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## Devulcanization of natural rubber industry waste in supercritical carbon dioxide combined with diphenyl disulfide

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30 (SEM) images strengthened these results. Finally, it was concluded that the developed  
31 device is appropriate to perform rubber recycling, which contributes to the progress in the  
32 environmental protection.

33 *Keywords:* Recycling, natural rubber, devulcanization, supercritical CO<sub>2</sub>, diphenyl  
34 disulfide.

### 35 **1. Introduction**

36 Rubber parts and tires manufacturing industries are constantly growing. Nonetheless, the  
37 inability to recycle their wastes represents a thorny environmental problem (Liu et al.,  
38 2020; Sabzekar et al., 2016). Because of the three dimensional structure of rubbers and  
39 their composition that includes numerous components, these kinds of polymers are indeed  
40 difficult to recycle (Hejna et al., 2020; Sienkiewicz et al., 2017; Kroll and Hoyer, 2019).  
41 One of the alternatives to throw off the mentioned wastes is to accumulate them in stocks,  
42 however they are focus of illnesses and fires (Adhikari et al., 2000; Mohajerani et al.,  
43 2020). Another way is to use them as an energy source by burning them, but this route is  
44 hazardous and generates environmental contamination (Molino et al., 2018; Pehlken and  
45 Müller, 2009). Consequently, these two methods are not recommended. With the aim of  
46 reducing this environmental problematic, several processes have been developed, especially  
47 the devulcanization technique (Asaro et al., 2018; Cheng et al., 2018 ; Bockstal et al.,  
48 2019), during the last few decades. Rubber devulcanization is a process where poly-, di-,  
49 and mono-sulfidic bonds, formed during vulcanization, are totally or partially broken, i.e. a  
50 process that causes a selective breakup of sulfidic bonds without degrading the polymer  
51 (Isayev, 2013; Asaro et al., 2018). Performing a successful devulcanization is a great

52 challenge, since the energies needed to break the sulfur-sulfur (S-S) and carbon-sulfur (C-  
53 S) bonds (227 and 273 kJ/mol, respectively) are not so different from the energy required to  
54 break the rubber main chains i.e. the carbon-carbon (C-C) bonds (348 kJ/mol) (Rooj et al.,  
55 2011; Karger-Kocsis et al., 2013; Ramarad et al., 2015; Sabzekar et al., 2015). Several  
56 devulcanization processes have been developed and presented in the literature, including:  
57 biological (Yuanhu et al., 2011; Yao et al., 2013), chemical (le Beau, 1967; Zhang et al.,  
58 2018; Anu Mary et al., 2016), ultrasound (Isayev et al., 2014; Mangili et al., 2015; Hon et  
59 al., 2015), microwave (Novotny et al., 1978; Aoudia et al., 2017; Simon et al., 2020),  
60 mechanochemical (Jana et.al, 2005), and thermo-mechanical (Seghar et al., 2019b; Diaz et  
61 al., 2018). Usually, the mentioned devulcanization processes are followed by the  
62 characterization of the obtained materials. The aforementioned characterization serves both  
63 to evaluate the devulcanized material as well as the devulcanization process. Because direct  
64 access to the changes generated by the devulcanization process at molecular level is non-  
65 trivial for rubber materials, an indirect method is required. The most widely used indirect  
66 technique is based on the swelling test (ASTM D 6814-02). Through this test, it is possible  
67 to measure the crosslink density of the devulcanized material and compare it with that of  
68 the virgin vulcanized rubber. Then, the degree of devulcanization is estimated as the  
69 decrease in the material crosslink density. Other characteristics such as the degree of  
70 swelling, the soluble and gel fractions, etc., are also obtained by this technique. It is worth  
71 mentioning that the swelling test results are also used to perform the Horikx chart (Horikx,  
72 1956). This diagram allows analyzing the quality of the performed devulcanization by  
73 means of crosslink scission versus main chain scission. The development of the Horikx  
74 theory (Horikx, 1956) is based on the work of Charlesby (Charlesby, 1953). It is well  
75 developed in the literature (Verbruggen et al., 1999), and its application in the rubber

76 devulcanization analysis was recently experimentally proved (Verbruggen et al., 2016;  
77 Seghar et al., 2019a).

78 The chemical devulcanization in a pressurized reactor in scCO<sub>2</sub> atmosphere has been  
79 already analyzed. It is expected that, during the devulcanization process, the supercritical  
80 carbon dioxide swell the polymer, facilitating the sulfidic bonds scission. A more detailed  
81 explanation of the devulcanization mechanism in scCO<sub>2</sub> is given afterwards. Kojima et al.  
82 (Kojima et al., 2003; Kojima et al., 2004; Kojima et al., 2005a; Kojima et al., 2005b) have  
83 devulcanized different kinds of rubbers in an autoclave, with supercritical carbon dioxide  
84 (scCO<sub>2</sub>) and diphenyl disulfide (DD) as devulcanizing reagents, among others. The most  
85 suitable conditions for the devulcanization of the sulfur-cured unfilled natural rubber (NR)  
86 were 60 min at 10 MPa and 180 °C, with 11wt% of DD. They concluded that scCO<sub>2</sub> helps  
87 in the penetration of the devulcanizing reagent DD into the rubber. In order to understand  
88 the reaction that occurs between DD and the rubber during the devulcanization, they  
89 proposed a reaction mechanism scheme that is presented in Fig. 1. It was pointed out that,  
90 firstly, the DD molecules solvated by the scCO<sub>2</sub> will get into the NR previously swollen by  
91 the scCO<sub>2</sub>. Then, these molecules will contribute to the sulfur bonds cleavage, giving as a  
92 result a devulcanized rubber.

93 The analysis of the devulcanized material was based on the variation of the sol fraction  
94 content. Jiang et al. (Jiang et al., 2013) studied the devulcanization of sulfur-cured butyl  
95 rubber in a high-pressure reactor with scCO<sub>2</sub>, by using DD as a devulcanizing reagent. The  
96 devulcanization degree of the treated materials was evaluated with respect to the sol  
97 content. It was pointed out that the revulcanization of the recycled material could be  
98 affected by the amount of DD used during the devulcanization process, and therefore  
99 excessive quantities of DD should be avoided. A devulcanization mechanism, including the

100 reaction between the butyl rubber and DD, and the material thermal degradation, was  
101 proposed. Mangili et al. (Mangili et al., 2014a; Mangili et al., 2014b) analyzed the  
102 devulcanization of ground tire rubber (GTR) with scCO<sub>2</sub>, using DD as devulcanizing  
103 reagent. DD fraction, temperature and their interaction were identified as the main  
104 parameters affecting the devulcanization process. The devulcanization degree, obtained by  
105 swelling measurements, was about 50 %. It was shown that the use of DD in the  
106 devulcanization process favors the increase of the strain at break and the decrease of the  
107 Young modulus of the blends containing the devulcanized GTR. The devulcanization of  
108 waste tire rubber (WTR) by using scCO<sub>2</sub> as reaction medium and DD as devulcanizing  
109 reagent, in an autoclave, was also performed by Liu et al. (Liu et al., 2015). The effect of  
110 time, temperature, pressure, and DD concentration on the devulcanization process were  
111 studied. In each case, the quality of the devulcanization was analyzed using the Horikx  
112 theory (Horikx, 1956). It was found that the concentration of DD was the most important  
113 variable during the process. It was also shown that an excessive increase in time and  
114 temperature just lead to polymer degradation. A combination between sulfur bond scission  
115 and main chain scission, commonly named regeneration, was obtained in all cases, with a  
116 maximum devulcanization degree near to 50 %.

117 Despite the several works carried out on the static devulcanization of rubber in scCO<sub>2</sub>  
118 atmosphere with DD, to the best of our knowledge, no published paper has reported the  
119 achievement of a high devulcanization degree of good quality, i.e. mostly scission of the  
120 sulfur-sulfur bonds with little degradation of the polymer.

121 The aim of this work is to develop a novel device allowing to perform successful rubber  
122 devulcanization, under scCO<sub>2</sub> atmosphere. In fact, a triaxial compression reactor was  
123 developed. It is integrated into a dynamic hydraulic universal testing machine equipped

124 with a heating chamber. Rubber devulcanization tests were carried out in this reactor, under  
125 scCO<sub>2</sub> atmosphere, using DD as devulcanizing reagent, at different temperatures. The  
126 degree and quality of devulcanization of the treated materials were evaluated by the  
127 swelling test combined with the Horikx theory. The mentioned theory was recently proved  
128 as efficient and as one of the fundamental tools in the devulcanization analysis (Seghar et  
129 al., 2019a). It was found that, when optimal conditions are used in the developed device,  
130 the degree of successful devulcanization reaches 90 %. To the extent of our knowledge, no  
131 similar results have been reported in the literature, using a comparable devulcanization  
132 process.

## 133 **2. Experimental**

### 134 *2.1. Devulcanization equipment*

135 A novel laboratory device allowing to perform rubber devulcanization tests was developed  
136 (Fig. 2). It mainly consists of a cylinder and a piston that let to apply triaxial compression  
137 on the rubber to be devulcanized. This reactor is integrated into a dynamic hydraulic  
138 universal testing machine (100 kN) equipped with a heating chamber. It allows to contain  
139 the rubber particles in a controlled atmosphere, in our case CO<sub>2</sub>, and all necessary  
140 devulcanizing reagents. The compression loading generated by the testing machine results  
141 in an increase of the pressure of the gas surrounding the rubber particles, turning the CO<sub>2</sub>  
142 from the gaseous state to the supercritical state. The main idea is to devulcanize the rubber  
143 by submitting it to an equi-triaxial mechanical stress (hydrostatic pressure loading) and by  
144 using small quantities of CO<sub>2</sub> (less than 5 wt%).

145 As shown in Fig. 2, the pressure inside the reactor is controlled by the movement of a  
146 piston (38 mm diameter), using the testing machine software (WaveMatrix). This  
147 movement has to be gradual, during unloading, to avoid the rapid gas decompression that  
148 could damage the rubber seals and the studied rubbers. The procedure followed to obtain a  
149 desired pressure by moving the piston can be summarized as follows.

150 First two compression loading tests were carried out, with and without CO<sub>2</sub> in the reactor.  
151 From the difference between the obtained force-displacement curves, the experimental gas  
152 pressure-full load curve was deduced. Then, the force to be imposed to reach a desired gas  
153 pressure was obtained from the mentioned curve. Finally, the piston was moved till reached  
154 the mentioned force, and the gas pressure was satisfactorily achieved.

155 It was assumed that, during the fast compression of the CO<sub>2</sub> and the rubber particles, the  
156 rubber remained unchanged.

157 The initial CO<sub>2</sub> pressure, before moving the piston, was calculated using the CO<sub>2</sub> state law  
158 proposed by Duschek et al. (Duschek et al., 1990), knowing the mass of CO<sub>2</sub> and the empty  
159 volume of the reactor cavity. Hypotheses of rubber incompressibility and isothermal  
160 transformations were considered.

161 The parameters that can be controlled during a test are: CO<sub>2</sub> content, CO<sub>2</sub> pressure,  
162 temperature (up to 160 °C), amount of rubber, amount of devulcanizing reagent, time, and  
163 compression loading and unloading steps.

## 164 *2.2. Materials and devulcanization process*

165 Sulfur-cured NR was obtained from the production waste of an industry. The requirements  
166 for the parts made with this material were high elasticity and high resistance to fatigue. The  
167 global formulation of the mentioned NR is detailed in Table 2. The rubber was used as



168 received, in the form of particles. The average size of the particles, determined by sieving  
169 was less than 4 mm. Because of confidentiality reasons, no further details about the studied  
170 material were provided by our industrial partner.

171 Diphenyl disulfide (DD) purchased from Sigma Aldrich Corporation was used as  
172 devulcanizing reagent in a proportion of 15 wt% in all cases. This proportion is similar to  
173 those already considered in the literature (Kojima et al., 2004; Kojima et al., 2005b; Jiang  
174 et al., 2012; Mangili et al., 2014b). The amount of DD actually consumed during the  
175 devulcanization process was not measured. Taking into account that excessive DD could  
176 affect the revulcanization process, measurement and recovery of the eventual unused DD  
177 reminds as a challenge to be addressed. DD chemical structure is given in Fig. 3.

178 The reaction medium during the devulcanization was CO<sub>2</sub> because its supercritical state is  
179 easy to reach (31.1 °C and 7.38 MPa), it is non-toxic, cheap, easily removable from the  
180 rubber, and non-flammable (Kojima et al., 2003; Ikeda, 2014). In the supercritical state the  
181 CO<sub>2</sub> has high diffusivity and acts as an excellent swelling agent in the rubber, which helps  
182 in the devulcanization process (Mueller et al., 2005; Liu et al., 2015; D'hooge et al., 2016).  
183 The purity of the used CO<sub>2</sub> was  $\geq 99.7\%$ .

184 Before running the devulcanization test, 20 g of NR were mixed with 3 g of DD and placed  
185 in the cavity of the reactor, at room temperature. Then the device was closed, positioned in  
186 the machine chamber and heated to the desired temperature. The air inside the reactor was  
187 removed using a vacuum pump, and then the CO<sub>2</sub> was injected. Afterwards, the  
188 compression ramp (Fig. 4) was executed in order to increase the pressure and allow the CO<sub>2</sub>  
189 to become supercritical. The imposed force was equal to -18 kN, inducing a pressure of 12  
190 MPa inside the reactor. Tests were carried out at 120, 140 and 160 °C, during 1 hour. At the

191 end of each test, the system was slowly decompressed and allowed to cool to room  
192 temperature. The treated rubber was extracted from the device in the form of one  
193 agglomerate piece. The devulcanization parameters (temperature and time) were chosen  
194 based on the data found in the literature (Kojima et al., 2004; Kojima et al., 2005b; Jiang et  
195 al., 2012; Mangili et al., 2014b), seeking to perform a satisfactory devulcanization by  
196 consuming a reasonable amount of energy. Greater temperature and/or time were supposed  
197 to be harsh conditions to be used in NR devulcanization tests, as they would induce  
198 material degradation.

### 199 2.3. Characterization

#### 200 2.3.1. Evaluation of the devulcanization degree

201 The devulcanization degree was evaluated by the swelling test, according to the Standard  
202 ASTM D 6814-02. Conforming to the procedure, the swelling was carried out after  
203 washing the rubber with acetone, in a 250 ml soxhlet extractor, during 16 h (Standard  
204 ASTM D297-02). Afterwards, the specimen was dried and weighed ( $m_i$ ), and then swelled  
205 in toluene at ambient temperature, during 72 h. The solvent was refreshed every 24 h. The  
206 sample impregnated with toluene was weighed ( $m_t$ ) and then dried in an oven at 70 °C  
207 during a night. The dried sample was finally weighed ( $m_d$ ). Three samples were tested for  
208 each material.

209 The soluble fraction %S was evaluated using the following equation:

$$210 \quad \%S = \frac{m_i - m_d}{m_i} \times 100 \quad (1)$$

211 The Flory-Rehner equation was used for the evaluation of the crosslink density  $\nu_e$ :

$$212 \quad v_e = \frac{-[\ln(1-V_r)+V_r+\chi V_r^2]}{[V_1 (V_r^{1/3}-V_r/2)]} \quad (2)$$

213 where  $V_r$  is the rubber volume fraction in the swollen sample,  $\chi$  is the rubber-solvent  
 214 interaction parameter, and  $V_1$  is the molar volume of toluene. It is worth noting that  
 215  $\chi=0.391$  for NR-toluene interaction. This value was obtained from the Standard ASTM D  
 216 6814-02 and it has been already used in the literature (Kojima et al., 2004; Lamminmaki et  
 217 al., 2006; Ghorai et al., 2016).  $V_1=106.3$  mL/mol.

218  $V_r$  was calculated using the following equation:

$$219 \quad V_r = \frac{m_d/\rho_d}{m_d/\rho_d + m_s/\rho_s} \quad (3)$$

220 where  $m_d$  is the mass of the dried rubber,  $\rho_d$  is the density of this rubber,  $m_s$  is the mass of  
 221 the solvent absorbed by the sample, in our case toluene, and  $\rho_s$  its density at room  
 222 temperature. The density of the dried rubber ( $\rho_d$ ) was evaluated by hydrostatic weighing  
 223 procedure as explained in the Standard ASTM D 6814-02.

224 Finally, the devulcanization degree,  $\%Devulc.$ , was evaluated for each sample, as follows:

$$225 \quad \%Devulc. = \left[1 - \frac{v_f}{v_i}\right] \quad (4)$$

226 where  $v_i$  is the crosslink density of the rubber before devulcanization, and  $v_f$  is the crosslink  
 227 density after devulcanization.  $v_i$  and  $v_f$  were estimated with Eq. 2.

228 The reported values are the averages of the results obtained with the three tested samples.

### 229 2.3.2. Horikx analysis

230 The Horikx diagram (Horikx, 1956) allows to carry out an accurate analysis of the  
 231 performed devulcanization. In fact, in this chart, the devulcanization degree (Eq. 4) and the

232 soluble fraction (Eq. 1) of the rubber are related, so that both the degree and quality of  
233 devulcanization, in terms of crosslink against main chain scission, can be qualitatively  
234 estimated.

235 The theoretical variation of the soluble fraction is shown in Fig. 5, for the tested NR, as a  
236 function of the devulcanization degree. The dashed line corresponds to only main chain  
237 scission, and the solid line corresponds to only selective crosslink scission. The initial  
238 soluble fraction of the studied vulcanized NR was evaluated by the swelling test and was  
239 found to be equal to 1.17 %. When carrying out the analysis, it is considered that the  
240 experimental points located near the solid curve correspond mostly to the scission of sulfur  
241 bonds, and those positioned near the dashed curve correspond to the rupture of the carbon-  
242 carbon chains i.e. the polymer degradation. If there are points located between the two  
243 curves, they are considered to undergo regeneration i.e. a combination between  
244 devulcanization and degradation of the rubber.

### 245 *2.3.3. Thermogravimetry*

246 Thermogravimetric analyses (TGA) were performed in a Perkin Elmer Diamond TG/DTA.  
247 Samples of about 10 mg were heated from room temperature up to 800 °C, at a heating rate  
248 of 10 °C/min and under nitrogen atmosphere, after soxhlet extraction and swelling in  
249 toluene (see section 2.3.1). The mass variation of the samples was gradually measured  
250 during the thermal degradation of the material.

### 251 *2.3.4. Scanning electron microscopy*

252 Morphological analysis of the virgin and devulcanized NR was achieved by scanning  
253 electron microscopy (SEM) performed in a TESCAN MIRA3 FEG-SEM. The working  
254 accelerating voltage was 20 kV. Sample surfaces were prepared by cryofracture.

### 255 **3. Results and discussion**

256 The evaluation of the variation in the soluble fraction, before and after devulcanization  
257 treatment, is not enough to conclude about the devulcanization quality, because it cannot  
258 distinguish between crosslinks breaking (devulcanization) and rubber main chains breaking  
259 (degradation) (Li et al., 2005; Yazdani et al., 2011). In this work, the evaluation of the  
260 devulcanization quality was performed using the Horikx diagram (section 2.3.2.). Swelling  
261 tests results and the Horikx theoretical curves corresponding to the studied material are  
262 reported in Fig. 6. This figure shows that all the experimental points are near the lower  
263 curve corresponding to sulfur bond scission. Thus, the devulcanization was effective, with a  
264 selective bonds breaking and little or no polymer degradation. Fig. 6 also highlights that, as  
265 the temperature increases, the experimental points are moved to the right side of the chart  
266 i.e. to higher devulcanization levels. The devulcanization degree reaches a maximum value  
267 of ~90 %. To the extent of our knowledge, there are no similar results in the literature  
268 dealing with NR static devulcanization in scCO<sub>2</sub>.

269 Mangili et al. (Mangili et al., 2014a) has proposed a devulcanization mechanism for sulfur-  
270 cured rubber, in the presence of DD. It is explained that the devulcanization process starts  
271 with the DD decomposition, which leads to the creation of two active radicals that are  
272 capable to open the sulfur bonds. The allylic hydrogen from the rubber is subtracted by the  
273 benzene-sulfide radical creating intermediate products (Rajan, 2005). Different  
274 combinations can take place during the reaction, afterwards new active crosslinking sites

275 are created making the devulcanized rubber ready to be revulcanized (Vega et al., 2008;  
276 Anu Mary et al., 2016; Asaro et al., 2018).

277 According to the preceding explanation, it is not possible to obtain a high devulcanization  
278 degree if the temperature is not enough to dissociate the DD, which was the case of the test  
279 carried out at 120 °C (Fig. 6). It can be concluded that the reactivity of DD increases at  
280 high temperature, and that 160 °C was the optimum one in this study. In addition, all the  
281 above results prove that the developed device works well and that it can be used to carry  
282 out rubber devulcanization under different experimental conditions. As stated in the  
283 literature, generally, the initial mechanical properties of the rubbers are not entirely  
284 recovered after the devulcanization and revulcanization processes, whatever the used  
285 devulcanization technique (Li et al., 2005; Mangili et al., 2014a; Isayev et al., 2014). As  
286 shown in Fig. 6, the experimental points obtained in this study are located on the solid  
287 curve of the Horikx chart, which means that the material has underwent mostly sulfur  
288 bonds scission. This suggests that the proposed devulcanization process would not have a  
289 significant influence on the mechanical properties of the revulcanized NR.

290 Although a satisfactory devulcanization was confirmed by the Horikx analysis, TGA and  
291 SEM tests were made to strengthen this result.

292 As explained by Kleps et al. (Kleps et al., 2000), the thermogravimetric analysis is useful to  
293 control and evaluate the devulcanization process. Therefore, thermal degradation of the  
294 virgin NR and the most devulcanized NR were studied by thermogravimetry, and the  
295 results are presented in Fig. 7. It is noticeable that the devulcanized material starts to  
296 degrade slightly before the virgin one. This could be related to the breaking of the  
297 tridimensional network of the treated rubber, during the devulcanization process, which is  
298 in accordance with the swelling test results presented in the Horikx diagram (Fig. 6).

299 Similar results were found by Valetini et al. (Valentini et al., 2020) when studying the  
300 thermal degradation of devulcanized tire rubber. Moreover, the thermal degradation rate is  
301 higher for the virgin material, result that could be associated to a higher sulfur content,  
302 which plays the role of thermal degradation accelerator. It is worth underlining that the  
303 average degradation temperature (375 °C) is the same for both materials, suggesting that  
304 the devulcanization process mainly breaks the sulfur bonds without breaking the main  
305 chains of the rubber. Finally, the residual mass corresponding to the virgin rubber amounts  
306 to about 20 % while that of the devulcanized rubber is about 34 %. The difference between  
307 the obtained values could be explained on the basis of carbon black content (Table 2). In  
308 fact, both materials had the same carbon black content, however, during devulcanization  
309 and washing processes, the treated material was separated into the gel and sol fractions, and  
310 only the gel part was used in the thermogravimetric test, the sol fraction was removed  
311 during the swelling test and washing (see section 2.3.1). Consequently, the relative carbon  
312 black content of the devulcanized rubber is higher, and is observed as a higher residual  
313 mass.

314 The microstructures of the rubber before and after devulcanization were analyzed by SEM.  
315 The obtained images are presented in Fig. 8. The microstructure of the virgin NR is  
316 continuous and smooth (Fig. 8a), which is a signature of a homogeneous and cohesive  
317 material. The material devulcanized at 120 °C (Fig. 8b) presents slight changes compared  
318 to the virgin NR, suggesting that the rubber underwent little modifications during the  
319 devulcanization process. The microstructure of the NR devulcanized at 140 °C (Fig. 8c)  
320 presents two phases, a homogeneous cohesive phase and a discontinuous non-cohesive  
321 phase, corresponding respectively to the devulcanized and non-devulcanized zones of the

322 rubber. This result means that the rubber was only partially devulcanized. Fig. 8d reveals  
323 that the microstructure of the material devulcanized at 160 °C is homogeneous, continuous  
324 and smooth, confirming that the rubber was highly and effectively devulcanized, as  
325 concluded from the Horikx analysis (Fig. 6).

#### 326 **4. Conclusion**

327 A novel device allowing to perform rubber devulcanization was developed. It consists of a  
328 triaxial compression reactor integrated into a dynamic hydraulic universal testing machine  
329 with a heating chamber. NR industry waste was devulcanized in the mentioned device at  
330 different temperatures, in scCO<sub>2</sub> and using DD as devulcanizing reagent. A very high  
331 devulcanization degree (~90 %) was reached in the specimen tested at 160 °C. From the  
332 Horikx analysis, it was found that the devulcanization was successful, with almost no  
333 polymer degradation. It is worth noting that the devulcanization test conditions needs to be  
334 optimized to obtain similar results with another type of rubber. Thermogravimetric tests  
335 revealed that the material treated at 160 °C begun to degrade before the virgin one, which  
336 was an indication of crosslinks breaking in the rubber, confirming its successful  
337 devulcanization. In addition, SEM images showed that its morphology is homogeneous,  
338 continuous and smooth, which is another proof of its successful devulcanization, in  
339 accordance with the results obtained by Horikx and thermogravimetric analyses.

340 The results from this work suggested that the NR industry waste could be highly  
341 devulcanized by the proposed process. This means that the developed reactor is appropriate  
342 to perform rubber recycling, which contributes to the progress in the waste management  
343 and thus in the environmental protection.



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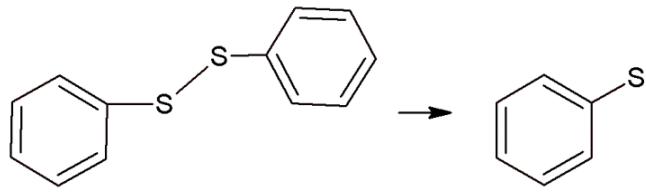
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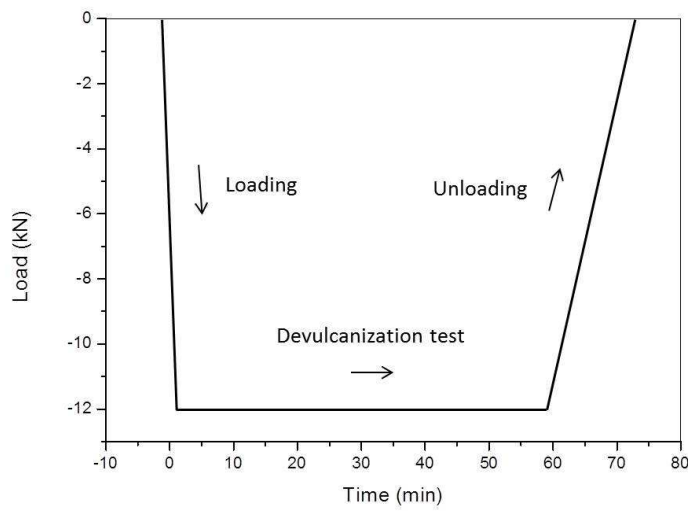


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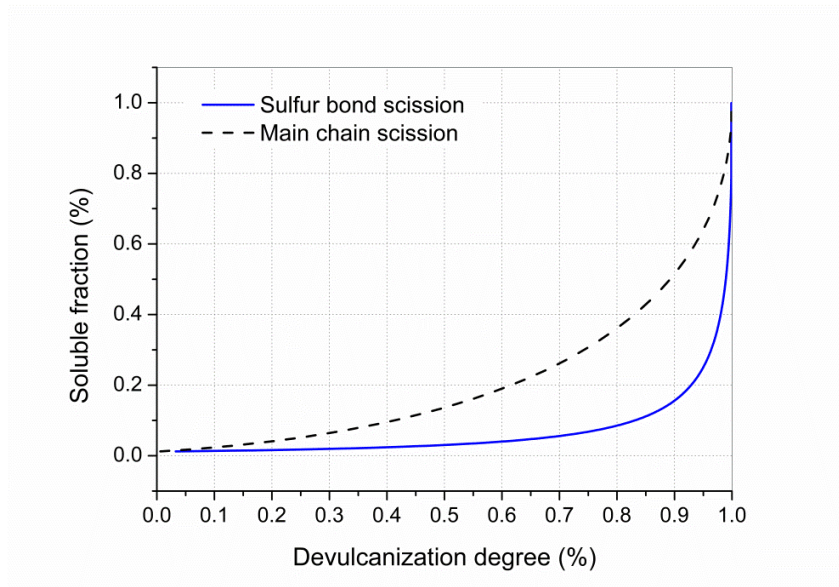
**Fig. 3.** Diphenyl disulfide chemical structure.



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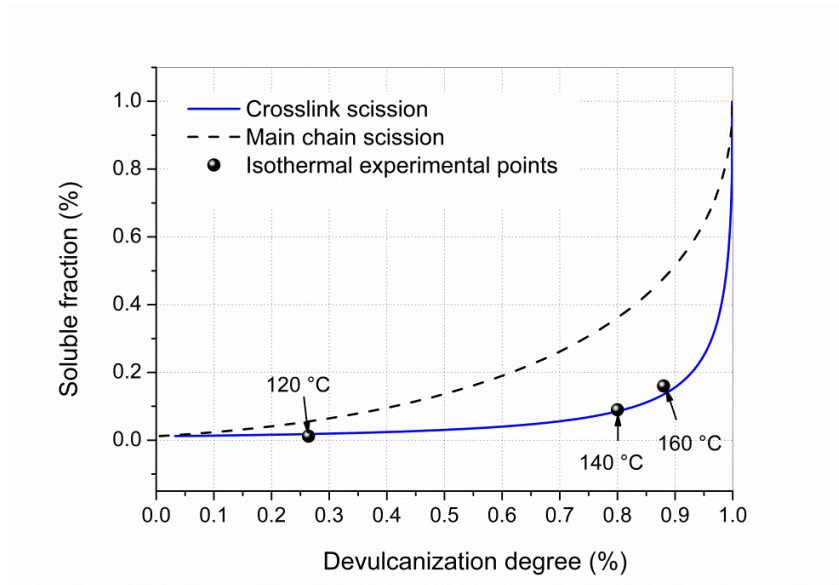
**Fig. 4.** Loading-unloading cycle carried out during the devulcanization test.



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**Fig. 5.** Theoretical Horikx diagram of the studied NR.



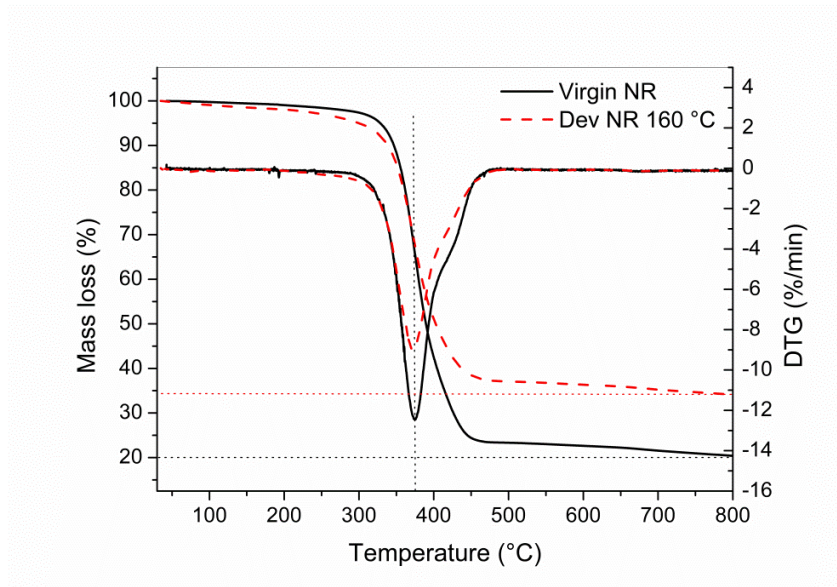
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**Fig. 6.** Theoretical and experimental soluble fractions as a function of the devulcanization

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degree for the studied NR.



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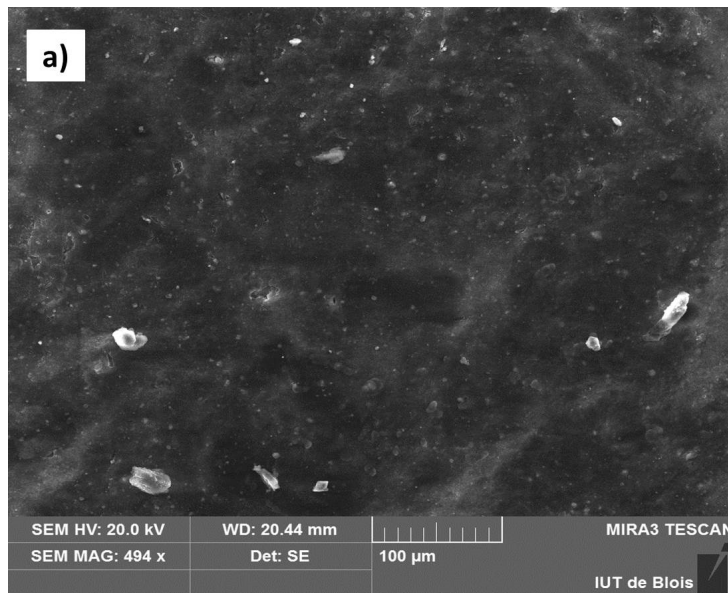
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**Fig. 7.** Mass loss and its derivative (DTG) as a function of temperature for virgin

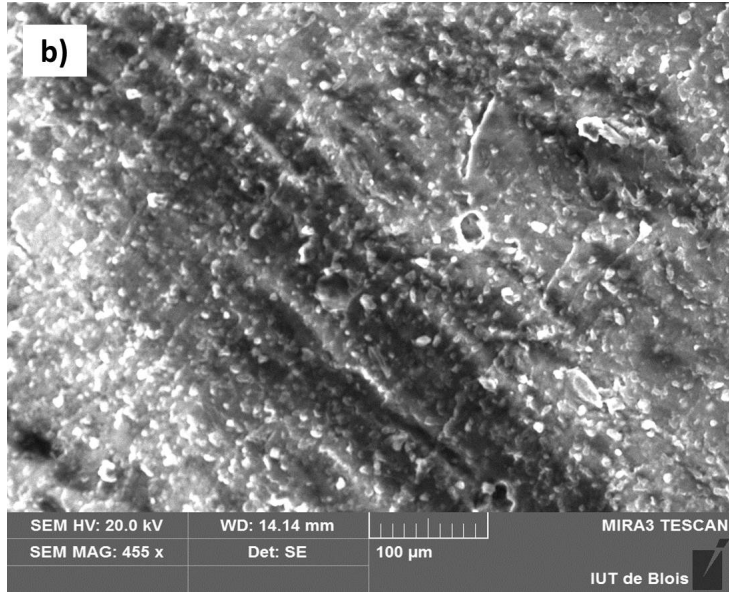
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NR and NR devulcanized at 160 °C.

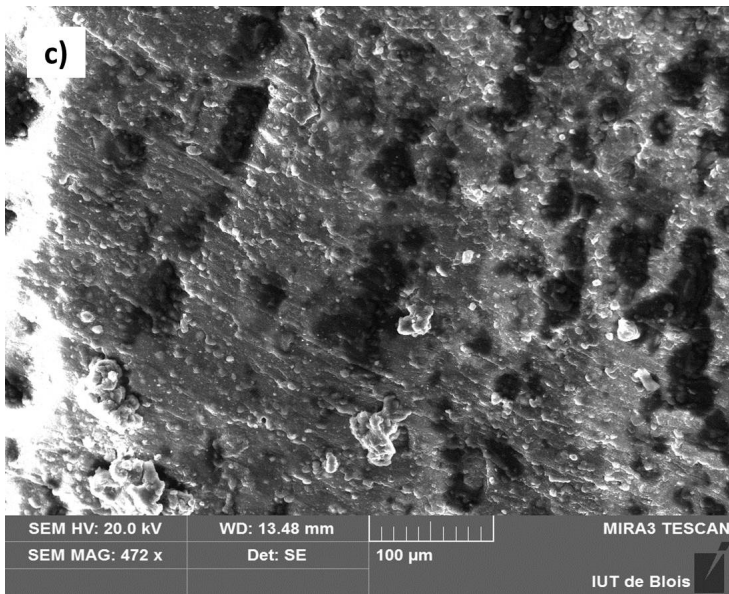
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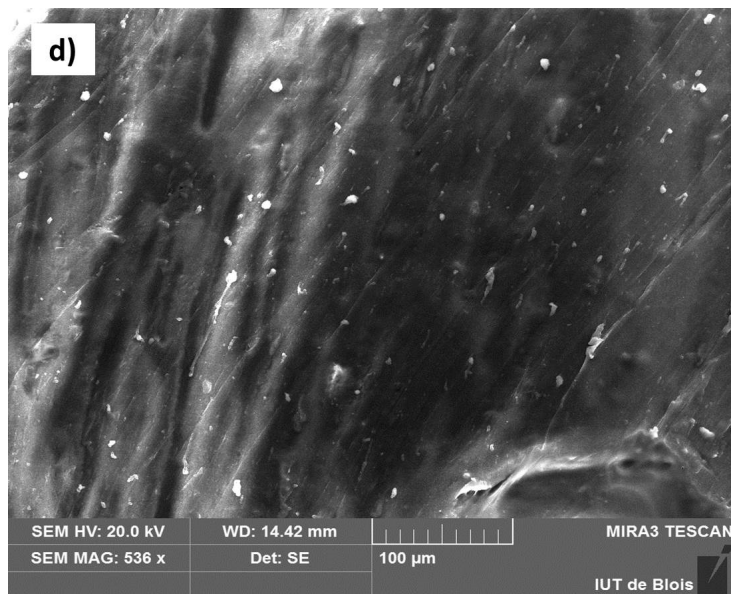
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555 **Fig. 8.** SEM images of a) virgin NR, b) NR treated at 120 °C, c) NR treated at 140 °C, and

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d) NR treated at 160 °C.

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558 **Table 1** Table of symbols and notations.

Symbols and notations	Explanation
C-C	Carbon-carbon bond
CO <sub>2</sub>	Carbon dioxide
C-S	Carbon-sulfur bond
DD	Diphenyl disulfide
DTG	Mass loss derivative
GTR	Ground tire rubber
NR	Natural rubber
scCO <sub>2</sub>	Supercritical carbon dioxide
SEM	Scanning electron microscopy
S-S	Sulfur-sulfur bond
TGA	Thermogravimetry
$m_i$	Initial mass

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$m_d$	Mass of the dried rubber
$m_t$	Mass of the sample impregnated with toluene
%S	Soluble fraction
$\nu_e$	Crosslink density
$V_r$	Rubber volume fraction in the swollen sample
$\chi$	Rubber-solvent interaction parameter
$V_l$	Molar volume of toluene
$m_s$	Mass of the solvent absorbed by the sample
$\rho_s$	Density of the dried rubber
$\rho_d$	Density of toluene at room temperature
%Devulc	Devulcanization degree
$\nu_i$	Crosslink density of the rubber before devulcanization
$\nu_f$	Crosslink density of the rubber after devulcanization

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560 **Table 2** NR formulation.

Component	Sulfur-cured NR (phr)
NR	100
Carbon black	35
Processing oil	3
Stearic acid	1
CBS*	1
Sulfur	1.5

561 \*CBS: N-Cyclohexyl-2-benzothiazole sulfonamide

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