

Preparation and Characterization of Composites: Ethylene–Propylene–Diene Terpolymer-graft-Maleic Anhydride/CaCO₃

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ABSTRACT: In this paper, a new method was applied to form crosslinking networks in the ethylene–propylene–diene terpolymer (EPDM) matrix with calcium carbonate (CaCO₃) particles, which were chemically treated by maleic anhydride (MAH). The tensile test showed that the tensile strength and the elongation at break of the composites were improved significantly, and when the content of CaCO₃ was about 20 wt % in the composites, the maximum tensile properties were achieved. The results of swell and solution text showed that the composites had evident crosslinking structure. The results of attenuated transmission reflectance–Fourier transform infrared (ATR-FTIR) spectrum proved

that the Acid-Base reaction between CaCO₃ and MAH had happened. SEM micrographs showed that the interfacial adhesion between CaCO₃ and copolymer was well. The thermogravimetric analysis curves showed that the composites had a new change in mass between 655 and 700°C, which might be the decomposition temperature of calcium maleate. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1810–1815, 2006

Key words: grafting; calcium carbonate (CaCO₃); maleic anhydride; ethylene–propylene–diene terpolymer

INTRODUCTION

Ethylene–propylene elastomer is a family of synthetic rubber that is prepared by a polymerization of ethylene, propylene, and, optionally, a nonconjugated diene. There are two classes: ethylene–propylene copolymers (EPM) and ethylene–propylene–diene terpolymer (EPDM). The EPDM is a low unsaturated synthetic rubber that was developed by DuPont in the 1960s. Because EPDM has a low degree of unsaturation, it not only contains excellent weatherability and heat resistance similar to that of EPM, but also contains a small portion of double bonds for further crosslink.^{1–8} However, when compared with major synthetic elastomers and natural rubber, EPDM is difficult to crosslink because of its fewer double bonds.

EPDM is a noncrystallizable polymer, and its noncrystallizability dominates its low stretch strength. The raw elastomer is seldom used solely because of this disadvantage. Usually, they are compounded with oils, fillers, and curatives, followed by crosslinking using sulfur or peroxide-based curing systems. Talc, calcium carbonate (CaCO₃), silicon dioxide, and

graphite are the most common fillers for EPDM to improve the mechanical properties.

It is well-known that the adhesion properties of EPDM are not good enough for application. Grafting modification is a good method to improve the adhesion properties of EPDM.^{9–11} Solution grafting of maleic anhydride (MAH) onto EPDM was reported previously. In this article, the reaction of EPDM with MAH in the presence of xylene was carried out. After the reaction was finished, calcium carbonate was added into the reactive product, and finally, acetone was added dropwise into the mixture as a precipitant. The composites were obtained after the precipitates were dried in vacuum.

The tensile strength and the solution and swell test showed that the composites were indeed crosslinked. The tensile strength and the elongation at breaking were improved significantly. When the contents of CaCO₃ were about 20 wt %, the composites had the maximal mechanical properties. The images of scanning electron microscopy (SEM) showed that adhesion between EPDM and CaCO₃ is very good. It could be explained by the fact that CaCO₃ particles became the centers of crosslink and improved the mechanical properties of the composites by reacting with MAH and forming a large network. The results of FTIR and SEM confirmed this conjecture.

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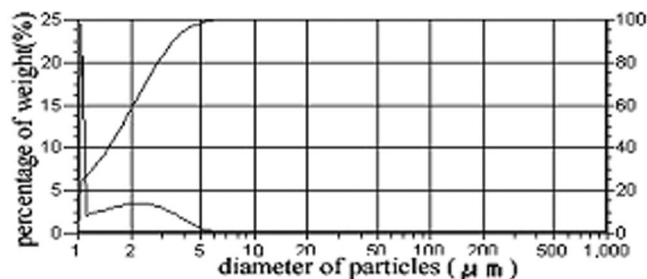


Figure 1 Integral curves of size distribution of CaCO_3 ; 2500 mesh (10×3 times).

Compared with the method using common crosslink agents and reinforcing agents, the present method has following advantages: (1) the composites are not blended, which reduces the possibility of macrophase separation; and (2) the crosslink reaction is carried out under low viscosity conditions, which provides a good reaction condition to form a uniform structure.

EXPERIMENTAL

Materials

Ethylene-propylene-diene terpolymer (EPDM) was provided by Yangtze Chemical (Nanjing, China). Maleic anhydride (MAH, AR) and benzoyl peroxide (BPO, AR) were purchased from Sanaisi Chemical Reagent (Shanghai, China) and Shanghai Chemical Reagent (Shanghai, China), respectively. Both MAH and BPO were further purified by recrystallization. AR grade xylene and acetone were used as received without further purification.

Measurement of size gradation of CaCO_3

The size gradation of different CaCO_3 samples were measured by LS-CWM(2) laser particle sizer (OMEC, China). The characteristic and size of CaCO_3 were: D25, $0.56 \mu\text{m}$; D50, $1.32 \mu\text{m}$; D75, $2.57 \mu\text{m}$; D90, $4.20 \mu\text{m}$. The content of CaCO_3 was above 98.0 wt % in all the samples. The integral coefficients of the samples are shown in Figure 1.

Grafting procedure

The reaction of EPDM and MAH was carried out in a four-necked flask equipped with overhead stirrer, dropping funnel, thermometer, and a nitrogen gas inlet. The temperature was maintained within an accuracy of $\pm 0.5^\circ\text{C}$ by using a contact thermometer in an oil bath. EPDM (8.0 g) and MAH (1.4 g) were dissolved in 200 mL xylene at 100°C . Nitrogen gas was purged throughout the reaction to avoid possible oxygen during the reaction. BPO (0.1 g) was dissolved in

40 mL xylene and was added dropwise into the four-necked flask at 100°C . The reaction was continued for 4 h.

Measurement of graft ratio

A control experiment was carried out under identical conditions, and was used to measure the graft ratio. One hundred and twenty milliliters of acetone was added dropwise into the control sample under vigorous stirring at 60°C for 6 h. The graft copolymer was filtrated, washed by acetone, and dried in vacuum at room temperature. The graft ratio was determined by using eq. (1):

$$\text{Graft (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where W_0 was the weight of the original EPDM; W_1 was the weight of the grafted EPDM after complete removal of unreacted MAH and solvent under vacuum.

Preparation of composites

A known amount of CaCO_3 was added into grafting reactive product (2.3) under vigorous stirring after the temperature went down to 60°C . The reaction was continued for 1 h at 60°C . One hundred and twenty milliliters of acetone was added dropwise into the reaction mixture. The process was continued for 6 h. The deposition was isolated and dried in vacuum at room temperature. Table I lists the contents of CaCO_3 in the different composites.

Measurement of swell and solution

The results of swell and solution were used to confirm the degree of crosslinking of the elastomer. One EPDM-g-MAH sample and two EPDM-g-MAH/ CaCO_3 composite samples (No. 1 and No. 5) were prepared, and each was divided into six portions, respectively. Each portion was weighed accurately (W_0). These samples were put into xylene and the reaction was continued for 1, 3, 6, 12, 24, and 48 h at 35°C . Then the samples were wiped quickly and weighed accurately (W_1). Finally the samples were

TABLE I
Different Content of CaCO_3 in 8g EPDM

	Sample no.				
	1	2	3	4	5
Content of CaCO_3	1.0	1.5	2.0	2.5	3.0
Content of CaCO_3 in composites (wt %)	11	16	20	24	27

TABLE II
The Stretch Parameter of Samples

Content of CaCO ₃ in 8g EPDM(g)	Tensile strength (MPa)	Elongation at max load (%)	Elongation at break (%)	Modulus (Aut Young) (MPa)
0.0	2.017	612.0	612.0	1.962
1.0	3.371	753.7	753.7	2.902
1.5	3.357	900.0	900.0	3.352
2.0	3.884	961.2	961.2	3.154
2.5	3.714	908.2	908.2	3.329
3.0	3.300	960.3	960.3	3.070

dried in vacuum at room temperature and weighed again (W_2). The rates of swell and solution were determined by using the following equations.

$$\text{Swell (\%)} = \frac{W_1 - W_2}{W_2} \times 100 \quad (2)$$

$$\text{Solution (\%)} = \frac{W_0 - W_2}{W_0} \times 100 \quad (3)$$

Tensile measurement

For mechanical testing, the plates (about 1 mm thickness) were conditioned at 20°C and were cut and modeled into 15-mm span tensile test specimens. Tensile tests to determine the modulus, tensile strength, and elongation at break were performed with a cross-head speed of 200 mm/min on an Instron 4200 (Instron, UK).

Measurement of ATR-FTIR

The attenuated transmission reflectance (ATR) technique was used to determine the chemical modification produced on the most external 5- μm rubber surface, after the treatment was carried out. A Nexus 870 Fourier transform infrared (FTIR) spectrophotometer was used to obtain the ATR-FTIR spectra of the samples. A Germanium crystal (absorption at 690–4000 cm^{-1}) was used and 200 scans per sample were taken.

Measurement of SEM

The break surface of tensile samples was observed on X650 scanning electron microscope (Hitachi, Japan). the operation voltage was 20 kV.

Measurement of TGA

Thermogravimetric analysis (TGA) measurements of Samples 1–5 and EPDM-g-MAH were carried out on a Pyres 1 TGA under the following conditions: samples weight ranging from 10 to 15 mg, at a rate of 20°C/

min from room temperature to 800°C under atmosphere.

Blend 8 g EPDM and 2 g calcium maleate that was named blend was measured by TGA under the same conditions as that for Samples 1–5 and EPDM-g-MAH.

RESULTS AND DISCUSSION

Graft ratio

In this experiment, W_0 was 8.014 g, and W_1 was 8.936 g. The graft ratio, obtained from eq. (1), of our samples was 11.50 wt %.

Tensile strength

Table II shows the tensile strength of samples with different CaCO₃ contents. From this table, it can be seen that with the increase of CaCO₃ contents in the composites, the elongation at breaking and tensile strength were increased, when the contents of CaCO₃ are not more than 2 g in 8 g EPDM. The span of tensile strength was between 3.371 MPa, for 1 g CaCO₃ sample, and 3.884 MPa, for 2 g CaCO₃ sample. The span of the elongation at breaking was between 753.8%, for 1 g CaCO₃ sample, and 961.2%, for 2 g CaCO₃ sample. However, when the content of CaCO₃ is more than 2 g in 8 g EPDM, the elongation at breaking and tensile strength of the composites were decreased. The control experiments by the same method showed that the stretch parameter of EPDM and EPDM-g-MAH samples were very poor and weren't used as materials.

Crosslinking of different samples

The results of swell and solution are used to measure the degree of crosslinking of elastomer. The lesser the swell and solution of the elastomer the higher the degree of crosslinking.

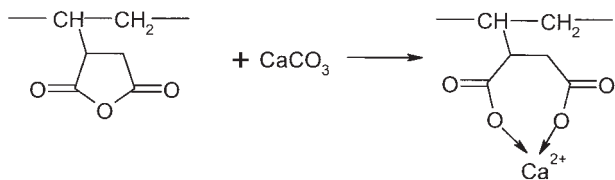
The results of swell and solution of three samples, one EPDM-g-MAH sample and two kinds of EPDM-g-MAH/CaCO₃ (1.0 g CaCO₃ and 3.0 g CaCO₃) samples, are shown in Table III and Table IV. These two tables show that the rates of swell and solution of

TABLE III
The Swell Ratio of Samples at Different Times

Sample	The swell ratio of samples in different time (%)					
	1 h	3 h	6 h	12 h	24 h	48 h
EPDM-g-MAH	734	1101	1226	1525	1890	1970
3.0 g CaCO ₃ in composites	96	111	116	118	124	122
1g CaCO ₃ in composites	240	304	320	325	339	340

EPDM-g-MAH/CaCO₃ samples was much smaller than those of EPDM-g-MAH sample, and the higher CaCO₃ content sample had slower swell and solution than the lower CaCO₃ content sample. Under the same condition, pure EPDM had been dissolved completely within less than 0.5 h. These indicated that the composites were efficiently crosslinked by introducing CaCO₃ particles. The more the CaCO₃ particles were added, the higher degree of crosslinking the composites had.

Acid-Base theory could be used to explain the current experimental results. Since the grafted MAH was acidic, it might react with CaCO₃ in xylene, which is an alkalescence. This reaction generated random coils from EPDM chains, anchored by a filler of CaCO₃. The random coils of EPDM were anchored by several fillers of CaCO₃, through the reaction between their branched chains (MAH) and fillers (CaCO₃). These two reasons resulted in the crosslinking of composites (Figs. 2 and 3). With the increase of the content of CaCO₃, the crosslinking points of the composites increased. The degree of crosslinking was increased. Thus the tensile strength and tensile modulus of the composites were improved as well. However, the elongation at breaking of composites was decreased.



ATR-FTIR analysis

Figure 4 showed the ATR-IR spectra of the CaCO₃, EPDM, EPDM-g-MAH, and Samples 1–5. The ATR-

FTIR spectrum of EPDM-g-MAH showed a band at 1710 cm⁻¹ attributed to anhydride —C=O groups, which did not appear at the spectrum of the as-received EPDM. It indicated that the grafting reaction had taken place after introducing MAH. The ATR-FTIR spectrum of CaCO₃ showed a strong band at 1429cm⁻¹ attributed to its —C=O groups. Compared with the IR spectrum of EPDM-g-MAH, the spectra of Samples 4 and 5 had an additional peak between 1420 and 1450 cm⁻¹, which might attributed to —C=O groups of CaCO₃. However, the peak at 1710 cm⁻¹ disappeared. The Samples 1, 2, and 3 had no peaks between 1420 and 1450 cm⁻¹, and the peak at 1710 cm⁻¹ decreased significantly compared with the IR spectrum of EPDM-g-MAH. A comparison between the strength of absorption of the peak at 1710 cm⁻¹ for the Samples 1–3 showed that Sample 1 had the strongest absorption among the three samples, and Sample 2 has a stronger absorption than Sample 3. These results indicated that the reaction between MAH and CaCO₃ had taken place and the Samples 4 and 5 had excess amount of CaCO₃ over MAH, while the Samples 1–2 have the opposite situation, i.e., MAH over CaCO₃. The results of ATR-FTIR confirmed the supposition of the crosslinking.

SEM analysis

Scanning electron microscopy (SEM) micrographs of the tensile break surface of EPDM-g-MAH/CaCO₃ are shown in Figure 5. The small bright spots represent CaCO₃, while the white spots were chips of EPDM, which were pulled out from the matrix and could be proved by the size of chips and fillers. From the images, it could be concluded that most of fillers had been embedded completely within the rubber and the adhesion between EPDM.

TABLE IV
The Solution of Samples at Different Times

Sample	The solution ratio of samples in different time (%)					
	1 h	3 h	6 h	12 h	24 h	48 h
EPDM-g-MAH	16.2	24.0	28.8	24.2	25.9	38.5
3.0 g CaCO ₃ in composites	0.55	1.42	1.55	1.76	2.33	2.29
1.0 g CaCO ₃ in composites	0.54	2.11	2.17	2.63	2.54	2.99

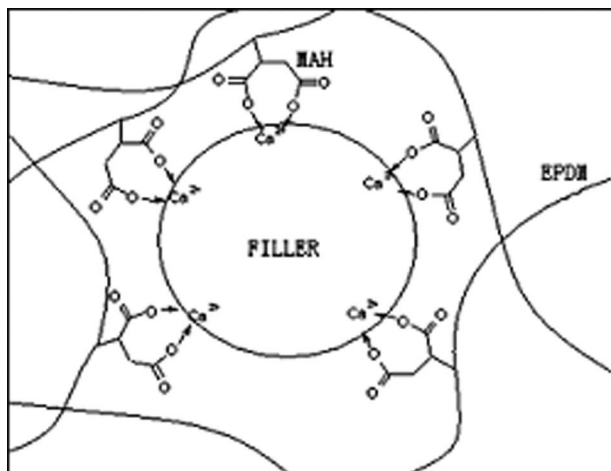


Figure 2 Schematic illustration of adhesion between MAH (branched chain) and CaCO_3 (filler).

TGA analysis

The TGA curves of samples in atmosphere were shown in Figure 6. It showed that the heat decomposed temperature in the sample of EPDM-g-MAH was between 385 and 465°C, which was nearly the heat decomposed temperature of EPDM in the sample of blend, and those of Samples 1–5 were between 445 and 490°C. It was in accord with the decompose temperature of EPDM that had been crosslinked. It was also shown that the heat resistance of the Samples 1–5 was better than EPDM-g-MAH, which was also a proof that the Samples 1–5 had been effectively crosslinked. Moreover, the Samples 1–5 had a small change in mass between 655 and 700°C that was nearly the heat decomposed temperature of calcium maleicate in the sample of blend. We considered that

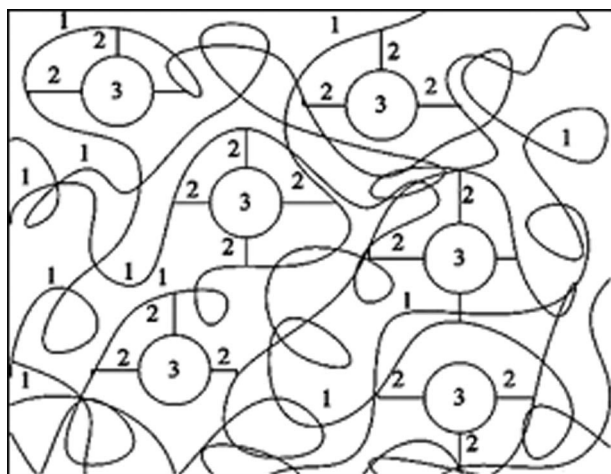


Figure 3 Schematic illustration of crosslink in EPDM-g-MAH/ CaCO_3 composites. EPDM (random coil), 1; MAH (branched chain), 2; CaCO_3 (filler), 3.

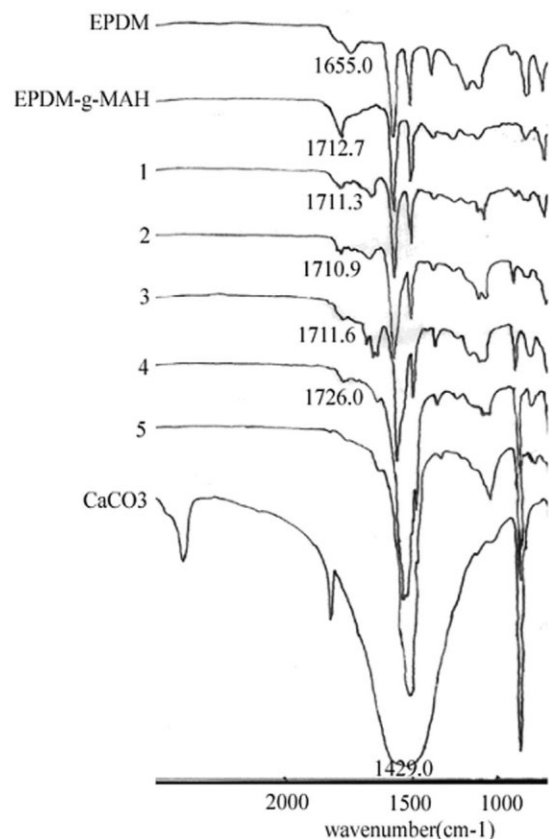


Figure 4 ART-FTIR spectrum of Samples 1–5 and CaCO_3 , EPDM, and EPDM-g-MAH.

might be the decomposed temperature of calcium maleicate.

CONCLUSIONS

Precipitation could be used to synthesize EPDM-g-MAH/ CaCO_3 composites. In this method, crosslink

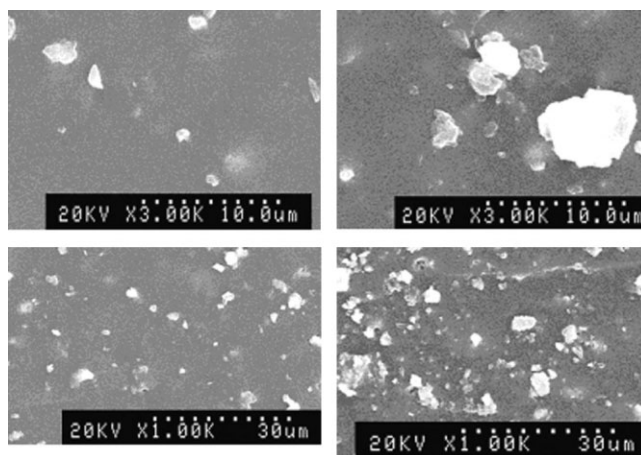


Figure 5 SEM of tensile break surface of EPDM-g-MAH/ CaCO_3 . (a) Sample 1 ($\times 3000$), (b) Sample 3 ($\times 3000$), (c) Sample 1 ($\times 1000$), (d) Sample 3 ($\times 1000$).

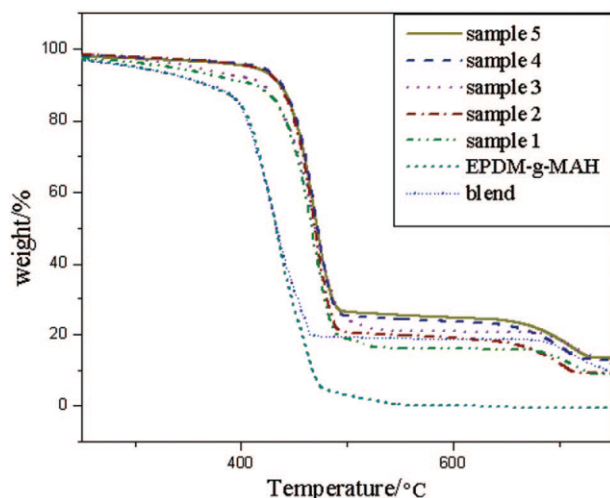


Figure 6 TGA of Samples 1–5, EPDM-g-MAH and blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

between EPDM-g-MAH and CaCO_3 was generated. The tensile strength, tensile modulus, and the elongation at breaking of the composites of EPDM-g-MAH/ CaCO_3 were remarkably improved compared with those of the original EPDM. The degrees of solution and swell of the composites were decreased greatly after the crosslink. The results of ATR-FTIR spectrum showed that the Acid-Base reaction between CaCO_3 and MAH had been taken place. The results of SEM

showed that the adhesion of interface between CaCO_3 and copolymer was well. The results of TGA showed that the composites had a small change in mass between 655 and 700°C, which might be the decomposed temperature of calcium maleicate.

NOMENCLATURE

MAH	Maleic anhydride
EPDM	Ethylene-propylene-diene terpolymer
BPO	Benzoyl peroxide
ATR-FTIR	Attenuated transmission reflectance-Fourier transform infrared
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis

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