Graft Reaction of Acrylic Acid onto Metallocene-Based Polyethylene-Octene Elastomer

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ABSTRACT: In this study, grafting of acrylic acid (AA) onto metallocene-based polyethylene-octene elastomer (POE) was investigated by using benzoyl peroxide as an initiator. Grafted product was characterized by using Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction spectroscopy, and differential scanning calorimetry (DSC). Both the grafting percentage and the gel yield, at equilibrium, were higher for POE containing lower degree of comonomer content. In all cases, the crosslinking reaction was accompanied by the predominant graft reaction due to the competition of POE macroradical and excited AA. From the result of DSC and X-ray characterizations, it was found that the change of crystallinity is slight when the gel is removed from POE-*g*-AA copolymers. It was also proven that the effect of gel formation on the properties of the copolymer could be neglected because of the low gel yield. So, the graft method proposed in this article can produce low gel yield copolymer. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2905–2912, 2002

Key words: graft copolymer; acrylic acid; polyethylene

INTRODUCTION

Free-radical grafting of copolymerization of unsaturated carboxylic derivatives on polyolefins, to impart a certain degree of functionality, was widely employed in industrial applications. Articles related to graft reaction of unsaturated monomers on polyolefins, such as polyethylene, polypropylene, ethylene propylene copolymer, and poly(ethylene terephthalate) fibers, are too numerous to enumerate. Naqvi and Reddy[1] studied the grafting of acrylic acid (AA) and ethyl methacrylate on low-density polyethylene (LDPE)

under melt-processing conditions and showed that it would be a highly cost-effective way of diversifying the properties and applications of LDPE. By use of dicumyl peroxide as the initiator, Ghoshet et al.[2] modified LDPE by graft copolymerization with AA, ethyl acrylate, and butyl acrylate and showed that the grafting efficiency was highest when AA was employed. For the biodegradable system of linear low-density polyethylene (LLDPE)/starch, grafting of maleic anhydride (MAH) or AA on LLDPE can effectively improve the compatibility between LLDPE and starch.[3] The thermal analysis of ethylene propylene copolymer-*g*-AA was examined and the result showed that the crystallization temperature and melting enthalpy increased about 8–12°C and 4–6 J/g, respectively.[4] The effect of solvents on the benzyl

peroxide initiated graft copolymerization of poly-(ethylene terephthalate) fibers with AA was studied by Sacak and Oflaz.[5] In addition to the method of free-radical graft copolymerization, the reactive extrusion method and the vapor phase photografting method were also employed.[6-8] In the research of Park et al.,[8] AA was grafted on polypropylene fabric by a preirradiation method by using a [60]Co γ-ray and their result showed that an Ag-complexed fabric had a strong biocidal effect upon all bacteria.

Recently, the metallocene-based polyethylene-octene elastomer (POE), developed by using a metallocene catalyst by Dow and Exxon, has received much attention because of its unique uniform distribution of comonomer content and narrow molecular weight distribution.[9,10] The POE-*g*-MAH was used as the compatibilizer in the nylon6/POE-*g*-MAH system and the result showed that the impact strength of nylon6 was enhanced considerably.[11-13] For the case of POE-*g*-AA, it seems that it was not previously studied. As the reactivity of polyolefins stems from their hydrogen atoms along the hydrocarbon skeleton that is subjected to free-radical attack, crosslinking or degradation may occur simultaneously apart from the desired grafting.[1-3] There is still limited literature discussing extensively both the grafting reaction and the gel formation for POE. The purpose of this article is devoted to systematically investigate the effects of peroxide initiator and AA on the aforementioned phenomena. By using xylene as an interface agent and benzoyl peroxide as an initiator, we studied the graft reaction of AA onto molten POE. Moreover, we also searched the competition between the grafting and the crosslinking reactions to understand the reason for deterioration of mechanical properties. FTIR, NMR, X-ray diffraction, and DSC were used to characterize the grafting product.

EXPERIMENTAL

Materials

POE with different comonomer contents, 18% (Engage 8003) and 24% (8100), was obtained from Dow Chemical Corp. Acrylic acid, a commercial product of Aldrich, was purified by recrystallization from chloroform before use. The free-radical initiator used in this study was benzoyl peroxide (BPO) and it was used as received.

Graft Reaction and Sample Preparation

A mixture of AA and BPO was added in four equal portions at 2-min intervals to the molten POE. The reactions were carried out under a nitrogen atmosphere at 85 ± 2°C. Preliminary experiments showed that reaction equilibrium was approached after 5 h. To confirm that reaction equilibrium was established, all the reactions lasted for 6 h with a rotor speed of 60 rpm. The grafting product (4 g) was dissolved in 200 mL refluxing xylene at 85°C and then the hot solution was filtered through several layers of cheesecloth. The xylene-insoluble product remaining on the cheesecloth was washed by acetone to remove the unreacted AA before measuring the gel yield and then it was dried in a vacuum oven at 80°C for 24 h. The percentage ratio of the dry xylene-insoluble product to the crude copolymer (4 g) is called the gel yield in this article.[14] The xylene-soluble product is extracted five times from the filtrate by using 600 mL cold acetone for each extraction operation. Then, the acetone insoluble polymer, which was dried at 80°C overnight, was used to measure the grafting percentage by a titration method.[14]

Determination of Grafting Percentage

In this study, the AA loading of the xylene-soluble polymer is calculated from the acid number and the result is expressed as the grafting percentage. The acid number was determined by heating approximately 2 g of copolymer for 2 h in 200 mL of refluxing xylene. The hot solution was then titrated immediately with 0.03N enthanolic KOH solution, standardized against a solution of potassium hydrogen phthalate, by using phenolphthalein as an indicator. The acid number and the grafting percentage were calculated from the following equations[14]:

Acid number (mgKOH/g)

$$= \frac{V_{KOH} \text{ (ml)} \times C_{KOH} \text{ (N)} \times 56.1}{\text{polymer(g)}} \quad (1)$$

Grafting percentage (%)

$$= \frac{\text{Acid number} \times 72}{2 \times 561} \times 100\% \quad (2)$$

Characterization of the Graft Products

The POE 8003, due to its higher crystallinity, was chosen as the representative material for charac-

terization of the grafting product. Bruker AMX400 ^{1}H-NMR and ^{13}C-NMR spectrometers, using trichlorobenzene/benzene (TCB/C_6D_6) as the solvent and sealed in NMR tubes (10 mm OD) after degassing, operated at 100.6 and 50.3 MHz, respectively. Infrared spectra were obtained from Bio-Rad FTS-7PC type FTIR spectrophotometer by using thin films. The X-ray diffraction intensity curves were recorded with Rigaku D/max 3V X-ray diffractometer, with $CoK\alpha$ radiation at a scanning rate of 2°/min, to study the change of crystal structure. The melting temperature (T_m) and the heat of fusion (ΔH_f) were determined from a TA Instrument 2010 DSC system. For DSC tests, sample sizes ranged from 4 to 6 mg and the melting curves were taken a temperature range of -30 to 150°C scanned at a rate of 10°C/min. The crystallinity of various samples was determined from[15,16]

$$\% \text{ crystallinity} = \frac{\Delta H_f}{\Delta H_f^0} \times 100\% \qquad (3)$$

where ΔH_f^0 is the fusion heat of 100% crystalline LDPE[15] and ΔH_f is the fusion heat of grafted copolymer.

RESULTS AND DISCUSSION

Effects of Ingredients on the Graft Reaction

Effect of Peroxide Loading

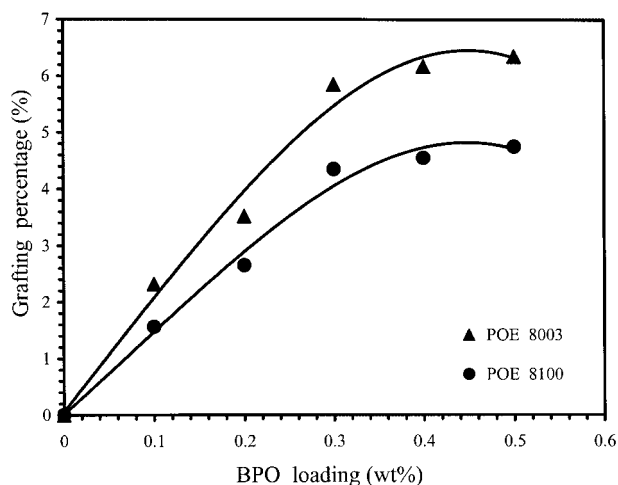Figure 1 and black solid symbols in Figure 2 show the effect of BPO loading on the grafting percent-

Figure 1 Effect of BPO loading on the grafting percentage for POEs 8003 and 8100 at 10 wt % AA.
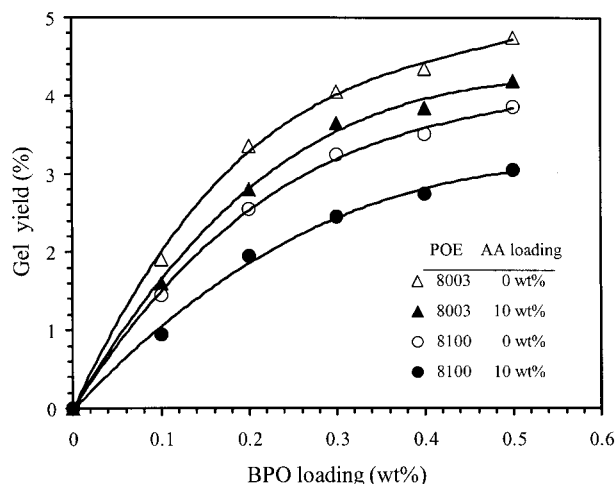

Figure 2 Effect of BPO loading on the gel yield for POEs 8003 and 8100.

age and the gel yield for POEs 8003 and 8100 when AA loading is kept at 10 wt %. It was found that both the grafting percentage and the gel yield increase steadily when the BPO loading was increased to 0.3 wt %. When the BPO loading was beyond 0.3 wt %, the grafting percentage and gel yield approached constant values for all cases. Meanwhile, grafting percentage and gel yield increase with increasing initiator loading. Apparently, grafting reaction is accompanied with the crosslinking of POE macroradicals to induce a microgel. The result mentioned above is similar to the case of some proposed articles.[14,17,18] A controlled crosslinking reaction without addition of monomer, to compare the crosslinking reaction with the gel formation, was performed and the result was given as a hollow circle and triangle symbols in Figure 2. As expected, gel yield in the case of crosslinking reaction was higher than that of graft reaction.

From the results of Figures 1 and 2, it is apparent that the grafting percentage and the gel yield for POE 8003 are both higher than those for POE 8100, which is attributed to the difference in the microstructure for both resins. Presumably, POE 8003 with a low degree of octene content exhibits a higher number of active hydrogen subjected to the attack of free radicals generated from the decomposition of peroxide. A similar example is that high-density polyethylene with fewer branches has a higher activity in the presence of peroxide than low-density polyethylene. Thus, high-density polyethylene normally exhibits a higher degree of crosslinking efficiency.
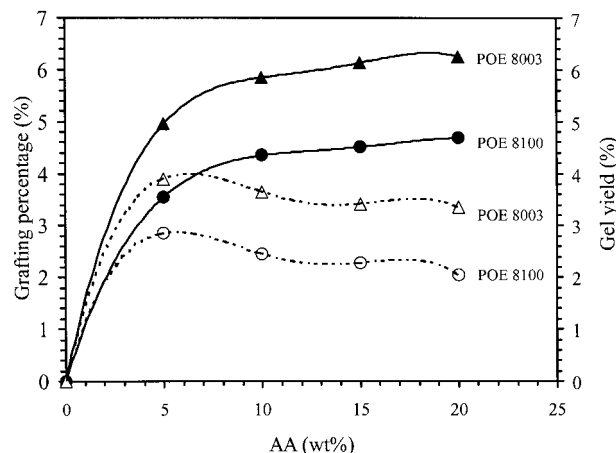
Figure 3 Effect of acrylic acid loading on the gel yield and grafting percentage for POEs 8003 and 8100 at 0.3 wt % BPO. (The solid and dotted lines indicate grafting percentage and gel yield, respectively.)

Effect of AA Loading

Figure 3 illustrates the effect of AA loading ranging from 5 to 20 wt % on the grafting percentage and the gel yield when BPO loading is kept at 0.3 wt %. As shown in Figure 3, the grafting percentage and the gel yield are both enhanced as AA loading is increased, but they are increased and decreased slightly, respectively, when AA loading is beyond 5 wt %. For grafting reaction, it may be explained by the fact that at low AA loading, the diffusion of monomer molecules toward the free-radical sites on the POE backbone governs the grafting extent, whereas at higher concentrations of monomer, the percentage grafting remains almost constant as the number of free-radical sites available on the POE backbone becomes a limiting factor.[19] Figure 3 also shows that at low AA loading, the rate of change of grafting percentage with AA loading is larger than that of gel yield. So, at a higher concentration of monomer, the gel yield is decreased while the AA loading is increased because of the fact that more free-radical sites on the POE backbone proceeds graft reaction.

The Characterization of POE-*g*-AA

FTIR was used extensively to investigate the grafting reaction of AA onto POE. The FTIR spectra of the unmodified POE 8003 and the POE-*g*-AA are illustrated in Figure 4(A,B), respectively. From the result of Figure 4, it can be seen that all the characteristic peaks of POE at 2840–

2928, 1465, and 720 cm^{-1} appear in both polymers.[15] It is also observed that there are two extra peaks (1710 and 1247 cm^{-1}), which are the characteristic peaks of —C=O and —C—O, and a broad O—H stretching absorbance in 3000–3600 cm^{-1} for the modified POE. Similar results can be found in some proposed articles.[15,20,21] So, it can be confirmed that AA is really grafted onto POE because the discernible shoulder near 1710 cm^{-1} based on free acid appears in the spectrum of the modified polymer.

Figure 5(A,B) gives the ^{1}H-NMR spectra of the unmodified POE 8003 and the POE-*g*-AA, respectively. For unmodified POE 8003, it can be seen from Figure 5(A) that only the functional groups of POE: 1° (—CH$_3$), 2° (—CH$_2$—), and 3° (—CH—) appear at 0.8–1.0, 1.1–1.3, and 1.4–1.6 ppm, respectively.[22] The ^{1}H-NMR spectrum of POE-*g*-AA [Fig. 5(B)] shows that some peaks occur at 4 (δ: 1.7–1.9 ppm), 5 (δ: 2.2–2.4 ppm), 6 (δ: 4.7 ppm), and 7 (δ: 5.3 ppm) in addition to the original —CH$_3$ and —CH$_2$— peaks of the unmodified POE 8003. The appearances of peaks 4, 5, and 7 are due to AA grafted onto the main or branch chain of POE skeleton.[21,23,24] In addition, from the re-
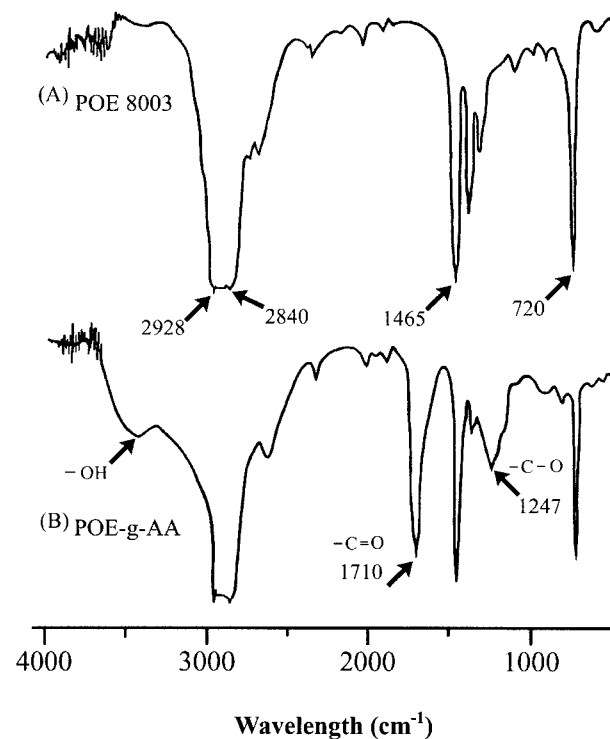

Figure 4 FTIR spectra of unmodified POE 8003 and POE-*g*-AA obtained from the conditions of 10 wt % AA and 0.3 wt % BPO.
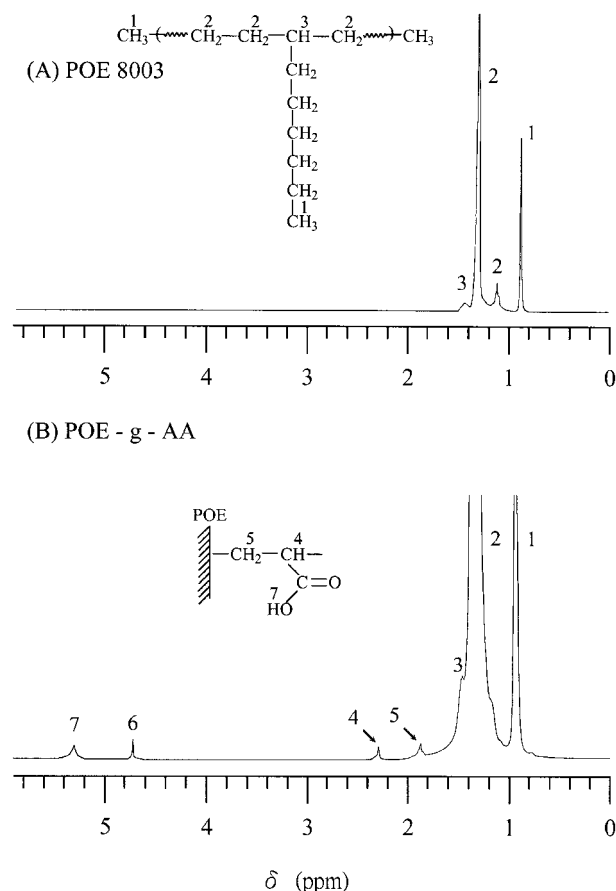
Figure 5 ^{1}H-NMR spectra of unmodified POE 8003 and POE-*g*-AA obtained from the conditions of 10 wt % AA and 0.3 wt % BPO.

sult that the integral ratio of peak 4 to peak 5 is equal to 1 : 2, it is clear that peaks 4 and 5 are from the functional group of AA. In the article of Kim and Tirrel,[21] the functional group of carboxylic acid appears at $\delta = 5.3$ ppm. We think that peak 7 (δ: 5.3 ppm; δ: 4.7 ppm) is due to the fact that the carboxylic acid is grafted onto POE. In Figure 5(B), there is also an extra peak at δ: 4.7 ppm. The appearance of peak 6 at δ: 4.7 ppm, which is similar to the result of some articles,[25,26] implies that the gel formation is accompanied by the POE-*g*-AA reaction.

To further understand the formation of grafting and gel, ^{13}C-NMR is used to study the structure change of POE-*g*-AA copolymer. The ^{13}C-NMR spectra of the unmodified POE 8003 and the POE-*g*-AA are given in Figure 6(A,B), respectively. Figure 6(A) illustrates that the structure of POE is similar to the result of Pooter et al.,[27] in which polyethylene octane copolymers were studied. The comparison between Figure 6(A) and Figure 6(B) shows that seven extra peaks β_H (δ: 28.467 ppm), α_H (b: 31.905 ppm), C_α (δ: 35.625 ppm), Y-*cross*-Links (δ: 39.725 ppm), H-Links (δ: 40.845 ppm), C_α (δ: 42.189 ppm), and —C=O (δ: 175.042 ppm) appear for the modified POE. The extra peaks C_β, C_α, and —C=O are due to the grafting of AA onto POE and the corresponding structures are illustrated in Figure 6(B). The appearances of the above three peaks (C_β, C_α, and —C=O) are in agreement with the results proposed by Pham et al.[23] and Lin et al.[24] The structures of peaks b_H, a_H, Y-*cross*-Links, and H-Links can be assigned to H-Links and Y-*cross*-Links.[28–30] These phenomena are similar to the result of Baojun et al.,[28] who studied the peaks produced from crosslinks of classical polyethylene. So, it is proven that the gel formation stemmed from the POE-*g*-AA reaction. From the ^{13}C-NMR result mentioned above, it is clear that both the grafting reaction and the gel formation occur simultaneously during the period of POE-*g*-AA reaction. Finally, from the results of FTIR, ^{1}H-NMR, and ^{13}C-NMR, it is certain that AA is really grafted onto POE and that the gel formation is accompanied by the POE-*g*-AA reaction.

Effect of Grafting and Gel on Crystallization

X-ray Diffraction Analysis

In this study, the X-ray diffraction analysis is examined to study the change of crystalline structures of the unmodified POE 8003 and POE-*g*-AA. For unmodified POE 8003, Figure 7(A), which is similar to the results of Perez et al.,[31] shows that there are two peaks at about $2\theta = 19.8°$ and $2\theta = 21.4°$. Figure 7(B) illustrates the spectrum of POE-*g*-AA copolymer with grafting percentage = 5.85% and gel yield = 3.65%. When the gel was removed from the POE-*g*-AA copolymer, the X-ray diffraction spectrum is shown in Figure 7(C). From the result of Figure 7(B,C), it is clear that there is only one peak at about $2\theta = 21.4°$. The disappearance of the peak at $2\theta = 19.8°$ may be due to the change of coordination features of POE molecules when AA is grafted onto POE. As the result, the crystalline structure of POE is actually changed when AA was grafted onto POE.

Differential Scanning Calorimetry Tests

DSC was used to understand the effects of grafting percentage and the gel yield on the thermal properties of POE-*g*-AA copolymer. The DSC heating thermograms of POE-*g*-AA with different
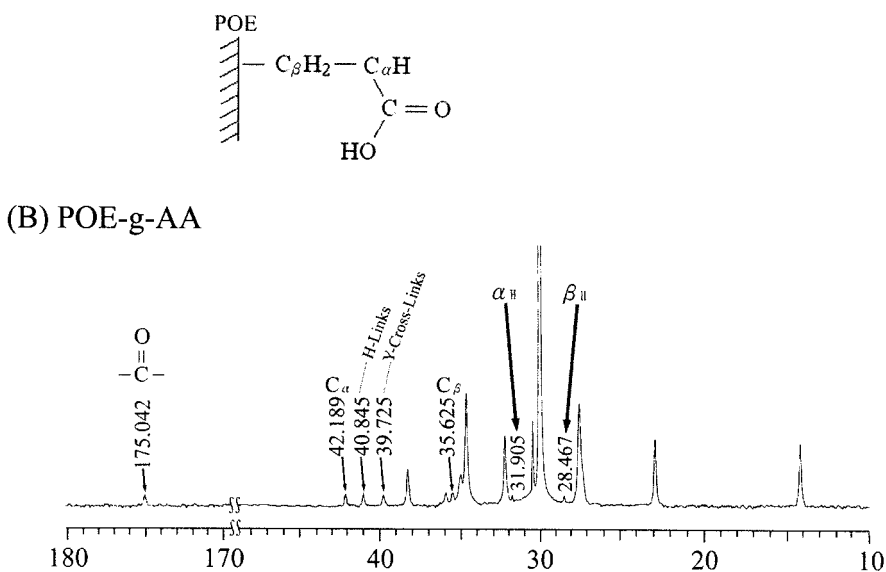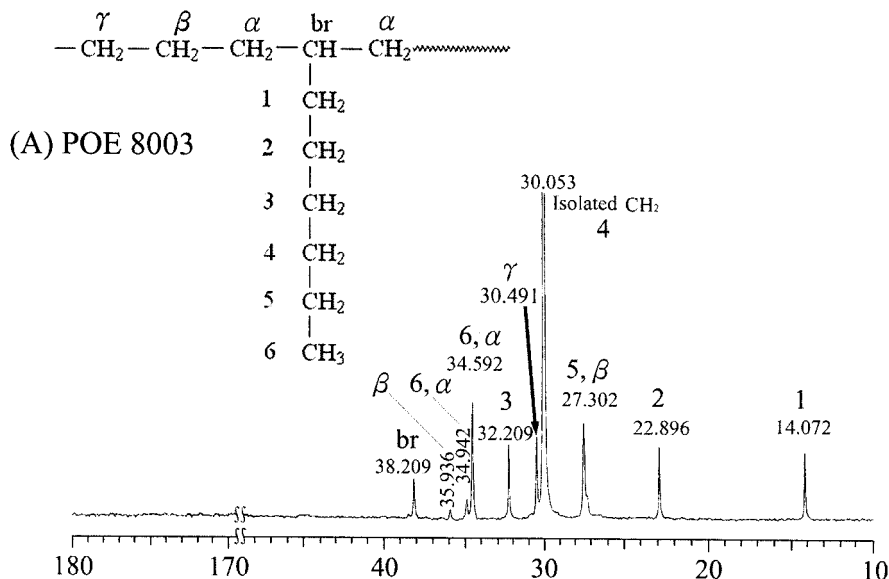
Figure 6 ^{13}C-NMR spectra of unmodified POE 8003 and POE-g-AA obtained from the conditions of 10 wt % AA and 0.3 wt % BPO.

grafting percentages and pure POE 8003 are shown in Figure 8. For unmodified POE, the corresponding values of melting temperature (T_m) and the heat of fusion (ΔH_f) are 83.1°C and 50.8 J/g, respectively. For POE-g-AA copolymers, it was determined that the melting temperatures (T_m) with increasing grafting were 82.2, 81.8, 81.0, 80.7, and 80.3°C, and their heats of fusion (ΔH_f) were 46.2, 42.0, 36.0, 34.0, and 32.1 J/g. The

decrease in heat of fusion was probably due to the grafted branches, which disrupted the regularity of the chain structures in POE and increased the spacing between the chains.[32] It was probably caused by the increase in difficulty in polymer chain arrangements as the grafted branch chains prohibited the movements of the polymer segments.[33,34] Figure 9 shows the change of heating thermograms, for grafting percentages of 2.32
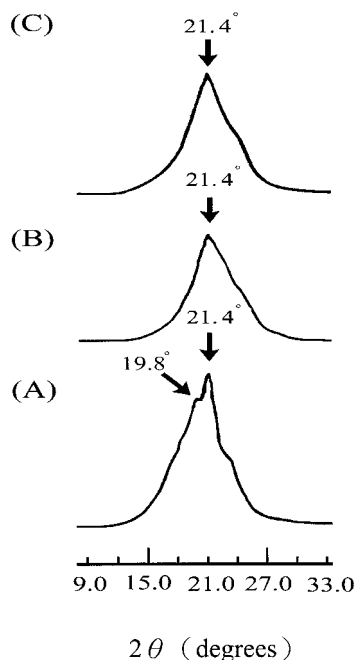
Figure 7 X-ray diffraction spectra of unmodified POE 8003 and POE-*g*-AA obtained from the conditions of 10 wt % AA and 0.3 wt % BPO. (A) indicates POE 8003; (B) indicates that gel is not removed from POE-*g*-AA; (C) indicates that gel is removed from POE-*g*-AA.

and 5.85%, when the gel is removed from the POE-*g*-AA copolymer. It can be seen that the values of T_m and ΔH_f decrease from 82.2°C/46.2 J/g to 81.0°C/36.1 J/g and from 82.4°C/47.4 J/g to
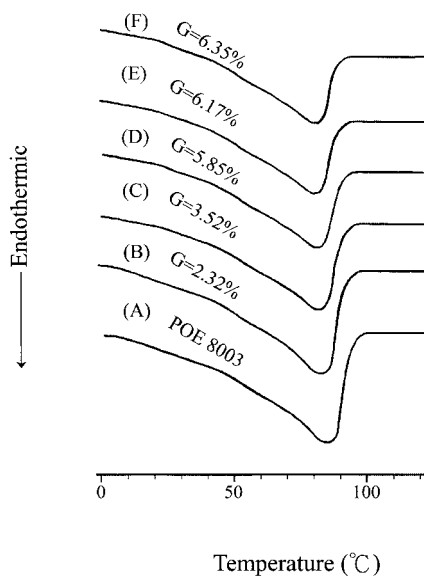

Figure 8 DSC heating thermograms of POE 8003 and POE-*g*-AA with different grafting percentages.
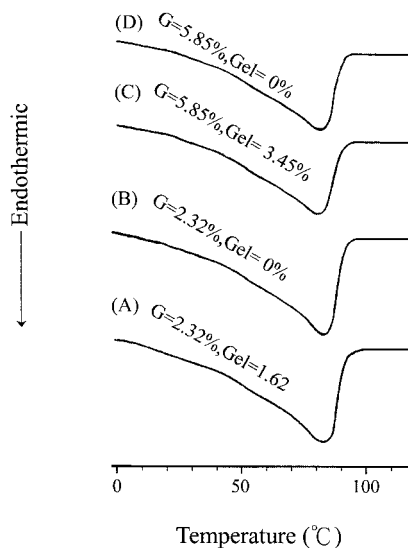

Figure 9 Effect of gel formation on the DSC heating thermograms of POE-*g*-AA.

81.4°C/38.6 J/g, respectively, for grafting percentages of 2.32 and 5.85%. From the results of Figure 9, it is found that the decrements of T_f and ΔH_f are both smaller than 1°C and 3 J/g, respectively, when the gel is removed from the POE-*g*-AA product. According to the results of DSC heating thermograms, the effect of gel formation on the thermal properties of POE-*g*-AA can be neglected. This result is similar to the work of grafting of MAH onto polypropylene proposed by Ko and Ning.[32] The percentage crystallinity can be calculated from eq. (3) and the results are given in Table I. Table I also proves that the percentage crystallinity decreases as the extent of grafting is increased and it is almost unchanged when the gel is removed from the POE-*g*-AA copolymer.

Table I The Percent Crystallinity of POE 8003-*g*-AA with 10 wt % AA for Different BPO Loadings

BPO Loading (wt %)	Grafting Percentage (%)	Gel Yield (%)	% Crystallinity Unremoving Gel	Removing Gel
0	0	0	17.53	17.53
0.1	2.32	1.62	15.98	16.39
0.2	3.52	2.83	14.55	15.18
0.3	5.85	3.45	12.48	13.34
0.4	6.17	3.65	12.05	12.65
0.5	6.35	3.83	11.13	11.76

CONCLUSION

Graft reaction of AA onto two POEs 8003 and 8100 was investigated in this article. According to the spectra of FTIR, ^{1}H-NMR, and ^{13}C-NMR, it is confirmed that AA is essentially grafted onto POE. Yet, the presence of BPO induces not only the graft reaction of AA but also the crosslinking reaction of POE. Both the graft percentage and the gel yield increase with increasing initiator content. It is proven that POE with a low degree of comonomer content provides higher equilibrium grafting percentage and gel yield. It also shows that the higher the AA loading, the higher the graft percentage and the lower the gel yield. The X-ray spectrum shows there are two peaks at $2\theta = 19.8°$ and $2\theta = 21.4°$ for the unmodified POE 8003 but the peak at $2\theta = 19.8°$ vanishes for POE-g-AA. As the results mentioned above, it is proven that the gel formation is accompanied by the POE-g-AA reaction. From the result of DSC test, it is found that all the values of ΔH_f and T_m decrease as the graft percentage is increased. It is also seen that the changes of crystallinity, ΔH_f and T_m, are slight for POE-g-AA copolymers with and without removing gel. Due to the low gel yield, the effect of gel formation on the crystalline structure and the thermal properties of the copolymer can be neglected. Finally, the graft method proposed in this article can produce low gel yield copolymer whose crystalline structure and thermal properties are not affected by the formation of gel.

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