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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

STRUCTURAL EFFECTS ON THE DECOMPOSITION KINETICS OF EPDM ELASTOMERS BY HIGH-RESOLUTION TGA AND MODULATED TGA

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Abstract

Effects of ethylene content and maleated EPDM content on the thermal stability and degradation kinetics of ethylene propylene diene monomer (EPDM) have been studied using high resolution thermogravimetric analysis (Hi-Res TGA) and Modulated TGA (MTGA). Modulated TGA shows that EPDM degradation is complex, with activation energy of degradation increasing throughout the degradation. Values from both dynamic and constant heating rate experiments are in good agreement with each other and with the literature value. However, the dynamic heating rate experiment shows that if the difference of peak temperature of components in a system is less than 5°C, Hi-Res TGA does not resolve them.

Keywords: blends, EPDM, high resolution TGA, maleated EPDM, modulated TGA

Introduction

Ethylene propylene diene (EPDM) polymers are the fastest growing general-purpose elastomers on the market today. Ethylene propylene polymers have several advantages including high resistance to ozone and oxidation without the use of antidegradants, low temperature flexibility, colour stability, and the ability to accommodate large quantities of filler and oil without creating unnecessary instability. EPDM rubber and its composites are well suited for many outdoor applications due to its outstanding ozone and weathering resistance that is inherent to both its hydrocarbon nature and its almost saturated backbone. Unsaturation is introduced by copolymerising a small quantity (up to 5%) of diene with ethylene and propylene. The unsaturated linkages formed by the diene monomers are required for sulphur curing or vulcanization [1]. These points of unsaturation must be located on a side chain, not in the hydrocarbon backbone, so that no deficiency in the ozone and oxidation resistance of the rubber occurs. Ethylidene norbornene, dicyclopentadiene and 1,4-hexadiene are

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the three main types of dienes used in commercial EPDM, though other dienes may be used for special applications.

The EPDM itself may vary in ethylene and propylene proportions, as well as in the amount and type of diene used [2]. The final performance of the EPDM and its formulated rubber compound is sensitive to the variation in polymer microstructure. Structural effects such as microstructural and compositional variation could greatly affect the degradation characteristics of the EPDMs and their composites [3]. However, there remains no systematic study of the effect of microstructure on the long-term performance and degradation behavior of the EPDM and its composites. Therefore, it is important to understand the effects of microstructure and compositional variables on the thermal properties and degradation behavior of EPDM. The quantity ratio of the monomers confers particular properties on the final elastomer [4]. All the types of EPDM currently available on the market have an ethylene content between 45 and 75% by mass. Usage of the high ethylene content will produce polymers with high green strength, whereas the low and medium values will produce softer and more elastic polymers.

As a non-polar hydrocarbon elastomer, EPDM has excellent insulating properties. It is widely used in many products including hose, molded parts for automobile applications, cable insulation, connectors in the electrical industry, and sheet goods. However, EPDM is often blended with other elastomers to modify many properties in a particular way. The development of blends of natural rubber (NR) with EPDM, with the aim of combining the excellent physical properties of NR with ozone resistance of EPDM, has received much attention over the past three decades [5]. Blends of other polar and unsaturated rubbers with EPDM have been developed in order to achieve better thermal stability and wettability [6]. For example synthetic polyisoprene rubber (IR) blends with EPDM exhibit greater thermal stability than natural rubber [7]. Thermogravimetric analysis (TGA) is one of the most commonly used techniques to study the primary reactions of decomposition of polymers and other materials. Despite a lot of work that has been done on blends of EPDM rubber by TGA [8], nothing has been reported on the use of high resolution TGA (Hi-Res TGA); a very useful tool for the characterization and evaluation of thermal stability of those blends.

Although structural changes due to blending improves the desired properties; it may interfere with the thermal stability of the parent polymer. Such change may lead to a structure where the polymer chain is more susceptible to degradation. Degradation usually starts from a labile centre, e.g. head to head structure, site of unsaturation or tertiary carbon atom. In most cases, the kinetics of such decomposition initially is rate controlled, however, in the final stage it becomes more diffusion controlled, due to morphological changes [2]. Therefore, it is very interesting to study the influence of various structural factors on the thermal stability of EPDM with help of Hi-Res TGA.

The present study focuses on studying the effects of ethylene content, maleated EPDM and its proportion on the thermal stability of EPDM rubber using Hi-Res and Modulated TGA.

Modulated TGA (MTGA) [9], patented by TA Instruments in 1998, is a method for calculating activation energy of degradation in a single, rapid experiment, without resorting to kinetic models of degradation. While many polymers decompose in a single step, there are others such as blends or block copolymers etc., in which total decomposition involves more than one stage. The application of the Hi-Res TGA is very useful in the study of those multi-component systems. It permits continuous, smooth variation of the heating rate in response to the sample's measured rate of mass loss. Consequently, it provides increased resolution without increasing the experimental time. There are very few reports on the use of Hi-Res and MTGA for studying complex polymers and composite systems [10, 11].

Experimental

Materials

The effect of microstructure variation was studied using various EPDM gums. Ten EPDM gum rubber samples used (ASTM standard materials with ethylene contents ranging from 40.1 to 78.6%) were received from Exxon Chemicals USA. Samples were used as received, and are designated as PEx, where x is the ethylene content of the gum rubber. In order to study the effect of maleated rubber and other additives, EPDM rubber (JSR EP 103AF, iodine number 15, specific gravity 0.86) manufactured by Japan Synthetic Rubber JSR, Japan, was used. Two different maleated EPDMs; Royaltuf 485 (ethylene content 75%, iodine number 10, specific gravity 0.85, total maleic anhydride 0.5%) and Royaltuf 490, (ethylene content 55%, iodine number 17, specific gravity 0.89, total maleic anhydride 1.0%) manufactured by Uniroyal, USA, were used. Continental Carbon black (N660) was received from Cabot, Australia.

Blending and compounding

Blending of different maleated EPDM with gum EPDM was done in an open two-roll mill. After blend formation, a black masterbatch was prepared first. Table 1 shows the blend composition. The formulation of masterbatch is: Particular blend 100, Carbon black (N660) – 138, ZnO 5, Aktiplast 3, hydrocarbon resin 2, polyethylene glycol 1.5, factice 10, stearic acid 1, PE wax 3, oil 80 and antioxidant 0.5 phr. The second stage involved addition of curatives namely sulfur and accelerator (Efficient Vulcanization/EV system). A compression-molding machine (IDM Australia) was used to carry out the vulcanization of the rubber compound at 180°C to the optimum cure.

Photoacoustic infrared spectroscopy (PA-FTIR)

The ethylene/propylene contents of all EPDM used in the study were known except for sample S_0 (JSR EP 103AF). PA-FTIR was used to determine the ethylene content of the control sample S_0 (gum EPDM) using previously published methods [12], and the ASTM samples PE40 to PE79 to generate the calibration curve. PA-FTIR spectra were obtained by using a Nicolet Magna Spectrometer (Model 750) equipped with a MTech photoacoustic attachment. Samples were placed in circular stainless steel cups, 3 mm deep with a 10 mm diameter, and sealed in a device with a potassium bromide salt window. Samples were also sealed in a high-purity helium atmosphere to promote good heat transfer. PA-FTIR spectroscopy was carried out with 2000 scans at a resolution of 8 $\mathrm{cm^{-1}}$. All FTIR spectra were ratioed *vs*. a reference background spectrum of carbon black. The calibration curve was generated by plotting the ratio of the intensity of the 1462 and 1377 $\mathrm{cm^{-1}}$ bands *vs.* the ethylene content of samples. The 1462 to 1377 $\mathrm{cm^{-1}}$ band ratio of sample S_0 (gum JSR) was then used to determine its ethylene content using the calibration curve.

Table 1 Composition of blends of EPDM with maleated EPDM

Components/%	100/0/%	75/25/%	50/50/%	0/100/%
JSR EP 103AF	S_{1c}*	–	–	–
JSR/Royaltuf 485	–	M_{1c}	M_{2c}	M_{4c}
JSR/Royaltuf 490	–	P_{1c}	P_{2c}	P_{4c}

*Suffix *c* indicates carbon black and curative present in the compound

Thermogravimetric analysis (TGA)

All TGA analyses were conducted using a TA Instruments Hi-Res/Modulated TGA 2950 thermal analyser, using conventional (constant heating rate), modulated and high-resolution modes operating from room temperature to 600°C. The thermal analyser was temperature calibrated between experimental methods using the Curie point of Nickel as a reference. Experiments were performed on ~7.5 and ~20 mg samples for pure and compounded EPDM respectively. All experiments were carried out under a nitrogen atmosphere at a purge rate of 50 ml $\mathrm{min^{-1}}$.

In conventional TGA for gum EPDMs, the samples were temperature equilibrated to 300°C before being heated to 500°C at different heating rates. As PE79 showed appreciable degradation before 300°C at 2°C $\mathrm{min^{-1}}$, the experiment was repeated for PE79 from ambient temperature to 500°C at 2°C $\mathrm{min^{-1}}$. The onset and peak degradation temperatures were determined from the 8°C $\mathrm{min^{-1}}$ heating rate. For compounded EPDM sample, the samples were heated from ambient temperature to 600°C at different heating rates. The activation energies of degradation of the EPDM samples were determined using the isoconversion method of Flynn, Wall [13] and Ozawa [14, 15]

In isothermal TGA, the samples were heated from ambient temperature to 420°C at a heating rate of 20°C $\mathrm{min^{-1}}$ before being held in isothermal mode until less than 1% of the polymer sample was remaining. In MTGA experiments, the samples were temperature-equilibrated to 300°C before being heated to 500°C at a heating rate of 2°C min^{-1}, with temperature amplitude of ±5°C and a period of 200 s. In Hi-Res TGA, the samples were heated from ambient temperature to 600°C at initial heating rate of 10°C min^{-1} with different resolutions and fixed sensitivity 3. Kinetic parameters were calculated using the method proposed by Kissinger [16], and later Seferis *et al.* [17].

Results and discussion

Characterization of EPDM rubber

PA-FTIR was used to characterize the gum EPDM (S_0) using previously published methods [12]. A typical FTIR spectrum of EPDM is shown in Fig. 1. To determine the ratio of ethylene to propylene of sample S_0, a calibration curve was constructed from the set of standard EPDM gum samples, PE49 to PE79. The ratio of the intensity of the 1462 cm^{-1} methylene/methyl bending vibration to the intensity of the 1377 cm^{-1} methyl bending band was plotted as a function of the % ethylene of the ten ASTM samples (P40 to P79), as shown in Fig. 2. Using the least squares linear regression of these data, the ethylene content of the sample S_0 was determined to be 61.5%.

Non-isothermal TGA of EPDM gum

Conventional TGA mass loss curves of samples P40 to P79, performed at a constant heating rate of 8°C min^{-1}, are shown in Fig. 3. Heating curves of the samples show only one step with no oil and little or no residue or filler, indicating that the overall decomposi-

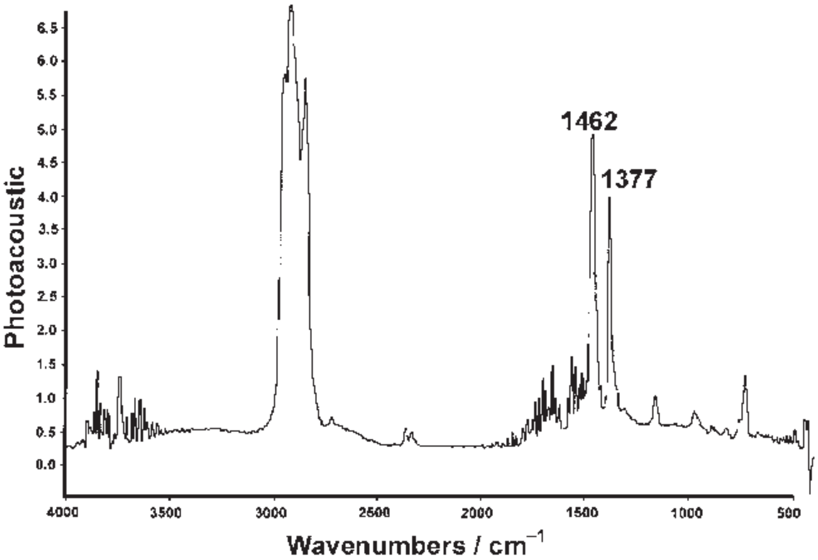

Fig. 1 Photoacoustic infrared spectrum of EPDM sample S_0

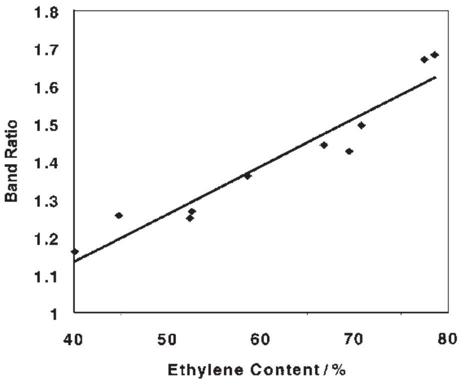

Fig. 2 Calibration curve showing the ratio of 1462 and 1377 cm^{-1} peak heights for EPDM samples

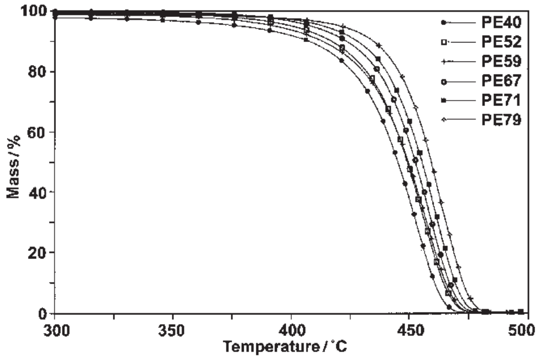

Fig. 3 Heating curves of EPDM gum samples at 8 °C min^{-1} from conventional TGA

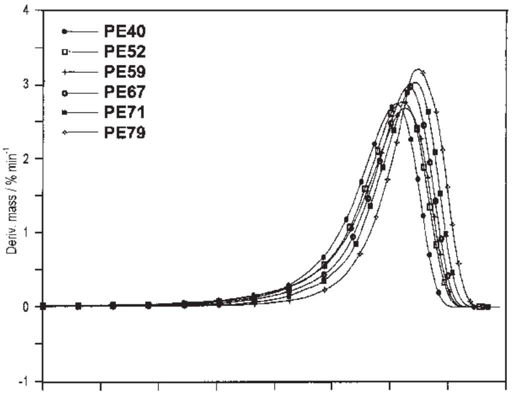

Fig. 4 DTA curves of EPDM gum samples at 8 °C min^{-1} from conventional TGA

tion takes place in a single step. From the first derivative (DTGA) curves of these degradations, shown in Fig. 4, the temperatures of the peaks of degradation can be determined. The onset temperatures of degradation can then be calculated from the TGA curve by extrapolating from the curve at the peak of degradation back to the initial mass of the polymer. Table 2 clearly shows that the temperatures of onset and the peak of degradation are both increased for the samples with higher ethylene content, consistent with the generally held view that EPDM elastomers with higher ethylene contents have higher thermal stability.

Table 2 Onset and peak of decomposition temperatures for samples P40 to P79

Sample	Onset[a]/ T/°C[a]	Peak[a]/ T/°C[a]	Onset[b]/ T/°C[b]	Peak[b]/ T/°C[b]
P40	423.60	452.40	403.50	427.90
P52	426.80	455.40	405.00	432.30
P59	426.40	456.30	406.80	433.20
P67	430.30	458.00	409.50	434.00
P71	434.00	460.90	413.60	437.60
P79	437.60	462.20	416.90	440.70

[a]From TGA at 8 °C $\min^{-1}$. [b]From modulated TGA at 2 °C $\min^{-1}$

Multiple constant heating rate data can be used to calculate the activation energy of degradation by using the equation proposed by Flynn and Wall [13] and independently by Ozawa [14, 15],

$$\log\beta \cong -0.457\frac{E_a}{RT} + \left(\log\frac{AE_a}{R} - \log F(\alpha) - 2.315\right) \tag{1}$$

where 'β' is the heating rate in °C $\min^{-1}$, E_a is the activation energy, '$F(\alpha)$' is the degree of conversion, 'A' is the frequency factor and 'T' is the absolute temperature.

Activation energy can be obtained from the slope of the straight line by plotting $\log\beta$ *vs.* $1/T$ for any level of conversion. Conventional TGA of samples P40 to P79 were performed at constant heating rates of 2, 5 and 8 °C $\min^{-1}$. A typical $\log\beta$ *vs.* $1/T$ plots from 5 to 90% conversions for the degradation of EPDM gum sample is shown in Fig. 5. The activation energies of degradation of samples P40 to P79 from 5 to 90% conversions are shown in Fig. 6. This figure shows that the calculated activation energies of degradation for these samples remain relatively constant after 30% conversion. However, there is no clear trend between the activation energy of degradation and the ethylene content of these samples, although good correlation between the ethylene content of the samples and decomposition temperatures was observed. This could well be due to the random chain scission mechanism in different cases.

Isothermal TGA of EPDM gum

Isothermal TGA was performed to confirm the mechanism of degradation of the EPDM gum samples PE40 to PE79. The isothermal temperature of 420°C was chosen as degradation begins before this temperature, but the mass lost at this temperature in constant heating rate experiments was not excessive (within 5%).

Figures 7 and 8 show the mass loss and the rate of degradation for samples PE40 to PE79 at 420°C. As expected, a small amount of sample is degraded in 20 min while heating to 420°C. Figure 8 also shows that the peaks of degradation occur between 10 to 20 min after the isothermal temperature is reached. These maxima are characteristic of linear olefinic polymers [18], and indicate that the polymer is not degrading via a simple n^{th} order reaction, but via random degradation.

The maximum rate of degradation generally tends to decrease with increasing ethylene content for most samples. The samples with lower maximum rates of degradation also generally tend to have a longer time span between the peak of degradation and the start of isothermal degradation. Straus and Wall [18] have previously noted the same trends in isothermal experiments between polyethylene, polypropylene and ethylene-propylene copolymers with ethylene content between 66 and 94%.

MTGA of EPDM gum

Modulated TGA is based on a method first described by Flynn in 1968 [19]. It has recently been implemented [20, 21] and patented by TA Instruments. In MTGA, a sinusoidal temperature modulation is superimposed on the underlying linear heating rate profile used in traditional TGA (Fig. 9). This modulated temperature results in an oscillatory response in the rate of mass loss, deconvolution of which via a real time discrete Fourier transformation produces the desired kinetic parameters. The activation energy of degradation can then be determined at any point in the decomposition reaction from Eq. (2), where '*T*' is the average temperature, '*A*' is the temperature amplitude and '*L*' is the natural logarithmic ratio between the maximum and minimum

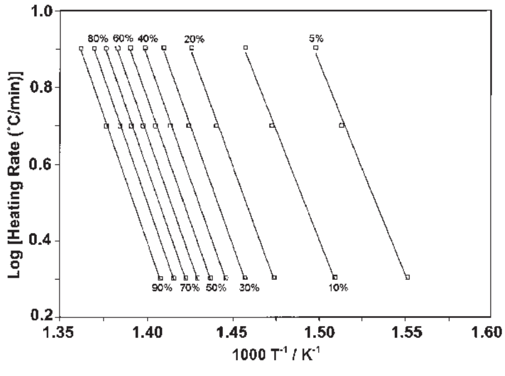

Fig. 5 Plots of logarithm of heating rate *vs*. inverse of absolute temperature at conversion levels from 5 to 95%

rates of degradation, as determined from the amplitude of the mass loss signal by discrete Fourier transformation [22]

$$E_a = \frac{R(T^2 - A^2)L}{2A} \tag{2}$$

Modulated TGA was performed on the samples P40 to P79 with a heating rate of 2°C min^{-1}, with modulation amplitude of 5°C min^{-1} and a period of 200 s. Average mass loss and average rates of mass loss (DTGA) curves are shown in Figs 10 and 11 respectively. The onset and peak degradation temperatures calculated from these curves are also shown in Table 2. Both the onset and peak degradation temperatures are increased in samples with higher ethylene content, consistent with the results obtained by conventional TGA.

The activation energies of the degradation of these samples throughout the entire mass loss are shown in Fig. 12. There is no clear trend between the activation energy of degradation and the ethylene content of these samples. However, there is a general

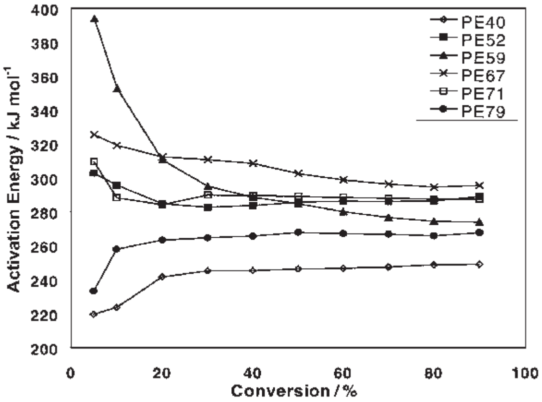

Fig. 6 Activation energies of EPDM gum samples at conversion levels from 5 to 95%

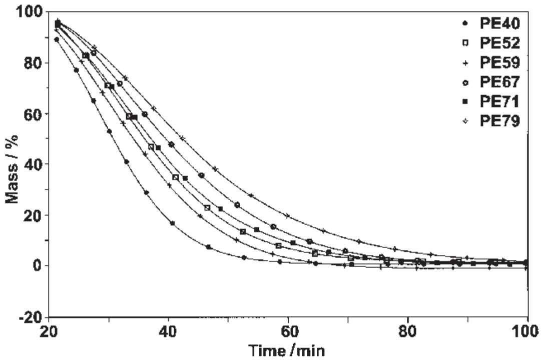

Fig. 7 Curves of EPDM gum samples from isothermal TGA

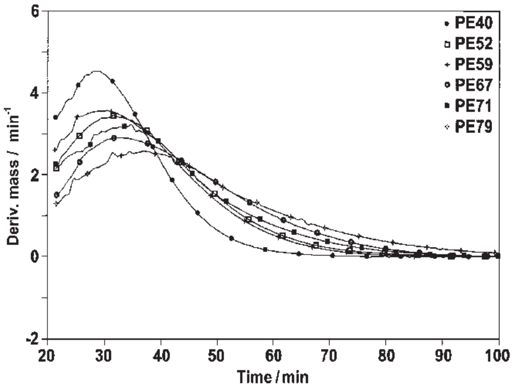

Fig. 8 DTGA of EPDM gum samples from isothermal TGA

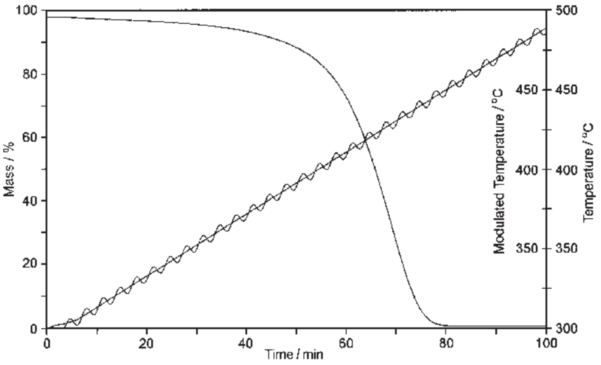

Fig. 9 Typical MTGA plot showing curve, underlying temperature and modulated temperature

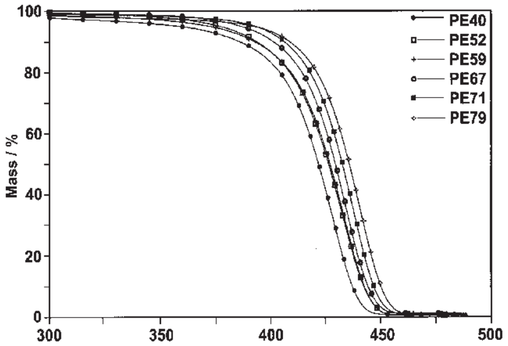

Fig. 10 Curves of EPDM gum samples from MTGA

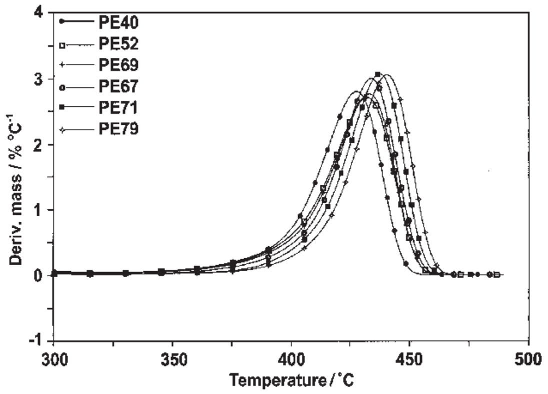

Fig. 11 DTGA curves of EPDM gum samples from MTGA

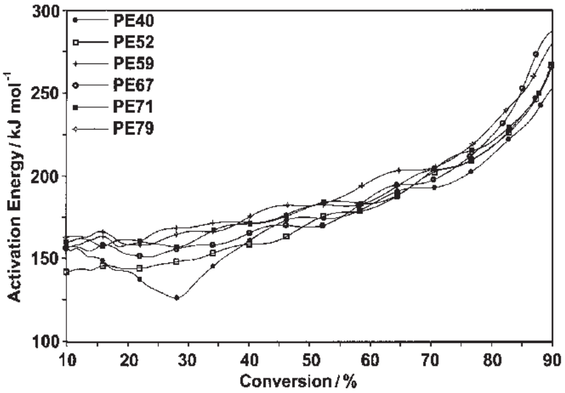

Fig. 12 Activation energies for EPDM gum samples from MTGA

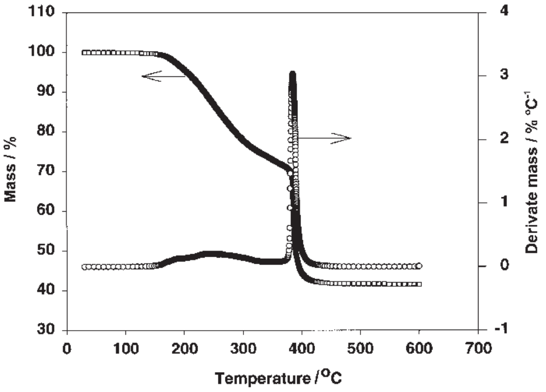

Fig. 13 A typical Hi-Res TGA curve for P_{1c}

trend in that the activation energy tends to increase across the reaction, and the activation energy for each sample is within 30 kJ mol^{-1} from each other. This trend suggests that the mechanism of degradation is similar for these samples, whereby the polymer chain becomes increasingly more difficult to break as the weakest points in the chain are progressively degraded.

It is interesting to note that the activation energies calculated from MTGA are much lower than those calculated from multiple constant heating rate data for these samples. Degradation usually proceeds though competing multi-step reactions and changing the heating rate may alter the balance of these degradation mechanisms. This problem is exacerbated in the multiple constant heating rate experiment, where any change in the mass loss curves is accumulated across the entire mass loss. The Flynn, Wall and Ozawa method assumes that the degradation occurs via a single n^{th} order reaction mechanism over the entire degradation [11]. Because MTGA calculates activation energy from one experiment using a model free equation, it obviously avoids the difficulty of comparing the degradation of samples under different conditions. It also has the advantage in that the experiments are quicker and activation energy is calculated throughout the entire degradation reaction in real time. However, this is noteworthy to mention that the period of oscillation in MDSC (particularly, if the period is short for the transients from thermal and material diffusion to die out) may have effect on the calculated activation energy [23]. MTGA experiments with the samples at different periods of 200, 300, 400 etc. is now under progress to address this issue.

TGA of blended EPDM

The unique ability of Hi-Res TGA to separate the closely overlapping peaks was used in studying the kinetics of decomposition of final cured blends of EPDM rubber and maleic anhydride grafted EPDM rubber. High-resolution analysis allows significant decomposition steps over a smaller temperature range because the heating rate is reduced once any significant mass loss commences. The derivative mass-loss peak is, consequently, narrower than with conventional TGA, allowing greater resolution and separating competing/overlapping mass losses.

A typical Hi-Res TGA curve for P_{1c} carried out at 10°C min^{-1} with resolution 6 and sensitivity 3 is shown in Fig. 13. From the figure, it is obvious that mass loss occurs in two major steps, revealing degradation of the oil, and then the polymer. From the first derivative (DTGA) curve the peak temperatures of degradation of oil and blend can be obtained. However, the expected two steps in degradation of the blend corresponding to the degradations of EPDM and grafted EPDM are not detected. The Hi-Res TGA of pure components (resolution 4) was undertaken in order to determine the peak temperature decomposition of S_0 (pure EPDM), M_4 (Royaltuf 485) and P_4 (Royaltuf 490). The peak temperatures of pure components of the blends are found to be 413.94, 410.58 and 412.99°C respectively. This indicates that use of high resolution can not resolve two close steps in degradation of the components of a blend unless they are separated by more than 5°C. Several authors [10, 17] have claimed that high resolution can be performed with higher heating rates 20, 35 and 40°C min^{-1}. Comparing the time spent on the high-resolution experiment carried out and 10 and 20°C min^{-1} heating rate with resolution 6 and sensitivity 3, no remarkable difference was found. However, Berbenni *et al.* [24] studied the dehydration process of alpha-cyclodextrin, applying Hi-Res TGA at similar initial heating rate (10°C min^{-1}).

For dynamic heating rate experiments, the heating rate and the temperature at maximum mass loss rate (minimum heating rate) are two essential parameters for calculation of kinetics. Salin and Seferis [17] proposed a simple method to determine the kinetic parameters from multiple dynamic heating rate experiments by using different resolution settings at one heating rate and sensitivity. Using this method, kinetics parameters can be obtained from Eq. (3)

$$\ln\left(\frac{\beta}{T^2}\right)=-\frac{E_\mathrm{a}}{R}\frac{1}{T}+\ln\left[\frac{AR}{E_\mathrm{a}}n(1-\alpha)^{\mathrm{n-1}}\right] \tag{3}$$

where, 'β' is the heating rate in °C min^{-1}.

Activation energy can be obtained from the slope of the straight line by plotting ln (β/T^2) *vs.* 1/T. The intercept gives the information about pre-exponential factor 'A' assuming that 'n' is known. If the degradation is a first order reaction, n=1 and 'A' becomes independent of conversion, at the maximum degradation rate. Figure 14a shows plot of ln(β/T^2) as a function of 1/**T** for decomposition of P_{1c} at different degree of conversions.

Hi-Res TGA of the EPDM blends were performed at 10°C min^{-1} using resolution settings of 2, 3, 4 and 6. Table 3 shows the heating rate and temperature of degradation of the oil as the first step and the blend as the second step at maximum conversion of 90%. This table clearly shows that increasing the resolution leads to a decrease in the minimum heating rate at the degradation maximum, and a shift of the peak degradation temperature to a lower value. In general, the peak temperature and heating rates are strongly affected by resolution whereas initial heating rate has less

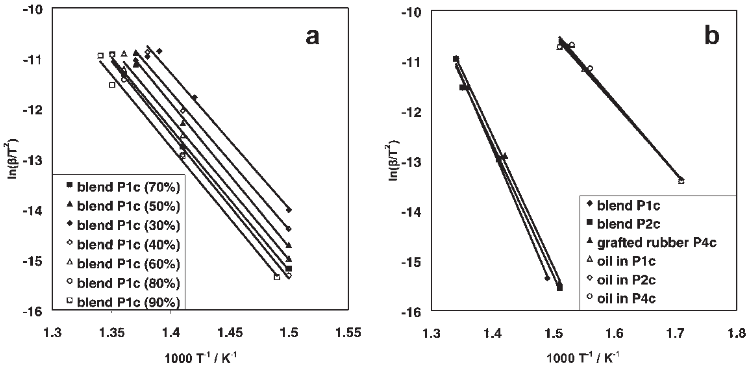

Fig. 14 Plot of ln(β/T^2) as a function of 1/T for decomposition of P_{1c} at different degree of conversions (a). Plot of ln(β/T^2) as a function of 1/T for two stages of P_{1c} decomposition (b)

of an effect. At any particular resolution, only one T_{max} value is observed for the blend components. As the T_{max} of the parent EPDMs do not differ significantly, the thermal stability of the blends is not affected drastically. Previous studies on degradation of blends of EPDM with silicone, by conventional TGA [24] showed the effect of degradation of the individual components on the thermal stability of the blends. However, in the present case, the two components are decomposing simultaneously, although their composition and chemical structure is different. The activation energy and pre-exponential factor '*A*' of the control sample S_{1c}, M_{4c} and their blends are presented in Table 3. Generally, the parameter E_a is a measure of the rate, and increases with temperature, while pre-exponential factor is seen to represent the rate at infinite temperature. From the table, an increasing trend of activation energy of decomposition of elastomer blend (M series) is observed compared to that of control sample. This is attributed to higher ethylene content (75%) of grafted rubber. The increasing level of grafted rubber in blends does not cause increase in activation energy of decomposition. Previous work on the non-isothermal TGA [25] of the polymer blends demonstrated that the degradation curve is not a simple overlay of the two pure polymers degradation process. This is because often the blends of two polymers are heterogeneous systems comprised of a continuous matrix of one polymer and the dispersed phase of the other. The size of the dispersed phase (domain) and the interaction at the interphase play the essential role in determining the long-term performance of the blend. When the activation energy of the blend is higher than the weighted-average activation energy of the respective pure polymers, the blend material has a higher thermal stability than the pure polymers. In the present system, none of the blends activation energy is lower than the pure EPDM rubber confirming that maleated EPDM does not accelerate the decomposition process of pure EPDM. There is no significant change in the activation energy of decomposition of the oil, as the same oil was used for all formulations. However, the M_{4c} shows the lowest activation energy of decomposition for the oil. In order to observe the effect of different methods on the kinetic parameters, conventional TGA of sample S_{1c} was also carried out at constant heating rates of 5, 10, 15 and 20°C min^{-1}. The activation energy of degradation of control sample S_{1c} at 90% conversion, calculated using the equation proposed by Flynn and Wall, is found to be 228.5 kJ mol^{-1}. This is in good agreement with the literature value of 232.8 kJ mol^{-1} (calculated from Kissinger method) [26] and value obtained from dynamic heating rate experiment (216.30 kJ mol^{-1}), indicating the similar overall decomposition in these cases.

The effect of blend ratio on the activation energy is shown in Fig. 14b, which reveals the plot of $\ln(\beta/T^2)$ *vs.* $1/T$ for P series. The activation energy is the highest for P_{1c} while P_{2c} and P_{4c} show similar value. The overlapping lines of oils obtained by plotting $\ln(\beta/T^2)$ *vs.* $1/T$ are due to the fact that the activation energy of decomposition of oils vary marginally in corresponding formulations. The effect of different maleated rubber on the thermal stability of the blends is shown in Fig. 15a. The blends show higher activation energy than the control sample. The value of activation energy of P_{1c} (234.30 kJ mol^{-1}) is comparable with M_{1c} (231.60 kJ mol^{-1}). Figure 15b presents the effect of grafting onto the activation energy of decomposition of 'P'

Table 3 Decomposition blends in nitrogen at fixed initial heating rate (10°C min^{-1}) using Eq. (3)

Operating parameters		First step Decomposition of oil				Second step* Decomposition of rubbers			
Compound	Resolution	Heating rate/ °C min^{-1}	T/ °C	E_a/ kJ mol^{-1}	Log$A$/ 1 min^{-1}	Heating rate/ °C min^{-1}	T/ °C	E_a/ kJ mol^{-1}	Log$A$/ 1 min^{-1}
S_{1c}	2	9.80	377.60			9.70	474.90		
	3	9.60	387.50	115.80	5.70	5.20	476.00	216.30	11.60
	4	6.20	372.10			1.30	440.80		
	6	0.50	310.00			0.09	395.40		
M_{1c}	2	9.80	383.20			9.70	473.30		
	3	9.60	393.70	113.10	5.40	5.10	462.80	231.60	12.90
	4	5.70	371.70			1.20	438.70		
	6	0.50	312.10			0.08	392.30		
M_{2c}	2	9.80	384.00			9.70	474.40		
	3	9.50	386.60	114.60	5.50	5.20	465.50	226.80	12.50
	4	5.60	375.90			1.00	437.70		
	6	0.50	310.00			0.09	393.70		
M_{4c}	2	9.80	387.50			9.70	476.00		
	3	9.60	398.60	103.20	4.50	4.70	465.00	231.70	12.80
	4	6.00	375.90			1.00	436.70		
	6	0.50	310.00			0.08	395.40		

Table 3 Continued

Operating parameters		First step Decomposition of oil				Second step* Decomposition of rubbers			
Compound	Resolution	Heating rate/ °C min^{-1}	T/ °C	E_a/ kJ mol^{-1}	Log$A$/ 1 min^{-1}	Heating rate/ °C min^{-1}	T/ °C	E_a/ kJ mol^{-1}	Log$A$/ 1 min^{-1}
P_{1c}	2	9.80	318.40			9.70	458.00		
	3	9.60	325.00	118.90	5.90	5.30	458.50	234.30	13.00
	4	5.80	315.20			1.20	434.20		
	6	0.50	256.90			0.09	392.80		
P_{2c}	2	9.80	386.20			9.70	473.80		
	3	9.60	388.80	113.80	5.50	5.30	465.50	218.00	11.90
	4	5.90	371.70			1.10	434.20		
	6	0.50	311.80			0.08	388.80		
P_{4c}	2	9.80	381.90			9.70	474.40		
	3	9.60	387.50	122.40	6.20	5.30	463.40	218.70	11.90
	4	5.90	368.80			1.20	432.20		
	6	0.50	313.50			0.08	390.60		

*Two rubbers decomposing simultaneously

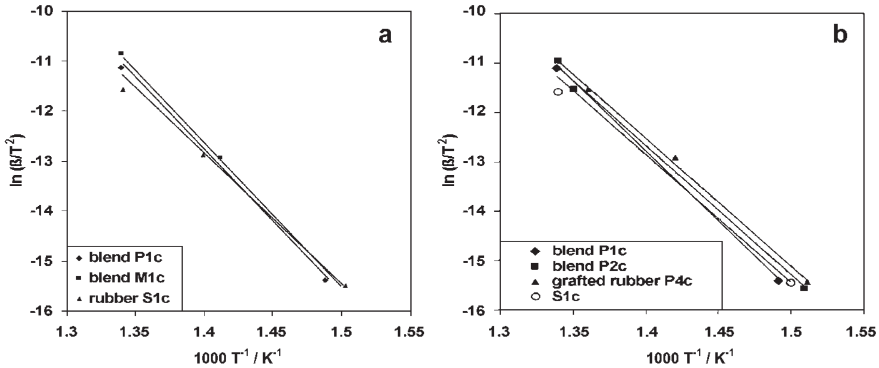

Fig. 15 Effect of different maleated EPDM onto the activation energy of decomposition of blends (a). Effect of level of grafting on the activation energy of decomposition of blends of P series (b)

compositions. The activation energy of the P_{1c} is the highest indicating the highest stability. In general, blends of 25% of grafted rubber show improved thermal stability over the control sample. However, further increase in proportion of grafted EPDM rubber in the blends does not affect the thermal stability of the parent EPDM rubber.

Conclusions

Although ethylene content controls the onset and peak degradation temperatures, and hence the thermal stability of the polymer, both MTGA and conventional TGA show that within the systems studied, the activation energy of degradation do not depend very much on the ethylene content of EPDM. MTGA has shown EPDM degradation complex, with a general increase in activation energy for degradation throughout the degradation. Isothermal TGA has confirmed the random degradation model for EPDM, though it is probable that different mechanisms are operating simultaneously. Values from both dynamic and constant heating rate experiments for pure EPDM (S_{1c}) are in good agreement with each other and with the literature value. Maleated EPDM in the blend does not affect the decomposition process of the pure EPDM. The dynamic heating rate experiment for the blends shows that if the difference in peak temperature of the components in a system is less than 5°C, Hi-Res TGA can not resolve them.

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