Preparation of Maleated Ethylene-Propylene-Diene Terpolymer (EPDM-g-MA) Modified with $\alpha,\omega$-Aminopropyl Polydimethylsiloxane

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Abstract: Maleic anhydride (MA) grafted ethylene-propylene-diene terpolymer (EPDM-g-MA) was prepared using both solution and reactive processes. The maleation of EPDM in the solution process was carried out using a benzoyl peroxide (BPO) initiator at 110 °C for 6 h. In the reactive process, the banbury-type internal mixer was used with dicumyl peroxide (DCP) as the initiator. The grafting ratios of the MA on the EPDM relative to the MA and initiator contents were measured. The maximum grafting ratios were 2.4% and 1.4% in the solution and reactive processes, respectively when 10 phr of MA and 0.25 phr of the initiator were used. EPDM-g-MA was mixed with $\alpha,\omega$-aminopropyl polydimethylsiloxane using roll mill techniques at room temperature and imidized by aging at 240 °C for 2 h. The curing of the maleated EPDM/PDMS was confirmed by measuring the FT-IR and the morphology was obtained by SEM.

Keywords: MA grafted EPDM, solution process, reactive process, $\alpha,\omega$-aminopropyl polydimethylsiloxane, maleated EPDM/PDMS

1. Introduction

The terpolymer of ethylene-propylene-diene (EPDM) is commonly used in the fields of automobile parts, electrical materials, and construction because of its good mechanical, thermal, and electrical properties. However, its poor surface characteristics and weather property limit its use as an outdoor insulating material. In addition, the EPDM terpolymer decomposes easily when used for a long time outdoors [1,2]. Accordingly, it has been modified by copolymerizing it with various monomers such as poly (EPDM-g-styrene) [3], poly (EPDM-g-acrylonitrile) [4], poly (acrylonitrile-EPDM-styrene) [5], and poly (vinyltrimethoxysilane-EPDM-styrene) [6] to increase its resistance to heat, light, and oxygen. The concept of an EPDM terpolymer/silicone rubber blend system has attracted much interest over the years because silicone rubber has a low surface energy, low temperature flexibility, excellent weather and thermal stability, ozone and oxygen resistance, and high dielectric strength and volume resistivity [7]. However, it is very difficult to blend the EPDM terpolymer/silicone rubber without using a compatibilizer.

The aim of this investigation is to maleate the EPDM terpolymer using a solution or reactive process based on the amounts of maleic anhydride and an initiator, and then modify the maleated EPDM terpolymer with $\alpha,\omega$-aminopropyl polydimethylsiloxane (PDMS) without using a compatibilizer.
The structure and morphology of EPDM-g-MA modified with \( a, \omega \)-aminopropyl group terminated PDMS were confirmed by the measurement of the FT-IR, NMR, and SEM.

2. Experimental

2.1. Materials

The Nordel® IP NDR-4640 (ethylene-propylene-diene terpolymer, Du Pont) containing 5-ethylidene-2-norbornene (ENB) with ethylene/propylene/ENB = 55/40/5 by weight %; specific gravity, 0.86; Mooney viscosity (ML1+4, 125 °C), 40; \( \eta_{\infty} \), 340000; \( \eta_{\infty}/\eta_{0} \), 1.5; was used as received. The benzoyl peroxide (BPO, Junsei Chemical) and dicumyl peroxide (DCP, Hercules) were used without further purification. The \( a, \omega \)-aminopropyl polydimethylsiloxane (PDMS, UCT Co.) with \( \eta_{\infty} \), 27000; viscosity, 2000 cps; amine %, 0.08~0.09; was used as received. The xylene, acetone, and methanol were distilled prior to use.

2.2. Maleation of EPDM by Solution Process

The maleation of EPDM by a solution process was carried out by referring Martin’s process [8]. For example, 40 g of EPDM, 4 g of MA, and 0.1 g of BPO dissolved in xylene respectively were added to a 1 L four-necked flask equipped with a reflux condenser, stirrer, thermometer, and nitrogen inlet. The reaction mixture was vigorously stirred at 110 °C for 6 h. After completing the reaction, the reaction mixture was poured into excess acetone with stirring. After removing any unreacted MA contained in the reaction mixture, the precipitate was filtered. The purification procedure was then repeated and the precipitate was finally dried in a vacuum at 80 °C for 24 h.

2.3. Maleation of EPDM by Reactive Process

The reaction was carried out in a banbury-type internal mixer (HAAKE RHEOMIX 600F). After 40 g of EPDM was charged in the chamber and heated at 130 °C for 5 min., various amounts of MA and DCP were added and mixed with a 50 rpm stirring rate for 25 min at the same temperature. After completing the reaction, the reaction mixture was dissolved in xylene, then the product was precipitated by pouring it into excess acetone with stirring. After removing any unreacted MA, the product was filtered. The purification procedure was then repeated and, the precipitate was finally dried in a vacuum at 80 °C for 24 h.

2.4. EPDM-g-MA Modified with PDMS

23 g of EPDM-g-MA prepared by the solution process was mixed with 3.91 g of \( a, \omega \)-aminopropyl terminated PDMS at room temperature for 2 h using the roll mill technique. This premixed sample was then mixed with 0.12 phr DCP to EPDM-g-MA at room temperature and a film was prepared using a hot press under 170 kgf/cm² at 130 °C, for 10 min.

2.5. Graft Ratio

The MA grafting ratio onto EPDM-g-MA was calculated using the titration method [9]. The sample was dissolved in xylene and titrated with 0.1 N isopropyl alcoholic KOH using a phenolphthalein indicator. The MA grafting ratio was calculated using the following equation.

\[
\text{Grafting Ratio} (\%) = \frac{M_{KOH} V_{KOH}}{2 \times \text{Sample weight}} \times 58.06 \times 100
\]

where, \( M_{KOH} = \) Molar concentration of isopropyl alcohol solution of KOH

\( V_{KOH} = \) Volume of KOH consumed

2.6. Instrumental Analysis

The \(^1\text{H-NMR} \) spectrum was measured using a Varian Gemini 2000-200MHz spectrometer with TMS and deuterohloroform as the internal reference. The FT-IR spectra were measured with a Perkin Elmer Spectrum GX. The molecular weight was measured with a Tosho GPC HLC-8020 system equipped with three stragel columns of 10³, 10⁴, and 10⁵A. THF was used as the eluant with a flow rate of 1.0 mL/min at 30 °C. The morphology for the EPDM modified with PDMS was measured using a Philips XL-30 Scanning Electron Microscope.

3. Results and Discussion

3.1. Maleation of EPDM

The maleation of EPDM was carried out using solution and reactive processes to compare the grafting ratio relative to the amount of MA and initiator. The maximum grafting ratio of MA onto EPDM was 1.47 wt%, when 10 phr of MA and 0.25 phr of DCP were used. Figure 1 shows the results of the grafting ratio to the maleated EPDM product according to the reactive processes. The amount of MA grafted onto the EPDM backbone increased with an increasing amount of MA and reached limit a value of 1.47 wt% by reacting with more than 12 phr of MA. This grafting ratio indicates that 36 mol% of the MA was grafted onto the EPDM in comparison with the total concentration of the double bond of the EPDM sample.
Figure 1. Grafting ratio relative to amount of MA with maleation of EPDM by reactive process (DCP : 0.25 phr).

Figure 2. Grafting ratio relative to amount of initiator with maleation of EPDM by reactive process (MA : 10 phr).

Figure 3. Grafting ratio relative to the reaction time with maleation of EPDM by solution process (BPO/MA/EPDM = 0.25 phr /10 phr /100 plu).

Scheme 1. Preparation of EPDM-g-MA.

grafting ratio of the MA is obtained at 2.4 wt%, and reached the limit value after 6 h of reaction time at 110 °C reaction temperature. In the maleation of EPDM using the solution process, 59 mol% of the MA was grafted onto the EPDM in comparison with the total concentration of the double bond of the EPDM sample.

The maleation mechanism of EPDM is shown in Scheme 1. As shown in Scheme 1, DCP decomposes
at 130 °C to form radicals, which abstract hydrogen H₆ or H₇ from the allyl hydrogen of EPDM. Thereafter, MA molecules are added to EPDM radical (1) or (II), and the MA or polymeric MA is grafted onto the EPDM. In the forming of EPDM radicals, it would seem that radical (1) is easily generated because H₆ with a ring strain is easier to eliminate than H₇. The chemical structure of EPDM-g-MA prepared from the solution process was confirmed by measuring the FT-IR and NMR, and the results are shown in Figures 4 and 5. In Figure 4, new absorption peaks appeared at 1784 cm⁻¹ and 1864 cm⁻¹ due to the C=O of the MA grafted onto the EPDM. In Figure 5, a new resonance peak appeared at 7.03 ppm due to the MA grafted onto the EPDM. The molecular weight of EPDM-g-MA for sample 4 (Table 1) was slightly higher than at about 9000 when compared with the EPDM sample.

3.2. EPDM-g-MA Modified with PDMS
EPDM-g-MA modified with PDMS was prepared from the direct blending of EPDM-g-MA with aminopropyl group terminated PDMS relative to the amount of PDMS used in the roll mill technique at room temperature. The reaction mechanism is shown in Scheme 2. The chemical structure of EPDM-g-MA/PDMS (17 phr of PDMS) was confirmed by measuring the FT-IR spectrum, and the result is shown in Figure 6. In Figure 6, absorption peaks appeared due to the symmetric and asymmetric stretching vibration of C=O in the maleic anhydride at 1864 cm⁻¹ and 1784 cm⁻¹, whereas other peaks appeared due to the stretching vibration of C=O in the amic acid at 1680 cm⁻¹ and 1710 cm⁻¹, and finally a Si-O-Si absorption peak appeared at 1020–1100 cm⁻¹. The FT-IR spectra for EPDM-g-MA/PDMS (17 phr of PDMS) were measured by changing the aging time at 240 °C to confirm the imidization.
reaction of the MA grafted onto the EPDM with the aminopropyl group of PDMS, and the result was shown in Figure 7. In Figure 7, the absorption peaks of C=O at 1770 cm\(^{-1}\) and 1710 cm\(^{-1}\) were increased due to imidization [8], C=O peak at 1784 cm\(^{-1}\) due to MA and C=O peak at 1680 cm\(^{-1}\) due to amide both decreased as the imidization progressed.

From these results, it would appear that the premixed sample of EPDM-g-MA/PDMS was imidized by aging at 240 °C.

3.3. Morphological Behavior of EPDM-g-MA/PDMS

The overall surface morphologies for the unaged and aged samples of EPDM-g-MA/PDMS were investigated on the surface of specimens broken in liquid nitrogen. A typical SEM micrograph of a fractured surface of unaged EPDM-g-MA/PDMS (17 phr of PDMS) is shown in Figure 8. Whereas Figure 9 shows a specimen after aging at 240 °C for 2 h.

As can be seen in Figure 8, \(\alpha,\omega\)-aminopropyl group terminated PDMS has uniformly dispersed throughout the EPDM-g-MA matrix. The length of the brighter phase particles varied from 20 \(\mu\)m to 200 \(\mu\)m. In addition, the specimen aged at 240 °C for 2 h shown in Figure 9 exhibited spherical shaped domains of PDMS with an average diameter of 50 \(\mu\)m. A careful inspection of the SEM micrograph of the cryogenic fractured surfaces of the EPDM-g-MA/PDMS showed no evidence of any separated phases of the EPDM-g-MA and PDMS.

Accordingly, the above observation would seem to be suggested that \(\alpha,\omega\)-aminopropyl group terminated PDMS was well dispersed into the EPDM-g-MA copolymer matrix without usage of a compatibilizer and imidized with the aminopropyl group of PDMS.

4. Conclusions

EPDM-g-MA was prepared using both solution and reactive processes. The maximum grafting ratios were 2.4 wt% and 1.47 wt% in the solution and reactive processes, respectively. The solution process proceeded at 110 °C and the reactive process was carried out using a banbury-type internal mixer with various amounts of MA and concentrations of DCP at 130 °C.

EPDM-g-MA modified with \(\alpha,\omega\)-aminopropyl PDMS was prepared from the direct blending of EPDM-g-MA with PDMS using roll mill techniques at room temperature without the use of compatibilizer. The morphology of EPDM-g-MA/PDMS blend was confirmed by SEM. The \(\alpha,\omega\)-aminopropyl polylimethyldisiloxane was well dispersed into the EPDM-g-MA matrix and the MA group of the EPDM matrix was imidized with amino group of PDMS.
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References