# ADVANCED CHARACTERIZATION OF RECYCLED RUBBER FROM END-OF-LIFE TIRES

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## ABSTRACT

There are currently many well-established applications for recycled rubber from end-of-life tires (ELT), but it is essential to investigate and seek new approaches to enhance the value of these products. Recent developments in new technologies and innovative recycling and devulcanization processes have opened up new perspectives for ELT crumb rubber. To promote the use of these products in newly added value applications, it is essential to develop and optimize methods that allow the characterization of parameters related to the ultimate properties of potential final applications. In this respect, a novel characterization methodology based on advanced $^1$H double-quantum (DQ) nuclear magnetic resonance experiments has been applied for the first time to quantify the key parameters that characterize the structure of ELT crumb rubber after diverse recycling processes: from simple mechanical grinding to complex devulcanization methods. This experimental approach enables the quantification of parameters that define the network structure of rubber, such as the nonelastic network defects (sol fraction, dangling chain ends, loops), the cross-link density, and the heterogeneity of the network, directly from rubber granulate and powder (without any additional sample preparation steps), overcoming most of the drawbacks and uncertainties that limit the application of traditional rubber characterization methods (e.g., equilibrium swelling experiments). By applying this experimental approach, it is possible to identify and quantify the actual technical limits for a complete selective devulcanization process of ELT crumb rubber. [doi:10.5254/rct.20.79963]

## INTRODUCTION

Circular economy is a concept that was created at the beginning of the past decade and promoted by the European Commission (EC) with ambitious action plans,[1,2] to drive the transformation from traditional production lines to the circularization of productive processes by creating closed cycles of materials and energy flows. Although great efforts have being made to reduce the production of waste according to the hierarchical organization promoted by the EC,[3] a large amount of waste continues to be generated and needs to be managed. As a tool of progress on this issue, the concept of extended producer responsibility was defined in the European Waste Framework Directive 2008/98/EC,[3] which involves the producers of those products that become waste in the phases of prevention and management organization.

Among the different waste streams, in the case of used tires, the industry has been active in taking action to organize the different players in the recovery chain with the creation of management systems for end-of-life tires (ELT) at a national level to collectively take responsibility for ELTs and organize their management chain: from the collection to the recycling of the derived materials. This contributes to the principles of circular economy strategies for the use of this waste as a resource, thus reducing the use of nonrenewable natural resources.

ELT are much more than just waste; they are a source of material and energy resources.[4] There are many advantages in using materials from ELTs, particularly rubber. The numerous applications in different market niches reflect the consolidation of ELT rubber as a material of technological and industrial interest.[4–7] Nevertheless, it is necessary to investigate and find new ways to give value to these products. Moreover, some high-added-value applications in the rubber industry are limited for recycled ELT rubber because of technological challenges related to its complex structure and

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composition (i.e., vulcanized blend of different filled rubbers). This is because tires have a complex design[8,9] and must fulfill demanding technical requirements in terms of security, fuel efficiency, and durability, among many others. To achieve these high-performance demands, different materials and ingredients are combined in the manufacture of different types of tires,[10] making complex the recycling processes to separate them (e.g., rubbers, reinforcing fillers, additives, textile fibers, steel).

Currently, used tires are collected and sorted by separating those that can be reused from ELTs. To produce granulates and powders for recycling in different applications,[4,11] ELTs must undergo several steps of size reduction (by shredding and grinding) and separation of rubber and nonrubber elements (steel is removed by magnetic separators, and textile fibers are separated by means of vacuum systems). It is then possible to obtain cuts, shreds, chips, granulates (particle size less than 10 mm), powders (particle size less than 1 mm), steel, and textile fibers. Among other existing methods, ambient grinding and cryogenic grinding (at low temperatures with liquid nitrogen) are the main industrial methods for obtaining fine rubber granulates and powders.[4,12,13] Ambient grinding is currently the most common method in the market based on high shearing forces and the production of irregular rubber particles with rough surfaces. Grinding at temperatures below the glass transition of the rubber blend is mainly based on impact forces on a brittle material, providing smaller powders with smoother surfaces. The cryogenic grinding minimizes the surface oxidation of rubber particles (in comparison with the ambient grinding) because the process temperature is much lower and it takes place in an inert atmosphere; however, it requires the use of liquid nitrogen.[4,11,13]

A step forward in the recycling of rubber from ELT is constituted by devulcanization processes,[4,11–22] such as thermomechanical (including those assisted by supercritical $CO_2$ and/or devulcanizing agents), chemical, ultrasonic, microwave, and biological methods. Thermomechanical processes comprise one of the most important approaches to be used at the industrial scale because they can be performed in a continuous process in co-rotating twin-screw extruders[11,23] with a high production ratio. They use the synergism between thermal energy, high shearing forces, and elongational strain to provide enough energy to break down the sulfur cross-links formed during the vulcanization process of rubber compounds but while minimizing the rubber chain scission (mainly formed by carbon–carbon bonds).[11,24,25] Devulcanization grade and selectivity (i.e., the ratio between cross-links breakdown/chain scission) reached in thermomechanical approaches depends on diverse factors and processing parameters,[18,23,26–29] and their optimization strongly depends on the rubber matrix. The effect of different and complex chemical processes that take place during devulcanization will be different according to the chemical structure of rubber matrices and their reactivity.[11] In the case of rubber granulates and powders from ELT, this fact limits the quality of devulcanized products because they are composed by a complex mixture of different blends of natural rubber (NR), styrene–butadiene rubber (SBR), butadiene rubber (BR), and halobutyl rubber (XIIR), fillers (silica modified with silane and/or carbon black), oils, and other ingredients coming from different components of the tire (e.g., tread, inner liner, sidewall) and different kinds of tires mixed during the grinding process.[28,30,31]

The application of recycled ELT rubber in new high-consuming markets and the opening of new applications and uses with higher added value for these secondary raw materials requires the establishment of measurable quality parameters that could be related to the properties of the end product. So far, the tests to characterize the technical specifications of ELT rubber granulates and powders have been mainly based on the determination of the particle size distribution and the impurity content.[32] However, structural key parameters at the molecular scale that could be related to crumb rubber quality and potential uses of these materials have not being investigated. In the case of devulcanized rubber from ELT, the most important parameters are the devulcanization degree and the process selectivity (i.e., the ratio between broken cross-links and chain scission).

The devulcanization rate of crumb rubber could be determined by extraction with acetone and the cross-link density by swelling experiments.[33] Nevertheless, this experimental approach strongly overestimates the obtained cross-link density for ELT crumb rubber (granulates and powders) because the swelling degree in filled rubber compounds is dominated by the filler–rubber interactions instead of the elasticity of the rubber network.[34,35] In addition, it has important uncertainties for determining the cross-link density because of the assumed model for rubber elasticity in swollen samples[36] and the exclusion of entanglement effects.[37] Furthermore, the obtained cross-link density strongly depends on the Flory–Huggins interaction parameter, which is different for each rubber–solvent pair and depends on the solvent fraction and changes for cross-linked or non-cross-linked polymers.[38,39] This is a critical issue for ELT crumb rubber, because it contains different rubber matrices with variable cross-link density when they are subjected to the devulcanization processes. Finally, this experimental approach considers perfect rubber networks and does not take into account network defects nor heterogeneities in the cross-link density, two key factors in the understanding of rubber elasticity.[40,41]

Finally, quantification of selectivity in the devulcanization process is a complex issue that is currently only addressed by applying the Horickx model.[42,43] This model has been validated for different rubber matrices and predicts the variation of sol fraction with the cross-link density in 2 extreme scenarios: the selective cleavage of sulfur cross-links or a random breakdown of rubber chains. Nevertheless, this experimental methodology has 2 main factors that promote uncertainties to the obtained results in ELT crumb rubber.[31] On one hand, the explained difficulties for quantifying the cross-link density by using swelling experiments should be addressed. On the other hand, it is mandatory to quantify both the soluble rubber fraction (sol fraction) and the network defects. In this sense, it is also necessary to take into account the fraction of dangling chain ends that, being produced during the devulcanization process (independently of the involved mechanism), remain attached to the rubber network and cannot be extracted by the action of solvents.[44,45]

According to these statements, it is mandatory to develop and optimize alternative experimental methods for addressing the difficulties to quantify the structure of recycled rubber from ELT. In this sense, a novel characterization methodology based on advanced $^1$H double-quantum (DQ) nuclear magnetic resonance (NMR) experiments[46,47] has been applied, for the first time, to quantify the key parameters that define the structure of ELT rubber granulates and powders after different recycling processes: from simple mechanical grinding to complex devulcanization methods. The main objective of this work is to quantify (1) the nonelastic network components that are defined by (a) the extractable fraction of organic ingredients, (b) the sol fraction of extractable rubber chain segments, and (c) the nonextractable dangling chain ends from the rubber network; (2) the cross-link density; (3) the spatial distribution of cross-links; and (4) the cross-link type (chemical structure), directly from the ELT crumb rubber (without any additional preparation step that could modify the rubber network structure), while overcoming most of the inconveniences and uncertainties that limit the application of traditional rubber characterization methods (e.g., swelling experiments). Finally, by applying this experimental approach, the actual technical limits will be identified and quantified for a complete selective devulcanization process of ELT rubber granulate.

## EXPERIMENTAL

### SAMPLES AND MATERIALS

Eleven ELT crumb rubber samples (four granulates and seven powders) were investigated in this work (see Table I). Samples obtained by mechanical grinding were supplied by Valoriza **?1** Medioambiente (Grupo Sacyr S.A., Madrid, Spain), whereas powder samples obtained by cryogenic grinding were supplied by Lehigh Technologies, Inc. (Atlanta, GA, USA). All samples

TABLE I

DESCRIPTION OF THE ELT CRUMB RUBBER SAMPLES

| Name | Supplier | Crumb rubber type | Nominal particle size (μm) | Grinding process | ELT origin |
|------|----------|-------------------|---------------------------|------------------|------------|
| GR2 | Valoriza Medioambiente | Granulate | 3000 | Ambient | Truck |
| GR2mix | Valoriza Medioambiente | Granulate | 3000 | Ambient | 50% truck, 50% passenger car |
| GR1 | Valoriza Medioambiente | Granulate | 2100 | Ambient | Truck |
| GR1mix | Valoriza Medioambiente | Granulate | 2100 | Ambient | 50% truck, 50% passenger car |
| POW 550 | Valoriza Medioambiente | Powder | 550 | Ambient | Truck |
| MD-830-TR | Lehigh Technologies | Powder | 595 | Cryogenic | Truck |
| MD-400-TR | Lehigh Technologies | Powder | 380 | Cryogenic | Truck |
| MD-184-TR | Lehigh Technologies | Powder | 338 | Cryogenic | Truck |
| MD-180-TR | Lehigh Technologies | Powder | 210 | Cryogenic | Truck |
| MD-105-TR | Lehigh Technologies | Powder | 110 | Cryogenic | Truck |
| MD-075-TR | Lehigh Technologies | Powder | 70 | Cryogenic | Truck |

were obtained from truck tires, except for GR1mix and GR2mix, for which 50% truck tires and 50% passenger car tires were used. Moreover, the samples were composed of a mixture of crumb rubber from all different tire parts (e.g., inner liner, tread, sidewalls), which have different chemical formulations. Nominal particle sizes (defined as the upper limit of the dimension (i.e., 90% w/w of the material has a smaller size than the given value) ranged from 3000 to 70 μm. All samples were characterized as received from the suppliers.

SAMPLING STRATEGIES

Crumb rubber used in this work is a complex and heterogeneous material composed of vulcanized rubber particles with different sizes coming from different tires (different origin, age, and degradation) and different parts of the tire (diverse compositions and formulations from tread, sidewall, or inner liner). In consequence, each rubber particle could have a different composition and properties, and it is mandatory to adapt the sampling strategies to prepare a representative test sample of this heterogeneous material according to the current standards. For the studied granulates and powders, a riffle splitter was used to reduce the sample mass (standard EN 14243-2:2018)[32] to obtain the representative test sample for each material (according to Annex B in the standard EN 15413:2011).[48]

SOLVENT EXTRACTION AND CLEAVAGE OF SULFUR CROSS-LINKS BY CHEMICAL PROBES

The complex composition of ELT crumb rubber samples makes essential the quantification of organic ingredients (essential oils, antidegradants, accelerants, and their by-products as well as extractable rubber chain segments) by solvent extraction. In this step, rubber samples were placed in weighted baskets made of stainless steel wire mesh (the mesh size was small enough to avoid sample loss). The baskets with the rubber samples were weighed before being immersed in toluene (individual containers) over 5 days. Swollen samples were protected against the light to avoid degradation.[36] Finally, the samples contained in the baskets were dried at room temperature until

they reached a constant weight. This extraction procedure was repeated three times per sample, quantifying the average weight loss during the extraction of organic ingredients from the rubber samples. It is important to note that extraction with toluene during 5 days quantifies a similar weight fraction of organic ingredients than a Soxhlet extraction procedure with acetone.

The latter extraction procedure was also used as a preliminary cleaning step for the rubber samples that were treated with chemical probes (based on thiol-amine chemistry) for cleaving of sulfur cross-links.[49–53] Initially, a weighted fraction of cleaned rubber sample (after extraction of the organic fraction) was swollen in toluene for 1 day. After that, such a swollen sample was immediately immersed in a solution of propane-2-thiol (0.4 M) and piperidine (0.4 M) in toluene during 4 h in nitrogen atmosphere for cleaving the polysulfidic cross-links. After treatment with chemical probes and subsequent cleaning with fresh toluene, the solid rubber was collected by using a basket of stainless steel wire mesh (the mesh size was small enough to avoid sample loss). Finally, the collected rubber was dried at room temperature until it reached a constant weight. The weight loss during the treatment quantifies the sol fraction (extractable rubber chain segments that are not bonded to the rubber network) produced by the cleavage of the polysulfidic cross-links.

The so-treated rubber was later immersed in a solution of n-hexane-1-thiol (2 M) and piperidine (4 M) in toluene during 48 h in nitrogen atmosphere to obtain a selective cleavage of the disulfidic cross-links. After cleaning with fresh toluene, the solid rubber collected by using a basket of stainless steel wire mesh was dried at room temperature until it reached a constant weight. The weight loss during the treatment quantified the sol fraction (extractable rubber chain segments do not bonded to the rubber network) produced by the cleavage of the disulfidic cross-links.

### THERMOMECHANICAL DEVULCANIZATION PROCEDURE

Thermomechanical devulcanization of the granulate sample GR1 was performed in an internal mixer (Haake rheomix) with a mixing chamber volume of 78 cm$^3$ and Banbury rotors. A fill factor of 0.6 was used (the high free volume between rubber particles makes it difficult to manage higher fill factors). The chamber temperature was 200 °C, and the rotor speed was set to 80 rpm. Two different processing times were performed (e.g., 15 and 30 min) to obtain different devulcanization degrees with different structures.

### $^1$H-DQ NMR EXPERIMENTS

$^1$H-DQ NMR experiments were carried out at 80 °C on a Bruker minispec mq20 spectrometer operating at 0.5 T with 90° pulses of 3.1 μs length and a dead time of 12 μs. In all performed experiments, the recycle delay time was fixed to 0.5 s. This time was used as a filter for the NMR signal because it is large enough to obtain complete magnetization (and acquisition) of rubber protons, with a characteristic longitudinal relaxation time $T_{1(rubber)}$ ∼60 ms, but it is too short to obtain information about other organic ingredients such as oils, which require magnetization times in the order of seconds to be measured. This is an important point to take into account in the quantification of the fraction of nonelastic components in rubber samples. The time-domain solid proton DQ NMR is one of the most quantitative and reliable methods for characterizing elastomer networks,[46,47,54–56] which can be applied on low-field spectrometers such as the Bruker Minispec (Billerica, MA, USA).

The ELT crumb rubber samples were introduced in the NMR sample tubes with a 10 mm outer and 8 mm inner diameter, reaching a maximum height of 5 mm to ensure that the rubber particles were placed in a position in the spectrometer where the magnetic field was homogeneous. All samples were protected from thermo-oxidative processes by creating a vacuum in the sample tubes before they were flame sealed.
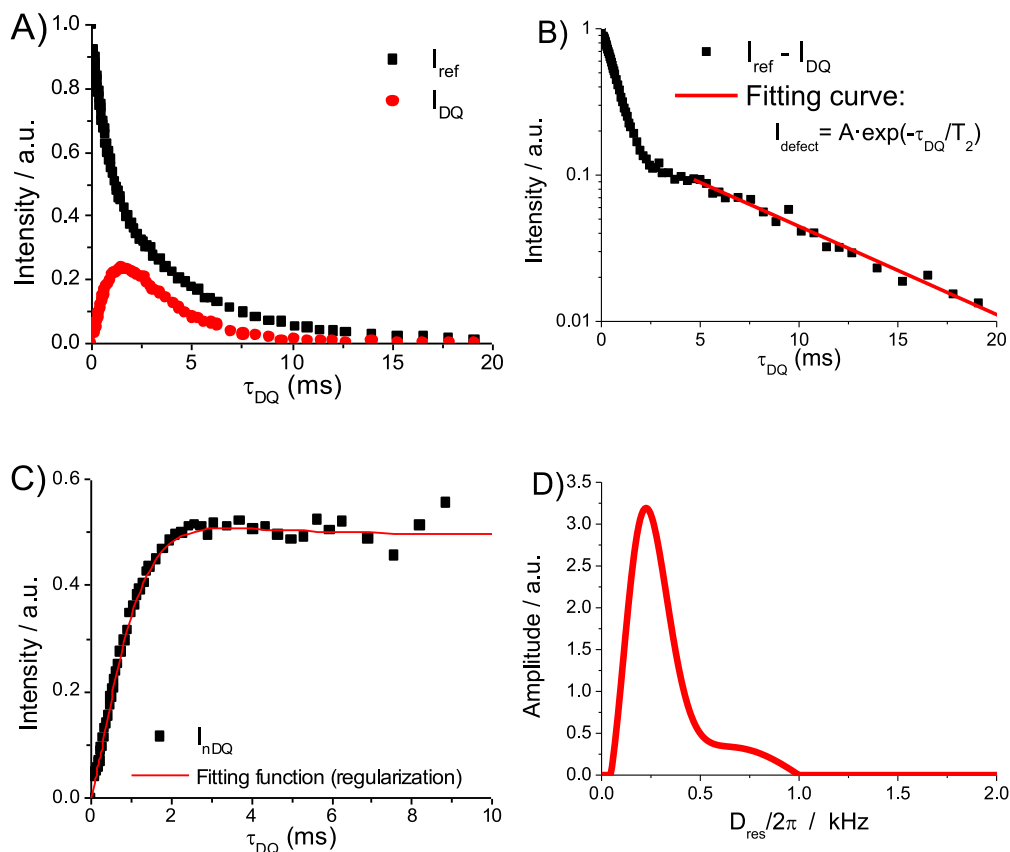
FIG. 1. — $^1$H-DQ NMR signals and data analysis for POW 550 sample. (A) Raw DQ buildup ($I_{DQ}$) and reference decay ($I_{ref}$) data as a function of the DQ evolution time $\tau_{DQ}$. (B) The difference $I_{ref} - I_{DQ}$ is used to identify the slower relaxing fraction of network defects. (C) The obtained $I_{nDQ}$ is used to analyze the residual dipolar couplings by using a numerical inversion procedure, obtaining the distribution of dipolar couplings that better fit to the experimental data, as shown in (D).

For cases in which swollen samples were analyzed by $^1$H-DQ NMR experiments, deuterated toluene was used to avoid the existence of NMR signal from the solvent.

## RESULTS AND DISCUSSION

ELT rubber in the form of granulate or powder does not represent any inconvenience for the application of NMR experiments for the structural characterization of these materials. The $^1$H-DQ NMR approach and data analysis widely applied to rubber samples in past years could be directly applied to crumb rubber samples without any substantial variation in the procedure. Nevertheless, some minimal but important issues should be adapted to take into account some particularities of these complex and heterogeneous rubber samples, as will be discussed in the following sections.

Two experimental signals (i.e., reference and DQ intensities) were obtained from the application of an improved Baum and Pines pulse sequence as a function of the DQ evolution time, $\tau_{DQ}$ (see Figure 1a).[57–59] Following the data analysis procedure explained elsewhere,[46] it is possible to identify and quantify the contributions of the isotropically mobile parts (see Figure 1b) by using the following exponential fitting function: $I_{defects} = A \cdot \exp(-\tau_{DQ}/T_2)$, where $A$ is the fraction of the sample with this behavior and $T_2$ is the transverse relaxation time. This sample fraction with slower

TABLE II
RUBBER NETWORK PARAMETERS OBTAINED FROM THE ANALYSIS OF $^1$H-DQ NMR EXPERIMENTS FOR PRISTINE ELT CRUMB RUBBER SAMPLES

| Sample | Rubber network defects, % | $D_{res}$, Hz | $\sigma/D_{res}$ |
|---|---|---|---|
| GR2 | 13 | 259 | 0.47 |
| GR2mix | 13 | 301 | 1.39 |
| GR1 | 13 | 271 | 0.54 |
| GR1mix | 14 | 319 | 1.32 |
| POW 550 | 18 | 317 | 0.66 |
| MD-830-TR | 8 ± 0 | 243 ± 0 | 0.45 ± 0.01 |
| MD-400-TR | 11 ± 0.5 | 221 ± 3 | 0.57 ± 0.03 |
| MD-184-TR | 8.5 ± 0.7 | 252 ± 5 | 0.56 ± 0.05 |
| MD-180-TR | 8 ± 0 | 248 ± 3 | 0.53 ± 0.04 |
| MD-105-TR | 11.5 ± 0.7 | 238 ± 4 | 0.55 ± 0.02 |
| MD-075-TR | 16.5 ± 0.7 | 264 ± 1 | 0.59 ± 0.03 |

exponential behavior is related to the rubber network defects ($A$), which are mainly composed by the sol fraction of extractable rubber chain segments and the nonextractable dangling chain ends from the rubber network because of the recycle delay time applied in these experiments (as will be discussed in the following sections). As shown in Figure 1c, the subtraction of the rubber network defects[45] allows for discriminating the information coming from the constraints to the movement of the chains (e.g., cross-links and entanglements) and for quantifying the corresponding residual dipolar coupling distribution according to a numerical inversion procedure explained elsewhere[60] (see Figure 1d). For a better comparison between samples, these distributions have been defined according their average value ($D_{res}$) and the distribution width. The latter parameter is defined by the standard deviation ($\sigma$) that is normalized with the average value ($\sigma/D_{res}$).

The correlation between $D_{res}$ (measured by DQ NMR) and the molecular weight between constraints ($M_x$) depends on the adopted model,[61,62] being in all cases the effective static dipolar couplings ($D_{stat}/k$) the proportionality factor of this relationship[62]:

$$D_{res} \frac{k}{D_{stat}} \propto \frac{1}{M_x}$$

In the case of homopolymers such as NR and BR, there are available apparent proportionality constant ($D_{stat}/k$) values for obtaining in a quantitative way the molecular weight between cross-links ($M_c$) from the $D_{res}$ measurements.[46] However, the cases of copolymers (e.g., SBR) and rubber blends are different because the existence of different co-monomers with different local coupling topologies and complex spin dynamics makes broader the dipolar coupling distribution,[3] as will be discussed in the following sections. In those cases, although the proportionality between $D_{res}$ and $M_c$ in these complex materials (including rubber samples from ELT) is completely valid, there is not a suitable constant in the literature that quantifies this relationship. For that reason, in this work the cross-link density will be given in terms of the average residual dipolar couplings ($D_{res}$), whereas the distribution width ($\sigma/D_{res}$) will be mostly related to (1) the spatial distribution of cross-links and (2) the rubber composition (blends composed by different fractions of diverse rubber matrices). These are important network parameters that have been successfully correlated with the elasticity and mechanical response of rubber samples.[61,63]

Results of the NMR analyses of pristine ELT crumb rubber samples are summarized in Table II and will be discussed in the following sections.

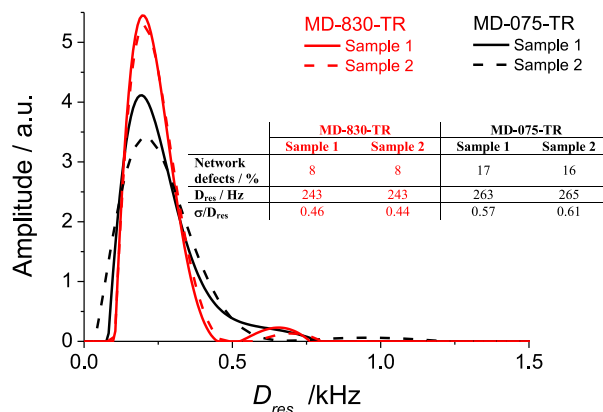| | MD-830-TR | | MD-075-TR | |
|---|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 1 | Sample 2 |
| Network defects / % | 8 | 8 | 17 | 16 |
| $D_{res}$ / Hz | 243 | 243 | 263 | 265 |
| $\sigma/D_{res}$ | 0.46 | 0.44 | 0.57 | 0.61 |

FIG. 2. — Repeatability of the residual dipolar couplings distributions for MD-830-TR and MD-075-TR samples. Two different test specimens were measured and compared per sample. The inserted table summarizes the most important rubber network parameters obtained from the analysis of these distributions.

ROBUSTNESS OF ^{1}H-DQ NMR EXPERIMENTS APPLIED TO ELT CRUMB RUBBER

The first step in the application of the ^{1}H-DQ NMR experiments for the advanced characterization of the network structure of ELT rubber is to determine the robustness of the method in terms of repeatability, taking into account the heterogeneity in the composition of the studied samples. Samples obtained by cryogenic grinding were measured twice (two specimens per sample), and the obtained average value and standard deviation for each sample are reported in Table II. As an example of those results, Figure 2 shows the dipolar coupling distribution for samples MD-830-TR and MD-075-TR.

According to the results shown in Table II and Figure 2, when results from the two test samples from the same material are compared, the greatest deviation obtained for the fraction of rubber network defects was about 8%. In the same way, although there are minimal variations in the shape of the dipolar coupling distributions (see Figure 2), the maximum difference found for the average value of the dipolar coupling (i.e., the cross-link density) is about 2% and less than 8% for the normalized distribution width (i.e., the spatial distribution of cross-links). Therefore, based on these results and being conservative, we could be sure that the values obtained by applying this experimental approach are subject to a relative error of less than 10%.

After establishing the confidence limit, the following sections will discuss the results, taking into account the different (1) grinding methods (ambient or cryogenic), (2) tire origins (100% truck or mixture 50% truck/50% passenger car), and (3) nominal particle sizes (from 3000 μm to 70 μm). These key factors have important effects on the properties of granulates and powders for recycling in different applications.[4,11,13,64,65] For this purpose, the fraction of nonelastic components and the parameters that define the rubber network structure (e.g., cross-link density, spatial distribution of cross-links, and distribution of the different types of cross-links, such as poly-, di-, and monosulfidic bonds), will be evaluated.

**?2**

NONELASTIC COMPONENTS IN CRUMB RUBBER FROM ELT

The nonelastic components in crumb rubber are defined by the extractable fraction of organic ingredients (e.g., processing oils, antidegradants, accelerants, and their by-products), the sol fraction of extractable rubber chain segments, and the nonextractable dangling chain ends from the
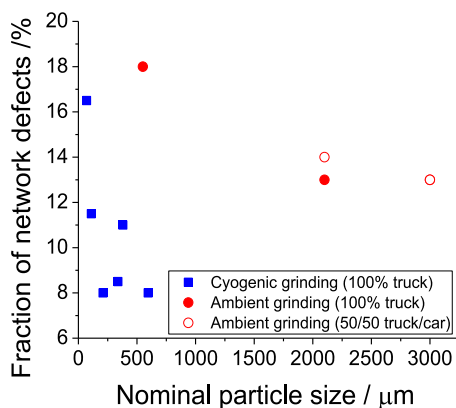
FIG. 3. — Variation of the rubber network defects the fraction with the nominal particle size for the ELT crumb rubber samples obtained by ambient and cryogenic grinding.

rubber network. Quantification of this fraction of nonelastic components will require the combination of ^{1}H-DQ NMR experiments with solvent extraction procedures in different steps.

*Characterization of Pristine Materials*. — Figure 3 shows the fraction of rubber network defects measured by ^{1}H-DQ NMR experiments for the studied samples (values are also summarized in Table I). As previously discussed in the "^{1}H-DQ NMR Experiments" section, this rubber fraction is composed exclusively by the extractable rubber chain segments and the nonextractable dangling chain ends from the rubber network because of the short recycle delay time applied in the NMR experiments (as will be demonstrated in the next section).

According to these results, it is possible to establish that the ambient grinding seems to generate a higher fraction of network defects in the samples as compared with the cryogenic grinding. Independently of the applied grinding technique, the reduction of the particle size seems to have an important effect on the fraction of rubber network defects generated. Finally, it was not possible to appreciate significant differences between granulates obtained from truck tires or from a mixture of truck/passenger car tires when they are produced by ambient grinding.

It is important to remark that observed differences in the rubber network defects between samples (from 8% to 17%) and different data trends discussed in this section would be caused by uncontrolled rupture of rubber network during the grinding processes.

*Characterization of Rubber Materials after Solvent Extraction*. — Quantification of the nonelastic components requires the application of the solvent extraction strategy widely explained in the "Experimental" section (see the "Solvent Extraction and Cleavage of Sulfur Cross-links by Chemical Probes" section). In this case, the sample POW 550 (obtained by ambient grinding with a nominal particle size of 550 μm) was used as a reference. The extraction was made in three different test sample specimens. By difference in mass, it was obtained that the extractable fraction of organic ingredients (e.g., processing oils, antidegradants, accelerants, and the sol fraction of extractable rubber chain segments) was 7.2% ± 1.5% w/w.

After the extraction procedure, the three cleaned rubber samples were again analyzed by ^{1}H-DQ NMR experiments. Figure 4 shows the analysis for determining the noncoupled network defects, establishing that extracted samples with toluene show a similar fraction of nonextractable dangling chain ends from the rubber network (20% in average) than the pristine sample (18%), as summarized in Table III. These results demonstrate that the $T_1$ filter applied in ^{1}H-DQ NMR has been effective (1) to be selectively sensitive to the rubber signal and (2) to shorten the experimental time of each measurement. In addition, it is possible to note that faster relaxation behavior for the
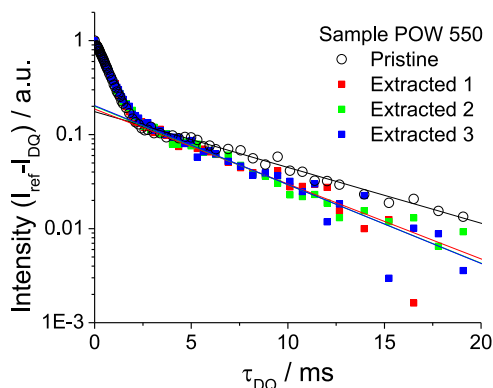
FIG. 4. — Noncoupling network defects for three solvent-extracted POW 550 test sample specimens and the corresponding pristine counterpart. Lines show the exponential fitting to the slow relaxing tails related to the rubber network defects.

rubber network defects in the extracted rubber samples should be related to the oil extraction that increases the mobility of this rubber fraction in the pristine powder.

The analysis of the rubber network structure for the three cleaned POW 550 sample specimens revealed that the applied solvent extraction procedure did not have any effect on the cross-link density or on the spatial distribution of cross-links, as shown in Table III.

*Characterization of Rubber Materials in the Swollen State*. — A previous work[54] demonstrated that the fraction of the rubber network defects obtained by $^1$H-DQ NMR experiments depends on the measurement temperature. This fact is caused by the slow relaxation of the entangled dangling chain ends and loops[44] that is enhanced by the increasing temperature. For that reason, to obtain a quantitative characterization of this important parameter, it is required to minimize the effect of entanglements by measuring the rubber samples in a swollen state.[45] Then, one of the solvent-extracted POW 550 sample specimens (named Extracted 1) was swollen during 24 h with deuterated toluene directly in the NMR tube and subsequently analyzed by $^1$H-DQ NMR according to the previously explained procedure.

Figure 5 shows the effect of solvent on the behavior of the rubber network defects. The release of most of the entanglement effect[37] on the rubber segments increases the measurable fraction of the network defects (reaching a maximum value of 24%) and, because of its increasing mobility, slows the relaxation of this rubber fraction.

Summarizing the results from the previous sections, the rubber phase of the sample POW 550 (taken as a reference in this work) is constituted by about 69% of the rubber network (i.e., cross-linked rubber segments) and 31% of nonelastic components (see Figure 6). The total nonelastic components in the ELT crumb rubber samples should be defined by summing up the extractable fraction of the organic ingredients (7% measured by a difference in weight after solvent extraction)

TABLE III
RUBBER NETWORK PARAMETERS OBTAINED FROM THE ANALYSIS OF $^1$H-DQ NMR EXPERIMENTS FOR PRISTINE AND THREE SOLVENT-EXTRACTED POW 550 SAMPLE SPECIMENS

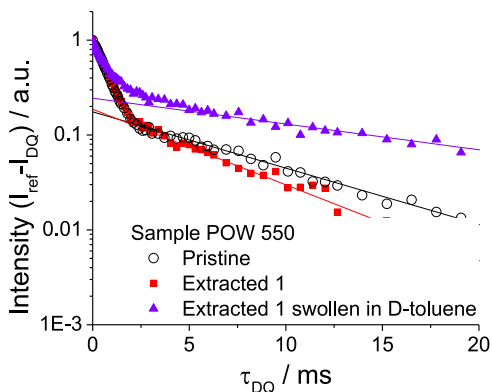| Parameter | Pristine | Extracted 1 | Extracted 2 | Extracted 3 |
|---|---|---|---|---|
| Network defects, % | 18 | 19 | 20 | 20 |
| $D_{res}$, Hz | 317 | 316 | 314 | 323 |
| $\sigma/D_{res}$ | 0.66 | 0.64 | 0.59 | 0.65 |

FIG. 5. — Noncoupling network defects for (1) pristine POW 550 sample, (2) solvent-extracted POW 550, and (3) solvent-extracted POW 550 swollen in d-toluene. Lines show the exponential fitting to the slow relaxing tails related to the rubber network defects for each sample.

and the nonextractable dangling chain ends from the rubber network (24% as measured by the ^{1}H DQ-NMR experiments in swollen samples).

### NETWORK STRUCTURE OF ELT CRUMB RUBBER

Once the diverse fractions that define the nonelastic components of the crumb rubber samples have been quantified, the network structure will be characterized and described in terms of cross-link density, spatial distribution of cross-links, and cross-link type (i.e. chemical structure of cross-links).

*Cross-link Density and Spatial Distribution of Cross-links*. — The residual dipolar coupling distribution measured by ^{1}H-DQ NMR and consequently the related factors that define the network structure of the studied samples will depend on (1) the ELT origin (truck or mixture truck/passenger
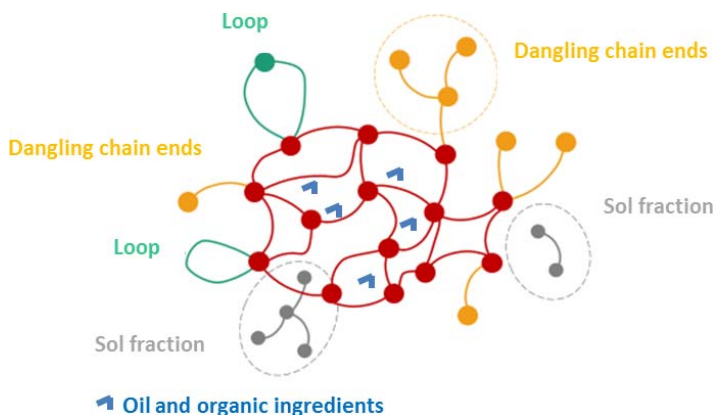


FIG. 6. — Schematic representation of the different components that conform the ELT crumb rubber particles: the rubber network (red) and the nonelastic network components. The latter is formed by the extractable fraction of organic ingredients (blue), the sol fraction of extractable rubber chain segments (gray), and the nonextractable rubber dangling chain ends (orange) and loops (green). To more easily understand this schematic picture, fillers and other ingredients or impurities that could be present in ELT crumb rubber particles have not been included.
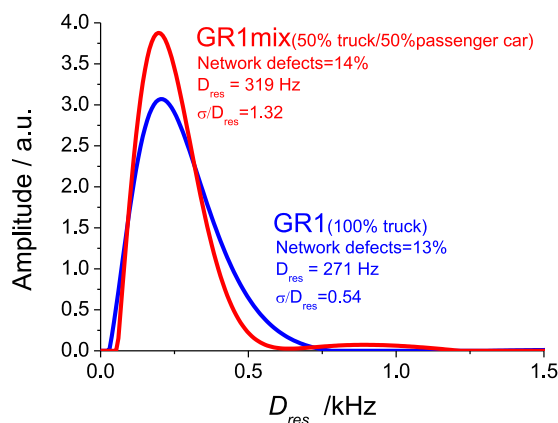
FIG. 7. — Dipolar coupling distribution for the GR1 sample (100% truck) and GR1mix (50% truck/50% passenger car). The main parameters that define these distributions (i.e., the average ($D_{res}$) and the width ($\sigma/D_{res}$) and fraction of the rubber network defects for each sample are shown.

car), (2) the particle size (related to grinding conditions), and (3) the grinding process applied (ambient or cryogenic).

Effect of the ELT origin. — Dipolar coupling distributions of 100% truck samples and 50% truck/50% passenger car (mixture) samples have been compared, as shown in Figure 7. The sample with the mixture is characterized by a broader distribution mainly caused by a certain bimodality shown in the high dipolar coupling range. These results would be mainly related to the higher fraction of SBR in the composition of passenger car tires as compared with truck tires.[66] However, in both cases, the complexity of the vulcanized rubber blends is evident because they contain rubber from the different tire parts: tread, sidewall, and inner liner. The existence of different co-monomers in SBR with different local coupling topologies and complex spin dynamics (in terms of NMR signal) makes the dipolar coupling distribution broader, minimizing the differences caused by the rubber network structure (number and spatial distribution of cross-links). As a consequence, by this methodology, it is not possible to compare the network structure of the ELT crumb rubber when the origin of the tire composition is quite different. Nevertheless, it is a powerful characterization tool when samples from the same origin are compared, as will be demonstrated in the following sections.

Effect of grinding process and particle size. — In this section, only samples from the same ELT origin will be compared. For that reason, the differences in the dipolar coupling distributions measured by NMR would be mainly related to changes in the rubber network structure generated during the grinding process. Figure 8 shows the evolution of the main parameters that define the dipolar coupling distribution as a function of the particle size: (1) the average value, $D_{res}$, which is related to the average cross-link density of the sample and (2) the distribution width, $\sigma/D_{res}$, which defines the spatial distribution of cross-links.

In the case of ambient grinding of 100% truck samples, the reduction of the nominal particle size from 3000 µm (granulate sample GR2) to 550 µm (powder sample POW 550) leads to a 20% increase in the cross-link density and makes the dipolar coupling distribution 40% broader. Figure 9 shows that changes in the dipolar coupling distribution are mainly related to the appearance of tails at higher dipolar coupling areas when the particle size is reduced. This could be due to the formation of some areas and/or particles with higher cross-link density during the grinding process.

It is important to note that the same trend is observed for all studied samples (i.e., also for the ambient grinding samples consisting of a mixture of truck and passenger car tires and the samples obtained by cryogenic grinding). For example, the sample with a nominal particle size of 70 µm
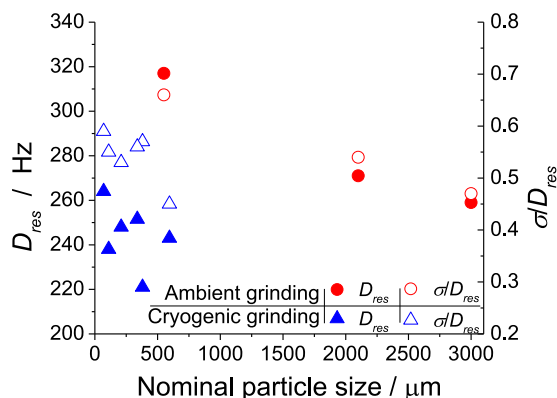
FIG. 8. — Average dipolar coupling $D_{res}$ and distribution width $\sigma/D_{res}$ as a function of the nominal particle size of the studied crumb rubber samples.

obtained by cryogenic grinding presents an increase of 9% in the cross-link density and 30% in the distribution width in comparison with the 595 µm sample (see Figure 8).

According to these results, it could be concluded that the lower the particle size (independently of the grinding process or the ELT origin), the higher the network defects and the average cross-link density of crumb rubber samples. In addition, the cryogenic grinding, which is able to reach a smaller particle size than ambient grinding, seems to reduce the modification on the network structure that may be associated to rubber degradation.

*Characterization of Different Type of Cross-links*. — The vulcanization systems used in the manufacture of tires are mainly based on the sulfur chemistry. Therefore, it is expected that the network structure of ELT crumb rubber samples is mainly formed by polysulfidic, disulfidic, and monosulfidic cross-links, although carbon–carbon bonds could also be present. Quantification of the different types of cross-links for the GR1 sample was made by combining chemical probes and ^{1}H DQ-NMR experiments.

As explained in the "Experimental" section, the first step in this process was a cleaning step (acetone extraction followed by a preswelling process in toluene) that causes the loss of 7% in weight because of the extraction of the organic ingredients fraction in the sample (e.g., processing oils, antidegradants, accelerants) and the extractable sol fraction of rubber chain segments. Such a
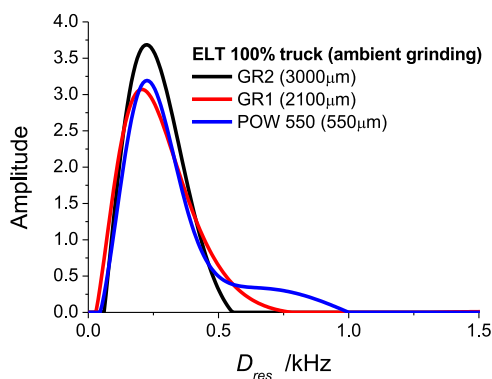


FIG. 9. — Dipolar coupling distribution for crumb rubber samples with different nominal particle size obtained by ambient grinding of ELT 100% truck.
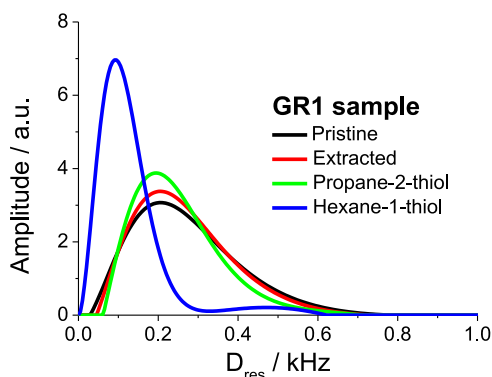
FIG. 10. — Dipolar coupling distribution for (1) the pristine GR1 sample, (2) after solvent extraction and after being treated with (3) propane-2-thiol for the selective cleavage of polysulfidic cross-links and (4) hexane-1-thiol for additional cleaving of disulfidic cross-links.

clean sample (after the drying process at room temperature) was characterized by $^1$H DQ-NMR experiments that showed a quite similar network structure to the pristine material, as shown in Figure 10. Approximately 11% of the rubber segments are network defects (dangling chain ends and loops), whereas the elastic network is characterized by a density of constraints (cross-links and entanglements) that provide a value of $D_{res} = 265$ Hz (see Table IV).

The breakdown of polysulfidic cross-links by treating the cleaned sample with propane-2-thiol (chemical probe) results in a mass loss of only 1% (sol fraction), leaving almost unaltered the measured network defects (11%) but decreasing the average cross-link density to $D_{res} = 249$ Hz. This variation in $D_{res}$ after the treatment with propane-2-thiol is mainly due to the breakdown of the polysulfide bonds, which constitute approximately 7% of the total number of cross-links in the pristine sample (see Table IV).

A further treatment with hexane-1-thiol is able to break the disulfidic cross-links, obtaining a sol fraction of 41% w/w. The remaining material is constituted by solid and cross-linked rubber particles due to the persistence of (1) monosulfidic and carbon–carbon cross-links that remain unaffected during these treatments and (2) fillers that are able to adsorb rubber segments (e.g., bound rubber in carbon black) or react with them by covalent bonds (e.g., silica modified with bifunctional silanes). The NMR analysis of these insoluble solid particles shows that their rubber networks are formed by 34% of dangling chain ends and loops with a remaining cross-link density defined by $D_{res} = 130$ Hz. This means that the fraction of disulfidic cross-links broken during this chemical treatment corresponds to about 55% of the initial cross-links, whereas the fraction of remaining monosulfidic and carbon–carbon cross-links represent 38% of the total cross-links of the pristine sample. Finally, the soluble rubber fraction after hexane-1-thiol treatment was recovered and dried, prior to being analyzed by $^1$H DQ-NMR experiments. The so-obtained $D_{res} \sim 47$ Hz provides information about the entanglement effect on the chain order at the measurement temperature (80 °C), and it has been used, in addition to the $D_{res}$ parameters summarized in Table IV, for determining the fraction of different types of sulfidic cross-links in the GR1 sample.

Nevertheless, the obtained fraction of network defects (34% w/w) is underestimated because of the effect of entanglements.[44,45,54] To minimize this effect, the sample treated with hexane-1-thiol was swollen in d-toluene to obtain the actual fraction of network defects, as was thoroughly explained in previous sections. As shown in Figure 11, the fraction of dangling chain ends and loops, when restrictions from entanglements are minimized by swelling, is considerably increased and was able to reach values of about 51% of the total rubber fraction in the sample.

TABLE IV

EXTRACTABLE FRACTION AND RUBBER NETWORK PARAMETERS OBTAINED FROM THE ANALYSIS OF $^1$H DQ-NMR EXPERIMENTS FOR GR1 SAMPLE AFTER DIFFERENT TREATMENTS (SOLVENT EXTRACTION AND TREATMENT WITH CHEMICAL PROBES) IN COMPARISON WITH THE PRISTINE COUNTERPART

| Treatment | Extractable fraction % w/w | Nonextractable fraction % w/w | Rubber network defects Fraction, % | Fraction, % | $D_{res}$, Hz | $\sigma/D_{res}$ | Rubber network Constraints | Cross-link fraction, % |
|---|---|---|---|---|---|---|---|---|
| Pristine | — | 100 | 13 | 87 | 271 | 0.54 | Polysulfidic + Disulfidic + Monosulfidic + C–C + entanglements | 100 |
| Extracted | 7 | 93 | 11 | 89 | 265 | 0.45 | | |
| Propane-2-thiol | 1 | 99 | 11 | 89 | 249 | 0.46 | Disulfidic + Monosulfidic + C–C + entanglements | 93 |
| Hexane-1-thiol | 41 | 59 | 34 (51)$^a$ | 64 (49)$^a$ | 130 | 0.71 | Monosulfidic + C–C + entanglements | 38 |
| Soluble fraction | 100 | — | | | 47 | | Entanglements | 0 |

$^a$ Value between brackets corresponds to the actual fraction of network defects obtained from the swollen sample in d-toluene.
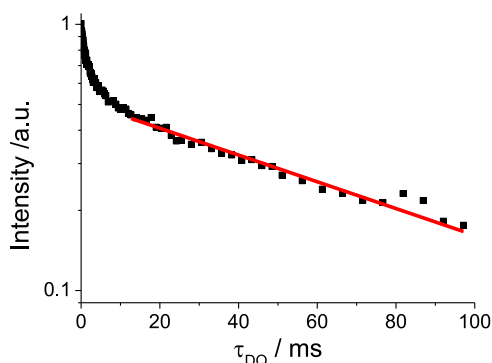
FIG. 11. — Determination of the fraction of the noncoupling network defects for the GR1 sample after treatment with hexane-1-thiol, obtained from the $^1$H-DQ NMR experiments performed on the swollen sample in d-toluene.

Finally, it is important to go deeper into the discussion about the change on the dipolar coupling distribution of GR1 sample after the treatment with hexane-1-thiol. As shown in Figure 10, the distribution after this chemical treatment is shifted toward lower $D_{res}$ values, because of the breakdown of sulfur cross-links, showing some bimodality in the shape.

EVALUATION OF DEVULCANIZED ELT RUBBER

The structural information obtained throughout this work by means of the application of advanced $^1$H-DQ NMR experiments could be a powerful tool for enhancing knowledge of the key steps to transform ELT rubber to a valuable secondary raw material along all the different recycling strategies, including devulcanization processes.

In the particular case of truck ELT samples, taking as reference the results for the GR1 sample, the rubber network structure is composed of the following:

1.  Polysulfidic cross-links: These links represent 7% of the total cross-links in the sample, being the most thermolabile and reactive cross-links and consequently the first fraction of bonds that could be broken in different processes of grinding and devulcanization. The several S–S bonds that form the polysulfidic cross-links have lower bond energy than C–C bonds in the polymer backbone; therefore, they could be selectively broken without damage of the rubber chains if the required conditions are applied.[11]

2.  Disulfidic cross-links: These links constitute about 55% of the total cross-links in the sample. They have only one S–S bond in their structure that reduces the lability and reactivity in respect to the polysulfidic cross-links but can still be broken in a selective way from the C–C cross-links in the grinding and devulcanization processes (if the recycling parameters would be optimized).

3.  Monosulfidic and C–C cross-links: These links constitute about 38% of the total cross-links in the sample, and they cannot be broken without chain scission in the rubber backbone because of the energetic similitude in their chemical bonds. As a consequence, they are the most important technological challenge to be addressed in rubber recycling, being actually the limit for selective devulcanization processes in this type of ELT rubber products.

It is important to point out that ELT crumb rubber treated with chemical probes is the most selective devulcanized example that could be obtained. Therefore, its structure could be considered
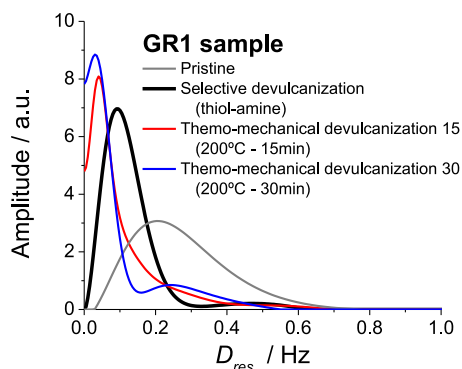
FIG. 12. — Variation of the dipolar coupling distribution of the pristine GR1 sample with different devulcanization treatments: (1) selective devulcanization with chemical probes (reference), (2) thermomechanical devulcanization 1, carried out in an internal mixer at 200 °C for 15 min; (3) thermomechanical devulcanization 2, carried out in an internal mixer at 200 °C during 30 min.

as the most precise limit for the state of the art of the devulcanization technology for ELT crumb rubber from a 100% truck tire without any damage to the backbone polymer chains. After the breakdown of approximately 62% of the initial total cross-links in the pristine sample (cleavage of poly- and disulfidic cross-links), almost half of the sample is soluble in toluene/acetone (i.e., organic ingredients and extractable rubber material that are not bonded to the rubber network). The remaining solid material recovered after the thiol treatment is composed of nonsoluble rubber material, mainly formed by rubber matrices and fillers. It is important to point out that the filler/rubber ratio obtained from the pristine material by thermogravimetric analysis (data do not shown) remains almost unaltered when it is measured in the soluble and the nonsoluble rubber fraction obtained after the treatment with chemical probes. Finally, the rubber fraction is formed by about 50% of nonextractable network defects (dangling chain ends and loops bonded to the rubber network) and 50% of chain segments in a network.

In addition, the dipolar coupling distribution of the remaining thiol-treated sample could be used as reference for checking the quality and selectivity of any devulcanization process that could be applied to this type of ELT crumb rubber materials as shown in Figure 12.

For this purpose, the GR1 sample was subjected to a devulcanization treatment based on a thermomechanical process in an internal mixer at 200 °C. The application of two different processing times (e.g., 15 and 30 min) results in two different samples. The structure of those samples was analyzed by $^1$H DQ-NMR experiments, and the so-obtained results were compared with the pristine and thiol-treated counterparts. Figure 12 and Table V show that the thermomechanical devulcanized samples present lower averaged residual dipolar couplings (i.e., lower cross-link density) and broader distributions (i.e., more heterogeneous distribution of cross-links) than the reference network obtained by the treatment with chemical probes because of two different factors:

1.  Breakdown of cross-links and chain scission processes take place simultaneously in a nonselective way, reaching cross-link density values below the reference sample obtained by the selective treatment with chemical probes.
2.  Rubber matrices containing butadiene monomers (e.g., BR and SBR) show thermo-oxidative mechanisms completely different than those rubbers based on isoprene units (NR). Whereas in NR, chain scission tends to be the dominant mechanism, in BR and SBR, the formation of new cross-links between rubber chains could take place to a higher

TABLE V
RUBBER NETWORK PARAMETERS OBTAINED FROM THE ANALYSIS OF $^{1}$H-DQ NMR EXPERIMENTS FOR PRISTINE AND TREATED GR1 SAMPLE

|  | Pristine | Selective devulcanization | Thermomechanical devulcanization 15 | Thermomechanical devulcanization 30 |
|---|---|---|---|---|
| Treatment conditions | — | Reaction with thiol-amine chemical probes | Temperature 200 ℃ Time 15 min | Temperature 200 ℃ Time 30 min |
| Network defects, % | 13 | 34 | 36 | 34 |
| $D_{res}$, Hz | 271 | 130 | 108 | 96 |
| $\sigma/D_{res}$ | 0.54 | 0.71 | 1.25 | 1.16 |

extent, resulting in a broadening of the obtained residual dipolar distribution when both matrices coexist in the same sample.

When the time of treatment is increased (from 15 to 30 min), these two effects are more evident, because both chain scission and cross-link breakage are produced to a higher extent but the ratio between them is modified, being more favorable to the chain scission and consequently losing the selectivity required for high-quality devulcanization processes.

CONCLUSIONS

Advanced $^{1}$H DQ-NMR experiments performed in an inexpensive and easy-to-use low-field spectrometer have been successfully applied to ELT crumb rubber samples, demonstrating their robustness to obtain a complete and quantitative characterization of the most important parameters that define the rubber network structure (at the molecular level) of these complex materials. This NMR experimental approach overcomes most of the drawbacks and uncertainties related to equilibrium swelling experiments for determining the cross-link density, but it also adds completely new evidence regarding the structural factors never evaluated before, such as the network defects fraction (composed by dangling chain ends and loops) or the spatial distribution of cross-links in the rubber network of these materials.

It has been demonstrated that the network structure of ELT crumb rubber changes during the grinding process. The reduction of the nominal size of crumb rubber particles, independently of the applied grinding process, increases the fraction of rubber network defects, average cross-link density, and width of the spatial distribution of cross-links. These changes in the rubber network structure may be associated with a local uncontrolled breakdown of the rubber network and reformation of cross-links between rubber chains in the framework of some complex degradation phenomena caused by the heat generated near the fracture surface during the grinding process. In this sense, cryogenic grinding, which is able to reach smaller particle sizes than ambient grinding, seems to reduce the modification on the network structure.

According to the NMR results, ELT crumb rubber samples contain an important fraction of network defects (even higher than 25% of the total rubber matrix). It is composed of dangling chain ends and loops attached to the network structure with the capability of creating entangled structures. In consequence, this fraction of network defects could have some relevance in the interaction of ELT crumb rubber with other polymer matrices and therefore in their properties and applications as secondary raw material, but this issue should be deeply evaluated in further studies.

A combination of NMR experiments and selective cleavage of sulfur cross-links by using chemical probes has allowed us (1) to quantify the fraction of the different types of cross-links that form the elastically active rubber network of these materials and (2) to obtain the most complete characterization of the network structure obtained by a completely selective devulcanization of ELT crumb rubber. On one hand, the ratio between poly-, di-, and monosulfidic cross-links play a key role in the devulcanization process of ELT crumb rubber, because their characteristic lability, reactivity, and bond energies in comparison with C–C bonds in the rubber backbone dictate the selectivity of the devulcanization processes. In this sense, the estimated fraction of monosulfidic cross-links (about 38% of the total cross-links) is the actual limiting factor for achieving a completely selective devulcanization process that could be able to avoid the rubber chain scission reaction.

On the other hand, the distribution of dipolar couplings of the thiol-treated sample could be used as a reference for checking the quality and selectivity of any devulcanized sample. In this sense, devulcanized samples by means of thermomechanical treatments have shown lower cross-link densities and more heterogeneous distribution of cross-links than our reference network, because in this process, both chain scission and cross-link breakage are produced simultaneously, losing the selectivity required for high-quality devulcanization processes.

According to our results, it is possible to conclude that $^1$H DQ-NMR experiments are powerful tools that provide unique information about the structure of devulcanized ELT rubber materials at the molecular level. This information could be used to address some of the limitations of experimental methodologies currently applied in this complex field. In light of the obtained results, the next step should be the implementation of these new insights obtained by means of the $^1$H DQ-NMR approach in the Horikx theory to enhance a combined experimental methodology that could improve the accuracy for determining, in a quantitative way, the quality and selectivity of any devulcanized rubber material (especially in the case of ELT crumb rubber) beyond the current state of the art.

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