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Thermo-mechanical devulcanization and recycling of rubber industry waste

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Declarations of interest: none

ABSTRACT

This work is focused on the recycling of natural rubber industry waste by means of thermo-mechanical devulcanization. With that aim, tests were carried out in an industrial twin-screw extruder, at different barrel temperatures, ranging from 80 to 220 °C. The extrusion was done with a screw profile specifically designed for the devulcanization process. The extent and quality of devulcanization were evaluated through the measurements of crosslink density, soluble fraction and Mooney viscosity, and by using the Horikx diagram. Results showed that a high degree of reclaiming (~90%) was obtained, independently of the barrel temperature. The samples with the best devulcanization quality, i.e. the samples with a more selective sulfur bond scission, were found to be those treated at a lower input temperature. This was explained by the effect of the rubber homogenous self-heating which contributes to the local increase of the material temperature, during the devulcanization process. Moreover, it was found that the properties of the devulcanized rubber/virgin rubber blends were not significantly affected by the addition of the treated rubber. Results suggest that the entire natural rubber industry waste could be recycled into new competitive products, with low energy consumption. This would present a real contribution to the industrial recycling and thus a noticeable improvement of the environment.

Keywords: Rubber industry waste, thermo-mechanical devulcanization, extrusion, recycling.

32 1. Introduction

33 The industrial rubber scraps and the end-of-life rubber products have become a serious
34 environmental problem (Garcia et al., 2015; Dunuwila et al., 2018). Despite the efforts made
35 to recycle waste rubber, an important fraction is still landfilled (Molino et al., 2018), which
36 represent a real environmental hazard (Burlakovs et al., 2017). In fact, the stacking of rubber
37 scraps promotes the growth of mosquitoes and rodents, and also they can produce
38 spontaneous heating resulting in fire (Colom et al., 2016). Because of their three-dimensional
39 structure and their composition that includes several components, recycling rubbers is
40 difficult and thus represents a current technological challenge (Shi et al., 2014; Sienkiewicz et
41 al., 2017). Nowadays, the majority of rubber wastes is burnt or discarded, causing diseases
42 and ecological contamination (Isayev, 2013; Molino et al., 2018; Pehlken and Müller, 2009).
43 However, during the last few decades, several processes have been developed to reuse the
44 waste rubber (Asaro et al., 2018). One solution is to recycle the discarded rubbers as fuel in
45 the cement industries. Another solution is to grind this waste to convert it into powder or
46 granulates which are then used in bituminous mixtures (Zanetti et al., 2015; Farina et al.,
47 2017), concrete (Si et al., 2018), or as reinforcing fillers in polymers (Sripornsawat et al.,
48 2016; S. L. Zhang et al., 2009). Nevertheless, the objective is to devulcanize the waste rubber
49 in order to reuse it in new competitive products (Gheni et al., 2017), trying to reach the same
50 properties of the materials obtained from virgin rubbers (Kim et al., 2015). This task consists
51 of breaking selectively the sulfur-sulfur (S–S) bonds or the carbon-sulfur (C–S) bonds without
52 affecting the main chain of the polymer i.e. the carbon-carbon (C–C) bonds. This is a difficult
53 process as the energies needed to break the S–S and C–S bonds (227 and 273 kJ/mol,
54 respectively) are not so different from the energy required to break the C–C bonds (348
55 kJ/mol) (Ramarad et al., 2015; Sabzekar et al., 2015). For practical purposes, several authors
56 have proposed schemes to describe different devulcanization mechanisms (Anu Mary et al.,
57 2016; Mangili et al., 2014; Zhang et al., 2018).

58 Many types of devulcanization processes are presented in the literature: chemical (Anu
59 Mary et al., 2016), microwave (Aoudia et al., 2017; Seghar et al., 2015), ultrasound (Mangili
60 et al., 2015; Mende et al., 2016), thermo-mechanical (Meysami et al., 2017), etc. However,
61 the most suitable technique to be industrially applied is the thermo-mechanical method. This

62 is because it is based on the use of an extruder which is common equipment in the rubber and
63 thermoplastic industry, and it can produce high degree of devulcanization (Fukumori et al.,
64 2006; Tzoganakis and Zhang, 2004; Yazdani et al., 2011). Also, this technique is adapted to
65 the mass production, is easy to implement, and it has the advantage of being continuous,
66 allowing the treatment of large quantities of rubber waste. Thermo-mechanical
67 devulcanization has been widely analyzed in the literature, particularly during the last decade.
68 Maridass and Gupta et al. (Maridass and Gupta, 2007) have worked on waste ground rubber
69 devulcanization, in a twin screw extruder, revealing that the temperature and the screw
70 rotation speed were the most important parameters throughout the process. They concluded
71 that it was possible to replace about 65 wt% of the virgin natural rubber (NR) by the recycled
72 rubber, in several applications. Ground tire rubber (GTR) devulcanization in a pan-mill
73 mechano-chemical reactor was done by Zhang et al. (X. Zhang et al., 2009). They found that
74 the quality of the devulcanized material was governed by the screw speed and temperature.
75 Moreover, they showed that the properties of NR/devulcanized GTR blends were higher than
76 those of the NR/non devulcanized GTR materials, which was associated to the improved
77 interfacial interaction between NR and the devulcanized GTR. In 2013, Formela et al.
78 (Formela et al., 2013) have worked on rubber devulcanization in an extruder equipped with a
79 specific screw. They found that it was possible to use a lower devulcanization temperature
80 with the addition of a plasticizing system that promotes high shear strain in the rubber. It was
81 also highlighted that the devulcanization degree increases by increasing the screw speed. The
82 mechanical behavior of the final recycled materials was comparable to those based on
83 commercial recycled rubber. In the same year, Shi et al. (Shi et al., 2013) have studied GTR
84 reclamation by several techniques, one was done in a twin screw extruder at different
85 temperatures. The authors concluded that high shear forces, high temperature and oxygen
86 have negative effects on the devulcanization, because all these parameters promote the main-
87 chain breakage. In 2016, Ghorai et al. (Ghorai et al., 2016a) worked on the NR
88 devulcanization in an open roll mixing mill. They mainly found that the rate of curing
89 increases and the optimum cure time decreases with devulcanization time. They also showed
90 that the elongation at break and the tensile strength of the revulcanized rubber increases with
91 the devulcanization time. In 2017, Barbosa et al. (Rafael Barbosa, Anderson Thadeu Nunesa,
92 2017) have analyzed the thermo-mechanical devulcanization of vulcanized NR with three

93 different crosslink densities. It was shown that the material with higher initial crosslink
94 density was the most devulcanized. This was explained by the fact that when the material has
95 more sulfur bonds, these are more susceptible **to be broken** by a combination of shear stress
96 and temperature. **Other** authors also **studied** the continuous devulcanization of waste rubber in
97 supercritical CO₂ (Jeong et al., 2014; Jiang et al., 2013; Meysami et al., 2017, 2014). Results
98 **revealed** that CO₂ facilitates the permeation of **devulcanization agents inside** the rubber
99 network, allowing obtaining high devulcanization levels.

100 In this work, the recycling through devulcanization of post-production NR was studied.
101 The rubber devulcanization was performed in a large scale twin-screw extruder, at different
102 barrel temperatures, **ranging** from 80 to 220 °C. Effects of the input temperature and the
103 rubber self-heating on the devulcanization quality were studied. The self-heating phenomenon
104 is induced by the friction between the polymer macromolecules during the mechanical
105 shearing of the material, and contributes in the local increase of the material temperature. It
106 was concluded that the NR industry waste could be recycled and reused, without significantly
107 altering the properties of the final products. To the extent of our knowledge, the effect of the
108 material self-heating **during** the rubber devulcanization, and the presented results have never
109 been reported in the literature, at least, in the case of NR thermo-mechanical devulcanization.

110 **2. Experimental**

111 *2.1. Vulcanized material*

112 The rubber **waste** used in this study comes from NR parts obtained by injection molding.
113 The rubber composition was determined by **thermogravimetric analysis** (TGA) according to
114 ASTM Standard D6370-99(2014). A sample of about 10 mg was heated from room
115 temperature to 550 °C, under nitrogen (N₂) atmosphere. Then, it was cooled down to 300 °C,
116 **The** purge atmosphere was changed to air and the rubber was heated again to 800 °C. The
117 heating rates were 10 °C/min.

118 Before the devulcanization treatment, the NR waste was grinded to particles with a
119 reasonable economical size, i.e. 0.8 to 4 mm, using a knife mill. It is worth noting that the **cost**
120 **of grinding rubber is approximately 120 €/ton** for particles of 1-3 mm size, 130 **€/ton** for

121 particles of 0.8-2.5 mm size and 300 €/ton for particles with dimension under 0.8 mm (Phenix
122 Technologies, 28800 Sancheville, France).

123 2.2. Devulcanization process

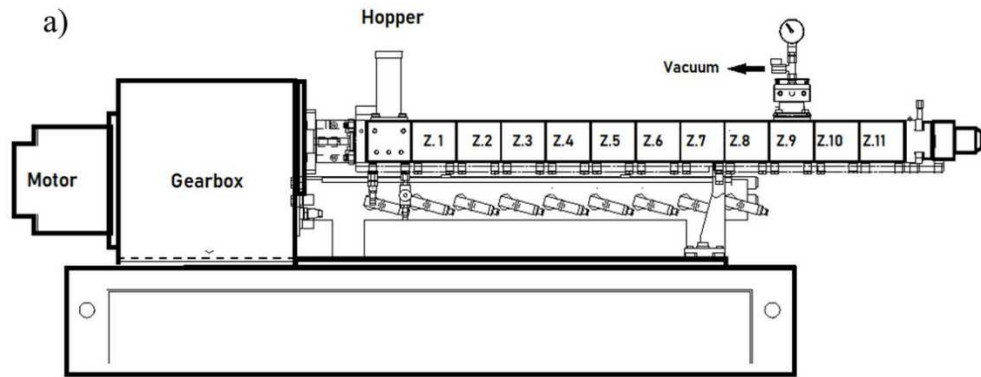
124 Thermo-mechanical devulcanization of NR was conducted in a large scale twin screw
125 extruder Leistritz ZSE 27 MAXX 48D, schematically presented in Fig. 1a. The mentioned
126 machine is a semi-industrial extruder that is used in the industry to devulcanize rubber with a
127 maximum flow rate of 30 kg/h. It is also used to optimize the devulcanization parameters and
128 then apply them to larger-scale extruders. The extrusion was done with a screw profile of 28
129 mm diameter that was specifically designed for rubber recycling. Fig. 1b illustrates the
130 geometry and configuration of the screw. It is divided in three zones as in the work presented
131 by Fukumori et al. (Fukumori et al., 2001). The first part is composed by conveying and
132 kneading elements that prepare the material to be devulcanized. The second part is the central
133 devulcanization zone followed by a vacuum extraction and finally the discharge. Conveying
134 elements of different lengths and pitches were used to control the pressure during the
135 extrusion process. Kneading elements of different lengths, offsets and pitch angles were used
136 to control the rubber shearing into the extruder.

137 The used barrel temperatures were 80, 100, 120, 140, 160, 180, 200 and 220 °C. In each
138 test, the temperature was constant along the 11 zones of the barrel (Fig. 1a). The devulcanized
139 samples were named as dNR-X, where X corresponds to the barrel temperature. The extruder
140 screw speed was 240 rpm, the material feed rate was 5 kg/h, and the die temperature was 80
141 °C. All the mentioned parameters remained constant during the tests.

142 Considering that the applied shear induces an increase in the local temperature of the
143 rubber, the real temperature of the material is a balance between the average temperature
144 provided by the barrels and the one generated by the materials' self-heating. To qualitatively
145 take into account this phenomenon in the analysis of the results, the temperature of each
146 sample was measured at the output of the extruder with a laser thermometer.

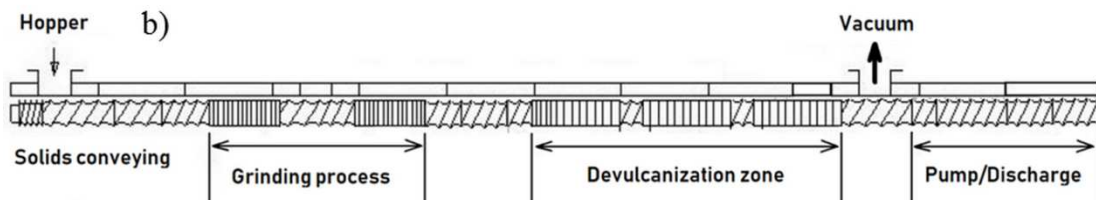
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Fig. 1. (a) Twin screw extruder and (b) screw configuration used to perform thermo-mechanical devulcanization

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2.3. Revulcanization process

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Eight materials were obtained after devulcanization process. Three of those materials devulcanized at low, middle, and high temperatures, i.e. dNR-100, dNR-160 and dNR-220, were revulcanized according to a common industrial formulation given in Table 1 (Ghorai et al., 2016a; Rooj et al., 2011). The selection of dNR-100 over dNR-80 as low devulcanization temperature will be discussed later, in section 3.2, based on the results presented in Fig. 6.

The material presenting the best mechanical properties (dNR100) was added to the virgin rubber, in quantities of 5, 10 and 20 wt% (Table 2).

During processing, the exact amounts of components (Table 1 or Table 2) were mixed in a roll mixing mill and then revulcanized during 5 minutes, at 150 MPa and 160 °C, in a 150 x 200 x 2 mm³ mold. In this revulcanization process, the same amount of sulfur and accelerator (CBS) was used, which gives rise to the formation of sulfur links with different lengths, i.e. mono-, di- and poly-sulfur links. The mentioned formulations could be used in real

167 applications without any change. The **obtained** materials were named as dNRv-X, where X
 168 corresponds to the devulcanization temperature. A schematic representation of the
 169 experimental procedure carried out in this work is shown in Fig. 2.

170 **Table 1**

171 Formulation for revulcanizing the devulcanized rubber

Material	Devulcanized NR (phr)			Components (phr)			
	dNR-100	dNR-160	dNR-220	Stearic Acid	ZnO	CBS*	S
dNRv-100	100	0	0	2	4	1.5	1.5
dNRv-160	0	100	0	2	4	1.5	1.5
dNRv-220	0	0	100	2	4	1.5	1.5

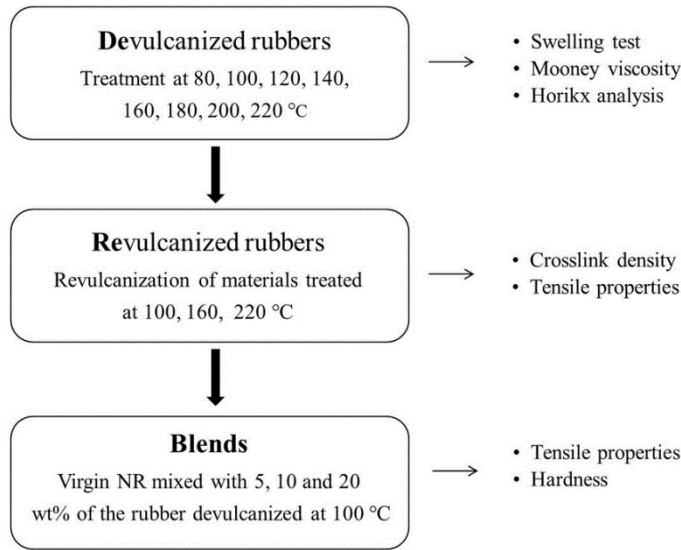
172 *CBS: N-Cyclohexyl-2-benzothiazole sulfonamide

173 **Table 2**

174 Formulation for revulcanizing the **dNR-100/virgin NR blends**

Material	Components						175
	Virgin NR (wt%)	dNR-100 (wt%)	Stearic Acid (phr)	ZnO (phr)	CBS* (phr)	S (phr)	
Virgin NR	100	0	2	4	1.5	1.5	
dNR-100(5)	95	5	2	4	1.5	1.5	
dNR-100(10)	90	10	2	4	1.5	1.5	
dNR-100(20)	80	20	2	4	1.5	1.5	

176 *CBS: N-Cyclohexyl-2-benzothiazole sulfonamide



177

178

Fig. 2. Experimental procedure

179 *2.4. Characterization of reclaimed rubber*

180 *2.4.1. Degree of devulcanization*

181 The degree of devulcanization was evaluated by the swelling test, after **the** extraction
 182 process in a Soxhlet extractor. The extraction was done with acetone during 16 h, according to
 183 the Standard ASTM D297-02. After drying, the sample was weighted (m_i) and swelled in
 184 toluene, at ambient temperature, during 72 h, with refreshing solvent every 24 h, according to
 185 ASTM D 6814-02. The swollen sample was weighed (m_t) and then dried in an oven, at 70°C
 186 overnight. Finally, the dry sample was weighted (m_d). This procedure was done in triplicate
 187 for each material.

188 The soluble fraction was given by equation (1):

189
$$\%S = \frac{m_i - m_d}{m_i} \times 100 \quad (1)$$

190 The density of the rubber (ρ_r) was evaluated by **the** hydrostatic weighing procedure. The
 191 sample was weighed in air (m_{air}) and weighed again while immersed in methanol ($m_{methanol}$),
 192 then the density was calculated using equation (2):

193
$$\rho_r = \rho_{methanol} \times \frac{m_{air}}{m_{air} - m_{methanol}} \quad (2)$$

194 where $\rho_{methanol}$ is the methanol density at room temperature.

195 The crosslink density ν_e was estimated using Flory-Rehner's model given by equation (3):

$$196 \quad \nu_e = \frac{-[\ln(1-V_r)+V_r+\chi V_r^2]}{[V_1(V_r^{1/3}-V_r/2)]} \quad (3)$$

197 where V_r , χ and V_1 are, respectively, the rubber volume fraction in the swollen sample, the
198 rubber-solvent interaction parameter ($\chi = 0.391$ for NR-toluene) and the molar volume of
199 toluene (106.3 mL/mol).

200 The rubber volume fraction V_r was calculated with equation (4):

$$201 \quad V_r = \frac{m_d/\rho_d}{m_d/\rho_d + m_s/\rho_s} \quad (4)$$

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

204 The degree of devulcanization of each sample was calculated using the following equation:

$$205 \quad \%Devulc. = \left[1 - \frac{\nu_f}{\nu_i}\right] \times 100 \quad (5)$$

206 where ν_i and ν_f are, respectively, the crosslink densities of the rubber before and after
207 devulcanization, evaluated using equation (3).

208 2.4.2. Horikx diagram

209 The analysis of the decrease in crosslink density and the variation of the soluble fraction
210 was done by using the Horikx diagram (Horikx, 1956). In this diagram the decrease in
211 crosslink density is related to the amount of soluble fraction in the rubber, in such a way that
212 both the degree and quality of devulcanization, in the sense of crosslink against main chain
213 scission, can be qualitatively deduced. The Horikx theory, based on the work of Charlesby
214 (Charlesby, 1953), has been extensively described in the literature (Verbruggen et al., 1999)
215 and was recently checked experimentally by Verbruggen et al. (Verbruggen et al., 2016).

216 2.4.3. Mooney viscosity

217 The viscosity of the devulcanized rubber was measured with a Mooney Viscometer
218 MV2000 from Alpha Technologies, according to the ASTM D1646 Standard. The test
219 consists of the slow and continuous rotation of a disk in a heated chamber filled with rubber,

220 for a given time. The resistance to this rotation induced by the rubber is measured, in arbitrary
221 torque units, as the Mooney viscosity of the **tested material**. In this study samples were
222 preheated during 1 minute, and the viscosity was measured after 4 minutes of testing, at 100
223 °C. **The** results are presented as ML (1+4) 100 °C. At least, 3 measurements were carried out
224 for each material.

225 2.4.4. Hardness Shore A

226 The hardness was measured for the materials dNR-100(5), dNR-100(10), dNR-100(20),
227 obtained by mixing the devulcanized NR with virgin NR (Table 2). Tests were performed
228 with a digital durometer Sama Tools SA6610A, according to the Standard ISO 7619-1:2010.

229 2.4.5. Mechanical properties

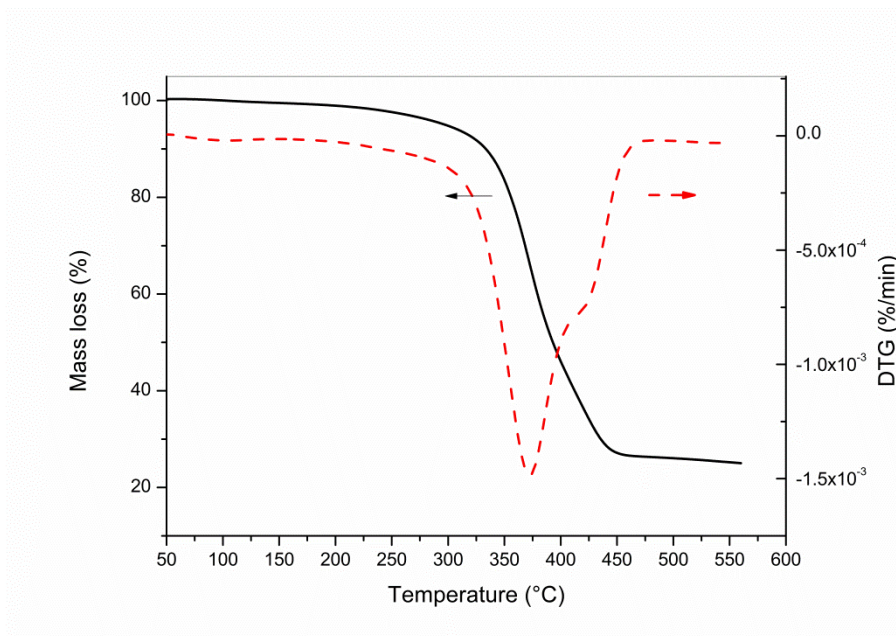
230 Tensile tests were achieved on the revulcanized rubbers (Tables 1 and 2), according to the
231 ISO-37 Standard, using a Shimadzu AGS-X traction machine equipped with a 5 kN load cell,
232 at ambient temperature. H2 dumbbell specimens of 2 mm thickness were used. The crosshead
233 speed was 500 mm/min and the strain was measured with an extensometer, during the test.

234

235 3. Results and discussions

236 3.1. Waste material characterization

237 The rubber composition was determined by TGA. NR mass loss and its derivative (DTG)
238 are reported, as a function of temperature, in Fig. 3. **Between 200 and 300 °C, the first mass**
239 **reduction under N₂ atmosphere (about 6 wt%),** corresponds to the volatilization **of**
240 **components of low boiling points and the processing oils**. The next mass reduction, still under
241 N₂ atmosphere (about 70 wt%), corresponds to the elastomer. The second part of the cycle,
242 carried out in air, **does not** affect the final mass of the sample. Thus, the last 24 wt%
243 corresponds to the mineral fillers. Similar analyzes are reported in (de Sousa et al., 2017;
244 Ghorai et al., 2016b; Mangili et al., 2014).



245

246

Fig. 3. NR mass loss and its derivative (DTG) as a function of temperature

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3.2. Devulcanization analyzes

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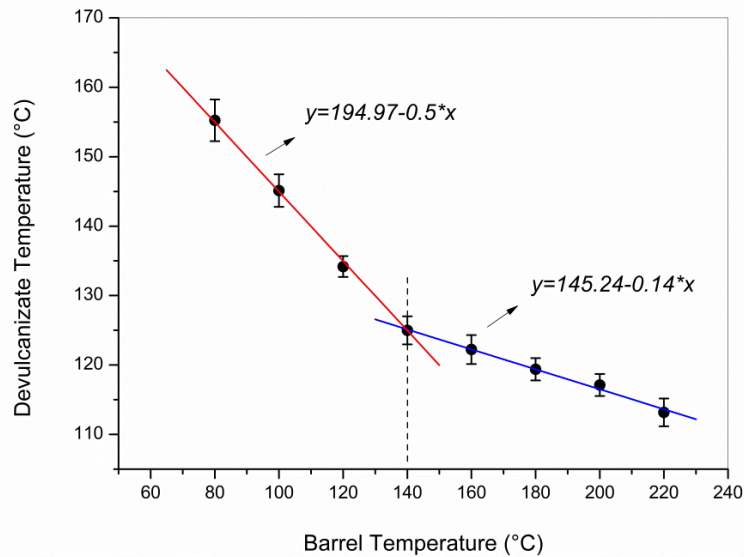
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When a rubber is subjected to shear strains, the friction produced between its chains dissipates a part of the total received energy in the form of heat, which results in a local temperature increase known as self-heating. To qualitatively evaluate this phenomenon in the devulcanization process, the temperature of the devulcanized rubber was measured at the exit of the extrusion die. The results are reported, as a function of the barrel temperature, in Fig. 4. This figure shows that the devulcanizate temperature linearly decreases from ~155 °C to ~113 °C when the barrel temperature increases from 80 °C to 220 °C, with a slope break at the barrel temperature of 140 °C. The slope of the curve below this threshold point is ~3.5 times greater than the slope displayed at barrel temperatures superior to 140 °C. This result suggests that the self-heating phenomenon happens at all input temperatures and its effects quickly increase as the barrel temperature decreases, in the range from 80 °C – 140 °C. This growth is less significant for higher input temperatures (> 140 °C). The self-heating phenomenon mainly results from friction between the rubber macromolecules. It could be expected that increasing input barrel temperature reduces entanglements between macromolecules and facilitate their mobility, and therefore decreases the friction and the self-heating. The trend of

263 this decrease is less significant beyond the input temperature threshold value of 140 °C.
264 Actually, the average temperature of the rubber during the devulcanization treatment could be
265 considered as a balance between the barrel temperature and the temperature induced by the
266 material self-heating.



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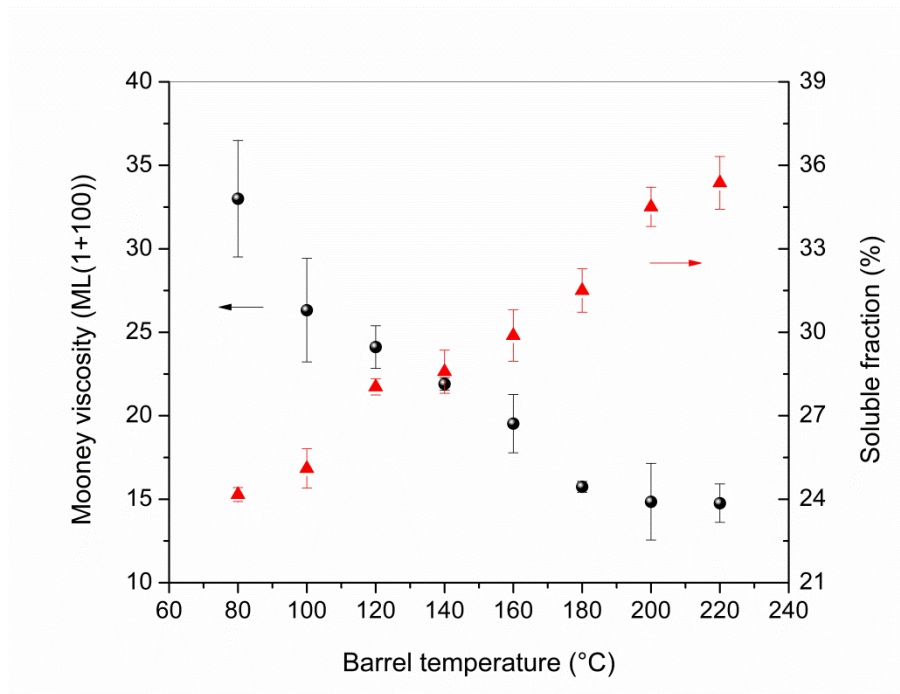
268 **Fig. 4.** Temperature of the material at the exit of the extruder die as a function of the barrel
269 temperature (3 measurements were done in each condition)

270 The rubber Mooney viscosity can be readily and quickly measured, and it is obviously
271 related to the network configuration of the material. Also, it is possible to evaluate the
272 processability of the rubber by Mooney viscosity measurements. Indeed, a high viscosity
273 limits the rubber to be processed in a precise shape, while a very low viscosity hinders
274 processing (Zhang et al., 2018).

275 Fig. 5 shows that the Mooney viscosity of the devulcanized NR decreases strongly as the
276 barrel temperature **increases** up to 180 °C, and remains almost constant for higher
277 temperatures. It should be noticed that the lower the Mooney viscosity values of the treated
278 rubber, the higher the number of broken bonds during the devulcanization process, as reported
279 by Si et al. (Si et al., 2013) during the devulcanization of ground tire rubber in a twin-screw
280 extruder. However, this parameter cannot give an idea about the quality of the performed
281 devulcanization treatment, i.e. if was done by crosslink scission or main chain scission. Thus,

282 additional characterizations are necessary to deeply analyze the results with the Horikx
283 theory.

284 The values corresponding to the soluble fraction %S (Eq. 1) are also reported in Fig. 5. The
285 curve shows that the soluble part of the polymer increases **when** increasing the barrel
286 temperature, confirming that the quantity of low molecular weight compounds becomes
287 higher as the input temperature grows, which is in agreement with the Mooney viscosity
288 results. The soluble fraction evolution reflects the changes in the 3D-macromolecular network
289 of the treated rubber. The analysis of this aspect with the Horikx diagram is presented
290 hereafter.



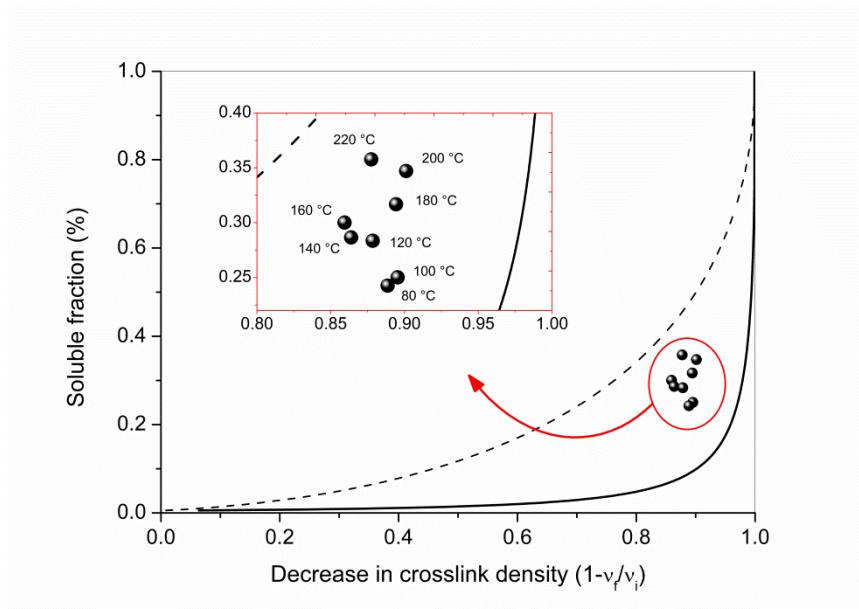
291
292 **Fig. 5.** Mooney viscosity and soluble fraction of the devulcanized NR as a function of the
293 barrel temperature (3 samples were tested in each condition)

294 Theoretical Horikx curves and the experimental points are presented in Fig. 6. The analysis
295 **consists of considering** that the experimental points positioned near the lower curve (solid
296 line) correspond to **a** more selective sulfur scission, and those located near the upper curve
297 (dash line) correspond to main chain scission and polymer degradation. The points between
298 the two curves undergo reclaiming, a combination between devulcanization (sulfur bond
299 scission) and degradation (main chain scission). It can be seen that the experimental points are

300 positioned between the two theoretical Horikx curves, which means that the treated rubbers
301 underwent a reclaiming process. Moreover, it can be observed that a high degree of
302 reclaiming, near 90%, was obtained for all the samples, while the soluble fraction increases
303 with increasing the barrel temperature. This means that a rise in the barrel temperature just
304 induces polymer degradation, without improving devulcanization quality. It was reported by
305 several authors (Jiang et al., 2013; Meysami et al., 2017; Rooj et al., 2011) that it is possible
306 to reach a very high devulcanization degree by selecting the optimum devulcanization
307 conditions. In the case of thermomechanical devulcanization some of the parameters that can
308 be modified are the screw profile, temperature, speed, etc. The most devulcanized samples
309 were those treated at 80 °C and 100 °C, corresponding to the experimental points that are
310 closer to the lower theoretical curve of Horikx. The point representing dNR-100 is in the right
311 of the point representing dNR-80, which means that the first material has a greater
312 devulcanization degree than that of the second one. Even though the difference is very slight,
313 100 °C was selected as the lower devulcanization temperature. It should be noticed that these
314 samples displayed the highest temperatures, ~155 °C and ~145 °C respectively (Fig. 4), at the
315 exit of the extrusion die, i.e. they underwent the most pronounced self-heating. It is worth
316 clarifying that the temperature induced by the rubber self-heating is quite homogeneous in the
317 material, while the distribution of the barrel temperature depends on the thermal conductivity
318 of the treated rubber.

319 It is clear that the self-heating, which depends probably on many factors (type of material,
320 quantity and kind of fillers, crosslink density, input temperature, shear rate), has a helpful
321 effect on the devulcanization quality. Therefore, it is necessary to include this phenomenon in
322 the analysis of the thermo-mechanical devulcanization. The high devulcanization level
323 reached in this study, ~90%, is an important finding, as the proposed procedure could be
324 directly applied on an industrial scale to recycle greater quantities of waste rubber. In
325 addition, the obtaining of such devulcanization degree at low input temperature (100 °C)
326 represents a significant energy saving. The consumed energy during the extrusion, at 100 °C,
327 was approximately 0.35 kWh/kg.

328



329

330 **Fig. 6.** Soluble fraction of devulcanized NR against relative decrease in crosslink density

331 *3.3. Revulcanized materials properties*

332 *3.3.1. Revulcanized materials based entirely on recycled rubbers*

333 To better understand the changes in the rubber structure of dNRv-100, dNRv-160 and
 334 dNRv-220, induced by the devulcanization and revulcanization processes, the crosslink
 335 densities and soluble fractions of these materials were evaluated. **The results with their**
 336 corresponding standard deviation are shown in Table 3. The higher crosslink density of the
 337 dNRv-100 denotes the better ability of this material to be revulcanized, fact that could be
 338 associated to a probable preservation of long polymer chains during the devulcanization
 339 treatment. **Also**, the increase in the soluble fraction with higher devulcanization temperatures
 340 denotes the increase in the quantity of low molecular weight compounds, which suggest **a** rise
 341 in rubber degradation when the **input** temperature grows. The modulus E at 100% of
 342 deformation (M 100%), stress at break, and elongation at break of the dNRv-100, dNRv-160
 343 and dNRv-220 are also presented in Table 3. In accordance with the changes in the crosslink
 344 density, the mechanical properties of these materials decrease as the barrel temperature
 345 increases. These results are in agreement with those reported by Shi et al. (Shi et al., 2013)
 346 who mainly concluded that high temperature reclamation leads to materials with low
 347 mechanical properties. The highest mechanical properties were obtained for the revulcanize

348 produced with the rubber devulcanized at 100 °C, the lower barrel temperature, namely the
 349 condition that favors the material self-heating (Fig. 4). As indicated in Rooj et al. (Rooj et al.,
 350 2011), only at an appropriate devulcanization level, the structure of the rubber is destroyed
 351 but still has a certain degree of deformability and plasticity. **Therefore**, the revulcanized
 352 materials mechanical properties suggest that dNR-100 is the best devulcanized material to be
 353 blend with virgin rubber.

354 **Table 3**

355 Crosslink density, soluble fraction and mechanical properties of the revulcanized materials

Material/ Property	Soluble fraction [%]	Crosslink density [x 10⁻⁴ mol/cm³]	M 100% [MPa]	Stress at break [MPa]	Elongation at break [%]
dNRv-100	4.57 ± 0.31	2.325 ± 0.026	1.25 ± 0.03	11.00 ± 0.29	518 ± 8
dNRv-160	5.73 ± 0.06	2.059 ± 0.040	1.11 ± 0.01	10.20 ± 0.49	488 ± 11
dNRv-220	7.55 ± 0.58	1.812 ± 0.029	1.06 ± 0.04	8.87 ± 0.08	481 ± 13

356 *3.3.2. Revulcanized blends with virgin rubber*

357 The devulcanized rubber with high degree and best quality of devulcanization, dNR-100,
 358 was blended with virgin NR, in different quantities (Table 2). According to the Horikx theory,
 359 the devulcanization quality **is improved** as the experimental points are near to the Horikx
 360 curve that represents crosslink scission (Fig. 6).

361 Tensile test results of the blends are presented in Table 4. It can be seen that the rigidity
 362 modulus of the material decreases as the quantity of devulcanized rubber increases, which
 363 means that the blends become more ductile with the devulcanized rubber content. Moreover,
 364 for 5 and 10 wt% of recycled rubber, the decrease in the stress at break of the blends is of
 365 **approximately** 6% and 3%, respectively. However, when this quantity increases to 20 wt%,
 366 the reduction in the stress at break is more pronounced, **approximately** 14%. The decrease in
 367 this property was attributed to the **initial crosslinking** of the devulcanized NR, that induced a
 368 poor compatibility between the virgin and devulcanized rubbers, and to the possible presence
 369 of short polymer chains in the devulcanized NR that reduces the stress transmission. The
 370 elongation at break was not affected by the incorporation of devulcanized rubber in the virgin
 371 NR, suggesting that the global stretching of the material was not altered by the local changes

372 in the 3D-macromolecular network produced by the presence of the recycled NR. The surface
 373 hardness of the blends has not changed appreciably by the addition of recycled rubber in the
 374 virgin NR. Similar results were reported by Rooj et al. (Rooj et al., 2011) when they studied
 375 the mechanical properties of blends based on devulcanized NR with different proportions of
 376 virgin rubber. Finally, it can be concluded from the above results that the rubber industry
 377 wastes can be devulcanized and reintroduced into the production without considerably
 378 affecting the quality of the final materials. This will **allow** manufacturers to eliminate a
 379 **considerable** quantity of the waste rubber, at a relatively low cost, which represents an
 380 advance in the industrial recycling and thus a noticeable **improvement of the environment.**

381 **Table 4**

382 **Mechanical properties of virgin rubber/recycled rubber blends**

Material/Property	M 100%	Stress at break [MPa]	Elongation at break [%]	Hardness Shore A
Virgin NR	2.3 ± 0.2	28.8 ± 0.7	643 ± 8	60 ± 1
dNR-100(5)	2.1 ± 0.1	27.1 ± 0.6	628 ± 15	60 ± 2
dNR-100(10)	2.0 ± 0.1	28.0 ± 0.8	655 ± 17	59 ± 1
dNR-100(20)	1.8 ± 0.2	25.3 ± 0.5	648 ± 9	57 ± 1

383 **4. Conclusion**

384 Devulcanization of post-production NR was performed in a large scale twin-screw
 385 extruder, at different temperatures, with a screw profile **specifically** designed for rubber
 386 recovery. High degree of reclaiming (~90%) was obtained. The Horikx diagram was used to
 387 analyze the swelling test results and it was found that the samples with more selective sulfur
 388 bond scission were those treated at 80 and 100 °C. This was explained by the effect of the
 389 rubber self-heating which have increased the temperature of these samples up to, respectively,
 390 ~155 °C and ~145 °C, during the devulcanization process. It is therefore necessary to include
 391 the material self-heating phenomenon in the analysis of the thermo-mechanical
 392 devulcanization. It was also revealed that an increase in the input temperature does not
 393 necessary promotes devulcanization. In this study, higher screw temperatures just induced

394 polymer degradation, without any increase in the devulcanization degree and without any
395 improvement in the devulcanized materials properties. Analysis of the mechanical properties
396 of the dNR-100/virgin NR blends led to conclude that the NR industry waste can be
397 devulcanized at low input temperature and reintroduced into the production without
398 significantly affecting the quality of the final products. Results suggest that the NR industry
399 waste could be almost entirely recycled with low energy consuming, which represents a real
400 contribution to the industrial recycling. As a perspective, it would be interesting to analyze the
401 effects of parameters such as the type of material, the quantity and the kind of fillers, the
402 crosslink density, and the shear rate, on the rubber self-heating during devulcanization.

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407 References

- 408 Anu Mary, J., Benny, G., Madhusoodanan, K.N., Rosamma, A., 2016. The current status of
409 sulphur vulcanization and devulcanization chemistry: devulcanization. *Rubber Sci.* 29,
410 62–100.
- 411 Aoudia, K., Azem, S., Aït Hocine, N., Gratton, M., Pettarin, V., Seghar, S., 2017. Recycling
412 of waste tire rubber: Microwave devulcanization and incorporation in a thermoset resin.
413 *Waste Manag.* 60, 471–481. <https://doi.org/10.1016/j.wasman.2016.10.051>
- 414 Asaro, L., Gratton, M., Seghar, S., Aït Hocine, N., 2018. Recycling of rubber wastes by
415 devulcanization. *Resour. Conserv. Recycl.* 133, 250–262.
416 <https://doi.org/10.1016/j.resconrec.2018.02.016>
- 417 **Burlakovs, J., Kriipsalu, M., Klavins, M., et. al., 2017. Paradigms on landfill mining: From**
418 **dump site scavenging to ecosystem services revitalization. *Resour. Conserv. Recycl.* 123,**
419 **73–84. <http://dx.doi.org/10.1016/j.resconrec.2016.07.007>**
- 420 Charlesby, A., 1953. Solubility and molecular size distribution of crosslinked polystyrene. *J.*
421 *Polym. Sci.* 11, 513–520. <https://doi.org/https://doi.org/10.1002/pol.1953.120110601>

422 Colom, X., Faliq, A., Formela, K., Cañavate, J., 2016. FTIR spectroscopic and
423 thermogravimetric characterization of ground tyre rubber devulcanized by microwave
424 treatment. *Polym. Test.* 52, 200–208.
425 <https://doi.org/10.1016/j.polymertesting.2016.04.020>

426 de Sousa, F.D.B., Scuracchio, C.H., Hu, G.H., Hoppe, S., 2017. Devulcanization of waste tire
427 rubber by microwaves. *Polym. Degrad. Stab.* 138, 169–181.
428 <https://doi.org/10.1016/j.polymdegradstab.2017.03.008>

429 **Dunuwila, P., Rodrigo, V.H.L., Goto, N., 2018. Sustainability of natural rubber processing
430 can be improved: A case study with crepe rubber manufacturing in Sri Lanka. *Resour.
431 Conserv. Recycl.* 133, 417–427. <https://doi.org/10.1016/j.resconrec.2018.01.029>**

432 **Farina, A., Zanetti, M.C., Santagata, E., Blengini, G.A., 2017. Life cycle assessment applied to
433 bituminous mixtures containing recycled materials: Crumb rubber and reclaimed asphalt
434 pavement. *Resour. Conserv. Recycl.*, 117, 204–212.
435 <http://dx.doi.org/10.1016/j.resconrec.2016.10.015>**

436 Formela, K., Cysewska, M., Haponiuk, J., Stasiak, A., 2013. The influence of feed rate and
437 shear forces on the devulcanization process of ground tire rubber (GTR) conducted in a
438 co-rotating twin screw extruder. *Polimery/Polymers* 58, 906–912.
439 <https://doi.org/10.14314/polimery.2013.906>

440 Fukumori, K., Matsushita, M., Mouri, M., Okamoto, H., Sato, N., Takeuchi, K., Suzuki, Y.,
441 2006. Dynamic devulcanization and dynamic vulcanization for recycling of crosslinked
442 rubber. *KGK. Kautschuk, Gummi, Kunststoffe* 59, 405–411.

443 Fukumori, K., Mouri, M., Sato, N., Okamoto, H., Matsushita, M., 2001. Continuous recycling
444 of vulcanisates 28, 5–11.

445 Garcia, P.S., de Sousa, F.D.B., de Lima, J.A., Cruz, S.A., Scuracchio, C.H., 2015.
446 Devulcanization of ground tire rubber: Physical and chemical changes after different
447 microwave exposure times. *Express Polym. Lett.* 9, 1015–1026.
448 <https://doi.org/10.3144/expresspolymlett.2015.91>

449 Gheni, A.A., Abdelkarim, O.I., Abdulazeez, M.M., ElGawady, M.A., 2017. Texture and
450 design of green chip seal using recycled crumb rubber aggregate. *J. Clean. Prod.* 166,
451 1084–1101. <https://doi.org/10.1016/j.jclepro.2017.08.127>

452 Ghorai, S., Bhunia, S., Roy, M., De, D., 2016. Mechanochemical devulcanization of natural

453 rubber vulcanizate by dual function disulfide chemicals. *Polym. Degrad. Stab.* 129, 34–
454 46. <https://doi.org/10.1016/j.polymdegradstab.2016.03.024>

455 Horikx, M., 1956. Chain scissions in a polymer network. *J. Polym. Sci. Part B Polym. Phys.*
456 19, 445–454. <https://doi.org/https://doi.org/10.1002/pol.1956.120199305>

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

459 Jeong, K.M., Hong, Y.J., Saha, P., Park, S.H., Kim, J.K., 2014. Novel polymer composites
460 from waste ethylene-propylene-diene-monomer rubber by supercritical CO₂ foaming
461 technology. *Waste Manag. Res.* 32, 1113–1122.
462 <https://doi.org/10.1177/0734242X14545375>

463 Jiang, K., Shi, J., Ge, Y., Zou, R., Yao, P., Li, X., Zhang, L., 2013. Complete devulcanization
464 of sulfur-cured butyl rubber by using supercritical carbon dioxide. *J. Appl. Polym. Sci.*
465 127, 2397–2406. <https://doi.org/10.1002/app.37542>

466 Kim, K.G., Saha, P., Kim, J.H., Jo, S.H., Kim, J.K., 2015. Novel elastomer nanocomposite
467 with uniform silica dispersion from polybutadiene rubber treated with epoxidized
468 soybean oil. *J. Compos. Mater.* 49, 3005–3016.
469 <https://doi.org/10.1177/0021998314559061>

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

474 Mangili, I., Lasagni, M., Huang, K., Isayev, A.I., 2015. Modeling and optimization of
475 ultrasonic devulcanization using the response surface methodology based on central
476 composite face-centered design. *Chemom. Intell. Lab. Syst.* 144, 1–10.
477 <https://doi.org/10.1016/j.chemolab.2015.03.003>

478 Maridass, B., Gupta, B.R., 2007. Effect of extruder parameters on mechanical properties of
479 revulcanized ground rubber tire powder. *Polimery/Polymers* 52, 456–460.

480 Mende, H., Olenik, D., Schleppers, A., 2016. G-DRG-Version 2016 - Auswirkungen auf
481 unser Fachgebiet. *Anesthesiol. und Intensivmed.* 57, 147–151.
482 <https://doi.org/10.1002/pen>

483 Meysami, M., Mutyala, P., Zhu, S., Tzoganakis, C., 2014. CONTINUOUS

484 DEVULCANIZATION OF SCRAP EPDM RUBBER WITH SUPERCRITICAL CO₂ :
485 EFFECT OF PROCESS PARAMETERS ON DEVULCANIZED RUBBER
486 PROPERTIES Materials 1025–1032.

487 Meysami, M., Tzoganakis, C., Mutyala, P., Zhu, S.H., Bulsari, M., 2017. Devulcanization of
488 Scrap Tire Rubber with Supercritical CO₂: A Study of the Effects of Process
489 Parameters on the Properties of Devulcanized Rubber 183–193.

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

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

496 Rafael Barbosa, Anderson Thadeu Nunesa, J.D.A., 2017. Devulcanization of Natural Rubber
497 in Composites with Distinct Crosslink Densities by Twin-Screw extruder.

498 Ramarad, S., Khalid, M., Ratnam, C.T., Chuah, A.L., Rashmi, W., 2015. Progress in
499 Materials Science Waste tire rubber in polymer blends: A review on the evolution ,
500 properties and future 72, 100–140. <https://doi.org/10.1016/j.pmatsci.2015.02.004>

501 Rooj, S., Basak, G.C., Maji, P.K., Bhowmick, A.K., 2011. New Route for Devulcanization of
502 Natural Rubber and the Properties of Devulcanized Rubber. J. Polym. Environ. 19, 382–
503 390. <https://doi.org/10.1007/s10924-011-0293-5>

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

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

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

512 Seghar, S., Aït Hocine, N., Mittal, V., Azem, S., Al-Zohbi, F., Schmaltz, B., Poirot, N., 2015.
513 Devulcanization of styrene butadiene rubber by microwave energy: Effect of the
514 presence of ionic liquid. Express Polym. Lett. 9, 1076–1086.

515 <https://doi.org/10.3144/expresspolymlett.2015.97>

516 Shi, J., Jiang, K., Ren, D., Zou, H., Wang, Y., Lv, X., Zhang, L., 2013. Structure and
517 performance of reclaimed rubber obtained by different methods. *J. Appl. Polym. Sci.*
518 129, 999–1007. <https://doi.org/10.1002/app.38727>

519 Shi, J., Zou, H., Ding, L., Li, X., Jiang, K., Chen, T., Zhang, X., Zhang, L., Ren, D., 2014.
520 Continuous production of liquid reclaimed rubber from ground tire rubber and its
521 application as reactive polymeric plasticizer. *Polym. Degrad. Stab.* 99, 166–175.
522 <https://doi.org/10.1016/j.polymdegradstab.2013.11.010>

523 Si, H., Chen, T., Zhang, Y., 2013. Effects of high shear stress on the devulcanization of
524 ground tire rubber in a twin-screw extruder. *J. Appl. Polym. Sci.* 128, 2307–2318.
525 <https://doi.org/10.1002/app.38170>

526 Si, R., Wang, J., Guo, S., Dai, Q., Han, S., 2018. Evaluation of laboratory performance of
527 self-consolidating concrete with recycled tire rubber. *J. Clean. Prod.* 180, 823–831.
528 <https://doi.org/10.1016/j.jclepro.2018.01.180>

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

532 Sripornsawat, B., Saiwari, S., Pichaiyut, S., Nakason, C., 2016. Influence of ground tire
533 rubber devulcanization conditions on properties of its thermoplastic vulcanizate blends
534 with copolyester. *Eur. Polym. J.* 85, 279–297.
535 <https://doi.org/10.1016/j.eurpolymj.2016.10.031>

536 Tzoganakis, C., Zhang, Q., 2004. Devulcanization of recycled tire rubber using supercritical
537 carbon dioxide, in: *Antec Conference Proceedings*. pp. 3509–3513.

538 Verbruggen, M.A.L., van der Does, L., Dierkes, W.K., Noordermeer, J.W.M., 2016.
539 Experimental Validation of the Charlesby and Horikx Models Applied To De-
540 Vulcanization of Sulfur and Peroxide Vulcanizates of Nr and Epdm. *Rubber Chem.*
541 *Technol.* 89, 671–688. <https://doi.org/10.5254/rct.16.83776>

542 Verbruggen, M.A.L., van der Does, L., Noordermeer, J.W.M., van Duin, M., Manuel, H.J.,
543 1999. Mechanisms Involved in the Recycling of NR and EPDM. *Rubber Chem. Technol.*
544 72, 731–740. <https://doi.org/10.5254/1.3538830>

545 Yazdani, H., Karrabi, M., Ghasmi, I., Azizi, H., Bakhshandeh, G.R., 2011. Devulcanization of

546 waste tires using a twin-screw extruder: The effects of processing conditions. *J. Vinyl*
547 *Addit. Technol.* 17, 64–69.

548 Zanetti, M.C., Fiore, S., Ruffino, B., Santagata, E., Dalmazzo, D., Lanotte, M., 2015.
549 Characterization of crumb rubber from end-of-life tyres for paving applications. *Waste*
550 *Manag.* 45, 161–170. <https://doi.org/10.1016/j.wasman.2015.05.003>

551 Zhang, S.L., Xin, Z.X., Zhang, Z.X., Kim, J.K., 2009. Characterization of the properties of
552 thermoplastic elastomers containing waste rubber tire powder. *Waste Manag.* 29, 1480–
553 1485. <https://doi.org/10.1016/j.wasman.2008.10.004>

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

557 Zhang, X., Zhu, X., Liang, M., Lu, C., 2009. Improvement of the Properties of Ground Tire
558 Rubber (GTR)-Filled Nitrile Rubber Vulcanizates Through Plasma Surface Modification
559 of GTR Powder. *J. of Applied Polymer Sci.* 114, 1118–1125.

