

## Evaluation and rationale of the performance of several elastomeric composites incorporating devulcanized EPDM

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### ABSTRACT

Ethylene Propylene Diene rubber (EPDM), is present in many applications. However, its crosslinked structure makes difficult its recycling. The use of devulcanized EPDM, (dEPDM) as a component of elastomeric composites, is a real possibility to reuse EPDM scraps. In this study, three matrices (natural rubber (NR), styrene butadiene rubber (SBR) and EPDM rubber) have been tested including devulcanized EPDM as a recycled component. The EPDM previously was devulcanized using a thermomechanical process followed by microwave irradiation. The resulting devulcanized EPDM was blended with the matrixes and then the new compound was vulcanized again. The samples showed a general increase of their mechanical properties and their thermal stability specially marked for NR and SBR. Compositions including about 40 phr dEPDM within the EPDM matrix exhibited a difference in their general behavior that it was manifested by a general decrease in properties compared with lower amounts of dEPDM. In order to further understand this behavior, the samples were analyzed in terms of cross-link density, swelling degree, and scanning electron microscopy. The study of the microstructure of the samples indicated that microagglomerates of dEPDM are formed inside the samples. In case of NR or SBR the agglomerates were very linked to the matrix through the covalent bonds established in the crosslinking process. In the case of the EPDM matrix, the agglomerates presented less interfacial cross-links. The cross-linking takes place preferentially within the dEPDM microdomains and this results in a relative decrease in mechanical properties and thermal stability when compared to NR and SBR.

### 1. Introduction

21<sup>st</sup> century faces the important challenge of transitioning to an optimized energy management. The proposals agreed in Sharm el-Sheikh (COP 27) about generating zero emissions are related to this evolution. To achieve these ambitious goals, a wider array of decarbonization pathways are necessary [1]. The change in the origin of energy, opting for renewable and the quest for new storage technologies must be accompanied by an efficient use of the industrial resources that is committed to circular economy and the recycling of materials. Industrial production of new materials should involve minimal environmental impact. Certainly, the reuse and recycling of the waste is a strategy that every government should support.

Elastomeric compounds, and among them Ethylene Propylene Diene Monomer (EPDM), are high-performance materials that are present in many applications. However, their cross-linked structure obtained by the vulcanization process makes their recycling difficult. In order to overcome this situation, given their high production and disposal, it is

essential to find new devulcanizing methods that allow the reuse of the rubber waste as component within new composite materials. During the last decade, a large number of devulcanization methods have been proposed such as microwave irradiation [2–5], thermo-mechanical treatments [6,7], mechanochemical processes [8,9], supercritical dioxide [10], applying ultrasounds [11] or by enzymatic action [12].

The geopolitical trend due to the conflict between Russia and Ukraine has caused a significant increase in the price of raw materials [13]. The price of a barrel of oil has increased by 40%, directly affecting the price of manufacturing synthetic elastomers. Although it is a circumstantial aspect, it is important to take it into account in order to promote research into new recycling processes for polymer waste that may decrease the need of raw materials.

For several years, POLQUITEX research group from Universitat Politècnica de Catalunya, has been working on devulcanization of elastomers using microwaves. The obtained results have been very good at laboratory level but not so easy to apply in industrial processes. For this reason, during the last two years, we have opted for a combined

*Abbreviations:* EPDM, Ethylene Propylene Diene rubber; dEPDM, devulcanized EPDM; NR, natural rubber; SBR, styrene butadiene rubber; ENB, ethylidene Norbornene; BPO, benzoyl peroxide; TBBS, N-tert-butyl-2-benzothiazole sulfonamide; TMTD, tetramethylthiuram disulfide; TGA, Thermogravimetric analysis; SEM, scanning electron microscope; TS, Tensile strength; TdT, thermal decomposition temperatures.

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thermomechanical and microwave method. The results obtained on EPDM evaluated using the Horikx charts have been very satisfactory [14].

Since the aim of devulcanizing EPDM waste is to use it as component in elastomeric compounds and composites, in this study the feasibility of combining devulcanized EPDM (dEPDM) with three common elastomers (natural rubber (NR), styrene butadiene rubber (SBR) and EPDM) was examined. Their mechanical and thermal performance was evaluated and also the effect of the incorporation of dEPDM in the microstructure of the material that may be useful also as a reference for other blends and composites was studied. The effect on disulfide bridges S-S produced by the vulcanization was assessed by the determination of the swelling degree and cross-link density.

## 2. Experimental

### 2.1. Materials

Natural Rubber NR (Vietnam Natural Rubber), ash content max. 0.5% wt., volatile matter 0.8% wt., Plasticity Retention Index (PRI) 60, density 0.92 g/cm<sup>3</sup> was supplied by VIGAR Rubí (Spain). SBR stabilized with BHT antioxidant of 0.375%, bound styrene 24% and organic acid 5.5% and EPDM with a Mooney viscosity of 25 MU, ethylene content 58,0 % wt. and ethylidene Norbornene (ENB) content 4,0 %wt. were both supplied by Brenntag Iberia (Barcelona).

Waste EPDM of commercial, industrial and residential roofing origin was supplied by Firestone Building Products Terrassa (Spain).

The additives and curing agents used for curing, namely benzoyl peroxide (BPO), vulcanization accelerators (TBBS- N-tert-butyl-2-benzothiazole sulfonamide, TMTD - tetramethylthiuram disulfide), carbon black N550, stearic acid, zinc oxide and sulfur with technical purity, were supplied by VIGAR Rubí (Spain).

### 2.2. Devulcanization of EPDM

Devulcanization process of EPDM by combined thermomechanical/microwave procedures, was carried out according to the procedure already tested and published by our group in a previous paper [14].

Following this procedure, the thermo-mechanical treatment was carried out in a Brabender plastograph at two temperatures, 80 °C and 110 °C, including the addition of different amounts of benzoyl peroxide which helps the thermomechanical devulcanization. The microwave irradiation takes place in a prototype microwave oven with a motorized stirring adapted in our laboratory. The microwaves devulcanization process was performed setting the magnetron power to 700W, 80 rpm of the stirrer and 3 min of MW exposure.

The resulting material after this process is named dEPDM in this paper.

In case of peroxide-cured EPDM, where no -S-S- bonds are present, the devulcanization process would produce the cleavage of the -C-C- bonds and would also be reflected in changes in the mentioned properties. As comment previously, the BPO acts as a devulcanization agent.

### 2.3. Samples preparation

Elastomeric composites were prepared at 70 °C using also the Brabender plastograph (Brabender GmbH, Duisburg, Germany) batch mixer. The rotational speed of the rollers was 100 rpm. The total mixing time was 8 min, which included 2 min of preliminary plasticization of the fresh elastomer (NR, SBR or EPDM), 4 min of mixing with 30phr of carbon black and dEPDM and 2 min of mixing the blend with the sulfur curing system. The devulcanized EPDM content in the samples was 0, 20, 40 and 50 parts per hundred of rubber (phr).

The curing system composition (phr) was: zinc oxide 5.0; stearic acid 3.0; TBBS 1.0; TMTD 0.25; sulfur 2.0. The same curing system was used for all the samples.

The resultant elastomeric compounds were compressed in a Dr. Collin GmbH (Germany) hot plate press and molded into 3 mm thick plates at 160 °C and 4.9 MPa. These conditions correspond to the optimum cure time (t<sub>90</sub>) determined by the vulcanization characteristics of vulcanizable rubber compounds according to ASTM D2084, with an Oscillating Disc Rheometer R 100, Monsanto, (Akron, Ohio, USA), at 162 ± 1 °C. Fresh elastomers (NR, SBR and EPDM), were processed in the same conditions and used as reference samples.

### 2.4. Measurements

Tensile strength and elongation at break of the obtained vulcanized elastomers compounds were tested according to the standard ISO 37 using an Instron testing machine with load cell capacity of 20 kN. The dumbbell shaped specimen, with a thickness of 3 mm, was gripped in the machine and slowly pulled until the sample fractured. The crosshead speed 500 mm/min was used and the average value of tensile strength, elongation at break, modulus at 100% elongation (M100) were obtained. Hardness was determined using a Zwick 3130 durometer Shore A (Zwick, Germany) in accordance with the standard ISO 7619-1. The reported results are the average of 5 measurements per sample.

Swelling degree of elastomers compounds (0.2 g samples) was determined by equilibrium swelling in toluene (room temperature) after immersing the samples in the medium for 72 h. Swelling degree was calculated in accordance to formula (1):

$$Q = \frac{m_t - m_0}{m_0} \times 100\% \quad (1)$$

where: Q – swelling degree; m<sub>t</sub> – mass of the sample swollen (g); m<sub>0</sub> – initial mass of sample (g).

The crosslink density was determined according to ASTM D6814-02 standard method through swelling measurements of the rubber composites which were let to swell in cold toluene for 72 h refreshing the solvent every 24 h [5,14,15]. The Flory Rehner equation [16] was used to calculate the crosslink density.

The  $\chi$  interaction parameter between rubber and swelling solvent was set equal to 0.39, considering NR as main polymer, 0.377 considering SBR as a main polymer [17], 0.496 considering EPDM as a main polymer [18] and in all cases toluene as solvent. Kraus correction model was applied due to the presence of carbon black as a filler [19]. The carbon black density was chosen equal to 1.85 g/cm<sup>3</sup> and the K constant was chosen to be 1.17 [18]. equations (2) and (3) were used for cross-link density calculations.

$$\nu_e = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{[V_1(V_r^{1/3} - V_r/2)]} \quad (2)$$

Where:  $\nu_e$  – cross-link density, mol/cm<sup>3</sup>; V<sub>1</sub> – solvent molar volume (toluene = 106.2, cm<sup>3</sup>/mol) and V<sub>r</sub> means the volume fraction of rubber in the swollen sample, which can be determined with Ellis and Welding equation [20]

$$V_r = \frac{\frac{m_p}{\rho_p}}{\frac{m_p}{\rho_p} + \frac{m_s}{\rho_s}} \quad (3)$$

where: m<sub>p</sub> – the weight of the dry polymer;  $\rho_p$  – the density of the dry polymer g/cm<sup>3</sup>; m<sub>s</sub> – the weight of solvent absorbed by polymer;  $\rho_s$  – the density of the solvent.

Cross-link density with Kraus correction was calculated according equations (4) and (5):

$$\nu_{after\ correction} = \frac{\nu_e}{1 + K \times \Phi} \quad (4)$$

$$\Phi = \frac{\rho_f \times \rho_r \times m_0}{\rho_f \times m_{dry}} \quad (5)$$

Where,  $\nu_e$  – the measured chemical cross-link density, mol/cm<sup>3</sup>;  $\nu_{\text{after correction}}$  – the actual chemical cross-link density, mol/cm<sup>3</sup>;  $K$  – constant characteristic of the filler but independent of the solvent;  $\varphi_f$  – the volume fraction of filler in the sample which is calculated;  $\rho_r$  – the density of studied compound, g/cm<sup>3</sup>;  $m_0$  – the weight of sample before extraction;  $\rho_r$  – the density of filler, g/cm<sup>3</sup>;  $m_{\text{dry}}$  – the weight of sample after extraction.

Sol fraction was obtained by 24 h Soxhlet extraction method using toluene as solvent. The weight of the rubber composites samples was measured before ( $W_1$ ) and after extraction ( $W_2$ ), according to equation (6):

$$\text{Sol fraction} = \frac{W_1 - W_2}{W_1} \times 100 \% \quad (6)$$

The density of the samples was measured based on the Archimedes method, as described in ISO 2781. Accordingly, all measurements were performed at room temperature in methanol medium.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851 apparatus. Elastomers compounds weighing approximately 10 mg were placed in a corundum dish. The measurement was conducted in the temperature range 50–800 °C and under nitrogen atmosphere (30 ml/min), at a heating rate of 20 °C/min. At the end of the experiment, air was introduced in the chamber in order to allow the decomposition of the carbon black present in the samples.

The morphology of rubber composites after extraction in toluene (at room temperature, 72 h) was observed with a JEOL 5610 scanning electron microscope. Before measurement, the samples were covered with a fine gold-palladium layer in a vacuum chamber in order to increase their conductivity.

### 3. Results and discussion

#### 3.1. Characterization of NR, SBR and EPDM compounds

As observed in Table 1, swelling degree and crosslinking density are inversely related within the same type of elastomer. Increasing the cross-link density implies a tighter polymeric network, that does not allow the toluene entering within the structure and therefore, less swelling will result.

When comparing the swelling degrees for the different types of elastomers, the chemical structure has an effect beyond the crosslinking density. So, NR, because of its structure swells more than SBR and SBR swells more than EPDM. This can be related to the superior crosslinking density in the case of SBR but also to the presence of big groups in both SBR (phenyl) and EPDM (norbornene) that may contribute to a reduction in swelling.

The incorporation of dEPDM to the samples based on NR and SBR causes an increase of crosslinking that is especially noticeable in NR. Both NR and SBR, even after vulcanization, have unsaturations that are

**Table 1**  
Swelling degree and crosslinking density of the elastomeric composites.

Sample	Swelling Degree (%)	Crosslinking Density (mol/cm <sup>3</sup> )
100EPDM	161	1.02·10 <sup>-4</sup>
EPDM-dEPDM20	170	8.61·10 <sup>-5</sup>
EPDM-dEPDM40	175	7.54·10 <sup>-5</sup>
EPDM-dEPDM50	179	4.97·10 <sup>-5</sup>
100NR	229	5.12·10 <sup>-4</sup>
NR-dEPDM20	184	8.10·10 <sup>-4</sup>
NR-dEPDM40	173	9.08·10 <sup>-4</sup>
NR-dEPDM 50	143	1.03·10 <sup>-3</sup>
100SBR	169	6.05·10 <sup>-4</sup>
SBR-dEPDM20	136	8.18·10 <sup>-4</sup>
SBR-dEPDM40	123	9.06·10 <sup>-4</sup>
SBR-dEPDM50	132	7.64·10 <sup>-4</sup>

potential sites to start a curing reaction with the dEPDM. When adding dEPDM it reacts with these sites providing additional crosslinks resulting in a higher crosslinking degree. Contrarily, the data shows that the EPDM matrix decreases its crosslink when including dEPDM, The EPDM is a highly saturated elastomer, with few unsaturations that act as potential sites to establish crosslink with the dEPDM, some of these unsaturations are situated in the norbornene group. Then, even when the dEPDM has potential to start a curing reaction, the possibilities of increasing the crosslink with EPDM are very limited and the access to the unsaturations in the norbornene group is difficult. The crosslinking process consists basically in the revulcanizing of the dEPDM itself.

The swelling of the samples was also affected by the addition of dEPDM decreasing when the crosslinking increases and vice versa.

The results of the cross-link density importantly affect to other properties of the samples, as will be discussed in the next sections.

#### 3.2. Mechanical properties

##### 3.2.1. Tensile strength

Fig. 1a shows a comparative study of the tensile strength (TS) of all analyzed samples. Neat NR had the highest values. Its tensile strength was equal or only slightly superior than SBR, but significantly higher than EPDM. These values are in consonance with those reported by other authors [21,22] and show that even when the cross-link density of the NR is not the highest other structural features positively affect to its resistance.

However, the NR samples including dEPDM showed a significant increase in the TS when the amount of dEPDM did not exceed 40 phr. With 50 phr TS is lower. The increase in tensile strength was expected from the values of cross-link density presented in the previous point, (higher cross-linking when adding dEPDM results in higher TS). However, the decrease of TS at 50 phr is related to other phenomena. dEPDM not only produces interactions in the sample through the vulcanization by sulfur bridges but there are also interactions involving physical entanglements and secondary chemical forces between the olefinic chains of both NR and dEPDM. When the amount of dEPDM is very high, the interactions between NR and dEPDM are reduced due to the tendency of dEPDM to interact mainly with its own polymeric chains and even to form agglomerates (see SEM micrographs). This circumstance affects the mechanical behavior [23]. The NR macromolecules, with a lineal structure without any big pendant groups, have a higher ability to develop interactions with the dEPDM than SBR and also to form S-S bridges with its unsaturations [24,25].

##### 3.2.2. Elongation at break

The mentioned development of dEPDM agglomerates within the NR matrix explains the elongation at break values shown in Fig. 2. The dEPDM microdomains are constituted by an elastomer that is cross-linked mainly with disulfur bridges, with stronger interactions tightening the agglomerates and that is stiffer than the matrix formed by NR, SBR and EPDM. NR and SBR are able to establish some interactions with these agglomerates and for this reason showed a progressive decreasing of their elongation at break. EPDM matrix does not establish these interactions and then its elongation decreases smoothly with the dEPDM content.

##### 3.2.3. Young's modulus

The values of Young's Modulus are shown at Fig. 3. EPDM was stiffer than the other elastomers (NR and SBR), because of its chemical structure, containing norbornene. Similar to the previous discussion, the effect of the dEPDM agglomerates is also noticeable in the values obtained for NR and SBR. According to the results, NR is able to form stronger interactions than SBR [24,25] This is related to the decrease of the value of Young's Modulus at low dEPDM content that is followed by an increase when the dEPDM amount is higher.

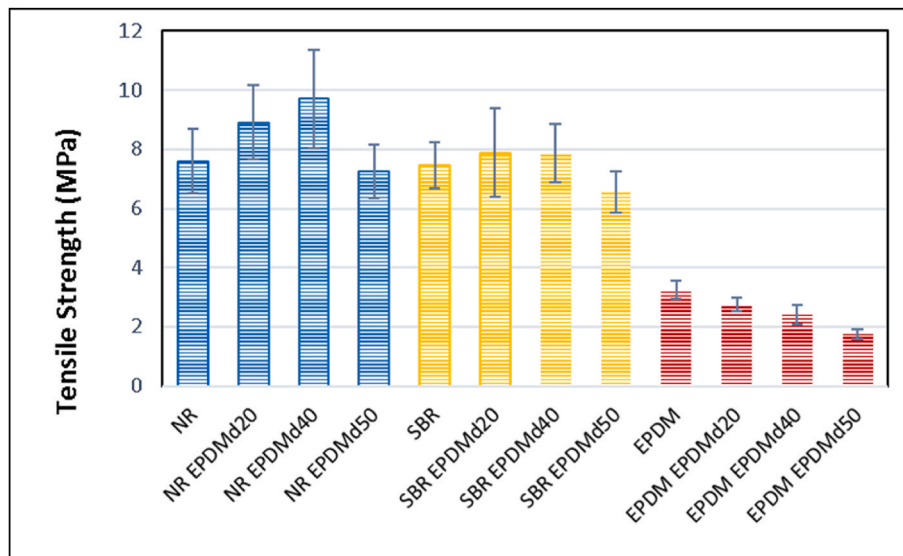


Fig. 1. Tensile strength of the elastomeric composites.

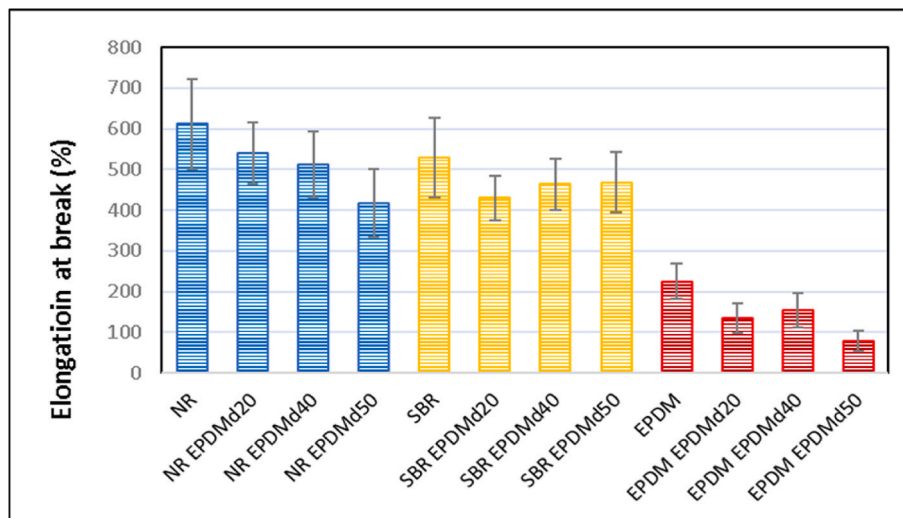


Fig. 2. Elongation at break of the elastomeric composites.

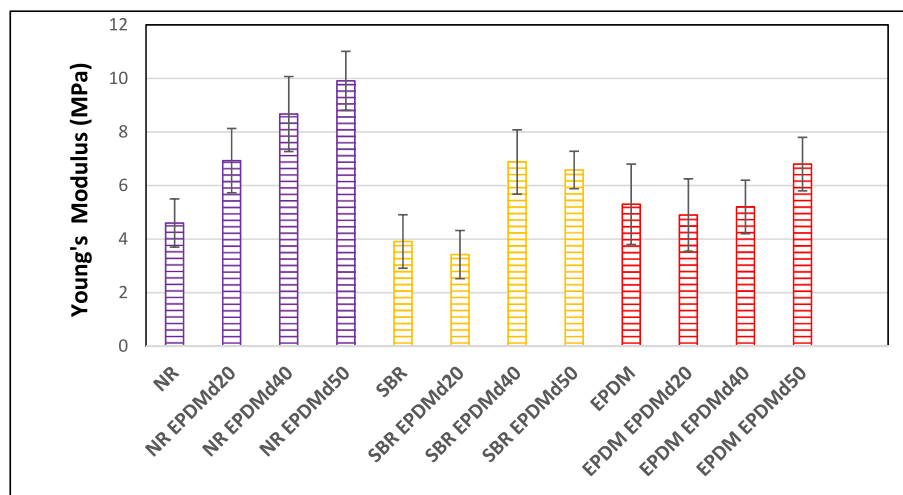


Fig. 3. Young's modulus of the elastomeric composites.

### 3.2.4. Hardness

Hardness values presented at Fig. 4 are in consonance with the other mechanical properties. Hardness shows an outstanding increase in the elastomeric composite with a NR matrix where the incorporation of dEPDM produces a change from 45 to 67 Shore A. In case of the samples SBR, the increase also exists, but is less notorious, from 48 to 55 Shore A. EPDM showed a constant value of 67 Shore A which was the highest of the three.

The increases of hardness produced by the dEPDM in NR and SBR matrixes is justified for the higher hardness of the EPDM. The higher increase of hardness in the matrix of NR compared to the SBR matrix is related, as in the previous section to the greater ability of the NR to form interactions with dEPDM.

### 3.3. Scanning electronic microscopy

Fig. 5 shows SEM microphotographs of the samples. The proposed model of dEPDM agglomerates formation is consistent with the findings from the SEM microphotographs. As observed, in the samples containing higher amount of dEPDM there are agglomerates that differ in size and dispersion according to the matrix, being bigger in case of NR and smaller and more dispersed in case of EPDM. This causes the increase of the Young's modulus of the samples, as discussed in previous sections. Red circles mark the presence of agglomerates that have sizes comprised between 10 and 50  $\mu\text{m}$  in the samples NR-dEPDM40; 5–30  $\mu\text{m}$  in EPDM-dEPDM40 and between 5 and 20  $\mu\text{m}$  in SBR-dEPDM40 samples. The particle bonding of dEPDM particles is also worse in EPDM matrix and it is visible. In some microphotographs, ZnSt<sub>2</sub> crystals, already described in previous publications are also present [26,27]

### 3.4. Thermogravimetric analysis

Fig. 6 shows the thermogravimetric analysis (TGA) and derivative thermogravimetric analysis of the three elastomers used in the samples. The obtained results for EPDM, SBR and NR were quite different. The thermal decomposition temperatures (TdT) of the elastomers are the transitions observed in the range of temperatures comprised between 350 °C and 500 °C: 445 °C for EPDM, 415 °C for SBR and 375 °C for NR. The range of decomposition in SBR was wider than in the other elastomers, because it included two components (styrene and butadiene). As expected, EPDM, because of its chemical structure presented the highest TdT followed by SBR. NR, has usually less service temperature than the synthetic rubbers.

The thermogram of Fig. 6b shows more clearly the decompositions temperatures and makes evident the existence of a wide band, formed by

the overlapping of a double peak in the case of SBR, due to the styrene and butadiene present in its chemical structure.

The decomposition of carbon black present in the elastomers, over 600 °C, appears also in the thermograms included in Fig. 6. Additionally, a small transition around 325 °C was observed in the SBR. This corresponded to the decomposition of oils or additives and took place before the decomposition of the main elastomeric component.

Fig. 7 shows the evolution of the thermograms of the elastomeric composites including dEPDM. TdT increased in NR and SBR matrixes when adding dEPDM. This could be expected because EPDM has a higher TdT. At the same time, as discussed in previous sections, the presence of dEPDM causes an increase of the crosslinking density in these cases, an increase of the interactions and sulfur bridges that are also responsible for the improvement in mechanical properties that was observed for these samples. It is noticeable the increase of the TdT that was observed in the NR-dEPDM20 and NR-dEPDM50. The increase appeared as a new shoulder, indicating that there are separate microdomains, with a higher TdT, corresponding to the aggregates observed in the SEM images which are also related to the results of the mechanical properties. The unsaturations present in the accessible external layers of these aggregates interact by S-S bridges with NR and to a lesser extent with the SBR (a non-scale representation of this idea is shown in Fig. 8). In the case of the matrix constituted by EPDM, we found a change in the results obtained when the amount of dEPDM in the sample was above 40 phr. Similarly, to the previous discussions, when the dEPDM is lower than 40 phr, EPDM is quite dispersed in the matrix, but from a certain amount of EPDM on, the formation of agglomerates alters significantly the properties of the material. These samples do not contain interactions particle-matrix and hence the changes observed for these samples.

## 4. Conclusions

The use of dEPDM as a component of elastomeric composites, offers a real possibility in terms of recycling EPDM scraps.

The three matrixes tested in this study showed a general improvement of their mechanical properties and their thermal stability specially marked for NR and SBR.

Increasing the dEPDM concentration above 40 phr results on a worsening of the mechanical and thermal properties.

The SEM study of the microstructure of the samples indicated that agglomerates of dEPDM were formed inside the samples. In case of NR or SBR, the agglomerates were very linked to the matrix through the covalent bonds established in the crosslinking process. In the case of the EPDM matrix, the agglomerates presented less interfacial crosslink. The crosslinking took place preferentially within the own dEPDM

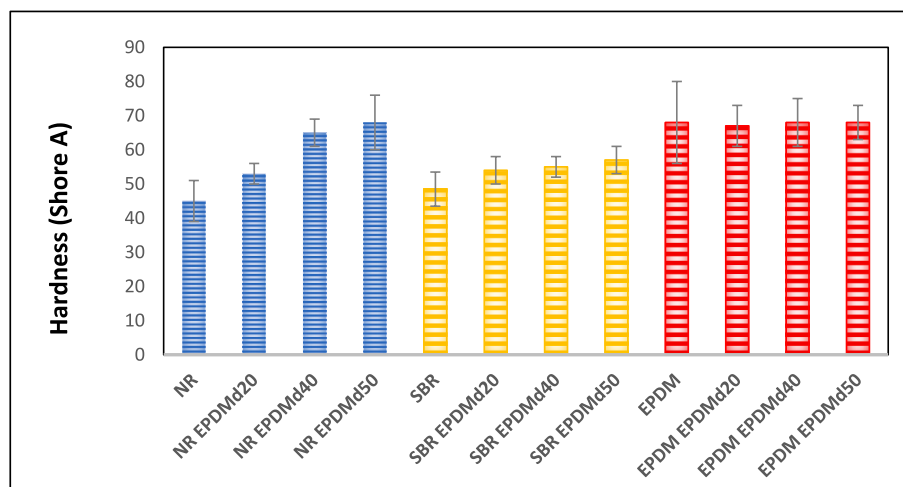


Fig. 4. Hardness of the elastomeric composites.

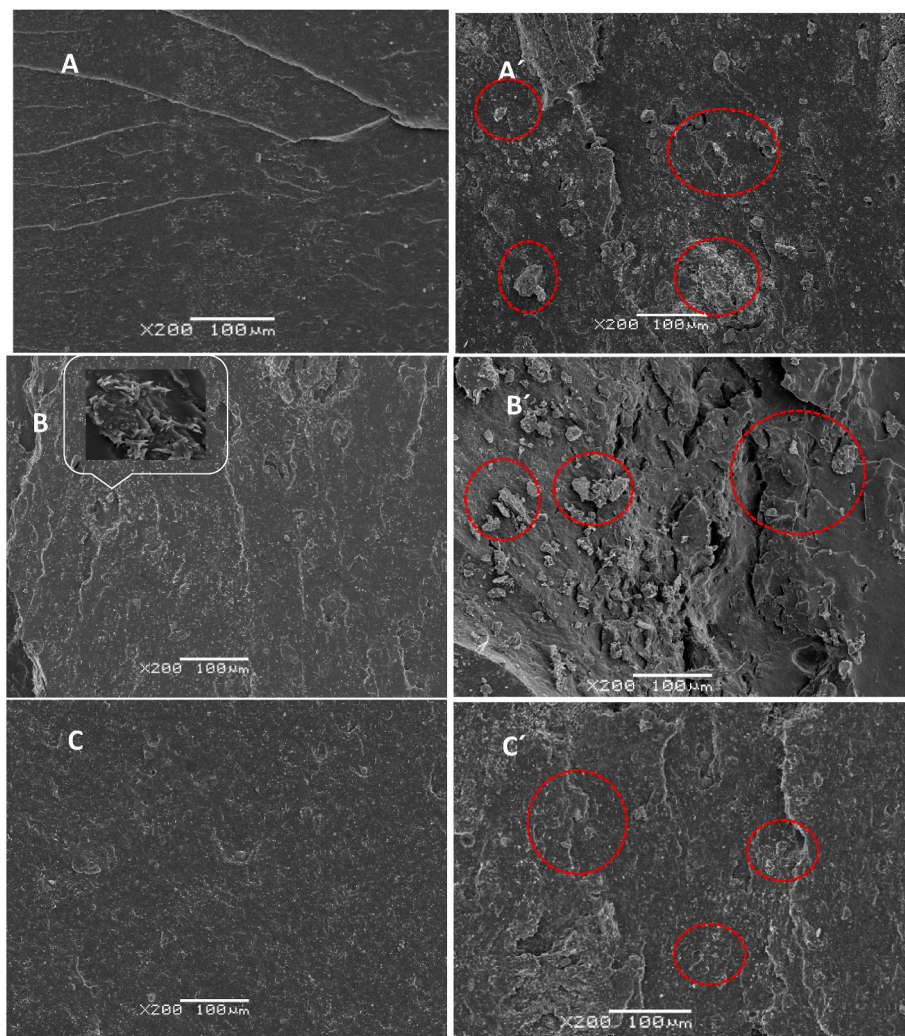


Fig. 5. SEM microphotographs of the elastomeric composites: A 100NR; A' NR-dEPDM40; B 100EPDM (presented in white frame crystals of zinc stearate was observed at  $\times 1500$  magnification); B' EPDM-dEPDM40; C 100SBR; C' SBR-dEPDM40.

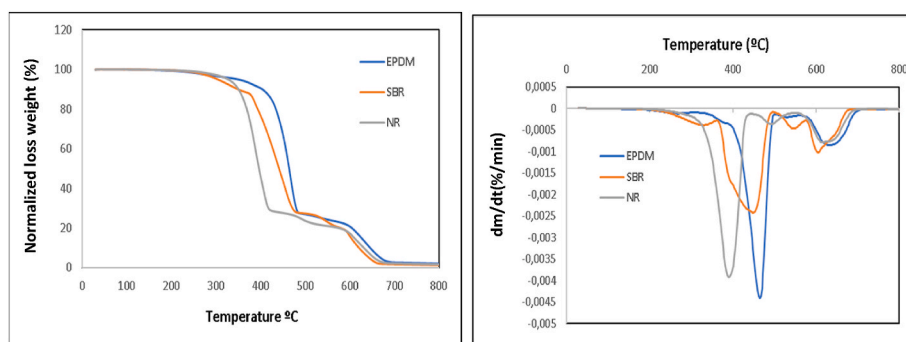


Fig. 6. a) Thermogravimetric analysis of the three elastomers used in the samples b) Derivative Thermogravimetric analysis of the three elastomers used in the samples.

microdomains and this resulted in a relative decrease in mechanical properties and thermal stability of EPDM when compared to NR and SBR. The formation of agglomerates was corroborated by the TGA analysis. The size of the agglomerates, bigger in NR than EPDM, correlated with the mechanical and thermal properties of the studied composites.

Author statement

Conceptualization, X.C. and J.C.; methodology, X.C. and J.C.; investigation, X. C, K.F, M.M.; resources, F.C.-N. K.F; writing—original draft preparation, X.C. M.R.S. and J.C.; writing—review and editing, F. C.-N.; project administration, M.R.S.; funding acquisition, X.C. All authors have read and agreed to the published version of the manuscript.

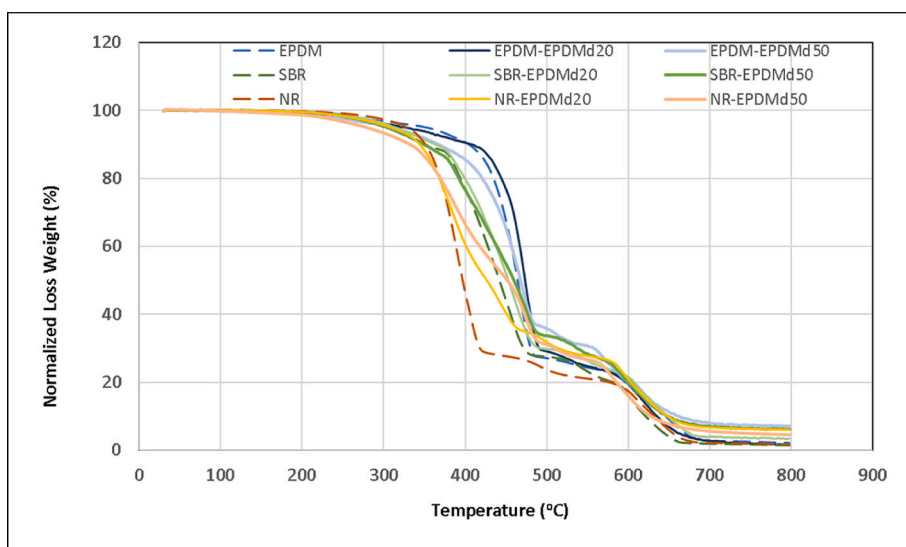


Fig. 7. Thermogravimetric analysis of the elastomeric composites including the three matrixes studied.

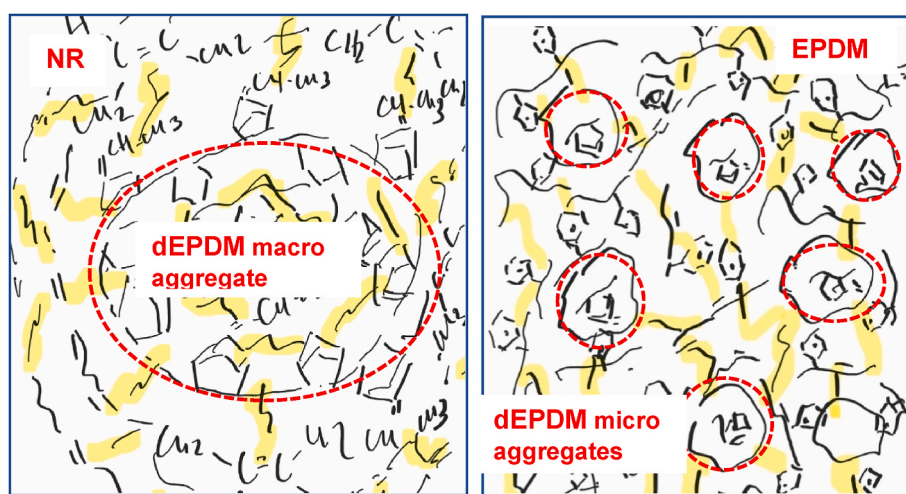


Fig. 8. dEPDM aggregate schema. a) macro aggregate with a NR matrix, b) dispersed micro aggregate with EPDM matrix.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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