



HAL
open science

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

Lucia Asaro, Michel Gratton, Nathalie Poirot, Said Seghar, Nourredine Aït Hocine

► **To cite this version:**

Lucia Asaro, Michel Gratton, Nathalie Poirot, Said Seghar, Nourredine Aït Hocine. Devulcanization of natural rubber industry waste in supercritical carbon dioxide combined with diphenyl disulfide. Waste Management, 2020, 118, pp.647-654. 10.1016/j.wasman.2020.09.026 . hal-03605252

HAL Id: hal-03605252

<https://hal.science/hal-03605252>

Submitted on 17 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

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 CO₂, 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 scCO₂ 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 scCO₂ 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 (scCO₂) 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 scCO₂ 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 scCO₂ will get into the NR previously swollen by
91 the scCO₂. 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 scCO₂, 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 scCO₂, 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 scCO₂ 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 scCO₂
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 scCO₂ 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 scCO₂ 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 CO₂, 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 CO₂
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 CO₂ (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 CO₂ 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 CO₂ and the rubber particles, the
156 rubber remained unchanged.

157 The initial CO₂ pressure, before moving the piston, was calculated using the CO₂ state law
158 proposed by Duschek et al. (Duschek et al., 1990), knowing the mass of CO₂ 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: CO₂ content, CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ was injected. Afterwards, the
188 compression ramp (Fig. 4) was executed in order to increase the pressure and allow the CO₂
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 ν_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, χ 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, ρ_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 ρ_s its density at room
 222 temperature. The density of the dried rubber (ρ_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 scCO₂.

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 scCO₂ 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.

344 **Acknowledgements**

345 The authors are grateful to la Région Centre Val de Loire, France for the financial support
346 received through the VALESTO project.

347 **References**

- 348 Adhikari, B., De, D., Maiti, S., 2000. Reclamation and recycling of waste rubber. *Prog.*
349 *Polym. Sci.* 25, 909–948. [https://doi.org/10.1016/S0079-6700\(00\)00020-4](https://doi.org/10.1016/S0079-6700(00)00020-4)
- 350 Anu Mary, J., Benny, G., Madhusoodanan, K.N., Rosamma, A., 2016. The current status of
351 sulphur vulcanization and devulcanization chemistry: devulcanization. *Rubber Sci.* 29,
352 62–100.
- 353 Aoudia, K., Azem, S., Aït Hocine, N., Gratton, M., Pettarin, V., Seghar, S., 2017.
354 Recycling of waste tire rubber: Microwave devulcanization and incorporation in a
355 thermoset resin. *Waste Manag.* 60, 471–481.
356 <https://doi.org/10.1016/j.wasman.2016.10.051>
- 357 Asaro, L., Gratton, M., Seghar, S., Aït Hocine, N., 2018. Recycling of rubber wastes by
358 devulcanization. *Resour. Conserv. Recycl.* 133, 250–262.
359 <https://doi.org/10.1016/j.resconrec.2018.02.016>
- 360 Bockstal, L., Berchem, T., Schmetz, Q., Richel, A., 2019. Devulcanisation and reclaiming
361 of tires and rubber by physical and chemical processes: A review. *J. Clean. Prod.* 236,
362 117574. <https://doi.org/10.1016/j.jclepro.2019.07.049>
- 363 Charlesby, A., 1953. Solubility and molecular size distribution of crosslinked polystyrene.

364 J. Polym. Sci. 11, 513–520.
365 <https://doi.org/https://doi.org/10.1002/pol.1953.120110601>

366 Cheng, X., Song, P., Zhao, X., et. al., 2018. Liquefaction of ground tire rubber at low
367 temperature. *Waste Management*, vol. 71, 301-310.
368 <https://doi.org/10.1016/j.wasman.2017.10.004>

369 D’hooge, D.R., Van Steenberge, P.H.M, Reyniers, M.F., et al., 2016. The strength of multi-
370 scale modeling to unveil the complexity of radical polymerization. *Progress in*
371 *Polymer Science*, Volume 58, 59-89.
372 <https://doi.org/10.1016/j.progpolymsci.2016.04.002>

373 Diaz, R., Colomines, G., Peuvrel-Disdier, E., Deterre, R., 2018. Thermo-mechanical
374 recycling of rubber: Relationship between material properties and specific mechanical
375 energy. *J. Mater. Process. Technol.* 252, 454–468.
376 <https://doi.org/10.1016/j.jmatprotec.2017.10.014>

377 Duschek, W., Kleinrahm, R., Wagner, W., 1990. Measurement and correlation of the
378 (pressure, density, temperature) relation of carbon dioxide I. The homogeneous gas
379 and liquid regions in the temperature range from 217 K to 340 K at pressures up to 9
380 MPa. *The Journal of Chemical Thermodynamics.* 22, 827-840.
381 [https://doi.org/10.1016/0021-9614\(90\)90172-M](https://doi.org/10.1016/0021-9614(90)90172-M)

382 Ghorai S., Bhunia S., Roy M., et al., 2016. Mechanochemical devulcanization of natural
383 rubber vulcanizate by dual function disulfide chemicals. *Polymer Degradation and*
384 *Stability*, 129, 34-46. <http://dx.doi.org/10.1016/j.polyimdegradstab.2016.03.024>

385 Hejna, A., Korol, J., Przybysz-Romatowska, M., Zedler, Ł., Chmielnicki, B., Formela, K.,

386 2020. Waste tire rubber as low-cost and environmentally-friendly modifier in
387 thermoset polymers – A review. *Waste Manag.* 108, 106–118.
388 <https://doi.org/10.1016/j.wasman.2020.04.032>

389 Hon, Y.J., Jeong, K.M., Saha, P., Suh, J., Kim, J.K., 2015. Processing and Characterization
390 of Microwave and Ultrasonically Treated Waste-EPDM/LDPE Polymer Composites.
391 *Polym. Eng. Sci.* <https://doi.org/DOI 10.1002/pen.23916>

392 Horikx, M., 1956. Chain scissions in a polymer network. *J. Polym. Sci. Part B Polym.*
393 *Phys.* 19, 445–454. <https://doi.org/https://doi.org/10.1002/pol.1956.120199305>

394 Ikeda, Y., 2014. Recycling of sulfur cross-linked natural rubber (NR) using supercritical
395 carbon dioxide. *Chem. Manuf. Appl. Nat. Rubber* 436–451.
396 <https://doi.org/10.1533/9780857096913.3.436>

397 Isayev, A.I., 2013. Recycling of Rubbers. *Sci. Technol. Rubber* 697–764.
398 <https://doi.org/10.1016/B978-0-12-394584-6.00020-0>

399 Isayev, A.I., Liang, T., Lewis, T.M., 2014. Effect of particle size on ultrasonic
400 devulcanization of tire rubber in twin-screw extruder. *Rubber Chemistry and*
401 *Technology*, 87, 86-102. <https://doi.org/10.5254/RCT.13.87926>

402 Jana G.K, Das C.K., 2005. Devulcanization of Natural Rubber Vulcanizates by
403 Mechanochemical Process. *Polymer-Plastics Technology and Engineering*, 44: 8-9,
404 1399-1412. DOI: 10.1080/03602550500209853

405 Jiang, K., Shi, J., Ge, Y., Zou, R., Yao, P., Li, X., Zhang, L., 2013. Complete
406 devulcanization of sulfur-cured butyl rubber by using supercritical carbon dioxide. *J.*

407 Appl. Polym. Sci. 127, 2397–2406. <https://doi.org/10.1002/app.37542>

408 Karger-Kocsis, J., Mészáros, L., Bárány, T., 2013. Ground tyre rubber (GTR) in
409 thermoplastics, thermosets, and rubbers. *J Mater Sci* 48, 1–38.
410 <https://doi.org/10.1007/s10853-012-6564-2>.

411 Kleps, T., Piaskiewicz, M., Parasiewicz, W., 2000. Use of thermogravimetry in the study of
412 rubber devulcanization. *J. Therm. Anal. Calorim.* 60, 271–277.
413 <https://doi.org/10.1023/A:1010134315762>

414 Kojima, M., Kohjiya, S., Ikeda, Y., 2005a. Role of supercritical carbon dioxide for
415 selective impregnation of decrosslinking reagent into isoprene rubber vulcanizate.
416 *Polymer (Guildf)*. 46, 2016–2019. <https://doi.org/10.1016/j.polymer.2004.12.053>

417 Kojima, M., Ogawa, K., Mizushima, H., Tosaka, M., Kohjiya, S., Ikeda, Y., 2003.
418 Devulcanization of Sulfur-Cured Isoprene Rubber in Supercritical Carbon Dioxide.
419 *Rubber Chem. Technol.* 76, 957–968. <https://doi.org/10.5254/1.3547784>

420 Kojima, M., Tosaka, M., Ikeda, Y., 2004. Chemical recycling of sulfur-cured natural rubber
421 using supercritical carbon dioxide. *Green Chem.*, 6, 84–89. DOI:10.1039/b314137c.

422 Kojima, M., Tosaka, M., Ikeda, Y., Kohjiya, S., 2005b. Devulcanization of carbon black
423 filled natural rubber using supercritical carbon dioxide. *J. Appl. Polym. Sci.* 95, 137–
424 143. <https://doi.org/10.1002/app.20806>

425 Kroll, L., Hoyer, S., 2019. Zero-waste production: Technology for the in-house recycling of
426 technical elastomers. *Procedia Manuf.* 33, 335–342.
427 <https://doi.org/10.1016/j.promfg.2019.04.041>

428 Lamminmaki, J., Li, S., Hanhi, K., 2006. Feasible incorporation of devulcanized rubber
429 waste in virgin natural rubber. *J Mater Sci*, 41:8301–8307. DOI: 10.1007/s10853-006-
430 1010-y.

431 le Beau, D. S., 1967. Science and Technology of Reclaimed Rubber. *Rubber Chemistry and*
432 *Technology* 40, 1, 217–237. <https://doi.org/10.5254/1.3539043>

433 Li, S., Lamminmäki, J., Hanhi, K., 2005. Effect of ground rubber powder and
434 devulcanizates on the properties of natural rubber compounds. *J. Appl. Polym. Sci.* 97,
435 208–217. <https://doi.org/10.1002/app.21748>

436 Liu, H.L., Wang, X.P., Jia, D.M., 2020. Recycling of waste rubber powder by mechano-
437 chemical modification. *J. Clean. Prod.* 245, 118716.
438 <https://doi.org/10.1016/j.jclepro.2019.118716>

439 Liu, Z., Li, X., Xu, X., Wang, X., Dong, C., Liu, F., Wei, W., 2015. Devulcanization of
440 waste tread rubber in supercritical carbon dioxide: Operating parameters and product
441 characterization. *Polym. Degrad. Stab.* 119, 198–207.
442 <https://doi.org/10.1016/j.polymdegradstab.2015.05.017>

443 Mangili, I., Collina, E., Anzano, M., Pitea, D., Lasagni, M., 2014a. Characterization and
444 supercritical CO₂ devulcanization of cryo-ground tire rubber: Influence of
445 devulcanization process on reclaimed material. *Polym. Degrad. Stab.* 102, 15–24.
446 <https://doi.org/10.1016/j.polymdegradstab.2014.02.017>

447 Mangili, I., Lasagni, M., Huang, K., Isayev, A.I., 2015. Modeling and optimization of
448 ultrasonic devulcanization using the response surface methodology based on central

449 composite face-centered design. *Chemom. Intell. Lab. Syst.* 144, 1–10.
450 <https://doi.org/10.1016/j.chemolab.2015.03.003>

451 Mangili, I., Oliveri, M., Anzano, M., Collina, E., Pitea, D., Lasagni, M., 2014b. Full
452 factorial experimental design to study the devulcanization of ground tire rubber in
453 supercritical carbon dioxide. *J. Supercrit. Fluids* 92, 249–256.
454 <https://doi.org/10.1016/j.supflu.2014.06.001>

455 Mohajerani, A., Burnett, L., Smith, J. V., Markovski, S., Rodwell, G., Rahman, M.T.,
456 Kurmus, H., Mirzababaei, M., Arulrajah, A., Horpibulsuk, S., Maghool, F., 2020.
457 Recycling waste rubber tyres in construction materials and associated environmental
458 considerations: A review. *Resour. Conserv. Recycl.* 155, 104679.
459 <https://doi.org/10.1016/j.resconrec.2020.104679>

460 Molino, A., Donatelli, A., Marino, T., Aloise, A., Rimauro, J., Iovane, P., 2018. Waste tire
461 recycling process for production of steam activated carbon in a pilot plant. *Resour.*
462 *Conserv. Recycl.* 129, 102–111. <https://doi.org/10.1016/j.resconrec.2017.10.023>

463 Mueller, P.A., Storti, G., Morbidelli, M., 2005. Detailed modelling of MMA dispersion
464 polymerization in supercritical carbon dioxide. *Chemical Engineering Science*,
465 Volume 60, Issue 7, 1911-1925. <https://doi.org/10.1016/j.ces.2004.11.029>

466 Novotny et al. 1978. US Patent 4,104,205. Microwave devulcanization of rubber.

467 Pehlken, A., Müller, D.H., 2009. Using information of the separation process of recycling
468 scrap tires for process modelling. *Resour. Conserv. Recycl.* 54, 140–148.
469 <https://doi.org/10.1016/j.resconrec.2009.07.008>

470 Rajan, V.V., 2005. Devulcanization of NR Based Latex Products for Tyre Applications.
471 Ph.D Thesis. University of Twente, Enschede, The Netherlands (ISBN 90 365 22579).

472 Ramarad, S., Khalid, M., Ratnam, C.T., Chuah, A.L., Rashmi, W., 2015. Waste tire rubber
473 in polymer blends: A review on the evolution, properties and future. *Prog. Mater. Sci.*
474 72, 100–140. <https://doi.org/10.1016/j.pmatsci.2015.02.004>

475 Rooj, S., Basak, G.C., Maji, P.K. et al., 2011. New Route for Devulcanization of Natural
476 Rubber and the Properties of Devulcanized Rubber. *J Polym Environ* 19, 382–390.
477 <https://doi.org/10.1007/s10924-011-0293-5>.

478 Sabzekar, M., Chenar, M.P., Mortazavi, S.M., Kariminejad, M., Asadi, S., Zohuri, G.,
479 2015. Influence of process variables on chemical devulcanization of sulfur-cured
480 natural rubber. *Polym. Degrad. Stab.* 118, 88–95.
481 <https://doi.org/10.1016/j.polymdegradstab.2015.04.013>

482 Sabzekar, M., Zohuri, G., Chenar, M.P., Mortazavi, S.M., Kariminejad, M., Asadi, S.,
483 2016. A new approach for reclaiming of waste automotive EPDM rubber using waste
484 oil. *Polym. Degrad. Stab.* 129, 56–62.
485 <https://doi.org/10.1016/j.polymdegradstab.2016.04.002>

486 Saiwari, S., Dierkes, W.K., Noordermeer, J.W.M., 2013. Devulcanization of whole
487 passenger car tire material. *KGK Kautschuk Gummi Kunststoffe* 66, 20–25.

488 Saiwari, S., Dierkes, W.K., Noordermeer, J.W.M., 2013. Comparative investigation of the
489 devulcanization parameters of tire rubbers. *Rubber Chem. Technol.* 87, 31–42.

490 Seghar, S., Asaro, L., Aït Hocine, N., 2019a. Experimental Validation of the Horikx Theory

491 to be Used in the Rubber Devulcanization Analysis. *J. Polym. Environ.* 27, 2318–
492 2323. <https://doi.org/10.1007/s10924-019-01513-z>

493 Seghar, S., Asaro, L., Rolland-Monnet, M., Aït Hocine, N., 2019b. Thermo-mechanical
494 devulcanization and recycling of rubber industry waste. *Resour. Conserv. Recycl.* 144,
495 180–186. <https://doi.org/10.1016/j.resconrec.2019.01.047>

496 Sienkiewicz, M., Janik, H., Borzędowska-Labuda, K., Kucińska-Lipka, J., 2017.
497 Environmentally friendly polymer-rubber composites obtained from waste tyres: A
498 review. *J. Clean. Prod.* 147, 560–571. <https://doi.org/10.1016/j.jclepro.2017.01.121>

499 Simon, D.Á., Pirityi, D., Tamás-Bényei, P., Bárány, T., 2020. Microwave devulcanization
500 of ground tire rubber and applicability in SBR compounds. *J. Appl. Polym. Sci.* 137,
501 1–8. <https://doi.org/10.1002/app.48351>

502 Valentini, F., Dorigato, A., Pegoretti, A., 2020. Evaluation of the Role of Devulcanized
503 Rubber on the Thermo-mechanical Properties of Polystyrene. *J. Polym. Environ.*
504 <https://doi.org/10.1007/s10924-020-01717-8>

505 Vega, B., Montero, L., Lincoln, S., Agullo, N., 2008. Control of
506 Vulcanizing/Devulcanizing Behavior of Diphenyl Disulfide with Microwaves as
507 the Heating Source. *J. Appl. Polym. Sci.* 108, 1969–1975.
508 <https://doi.org/10.1002/app.27578>

509 Verbruggen, M.A.L., van der Does, L., Dierkes, W.K., Noordermeer, J.W.M., 2016.
510 Experimental Validation of the Charlesby and Horikx Models Applied To De-
511 Vulcanization of Sulfur and Peroxide Vulcanizates of N_r and E_{pdm}. *Rubber Chem.*

512 Technol. 89, 671–688. <https://doi.org/10.5254/rct.16.83776>

513 Verbruggen, M.A.L., van der Does, L., Noordermeer, J.W.M., van Duin, M., Manuel, H.J.,
514 1999. Mechanisms Involved in the Recycling of NR and EPDM. Rubber Chem.
515 Technol. 72, 731–740. <https://doi.org/10.5254/1.3538830>

516 Yao, C., Zhao, S., Wang, Y., Wang, B., Wei, M., Hu, M., 2013. Microbial desulfurization
517 of waste latex rubber with Alicyclobacillus sp. Polym. Degrad. Stab. 98, 1724–1730.
518 <https://doi.org/10.1016/j.polymdegradstab.2013.06.002>

519 Yazdani, H., Karrabi, M., Ghasmi, I., Azizi, H., Bakhshandeh, G.R., 2011. Devulcanization
520 of waste tires using a twin-screw extruder: The effects of processing conditions. J.
521 Vinyl Addit. Technol. 17, 64–69.

522 Yuanhu L., Suhe Z., Yaqin W., 2011. Microbial desulfurization of ground tire rubber by
523 Thiobacillus ferrooxidans. Polymer Degradation and Stability, Vol 96, 9, 1662-1668.
524 <https://doi.org/10.1016/j.polymdegradstab.2011.06.011>

525 Zhang, X., Saha, P., Cao, L., Li, H., Kim, J., 2018. Devulcanization of waste rubber powder
526 using thiobisphenols as novel reclaiming agent. Waste Manag. 78, 980–991.
527 <https://doi.org/10.1016/j.wasman.2018.07.016>

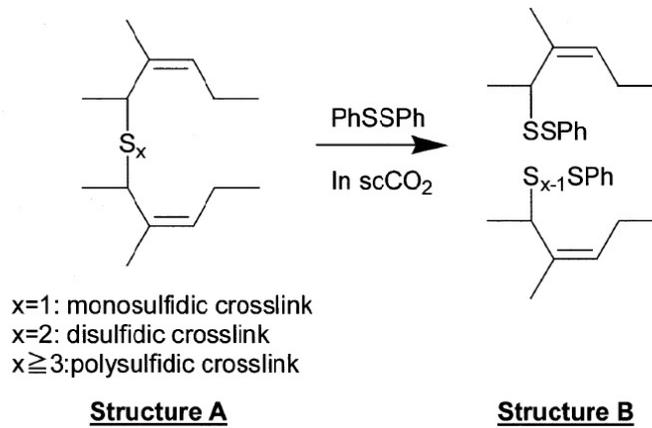
528

529

530

531

532 **Figures and tables.**

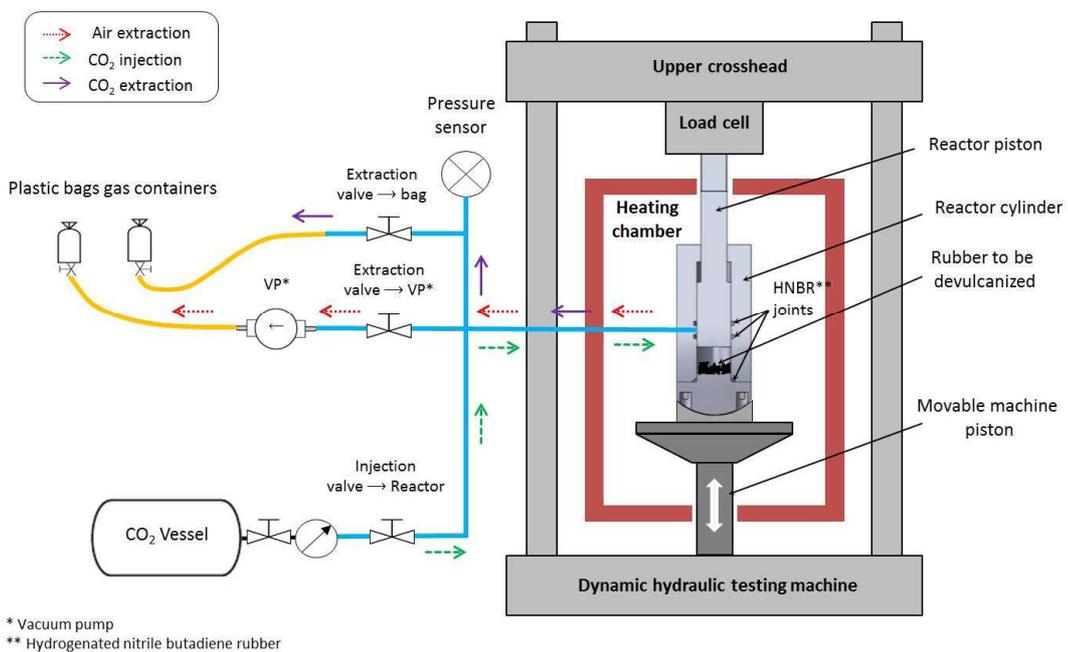


533

534 **Fig. 1.** Crosslink cleavage reaction of NR in the presence of DD and scCO₂ proposed by

535

Kojima et al. (Kojima et al., 2004).

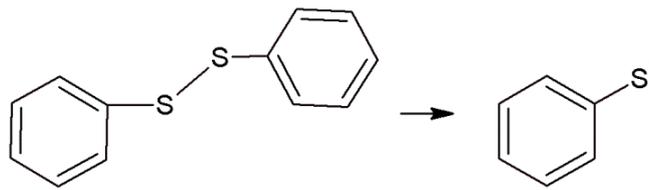


536

537

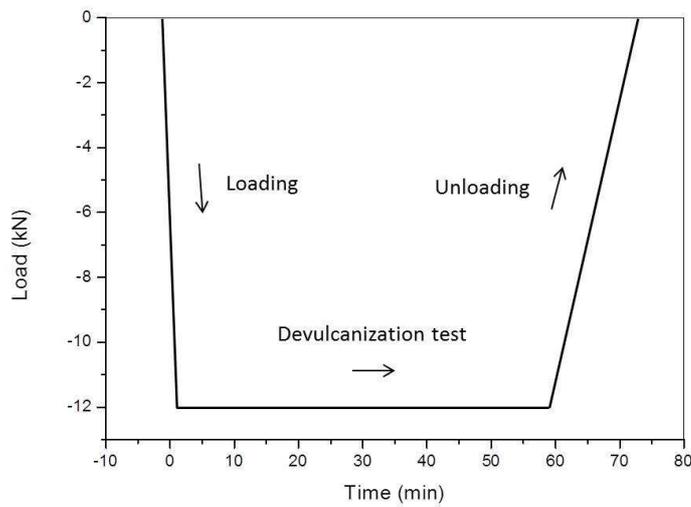
Fig. 2. Devulcanization device scheme.

538



539

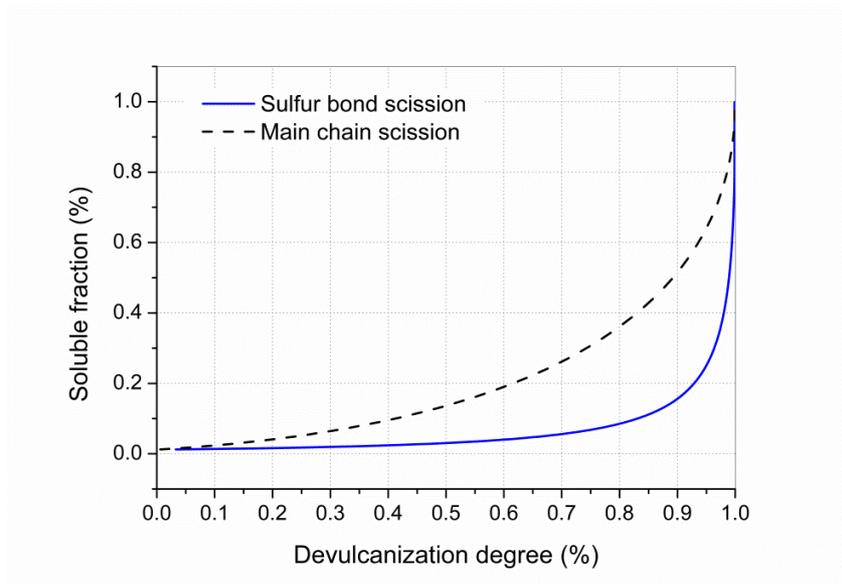
Fig. 3. Diphenyl disulfide chemical structure.



540

541

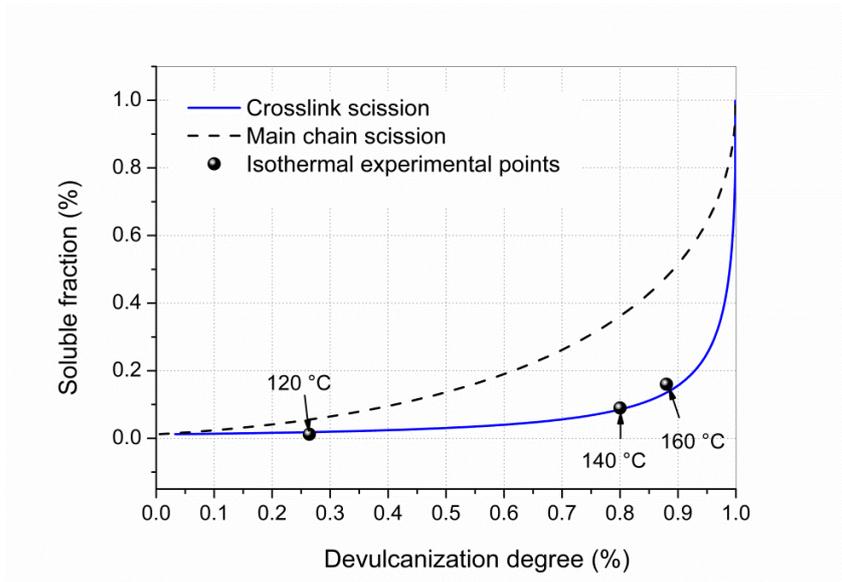
Fig. 4. Loading-unloading cycle carried out during the devulcanization test.



542

543

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

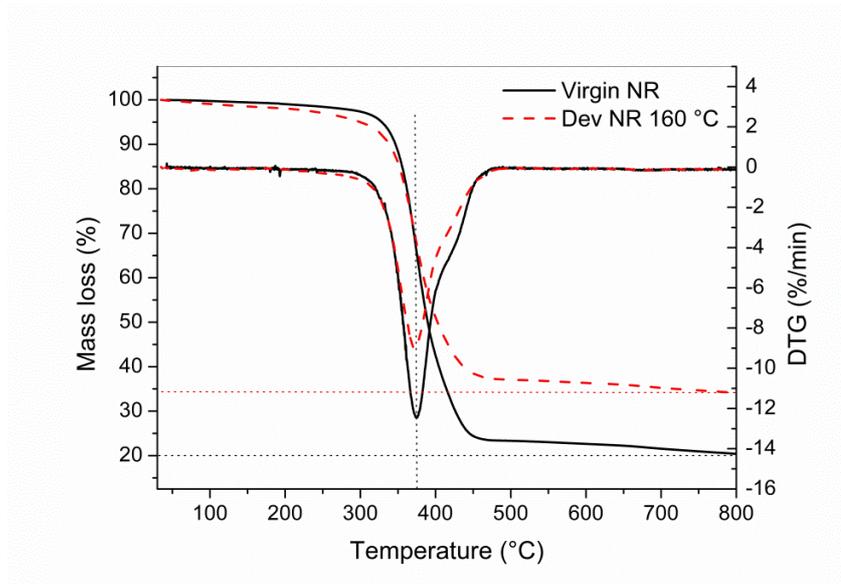


544

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

546

degree for the studied NR.



547

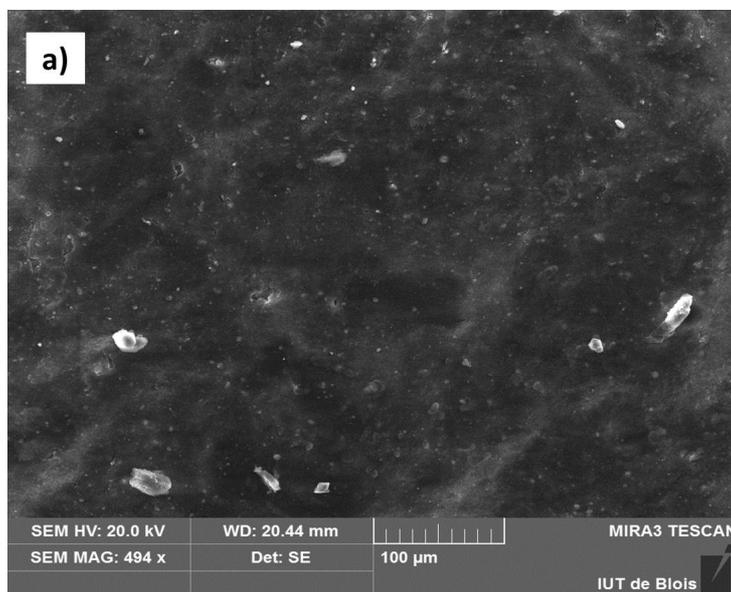
548

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

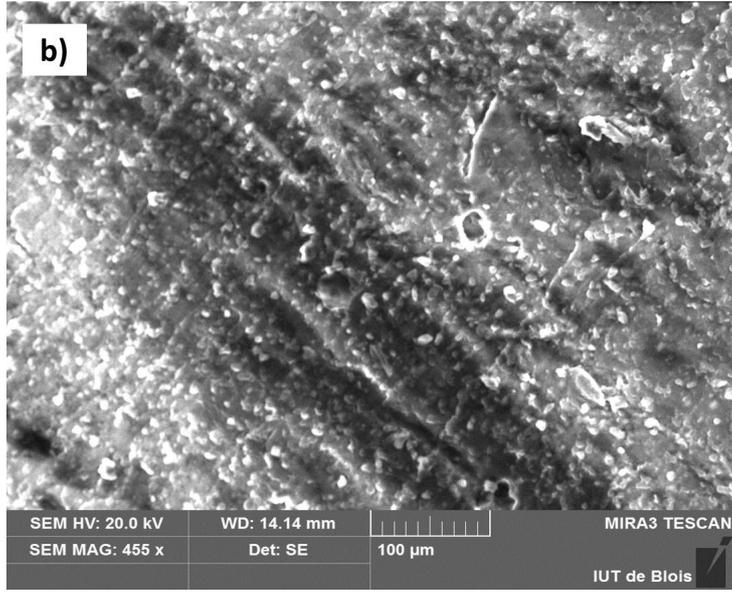
549

NR and NR devulcanized at 160 °C.

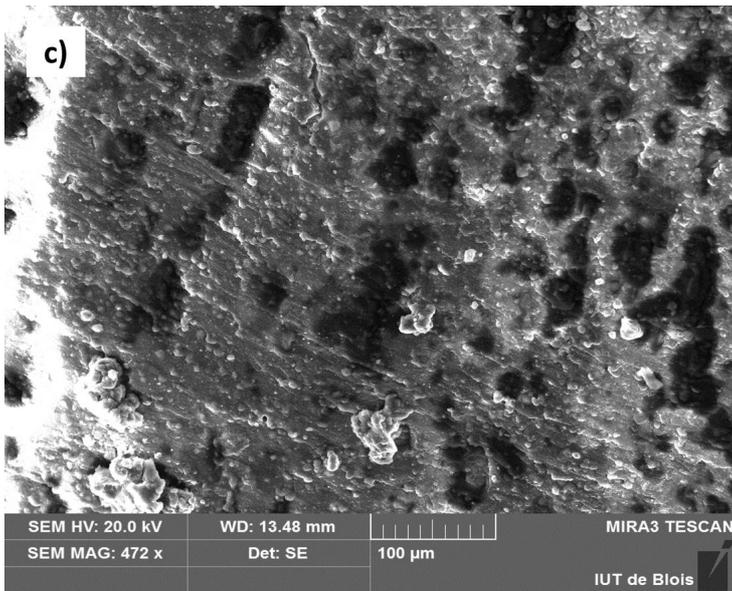
550



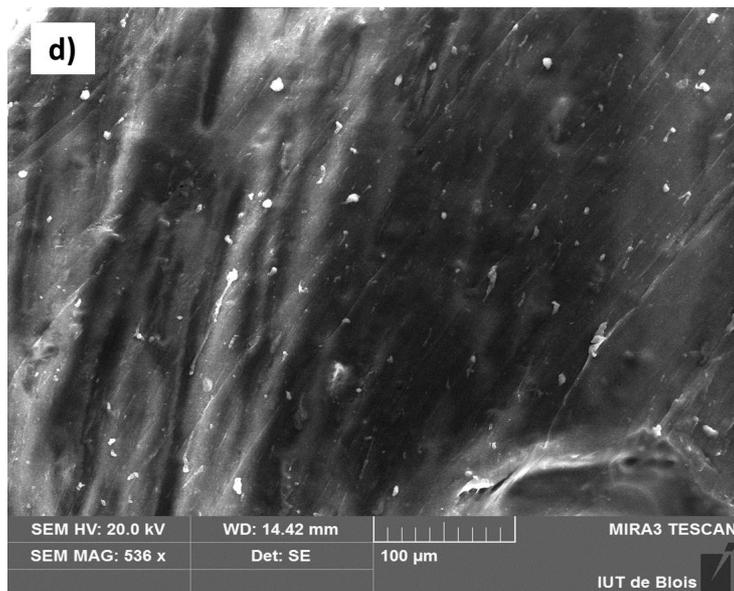
551



552



553



554

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

556

d) NR treated at 160 °C.

557

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

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

m_d	Mass of the dried rubber
m_t	Mass of the sample impregnated with toluene
%S	Soluble fraction
ν_e	Crosslink density
V_r	Rubber volume fraction in the swollen sample
χ	Rubber-solvent interaction parameter
V_l	Molar volume of toluene
m_s	Mass of the solvent absorbed by the sample
ρ_s	Density of the dried rubber
ρ_d	Density of toluene at room temperature
%Devulc	Devulcanization degree
ν_i	Crosslink density of the rubber before devulcanization
ν_f	Crosslink density of the rubber after devulcanization

559

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

562

563