initial state (stage 1). However, when the temperature goes over the ceiling temperature, only Rxn-2 proceeds and the long GMA side chain produced by Rxn-1 depolymerizes (stage 2). Finally, Rxn-2 also stops due to the complete exhaustion of the initiator introduced and results in some compensation of the GMA grafting amount (stage 3). Thus, the drop of the GMA graft yield in the Figures 8 and 9 is thought to be observed at stage 2 followed by the recovering the amount of grafted GMA by Rxn-2.
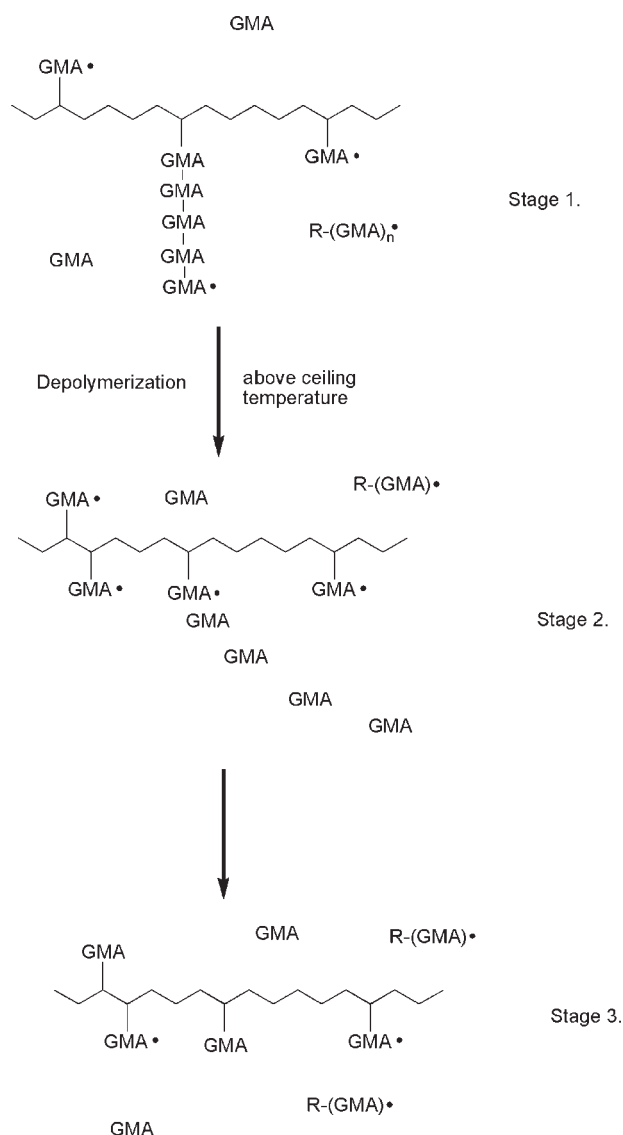

Figure 8 Effect of reaction time on GMA graft yield measured by titration method. [GMA]$_i$ = 5 phr, temperature = 160°C.

Figure 10 Schematic diagram of the proposed mechanism with the reaction time.

Crystallinity of the HDPE-*g*-GMA

The crystallinity of prepared HDPE-*g*-GMA was measured to investigate the effect of grafted GMA. Figures 11 and 12 illustrate the heat of fusion of HDPE grafted with GMA as a function of GMA content and reaction time. The crystallinity of HDPE-*g*-GMA was estimated from the ratio of the experimentally determined ΔH_m to the ΔH_m value of 282.8 J/g for the perfect crystalline HDPE. As shown in Figure 11, ΔH_m and crystallinity decrease monotonically with the increase in GMA content, that is, the increase in grafting yield (as in Fig. 7). It reflects that the supermolecular structure and crystallinity are affected by grafting. In other words, with the incorporation of GMA, crystallinity of HDPE decreases. GMA grafted site acted as defects for the
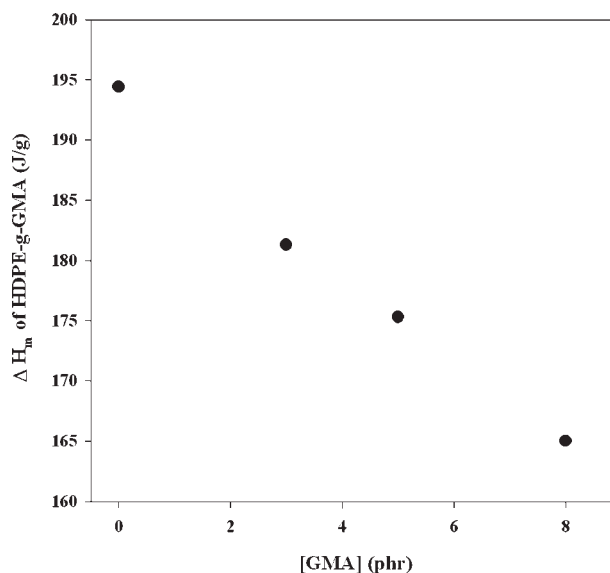

Figure 11 Effect of introduced GMA on the heat of fusion of HDPE-*g*-GMA.

crystalline structure. This brought about the decrease in crystallinity. Figure 12 illustrates the difference in the heat of fusion with reaction time. Heat of fusion of the HDPE-*g*-GMA decreased for the both of the initiator used as reaction goes on. This result is consistent with the proposed mechanism in the Figure 10, which states steady increase of the GMA graft site by the Rxn-2. Though the amount of grafted GMA changes with reaction time, steady increase of end groups by Rxn-2 lowers the crystallinity of the HDPE-*g*-GMA.
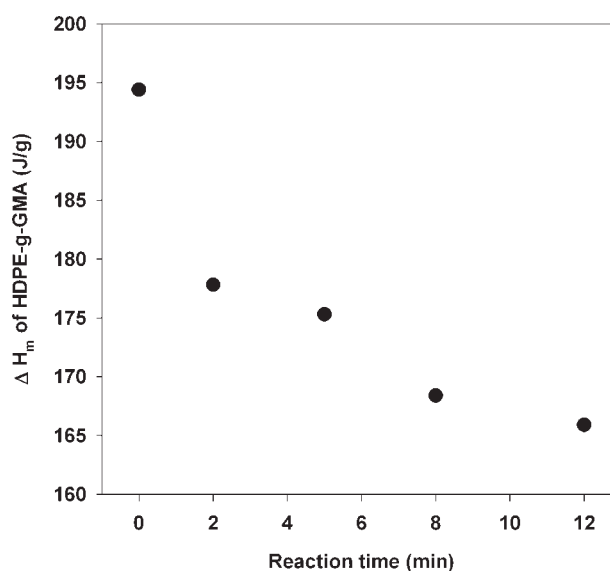

Figure 12 Effect of reaction time on the heat of fusion of HDPE-*g*-GMA.

CONCLUSIONS

Grafting of functional monomer onto the polymer is important issue in the field of reactive blending. Preparation of the functional polymer is governed by various factors. In this work, grafting of GMA onto the HDPE was investigated with the different initiator, amount of initiator, amount of GMA and reaction time. Some interesting aspects were found with the amount of graft GMA with the reaction time. It has been proposed that depolymerization of longer GMA resulted in change of the graft amount with the reaction time.

This study shows that reaction time effects on the grafting reaction, and it is one of the important variables for the preparation of functional polymer.

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