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Evaluation of the role of devulcanized rubber on the thermomechanical properties of expanded ethylenepropylene diene monomers composites

Francesco Valentini D | Andrea Dorigato | Daniele Rigotti | Alessandro Pegoretti

Department of Industrial Engineering and INSTM Research Unit, University of Trento, Trento, Italy

Correspondence

Francesco Valentini and Alessandro Pegoretti, Department of Industrial Engineering and INSTM Research Unit, University of Trento, Via Sommarive 9 38123 Trento, Italy. Email: francesco.valentini@unitn.it and alessandro.pegoretti@unitn.it

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Abstract

Various amounts of both devulcanized (DR) and non-devulcanized (NDR) recycled rubber were melt compounded with a virgin ethylene-propylene diene monomer (EPDM) rubber. The resulting compounds were then expanded by using azodicarbonamide. The role played by the presence of DR or NDR on the thermomechanical properties of the obtained materials was evaluated. Electron scanning microscope micrographs highlighted that DR particles were better encapsulated within the EPDM matrix with respect to the corresponding NDR ones. Moreover, a better interfacial adhesion was observed with DR, probably due the re-vulcanization process in which the free crosslinking sites that typically characterize DR could form linkages with the EPDM matrix. Tensile impact behavior of expanded EPDM/recycled rubber blends highlighted a strong improvement of the normalized total absorbed energy, of the normalized impact strength and of the elongation at break with respect to the neat expanded EPDM for all the investigated compositions, and especially with a DR content of 20 wt %. The preparation of expanded EPDM containing considerable amounts of devulcanized rubber was, therefore, demonstrated to be a practical route to reduce the costs and improve the properties and the environmental sustainability of rubber products.

K E Y W O R D S

elastomers, foams, recycling, rubber

1 | INTRODUCTION

It is well known that in tires production the different constituents are vulcanized together in order to form a crosslinked structure with elevated mechanical properties and dimensional stability.^[1,2] The crosslinked nature of rubber and the presence of additives, such as stabilizers, antioxidants, UV-stabilizers, antiozonants, is the reason why tires are extremely resistant to biodegradation, photochemical, and thermal degradation.^[3,4] In 2010, the worldwide consumption of rubber has been 24.8 ktons and it is estimated that almost 70% of this quantity was used for tires production.^[5] In spite of the different available techniques to manage end-of-life tires (ELT), it is estimated that around 800 million tires are discarded worldwide every year, even if in the European Union landfilling of rubber is forbidden since 1999.^[6,7] At the European level, the overall reuse rate within the rubber industry of the waste rubber coming from ELT is equal to 12%. The remaining rubber content is exported (11%) or it is subjected to energy recovery (22%), material recycling through non-rubber applications (21%), and landfill disposal

(34%).^[5] Due to the low recycling rate of rubber products and due to the high dependency of the European industry on rubber suppliers from non-EU countries, the European Commission decided to include natural rubber in the list of Critical Raw Materials in September 2017.^[8]

Despite the low reuse and recycling rates, recovered waste tires can be source of valuable raw materials: part of the worn tires is, indeed, still suitable for the on-road applications and it can be, therefore, reused.^[9] From the economical point of view, retreading is the most viable way of using ELT since it requires only 30% of energy and 25% of raw materials with respect to the production of a new tire.^[10] Several other techniques have been carried out to use ELT, for examples, recycling,^[11] reclamation,^[12-14] devulcanization.^[15-17] energy recovery.^[18,19] and pyrolysis.^[20,21] Moreover, ELT after being shredded into crumbs can be used for the production of sport tracks, artificial reefs, protection barriers, and flotation systems.^[4,21,22] The recycling process of rubber starts by grinding ELT in order to allow the separation of different materials and to reduce the size of the rubber matrix. It can be carried out through dry, wet, or cryogenic grinding.^[23] Cryogenic milling allows to obtain particles of small dimensions, but the high costs related to this operation make the process not viable at industrial scale.^[24] One of the most interesting processes for recycling rubber is represented by devulcanization and should results, in an ideal situation, in the breakage of the sulfur-carbon (C-S) or the sulfur-sulfur (S-S) bonds within rubber macromolecules, in order to obtain a material that can be handled and vulcanized similarly to virgin rubber.^[25-27] The devulcanization process can be performed through chemical methods, through ultrasound and microwaves, and through thermo-mechanical techniques.^[28] However, in many cases rubber recycling is carried out through the reclaiming process that consists in the breakage of the carbon-carbon (C-C) bonds and a consequent decrease of the molecular weight and of the properties of the resulting compounds.^[5,26,29] In this work, recycled rubber obtained through a devulcanization process will be considered. In fact, Rubber Conversion's devulcanization technology is performed by a chemical-modifier activated by the mechanical shear induced from refining rollers. The process is performed at ambient pressure and the working temperature is maintained below 90°C, in order to avoid rubber degradation. The process has no air or water emissions hence it is environmentally friendly, and the chemical modifier is patented and specifically engineered.^[30]

The use of devulcanized rubber (DR) in polymer blends could represent an interesting option for the valorization of rubber wastes. Considering that the worldwide plastics production has reached about 380 million tons in 2015,^[31] the addition of a small percentage of DR in virgin matrices could imply a huge consumption of DR.^[5] It will be, therefore, possible to produce materials with peculiar properties with respect to the pristine constituents, to substantially decrease the cost of the resulting compounds and to avoid the use of considerable amounts of raw materials. In literature, several examples can be found in which DR has been compounded with virgin rubber, and it was demonstrated that introduction of DR could strongly modify the processability and the mechanical performances of the resulting materials, with strong cost savings.^[24,32-34] Some attempts have been also performed in the preparation of novel blends between DR and thermoplastic matrices, such as polyethylene,^[33,35] polypropylene,^[34] and polystyrene.^[36]

Expanded polymers, thanks to the low density and the limited thermal conductivity values that allow their use for insulating applications, have gained great interest in the last years.^[37] Rubber foams are expanded materials, prepared using a blowing agent, consisting of a rubber matrix and a gas phase. Depending on the foaming parameters the morphology of the pores can be different (i.e., open-cell and/or closed-cell structure), and the resulting foams can be applied for different applications, such as thermal insulation panels, gaskets, and impact sound deadening products.^[38-40] The foaming process occurs through the generation of gases within the elastomeric matrix generated by the thermal decomposition of a chemical blowing agent that can have organic or inorganic nature.^[38,41,42] Inorganic blowing agents (such as sodium and potassium carbonates) decompose endothermically, releasing CO_2 and water under the action of heat. Organic blowing agents (such as azodicarbonamide and p.p'oxybis-(benzene sulfonyl hydrazide)), on the other side, decompose mainly exothermically releasing nitrogen.^[41] Rubber foams can be produced starting from several matrices, such as natural rubber (NR)^[43] or synthetic rubbers, such as styrene-butadiene rubber (SBR),^[44] acrylonitrile butadiene rubber, and ethylene-propylene diene monomer (EPDM).[40,45]

EPDM is a synthetic rubber made of ethylene and propylene polymerized with a non-conjugated diene monomer, and vulcanized at elevated temperature in order to allow the formation of sulfur bridges.^[46] EPDM rubber compounds are the most used ones at industrial scale, and they are generally obtained by mixing EPDM rubber with vulcanizing agents (such as sulfur), antioxidants, activators, fillers (carbon black), and accelerants.^[47] They are generally characterized by good mechanical properties, high resistance to aging, ozone, UV, and weathering.^[48] On the other side, they possess a limited resistance to polar fluids and oils. EPDM foams are used for the production of gaskets, O-rings, windows profiles, belts, electrical insulation of cables, and waterproofing membranes.^[48]

Despite the possible advantages deriving from the combination of an elastomeric foam filled with DR, no studies can be found in the open literature on this topic. Moreover, the recent decision of the European Commission to include NR in the list of Critical Raw Materials can represent a further stimulus for the development of materials containing a lower content of virgin rubber and to find possible applications for valuable materials, such as DR.^[49] Based on these considerations, this work investigates the effect of DR on the physical, thermal, and mechanical properties of expanded EPDM. Moreover, the properties of the resulting compounds were compared with the corresponding ones prepared with non-devulcanized rubber (NDR).

2 | EXPERIMENTAL PART

2.1 | Materials

Vistalon® 2504 EPDM rubber is an amorphous terpolymer, containing 58 wt% of ethylene and 4.7 wt% of ethvlidene norbornene, with a low Mooney viscosity (ML 1 + 4, 125°C) of 25 MU and was purchased from Exxon mobil (Irving, TX, USA). Zinc oxide (curing activator), stearic acid (curing activator and lubricating agent), and sulfur (vulcanizing agent) were supplied by Rhein Chemie (Cologne, Germany). The accelerants, tetramethylthiuram disulphide and zinc dibutyl dithiocarbamate were obtained from Vibiplast srl (Castano Primo [MI], Italy). As reinforcing filler, carbon black N550 was used, obtained from Omsk Carbon group (Omsk, Russia). DR and NDR, kindly provided by Rubber Conversion srl (Verona, Italy), were used for the preparation of EPDM/recycled rubber blends. NDR consisted of ground-tire-rubber coming from truck tires, and it was constituted by a mixture of NR and SBR. DR was produced starting from the corresponding NDR through a patented chemical devulcanization process (see the details reported in the introductive section [Section 1]). Both DR and NDR were provided in form of fluffy material with irregular size and heterogeneous dimensional distribution; in order to homogenize the size of the rubber particles, both DR and NDR were cryo-milled using liquid nitrogen and consequently sieved with a 300 µm mesh size.

Azodicarbonamide (ADCA), obtained from Thermo Fischer Scientific (Massachusetts, USA), was used as foaming agent. The expansion through ADCA occurs thanks to the decomposition of the material that take place at around 210°C, and the reaction products are N₂, CO, and solid residues.^[41] In order to lower the decomposition temperature of ADCA, that would be too high for



EPDM rubber processing, ADCA was mixed with zinc oxide in weight ratio 9:1, as reported by Stehr and by Bhatti et al.,^[41,50] and a decomposition temperature of around 185°C was thus obtained. In preliminary studies, the density as a function of the blowing agent concentration was investigated, and an optimum ADCA concentration equal to 2 wt% was selected to obtain the lowest possible density values. Table 1 reports the composition of the samples in this work (the quantities are expressed in phr). All the materials were used as received.

2.2 | Samples preparation

EPDM/recycled rubber compounds with different DR/NDR contents (from 10 to 30 wt%) were prepared by melt compounding through an internal mixer (Thermo Haake Rheomix® 600), equipped with counter-rotating rotors. The compounding temperature was kept at 40°C, while the rotor speed was set at 50 rpm. First, EPDM was fed into the mixer with the carbon black and mixed for 5 min, and then the vulcanizing agent and the additives were added and mixed for other 5 min in order to reach a good homogeneity of the compound. Then, different procedures were followed to prepare the samples:

- To produce the neat EPDM compound, after a mixing time of 10 min, the material was vulcanized in a closed mold at a pressure of 8 bar and a temperature of 190°C for 7 min. In this way, square sheets (110 × 110 × 5 mm³) were obtained.
- To produce expanded sample, after a mixing time of 10 min, the foaming agent was added and mixed for 5 min. The foaming and the vulcanization process of the resulting compounds were then carried out simultaneously under a hydraulic press at a pressure of 2 bar and at a temperature of 190°C. After 5 min, the

TABLE 1Composition of the elastomeric compound used forthe preparation of the composites

Material	Quantity (phr)
Vistalon® 2504	100
Sulfur	3
Zinc oxide	3
Stearic acid	1
Carbon black	20
TMTD	0.87
ZDBC	2.5

Abbreviations: TMTD, tetramethylthiuram disulphide; ZBDC, zinc dibutyl dithiocarbamate.

pressure was released in order to allow the expansion of the material, and the samples were left for further 2 min, in order to allow the completion of the vulcanization process. In this way, square sheets $(110 \times 110 \times 6 \text{ mm}^3)$ of the blends at different relative compositions were obtained.

• In case of expanded samples containing DR and NDR, after a mixing time of 10 min, the foaming agent and the recycled rubber were added and mixed for 5 min. The foaming and the vulcanization process of the resulting compounds were then carried out simultaneously under a hydraulic press at a pressure of 2 bar and at a temperature of 190°C. After 5 min, the pressure was released in order to allow the expansion of the material, and the samples were left for further 2 min, in order to allow the completion of the vulcanization process. In this way, square sheets ($110 \times 110 \times 6 \text{ mm}^3$) of the blends at different relative compositions were obtained.

Table 2 reports the list of the prepared samples together with their codes. The sample named "EPDM" refers to the neat EPDM bulk compound, whose composition is reported in Table 1.

2.3 | Experimental techniques

The cryofractured surfaces of the samples at different recycled rubber amounts were observed through a Zeiss Supra 40 field emission scanning electron microscope (FESEM), operating at an acceleration voltage of 4 kV. Before to be observed, the samples were metallized through the deposition of a thin electrically conductive coating of platinum palladium inside a vacuum chamber.

Pycnometric density (ρ_{picn}) measurements were carried out by means of a helium displacement pycnometry

TABLE 2 List of the prepared samples

Sample	ADCA (wt%)	DR (wt%)	NDR (wt%)
EPDM	0	0	0
EPDM_f	2	0	0
EPDM_10DR_f	2	10	_
EPDM_20DR_f	2	20	_
EPDM_30DR_f	2	30	_
EPDM_10NDR_f	2	—	10
EPDM_20NDR_f	2	_	20
EPDM_30NDR_f	2	_	30

Abbreviations: ADCA, azodicarbonamide; DR, devulcanized rubber; EPDM, ethylene-propylene diene monomers; NDR, non-devulcanized rubber.

system through an AccuPycII 1330 Pycnometer (Micrometrics Instrument Corporation, USA) at a temperature of 23°C. For each sample, 30 measurements were performed. A measure of the geometrical density (ρ_{geom}) (i.e., mass over the total volume inclusive of solid, closed, and open porosity) was also carried out. The geometrical density was measured on five cylindrical specimens by measuring their mass with a Gibertini E42 balance (0.1 mg resolution) and the volume by means of a caliper (resolution of 0.01 mm). According to ASTM D6226 standard, it was possible to calculate the total porosity (P_{tot}) and the fraction of open porosity (OP) and close porosity (CP) according to Equations (1-3):

$$P_{\text{tot}} = \left(1 - \frac{\rho_{\text{geom}}}{\rho_{\text{bulk}}}\right) \times 100,\tag{1}$$

$$OP = \left(1 - \frac{\rho_{geom}}{\rho_{picn}}\right) \times 100, \qquad (2)$$

$$CP = P_{tot} - OP, \qquad (3)$$

where ρ_{bulk} is the density of the material without porosity (i.e., 0.99 g/cm³ for the EPDM sample). In the case of materials containing recycled rubber, ρ_{bulk} values were determined by using the mixture law (ρ_{bulk} values of the DR and NDR were obtained from the data sheets and were equal to 1.18 and 1.14 g/cm³, respectively).

Thermogravimetric analysis (TGA) was performed through a TGAQ5000 thermobalance under a nitrogen flow of 10 ml/min in a temperature interval between 30 and 700°C, at a heating rate of 10°C/min. The temperature associated to a mass loss of 5% ($T_{5\%}$) and the temperatures associated to the maximum rate of degradation (T_{peak}) and the residual mass at 700°C (m_{700}) were determined.

Tensile properties under quasi-static conditions were measured testing ISO 527 type 1BA specimens through an Instron 5969 tensile testing machine equipped with a load cell of 50 kN. Tensile tests at break were performed at a crosshead speed of 100 mm/min. The elastic modulus was measured as a secant modulus at a strain value of 50%; moreover, the maximum tensile strength and the strain at break were determined. At least five specimens were tested for each composition. In order to consider the role of the porosity within the expanded samples, the resulting tensile properties were normalized to the geometrical density of each sample, whose values are reported in Table 3. Shore-A hardness measurements were performed with a Durometer Prufstander model OS-2 (Hildebrand, Germany) following the ASTM D2240 standard. At least five specimens were tested for each composition.

Tensile impact tests were performed by using an instrumented CEAST impact machine (Instron, USA) equipped with a 2.54 kg mass striker. ISO 527 type 1BA dogbone specimens were utilized, and at least five specimens for each composition were tested. An impact angle of 130° and an impact speed of 3.47 m/s were chosen. In this way, the maximum impact strength, the total absorbed energy, and the elongation at break under impact conditions were determined. The maximum impact strength values were normalized to the density while the total absorbed energy values were normalized to the density and to the cross section of the specimens.

The fracture surfaces of samples tested through quasistatic tensile tests and tensile impact tests were observed through a Zeiss Supra 40 FESEM, operating at an acceleration voltage of 4 kV. Before to be observed, the samples were metallized through the deposition of a thin electrically conductive coating of platinum palladium inside a vacuum chamber.

RESULTS AND DISCUSSION 3

SEM analysis on expanded samples was carried out in order to investigate their morphological features and to assess the effectiveness of the incorporation of recycled rubber within the expanded elastomeric matrices. Observing the FESEM micrograph of EPDM f sample reported in Figure 1(A), it is possible to see that the porosity is homogeneously distributed and that the pores have a mean dimension of around 10 μ m. In Figure 1(B)–(E) FESEM micrographs of the blends containing DR are compared with those additivated with NDR, considering recycled rubber amounts of 20 and 30 wt%.

It is evident that DR containing samples are characterized by a considerably higher degree of porosity with respect to the corresponding NDR blends. Morphology of EPDM_f is more similar to that of DR-based blends, and it can be thus concluded that the addition of NDR seems to hinder the expansion of the elastomeric matrix. It is probable that this difference could be due to the higher viscosity before the vulcanization of the EPDM/NDR blends with respect to the corresponding DR filled ones. In fact, in the literature it has been reported that the devulcanization process usually leads to a reduction of the viscosity of the material,^[51] because of the strong decrease of the crosslinking degree of the rubber. In future, rheological measurements will be performed to have a better comprehension of this phenomenon. Comparing FESEM micrographs of EPDM 30DR f and EPDM_30NDR_f samples, it can be noticed that DR particles seem to be better encapsulated inside the matrix. NDR is present in form of quite sharp large-sized



domains, with some void regions that are separating them from the matrix. Comparing EPDM_20DR_f with EPDM 30DR f samples and EPDM 20NDR with EPDM_30NDR one, a lower encapsulation of DR/NDR particles within the EPDM matrix at lower DR/NDR content can be observed. In general, in DR blends a better wetting with the EPDM matrix can be appreciated, and this is probably due to the stronger adhesion at the interface resulting from the re-vulcanization process during the hot pressing and foaming operations. In other words, DR has more sulfur-sites free that can participate in the crosslinking process with respect to NDR, that is, substantially a fully vulcanized rubber.^[52] Preliminary swelling tests performed both on DR and NDR powder (not reported in details for the sake of brevity) demonstrated that the devulcanization degree of DR was around 48%, while that of the NDR samples was practically zero.

It is clear that the morphology of the expanded materials is strictly connected to their density and their porosity. Therefore, the evaluation of the density was performed through both geometrical and pycnometric measurements, and the relative amount of open and close pores, and of the total porosity degree was thus determined. The results of the density measurements, reported in Table 3, reveal a progressive increase in the pycnometric and geometrical density for the expanded samples containing NDR, while by the addition of DR a minimum value of pycnometric and geometrical density is reached by the EPDM_20DR_f sample (0.80 and 0.67 g/cm^3 , respectively). Considering standard deviation values, it can be said that the density of the expanded samples with DR is very near to that of the neat EPDM expanded sample. It seems thus that the presence of NDR impairs the expansion process: this could be due to the higher viscosity of the EPDM/NDR samples with respect to the corresponding DR filled ones. Moreover, another reason for the lower expansion of EPDM/NDR samples could be the poor adhesion between NDR particles and EPDM matrix that results in the formation of defects during the foaming process with a consequent gas escape and a reduction of the porosity formation.^[53]

As already explained in FESEM observations, this could be also directly correlated to the role of the addition of recycled rubber on the viscosity of the prepared compounds before the crosslinking. Ultimately, the most favorable condition for the foaming resulted by adding a DR amount of 20 wt%. Comparing the geometrical density values of EPDM_20DR_f and EPDM samples, a reduction of about 32% was registered. According to SEM micrographs, porosity of DR filled samples is clearly greater than that of the corresponding NDR ones. Moreover, the total porosity reaches a maximum of 34.8% for the EPDM_20DR_f sample, that is, the double of the total



FIGURE 1 Scanning electron microscope (SEM) micrographs of (A) EPDM_f, (B) EPDM_20DR_f, (C) EPDM_30DR_f, (D) EPDM_20NDR_f, and (E) EPDM_30NDR_f samples (magnification 200×)

porosity values obtained for the EPDM_20NDR_f sample. Looking at the porosity type, it can be observed that in the case of the EPDM_20DR_f sample the OP content and the close one are almost the same, while in the case of the EPDM_20NDR_f sample the porosity is mainly open. It is thus evident that the observed morphological differences could strongly affect the thermo-mechanical behavior of the investigated materials.

The evaluation of the thermal degradation behavior of the prepared materials was carried out through thermogravimetric tests, in order to assess the influence of the addition of recycled rubber and of the foaming



TABLE 3 Results of density measurements and porosity evaluation of bulk EPDM sample and of the prepared samples

Sample	$ ho_{ m picn}$ (g/cm ³)	$ ho_{\rm geom}~({\rm g/cm^3})$	$ ho_{ m bulk}$ (g/cm ³)	OP (%)	CP (%)	P _{tot} (%)
EPDM	1.00 ± 0.01	0.99 ± 0.02	0.990	_	_	—
EPDM_f	0.82 ± 0.01	0.76 ± 0.02	0.990	7.3	15.9	23.2
EPDM_10DR_f	0.85 ± 0.01	0.77 ± 0.03	1.009	9.4	14.3	23.7
EPDM_20DR_f	0.80 ± 0.01	0.67 ± 0.03	1.028	16.3	18.6	34.8
EPDM_30DR_f	0.86 ± 0.01	0.75 ± 0.03	1.047	12.8	15.6	28.4
EPDM_10NDR_f	0.90 ± 0.01	0.82 ± 0.03	1.005	8.9	9.5	18.4
EPDM_20NDR_f	0.91 ± 0.01	0.86 ± 0.02	1.020	5.5	10.2	15.7
EPDM_30NDR_f	0.98 ± 0.01	0.87 ± 0.05	1.035	11.2	4.7	15.9

Abbreviations: CP, close porosity; EPDM, ethylene-propylene diene monomers; OP, open porosity.



FIGURE 2 Thermogravimetric analysis (TGA) curves of expanded ethylene-propylene diene monomers (EPDM) samples containing different amounts of (a) DR and (B) NDR [Color figure can be viewed at wileyonlinelibrary.com]

process on the degradation resistance of the prepared materials. In Figure 2(A),(B), thermogravimetric curves of the EPDM sample and of the expanded samples at different DR/NDR amounts, together with the corresponding derivative curves, are reported (the TGA curve of the unfoamed EPDM sample perfectly overlaps that of the EPDM_f sample and thus it was not inserted). The most significant results in terms of onset degradation temperature ($T_{5\%}$), maximum degradation rate temperature (T_{peak}) and mass residue at 700°C (m_{700}) are collected in Table 4.

Looking at the curves reported in Figure 2(A),(B), it can be observed that, in the case of EPDM_f, an initial weight loss of around 2%-3% occurs at around $200-300^{\circ}C$ corresponding to the evaporation of oils and plasticizers.

A more substantial mass loss, occurring in a single degradation step in the temperature interval between 400 and 500°C can be attributed to the thermal degradation of EPDM matrix.^[54] In the case of DR and NDR it is possible to observe that the main degradation starts at around 300°C and occurs in two steps: the first one (at around 370°C) can be associated to the degradation NR while the second one (at around 430°C) can be associated to the degradation of SBR contained in the recycled rubber.^[55] For samples filled with DR and NDR it is possible to observe that, due to the presence of NR, the main degradation starts progressively at lower temperatures increasing the recycled rubber content. From derivative curves it is evident that for expanded samples filled with recycled POLYMER ENGINEERING DNALS AND SCIENCE

Sample	T _{5%} (°C)	T _{peak1} (°C)	T _{peak2} (°C)	m ₇₀₀ (°C)
EPDM_f	341.7	_	460.5	3.7
DR NDR	250.6 272.2	374.0 373.3	433.5 420.2	33.5 36.3
EPDM_10DR_f	346.6	_	472.1	19.3
EPDM_20DR_f	339.0	_	474.6	22.0
EPDM_30DR_f	327.1	393.6	473.6	22.0
EPDM_10NDR_f	341.7	—	473.4	20.3
EPDM_20NDR_f	303.6	_	469.0	19.3
EPDM_30NDR_f	310.6	385.7	470.2	21.1

TABLE 4 Results of TGA tests on the prepared samples

Abbreviations: DR, devulcanized rubber; EPDM, ethylene-propylene diene monomers; NDR, non-devulcanized rubber; TGA, thermogravimetric analysis.

rubber (both DR and NDR) the main degradation peak is preceded by a small shoulder (typical of the degradation of NR^[55]), which becomes more and more relevant by increasing the content of recycled rubber within the blends. Correspondingly, the intensity of the main degradation peak decreases with the DR/NDR content. In the range 500–580°C the EPDM_f sample shows a mass loss due to the degradation of final residues of rubber components and, starting from 580 to 600°C, the thermolysis of carbon black can be observed. This behavior is only slightly visible in case of samples containing DR/NDR; they seem to be strongly influenced by the addition of DR and NDR particles that present a very limited degradation (of around 5 wt%) in this temperature range.

Looking at the results summarized in Table 4, it is possible to notice that $T_{5\%}$ decreases gradually by the addition of recycled rubber, leading to a worsening of the thermal stability (the $T_{5\%}$ of EPDM_30DR_f sample is 327°C, about 15°C lower than that of EPDM f). This result could be explained considering the presence of NR, whose thermal degradation generally starts at lower temperatures (375°C) with respect to that of EPDM rubber (460°C) .^[55] Despite the decrease of the T_{5%} upon addition of recycled rubber, it should be noticed that T_{peak2} shifts toward higher temperatures (of about 10°C) with the addition of recycled rubber particles. This behavior is due to the presence of SBR that reaches the maximum degradation at a temperature of around 475-480°C.^[55] The presence of NR in recycled rubber has a limited influence on the thermal resistance of the samples at high temperature and the T_{peak1} can be detected only for EPDM_30DR_f and EPDM_30NDR_f samples.

The char residue at 700°C (m_{700}) of the EPDM_f sample amounts to about 3.7% of the initial weight of the sample and strongly differs from the m_{700} value obtained for EPDM/DR blends, which is around 20% for all the compositions. This may be accounted for the increase in

carbon black content, since its typical amount in truck tires reaches the 21–27%.^[5,55] From these thermograms, it seems that the thermal degradation behavior of NDR and DR filled expanded materials is rather similar, but EPDM/DR blends present slightly higher $T_{5\%}$ values with respect to the corresponding EPDM/NDR blends, especially at low recycled rubber loadings. It could be thought that the better adhesion between EDPM and DR obtained upon the crosslinking process could slightly improve the onset degradation resistance of the materials, but further tests will be required to better elucidate this aspect.

Quasi-static tensile tests were carried out in order to verify the influence of addition of recycled rubber on the mechanical properties of the produced samples. Figure 3 (A),(B) shows the representative stress–strain curves of EPDM_f and of the corresponding blends with different amounts of DR and NDR, respectively. In Table 5 the most significant mechanical properties in terms of normalized elastic modulus (E_{50}^*), normalized stress at break (σ_b^*), and strain at break (ε_b) are reported.

As it could be expected, the expansion process produces a general decrease of the elastic and failure mechanical properties. Considering that the density decrease produced during the foaming operation was not so pronounced (see Table 3) the properties drop experienced for the EPDM f sample is not dramatic, especially if E₅₀* are considered. The trends of normalized values of elastic modulus clearly suggest a decreasing tendency for the expanded samples by increasing the rubber content, even at limited amounts. For instance, E₅₀* values of EPDM_f passes from 1.51 MPa·cm³/g to 1.29 MPa·cm³/g for a DR content of 10 wt%, while a harsher decrease (up to 0.84 MPa·cm³/g) can be detected rising the DR amount up to 30 wt%. This decreasing trend involves also the normalized values of the stress at break, which considerably drops even for an addition of recycled rubber of 10 wt%. Referring to the values of tensile strain at break



FIGURE 3 Stress-strain curves of bulk EPDM sample and of expanded samples containing different amounts of (A) devulcanized rubber (DR) and (B) non-devulcanized rubber (NDR) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 5 Results of quasi-static tensile tests and of Shore-A hardness tests on the prepared samples	Sample	E ₅₀ * (MPa*cm ³ /g)	σ_b^* (MPa*cm ³ /g)	ε _b (%)	Shore-A
	EPDM	1.60 ± 0.06	5.20 ± 0.80	509 ± 67	57 ± 1
	EPDM_f	1.51 ± 0.04	3.93 ± 0.12	348 ± 10	48 ± 1
	EPDM_10DR_f	1.29 ± 0.09	2.00 ± 0.08	293 ± 11	43 ± 1
	EPDM_20DR_f	0.94 ± 0.09	2.13 ± 0.12	460 ± 14	35 ± 1
	EPDM_30DR_f	0.84 ± 0.05	0.84 ± 0.19	447 ± 12	34 ± 2
	EPDM_10NDR_f	1.23 ± 0.02	1.63 ± 0.18	302 ± 18	44 ± 2
	EPDM_20NDR_f	1.02 ± 0.05	2.80 ± 0.12	772 ± 21	43 ± 1
	EPDM_30NDR_f	1.14 ± 0.03	1.28 ± 0.05	541 ± 9	43 ± 2

Abbreviations: DR, devulcanized rubber; EPDM, ethylene-propylene diene monomers; NDR, nondevulcanized rubber.

presented in Table 5, it seems that addition of recycled rubber positively affects $\varepsilon_{\rm b}$ values, especially for elevated NDR amounts. The progressive increase in the ε_b values with the recycled rubber content could suggest that the deformation at break values of DR/NDR materials were superior to those of the neat EPDM matrix. Strain at break values of DR filled materials result to be lower than those of the corresponding NDR filled samples, probably because the higher porosity detected in DR blends negatively affects the extensibility of these samples (see Table 3). This assumption is confirmed looking at the SEM micrographs of tensile fracture surfaces of EPDM_30DR_f and EPDM_30NDR_f shown in Figure 4. In both samples a good adhesion between DR/NDR particles and the EPDM matrix can be observed but the porosity content of EPDM_30DR_f is definitely higher respect to EPDM 30NDR f, resulting in a lower deformation at break.

Shore A hardness values reported in Table 5 substantially reflect the trends of the elastic modulus. Hardness values decrease by adding recycled rubber into the EPDM matrix, but the trend results to be also strongly influenced by the porosity fraction. The decreasing tendency in Shore A values is more evident in the case of DR filled samples because of the higher pore content; while it is mitigated for NDR filled ones.

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The most interesting features obtained upon addition of recycled rubber can be probably appreciated testing the prepared materials under impact conditions. Representative load-time curves from tensile impact tests are reported in Figure 5(A),(B), while the most significant numerical results are summarized in Table 6.

First of all, comparing the impact properties of EPDM and EDPM_f samples it can be concluded that the expansion process does not substantially impair the tensile impact behavior of the samples at elevated testing speed. Once again, this behavior is probably due to the fact that the utilized foaming procedure did not determine a harsh density decrease in the material (see Table 3). It is important to underline that, considering the standard deviation



FIGURE 4 Scanning electron microscope (SEM) micrographs of tensile fracture surfaces from quasi-static tensile tests of (A) EPDM_30DR_f, (B) EPDM_30NDR_f samples (magnification 200×). DR, devulcanized rubber; EPDM, ethylene-propylene diene monomers; NDR, non-devulcanized rubber

Signal A = SE2



FIGURE 5 Representatives curves from tensile impact tests on bulk ethylene-propylene diene monomers (EPDM) sample and of expanded samples containing different amounts of (a) DR and (B) NDR [Color figure can be viewed at wileyonlinelibrary.com]

values associated to these measurements, the decrease of the impact strength due to addition of recycled rubber is not so consistent, and the value registered for the EPDM 20DR f sample (6.40 MPa \cdot cm³/g) is even superior to that of the EPDM_f. An interesting behavior can be observed for the normalized values of specific total impact energy. The absorbed energy increases with the recycled content, and the specific energy absorbed at DR/NDR loadings of 20/30 wt% is much higher than that detected for the EDPM_f sample. For instance, normalized specific energy of EPDM_30DR_f sample (56.5 J·cm/ g) is almost the double of that of EPDM_f (29.2 J·cm/g). It is also interesting to notice that elongation at break values of the produced blends are equal or also superior to those displayed by EPDM_f sample. EPDM_30DR_f has a $\varepsilon_{\rm b}$ value of 578%, that is, 80% higher than that of EPDM_f. It is also important to underline that,

EHT = 4.00 k

differently from the conclusions reported in quasi-static tests, blends with DR show superior impact properties with respect to the corresponding NDR blends, in terms of impact strength, absorbed energy, and elongability. It could be thought that the lower crosslinking degree in DR and the better surface adhesion detected in DRbased blends (see Figure 1) could positively affect the mechanical behavior of the material, especially at elevated strain rate values. This behavior can be confirmed observing the SEM micrographs of fracture surfaces shown in Figure 6; looking at the fracture surface of EPDM_30NDR_f the presence of several detached particles can be detected while it cannot be observed in the case of EPDM 30DR f. Devulcanization technology seems thus to be extremely interesting if applied to the development of rubber-based blends with higher impact performances.



TABLE 6 Results of tensile impact tests on the prepared samples

Sample	Normalized impact strength (MPa*cm ³ /g)	Normalized total specific absorbed energy (J*cm/g)	ε _b (%)
EPDM	5.83 ± 0.21	32.4 ± 1.9	378 ± 54
EPDM_f	5.88 ± 0.63	29.2 ± 5.0	321 ± 42
EPDM_10DR_f	4.06 ± 0.40	21.1 ± 2.9	377 ± 41
EPDM_20DR_f	6.40 ± 0.27	52.5 ± 7.0	544 ± 17
EPDM_30DR_f	4.99 ± 0.33	56.5 ± 1.5	578 ± 23
EPDM_10NDR_f	3.16 ± 0.12	16.2 ± 1.5	260 ± 19
EPDM_20NDR_f	5.15 ± 0.47	29.6 ± 3.1	366 ± 32
EPDM_30NDR_f	4.39 ± 0.14	32.1 ± 0.5	371 ± 26

Abbreviations: DR, devulcanized rubber; EPDM, ethylene-propylene diene monomers; NDR, non-devulcanized rubber.



FIGURE 6 Scanning electron microscope (SEM) micrographs of tensile fracture surfaces from tensile impact test of (a) EPDM_30DR_f, (B) EPDM_30NDR_f samples (magnification 200×). DR, devulcanized rubber; EPDM, ethylene-propylene diene monomers; NDR, non-devulcanized rubber

4 | CONCLUSIONS

The present work investigates the potentialities of EPDM expanded materials obtained through the incorporation of recycled rubber (both devulcanized and non devulcanized) within an elastomeric matrix. SEM micrographs and density measurements on the prepared samples showed that the incorporation of DR particles results in lower density values and in a better encapsulation within the EPDM matrix with respect to the corresponding non-devulcanized materials. TGA highlighted a very limited influence of recycled rubber addition on the prepared samples that mainly results in a lowering of the initial degradation temperature of EPDM_30DR_f and EPDM_30NDR_f due to the presence of NR within recycled rubber particles. The incorporation of recycled rubber within EPDM expanded samples led to interesting results in terms of tensile impact

tests, highlighting a strong improvement of normalized total absorbed energy, normalized impact strength, and elongation at break with respect to EPDM_f for all the tested compositions, especially with a DR content of 20 wt%. Therefore, this work demonstrated the possibility of preparing novel rubber expanded materials containing devulcanized rubber with improved impact properties, allowing also a reduction of the materials costs, and a better environmental sustainability.

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ORCID

Francesco Valentini D https://orcid.org/0000-0001-9496-0501

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