

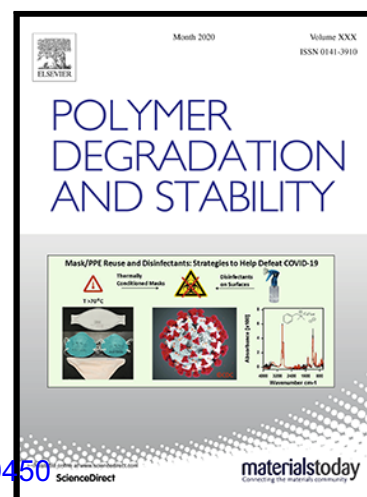
Assessment of the devulcanization process of EPDM waste from roofing systems by combined thermomechanical/microwave procedures

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Highlights

- Devulcanization based on a combined thermo-mechanical and microwave treatments has been suggested as an efficient way to recycle EPDM elastomeric waste
- Horikx plot show that the combined process is more specific than the thermomechanical, acting more selectively on the disulfide bonds.
- The statistical analysis indicates the difference in efficiency of the combined treatment founding that BPO has more influence in the devulcanization than the effect of the temperature
- This study provides a new and effective way to recycle EPDM and shows great application potentials.

Journal Pre-proof

Assessment of the devulcanization process of EPDM waste from roofing systems by combined thermomechanical/microwave procedures

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ABSTRACT

Ethylene-propylene-diene rubber (EPDM) is a elastomer widely used in common industrial applications. EPDM can be shaped into sheets and employed as isolating material for roofing systems. In this study, scraps of EPDM from commercial, industrial and residential roofing systems were treated by combined thermo-mechanical and microwave devulcanization processes including peroxide of benzoyl (BPO). The devulcanized EPDM (Dev-EPDM) was characterized by cross-link density, Horikx plot, sol fraction content, SEM and TGA analysis. In order to assess the effect of the different factors implied (type of devulcanization process, temperature and amount of BPO), the Fractional Factorial Design (FFD) method has been applied. The obtained



results show that, when thermo-mechanical and microwave methods are combined, produce an intense devulcanization effect. It was also found that the presence of BPO has significant influence in the devulcanization and that the effect of the temperature is related to the amount of BPO.

1. Introduction

Ethylene-propylene-diene monomer (EPDM) was introduced to the market of synthetic rubbers in 1963, and nowadays is one of the most used synthetic rubbers. It has found application in automotive (profiles, hoses, and seals), building and construction, cable and wire insulation, and appliances for a wide variety of molded articles. According to EPDM Market Size, Share & Trends Analysis Report by Application [1], over the period between 2016 and 2024, the development of the EPDM market will continue expanding, basically linked to the growth of the automotive industry. There are other key end-use industries that will also promote growth opportunities for the global EPDM market in the next few years. The EPDM market for the plastics (polymer modification) and construction industries will expand up to 5.2% and 5.5% CAGRs (compound annual growth rate), respectively, from 2016 to 2024. Part of this growth is related to the progressive replacement of other synthetic rubbers like SBR, NBR or BR by EPDM, due to its excellent properties. EPDM has high resistance to UV radiation, ozone, temperature and aging, presents high flexibility and elongation over 300% at wide temperature conditions, showing a good performance in building applications across different climate conditions worldwide.

Despite being an inert material with limited environmental impact, EPDM is used in a cross-linked form and this feature makes its recycling difficult. One of the effective industrial-scale methods for the reuse of EPDM waste is the reclaiming/devulcanization. During the devulcanization process, the three-dimensional network of cross-linked rubber is broken by means of thermal, mechanical or chemical energy. The devulcanization of elastomer wastes is suitable for the production of new elastomeric materials by mixing the devulcanized product with fresh synthetic or



natural rubber. An industrial method for EPDM recycling have been proposed by Mohaved et al. [2]

Formela et al. have studied different thermomechanical processes to reclaim ground tire rubber (GTR) by means a co-rotating extruder [3]. They have also reclaimed GTR at ambient temperature, in order to reduce the energy costs, using a two-roll mill [4] or by means of a mechano-chemical method using road bitumen 160/220, which was used as reactive plasticizer, combined with microwave radiation [5,6]. In order to reclaim/devulcanize GTR and industrial elastomers, many additional methods have been proposed, including other thermomechanical and microwave treatments [7,8], thermomechanical methods with dual function disulfide chemicals [9], thermomechanical utilizing silane-based tetrasulfides as devulcanizing agents [10,11], ultrasound processes [12,13], supercritical CO₂ [14], or microbial [15,16].

Microwave radiation constitutes an interesting and efficient technology to reclaim elastomeric materials at low temperature in a short processing time. The use of microwaves allows a controlled thermal degradation in a process of high efficiency combined with environmentally-friendly features. Compared to other heating methods based on convection or conduction, microwaves permit a precise and fast increase of the temperature inside the heated material, generated by dipole rotation, ionic conduction and interfacial polarization (Maxwell-Wagner effect) [17-19].

The application of microwaves (MW) to the devulcanization of rubber has also drawbacks: i) the rubber must be free of metals impurities and ii) some rubbers like EPDM are non-polar and non-affected by the microwave radiation. In this last case, the presence of a microwave absorbent like carbon black induces the heating of non-polar rubbers as demonstrated by several researchers. Kleps et al. [20] investigated the effect of microwave exposure time on structural changes in different elastomeric vulcanizates samples (NR, SBR, EPDM), using TGA as a characterization technique to analyze the crosslinking changes and the efficiency of devulcanization method. Colom et al. [21] analyzed by FTIR the effect of MW treatment on three different types of GTR, the obtained results indicate a strong correlation between the content of SiO₂ in the GTR and the achieved degree of devulcanization concluding that the presence of silica fillers improves microwave devulcanization efficiency. Formela et al [22] have

reported the recent progress in microwave treatments of vulcanized rubbers with different compositions. Special attention is devoted to the correlation between microwave processing parameters and devulcanization efficiency.

In order to analyze the degree of devulcanization related to the selective breaking of the crosslinking S-S bonds compared to the scission of the main polymeric chains, the Horikx plot can be very useful, allowing the comparison between different devulcanization processes. Sawairi et al. [23] used a Horikx plot to evaluate the ratio between random to cross-link scission in thermo-mechanical devulcanization of NR and EPDM, analyzing the influence of temperature and concentration of the devulcanization agent. Fabiula et al. [24] studied the chemical modifications and thermo-oxidative degradation of the GTR by microwaves as a function of the exposure time and found that NR phase of the GTR is more degraded than the SBR phase.

The present work is focused on waste rubber recycling as a continuation of the authors' research in this field [25-27]. In order to move a step forward towards the solution of this important issue, we propose a new devulcanizing method combining a thermomechanical (TM) and a microwave (MW) process, comparing the results to a plain thermomechanical method. The influence of the temperature and the presence of benzoyl peroxide (BPO) will be also analyzed. In order to understand the influence of each one of these factors, the cross-link degree (CLKD), sol fraction (SF), Horikx plot, SEM and thermal stability of the devulcanized samples by thermogravimetric analysis (TGA) have been studied. Also, a statistical analysis has been carried out to evaluate the effects of different parameters on the response variables.

2. Experimental

2.1.- Materials

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



2.2.- Devulcanization

Combined thermo-mechanical and microwave devulcanization processes have been performed in two steps: thermo-mechanical treatment in a Brabender plastograph equipment and microwave irradiation in a prototype microwave oven adapted with a motorized stirring system made of PTFE according to a design that has been used in our previous research [27].

The microwave oven has been constructed in our lab. As mentioned above, the system is based in a conventional microwave oven provided with a sample container of PTFE adapted with a motorized stirring system in PTFE. The design of the container and the stirrer favors a homogeneous irradiation of the sample. Power and time of irradiation can be controlled independently. Samples of 60 g GTR were used. The devulcanization process was performed setting the magnetron power to 700W, 80 rpm of the stirrer and 3 minutes of MW exposure. According to Pistor et al [19] microwave devulcanization process has been carried out for 3 minutes in order to avoid auto-ignition phenomena that could burn the sample.

The thermo-mechanical devulcanization of the waste EPDM in the Brabender plastograph included the addition of different amounts of benzoyl peroxide (0,2,4 phr) at two temperatures of 80 and 110 °C. The weight of the obtained sheets of waste EPDM was 60 g. They were previously chopped with a cutting mill (Retsch SM100, Germany) using an aperture size ring of 2 mm and fed into the hopper of the mixer. The rotor speed of the mixer was kept constant at 60 rpm and the processing time was 30 minutes.

After devulcanization process, the samples were homogenized in a laboratory two-roll mills and were named as 80 or 110 according to the thermo-mechanical devulcanization temperature. The nomenclature for the different samples is shown in table 1.



Table 1.- Nomenclature of the samples

	80 °C		110 °C
1/80	TM 0BPO 80	1/110	TM0 0BPO 110
2/80	TM/MW 0BPO 80	2/110	TM/MW 0BPO 110
3/80	TM 2BPO 80	3/110	TM 2BPO 110
4/80	TM/MW 2BPO 80	4/110	TM/MW 2BPO 110
5/80	TM 4BPO 80	5/110	TM 4BPO 110
6/80	TM/MW 4BPO 80	6/110	TM/MW 4BPO 110

2.1.- Measurements

The **swelling degree** of the samples (0.2 g) was determined by equilibrium swelling in toluene (room temperature) after immersion in the medium for 72h. The swelling degree was calculated in accordance with the formula (1):

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

where: Q – swelling degree; m_t – mass of the sample swollen (g); m_o – initial mass of sample (g).



The **cross-link density** was determined by equilibrium swelling in toluene (room temperature, 72 h, refreshing the solvent every 24 h), according to the Flory-Rehner equation [28] (2):

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

where: v_e – cross-link density, mol/cm³; V_r – gel volume in the swollen sample; V_1 – solvent molar volume (toluene = 106.2, cm³/mol); χ – polymer-solvent interaction parameter (in the calculations, it was assumed to be 0.48) [29]

Gel volume in the swollen sample was calculated according equation (3):

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

where: m_p – the weight of the dry polymer, g; ρ_p – the density of the dry polymer g/cm³; m_s – the weight of solvent absorbed by polymer, g; ρ_s – the density of the solvent.

The Flory-Rehner equation can be applied for non-filled compounds, but the studied samples contain carbon black. Kraus correction for filled compounds was applied to calculate the actual remaining cross-link density according equations [30] (4) and (5):

$$v_{\text{after correction}} = \frac{v_e}{1 + K \times \Phi} \quad (4)$$

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

where: v_e – the measured chemical cross-link density, mol/cm³; $v_{\text{after correction}}$ – the actual chemical cross-link density, mol/cm³; K – constant characteristic of the filler but independent of the solvent; φ_f – the volume fraction of filler in the sample which is calculated; ρ_r – the density of studied compound, g/cm³; m_0 – the weight of sample before extraction, g; ρ_f – the density of filler, g/cm³; m_{dry} – the weight of sample after extraction, g

Sol fraction was calculated as mass difference of EPDM devulcanized before swelling (W_1) and after extraction (W_2), according to equation (6):

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

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851 apparatus (USA). EPDM elastomers weighing approx. 15 mg were placed in a corundum dish. The measurement was conducted in the temperature range 25-800 °C and under oxygen atmosphere (50 ml/min), at a heating rate of 20 °C/min.

Scanning Electron Microscopy (SEM) was used to qualitatively examine the surface of the samples devulcanized/reclaimed by different methods. Several images of the samples were taken in a JEOL 5610 microscope. Previously to the observations the samples were covered with a fine layer of gold-palladium to increase their conductivity in a vacuum chamber.

Horikx Plot is a useful tool to further understand the devulcanization mechanism developed by Horikx [31] where the cross-link density of the rubber gel fractions and the rubber sol fraction of the devulcanizates are interrelated. Horikx derived a theoretical relationship between the soluble fraction generated after degradation of a polymer network and the relative decrease in cross-link density, as a result of either main-chain scission or cross-link rupture. Horikx plot can be applied to rubber devulcanization, in which also a mix of main-chain scission and cross-link rupture takes



place. When main-chain scission takes place, the relative decrease in cross-link density is given according equation (7):

$$1 - \frac{\nu_f}{\nu_i} = 1 - \left[\frac{(1 - s_f^{1/2})^2}{1 - s_i^{1/2}} \right] \quad (7)$$

where s_i is the soluble fraction of the rubber network before reclaiming, s_f is the soluble fraction of the reclaimed sample, ν_i is the cross-link density of the network prior to devulcanized treatment, and ν_f is the cross-link density of the reclaimed sample. For only cross-link scission, the soluble fraction is related to the relative decrease in cross-link density according equation (8):

$$1 - \frac{\nu_f}{\nu_i} = \left[\frac{\gamma_f (1 - s_f^{1/2})^2}{\gamma_i (1 - s_i^{1/2})^2} \right] \quad (8)$$

where the parameters γ_f and γ_i are the average number of cross-links per chain in the insoluble network after and before devulcanization, respectively. The values for γ_f and γ_i are determined as described by Verbruggen et al. [32].

Fractional Factorial Design (FFD)

Fractional factorial design has been used to investigate the effect of different parameters on the response variables. To reduce the total number of experiments, fractional factorial designs involve a carefully chosen fraction of the experimental setting, instead of trying all possible combinations of settings (full factorial designs).

In this paper we use different control factors like: system of devulcanization process (devulc process), temperature (T) and content of BPO (BPO). Each systems has two levels, high and low, and these two levels correspond to the conditions included in Table 2. A 2^{3-1} fractional factorial design with 2 replicates is used to study the effects of the control factors on the responses.

Table 2.- Factor sampling values

Factors	Low level	High Level 1	High Level 2
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Nature of devulcanization	TM	TM/MW	TM/MW
Temperature	80	110	110
Content of BPO	0	2	4

3. Results and Discussion

3.1. Cross-link density and sol fraction of EPDM

As shown in the Figure 1, samples that have been devulcanized using the combined method TM/MW at 80°C have a lower degree of cross-linking than samples at same temperature that have been treated only with the TM method. This means that the method TM/MW is more efficient than the TM method, and the samples treated with a combination of thermo-mechanical and microwave devulcanization are more devulcanized. The effect of the temperature is not so clear. When the temperature is increased from 80 to 110 °C the cross-linking degree does not show a substantial variation, except with samples with 0BPO. In a first look, seems that the treatment at 80°C provides more devulcanization than the one at 110°C.

The influence of the addition of BPO to the devulcanization process can be observed in figure 1. BPO appears to be more effective in samples submitted to a combined TM/MW devulcanization than in a TM process. The addition of 2 and 4 phr of BPO reduces the crosslinking of TM/MW samples mainly with 2BPO. According to Rooj et al. [33] at 80 °C, benzoyl peroxide undergoes free radical chain scission, which produces highly unstable benzoyl radicals used as initiators in typical polymerization reactions. Due to their instability, the radicals spontaneously react with the sulfur present in the cured rubber. Obtained results show that the reduction of crosslinking is higher using 2 phr BPO than 4 phr BPO, this is due that after the scission of S-S; C-S and C-C bonds, it is possible a recombination of some of the produced macro radicals (i.e., re-crosslinking). This phenomenon, known as cage effect, may have also led to decrease of the sol fraction. According to Malihe Sabzekar et al. [34] an increase of the



temperature in devulcanization process also caused cage effect with concentration of 4 phr BPO.

Figure 2 shows sol fraction results as a function of the BPO content. As can be seen, the TM/MW combined devulcanization process produces better results than the devulcanization with TM. The best results are obtained at 80°C with 2 phr BPO, although with a content of 4 phr BPO better results than without BPO have been observed. As commented previously, the cage effect provokes these reductions of sol content in samples with 4phr BPO compared with the 2phr BPO samples. It seems that this effect takes place during the MW treatment.

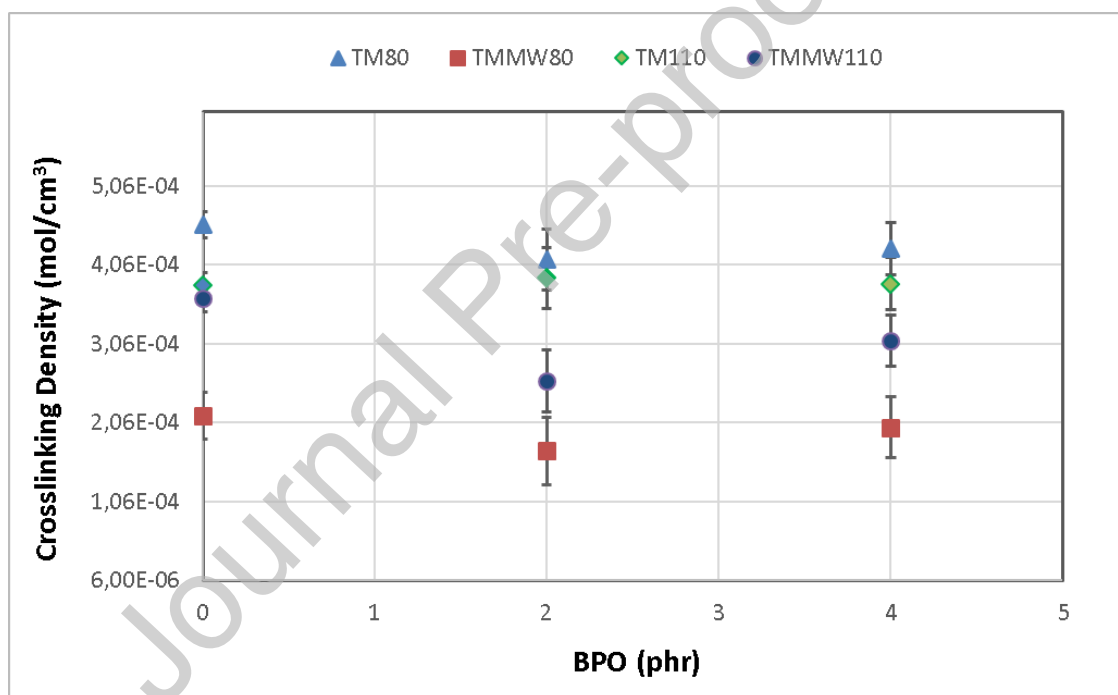


Figure 1. Crosslink density of EPDM devulcanizates as a function of amount of BPO (0,2,4). Reference value of crosslink density of not devulcanized EPDM is $5,25E-04 \text{ mol/cm}^3$



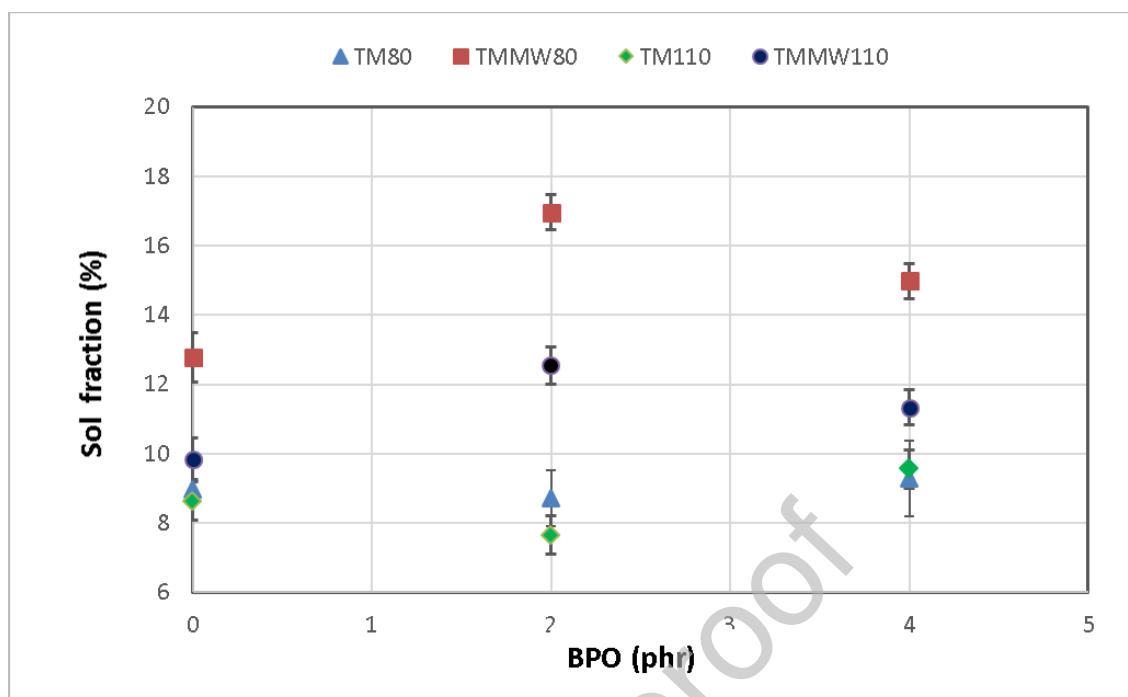


Figure 2. Sol fraction of EPDM devulcanizates as a function of amount of BPO (0,2,4). Reference value of sol fraction of not devulcanized EPDM is 4,5%.

The best results are obtained at 80°C with the combined TM/MW process, this is due to the fact that the devulcanization with the TM process is less aggressive, and BPO does not suffer thermal decomposition [35] and can improve the consecutive vulcanization with MW. In the devulcanization process using only TM, the sol content values obtained are independent of the temperature and the BPO content, this means that the BPO acts basically in the MW process. Therefore, a reasonable content of not degraded BPO (2phr) improves the devulcanization by MW and it is related to the observed sol content increase.

The breaking of the S-S bridges or the C-C of the main chain in the elastomeric material depends on the type of process used, the amount of BPO and the temperature. In order to differentiate the type of bond breaking that has taken place, the Horikx plot can be used. The main goal is comparing the type of scission (S-S vs C-C) that occurs during the studied devulcanization processes.

The Horikx plot with the studied samples is presented at Figure 3. It can be observed that the samples that have been devulcanized using the combined TM/MW method (coloured blue) have undergone a more selective type of scission than the samples devulcanized only by the TM process (yellow points). The 70% of the samples devulcanized using TM/MW have a relative decrease in crosslinking density higher than 0,50 and are close to the crosslinking scission line. On the other hand, samples devulcanized only with the TM process are quite close to the reference EPDM value, which means that decrease in crosslinking density is low and the not very high compared to the values of the waste EPDM reference.

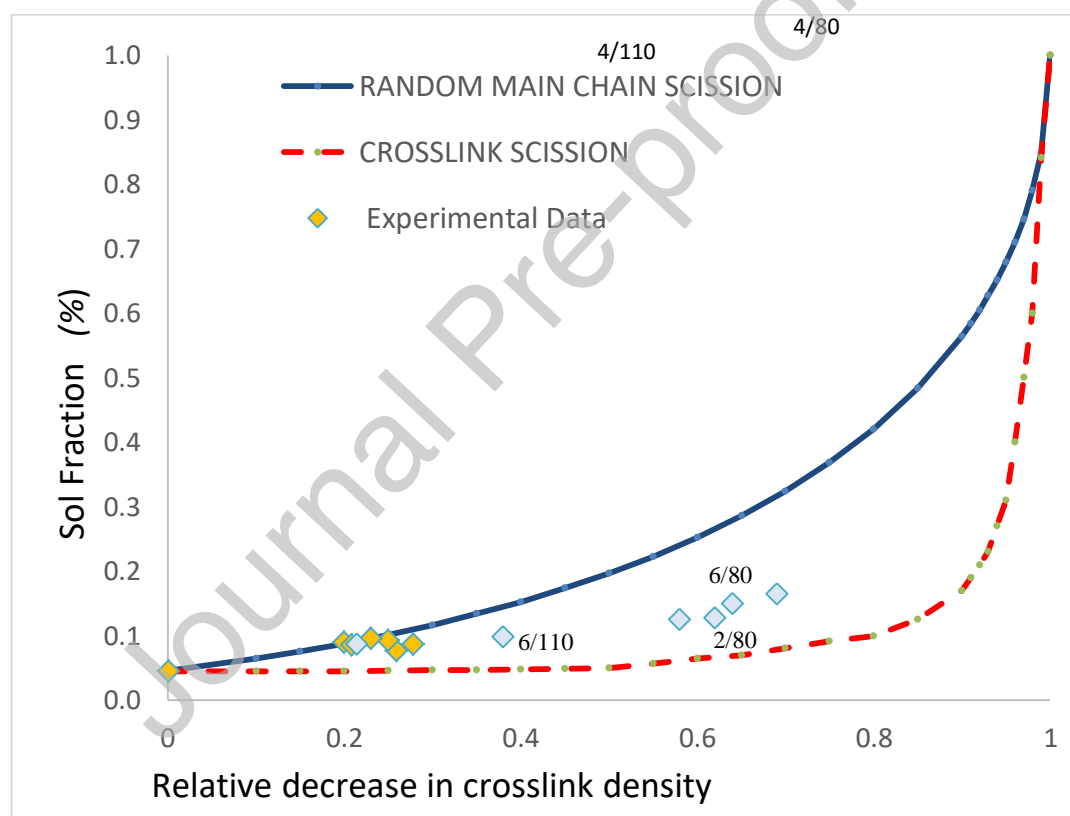


Figure 3. Random main chain scission and crosslink scission curves in a Horikx plot for EPDM devulcanized samples. The points colored in yellow correspond to samples devulcanized by TM and the blue to samples devulcanized by TM/WM.

The Horikx plot shows also a difference in the selectivity of the processes, the blue points related to the TM/WM are clearly situated around the crosslinking scission line, while the yellow (related to TM process), even at the lower decreases of crosslinking density remarked above, tend to be closer to the random main scission.

In terms of efficiency of the devulcanization, the best results correspond to the combined TM/WM devulcanization process at 80°C with 2phr of BPO (4/80). Samples devulcanized at higher temperature show less decrease of the crosslinking degree. This phenomenon can be related to the mechanism of reaction of the BPO and the effect of the temperature. As described previously, BPO experiences homolytic free radical scission, which produces highly unstable benzoyl radicals. According to the mentioned study of Rooj et al. [33] the reaction mechanism of BPO with EPDM can be divided in three steps. In the first step, BPO suffer homolytic cleavage resulting the formation of benzoyl radical (PhCOO^*). In the next immediate step, benzoyl radical will undergo further cleavage to form a phenyl radical. The phenyl radical is highly unstable in nature and readily reacts with the weakest S–S bond of the vulcanized EPDM at the transverse position and causes, in the final step, a crosslink scission. In this case, the radicals react equally with the sulfur included in the waste EPDM.

Verbruggen et al. [32] observed that, when curing EPDM with sulfur, at high temperatures, the reactivity was higher using disulfides than peroxides and, at low temperatures, the reactivity of peroxides is higher than disulfides. The effect of a temperature increase is not related to an increase of the reactivity of the BPO, hence the effects obtained at 80°C are more intense than at 110°C.

The increase in the concentration of BPO (4phr) does not provide an increase of the efficiency of the process. According to the Horikx plot, samples with 4phr BPO tend to be closer to the line related to the scission of C-C bonds. Probably the excessive presence of radicals produces an indiscriminate reaction that affects both S-S and C-C bonds. The optimal concentration was 2 phr.



As conclusion, the presence of BPO improves the results obtained in the treatment by microwave. The presence of the benzoyl radical in contact with the waste EPDM particles, favours the scission of polysulfide and disulfide cross-links, leaving a structure of devulcanized samples constituted basically by monosulfide cross-links [36].

3.2. Thermogravimetric analysis of EPDM

The thermogravimetric analysis (TGA) of the devulcanized samples was conducted in air atmosphere. These conditions allow a thermo-oxidative degradation in the presence of oxygen. The experiments were carried out until the complete degradation of the organic components and carbon black of the sample, in order to determine the stability of the samples after the devulcanization process and to obtain the amount of inorganic residues. According to Zanchett et al. [35] the TGA of EPDM from 25 to 800°C (Figure 4) presents different steps: first at 380°C (peak temperature of DTG curve) a change due to the action of the heat on plasticizers, second step (peak temperature of DTG curve at 480°C) with a mass loss of 38% assigned to the decomposition of EPDM, third at 520°C the thermal degradation of inorganic filler, and four, a broad band at 673°C corresponding to oxidative reaction of carbon black to CO₂. The final residua (lower than 10%) corresponds to inorganic decomposition products.

The data obtained by TGA, DTG and cross-link density corroborated the previous results, showing that the combined TM/MW process produces a more efficient devulcanization than the TM.



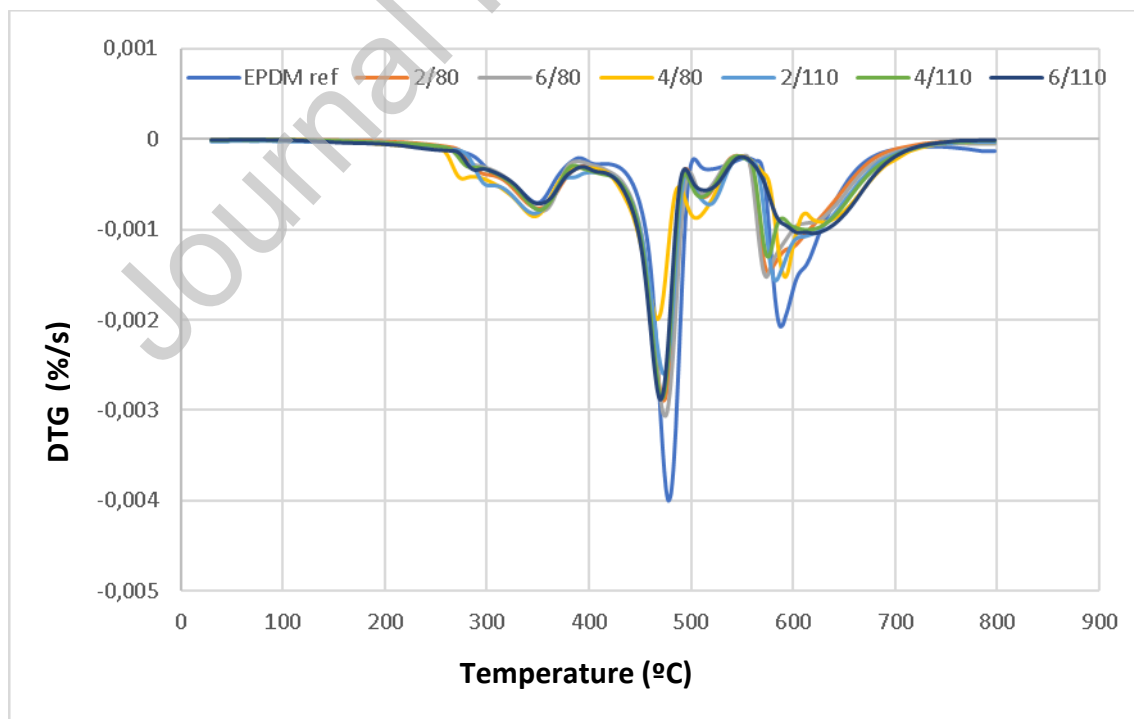
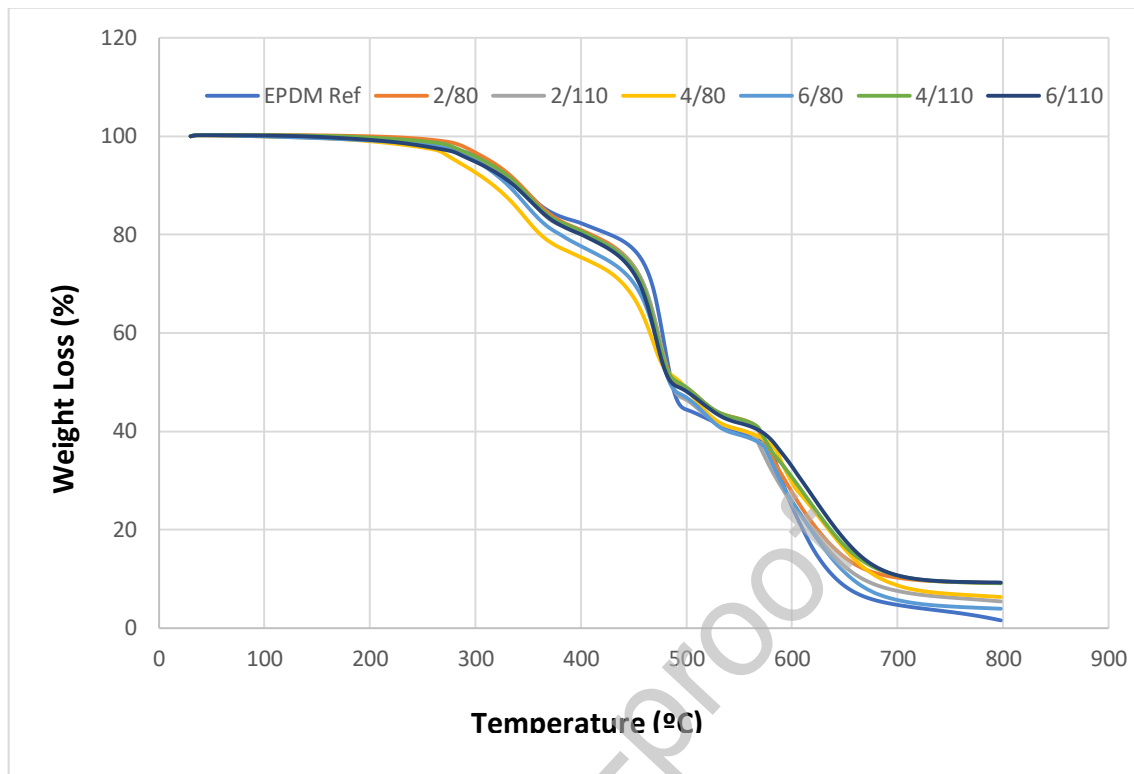


Figure 4. TGA and DTG curves measured in air atmosphere and heating rate of 20°C/min. DTG (derivative thermogravimetry), TGA (thermogravimetric analysis). TM (Thermo-mechanical devulcanization) with Brabender at 80 or 110°C and 0,2,4 BPO means amount of benzoyl peroxide, TM/MW (Thermomechanical and Microwave devulcanization at 80 or 110°C and 0,2,4 BPO denotes to amount of Benzoyl Peroxide)

The results of TGA and DTG of different samples devulcanized using TM and TM/MW at the two temperatures studied (80 and 110°C) with 2 and 4BPO are presented in Figure 3 and summarized in Table 3. The maximum thermal stability corresponds to the EPDM reference with a value of 481°C, and thermal stability decrease as a function of degree of devulcanization. Thermal stability of devulcanized samples with TM/MW and TM define values lower to 473°C. it means that the devulcanized process reduce their thermal stability. Both processes cause a lower temperature of degradation compared to the reference, but the TM/MW has a higher effect in the scission of main chain and S-S bridges than TM, giving values of thermal stability slightly lower, corroborating the results discussed previously.

Table 3 shows the content of volatile compounds, EPDM and residua (%) for each devulcanized sample. According to the obtained values, the devulcanization processes reduces the weight of volatile compounds and overall the amount of EPDM rubber in all the samples. The devulcanization by TM and combined TM/MW process shreds and shears the sample while the MW heats it, thereby releasing part of the plasticizer that decrease slightly as well as the EPDM. The weight of inorganic residua increases significantly from 2,1% until values higher to 9%. This increase of the relative content of residua is due to the modification of the percentages of the components of the sample caused by the treatments. The decrease of EPDM rubber is slightly higher in TM/MW samples than TM and in samples treated at 110 than 80°C. The same behavior has been observed by Colom et al [21] analyzing the MW devulcanization of GTR.

Table 3. Thermal decomposition data and volatile compounds, EPDM and residues content (%) for each devulcanized sample and reference

Sample	Volatile (%) Compounds	EPDM rubber (%)	Residues (%)	Thermal Decomposition EPDM (°C)
EPDM ref	21.7	38.0	2.1	481
1/80	18.0	34.0	7.5	472
2/80	18.2	32.3	8.5	470
3/80	18.2	33.8	9.1	473
4/80	18.2	33.5	7.6	469
5/80	17.6	35.0	8.2	471
6/80	19.0	33.5	6.2	467
1/110	16.8	32.5	9.3	472
2/110	18.8	32.5	4.9	472
3/110	17.1	33.1	8.2	472
4/110	18.1	32.2	8.1	470
5/110	17.8	33.0	6.5	471
6/110	18.4	32.3	4.6	470

3.3. Scanning Electron Microscopy of EPDM

Figure 4 show the surface morphology, of waste EPDM treated by TM and TM/MW devulcanization. The picture A shows the sample 5/80 (TM80 0BPO), which presents more heterogeneity than other samples. The treatment with microwaves (picture B-D) reduce the heterogeneities and generates a smoother surface with particles smaller than 10 microns. The shapes of the particles of sample 4/80 picture C is more regular than particles B and D. The surface is polished due to the MW treatment. When the particles are submitted to the microwave process, the size of the particles remains

relatively constant, but the surface appearance changes as a function of the amount of BPO. In EPDM waste particles submitted at TM80 0BPO, the surface shows roughness and sometimes even holes and pores. As exposed before, this roughness decreases with MW treatment, which reduces and removes partially some of the conglomerates that are generated with the thermo mechanical devulcanization (picture B) The effect also includes volatilization of plasticizers (temperatures higher to 320°C), decomposition of EPDM additives and, oxidation of carbon black to CO₂ [20]. The presence of BPO decrease the development of a roughness surface (picture C) and the action of MW also reduce the volume of agglomerated particles (picture D).

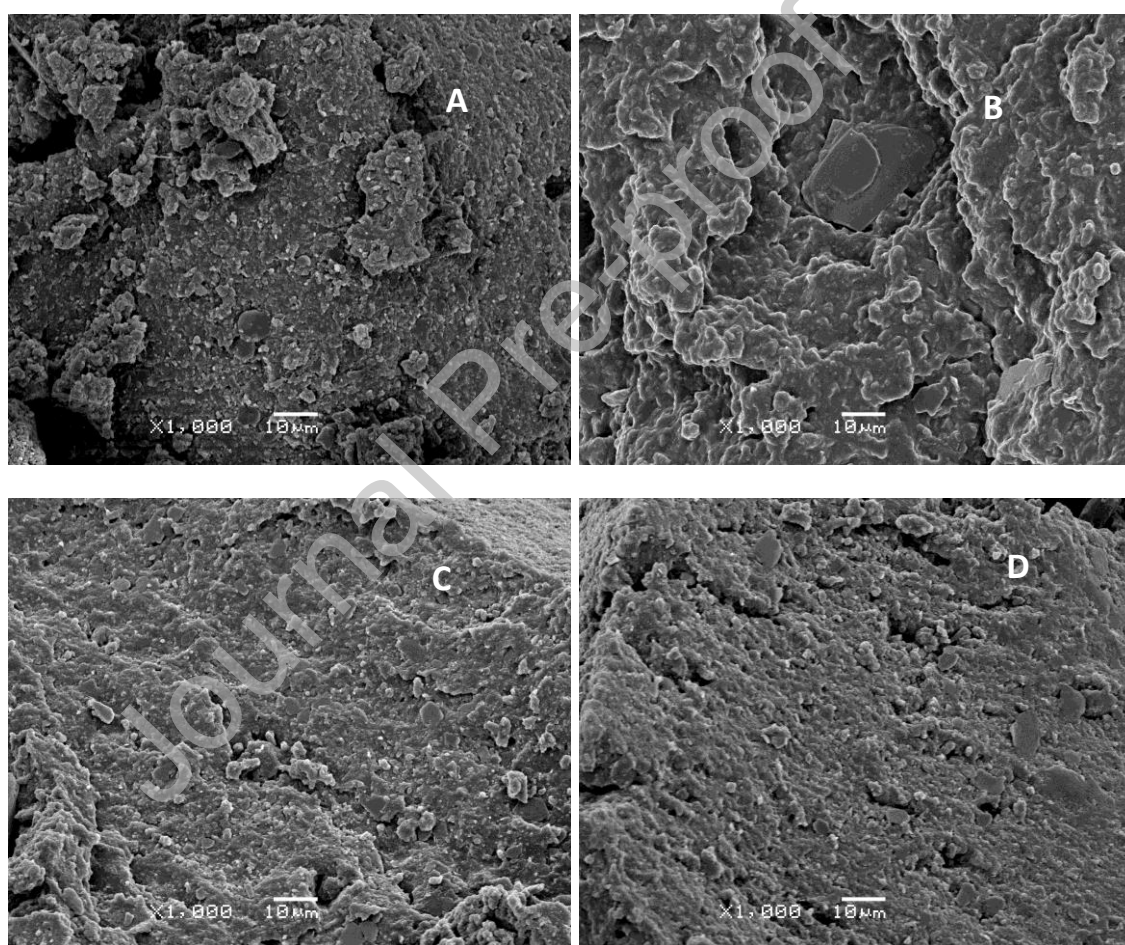


Figure 4. SEM microphotography of a) TM80 0BPO, b) TM/MW80 0BPO, c) TM80 4BPO, d) TM/MW80 4BPO

3.4. Statistical analysis of the influence of amount BPO and temperature in the cross-linking degree for samples

The assessment of the results using fractional factorial design (FFD) implies that it is possible to estimate the main effects of the factors, but it is not possible to estimate their interactions [36]. In fact, the interactions in this scheme are so-called confounded, and the main effects can only be analyzed by assuming that these interactions are ignored. Tables 4 and 5 show the variance analysis of the results, where cross-linking has been chosen as an experimental response (CLK02 corresponding to 2phr BPO and CLK04 to 4phr BPO). Results show that the type of devulcanization process is significant, the temperature factor is not and the amount of BPO factor is partially significant (with α equal to 0.1 significant).

The regression model considering all factors for CLK02 is:

$$\text{CLK02} = 6.298 - 1.438 \text{ Devulcanization} + 0.198 \text{ Temp} - 0.707 \text{ BPO}$$

The coefficient R^2 has been calculated and the value was 88.61%, indicating that this is a good model for describing response variables.

According with this regression model and P-Value parameter, devulcanization process with a P-value of 0.008 has great influence in crosslinking results, amount of BPO (P-Value 0.071) is significant and temperature isn't significant and depends of amount of BPO.

Table 4 Variance analysis of CLK02

Source	DF	Adj SS	Adj MS	F-Value	P-Value
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Model	3	5.21194	1.73731	10.38	0.023
Linear	3	5.21194	1.73731	10.38	0.023
Devulc	1	4.13281	4.13281	24.69	0.008
Temp	1	0.07801	0.07801	0.47	0.532
BPO	1	1.00111	1.00111	5.98	0.071
S	R-sq	R-sq(adj)	R-sq(pred)		
0.409161	88.61%	80.08%	54.46%		

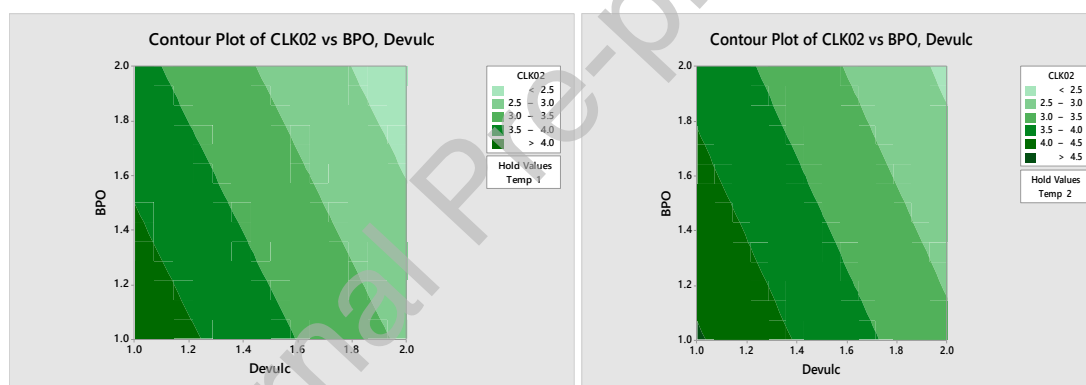


Figure 5.- Contour Plot of crosslinking degree for the sample 0 and 2 BPO a) 80°C and b) 110°C

Table 5 variance analysis of CLK04

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	3	7.9885	2.6628	17.92	0.009
Linear	3	7.9885	2.6628	17.92	0.009

Devulc	1	3.9060	3.9060	26.28	0.007
Temp	1	1.5400	1.5400	10.36	0.032
BPO	1	2.5425	2.5425	17.11	0.014
S	R-sq	R-sq(adj)	R-sq(pred)		
0.385535	93.07%	87.88%	72.29%		

In case of CLK04 the coefficient (R^2) is 93,07%, indicating that this is a good model quality for describing response variables. The regression model considering all factors for CLK04 is:

$$\text{CLK04} = 6.063 - 1.398 \text{ Devulcanization} + 0.878 \text{ Temp} - 1.127 \text{ BPO}$$

P-Value parameters are higher when comparing the degree of crosslinking using 4 than 2 phr of BPO. That means that the influence of BPO in devulcanization process is higher when the amount of BPO increase (i.e 0.007 in front of 0.008), although the difference is minimum. This statistical analysis corroborates the results obtained by Horikx plot.

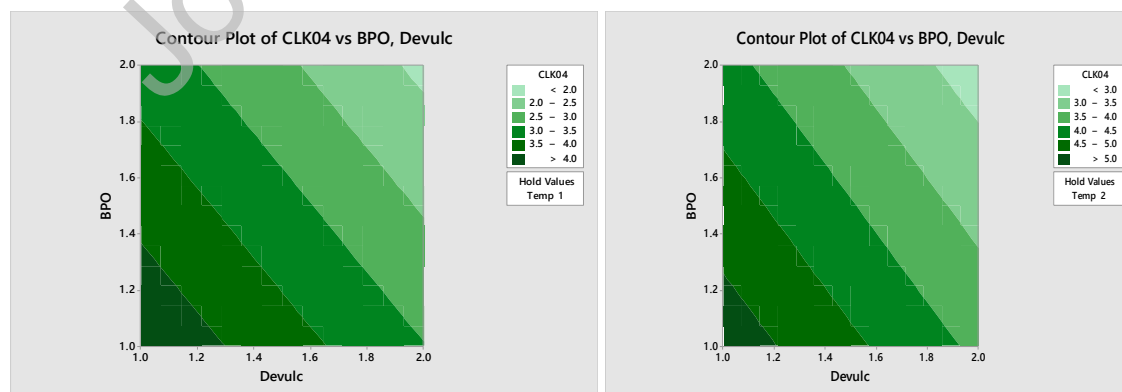


Figure 6.- Contour Plot of crosslinking degree for the sample 0 and 4 BPO a) 80°C and b) 110°C

4.- Conclusions

The use of a devulcanization process based on a combined thermo-mechanical and microwave treatments has been postulated as a way to recycle EPDM waste. Results show that the combined process is more efficient, causing a higher decrease of cross-linking determined by sol fraction, cross-link density and thermogravimetric analysis. At the same time, the process is more specific, acting more selectively on the disulfide bonds and sparing the main polymeric chain, obtaining a product that is more similar to the original fresh EPDM.

The addition of BPO increases the efficiency of the treatment because of the radicals reacting with the disulfide bonds and causing its scission. The optimum concentration of BPO is around 2phr, higher values do not provide better results.

The temperature also has an effect in the process, the treatment at 80°C provides better results than at 110°C. This effect is related to the mechanism of decomposition of BPO.

Microwave treatment combined to the thermo-mechanical, provides at the same time a material that is more homogeneous.

The statistical analysis of the results indicates the big difference in efficiency of the combined treatment compared to the thermo-mechanical and highlights the importance of the presence of BPO instead of temperature that is not a significant parameter in studied conditions.

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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.

References

- 1.- Ethylene Propylene Diene Monomer (EPDM) Market Size, Share & Trends Analysis Report By Application (Electrical & Electronics, Building & Construction, Wires & Cables), And Segment Forecasts, 2019 – 2025
<https://www.grandviewresearch.com/industry-analysis/ethylene-propylene-diene-monomer-epdm-market> (June 2020)
- 2.- Mohaved, S. O; Ansarifar, A; Nezhad, S.K; Atharyfar, S. A novel industrial technique for recycling ethylene-propylene-diene waste rubber, *Polymer Degradation and Stability*, Volume 111, (2015) 114-123
- 3.- Formela, K. Cysewska, M. Efficiency of thermomechanical reclaiming of ground tire rubber conducted in counter-rotating and co-rotating twin screw extruder, *Polimery* 59 (3) (2014) 231-238.
- 4.- Formela, K. Klein, M. Colom, X. Saeb M. R. “Investigating the combined impact of plasticizer and shear force on the efficiency of low temperature reclaiming of ground tire rubber (GTR)” *Polymer Degradation and Stability* 125 (2016) 1-11.



- 5.- Formela, K., Sulkowski, M., Saeb, M.R., Colom, X., Haponiuk, J.T. Assessment of microstructure, physical and thermal properties of bitumen modified with LDPE/GTR/elastomer ternary blends *Construction and Building Materials* 106, (2016) 160-167
- 6.- Zedler Ł, Klein M, Saeb, M. R. Colom, X. Cañavate, J. Formela K. "Synergistic Effects of Bitumen Plasticization and Microwave Treatment on Short-Term Devulcanization of Ground Tire Rubber" *Polymers* 2018, 10, 1265.
- 7.-Jana, G.k, Das, C. K. "Devulcanization of Natural Rubber Vulcanizates by Mechanochemical Process," *Polymer-Plastics Technology and Engineering*, vol. 44, (2005) pp. 1399-1412,
- 8.- Microwave devulcanization of rubber." U.S. Patent No. 4,104,205. 1 Aug. 1978.
- 9.- Ghorai, S; Bhunia, S; Roy, M; De, D; Mechanochemical devulcanization of natural rubber vulcanizate by dual function disulfide chemicals, *Polym. Degrad. Stab.* 129 (2016) 34-46, doi.org/10.1016/j.polymdegradstab.2016.03.02
- 10.- Ghorai S, Mondal D, Hait S, Ghosh AK, Wiessner S, Das A, De D. Devulcanization of Waste Rubber and Generation of Active Sites for Silica Reinforcement. *ACS Omega*. 2019 (18):17623-17633. doi: 10.1021/acsomega.9b01424. PMID: 31681869; PMCID: PMC6822114.
- 11.- Ghosh, J; Hait, S; Ghorai, S; Mondal, D; Wießner, S; Das, A; De, D. Cradle-to-cradle approach to waste tyres and development of silica based green tyre composites, *Resources, Conservation and Recycling*, Volume 154, (2020) 104629, ISSN 0921-3449, <https://doi.org/10.1016/j.resconrec.2019.104629>.
- 12.- Tukachinsky A, Schworm D, Isayev A.I. Devulcanization of waste tire rubber by powerful ultrasound. *Rubber Chem Technol* 1996; 69:92-103.
- 13.- Isayev, A., T. Liang and Todd M. Lewis. "Effect of particle size on ultrasonic devulcanization of tire rubber in twin-screw extruder." *Rubber Chemistry and Technology* 87 (2014): 86-102.
- 14.- Mangili, I. Collina, E. Anzano, M. Pitea, D. Lasagni, M. Characterization and supercritical CO₂ devulcanization of cryo-ground tire rubber: influence of devulcanization process son reclaimed, *Polymer Degradation and Stability* 102 (2014) 15-24.



- 15.- Yao C, Zhao S, Wang Y, Wang B, Wei M, Hu M. Microbial desulfurization of waste latex rubber with Alicyclobacillus sp. *Polym Degrad Stab* 2013;98:1724-30.
- 16.- Li Y, Zhao S, Wang Y. Microbial desulfurization of ground tire rubber by thiobacillus ferrooxidans. *Polymer Degradation and Stability* 2011; 96:1662-68
- 17.- Menéndez J. A., Arenillas A., Fidalgo B., Fernández Y., Zubizarreta L., Calvo E. G., Bermúdez J. M.: Microwave heating processes involving carbon materials. *Fuel Processing Technology*, 91, (2010) 1–8
- 18.- Kwon S. K., Ahn J. M., Kim G. H., Chun C. H., Hwang J. S., Lee J. H.: Microwave absorbing properties of carbon black/silicone rubber blend. *Polymer Engineering and Science*, 42, (2002) 2165–2171.
- 19.- Pistor V., Scuracchio C. H., Oliveira P. J., Fiorio R., Zattera A. J.: Devulcanization of ethylene-propylene diene polymer residues by microwave – Influence of the presence of paraffinic oil. *Polymer Engineering and Science*, 51, (2011) 697–703
- 20.- Kleps T., Piaskiewicz M., Parasiewicz W.: The use of thermogravimetry in the study of rubber devulcanization. *Journal of Thermal Analysis and Calorimetry*, 60, (2000) 271–277
- 21.- Colom, X. Faliq, A. Formela, K. Cañavate J. FTIR spectroscopic and thermogravimetric characterization of ground tire rubber devulcanized by microwave treatment, *Polymer Testing* 52 (2016) 200-208.
- 22.- Formela, K. Hejna, A. Zedler, Ł. Colom, X. Cañavate J. Microwave treatment in waste rubber recycling -recent advances and limitations *eXPRESS Polymer Letters* Vol.13, No.6 (2019) 565–588
- 23.- Saiwari, S. Van Hoek, J.W. Dierkes, W. K. Reuvekamp, L. E.A.M. Heideman, G. Blume, A, Noordermeer: J. W.M. Upscaling of a Batch De-Vulcanization Process for Ground Car Tire Rubber to a Continuous Process in a Twin-Screw Extruder, *Materials* 2016, 9, 724
- 24.- Fabiula D. B. de Sousa, Scuracchio, C. H. Guo-Hua Hu, Hoppe S, Devulcanization of waste tire rubber by microwave. *Polymer Degradation and Stability*, 2017, 138, pp.169 - 181
- 25.- Cañavate, J. Casas, P. Colom, X. Nogués F. “Formulations for thermoplastic vulcanizates based on high density polyethylene, ethylene-propylene-diene monomer, and ground tire rubber” *Journal of Composite Materials* 45(11) (2011) 1189-1200



- 26.- Orrit-Prat, J. Mujal-Rosas, R. Rahhali, A. Marin-Genesca, M. Colom, X. Belana-Punseti J. "Dielectric and mechanical characterization of PVC composites with ground tire rubber" *Journal of Composite Materials* 45(11) (2010)1233–1243
- 27.- Colom, X. Marín-Genesca, M. Mujal, R. Formela, K. Cañavate J. Structural and physico-mechanical properties of natural rubber/GTR composites devulcanized by microwaves: Influence of GTR source and irradiation time. *Journal of Composite Materials* 52(22) (2018), 3099–3108
- 28.- Flory PJ and Rehner J. Statistical mechanics of crosslinked polymer networks I. rubberlike elasticity. *J Chem Phys*; 11: (1943) 512–520.
- 29.- Hrnjak-Murčić, Z. Jelenčić, J. Bravar, M. Marović M. Influence of the network on the interaction parameter in system EPDM vulcanizate–solvent, *Journal of Applied Polymer Science* 65: (1997) 991-999.
- 30.- Kraus GJ. Swelling of filler-reinforced vulcanizates. *Journal Applied Polymer Science* 7, (1963), 861–871.
- 31.- Horikx M. M. Chain Scissions in a Polymer Network, *Journal of Polymer Science* 19, (1956) 445.
- 32.- Verbruggen, M. A. L. Van der Does, L. Noordermeer, J. W. M. Van Duin, M. Manuel H. J. "Mechanisms Involved in the Recycling of NR and EPDM". *Rubber Chemistry and Technology*: September 72, 4(1999) 731-740.
- 33.- Rooj S, Basak, G. C. Maji, P. K. Bhowmick A. K. New Route for Devulcanization of Natural Rubber and the Properties of Devulcanized Rubber, *Journal Polymer Environment* 19 (2011) 382–390.
- 34.- Malihe Sabzekar, Mahdi Pourafshari Chenar, Seyed Mohammadmahdi Mortazavi, Majid Kariminejad, Said Asadi, Gholamhossein Zohuri. "Influence of Process Variables on Chemical Devulcanization of Sulfur-Cured Natural Rubber" *Polymer Degradation and Stability* 118, 2015, 88
- 35.- Yueqi Shen, Wen Zhu, Maria Papadaki, M.Sam Mannan, Chad V.Mashuga, Zheng dong Cheng, "Thermal decomposition of solid benzoyl peroxide using Advanced Reactive System Screening Tool: Effect of concentration, confinement and selected acids and bases" . *Journal of Loss Prevention in the Process Industries* Vol 60, (2019) 28-34.



36.- Molanorouzi, M. Mohaved S. O. Reclaiming waste tire rubber by an irradiation technique, *Polymer Degradation and Stability* 128 (2016) 115-125.

37.- Zanchet, A. Bandeira A. L. Fabiula D. Bastos de Sousa "Relationship among Vulcanization, Mechanical Properties and Morphology of Blends Containing Recycled EPDM" *Recycling* 2, (2017)16.

38.- D.C. Montgomery "Design and analysis of Experiments" 6^aEd. John Wiley and Sons. INC. (USA) 2005.

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