

Influence of ethylene–propylene ratio on the thermal degradation behaviour of EPDM elastomers

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Abstract

The effect of ethylene/propylene content on the thermal degradation behaviour of ethylene–propylene–diene (EPDM) elastomers was investigated using conventional non-isothermal and isothermal thermogravimetric analysis (TGA) as well as modulated thermogravimetric analysis (MTGA[®]). Kinetic parameters of degradation were evaluated using single heating rate data under a pseudo-first order assumption; the Flynn–Wall–Ozawa isoconversional method; isothermal methods; and MTGA[®]. Although the ethylene/propylene ratio influences the onset and peak temperatures of degradation, it appears that not only the ethylene content but microstructure is also a controlling factor in determining the activation energy of degradation. Pseudo-first order analyses show that at least two different first-order degradation reaction mechanisms dominate the degradation process. MTGA[®] analyses show that the activation energy of degradation increases throughout the reaction. Isothermal TGA confirms that the degradation processes for PE, PP and EPDM are complicated and do not follow an *n*th order reaction path, rather they follow a random degradation process. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

EPDM polymers are the fastest growing general-purpose elastomers on the market today. They 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. This is inherent to both its hydrocarbon nature and its almost saturated backbone.

The EPDM elastomers may vary in ethylene and propylene ratio, as well as in the amount and type of diene used [1]. Structural effects such as microstructural and composition variation could greatly affect the degradation characteristics of the EPDM and their composites [2,3]. The quantitative ratio of the monomers confers particular properties on the final elastomer [4]. For example, usage of high ethylene content will produce polymers with high green strength, whereas low and medium values will produce softer and more elastic polymers. However, there remains no systematic study of the effects of composition and microstructure on the long-term performance and

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degradation behaviour of the EPDM and its composites.

The present investigation focuses on the effects of ethylene content on the degradation behaviour of EPDM using conventional and temperature modulated thermogravimetric analysis (MTGA[®]). MTGA[®] is based on a method first described by Flynn in 1968 [5], and has recently been implemented [6,7] and patented by TA Instruments. Like TGA, it is used to investigate the decomposition behaviour of materials. However, it has also the unique capabilities of providing continuous calculation of kinetic parameters in real-time from a single run without resorting to reaction modelling. There are very few reports on the use of MTGA[®] for studying complex polymeric systems [8].

2. Experimental

The EPDM samples (ASTM standard materials with ethylene contents ranging from 40.1 to 77.9%) were received from Exxon Chemical, USA. Pure polyethylene (ultra-high molecular weight) and polypropylene (melt index 4) were purchased from Aldrich. Samples were used as received, and are designated PE_x (Table 1), where *x* is the ethylene content of the sample.

All TGA analyses were conducted using a TA Instrument's Modulated TGA 2950 thermal analyser, using conventional (constant heating-rate), and modulated modes operating from room temperature to 500°C. The thermal analyser was temperature calibrated between experimental methods using the Curie point of nickel as a reference. All experiments were carried out under a nitrogen atmosphere at a purge rate of 50 ml min⁻¹.

In conventional TGA, ~7.5 mg samples were temperature-equilibrated to 300°C before being heated to 500°C at different heating rates (2, 5 and 8°C min⁻¹). The onset and peak degradation temperatures were determined from the thermogram obtained using a heating rate of 2°C min⁻¹. In MTGA[®], ~7.5 mg samples were temperature-equilibrated to 300°C before being heated to 500°C at a heating rate of 2°C min⁻¹, with temperature modulation amplitude of ±5°C with a period of 200 s. Isothermal TGA of the EPDM samples were performed on ~7.5 mg samples. The samples were heated from ambient temperature to the isothermal temperature (410, 420, 430 or 440°C) at a heating rate of 20°C min⁻¹ before being held in isothermal mode until less than 1% of the polymer sample remained.

3. Results and discussion

3.1. Theory

The kinetics of thermal transformation of a solid state chemical reaction is generally described for a single step reaction by [9]:

$$r = \frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where $f(\alpha)$ is the reaction model, α the extent of reaction, $k(T)$ the temperature dependent rate constant, T the temperature, t the time and r the rate of degradation. $k(T)$ is normally assumed to obey the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

Table 1
Kinetic parameters for the degradation of EPDM calculated using the pseudo-first order method at 2°C min⁻¹

Sample	Ethylene content (%)	Region I		Region II	
		ln A (min ⁻¹)	E (kJ mol ⁻¹)	ln A (min ⁻¹)	E (kJ mol ⁻¹)
PE ₀	0	14.1	105	61.4	367
PE ₄₀	40	21.4	144	55.5	334
PE ₅₂	52	28.2	183	57.0	346
PE ₅₉	59	26.4	173	57.6	345
PE ₇₁	71	30.3	197	55.4	338
PE ₇₈	78	30.9	203	59.6	364
PE ₁₀₀	100	20.0	143	63.2	389

where E is the activation energy of the kinetic process, A the pre-exponential factor and R the universal gas constant.

The conversion dependent function, $f(\alpha)$, is generally complicated and valid only for a limited range of experimental conditions. If it is assumed that the degradation reaction is a simple n th order reaction, the conversion dependant term can be expressed as

$$f(\alpha) = (1 - \alpha)^n = (W)^n \quad (3)$$

where W is the weight fraction remaining, and n the order of reaction.

Most published methods for deriving kinetic parameters from TGA are based upon these three equations. These methods involve analysis of either a single heating rate thermogram, multiple thermograms with different heating rates, isothermal thermograms, or thermograms obtained via dynamic or modulated heating rates.

3.2. Onset and peak degradation temperatures

Conventional non-isothermal TGA weight loss curves of the samples performed at a constant heating rate of 2°C min^{-1} are shown in Fig. 1. Thermograms of the samples show only one step with no oil and little or no residue or filler, indicating that the overall decomposition takes place in a single step. From the first derivative (DTG) curves of these degradations, shown in Fig. 2, the peak temperatures of

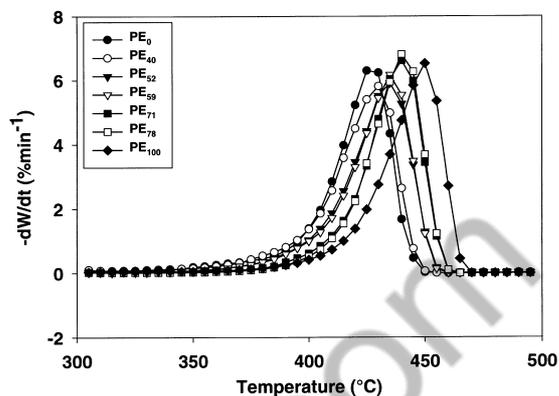


Fig. 2. Differential thermograms of different EPDM samples, heating rate 2°C min^{-1} .

degradation can be determined. It is clearly observed from the curves that the TGA and DTGA curves progressively shift towards the higher temperature with increase in ethylene content in the samples. The onset temperatures of degradation can be calculated from the TGA curves by extrapolating from the curve at the peak of degradation back to the initial weight of the polymer. Fig. 3 clearly shows that the onset and peak degradation temperatures are both increased in a linear fashion as the ethylene content increases above 40%. However, there is no significant difference in the onset and peak degradation temperatures of PE_0 and PE_{40} .

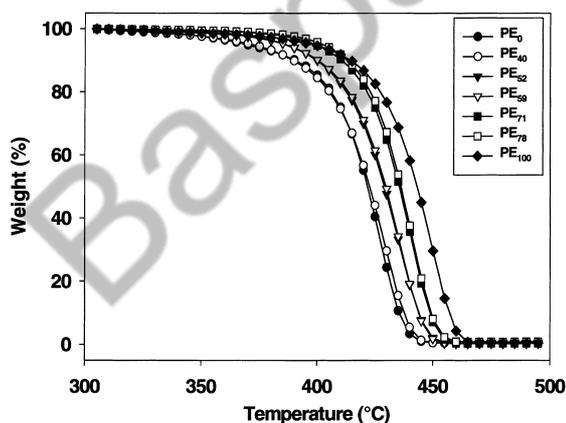


Fig. 1. Thermograms of the degradation of different EPDM samples, heating rate 2°C min^{-1} .

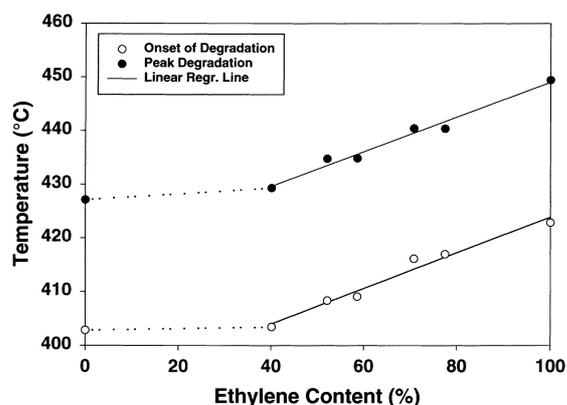


Fig. 3. Effect of PE content on the onset and peak degradation temperatures of EPDMs, heating rate 2°C min^{-1} .

3.3. Pseudo-first order analysis

For a first order reaction, Eqs. (1)–(3) may be reorganised as follows:

$$\ln\left(\frac{r}{W}\right) = E\left(-\frac{1}{RT}\right) + \ln A \quad (4)$$

Therefore, for a first order degradation process, a plot of $\ln(r/W)$ versus $-1/RT$ will be a straight line with slope equal to the activation energy [10]. Fig. 4 shows a typical plot of $\ln(r/W)$ plotted against $-1000/RT$ for a heating rate of 2°C min^{-1} for sample PE_{52} . These plots have a curvilinear trend, and it is observed that at least two straight lines are necessary to fit the data points for each heating rate. These regression lines, shown as solid lines in Fig. 4, can be considered as two pseudo-first order regions and are designated as region I and region II, respectively, with a transition zone between them. This observation indicates that at least two distinctly different types of reactions have dominated the degradation process. Similar results were obtained for all samples at heating rates of 2, 5 and 8°C min^{-1} , including pure polypropylene and polyethylene. Region I extends from zero to around 15% decomposition. A summary of the kinetic parameters obtained using the pseudo-first order method, shown in Table 1, indicate that region I has lower activation energies and frequency factors than region II. In region I the copolymer EPDMs have higher activation energies than pure PE and PP and the activation energy increase with increase in the PE content. In region II the activation energy values for the different systems are comparable (within 30 kJ mol^{-1}).

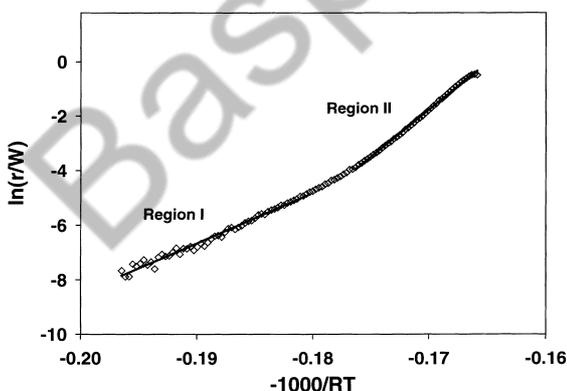


Fig. 4. Pseudo-first order plot for PE_{52} at 2°C min^{-1} .

3.4. Flynn–wall–ozawa isoconversional method

Where the temperature increases with time at a constant heating rate, $\beta = dT/dt$, Eqs. (1) and (2) may be represented as follows:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (5)$$

Writing Eq. (5) in the integral form, we obtain:

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (6)$$

By using Doyle's approximation to the Arrhenius integral in Eq. (5), Flynn and co-workers [11–13] derived a method for the determination of activation energy based on the equation

$$\log \beta \cong -0.457 \frac{E}{RT} + \left(\log \frac{AE}{R} - \log F(\alpha) - 2.315 \right) \quad (7)$$

If the mechanism of the degradation process does not depend on the heating rate, then $F(\alpha)$ is constant for constant α . The activation energy is then obtained from the slope of the plot of $\log \beta$ against T^{-1} for any level of conversion, independent of the $f(\alpha)$ model.

Conventional non-isothermal TGA of the sample was performed at constant heating rates of 2, 5 and 8°C min^{-1} . The thermogravimetric (TG) and derivative (DTG) curves for the pyrolysis of a typical sample (PE_{52}) at different heating rates are shown in Figs. 5 and 6, respectively. TG plot has been plotted against

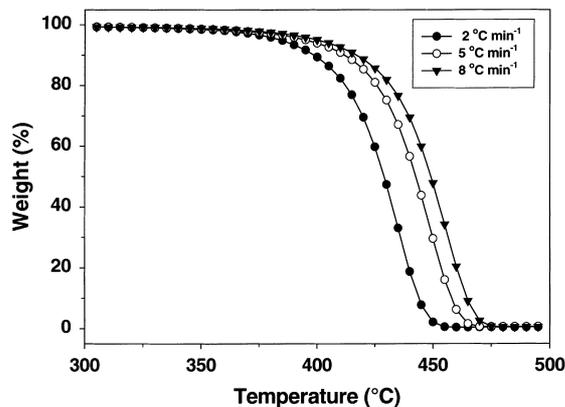


Fig. 5. Effect of heating rate on thermogram of PE_{52} , heating rates 2, 5 and 8°C min^{-1} .

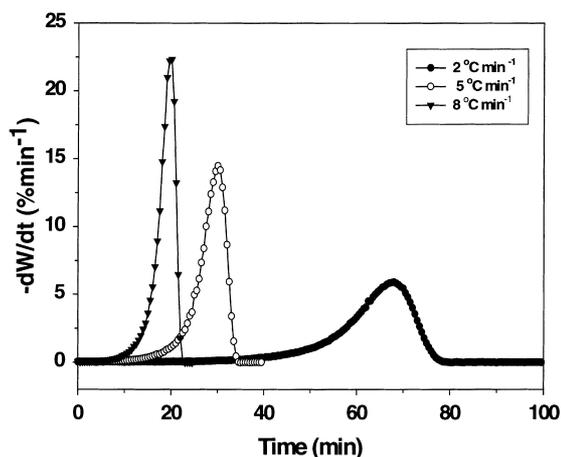


Fig. 6. Effect of heating rate on DTG of PE₅₂, heating rates 2, 5 and 8 °C min⁻¹.

temperature and DTG curve is plotted against time. It is clearly observed from the Fig. 5 that the TG thermograms shift to higher temperature as the heating rate increases. This shift in the onset of degradation to higher temperature is expected and is due to the shorter time required for a sample to reach a given temperature at the faster heating rates. This heating rate dependence is also evident in the DTG thermograms (Fig. 6).

A typical $\log \beta$ versus $-1000/RT$ plot from 5 to 90% conversion for the degradation of PE₅₂ is shown in Fig. 7. The activation energies of degradation calculated from these plots are shown in Fig. 8. It is evident

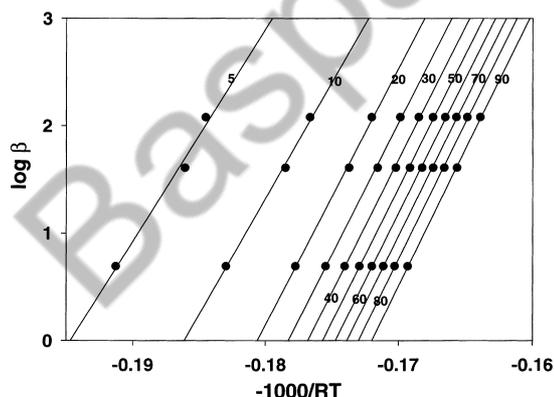


Fig. 7. Application of the Flynn–Wall–Ozawa method for PE₅₂ at 2, 5 and 8 °C min⁻¹ and conversions of (from left-hand side) 5, 10, 20, 30, 40, 50, 60, 70, 80, and 90%.

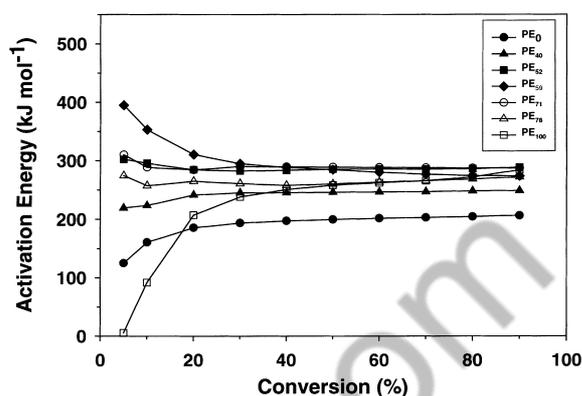


Fig. 8. Activation energies calculated as a function of conversion for EPDM using the Flynn–Wall–Ozawa method.

that the calculated activation energies of degradation for these samples remain relatively constant after 25% conversion. However, it appears that 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 differences in the random chain scission mechanism in different cases, or the degradation may depend on the microstructural features of the polymer rather than simply the composition.

3.5. Temperature modulated thermogravimetric analysis

In modulated TGA, the furnace, the thermocouple and the sample mass measurement system is used as in normal TGA, but a temperature oscillation (modulation) is overlaid on the conventional linear heating ramp. The actual variations in heating rate depend on three parameters: the underlying heating rate; the amplitude of modulation and the period of modulation. The modulated temperature program results in an oscillatory response in the rate of weight loss (Fig. 9), from which the activation energy of degradation can be calculated.

If Eq. (1) is evaluated at the peaks and valleys of the sinusoidal waveforms, we can write:

$$\frac{d\alpha_p/dt}{d\alpha_v/dt} = \frac{f(\alpha_p) \exp(-E/RT_p)}{f(\alpha_v) \exp(-E/RT_v)} \quad (8)$$

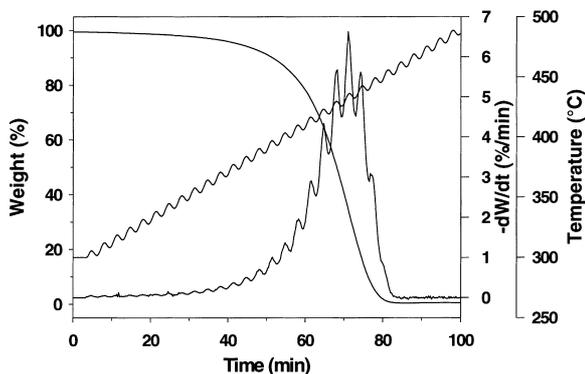


Fig. 9. Modulated temperature program, showing the weight loss and the rate of degradation for PE₅₂.

Under constant conversion conditions, $f(\alpha_p) = f(\alpha_v)$, and to calculate the activation energy, we can write [14],

$$E = \frac{R(T^2 - M^2)L}{2M} \quad (9)$$

where T is the average absolute temperature, M the amplitude, and L the amplitude of the $\ln(dx/dt)$ signal obtained by discrete Fourier transformation.

Modulated TGA was performed on the samples with a heating rate 2°C min^{-1} , with a modulation amplitude of $\pm 5^\circ\text{C min}^{-1}$ and period of 200 s. Both the onset and peak of degradation temperatures are increased in the samples with higher ethylene content, consistent with the results obtained by conventional TGA.

The activation energies of degradation for these samples throughout the entire weight loss are shown in Fig. 10. No clear trend between the activation energy of degradation and the ethylene content of these samples is observed. However, there is a general trend 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 using the Flynn–Wall–Ozawa method. The

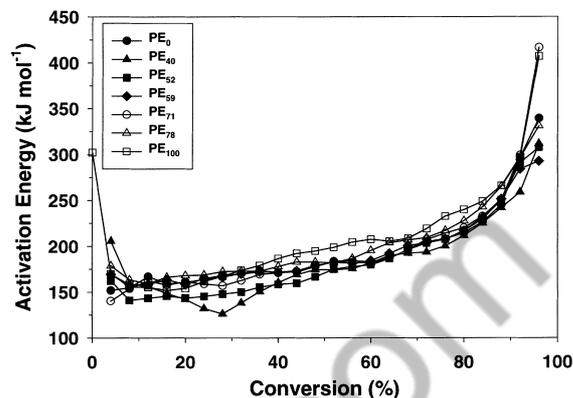


Fig. 10. Activation energies calculated as a function of conversion for EPDM using MTGA[®].

period of oscillation in MTGA[®] may have an effect on the calculated activation energy, particularly if the period is too short for the transients from thermal and material diffusion to die out. Currently, MTGA[®] experiments with the samples at different periods are under way to address this issue.

3.6. Isothermal analysis

Isothermal TGA was performed to confirm the mechanism of degradation of the EPDM samples. The isothermal temperatures of 410, 420, 430 and 440°C were chosen, as degradation began before these temperatures, but the weight lost at these temperatures in constant heating rate TGA was not excessive.

Figs. 11 and 12 show the weight loss and rate of degradation for the samples at 430°C . As expected, a small amount of sample is degraded in 20 min while heating to the isothermal temperature. Fig. 11 also clearly reveals that in the isothermal experiments also the degradation curve shifts systematically to the right side with increase in ethylene content in the polymer as observed for non-isothermal experiments. The DTG curve (Fig. 12) shows that with progressive increase in ethylene content not only does the entire degradation process occur over a longer period of time, but also the maximum rate of degradation decreases. This observation confirms the view that increasing the ethylene content increases the thermal stability of EPDM. Fig. 12 also illustrates that the peaks of degradation occur not at zero time, between 10 and 20 min after the isothermal temperature is reached,

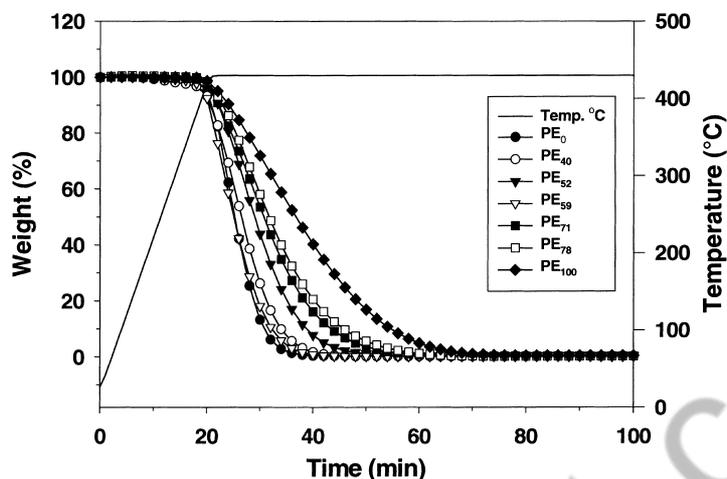


Fig. 11. Isothermal weight loss curves for EPDM at 430°C.

indicating that the polymers are not degrading via a simple n th order degradation, but via random degradation [15]. Straus and Wall [15] have previously noted the same trend in isothermal experiments of polyethylene, polypropylene and ethylene-propylene co-polymers. By substituting Eq. (3) into the natural logarithm of Eq. (1), we obtain

$$\ln\left(-\frac{dW}{dt}\right) = n \ln W + \ln k \quad (10)$$

Therefore, for an n th order degradation, a plot of $\ln(-dW/dt)$ against $\ln W$ should result in a straight

line with a slope equal to n , and an intercept on the $\ln(-dW/dt)$ axis of $\ln k$ [16]. A further plot of $\ln k$ against $1/T$ provides the activation energy from the slope, and $\ln A$ from the intercept on the $\ln k$ axis.

The plots of $\ln(-dW/dt)$ against $\ln W$ for isothermal degradations (Fig. 13) are not straight, confirming that EPDM does not undergo degradation via an n th order mechanism. There is, however, a region in each of these plots that can be fitted by a straight line and analysed using this method. These regions correspond to the region after the peak of degradation that undergoes an n th order-like exponential decay (Fig. 12). A

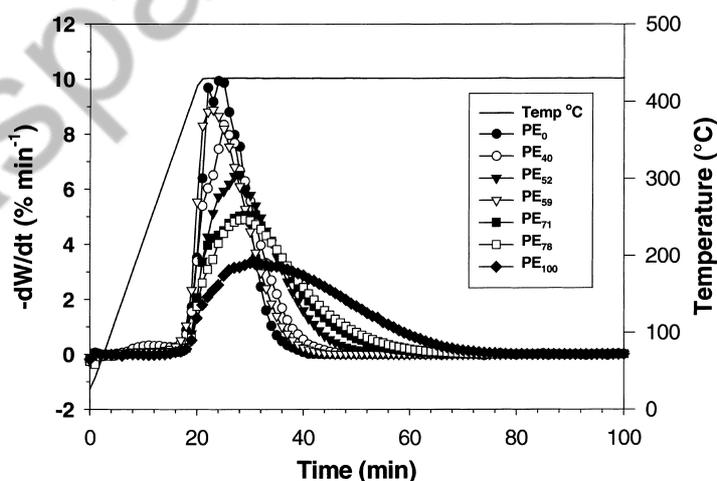


Fig. 12. Isothermal degradation rate curves for EPDM at 430°C.

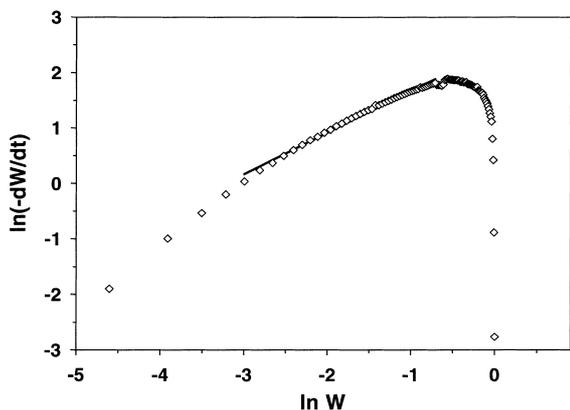


Fig. 13. Double log plot of degradation rate against fractional weight loss for PE₅₂ at 430°C.

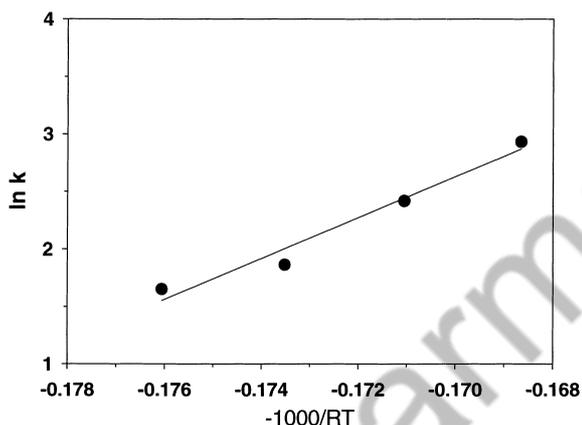


Fig. 14. Plot of $\ln k$ versus $1/RT$ plot for PE₅₂ at 410, 420, 430, and 440°C.

Table 2

Kinetic parameters for the degradation of EPDM calculated using the isothermal method

Sample	Ethylene content (%)	$\ln A$ (min^{-1})	E (kJ mol^{-1})	n
PE ₀	0	32.24	172.13	0.71 ± 0.03
PE ₄₀	40	35.74	193.74	0.74 ± 0.06
PE ₅₂	52	32.86	177.79	0.75 ± 0.10
PE ₅₉	59	33.29	180.36	0.68 ± 0.03
PE ₇₁	71	30.00	162.15	0.79 ± 0.06
PE ₇₈	78	32.95	180.32	0.77 ± 0.05
PE ₁₀₀	100	40.55	226.06	0.70 ± 0.07

plot of the $\ln k$ values, calculated from these lines, against $-1000/RT$ shows a good straight line fit (Fig. 14). The kinetic parameters calculated using this method for these regions are shown in Table 2. The order of reaction for these regions lay between 0.65 and 0.85, and there appears to be no relationship between the ethylene content and the calculated frequency factors or activation energies of degradation.

4. Conclusions

This study has shown that the degradation of EPDM in a nitrogen atmosphere is a complex, non- n th order reaction, where at least two reactions dominate, and the activation energy of degradation increases throughout the reaction. Increasing the ethylene content of EPDM increases the onset and peak temperatures in constant heating rate TGA, and decreases the maximum rate of degradation in isothermal TGA, indicating an increase in thermal stability. However, the activation energy of degradation does not seem to be controlled by the ethylene content alone, and it seems that the microstructure may be playing an important role in determining the activation energy. The activation energy of degradation calculated from MTGA is much lower than that using TGA.

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