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Thermal characterization of oil extracted from ethylene–propylene–diene terpolymer residues (EPDM-r)

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ABSTRACT

In this study, extender oil was extracted from automotive scraps of ethylene–propylene–diene terpolymer (EPDM-r). After extraction, the oil was characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). From the TGA analysis at multiple heating rates, the Flynn–Wall–Ozawa (FWO) method was used to determine the activation energy (E_a) of the degradation process. The FTIR results obtained showed that the extracted oil remained structurally stable after extraction, and no oxidation of the oil was observed. The DSC analysis revealed that the extender oil present in the elastomer composition has the characteristics of paraffinic oil. Thermogravimetric and E_a results showed that the extracted oil had higher thermal stability than the pure oil, since the extraction process can remove some additives and low molecular weight molecules present in the elastomer. Also, the vulcanization and extraction processes can affect the characteristics of the extender oil. This study showed that it is possible to reuse rubber-derivate residues, such as extender oil, without significantly modifying their initial characteristics.

1. Introduction

The recycling of polymers is a subject of increasing concern on a global level and many forms of reclaiming these materials have been tested. In recent years some methods for the regeneration of vulcanized elastomers have been studied as a means to ending the accumulation of these materials in landfills. Regeneration involves techniques used to break the three-dimensional network of the elastomer so that it can be reused. Devulcanization techniques, such as exposure to microwaves [1,2], ultra-sound [3] and mechanical shearing [4], have been described in the literature.

During the vulcanization of synthetic rubbers many additives are used, including oxides, peroxides, sulfur, carbon black and extender oil [5,6]. Extender oils of mineral origin are added during the preparation of vulcanized elastomers in order to decrease the viscosity of the raw elastomer [5]. The use of these oils favors the processing, ensuring a good surface finish. Many types of oil are used, such as paraffinic, naphthenic and aromatic; however, the most notable is paraffinic oil, since it has lower toxicity than the others [5]. Mineral oils are basically comprised of open-chain saturated hydrocarbons (alkanes), designated by the petroleum industry as paraffins (straight- or branched-chain). Closed-chain saturated hydrocarbons (cycloalkanes) are classified as naphthenes or aromatic hydrocarbons. The relative contents of these components define the base of the mineral oil as paraffinic or naphthenic [7]. These oils are discarded together with the rubber residues, and no appropriate recycling methods for the extender oils are currently available. According to the International Rubber Study Group [8], the estimate global consumption of rubber was 23.3 million tonnes in 2007 and 22.7 million tonnes in 2008. Also, it is cited in the literature that during industrial processing, approximately 50–100 parts of oil per hundred parts of rubber (phr) are usually incorporated into rubber compounds [5]. Hence, a large quantity of rubber is currently consumed annually, generating a substantial amount of residue containing a significant content of extender oil, which is not generally reclaimed.

In recycling studies, one of the most important issues is to characterize the material to be recycled, in order to ensure that it can be safely reused in its applications. In polymer science, many techniques can be used to evaluate the structural characteristics of these materials, such as thermal analysis and spectrometric techniques. This study aimed to physically extract the extender oil and characterize it in order to evaluate its potential for reuse.

2. Materials

The materials used in this study were vulcanized scraps of ethylene–propylene–diene terpolymer (EPDM-r), DSM South America, kindly donated by the Brazilian company Ciaflex Ltda. Pristine paraffinic oil was kindly donated by Ciaflex Ltda. and

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used for comparison with the extracted oil. The scraps where derived from automotive profiles; the Ciaflex company estimates that approximately 60 tonnes of such scraps are generated annually. Acetone P.A. (Merck) was used for the oil extraction.

3. Methods

3.1. Oil extraction

The oil extraction was carried out in Soxhlet (300 ml) using acetone (P.A.) for 16 h at 70 °C, according to ASTM D 297-93. The average of 32 extraction processes revealed that the oil content was 30.5% ± 0.087 in relation to the mass of the EPDM-r compound. The oil extracted was separated from the acetone by distillation; the oil was then heated at 50 °C in a vacuum oven for 24 h.

3.2. Fourier transform infrared (FTIR) spectroscopy

The Fourier transform infrared (FTIR) spectroscopy analysis was carried out with 32 scans, in the range of 4000–600 cm^{-1}, at a resolution of 4 cm^{-1}, using attenuated total reflectance (ATR).

3.3. Thermal analysis (DSC and TGA)

The DSC (DSC50 – Shimadzu) analysis was performed under N_2 atmosphere (50 ml min^{-1}) using approximately 10 mg of each sample. The samples were initially cooled from ambient temperature to −100 °C and then heated at a rate of 10 °C min^{-1} up to 100 °C. The TGA analysis (TGA50 – Shimadzu) was carried out under N_2 atmosphere (50 ml min^{-1}), from 25 to 910 °C. Approximately 20 mg of each sample was used. For the EPDM-r sample, the atmosphere was changed at 750 °C from N_2 to synthetic air, with the aim of determining the carbon black content. TGA analysis was carried out at four different heating rates (5, 10, 20 and 40 °C min^{-1}). The results obtained were used to determine the activation energy of degradation (E_a) using the Flynn–Wall–Ozawa (FWO) method [9,10].

3.4. Theoretical considerations

The activation energy (E_a) values for the degradation process were determined by the so-called isoconversional method of Flynn–Wall–Ozawa (FWO), according Eq. (1) [9,10].

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

where β is the heating rate, A is the pre-exponential factor, $\alpha(T)$ is the conversion at temperature T, E_a is the activation energy and R is the gas constant.

The FWO method is based on the Doyle [11] approximation and assumes that the reaction rate, at a specified conversion, is only a function of the temperature. Therefore, for different heating rates at a constant conversion, a linear relationship is observed by plotting $\log \beta$ *vs.* $1/T$ and E_a is obtained from the angular coefficient of the straight line.

4. Results and discussion

4.1. Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was carried out to evaluate the composition of both the extracted oil and the pristine oil. Fig. 1 shows the spectra for these materials. Absorption bands in the 2850–3000 cm^{-1} region can be observed, which are attributed to stretching of CH_3 and CH_2 in the aliphatic chains, and values in the range of 1370–1450 cm^{-1} refer to CH bending. An absorption band was also noted at 723 cm^{-1} related to CH rocking [12,13]. The possibility for oxidation of the oil due to mechanical wear or thermal processes is mentioned in the literature [13], in which case oxidation bands would be present in the region of 1700 cm^{-1} related to the carbonyl group (C=O); however, these bands were not observed for the extracted or pure oils. Fig. 1 shows that the oil analyzed in this study is paraffinic.

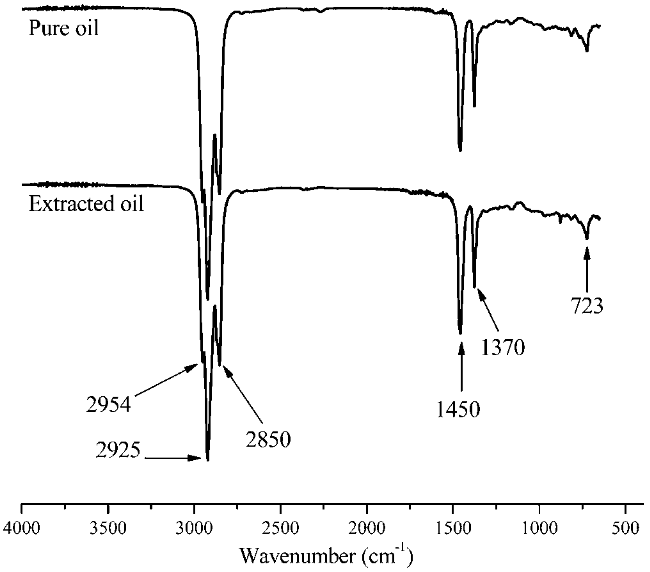

Fig. 1. FTIR spectra for pure oil and oil extracted from the terpolymer recycled ethylene–propylene–diene (EPDM-r).

4.2. Differential scanning calorimetry (DSC)

Fig. 2 shows the thermal behavior of the extracted oil where two endothermic phenomena can be observed, one at −55 °C and another only slightly visible at around −10 °C. Masson et al. [14] studied the melt temperature (T_m) and the glass transition temperature (T_g) for paraffinic and naphthenic oils. They reported modulated DSC (MDSC) transition values for paraffinic oil of around −50 °C and attributed this phenomenon to the T_g of the oil, and there were also values at around −10 °C which were attributed to the crystalline melting of the oil, related to the crystalline structure of the saturated hydrocarbons. These values corroborate those found for the oil extracted from the EPDM-r, which are also in agreement with the results of Fig. 1, indicating that the oil is paraffinic. DSC analysis also showed that there are no

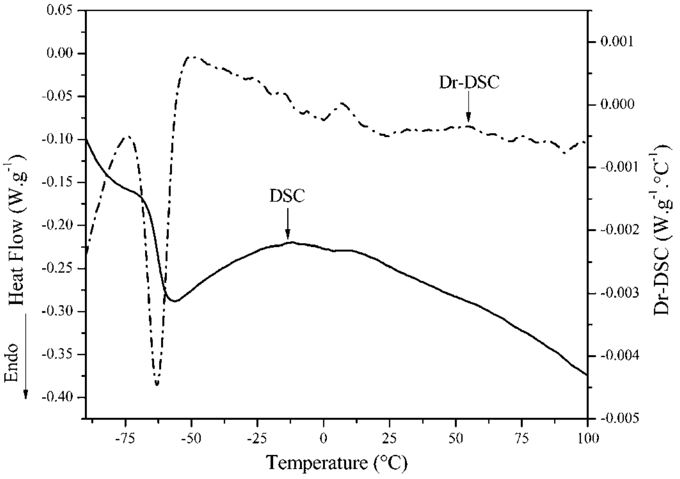

Fig. 2. Thermograms of DSC for sample of oil extracted from EPDM-r (β = 10 °C min^{-1}).

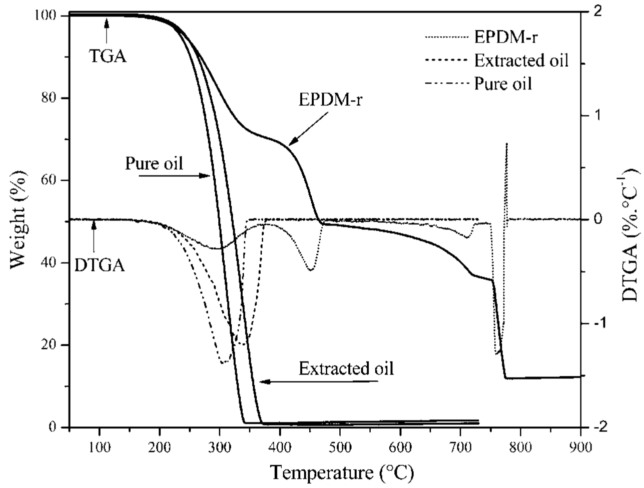

Fig. 3. Degradation curves for samples studied at a heating rate of 10 °C min^{-1}.

thermal transitions that could interfere in the extraction process.

4.3. Thermogravimetric analysis (TGA)

Fig. 3 shows the thermal degradation behavior for the extracted oil, pure oil and also for the EPDM-r. For the EPDM-r sample, four thermal degradation phenomena can be observed; the first, at 260–330 °C, is related to the quantity of oil found in the sample, which was approximately 30 wt.% Ginic-Markovic et al. [15] studied the composition of elastomers through thermal analysis and obtained degradation temperatures for extender oil of 200–400 °C under N_2 atmosphere, which was consistent with the values obtained in this study. Also, Scuracchio et al. [16] reported the decomposition of extender oil at between 200–350 °C. The second event in the range of 425–465 °C refers to the mass fraction of EPDM, which represented around 20 wt.% [13,17]. The third mass loss, at approximately 500–740 °C, corresponds to 10 wt.% of the inorganic filler, probably calcium carbonate ($CaCO_3$). With the changing of the atmosphere at 750 °C, the carbon black content was determined and the content of this material in the EPDM-r sample was approximately 30 wt.%. The residual mass was around 15%, which may be due to calcium and zinc oxides. Fig. 3 also shows the TGA data for the extracted and pure oils. The extracted oil showed higher thermal stability, and the mass loss was shifted to higher temperatures, compared to pristine oil. The higher thermal stability of the extracted oil can be attributed to the presence of additives and low molecular weight compounds present in the EPDM-r formulation that were extracted together with the oil [12,14].

4.4. Kinetic parameters

In the study on the degradation kinetics, the activation energies (E_a) of the oil incorporated in the elastomeric compound, the pure oil and the extracted oil were evaluated, in order to predict the structural modifications of the oil after extraction. Fig. 4 shows the thermograms of EPDM-r at heating rates of 5, 10, 20 and 40 °C min^{-1}. The residual mass was modified with the change in the heating rate, once the rate of weight loss change with heating rate.

In this study, the conversion (α) range analyzed was 0.05–0.25; these values were selected because the initial degradation process was related to oil, including in the case of the EPDM-r sample. From non-isothermal thermogravimetric analysis (α), can be determined by Eq. (2), [9,10]:

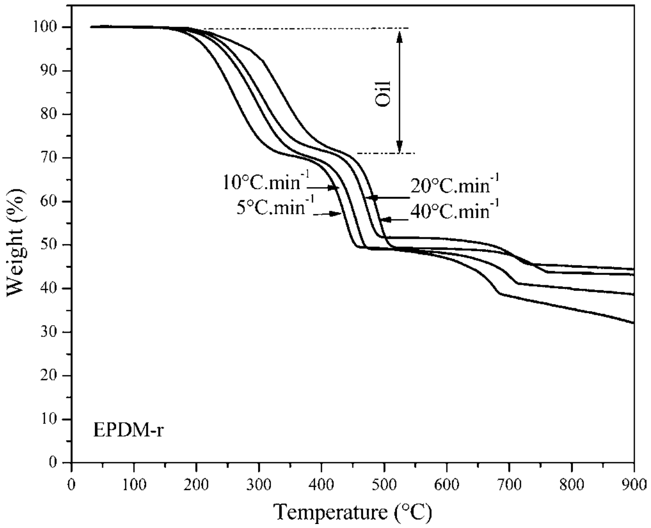

Fig. 4. Thermogravimetric curves at β = 5, 10, 20 and 40 °C min^{-1} for EPDM-r.

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{2}$$

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

Fig. 5 shows plots of log β *vs.* $1/T$ for EPDM-r at different conversion values. The pristine oil and extracted oil showed similar behavior. From the slope of each linear fit, the activation energy of degradation (E_a) was determined, and the results are shown in Fig. 6. The correlation coefficients (r), obtained from the linear fits at each α, were similar (between 0.98 and 0.99), and are showed in the detail of Fig. 6.

The E_a values were as follows: pure oil 71.7–73.2 kJ mol^{-1}; extracted oil 78.2–79.5 kJ mol^{-1}; and for the degradation of the oil in the EPDM-r sample 84.6–92.6 kJ mol^{-1}. The higher E_a values for the extracted oil compared to the pure oil are probably related to the presence of additives in the extracted oil [5,6]; moreover, the vulcanization process of the EPDM compound can lead to modifications in the paraffinic structure of the extender oil, which can induce branching or increase the molecular weight of the oil molecules. However, the FTIR spectra (Fig. 1) showed that the extracted oil has a chemical structure similar to that of pure

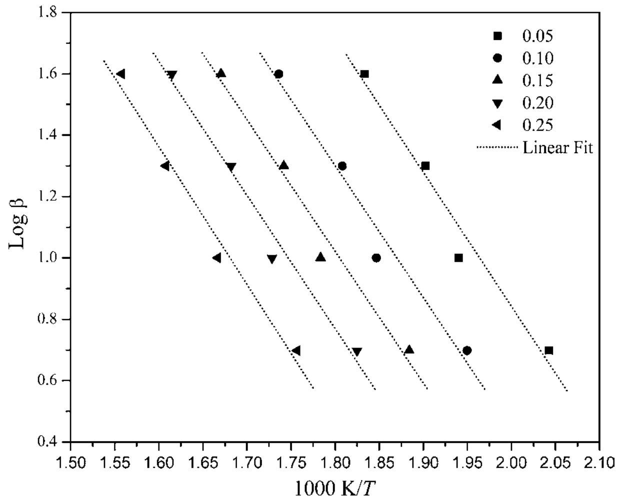

Fig. 5. Graph of log $\beta \times 1/T$ for the determination of the activation energy of degradation for the oil in the composition of EPDM-r.

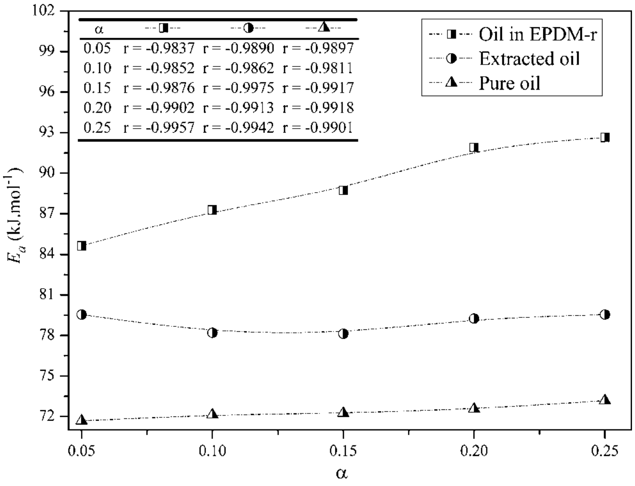

Fig. 6. Graph of E_a *vs.* α for pure oil, extracted oil and oil in EPDM-r.

oil, since no carbonyl, unsaturation or peroxide absorption bands were observed. According to Odian [18], chain transfer reactions can induce branching formation in hydrocarbon molecules, affecting the thermal stability.

On comparing the results for the pure and extracted oils with those for the oil present in the EPDM-r it can be observed that the latter has higher E_a values, showing a tendency toward an increase in the degradation as the conversion increases. This behavior may be related to the reduced diffusion of the oil molecules through the vulcanized EPDM structure during the TGA analysis; thus, the higher the conversion the lower the level of diffusion, promoting an increase in E_a.

The difference of around 10% between the E_a values of the extracted and pure oils indicates the possibility for the reuse of the extracted oil in new rubber compounds. Thus, these results show that the extender oil present in rubber compounds can be extracted and reused even if this oil contains other additives and its structure is slightly altered during the vulcanization and extraction processes. Also, it is possible that a shorter extraction process may be sufficient and more economically viable than the extraction period cited in ASTM D 297-93 (16 h).

5. Conclusions

This study evaluated a possible route for the reuse of extender oil used in the formulation of ethylene–propylene–diene terpolymer (EPDM-r) scraps, comparing the pure oil with the extracted oil.

The FTIR results showed that the pure and extracted oils have similar chemical structures, and the extraction process does not induce oxidation of the oil, suggesting that the extracted oil can be reused. Also, the FTIR results indicate that the studied oil is paraffinic and the DSC data corroborate this finding.

The values for the average activation energy of degradation (E_a), related to the elimination of the oil, were highest for the EPDM-r sample, probably due to the lower level of diffusion of the oil present in the vulcanized elastomer. The E_a values for the extracted oil were higher than those for the pure oil due to modification of the oil during the vulcanizing and extraction processes, and also due to the presence of additives and low molecular weight molecules derived from the rubber compound.

The results presented in this paper provide an initial insight into the potential for the use of a material that has received little attention in the recycling of vulcanized elastomers. This material thus merits further investigation by the industrial and scientific communities.

References

[1] T. Kleps, M. Piaskiewicz, W. Parasiewicz, J. Therm. Anal. Calorim. 60 (2000) 271–277.
[2] L. Landini, S.G. de Araújo, A.B. Lugão, H. Wiebeck, Eur. Polym. J. 43 (2007) 2725–2731.
[3] W. Feng, A.I. Isayev, E. von Meerwall, Polymer 45 (2004) 8459–8467.
[4] P. Sutanto, F. Picchioni, L.P.B.M. Janssen, Chem. Eng. Sci. 61 (2006) 7077–7086.
[5] A.K. Bowmick, H.L. Stephens, Handbook of Elastomers, 2001.
[6] K.A.J. Dijkhuis, J.W.M. Noordermeer, W.K. Dierkes, Eur. Polym. J. 45 (2009) 3302–3312.
[7] A.C.M. Wilson, Insulating Liquids: Their Uses, Manufacture And Properties. IEE Electrical and Electronic Materials and Devices Series 1, Peter Peregrius LTD, 1980.
[8] International Rubber Study Group, Rub. Ind. Rep. 8 (2009).
[9] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881–1886.
[10] J.H. Flynn, L.A. Wall, J. Polym. Sci. B: Polym. Lett. 4 (1966) 323–330.
[11] C.D. Doyle, J. Appl. Polym. Sci. 5 (1961) 285–292.
[12] R.M. Silverstein, F.X. Webster, D. Kielmle, Spectrometric Identification of Organic Compounds, 7th edition, 2005.
[13] M. Diaby, M. Sablier, A. Le Negrate, M. El Fassi, J. Bocquet, Carbon 47 (2009) 355–366.
[14] J.-F. Masson, G.M. Polomark, S. Bundalo-Perc, P. Collins, Melting and glass transition in paraffinic and naphthenic oils, Thermochim. Acta 440 (2006) 132–140.
[15] M. Ginic-Markovic, N.R. Chouddhury, M. Dimopoulos, D.R.G. Williams, J. Matisons Thermochim. Acta 316 (1998) 87–95.
[16] C.H. Scuracchio, D.A. Waki, M.L.C.P. da Silva, J. Therm. Anal. Calorim. 87 (2007) 893–897.
[17] T. Özdemir, Radiat. Phys. Chem. 77 (2008) 787–793.
[18] G. Odian, Principles of Polymerization, John Wiley & Sons, 2004.