Thermooxidative Aging and Kinetics of the Thermooxidative Degradation of Ethylene–Propylene–Diene Terpolymer-*graft*-Maleic Anhydride/Calcium Carbonate Composites

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ABSTRACT: We report the preparation of five different ethylene–propylene–diene terpolymer-*graft*-maleic anhydride/calcium carbonate samples with different calcium carbonate contents by precipitation and their mechanical properties and structural characterization.[1] In this study, we tried to analyze the thermooxidative aging and the kinetics of thermooxidative degradation with retained tensile testing for various thermal-aging times at 150°C and with hot-loading-recovery measurements. The results of the hot-loading-recovery measurements and retained tensile testing showed that the sample with the best cross-linked structure had the best thermooxidative-aging resistance of all the samples. The experimental results for the thermooxidative degradation kinetics showed that the sample with the best crosslinked structure had the highest activation energy of thermal decomposition. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2395–2401, 2007

Key words: ageing; blending; composites; elastomers; kinetics (polym.)

INTRODUCTION

Polymeric materials such as rubber usually suffer from oxidation and heat during processing, storage, and use. Ethylene–propylene–diene terpolymer (EPDM) is one of the fastest growing general-purpose elastomers on the market today. It has several advantages, such as high resistance to oxidant aging and heat aging without the use of antioxidants and low-temperature flexibility. EPDM and its composites are used in many outdoor applications because of their outstanding ozone and weather resistance.

EPDM is a low-unsaturation synthetic rubber developed by DuPont in the 1960s. Because EPDM has a low degree of unsaturation, it not only has excellent weatherability and heat resistance like ethylene-propylene monomer (EPM) but also contains a small number of double bonds for further crosslinking.[2–10] However, 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 this dominates its low stretching strength. The raw elastomer is seldom used solely because of this disadvantage. Usually, it is compounded with oils, fillers, and curatives, and this is followed by crosslinking with sulfur- or peroxide-based curing systems. Talc, calcium carbonate ($CaCO_3$), silicon dioxide, and graphite are the most common fillers used with EPDM to improve its mechanical properties.

In our previous experiments, the grafting reaction of EPDM with maleic anhydride (MAH) in the presence of xylene was carried out. After the reaction was finished, $CaCO_3$ was added to the reaction product, and finally, acetone was added dropwise to the mixture solution as a precipitant. Composites were produced after the precipitate was dried *in vacuo*. Compared with traditional methods, such as the use of popular crosslinking and reinforcing agents, this method does not involve blending, and the crosslinking is carried out in a lower viscosity solution.

Thermogravimetric analysis (TGA) is a useful technique for studying the decomposition reactions of sol-

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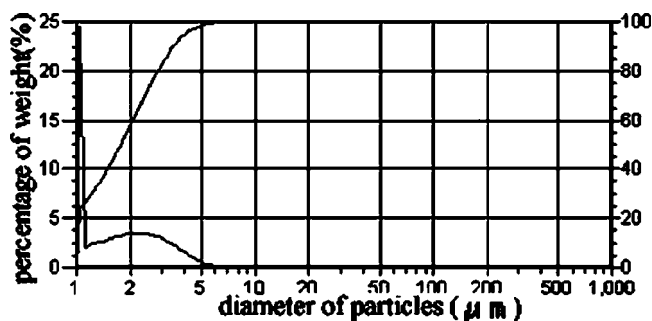
Figure 1 Integral and differential curves of the size distribution of 2500-mesh $CaCO_3$ (10×3 times).

ids, and it has been widely used to study the mechanisms and kinetics of the thermal decomposition of polymers.[11–15]

In this study, TGA at various heating rates was used to investigate the aging process and dynamic heat aging of ethylene–propylene–diene terpolymer-*graft*-maleic anhydride (EPDM-*g*-MAH)/$CaCO_3$ composites. The results showed that the sample with the best crosslinked structure had the highest activation energy of thermal decomposition. The results for the retained breaking strain and retained breaking load for the various thermal-aging times at 150°C showed that the sample with the best crosslinked structure had the best thermooxidative-aging resistance.

EXPERIMENTAL

Materials

EPDM was provided by Yangtze Chemical Co. (Nanjing, China). MAH (an analytical reagent) and benzoyl peroxide (BPO; an analytical reagent) were purchased from Sanaisi Chemical Reagent Co. (Shanghai, China) and Shanghai Chemical Reagent Co. (Shanghai, China), respectively. Both MAH and BPO were further purified by recrystallization. Analytical-reagent-grade xylene and acetone were used as received without further purification.

Measurement of the gradation size of $CaCO_3$

The size gradation of a $CaCO_3$ sample was measured with an LS-CWM (2) laser particle sizer (OMEC Co., Zhuhai, China). The sizes of $CaCO_3$ were as follows: for D25, 0.56 μm; for D50, 1.32 μm; for D75, 2.57 μm; and for D90, 4.20 μm. The concentration of $CaCO_3$ was greater than 98.0 wt % in 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 an overhead stirrer,

TABLE I
Different Contents of $CaCO_3$ in 8 g of EPDM

	Sample				
	1	2	3	4	5
$CaCO_3$ (g)	1.0	1.5	2.0	2.5	3.0

dropping funnel, thermometer, and nitrogen gas inlet. The temperature was maintained within an accuracy of ±0.5°C with a contact thermometer in an oil bath. EPDM (8.0 g) and MAH (1.4 g) were dissolved in 200 mL of 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 of xylene and was dropped into the four-necked flask at 100°C. The reaction was continued for 4 h. The attenuated total reflection/Fourier transform infrared spectra of the samples showed a peak at 1710 cm^{-1} that was attributed to anhydride —C=O groups; this indicated that the grafting reaction had taken place after the introduction of MAH.[1]

Measurement of the graft ratio

A control experiment was carried out under the same conditions used to measure the graft ratio.

Acetone (120 mL) was dropped into the control sample under vigorous stirring at 60°C for 6 h. The graft copolymer was filtered, washed with acetone, and dried *in vacuo* at room temperature.
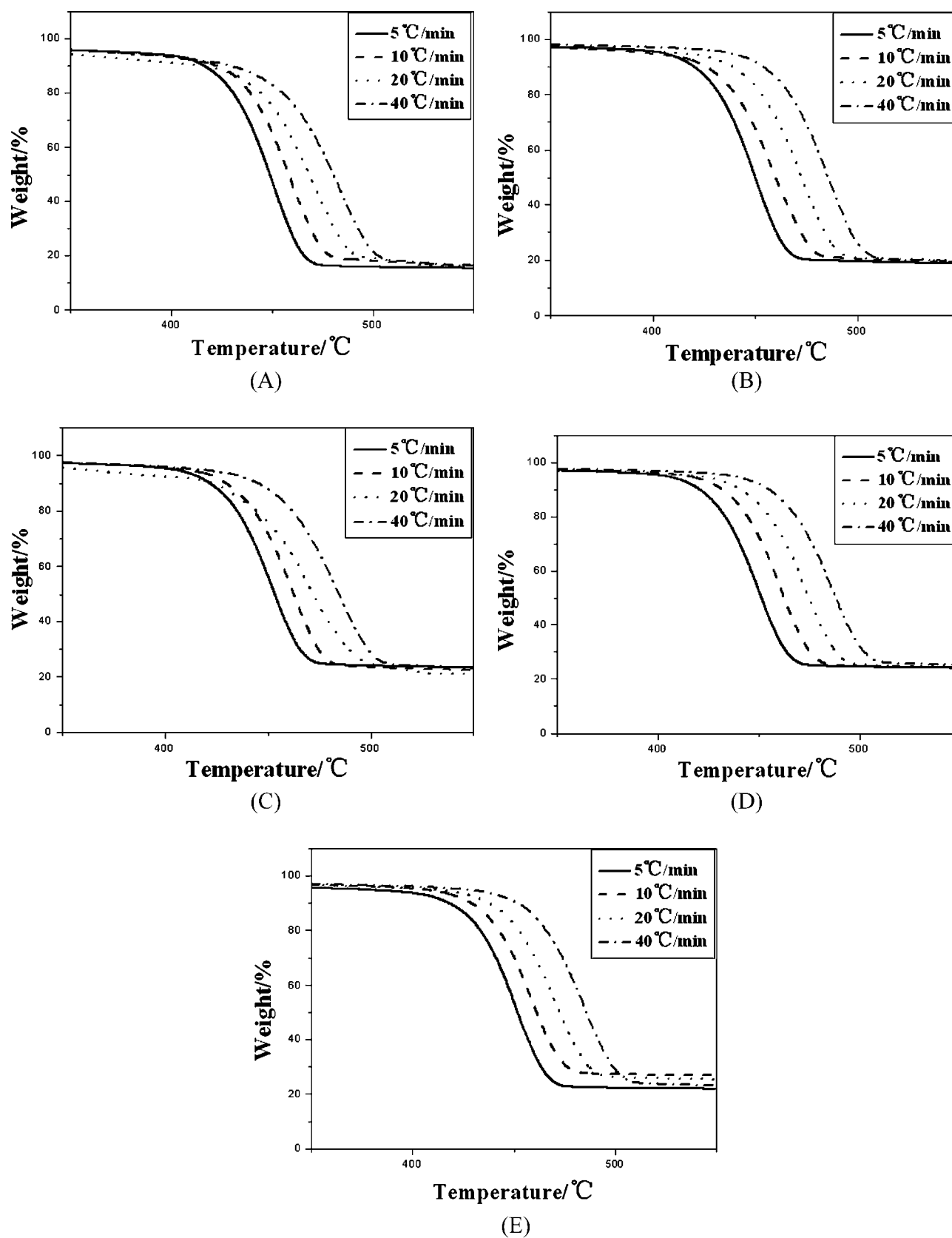
The graft ratio was determined as follows:

$$\text{Grafting } (\%) = (W_1 - W_0)/W_0 \times 100 \qquad (1)$$

where W_0 is the weight of the original EPDM and W_1 is the weight of the grafted EPDM after the complete removal of the unreacted MAH and solvent *in vacuo*.
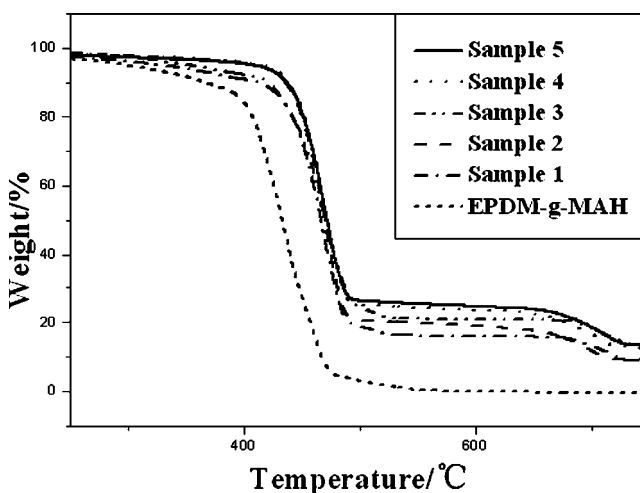
Figure 2 TGA of samples 1–5 and EPDM-*g*-MAH at a rate of 20°C/min from room temperature to 800°C in the atmosphere.

Figure 3 TGA of samples 1–5 at rates of 5, 10, 20, and 40°C/min in the atmosphere: (A) sample 1, (B) sample 2, (C) sample 3, (D) sample 4, and (E) sample 5.
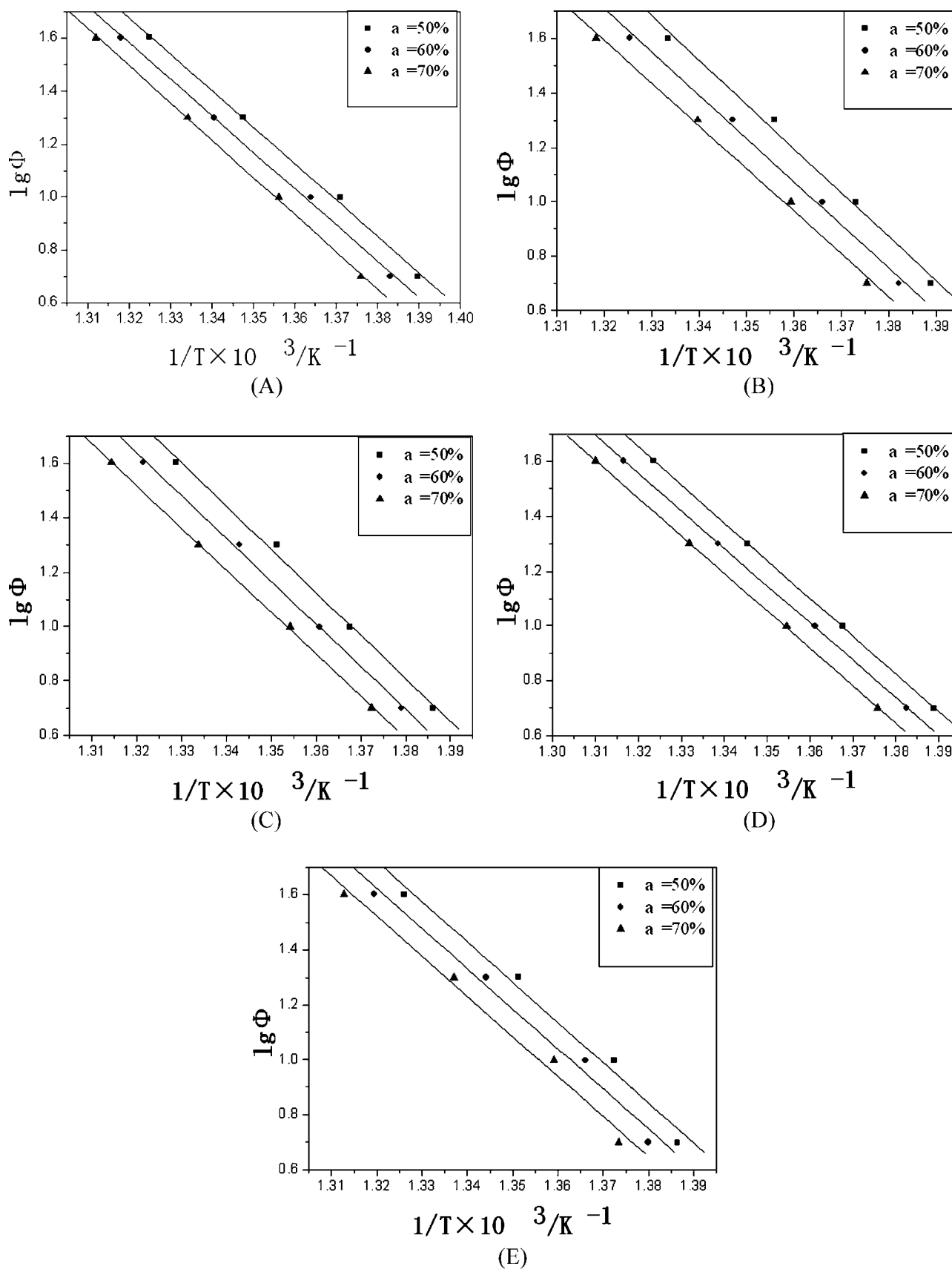
Figure 4 Plots of the logarithm of the heating rate (lg Φ) versus the reciprocal of the absolute temperature ($1/T$) for samples 1–5: (A) sample 1, (B) sample 2, (C) sample 3, (D) sample 4, and (E) sample 5. (a: massloss).

TABLE II
Thermal Aging Kinetic Parameters

	Sample				
	1	2	3	4	5
Activation energy of thermal decomposition (kJ/mol)					
50% weight loss	110.50	134.85	141.66	124.16	121.46
60% weight loss	110.51	131.47	140.39	122.97	120.85
70% weight loss	112.88	130.01	139.12	123.35	120.87

Preparation of the composites

A known amount of $CaCO_3$ was added to the grafting reaction product (2.3) under vigorous stirring after the temperature decreased to 60°C. The reaction was continued for 1 h at 60°C. Acetone (120 mL) was added dropwise to the reaction mixture. The process was continued for 6 h. The deposition was isolated and dried *in vacuo* at room temperature. Table I lists the contents of $CaCO_3$ in the different composites.

TGA measurements

TGA of samples 1–5 and EPDM-*g*-MAH was carried out on a Pyres 1 thermogravimetric analyzer (Perkin-Elmer, Inc., Wellesley, MA). All the samples were heated from room temperature to 800°C at a rate of 20°C/min in the atmosphere for the measurements.

Samples 1–5 were heated from room temperature to 600°C at the rates of 5, 10, 20, 40°C/min in the atmosphere for the measurements.

Tensile measurements

For mechanical tests, the thickness of the plates was about 1 mm. They were cut and machined into 15-mm tensile test specimens and were held from 0 to 168 h at 150°C before they were measured. Tensile tests of the tensile strength and break elongation were performed at a crosshead speed of 200 mm/min on an Instron 4200 (Instron, Inc., High Wycombe, UK). The tests were conditioned at 20°C. All tests were carried out five times.

Hot-loading recovery measurements

Specimens of each sample, tape-marked with a free 30-mm length (±0.02 mm) from a load of 0.2 MPa on the bottom up to a polytetrafluoroethylene support from which they hung, were allowed to hang vertically in circulatory air ovens at 120°C and were held from 24 to 72 h. Then, for the specimens, the load was eliminated, and the marked span from the top to the bottom was measured (±0.02 mm). All tests were carried out five times.

RESULTS AND DISCUSSION

Graft ratio

In this experiment, W_0 was 8.014 g, and W_1 was 8.936 g. The graft ratio of EPDM-*g*-MAH for our samples was 11.50 wt % according to eq. (1).

TGA results

The TGA curves for the samples in the atmosphere are shown in Figure 2. The loss of mass in the EPDM-*g*-MAH sample took place between 385 and 465°C, and that of samples 1–5 happened between 445 and 490°C. The heat resistance of samples 1–5 was therefore better than that of EPDM-*g*-MAH. Moreover, samples 1–5 experienced a small change in the mass between 655 and 700°C, which might have been the decomposition temperature of calcium maleicate.

Kinetics of nonisothermal degradation

To correlate the TGA experimental data with a kinetic expression, a dimensionless mass loss (α) has been defined as follows:

$$\alpha = \frac{M_0 - M}{M_0 - M_f} \tag{2}$$

where M, M_0, and M_f are the actual, initial, and final sample weights. For nonisothermal degradation, M_0 is the mass at the start of the degradation process (taken at room temperature), and M_f is the steady-state mass at the end of the degradation (taken at 600°C). The term $M_0 - M_f$ represents the total mass of the polymer available for reaction.

TABLE III
Stretching Parameters

$CaCO_3$ in 8 g of EPDM (g)	Stretching strength (MPa)	Strain at the maximum load (%)	Strain at the autobreak (%)	Young's modulus (MPa)
0.0	2.017	2.017	612.0	1.962
1.0	3.371	753.8	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

The approximate Flynn–Wall–Ozawa method might be shown as follows:

$$\lg \Phi = \lg AE/RF(\alpha) - 2.315 - 0.4567E/RT \quad (3)$$

where Φ is the heating rate of TGA, A is the pre-exponential factor, R is the universal gas constant, T is the absolute temperature, and E is the activation energy of thermal decomposition.

Thus, when the dimensionless mass loss is constant, a plot of the logarithm of the heating rate versus the reciprocal of the absolute temperature, obtained from thermograms recorded at several heating rates, should be a straight line whose slope allows an evaluation of the activation energy. The TGA curves corresponding to the thermooxidative degradation of samples 1–5 at heating rates of 5, 10, 20, and 40°C/min are shown in Figure 3, and plots of the logarithm of the heating rate versus the reciprocal of the absolute temperature of samples 1–5 are shown in Figure 4.

Table II shows the activation energies of thermal decomposition of samples 1–5. The activation energy of thermal decomposition of sample 3 was obviously higher than those of the others. We already reported that sample 3 had the best mechanical properties of all (Table III). Our previous research showed that the reaction between $CaCO_3$ and MAH was complete and the efficiency of crosslinking was good in sample 3. Thus, the good mechanical properties could be attributed to the best crosslinked structure (sample 3) but not to the highest crosslinking density (sample 5).[1]

It is well known that a higher activation energy of thermal decomposition can correspond to better thermooxidative-aging resistance. Therefore, the results are reasonable.

Hot-loading-recovery characterization

Table IV shows the set percentages of samples 1–5 held in circulatory air ovens at 120°C for 24 and 72 h. The composite sample that had more $CaCO_3$ had a lower set percentage. In these samples, more $CaCO_3$ implied more crosslinking points. The EPDM chains were anchored by more crosslinking points and were difficult to move.

TABLE IV
Hot-Loading-Recovery Parameters (mm)

	Sample				
	1	2	3	4	5
0 h	30	30	30	30	30
24 h	31.98	31.98	31.48	31.38	31.22
72 h	34.92	34.10	33.48	33.18	32.98

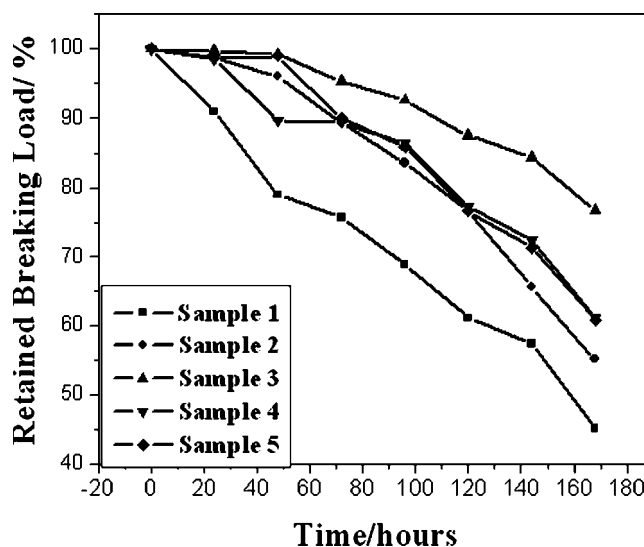Tensile loading = 0.2 MPa; temperature = 120°C.

Figure 5 Time dependence of the retained breaking load of samples 1–5 at 150°C.

Retained tensile properties during thermal aging

Figure 5 presents the effect of the retained breaking load for samples 1–5 for various thermal-aging times at 150°C. Sample 1 showed the lowest retained breaking load. Samples 2–5 had good results before 48 h of oven aging. The retained breaking load of sample 3 decreased mildly after 48 h of oven aging, but the retained breaking load of the other samples decreased rapidly after 48 h.

The effect of the retained breaking strain for samples 1–5 for various thermal-aging times at 150°C can be found in Figure 6. The retained breaking strain of sample 3 decreased mildly with time in oven aging, but the other samples showed a rapid decrease in their retained breaking strain. This implied that the
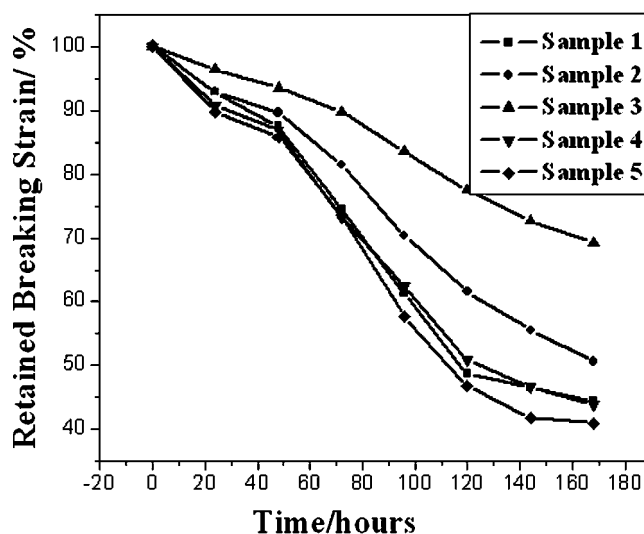

Figure 6 Time dependence of the retained break strain of samples 1–5 at 150°C.

sample with the best crosslinked structure had the best thermooxidative-aging resistance.

CONCLUSIONS

Samples of EPDM-*g*-MAH/CaCO$_3$ had the same thermooxidative-aging resistance as crosslinked EPDM. Sample 3 had the best thermooxidative-aging resistance and the highest activation energy of thermal decomposition of the samples. The fact that the sample had the best crosslinked structure could be used to explain these experimental results.

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