Kinetic Analysis of Thermal Degradation of NR/EPDM Blends: Effect of the Reactive Compatibilization

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ABSTRACT: The effect of mercapto-modified EPDM (EPDMSH) and thioacetate-modified EPDM (EPDMTA) on the thermal degradation of NR/EPDM (70 : 30 wt %) blends has been investigated under anaerobic and aerobic conditions. The anaerobic condition consisted of compression-molding the samples at different times, higher than the optimum curing time established by the oscillatory disk rheometer. The aerobic conditions consisted of ageing the samples in an air circulating oven. EPDMTA in the blend resulted in a reasonable retention of mechanical properties of sample ageing in an air-circulation oven, and a slight increase of crosslink density after ageing under anaerobic conditions.

EPDMSH resulted in an accentuated ageing degradation under anaerobic and aerobic conditions. The kinetic parameters of thermal degradation were evaluated from non isothermal TGA experiments taken at different heating rates. The presence of functionalized copolymers in a proportion as low as 2.5 wt % in the blends resulted in a substantial increase of the activation energy, indicating an increase of the resistance against thermal degradation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2669–2675, 2007

Key words: thermogravimetric analysis; activation energy; elastomer blend; compatibility; thermal degradation

INTRODUCTION

Elastomeric blends are important class of industrial materials, which are often employed in many critical service applications; especially in mining and industrial transportation.[1] Most of these blends are susceptible to thermal degradation because of the presence of unsaturated rubber. This phenomenon decreases the mechanical performance of these materials with time, whose extent is difficult to predict and depends upon several factors, such as, operating temperature, chemical environment, loading conditions, and type of rubber.[1,2] One of the most interesting and studied elastomer blends is that constituted by natural rubber (NR) and ethylene–propylene–diene rubber (EPDM). As a consequence, new materials can be developed by combining the excellent physical properties of NR and good ozone resistance of EPDM. However, due to differences in unsaturation level and structural characteristics, a mutual incompatibility can exist, which contributes for a decrease of mechanical performance.[2] To overcome these demerits, a third component, which is able to promote

an effective interaction between the phases, that is, a compatibilizing agent, is normally employed.[3–7] Recently we have developed new functionalized EPDM based on mercapto-modified EPDM (EPDMSH) and thioacetate-modified EPDM (EPDMTA) and used both as reactive compatibilizing system for NR/EPDM blends.[8–11] The addition of low amount of these functionalized copolymers (2.5 phr) resulted in an improvement on tensile properties.[8] The reactive compatibilization is based on the fact that thiol-based groups of the functionalized EPDM can react to the carbon–carbon double bond of the unsaturated rubber and form an effective anchorage between the rubber phases during processing.

The study of thermal degradation of these systems is of great interest since it can, in many cases, determine the upper temperature limit of use for these materials. Several papers employ thermogravimetric analysis to evaluate the thermal oxidative behavior of several polymeric materials, at different heating rates in air.[12–16] The kinetic parameters of the degradation process may be determined from dynamic TGA experiments, by using different models.[12,14] However, the most popular and versatile are the Kissinger[17] and Flynn-Wall-Ozawa[18] models, because it is not necessary for the knowledge of reaction mechanism.

Ozawa's method is an integral method that can determine the activation energy without knowledge of reaction order.[13,14] It is used to determine the activation energy at a given value of conversion by plotting the logarithm of the heating rate against $1/T$.

This paper investigates the effect of the functionalized EPDM copolymers (EPDMTA and EPDMSH) on
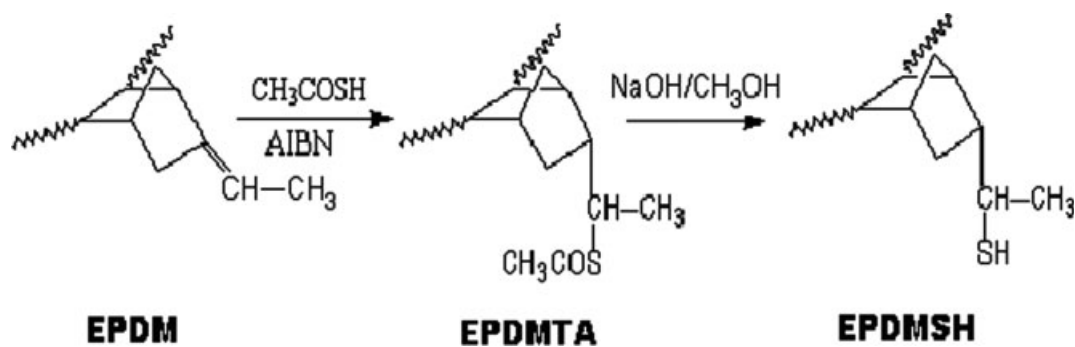
Figure 1 Scheme of the EPDM functionalization of EPDM with thioacetate (EPDMTA) and mercapto (EPDMSH) groups.

the kinetic parameters of the degradation process of NR/EPDM blends determined under aerobic conditions using TGA experiments performed in air. The anaerobic ageing of these blends was also investigated by performing the vulcanization at different times (higher than t_{90} given by the oscillating disk rheometer) and determining the swelling degree and mechanical properties of the samples as a function of curing time.

EXPERIMENTAL

Material

Natural rubber (*Hevea brasiliensis*) with Mw = 207,000, was kindly supplied by Michelin do Brasil S.A. (Rio de Janeiro, Brazil) EPDM rubber (Keltan 65; Mooney viscosity (ML 1 + 4 at 125°C) = 49.3; ethylene content = 51.7 wt %; ENB content = 9.11 wt %) was kindly supplied by DSM Elastomeros do Brasil S.A. (São Paulo, Brazil). Zinc oxide, stearic acid, sulfur, irganox 1010, and *n*-cyclohexil benzothiazyl sulfenamide (CBS) were of laboratory reagent grade and supplied by the local rubber industries. Thioacetic acid (TAA), analytical grade, from Sigma Chemistry, was used as received and Azo-bisisobutyronitrile (AIBN) from Merck S. A., was recrystallized from methanol/water solution.

Functionalization of EPDM

The preparation of the functionalized EPDM was carried out, according to previous report.[8] The functionalization has taken place in two steps (Fig. 1). The EPDMTA was prepared by a free radical addition of TAA and AIBN into a toluene solution of EPDM (10 wt %) at 70°C for 48 h. The TAA/AIBN and diene/TAA molar ratios were established as 10.0 and 1.0, respectively, to avoid crosslink during the synthesis. Then, the product was precipitated into methanol, filtered, washed several times with methanol and dried.

The EPDMTA was submitted to an alkaline methanolysis by slowly adding 5 wt % solution of NaOH,

followed by heating at 50–60°C. At these conditions, an amount of thioacetate or mercapto groups in the functionalized copolymers corresponding to 2.5 mmol/g has been achieved.

Blend preparation

Blends of NR and EPDM (as per formulation in Table I) were mixed in a two roll mill at 80°C. NR was masticated for 2 min and then EPDM and the functionalized compatibilizing (EPDMTA or EPDMSH) were subsequently added. After the homogenization of the rubber blend, the other ingredients were added. The processing time after each component addition was about 2 min.

Measurements of physical properties

Cure characteristics were studied using an oscillating disk rheometer, ODR (Tecnologia Industrial, mod T100) (Buenos Aires, Argentina) at 1° arc degree, according to ASTM D 2084-81 method. The samples were tested at a vulcanization temperature of 160°C. For tensile testing, the blends were vulcanized up to the optimum cure time, in a hydraulic press at 1500 lb/in.[2] (the optimum cure time, t_{90}, was established as the necessary time to reach 90% of the maximum torque). Then, dumbbell shaped tensile test specimens (DIN 53,540–testing number 2) were cut from the molded plaques and submitted to tensile test in an Emic Universal Testing Machine (São Paulo, Brazil),

TABLE I
Formulation of Compounds

Ingredients	Phr
Natural rubber (NR)	70
EPDM	30
Modified EPDM (EPDMTA or EPDMSH)	2.5
Zinc oxide	5.0
Stearic acid	1.5
Antioxidant (Irganox 1010)	1.0
Sulfur	2.0
N-cyclohexil-2-benzothiazole Sulfenamide (CBS)	1.0

Compatibilizer	M_L[a] (lb.in)	M_H[b] (lb.in)	M_H–M_L (lb.in)	t_{S1}[c] (min)	t_{90}[d] (min)	CRI[e] (min)$^{-1}$	V_r
Non compatibilized	1.7	20.4	18.7	3.02	6.0	33.56	0.179
EPDMTA	2.3	20.5	18.2	2.30	5.15	35.34	0.189
EPDMSH	1.4	21.7	20.3	1.63	4.0	42.19	0.198

[a] Minimum torque.
[b] Maximum torque.
[c] Scorch time.
[d] Cure time.
[e] Cure rate index.

at a crosshead speed of 200 mm/min. The experiments were performed before and after aging the specimens in an air-circulation oven at 70°C for 72 h.

For anaerobic ageing, the samples were also over cured at different curing time ($3.t_{90}$, $6.t_{90}$ and $9.t_{90}$) at 160°C, and submitted to tensile testing.

Crosslink densities of the blends were obtained from swelling experiments. Vulcanized (1 g) samples were accurately weighted (w) and immersed in toluene in closed bottles at room temperature, for 7 days. The surfaces were dried with filter paper and the samples were quickly weighted (w_1). The swollen samples were then dried completely at 60°C for 48 h under reduced pressure and weighted again (w_2). The volume fraction of the polymer in a swollen mass calculated by the following equation:

$$V_r = \frac{w_2(\delta_r)^{-1}}{w_2(\delta_r)^{-1} + (w_1 - w_2)(\delta_s)^{-1}} \quad (1)$$

where δ_r and δ_s are the rubber and solvent densities, respectively.

The thermogravimetric analysis (TGA) was performed in a TGA7 Perkin–Elmer. The samples (15 ± 0.1 mg) were placed on an open platinum sample pan, and the experiments were conducted in air, at a flow rate of 80 mL/min. Nominal heating rates of 10.0, 12.5, 15.0, 17.5, 20.0, and 30°C/min were used.

RESULTS AND DISCUSSION

Curing characteristics

The effect of compatibilizer on the curing characteristics and crosslink degree of NR/EPDM (70 : 30 wt %) blends is summarized in Table II. The presence of 2.5 phr of
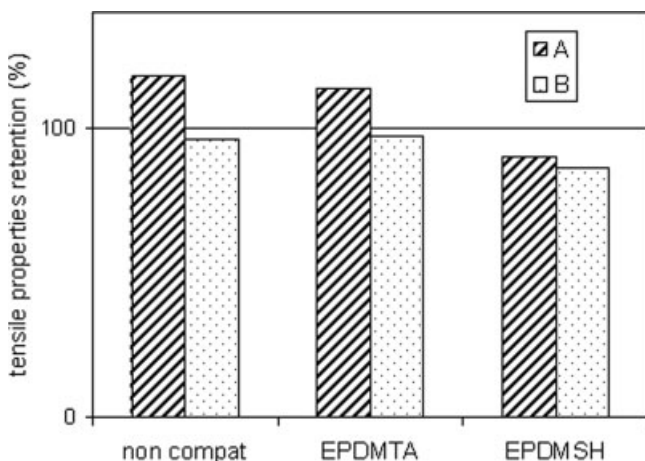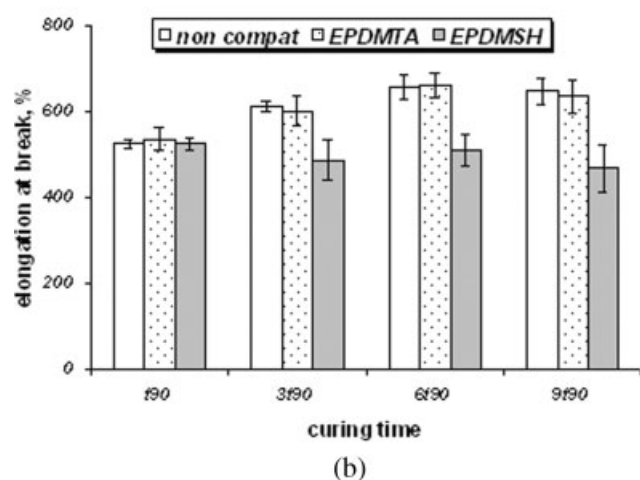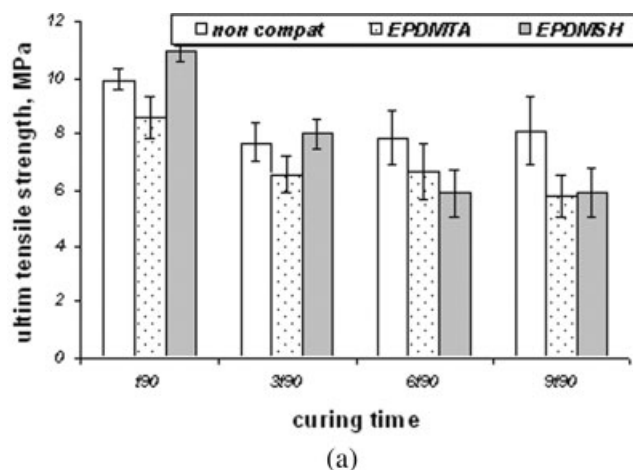

(a)

Figure 2 Retention of mechanical properties after ageing in an air-circullating oven. (A) ultimate tensile strength; (B) elongation at break.

(b)

Figure 3 Variation of tensile properties of the blends as a function of ageing time under anaerobic conditions.

TABLE III
Effect of EPDMTA or EPDMSH on V_r Values of NR/ EPDM (70 : 30 wt %) Blends Submitted to Different Ageing Time Under Anaerobic Conditions

Ageing time	Non compatibilized	EPDMTA	EPDMSH
t_{90}	0.179	0.189	0.198
$3t_{90}$	0.186	0.194	0.179
$6t_{90}$	0.184	0.181	0.172
$9t_{90}$	0.178	0.179	0.168

the functionalized EPDM resulted in an increase on cure rate index, determined by the following equation:

$$\text{CRI} = \frac{100}{(t_{90} - t_{s1})} \quad (2)$$

Also there was a decrease on both scorch time (t_{s1}) and optimum curing time (t_{90}) with the addition of the compatibilizer agents. The higher influence on curing parameters was observed by using EPDMSH as the compatibilizing agent. This behavior suggests that EPDMSH acts as an accelerator on the curing process. Indeed, the ability of EPDMSH in activating the vulcanization process by sulfur-based system was reported in our previous paper.[9] In that study, it was observed an accelerator effect of EPDMSH in samples cured at higher temperatures (180°C) without the presence of conventional accelerators.

The volume fraction of swollen rubber (V_r) also increased with the addition of the functionalized copolymers and this effect was more important in blends containing EPDMSH, indicating a substantial increase on crosslink density.

Tensile properties

Tensile properties of NR/EPDM blends were measured in samples submitted to aerobic and anaerobic ageing. The aerobic ageing was performed by putting the tensile testing specimens in an air-circulating oven at 70°C for 72 h. The retention of mechanical properties is illustrated in Figure 2. At this condition, the ageing resistance of blends containing EPDMSH was lower than the other blends. Non compatibilized blend and that containing EPDMTA resulted in an increase on tensile strength after ageing, suggesting an additional postcuring process in the oven.

The effect of anaerobic ageing on tensile properties of NR/EPDM blends was also investigated. For this purpose, the blends were compression-molded at different times (higher than the optimum curing time, t_{90}) and submitted to tensile testing. Figure 3 presents the variation of tensile properties of the blends as a function of ageing time under anaerobic conditions. All samples presented significant reduction of tensile strength after an ageing time corresponding to 3 times the t_{90}. This effect was more pronounced in blends containing EPDMSH, which also presented a decrease of elongation at break. These results suggest the occurrence of crosslink break, which was also confirmed from crosslink density obtained from swelling experiments.

Table III presents the variation of crosslink density (expressed in terms of V_r) as a function of the ageing time. Considering blends vulcanized for t_{90} min (the optimum curing time), that containing EPDMSH presented higher values of V_r, when compared to the other blends, which agrees with the tensile strength results. However, when EPDMSH-loaded blend was submitted to longer curing time, there was a substantial decrease on V_r, confirming the occurrence of crosslink break.

These results suggest that EPDMSH is able to improve the mechanical properties of NR/EPDM blends because of the compatibilizing effect promoted by the mercapto groups and a substantial increase on crosslink density. However, the network formed in this
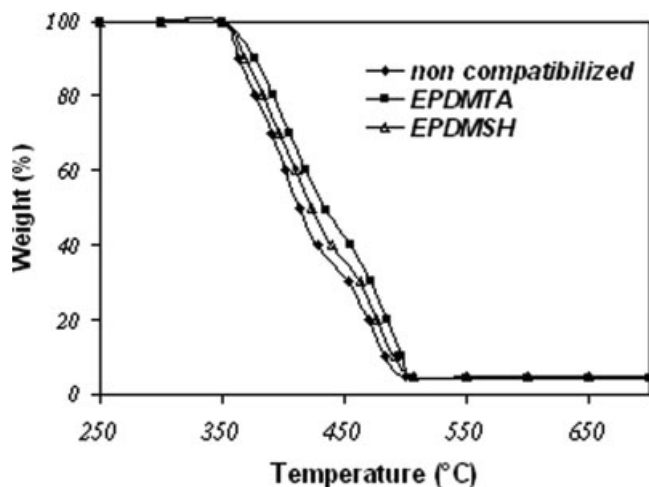

Figure 4 TGA curves of NR/EPDM blends obtained at a heating rate of 10°C/min.
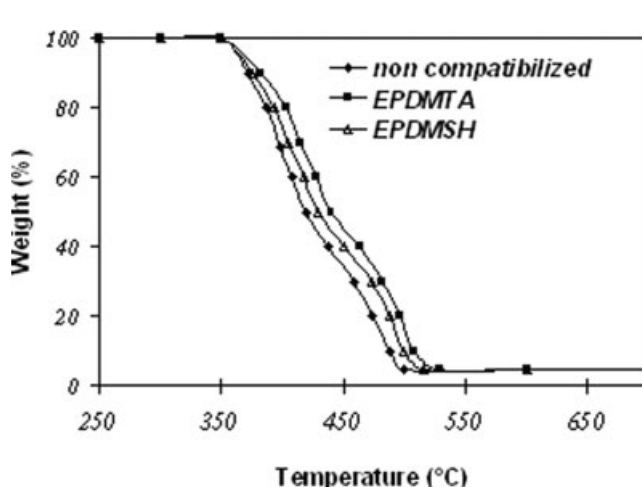

Figure 5 TGA curves of NR/EPDM blends obtained at a heating rate of 20°C/min.
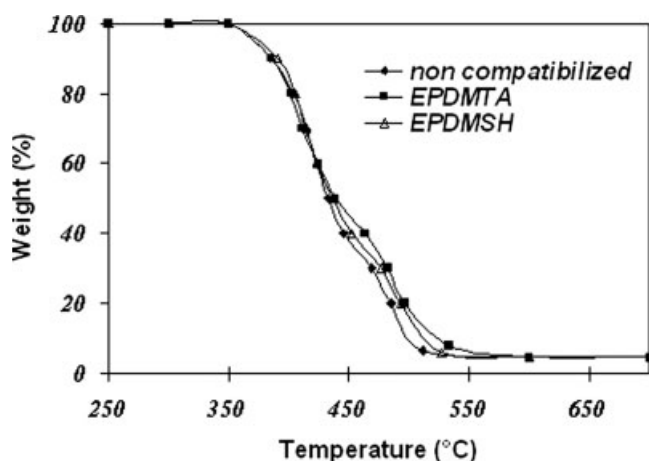
Figure 6 TGA curves of NR/EPDM blends obtained at a heating rate of 30°C/min.

system is not resistant to ageing under anaerobic or aerobic conditions.

Kinetic analysis of thermal degradation by TGA measurements

The effect of compatibilizing system on the degradation process of NR/EPDM blends during combustion was evaluated by thermogravimetric analysis (TGA) of samples cured at t_{90}. Figures 4–6 compare the thermal oxidative degradation curves of compatibilized and non compatibilized blends obtained from dynamic experiments carried out at different heating rates. The first degradation stage corresponds to the NR phase and the second stage is related to the EPDM phase, which is more resistant to thermal–oxidative degradation.[8] It can be easily observed in experiments carried out at lower heating rate (10 and 20°C/min) (Figs. 4 and 5) that the presence of modified EPDM shifted the degradation curves towards higher temperatures and this thermal stabilization effect was more significant in blends containing EPDMTA. At higher heating rate, there was no influence of the compatibilizing system on thermal stabili-

zation of NR phase, corresponding to the first step degradation.

The activation energy of the degradation process was determined using the method of Flynn-Wall-Ozawa, from a linear fitting of $ln\beta$ (heating rate) versus $1/T$ at different conversions. For this study, we have used the conversion values from 10 to 90%, whose results are summarized in Table IV. Figure 7 illustrates the dependence of $ln\beta$ versus $1/T$ at fixed conversions of 20 and 80%, to analyze the effect of the compatibilizing systems on the degradation process of the NR and EPDM phases, respectively. The fitting lines presented in Figure 7 are nearly parallel, indicating the applicability of this method to NR/EPDM blends in the conversions suggested. This fact suggests that a single reaction mechanism is operating in NR and EPDM phases.[15] Figure 8 presents the values of Ea as a function of the conversion, for NR/EPDM blends. The higher activation energy values found in blends with the functionalized EPDM is in agreement with the shift of the degradation temperature corresponding to the weight loss in TGA test, towards higher values. For conversion from 10 to 50%, the blend containing EPDMTA displayed the highest value of Ea. This degradation range corresponds to the decomposition of the NR phase. Therefore, the increase of Ea of degradation in this range of conversion indicates that EPDMTA presented higher efficiency in stabilizing the NR phase against thermal degradation. On the other hand, at the conversions from 60 to 90%, corresponding to the degradation of the EPDM phase, the presence of EPDMSH in the blend resulted in a little higher value of Ea when compared to blend containing EPDMTA, indicating that the thermal degradation of this phase was more difficult in the presence of EPDMSH, probably because of a preferential interaction of EPDMSH with the EPDM phase.

CONCLUSIONS

The above results show that modified EPDM copolymers (EPDMTA and EPDMSH) exert important influ-

TABLE IV
Determination of the Activation Energy of the Degradation Process for NR/EPDM Blends Using the Method of Flynn–Wall–Ozawa, at Different Conversions

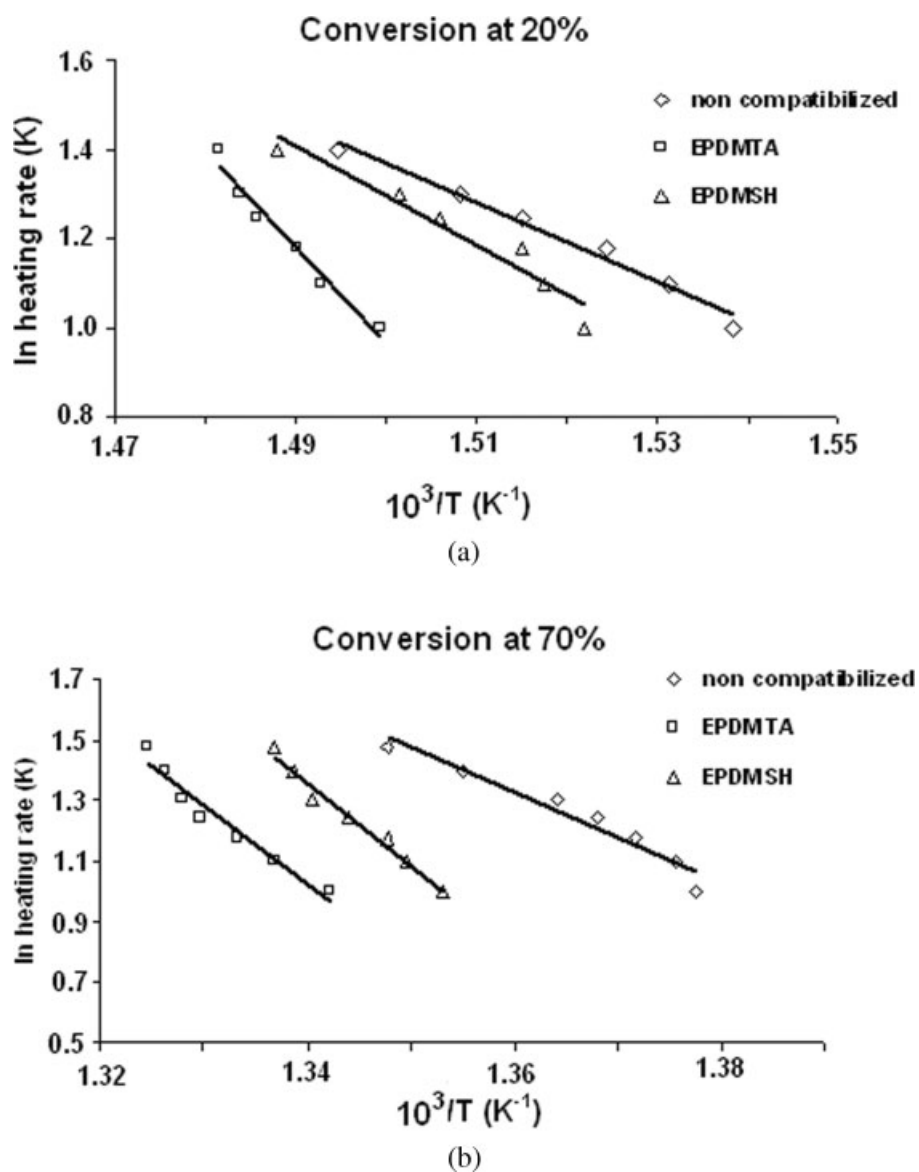| Conversion (α) (%)	Non compatibilized		EPDMTA		EPDMSH	
	Ea/R	r2	Ea/R	r2	Ea/R	r2
10	80	0.97	219	0.99	70	0.97
20	62	0.95	176	0.97	79	0.97
30	70	0.89	158	0.91	100	0.97
40	109	0.93	163	0.97	120	0.98
50	141	0.96	193	0.97	162	0.98
60	153	0.96	206	0.96	218	0.98
70	124	0.89	218	0.96	237	0.99
80	110	0.91	223	0.98	240	0.96
90	96	0.98	214	0.98	238	0.98

Figure 7   The Ozawa's plots of NR/EPDM blends at 20 and 80% of conversion.
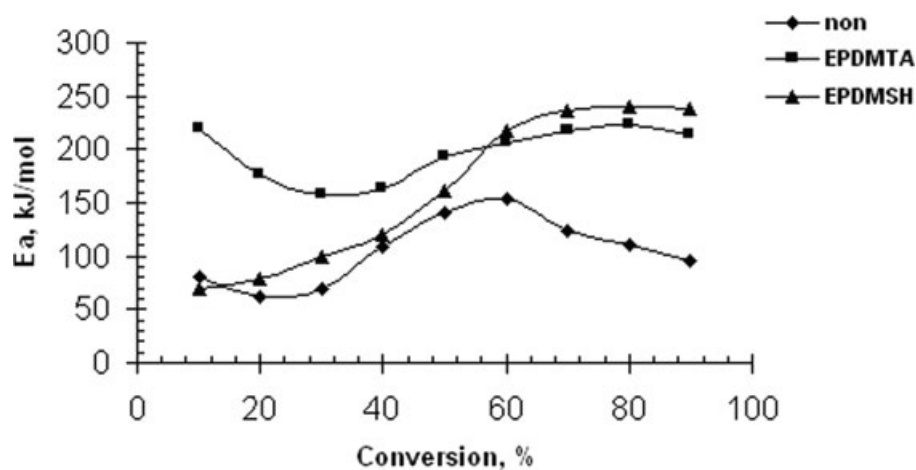

Figure 8   The dependence of the activation energy of the degradation process as a function of the conversion of weight loss, from TGA experiments.

ence on thermal degradation of NR/EPDM blends. The presence of EPDMTA in the blend resulted in a reasonable retention of mechanical properties of sample ageing in an air-circulation oven. By performing ageing under anaerobic conditions, this copolymer presented an increase on crosslink density of blend submitted to compression-molding for three times the optimum curing time ($3.t_{90}$), but displayed also a decrease on mechanical strength.

EPDMSH resulted in an accentuated ageing degradation under anaerobic conditions, as indicated by a decrease of both crosslink density (V_r) and mechanical strength after $3.t_{90}$ of curing time. This result is in agreement with the decrease on tensile strength of the sample aged in an air-circulating oven.

For the kinetic parameters obtained from non isothermal TGA experiments taken at different heating rates, it is possible to suggest that EPDMTA resulted in better resistance against thermal degradation of the NR phase, whereas EPDMSH increased the thermal resistance of the EPDM phase.

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