Modification of Fast-Cure Ethylene–Propylene Diene Terpolymer Rubber By Maleic Anhydride and Effect of Electron Donor

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ABSTRACT: Grafting of maleic anhydride (MA) onto fast-cure ethylene–propylene diene terpolymer rubber was studied. The effect of the amount of the MA, initiator (dicumyl peroxide), and electron donor (stearamide) on graft content are described. The potentiometric method and Fourier transform infrared spectroscopy are used to obtained the graft content. The stearamide suppresses the side reactions, such as crosslinking and chain scission. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1–5, 1998

Key words: ethylene–propylene diene terpolymer; maleic anhydride; melt functionalizing; stearamide; grafting

INTRODUCTION

In the past 2 decades, polymer alloying is widely used for the toughening of thermoplastics. Most of the widely used thermoplastic materials, such as isotactic polypropylene (iPP), polystyrene (PS), poly(vinyl chloride)(PVC), and polyamide (PA), show marked limitation in the end use because of poor impact resistance and toughness. These limitations may be overcome to a certain extent by adding to the thermoplastic materials a certain amount of a rubber component having much lower T_g by melt mixing, copolymerization, or other techniques.[1]

Most of the polymer pairs are immiscible. In this case, 1 phase is dispersed in the other. It is recognized that for fine dispersion, some degree of interfacial adhesion or coupling of 2 phases must exist, but some pairs of polymers, such as polar and nonpolar polymers, do not have sufficient affinity. This problem and, also, modification of blend morphology can be solved by incorporation of functionalizers or compatibilizers.

Ethylene propylene diene terpolymer (EPDM) can be modified by maleic anhydride (MA). Maleated EPDM rubber (m-EPDM) is mostly used as a component in reactive blending, that is for the impact modification of polyamides and polyolefins.[2–5]

This article reports the results of investigation of grafting reaction of the fast-cure EPDM, the influences of MA and SA on graft efficiency, and the comparison between 2 main techniques, potentiometric titration and Fourier transform infrared spectroscopy (FTIR) for analyzing g-MA content in modified polymers. We also determined the degree of grafting in partial crosslinked EPDM, and it is showed that the potentiometric method can be used in such samples.

EXPERIMENTAL

Materials

The EPDM used was Vistalon 7500, Exxon (ethylen content, 56 wt %; ENB content, 5.7 wt %). All

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other chemicals and solvents, including dicumyl peroxide (DCP, the initiator), maleic anhydride (MA, the reactive monomer), stearamide (electron donor), *tert*-butanol, and ortho dichloro benzene (ODCB), were of reagent grade.

Grafting Reaction

Composition of the reaction mixture was typically about 48 g EPDM, 0 to 6 phr MA, 0 to 0.06 phr of DCP, and 0 to 40 wt % (on MA) SA. The components were melt-mixed in a Haake–Buchler Rheomix 750 internal mixer. The rotor speed was 10 rpm in the first 1 min, and this increased to 60 rpm thereafter. The temperature of the mixing chamber was set at about 160°C.

Gel Content Determination

Gel content of the samples were determined by extraction procedure of refluxing in boiling ODCB (with 10 mg/L of 3.5 di-*t*-butyl-4-hydroxytoluene added as an antioxidant) for 6 h. The solution was subsequently filtered, and the insoluble materials were combined and dried under vacuum at 140°C for constant weight.

Fourier Transform Infrared Spectroscopy

The samples (maleated EPDM) were pressed at about 170°C to prepare films, which had been dried in a vacuum oven (1 day at 110°C). The IR spectra were taken using a Bruker IFS 48 FTIR spectrometer. The relative peak height of the anhydride absorption band of 1785 cm^{-1} asymmetric of carboxyl stretching, to the C—H stretch peak (715 cm^{-1}) was taken as an approximate indicator of the extent of MA grafting.

Potentiometric Titration

Two procedures were used to determined the *g*-MA in EPDM.

1. The amounts of *g*-MA was determined by potentiometric titration on vacuum-dried samples in 1,2-dichloroethane (ETOH) (9 : 1) and dissolved at 60°C, and titration was carried out with a 0.1M KOH solution in *t*-butanol.[6]
2. In other typical procedures, 0.3 g of EPDM-*g*-MA was cut into small pieces and was shaken in 100 mL of water for 24 hr. The polymer was washed repeatedly with acetone, dried in vacuum at 80°C for 24 h, dissolved
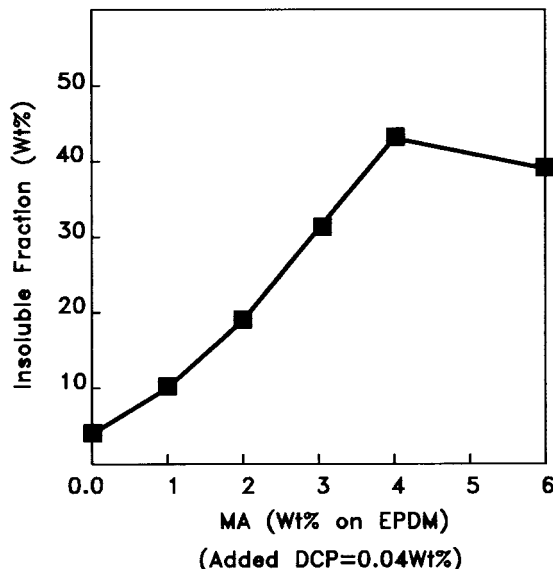

Figure 1   Effect of MA on the gel content of EPDM at constant DCP.

in 50 mL of an 0-dichlorobenzene–ethanol solution (9 : 1 v/v) and titrated with a 8.5 × 10^{-2}M solution of KOH in O-dichlorobenzene–EtOH (9 : 1 v/v).[7] The titration gave 2 inflection points corresponding to the 2 carboxylic groups.

RESULTS AND DISCUSSION

Effect of MA on Gel Content

Figure 1 shows the effect of MA on the crosslinking of EPDM at a constant initiator (DCP). It can be seen that by increasing the amount of MA, the gel content (insoluble fraction) increases up to 4 wt % MA and then decreases. Three reasons are described for this effect. First, according to Gaylord et al.,[8] the MA concentration of the polymer decreases with an increase in the MA concentration in the charge owing to the quenching of excited MA by increasing ground-state MA. Second, with high MA concentrations (4 wt %), phase separation of MA and rubber exists; part of the initiator is possibly lost in this separated MA phase, leading to a less efficient grafting reaction.[9] The third reason is attributed to the fact the MA in high concentration did not dissolve completely, which means that the 2 following phases are present: an EPDM phase with some MA and a separate MA phase.[6]
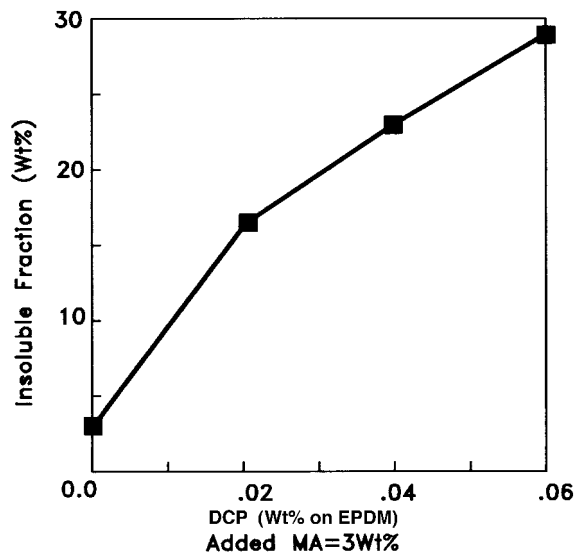
Figure 2 Effect of DCP on the gel content of EPDM at constant MA.

Effect of Initiator (DCP) on Gel Content

Figure 2 shows that by increasing the amount of initiator, the gel content increases. It is due to an increase in the DCP content number of the radicals and to an increase in active sites; thus, the chance of crosslinking and the gel content increases.

Graft Content

Figure 3 shows the graft content, which is determined by potentiometric titration versus MA per-
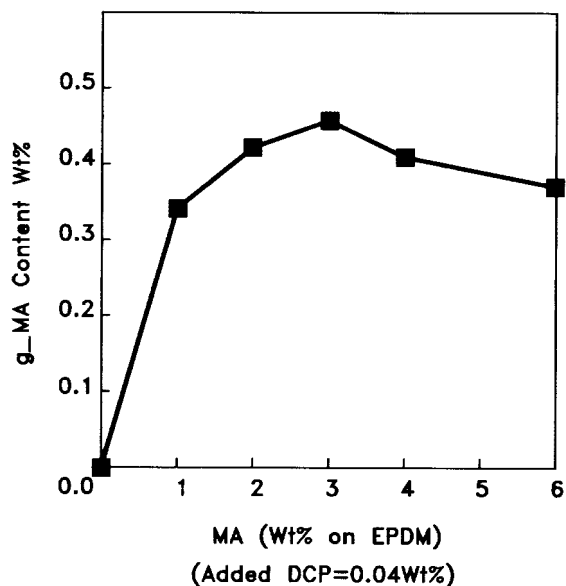

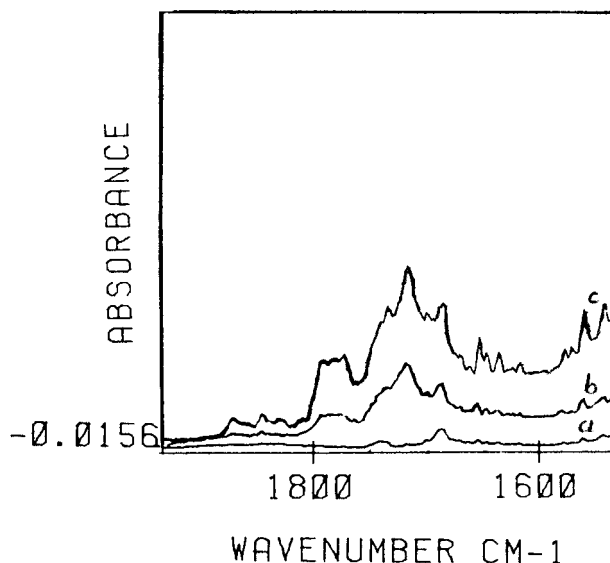**Figure 3** Graft content versus MA at constant DCP.

Figure 4 FTIR spectra of (a) EPDM, (b) EPDM with 1 wt % MA, and (c) EPDM with 2 wt % MA.

centage at constant DCP (0.04 wt %). It can be seen that by increasing the amount of MA, the graft content increases (up to 3%) and then decreases. The reasons of this effect are similar to effects of MA on gel content.

Figure 4 shows the FTIR spectra of EPDM and EPDM with different amounts of MA at 1600–1800 cm^{-1}. The height of the carboxyl group (1785 cm^{-1}) increases by increasing the amount of the MA.

The results of quotient of the absorbance peak of the carboxyl group at 1785 cm^{-1}, and the C—H stretching at 715 cm^{-1} are shown in Figure 5. It can be seen that by increasing the MA content, the graft content increases up to 3 wt % MA and then decreases. The results are correlated with potentiometric titration results (Fig. 3).

The incorporated MA content was also calculated from the integrated absorbances as follows[10]:

$$\%MA = 211 \frac{A_{1830-1750} + 0.83A_{1750-1660}}{A_{760-680}}$$

The results are shown in Figure 6. It can be seen that the grafted MA% increases by increasing the MA content up to 3 wt % and then decreases, and it is corrected with other 2 measurements.
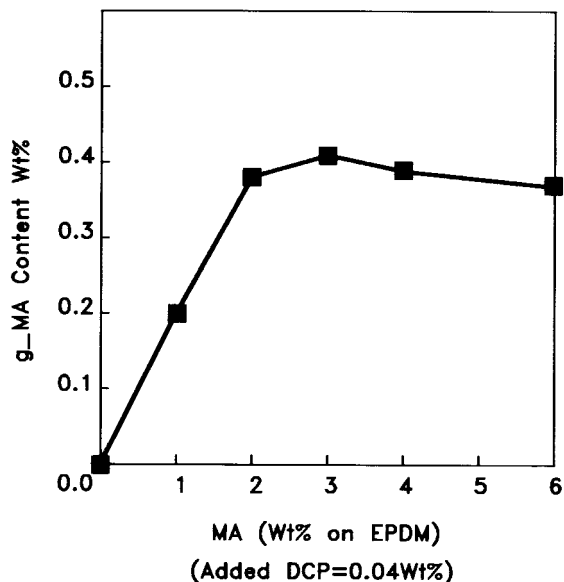
Figure 5 Effect of MA content on the graft content.

Effect of Initiator Concentration on the Graft Content

As is shown in Figure 7, the graft content increases with increasing the initiator concentration, but the undesirable reactions such as crosslinking and/or chain scission may occur simultaneously with the graft reactions. Rheology measurements showed that the melt viscosities of the functionalized rubber increased with increasing the initiator concentration.
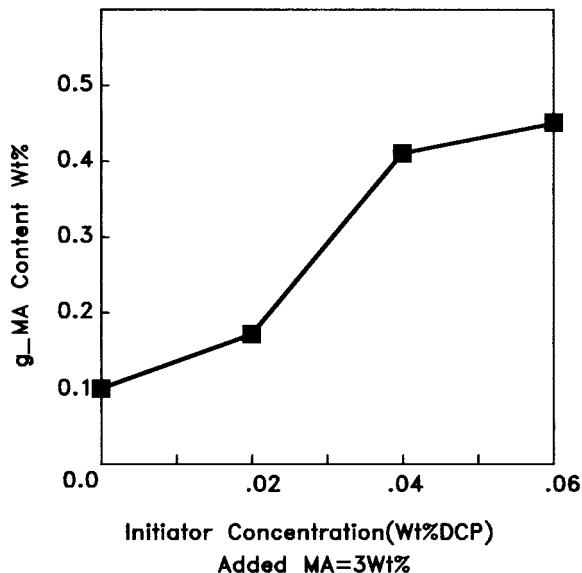

Figure 6 Effect of MA Content on the grafted MA percentage.

Figure 7 Effect of DCP on the graft content at constant MA.

Effect of Electron Donor

In this study, stearamide is used as electron donor for the suppression of side reactions of crosslinking and chain scission. Figure 8 shows the graft content versus the SA (wt % on MA) at constant MA (3 wt %) and DCP (0.04 wt %). It can be seen
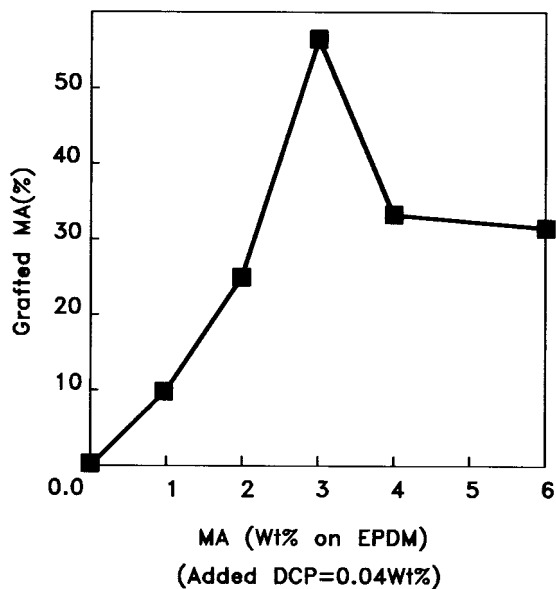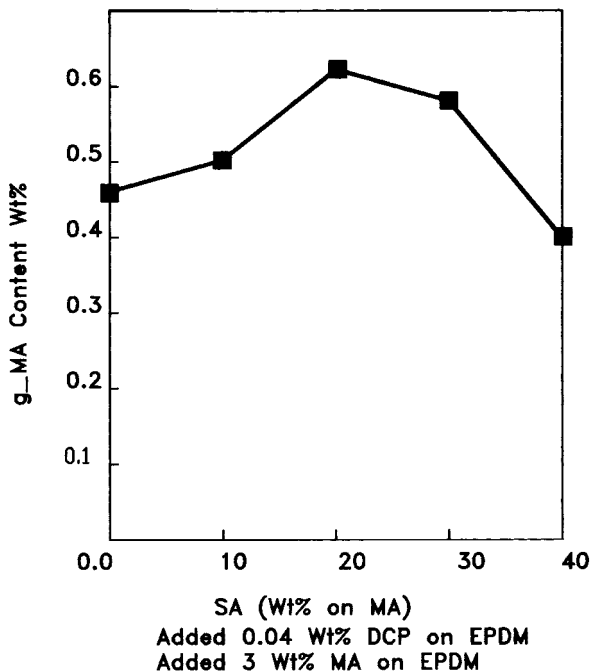

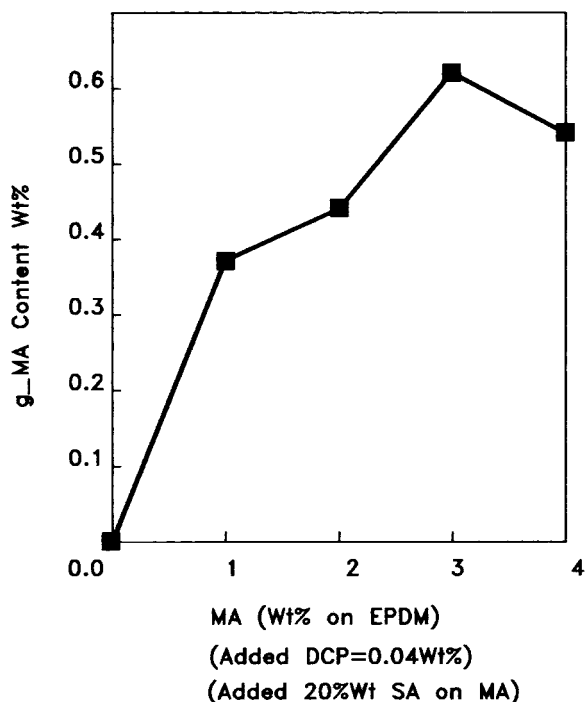**Figure 8** Effect of SA on the graft content at constant MA and DCP.

Figure 9 Graft content versus MA % at constant SA and DCP.

that by increasing the SA graft content increases and then decreases.

The results show that addition of 20 wt % of SA on MA in the mixtures increase the graft content. For investigation of the effect of SA on improvement, graft different samples with constant SA (20 wt % on MA) and DCP (0.04 wt %) with various MA content were made. The results show (Fig. 9) that in the present of SA at 3 wt % MA compare to absence of SA (Figs. 3 and 5). The graft content is increased about 38%. It seems that the added SA suppresses the undesirable reactions, such as crosslinking and scission reactions. Wu and Su[11] also believe that the effect of SA does not appear to be intrinsically selective; it tends to suppress the more populated radial reaction path.

CONCLUSION

On the basis of these studies, it can be calculated that functionalizing of fast-cure EPDM with MA is possible. The graft content increases by increasing the MA content up to 3 wt % MA and then decreases. The potentiometric method and FTIR both can be used for measurement of graft content and results correlated each other.

SA can be suppressed the undesirable reactions, such as crosslinking or scission. The results show that 20 wt % SA on MA is optimum for improvement of graft content.

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