

Degradation Kinetics of Vulcanized Ethylene–Propylene–Diene Terpolymer Residues

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ABSTRACT: In this study, ethylene–propylene–diene terpolymer residues (EPDM-r) from the automotive industry were analyzed by thermogravimetric analysis (TGA) for determination of the activation energy (E_a) of decomposition by the Flynn–Wall–Ozawa (FWO) method. The degradation mechanism was determined by the method of Criado et al. Analysis of the nonvulcanized EPDM gum (EPDM-g) and paraffinic oil used in the composition of the compound was also carried out. The E_a values for the decomposition of the EPDM-g and paraffinic oil remained constant with the conversion, but for the EPDM-r decom-

position, they changed due to the initial oil elimination followed by decomposition of the EPDM fraction. It was observed that removal of the paraffinic oil occurred less easily in the tridimensional vulcanized network, and there were differences in the elimination mechanism. The EPDM degradation mechanism was also affected by vulcanization and the fillers present in the compound. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1053–1057, 2011

Key words: EPDM; thermogravimetry; kinetics; FWO; Criado

INTRODUCTION

The characterization of synthetic elastomer residues is important in terms of their viable reclamation, because it permits proper disposal and/or specific treatments leading to a suitable and efficient recycling process. According to the International Rubber Study Group,¹ the production of synthetic elastomers in 2007–2008 was around 22 million tons. However, vulcanized elastomers contain a tridimensional network that hinders the reutilization of the postconsumed material.² Moreover, it is well known that this material has a great amount of impurities and additives in its composition.³ Some components like extender oils, carbon black (CB), zinc oxide, and calcium carbonate are commonly used in the formulation of rubber compounds.^{3–5} Pistor et al.,⁶ studying the influence of composition on the ethylene–propylene–diene terpolymer residues (EPDM-r) devulcanization process using microwaves, observed significant differences in the thermal stability of the components present in EPDM-r (oil, EPDM, CB, and inorganic fillers). Also, the authors observed that paraffinic oil interferes with the devulcanization process, reducing its efficiency.

Gamlin et al.⁷ studied the effects of the ethylene–propylene content on EPDM decomposition using the Flynn–Wall–Ozawa (FWO) method.^{8–10} The authors noted two distinct reactions during the degradation process. In the first stage (0–15% of weight loss), there was an increase in the activation energy (E_a) values with increasing ethylene content, and after 25% of weight loss, (second stage) the values remained constant. The authors did not observe a clear trend in the E_a values with an increase in ethylene content. This was attributed at a random decomposition mechanism, which may vary according to the microstructural characteristics of the polymer.

In addition to determining E_a of decomposition by thermogravimetric analysis (TGA), many methods that can be used to understand the degradation behavior of polymers. Albano and de Freitas¹¹ studied the thermal decomposition of degraded and nondegraded polypropylene and high-density polyethylene (HDPE) blends using the method proposed by Criado et al.¹² The authors observed that activation energies, as well reaction order, are not related to the HDPE content. Also, even if the global mechanism is not consistent with the real mechanisms, it is useful in terms of quantifying the overall reaction rate and gaining information on the polymer structure and the performance of the final product.

With the aim of complementing information on the decomposition kinetics of EPDM obtained in an

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TABLE I
Formulation of EPDM-r Residues

Contents	phr
EPDM	100.0
Zinc oxide	6.0
Stearic acid	1.8
Processing aid	2.0
Calcium carbonate	53.0
Calcium oxide	19.0
Sulfur	1.9
Accelerators	5.0
Carbon black	157.0
Paraffinic oil	147.0

earlier study,⁶ this article presents the E_a values and decomposition mechanisms determined using the FWO^{8–10} and Criado et al.^{12,13} methods.

EXPERIMENTAL

Materials

The materials used in this study were vulcanized EPDM rubber residues (EPDM-r), nonvulcanized EPDM gum (EPDM-g) from DSM South America and paraffinic oil used in the rubber formulation. The residue was kindly provided by the Brazilian rubber company CIAFLEX and where derived from automotive profiles. The basic formulation of the vulcanized elastomer used in the production of the profiles is shown in Table I. According to the company are manufactured around 1000 tons/year of these profiles, and are generated approximately 60 tons of scraps annually.

Thermogravimetric analysis

Thermogravimetric analysis (TGA50 – Shimadzu) was carried out under nitrogen atmosphere (50 mL min⁻¹), in the temperature range of 25–750°C, and in synthetic air from 750 to 910°C. The analysis was performed with approximately 20 mg of sample for each run and at four different heating rates (5, 10, 20, and 40°C min⁻¹). The results obtained were used for the determination of the degradation kinetics parameters.

Theoretical considerations

The values for the average activation energy (E_a) of degradation were estimated by the isoconversional FWO method according to eq. (1).^{7–10}

$$\log(\phi) = \log\left(\frac{AE_a}{R}\right) - \log(g(\alpha(T))) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (1)$$

where Φ is the heating rate, A is the frequency factor, $\alpha(T)$ is the conversion (which is dependent on the absolute temperature T), E_a is the activation energy, and R is the universal gas constant.

The FWO method is based on Doyle's integral approximations^{13,14} and presumes that the conversion is only a function of temperature. Thus, by carrying out the analysis at different heating rates, it is possible to obtain the E_a values from the slope of the plot of $\log \Phi$ versus $1/T$.⁷

The decomposition mechanism can be determinate applying the Criado et al. method^{12,13,15} according to eq. (2).

$$Z(\alpha) = \frac{d\alpha}{dT} \frac{E_a}{R} \exp\left(E_a/RT\right) Q(x) \quad (2)$$

where $Q(x)$ is a function initially proposed by Peterson¹³ and later Senun and Young¹⁶ proposed a rotational expression for $Q(x)$. The Criado method is used to determine the degradation mechanism in the solid state using theoretical master curves that represent the functions $[f(\alpha)]$ and $[g(\alpha)]$ found in the literature.^{12,13,17} Equation (3) is used to obtain these master curves.

$$Z(\alpha) = f(\alpha)g(\alpha) \quad (3)$$

The attainment of the theoretical curves [eq. (3)] and the superposition of the experimental data [eq. (2)] allow the nature of the mechanism involved in the degradation of the material studied to be identified.^{13,15}

RESULTS AND DISCUSSION

Figure 1 shows the thermograms (A) and its derivatives (DTGA) (B) for the vulcanized EPDM-r

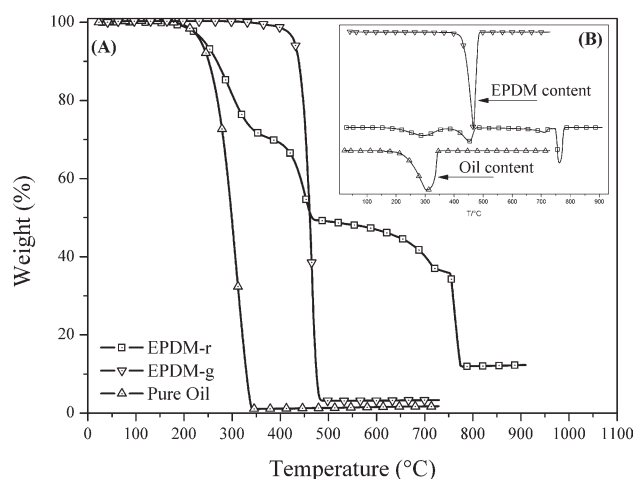


Figure 1 (A) Thermogravimetric curves for all samples studied (10°C min⁻¹) and (B) DTGA of the samples.

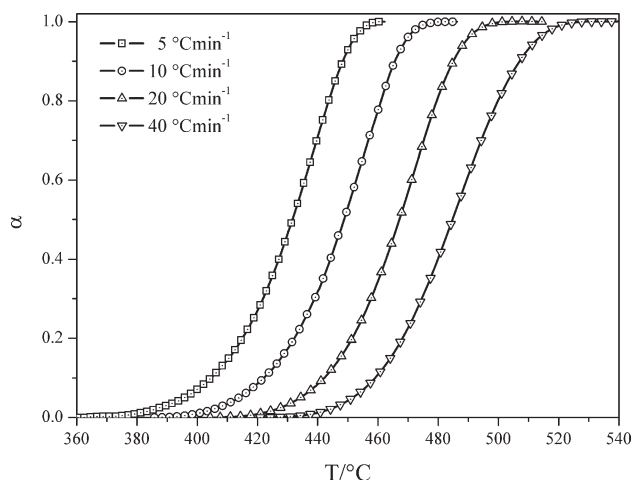


Figure 2 Conversion values as a function of temperature for the EPDM-g sample.

residues, nonvulcanized EPDM-g, and paraffinic oil. The thermogram and DTGA curves related to EPDM-r show four weight losses: paraffinic oil (200–350°C), EPDM decomposition (close to 450°C), inorganic additives (450–750°C), and CB elimination (750°C, with the change of the atmosphere from nitrogen to synthetic air).

The weight-loss temperature ranges of these components are consistent with values given in the literature.⁶ Also, it was observed that the degradation ranges associated with each component present in the EPDM-r are related to each individual material.

Having verified the presence of the characteristic components of the EPDM-r formulation, TGA analysis was performed at heating rates of 5, 10, 20, and 40°C min⁻¹ to determine the kinetics parameters. From nonisothermal thermogravimetric analysis, (α) can be obtained by the eq. (4),^{10,12,15,16,18}:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (4)$$

where m_0 is the initial mass, m is the mass monitored at a certain time t , and m_∞ is the final mass.

Figure 2 shows the conversion curves (α) obtained for the EPDM-g sample at different heating rates (Φ). All samples show a similar trend. It can be observed in Figure 2 that on increasing the heating rate, there was a shift in the weight loss curves to higher temperatures. This phenomenon is due to greater quantities of heat being provided in shorter time intervals, which increases the temperature difference in the sample, modifying the weight-loss behavior. From the data obtained, the isoconversional FWO method was applied.^{8,9} From applying eq. (1), the plot of $\log \Phi$ versus $1/T$ shown in Figure 3 was obtained for the EPDM-r sample, and the other samples showed similar behavior. From the

slope of the plots obtained for each conversion, the activation energies of decomposition were determined. The correlation coefficients (r) values were close to unity for all samples studied, with a confidence level of 95%.

Figure 4 shows the E_a results obtained from eq. (1) for the EPDM-g, oil and EPDM-r samples. The correlation coefficients (r), obtained from the linear fits, are included in Figure 4.

Figure 4 shows the E_a values for two distinct reactions for the EPDM-r sample, referring to the degradation and evaporation of the oil contained in the sample, with E_a values in the range of ≈ 70 – 100 kJ mol⁻¹ for $\alpha = 0.1$ – 0.4 and ≈ 170 – 210 kJ mol⁻¹ for the EPDM fraction decomposition. The increase in the E_a values with increasing conversion, in the lower α range (0.1–0.4), may be related to the restriction imposed by the tridimensional network of the elastomer in terms of the oil diffusion and elimination process. For the EPDM-r fraction, for $\alpha = 0.55$ and above, the E_a values are in agreement with those reported by Gamlin for EPDM samples containing over 52% of ethylene⁷ and also with the average value obtained by the Kissinger method.⁶ The E_a values for EPDM-g were similar to those for EPDM-r; however, for the EPDM-r, there was an increase in the E_a value with the conversion. According to Kurian et al.,¹⁹ the vulcanized EPDM structure comprises rigid domains and flexible regions. The rigid domains, related to polyethylene blocks and crosslinked dienes, probably inhibit the decomposition, increasing the E_a value. In addition, the presence of CB and inorganic fillers can reduce the diffusion rate of the decomposed compounds, also increasing the E_a value.

On comparing the E_a values obtained for the paraffinic oil and the oil present in EPDM-r, it was

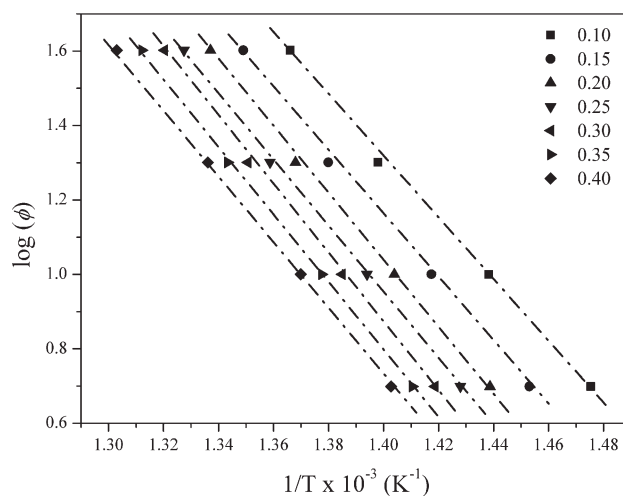


Figure 3 Superposition of the $\log \Phi$ versus $1/T$ values at different conversion (α) values for the oil fraction in the EPDM-r sample.

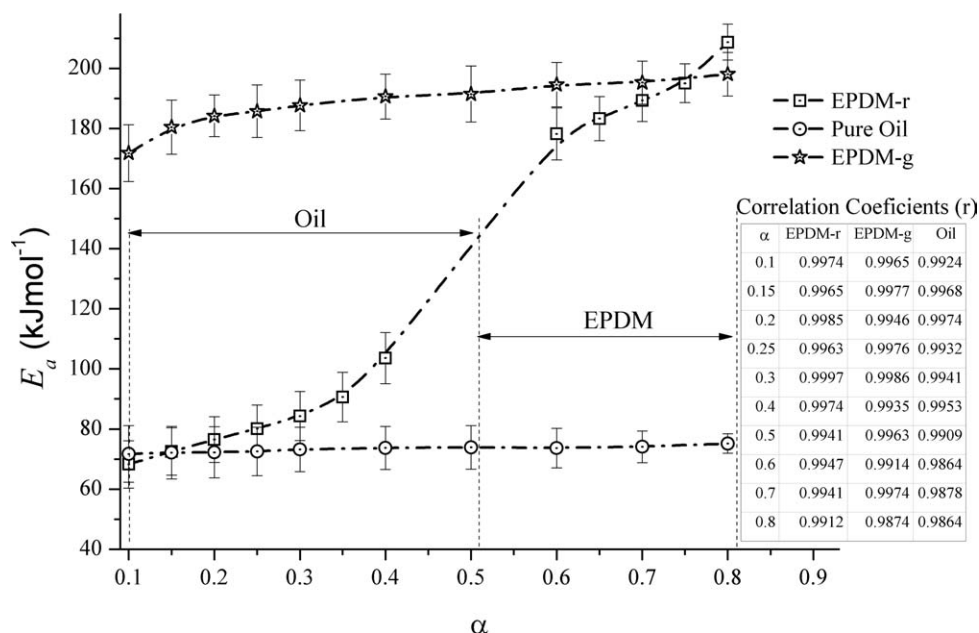


Figure 4 Activation energies as a function of conversion obtained by the FWO method.

observed that they show similar values up $\alpha = 0.2$; at higher conversions, the E_a values for the EPDM-r oil increase progressively, compared to the pure oil. This behavior may be due to reduced diffusion of the oil in the elastomer tridimensional network.

Figures 5 and 6 show the superposition of the theoretical master curves on those for the experimental data obtained from eqs. (2) and (3), respectively.

For oil decomposition up to $\alpha = 0.3$, the experimental data was superimposed on the curves D1, D2, and D3; these mechanisms being related to the diffusion process in one, two, and three dimensions, respectively.^{12,13,15} For α values higher than 0.3, the degradation mechanism was not in agreement with this behavior, which is consistent with the increase

in E_a values observed for the oil contained in the elastomer, showing that the oil diffusion process is restricted by the EPDM-r structure.

After the oil elimination, considering α values higher than 0.6, mainly related to EPDM decomposition, it was observed that the degradation mechanism was F3, which refers to a random nucleation with two cores of an individual particle.^{12,13,15} This trend shows that random nucleation may be related to the rupture of the tridimensional network and the formation of low molecular weight molecules during degradation.

Figure 6 shows the results obtained using the Criado method for EPDM-g and pure paraffinic oil. The EPDM-g degradation mechanism observed was

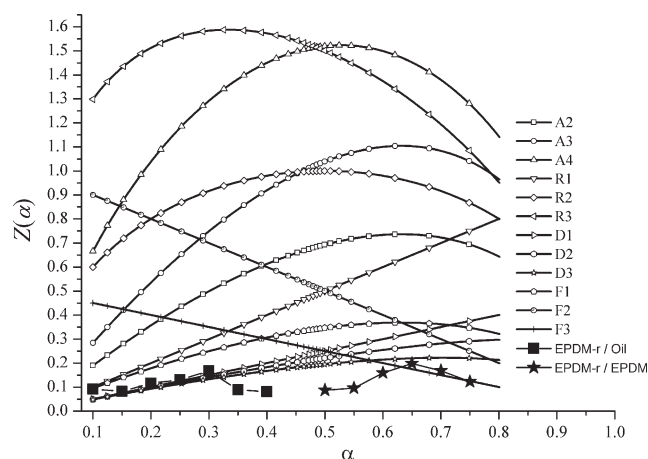


Figure 5 Theoretical and experimental curves obtained by the Criado et al. method for EPDM-r at a heating rate of $10^\circ\text{C min}^{-1}$.

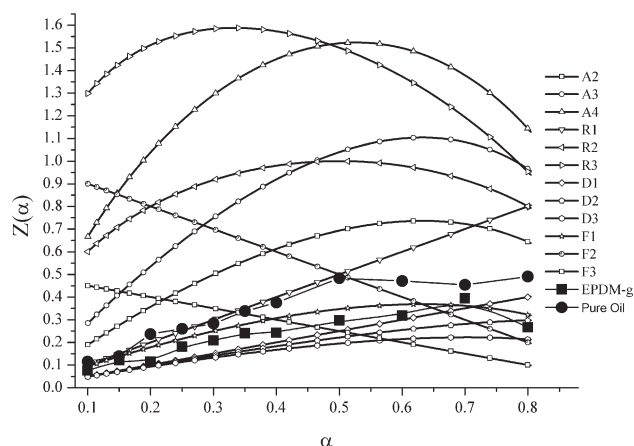


Figure 6 Theoretical and experimental curves obtained by the Criado et al. method for EPDM-g and pure paraffinic oil at a heating rate of $10^\circ\text{C min}^{-1}$.

F1, random nucleation with the core of an individual particle.^{12,13} This behavior differs from that observed for the EPDM fraction present in the EPDM-r compound. The F3 mechanism encountered for the vulcanized EPDM-r fraction can be attributed to the additives and fillers used in the elastomer formulation, because the presence of ionic aggregates,¹⁹ CB and a tridimensional network make the degradation mechanism of the vulcanized elastomer complex and heterogeneous. Pure oil shows the R1 decomposition mechanism, where the reaction is controlled by the edges of the shrinking volume moving in a single direction.¹⁷ In this manner, the degradation mechanism observed in the initial conversion, which is related to the D1, D2, and D3 diffusion processes (Fig. 5), is an event related to the elastomer structure. Thus, it is dependent on the diffusion and evaporation of the oil incorporated in the elastomer formulation, in agreement with the E_a results obtained.

CONCLUSIONS

The values for the average activation energy (E_a) of degradation obtained in this study were in agreement with those reported in the literature. However, it was observed that the E_a values for the oil contained in the elastomer for $\alpha > 0.2$ were higher than those for the pure oil, indicating that the EPDM structure hinders the oil degradation and evaporation.

The degradation mechanisms demonstrate the clear influence of a tridimensional network on the thermal stability of EPDM-r. It was noted that the first stage in the degradation of the EPDM-r compound showed lower E_a values and diffusional mechanisms related to the elimination of the oil fraction of the terpolymer. The EPDM degradation

mechanism is influenced by the crosslinking and fillers present in the rubber composition.

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