DEVULCANIZATION PARAMETERS AND MECHANICAL PROPERTIES OF EPDM/GROUND TIRE RUBBER COMPOUNDS

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ABSTRACT

Ground tire rubber (GTR) from end-of-life tires was mechanically devulcanized in a lab-made two-roll machine. Parameters such as rolling speed and number of rolling cycles were systematically changed, and their effects on the degree of devulcanization and on the chemical structure of the resulting materials were investigated. Milder devulcanization conditions promoted a selective scission of S–S bonds inside the macromolecular structure of GTR, whereas harsher processing parameters led to a more pronounced and undesired C–C and C–S scission in the rubber main chains. Next, two different amounts of GTR and devulcanized GTR (dGTR) were added through melt compounding to an EPDM. The effect of the devulcanization parameters and of the GTR/dGTR loading on the microstructural and thermomechanical properties of the resulting compounds was systematically investigated. A better interface was found for dGTR than GTR, due to revulcanization in which the restored cross-link sites could form chemical bonds with the EPDM compounds with tailorable properties with respect to the neat matrix and with a lower cost and raw material amount has thus been demonstrated. [doi:10.5254/rct.23.77949]

INTRODUCTION

The importance of rubber in modern society is evident: it was estimated that the worldwide production of NR in 2020 was 12.9 million metric tons, of which >70% was used in the production of tires.¹ The cross-linked nature of rubber and the presence of additives such as stabilizers, antioxidants, UV stabilizers, and antiozonants are the reasons for the elevated mechanical properties and dimensional stability of tires^{2,3} and therefore why they are extremely resistant to bio-, photochemical, and thermal degradation.^{4,5} A modern tire contains approximately 12–21 wt% metals, but also 45 wt% rubber.⁶ Because of the cross-linked structure of rubber and the presense of many constituents with different physical properties, tires are indeed difficult to recycle.^{7,8} It is estimated that approximately 800 million tires reach their end of life each year.⁹ In 2017, the low recycling rate of rubber products and the high dependence of European industry on rubber suppliers from third world countries led the European Commission to include NR in the list of critical raw materials.¹⁰ Waste tires can be a source of valuable raw materials, if properly disposed: part of the worn tires is still suitable for sports and playing surfaces; floor and walkway tiles; concrete; thermal and acoustic insulation; footwear; road and rail equipment; activated carbon production; artificial reefs; protection barriers; and flotation systems.^{5,11–13} Retreading is the most viable way of using end-of-life tires (ELTs), because it requires only 30% of the energy and 25% of the raw materials needed for the production of a new tire.¹⁴ In addition to this technology, many other processes have been evaluated to valorize ELTs, such as recycling,¹⁵ reclamation,^{16,17} energy recovery,^{18,19} and pyrolysis.11,20

From a circular economy perspective, it would be desirable to use secondary materials deriving from ELTs in the production of new tires. To achieve this goal, devulcanization technology is an interesting technological alternative. In an ideal situation, devulcanization should induce the breakage of the C–S and S–S bonds within rubber macromolecules, to obtain a material that can

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then be revulcanized, similarly to virgin rubber.^{21–23} Generally, devulcanization can be performed through chemical, ultrasonic and microwave-based, and thermomechanical methods.²⁴ Among the modern rubber-reclaiming technologies, thermomechanical methods are probably the most used.¹³ These methods are based on the application of mechanical shear stresses at elevated temperature $(\sim 200 \,^{\circ}\text{C})$ by using a two-roll milling machine or a twin-screw extruder. The temperature increase is provided by an external heat source and by the friction between the crumb rubber in a chamber with counter-rotating rolls.²⁵ The realization of selective bond breakage is based on the fact that S-S and C-S bonding energy is lower than that of C-C bonds. In these conditions, the probability of sulfur bridges scission is considerably larger than that of C-C scission within the main chain. However, in the literature, rubber devulcanization is often described as a simple reclaiming process that results in the breakage of C-C bonds, with a consequent decrease in the molecular weight and physical properties of the resulting compounds.^{1,22,26} Yazdani et al.²⁷ reported the effect of the devulcanization parameters on ground tire rubber (GTR), processed by using a twin-screw extruder. The barrel temperature seemed to have the most significant impact on devulcanization because a lower temperature increased the rubber viscosity, resulting in higher shear stress. At a screw speed of 120 rpm, devulcanization degree was higher at 220 °C (i.e., 88%) than at 280 °C (i.e., 85%). Similar results were achieved by Guo et al.²⁸ by using mechanical shear forces at low temperature and an environmentally friendly devulcanizing agent within a GTR compound, reaching a degree of devulcanization of approximately 85%. However, a lower screw speed led to a higher devulcanization rate at higher temperatures. Notably, by applying a proper combination of temperature and screw speed, devulcanization could be achieved without the use of a devulcanizing agent. In fact, Shi et al.²⁹ recommended a very careful selection of the process parameters, because the combination of elevated shear forces and high temperature tends to cause main-chain scission. Moreover, Zedler et al.³⁰ highlighted that the use of lower temperatures in a counter-rotating twinscrew extruder may result in significant energy savings, with a consequent reduction in the processing costs. Elevated shear forces applied to cross-linked rubber particles causes their mutual friction and generates exothermic reactions without providing external heating, allowing the production of reclaimed rubber having similar properties with respect to commercially available products. In fact, Seghar et al.³¹ found materials with the best devulcanization quality (i.e., with a more selective sulfur bond scission) to be those treated at a lower input temperature. Again this effect was explained by the effect of the rubber homogenously self-heating, which provides a local increase in the material temperature during devulcanization.

Results on devulcanized/virgin rubber blends indicated that all the NR industrial waste could be recycled, thereby generating competitive products with a lower energy consumption.³¹ Generally, the use of GTR in polymer blends could represent an interesting option for the valorization of rubber waste. Considering that the worldwide plastics production reached approximately 380 million in 2018,³² the addition of a small percentage of GTR in virgin matrices could imply a huge consumption of GTR.¹ It will therefore be possible to produce materials with peculiar properties with respect to the pristine constituents, to subtstantially decrease the cost of the resulting compounds, and to avoid the use of considerable amounts of raw materials.⁷ There are various examples in the literature wherein devulcanized rubber has been mixed with virgin rubber.^{33–36} Moreover, some efforts have been performed in the preparation of novel blends between GTR and thermoplastic polymers, such as polyethylene, ³⁵ polypropylene,³⁶ and polystyrene.³⁷ In our previous work,³⁸ EPDM compounds containing different amounts of GTR and thermochemically devulcanized GTR (dGTR) were developed. The resulting EPDM/GTR compounds showed a strong improvement in absorbed impact energy, impact strength, and elongation at break with respect to the neat EPDM, especially with a GTR content of 20 phr.

On the basis of these considerations, we focused on the effect of devulcanization parameters on the physical properties of EPDM compounds containing different amounts (20 and 40 phr) of as-



FIG. 1. — (a) Representative image of the lab-made two-roll mill and (b) its three-dimensional rendering.

received GTR and dGTR. A laboratory-scale replica of an industrial two-roll milling machine was built and used to devulcanize GTR. The change in the macromolecular structure of GTR due to devulcanization performed at different speeds and times was evaluated through the determination of the cross-link density and by thermogravimetric analysis (TGA) and infrared spectroscopy. The mechanical properties of the resulting EPDM/GTR and EPDM/dGTR compounds were then investigated.

EXPERIMENTAL

MATERIALS

The GTR coming from truck tires was provided by Rubber Conversion Srl (Verona, Italy) in the form of chips. It consisted of a mixture of NR and SBR. An EPDM rubber, Vistalon[®] 2504, containing 58 wt% ethylene and 4.7 wt% ethylidene norbornene and having a Mooney viscosity of ML_{1+4} @ 125 °C=25, was purchased by Exxon Mobil (Irving, TX, USA). Zinc oxide, stearic acid, and sulfur were supplied by Rhein Chemie (Cologne, Germany). Tetramethylthiuram disulfide and zinc dibutyl dithiocarbamate were obtained from Vibiplast Srl (Castano Primo, Milan, Italy). Carbon black N550 was supplied by Omsk Carbon Group (Omsk, Russia). All the materials were used as received.

PREPARATION OF SAMPLES

GTR Devulcanization. — Thermomechanical devulcanization of GTR was carried out in a labmade two-roll mill, adapted from a HAAKE Rheomix 600 melt compounder (Thermo Scientific, MA, USA), as shown in Figure 1. This roll mill was composed by two counter-rotating cylinders with a diameter of 20 mm, and the speed ratio between the two cylinders (i.e., the ratio between the speeds of the driven and master cylinders, respectively) was adjusted to 1.5 through an internal mechanical reduction system. In the following sections, the rolling speed (reported in rpm) is always related to the master cylinder. The gap between the rolls was fixed at 0.1 mm. The GTR was loaded on the top of the machine, masticated inside the rollers, and collected at the bottom. This procedure was manually repeated for the desired number of times. In this way, different dGTR

LIST OF DEVULCANIZED SAMPLES OF GTR PREPARED IN THIS STUDY					
Sample	Rolling speed, rpm	No. of cycles			
dGTR_A	100	40			
dGTR_B	100	80			
dGTR_C	200	40			
dGTR_D	200	80			

ΤΔΒΙΕ Ι

samples were obtained by varying the rotor speed and the number of rolling cycles. The codes of the samples, together with the processing conditions, are reported in Table I.

Preparation of EPDM/GTR Compounds. - EPDM-based compounds with two different GTR/dGTR contents—20 and 40 phr—were prepared by melt compounding through a HAAKE Rheomix 600 internal mixer, equipped with counter-rotating roller rotors. The compounding temperature was kept at 40 °C, and the rotor speed was set at 50 rpm. The EPDM was fed into the mixer with the carbon black and mixed for 5 min. Next, the vulcanizing agent and the additives were added and mixed for another 5 min. The recycled rubber was then added and mixed for 5 min. The resulting compounds were vulcanized in a hydraulic press at 5 MPa and 180 °C for 10 min. In this way, square sheets of samples with a thickness of 3 mm and at different relative compositions were obtained, according to previous work by our group.³⁸ The list of the prepared samples together with their codes is summarized in Table II.

EXPERIMENTAL TECHNIQUES

Characterization of GTR and dGTR. — The degree of devulcanization of GTR was evaluated by swelling tests, after the extraction process. The extraction was done in boiling acetone with a Soxhlet apparatus for a duration of 16 h, according to ASTM Standard D 297. After drying, the samples were weighted (m_i) and swelled in toluene at ambient temperature for 72 h, according to ASTM Standard D 6814. The swollen samples were weighed (m_t) and then dried in an oven at 70 °C overnight. Finally, the dried samples were weighted again (m_d) . This procedure was performed in triplicate for each material. The soluble fraction (% S) is given by Eq. 1:

$$\%S = \frac{m_{\rm t} - m_{\rm d}}{m_{\rm i}} \times 100\tag{1}$$

The cross-link density (v_e) was estimated using Flory–Rehner's model, whose expression is reported in Eq. 2:

$$v_{e} = -\frac{\ln(1 - v_{r}) + v_{r} + \chi v_{r}^{2}}{v_{s} \left(v_{r}^{\frac{1}{3}} - \frac{1}{2}v_{r}\right)}$$
(2)

Where v_r , χ , and v_s are the rubber volume fraction in the swollen sample, the rubber–solvent interaction parameter ($\chi = 0.391$ for NR-toluene),³⁹ and the molar volume of toluene (106.3 mL/ mol),³¹ respectively. The rubber volume fraction (v_r) was calculated with Eq. 3:

$$v_{\rm r} = \frac{m_d/\rho_d}{m_d/\rho_d + m_s/\rho_s} \tag{3}$$

where m_d and ρ_d are the mass and the density of dried rubber, respectively, and m_s and ρ_s are the mass of the toluene absorbed by the sample and its density at room temperature, respectively. The

	LIST OF EPDM/RECYCLED RUBBER COMPOUNDS				
	Recycled rubber content, phr	Rolling speed, rpm	No. of cycles		
EPDM	_	_	_		
EPDM_GTR_20	20	_	_		
EPDM_dGTR_A_20	20	100	40		
EPDM_dGTR_B_20	20	100	80		
EPDM_dGTR_C_20	20	200	40		
EPDM_dGTR_D_20	20	200	80		
EPDM_GTR_40	40	_	_		
EPDM_dGTR_A_40	40	100	40		
EPDM_dGTR_B_40	40	100	80		
EPDM_dGTR_C_40	40	200	40		
EPDM_dGTR_D_40	40	200	80		

TABLE II

degree of devulcanization (% dev) of each sample was calculated using Eq. 4:

$$\% \text{dev} = \left(1 - \frac{v_{\text{f}}}{v_{\text{i}}}\right) \times 100 \tag{4}$$

where v_i and v_f are the cross-link density of the rubber before and after devulcanization, respectively, evaluated using Eq. 2.

The analysis of the decrease in cross-link density and the variation of the soluble fraction upon devulcanization was performed by using the Horikx diagram.⁴⁰ The Horikx theory, originally based on the work of Charlesby,⁴¹ has been extensively described and experimentally evaluated in the literature.^{42,43} According to this approach, the decrease in cross-link density is related to the amount of the soluble fraction in the rubber in such a way that both the degree and the type of devulcanization (i.e., S–S, C–S, or C–C scission) could be qualitatively deduced.

The thermal degradation of GTR and dGTR was investigated through TGA by using a TGA Q5000IR machine (TA Instrument, DE, USA) at a temperature interval between 30 and 700 °C at a heating rate of 10 °C/min, both under a nitrogen flow of 100 mL/min and an air flow of 100 mL/min.

To obtain information about the possible chemical interactions between GTR/dGTR and the EPDM matrix in the compounds, Fourier transform infrared (FT-IR) spectroscopy of the GTR and dGTR compounds was performed with a Spectrum One spectrometer (Perkin-Elmer, MA, USA) in a wavenumber range from 640 to 4000 cm^{-1} .

Characterization of EPDM-Based Compounds. — Scanning electron microscopy (SEM) images of the cryo-fractured surface of the prepared compounds were taken with a Supra 40 microscope (Carl Zeiss, Deutschland) after Pt-Pd sputtering. Dynamic mechanical analysis (DMA) was performed by using a DMA Q800 machine (TA Instruments, DE, USA) in tensile configuration. Rectangular specimens ($20 \text{ mm}^3 \times 5 \text{ mm}^3 \times 3 \text{ mm}^3$) were tested between -120 and 100 °C at a heating rate of 3 °C/min, applying a frequency of 1 Hz and a strain amplitude of 0.05%. In this way, it was possible to determine the temperature dependence of the storage modulus (E'), the loss modulus, and the loss tangent (tan δ). Quasi-static tensile tests were carried out with a 4569 universal tensile testing machine (Instron, MA, USA), equipped with a load cell of 50 kN and set at a crosshead speed of 100 mm/min. An extensioneter for elastomers (Instron, MA, USA), with a gauge length of 25 mm, was used to monitor the deformation during the tests. At least five specimens for each formulation were tested to determine the elastic modulus (E), the tensile strength ($\sigma_{\rm B}$), and the strain at break ($\varepsilon_{\rm B}$). In addition, by the integration of the area under the stress–



FIG. 2. — (a) Maximum torque applied by the roll milling machine during devulcanization as a function of the number of rolling cycles and (b) thermal image of processed rubber at 200 rpm after 40 cycles.

strain curves, the tensile energy to break (TEB), corresponding to the total energy absorbed divided by the cross section of the specimens, was determined. The results of these tests were statistically analyzed through analysis of variance (ANOVA) and Tukey's tests.44

RESULTS AND DISCUSSION

CHARACTERIZATION OF DGTR

In Figure 2a, the trend of the maximum torque applied by the roll milling machine during devulcanization, as a function of the number of rolling cycles, is reported. Regardless to the rolling speed, the maximum torque progressively decreases, reaching a plateau level after 40 cycles at approximately7 N·m. According to the tendency lines, there is no correlation between the rotation speed and the applied torque. This decrease could be associated with a rise in the temperature of the material during the process, as verified through an infrared thermal camera after 40 cycles (Figure 2b), and also with the breakage of S-S (or C-C) bonds inside the rubber. In fact, the breakage of the bonds inside the rubber leads to a reduction of its viscosity and thus of the torque required by the machine to process the material.

Results from swelling tests in toluene of dGTR are summarized in Table III. The highest degree of devulcanization can be found for the sample treated at 100 rpm for 80 cycles (i.e., treatment B), with a cross-link density decrease of 82.4% compared with pristine GTR. This treatment provides an intense reduction of the cross-link degree with respect to the process performed at 200 rpm for 80 cycles (i.e., treatment D), whereas treatments A and C are not statistically different from treatment D. In harsher devulcanization conditions (i.e., D sample), it is not possible to exclude the onset of

	CROSS-LINK DENSITY AND DEGREE OF DEVULCANIZATION FOR TREATED SAMPLES OF GTR				
	Cross-link density of 10^{-4} mol/cm ³	Degree of devulcanization, %			
GTR	5.4 ± 4.4	_			
dGTR_A	1.4 ± 0.1	73.7 ± 2.6			
dGTR_B	0.9 ± 0.3	82.4 ± 5.4			
dGTR_C	1.5 ± 0.1	73.2 ± 0.1			
dGTR_D	2.7 ± 1.1	50.9 ± 20.7			

TABLE III

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FIG. 3. — Surface response curve for degree of devulcanization as a function of process parameters (N cycles and rolling speed). Adjusted R-squared = 0.496.

side reactions, such as reclamation rather than devulcanization, or the development of dynamic revulcanization processes.⁴⁵

Figure 3 shows a two-dimensional map, constructed via response surface methodology,⁴⁶ that reports an empirical model for the representation of the degree of devulcanization against the process parameters. Full quadratic response surface was used to model the influence of the considered factors on the degree of devulcanization of the treated GTR. The highest devulcanization values are obtained with a limited rolling speed, where side effects of the devulcanization treatment, such as the reclamation phenomenon, are negligible. This map identifies a suitable range of processability to obtain the maximum values of devulcanization.

To understand which phenomena took place during devulcanization, a Horikx plot was constructed that reported the soluble fraction as a function of the cross-link density. The main results are reported in Figure 4a. On this graph it is possible to identify each single treatment according to its soluble fraction, calculated according to Eq. 1, and its degree of devulcanization, calculated via Eq. 4. The plot shows that the experimental points are mainly distributed near the sulfur bonds scission curve, suggesting the preferential rupture of S–S and C–S bonds rather than C–C bonds upon the adopted devulcanization conditions. Figure 4b highlights that at the highest rolling speed and number of rolling cycles (dots related to treatment D) reclamation phenomenon could not be neglected, because the corresponding experimental points lie close to the C–C bond scission curve; thus, the higher cross-link density detected for treatment D could be explained by the concomitant occurrence of a reclamation process.

Evaluation of the thermal degradation behavior of GTR and dGTR was carried out through thermogravimetric tests, to assess the influence of processing parameters on the thermal degradation resistance of the tested materials. In Figure 5a–d, thermogravimetric curves of GTR and dGTR samples in nitrogen and air atmospheres, together with the corresponding derivative curves, are reported. A first mass reduction takes place between 200 and 300 °C (~5% of the total mass) that corresponds to the volatilization of processing oil, additives, and low-molecular-weight components within the rubber compound (Figure 5a).⁴⁷ As frequently reported in the literature,⁴⁸ thermogravimetric curves of GTR and dGTRs under nitrogen atmosphere (Figure 5a) show a main degradation step at approximately 390 °C, associated with NR degradation, without any influence of the devulcanization conditions. The shoulder visible at 440 °C in the DTG curves corresponds to the decomposition of the SBR fraction (Figure 5b).^{47,49}



FIG. 4. — (a) Horikx plot referred to the dGTR samples and (b) magnification of experimental points in the low soluble fraction region.



FIG. 5. — Thermogravimetric curves and relative derivative curves for GTR and dGTR in nitrogen (a, b) and air (c, d) atmospheres.



FIG. 6. — FT-IR spectra of GTR and dGTR samples.

When TGA tests are conducted in an oxidizing atmosphere, some differences between GTR and dGTR can be highlighted. Additional degradation steps appear (Figure 5c, d). According to the literature, the mass loss starts at 180 °C and has a peak in the rate of degradation at 280 °C that can be mainly related to the thermal decomposition of vulcanization cross-links (sulfur links), to the decomposition of links formed by zinc oxide, and to the partial breakage of the rubber backbone.^{50,51} The rate of degradation in this step, which can be related to the extent of broken bonds that are readily available to be thermally degraded, is higher for GTR treated at a higher number of cycles (dGTR B and dGTR D), thus underlining the major effect played by the number of rolling cycles with respect to the roller speed in devulcanizing the cross-linked structure. Peaks at 380 and at 440 °C are related to the thermal degradation of NR and SBR, respectively.⁵¹ The breakage of cross-links can thermally destabilize the rubber, promoting its degradation at lower temperatures and at a higher rate.⁵² In fact, the devulcanized samples show an increase in the degradation rate of both the NR and the SBR phases. Thermal oxidation of carbon black appears as a two-step phenomenon from DTG curves, in particular for GTR, and two peaks can be identified at 520 and 590 °C (Figure 5d). For the devulcanized samples, these peaks are shifted toward lower temperatures (490 and 530 °C, respectively) and have a higher intensity with respect to GTR. In particular the samples treated for a higher number of cycles show a higher rate of degradation than the samples treated for a shorter time, due to the higher effectiveness in breaking the chemical bonds.⁵¹ The mass residue at 700 °C can be attributed to inorganic constituents, prevalently residual carbon black and graphitized material.⁵³ No significant differences in mass residue can be detected between GTR and dGTR samples tested with the same atmosphere.

The FT-IR spectra of GTR and dGTR are presented in Figure 6. The bands of C–H bonds of CH₂ groups present in the aliphatic chains of the main backbone of the elastomeric phase are situated at 2915 and 2850 cm⁻¹, respectively. The absorption peaks at 1535 cm⁻¹, related to the aromatic C=C stretching vibration and at 961 cm⁻¹, corresponding to the –CH=CH– bending, are weakened in devulcanized samples, because of the breakage of sulfur cross-links and their

incorporation into the main rubber structure as benzene sulfide radicals,⁵⁴ or because of the cleavage of C=C bonds during the high shear treatment.⁵⁵ The characteristic signal at approximately 1370 cm⁻¹ corresponds to the C–H bonds of methyl groups and confirms the presence of natural rubber.³⁰ Other bands relative to the –CH₂– and C–H vibrations are located at 1430 and 812 cm⁻¹, respectively, whereas the bending vibration of –CH₃ is visible at 1300 cm^{-1.56} The intensity of the large band at 1050 cm⁻¹, assigned to sulfonyl groups, decreases in the devulcanized samples, suggesting that sulfur reacted with oxygen and hydrogen to form gas. These results confirm that oxidative degradation of sulfur bonds and rubber devulcanization could take place simultaneously during the treatment.⁵⁵ No further relevant differences between devulcanization conducted with different process parameters are highlighted by the FT-IR analysis.

CHARACTERIZATION OF EPDM-BASED COMPOUNDS

The SEM analysis on EPDM/GTR and EPDM/dGTR compounds was carried out to investigate their morphological features and to assess the effectiveness of the incorporation of recycled GTR within the EPDM matrix. By observing the cryo-fractured surface of the EPDM_GTR_20 sample (Figure 7a), a sharp cleavage fracture of the EPDM matrix that surrounds GTR particles can be seen. GTR particles incorporated in the EPDM matrix have a mean size of approximately 200 µm and sharp edges. As highlighted in Figure 7b, the interfacial adhesion between the two constituents is rather limited, and a neat separation between the GTR and the EPDM phases can be detected.

The cryo-fractured surface of the EPDM compound containing dGTR processed at 100 rpm for 40 cycles and 80 cycles is shown in Figure 7c-f. Even if the fracture of these specimens was performed in liquid nitrogen, a plastic failure mode, with the presence of a corrugated surface, can be detected. This effect could be caused by the presence of small and well-distributed dGTR particles inside the EPDM phase, with an average size of 70 µm for dGTR_A_20 that decreases to 50 µm, doubling the number of rolling cycles (Figure 7d–f). A stronger adhesion at the interface results from the revulcanization through hot-pressing. The dGTR has more free sulfur sites that can participate in the cross-link process with respect to as-received GTR that is substantially a fully vulcanized rubber. An increase of the rolling speed from 100 to 200 rpm leads to a visible decrease of the dimension of the dGTR particles, passing from an average size of 70 to 45 µm after 40 cycles (see treatment A vs treatment C). Figure 7g-j shows the fracture surface of EPDM_dGTR_C_20 and EPDM_dGTR_D_20 samples. The fracture surface appears more corrugated with respect to the previous specimen, which may be due to a better dispersion and a reduced particle size. In fact, a good adhesion between EPDM matrix and dGTR particles can be noticed, and dGTR particles appear better embedded inside the matrix. The size of dGTR_D_20 particles within the blend is very low (\sim 30 µm). As reported in some studies on similar systems, a good adhesion of dGTR domains could result in an improvement of the mechanical properties of the resulting compounds.⁵⁷ The SEMs of blends loaded at 40 phr present a similar microstructural behavior and are not presented for the sake of brevity.

In Figure 8a, b and Figure 9a, b, the influence of the incorporation of GTR and dGTR on the dynamic properties of EPDM, that is, E' and tan δ , for filler contents of 20 and 40 phr, respectively, is shown. The E' at low temperature (i.e., T < 50 °C) is similar for all the samples tested and seems to be not impaired by the presence of GTR or dGTR (Figures 8a and 9a). At -60 °C a sharp decrease in the E' occurs, due to the increased mobility of the EPDM macromolecules above the glass transition temperature.⁵² This drop is mitigated by the presence of GTR and at approximately 50°C it is possible to observe how the E' of samples with GTR and dGTR becomes lower with respect to the neat EPDM. For tan δ , a peak centered at -37 °C can be detected for all the samples, regardless to the GTR content and the devulcanization treatment. Once again, this peak corresponds to the glass



FIG. 7. — The SEM images of (a, b) EPDM_GTR_20, (c, d) EPDM_dGTR_A_20, (e, f) EPDM_dGTR_B_20, (g, h) EPDM_dGTR_C_20, and (i, j) EPDM_dGTR_D_20 taken at two different magnification levels.



FIG. 8. — The DMA analysis of EPDM samples filled with 20 phr of GTR and dGTR. Trends of (a) E' and (b) tan δ as a function of the temperature.

transition temperature of EPDM rubber.⁵⁸ At room temperature, an increase in the tan δ can be seen for EPDM compounded with recycled rubber compared with neat EPDM, with a higher magnitude for dGTR-filled samples. The observed increase in tan δ could be related to an improvement in the damping performances of the material, and the addition of dGTR can thus lead to an enhancement of the energy absorption capability of the resulting compounds.⁵⁹ Moreover, this increase is proportional to the dGTR content.

Quasi-static tensile tests were carried out to investigate the influence of devulcanization parameters on the mechanical properties of the produced blends. Figure 10a, b shows representative stress–strain curves of neat EPDM and the corresponding blends with a GTR/dGTR amount of 20 and 40 phr, respectively. In Table IV, the most important results in terms of E at a strain level of 50%, stress at break, ε_B , and specific TEB are summarized.

For the material loaded with 20 phr rubber, ANOVA states that speed and time of treatment significantly affect the stiffness of the prepared material (p value = 0.0007 and 0.0003, respectively), whereas their combination has no effect (p value=0.3). The E, calculated as the stress at 50% of deformation, is significantly lower (p value < 0.05) for the samples containing dGTR with respect to the blend filled with GTR, apart for the sample containing the GTR devulcanized with the mildest condition (EPDM_dGTR_A_20). Tukey test⁴⁴ highlighted a significative



FIG. 9. — The DMA analysis of EPDM samples filled with 40 phr of GTR and dGTR. Trends of (a) E' and (b) δ tan as a function of temperature.

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FIG. 10. — Representative stress-strain curves from quasi-static tensile tests on EPDM-based compounds with a GTR/ dGTR content of (a) 20 phr and (b) 40 phr.

difference in stiffness of the material between the two treatment durations considered in this study, but no difference between the two roller speeds applied. Therefore, devulcanization treatment seems to reduce the stiffness of the resulting compound, and this reduction is influenced in particular by the processing time. Stress at break is significantly higher for the samples filled with dGTR with respect to the samples with GTR, and the highest value can be found for EPDM_dGTR_C_20 (4.77 MPa). No differences can be detected between the samples containing devulcanized rubber and treated at different conditions. From Figure 10a, it appears that the addition of recycled rubber reduces the stress-at-break values, but the ε_B is significantly improved. Notably, when GTR is added to EPDM, the ε_B value is comparable with that of the neat EPDM matrix, suggesting the presence of a weak interphase between EPDM and rubber particles, but the situation changes dramatically when the rubber is devulcanized, reaching an improvement of 200% if EPDM_dGTR_D_20 is considered. The ε_B significantly increases upon dGTR addition, because of the improved interfacial adhesion between the constituents. The highest value of ε_B is reached by EPDM_dGTR_D_20 (580%) and reflects the possible dominance of reclamation over devulcanization in harsh working conditions (i.e., elevated rolling speed and number of cycles),

TABLE IV Mechanical Properties of epdm-Based Compounds with gtr/dgtr Content of 20 and 40 phr						
	E at 50%, MPa	Stress at break, MPa	$\epsilon_{\rm B},\%$	TEB, J/mm ²		
EPDM	1.55 ± 0.08	8.36 ± 0.53	286 ± 17	0.76 ± 0.09		
EPDM_dGTR_A_20	1.25 ± 0.07	4.55 ± 0.31	427 ± 26	0.74 ± 0.11		
EPDM_dGTR_B_20	1.09 ± 0.07	4.21 ± 0.13	508 ± 50	0.67 ± 0.07		
EPDM_dGTR_C_20	1.18 ± 0.10	4.77 ± 0.26	497 ± 68	0.71 ± 0.06		
EPDM_dGTR_D_20	1.07 ± 0.03	4.43 ± 0.15	580 ± 25	0.77 ± 0.05		
EPDM_GTR_20	1.32 ± 0.03	3.23 ± 0.64	265 ± 31	0.24 ± 0.12		
EPDM_dGTR_A_40	0.94 ± 0.04	1.33 ± 0.07	321 ± 40	0.18 ± 0.03		
EPDM_dGTR_B_40	0.82 ± 0.02	0.98 ± 0.02	310 ± 30	0.13 ± 0.01		
EPDM_dGTR_C_40	0.95 ± 0.02	1.28 ± 0.07	316 ± 27	0.16 ± 0.02		
EPDM_dGTR_D_40	0.88 ± 0.01	1.10 ± 0.05	263 ± 28	0.12 ± 0.01		
EPDM_GTR_40	1.08 ± 0.02	1.16 ± 0.13	185 ± 109	0.09 ± 0.04		

as also evidenced by the Horikx curves reported in Figure 4. In fact, the sample containing GTR devulcanized in mild conditions (EPDM_dGTR_A_20) shows a significantly lower ε_B value (427%), but the value is still higher than that of the sample loaded with nontreated GTR at the same concentration (265%). The ε_B of EPDM filled with GTR is close to that of neat EPDM. This could confirm the improved interphase between the EPDM matrix and the dGTR, due to breakage of S–S bonds upon devulcanization with respect to the use of nontreated GTR. Similar trends can be found for specific energy at break values. However, due to the improved elongation, energy adsorbed at break by the EPDM samples filled with dGTR is similar to that of the neat EPDM, with values approximately 0.77 J/mm² for all the samples loaded with dGTR at 20 phr.

Increasing the amount of GTR in the EPDM up to 40 phr leads to a worsening of all the mechanical properties (Figure 10b). According to ANOVA, both the speed and the duration of the devulcanization treatment significantly affect the E of the prepared materials (p value < 0.0001). The E is higher for the sample containing GTR than for the sample filled with dGTR. However, an E decrease of 30% has been recorded for the EPDM_GTR_40 sample compared with neat EPDM. Samples containing rubber devulcanized at the highest number of cycles (EPDM_dGTR_B_40 and EPDM_dGTR_D_40) show an E value significantly lower than that of the samples treated for shorter times, probably because of their higher degree of devulcanization. The stress at break dramatically decreases for all the samples at a filler loading of 40 phr, reaching a decrease of $\sim 85\%$ compared with the neat EPDM for the EPDM_dGTR_D_40 sample. Stress at break has been found to be significantly influenced only by the time of treatment (p value $< 10^{-8}$), whereas no significant influence has been observed by changing the roller speed (p value ~ 0.6). The $\varepsilon_{\rm B}$ decreases for all the samples loaded at 40 phr, compared with the material loaded up to 20 phr, and it shifts to values comparable with the neat EPDM matrix (2.8~3.1 mm/mm). According to ANOVA, this reduction in elongation at break is common to all the samples analyzed and does not seem to depend on the conditions of devulcanization. Because a decrease in the value of stress and ε_B has been recorded, the specific energy at break also decreases with respect to neat EPDM. Considering that stress at break is influenced by the treatment time and $\varepsilon_{\rm B}$ is the same for all the samples, the energy absorbed by the samples has been found to depend on the number of rolling cycles. In fact, higher TEB values can be detected for samples containing GTR treated for 40 cycles (i.e., 0.18 and 0.16 mm/mm for samples EPDM dGTR A 40 and EPDM dGTR C 40, respectively).

CONCLUSIONS

Devulcanization is becoming an important industrial method for rubber recycling that could allow to reintroduce the rubber waste into the manufacturing process of high-end products, promoting a circular economy approach for ELTs. The output of the devulcanization treatment is highly influenced by the adopted processing parameters. Therefore, the present work investigated the correlation between the process parameters and the resulting devulcanization degree of GTR. Milder processing conditions (low rolling speed and duration of the treatment) led to a high degree of devulcanization, reaching a reduction in cross-link density of 82.4% with a limited disruption of the C-C backbone, as also evidenced by the Horikx plot. Moreover, the effect of the adopted devulcanization parameters was correlated with the physical properties of EPDM-based compounds in which two different amounts of dGTR (20 and 40 phr) were added. According to DMA, the addition of dGTR brought an enhancement of vibration-damping properties compared with that of the neat EPDM. The E and stress at break were reduced by the presence of GTR/dGTR, whereas the failure properties were increased to comparable or even higher values with respect to the neat EPDM. This effect was explained by the improved interfacial interaction between dGTR and EPDM, as evidenced by the microstructural analysis, due to the increased amount of free sulfur sites in dGTR that can participate in the cross-link process during vulcanization of the compounds.

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This work demonstrated the possibility of preparing inexpensive and eco-sustainable rubber compounds containing devulcanized rubber from ELTs that show improved vibration absorption properties and elongation at break values with respect to those of the neat EPDM matrix. Investigated rubber compounds could be used for several applications, including soundproofing, insulation, vibration dampening, and sealing. They also possess many industrial purposes such as shock absorption, sealant for pipes, and tubing and tanks or can be used to make gaskets and seals for machinery.

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