

Thermo-mechanical devulcanization and recycling of rubber industry waste

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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.

1. Introduction

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

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

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

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

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

2. Experimental

2.1. Vulcanized material

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

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

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

2.2. Devulcanization process

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

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

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

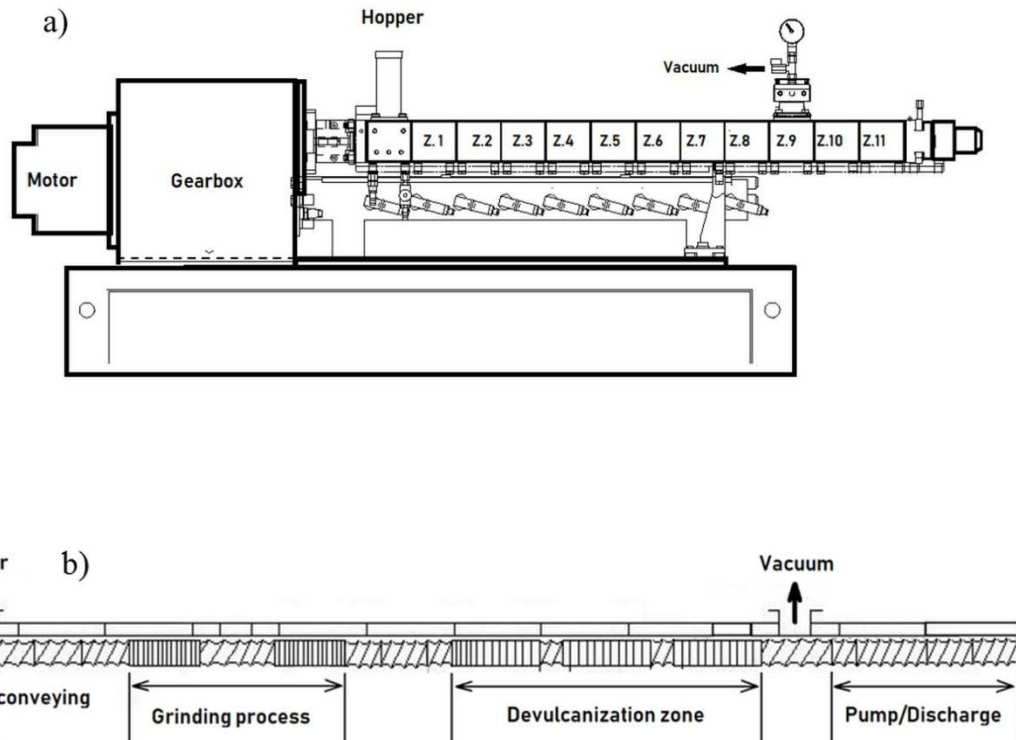


Fig. 1. (a) Twin screw extruder and (b) screw configuration used to perform thermo-mechanical devulcanization

2.3. Revulcanization process

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

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

Table 1

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

*CBS: N-Cyclohexyl-2-benzothiazole sulfonamide

Table 2

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	

*CBS: N-Cyclohexyl-2-benzothiazole sulfonamide

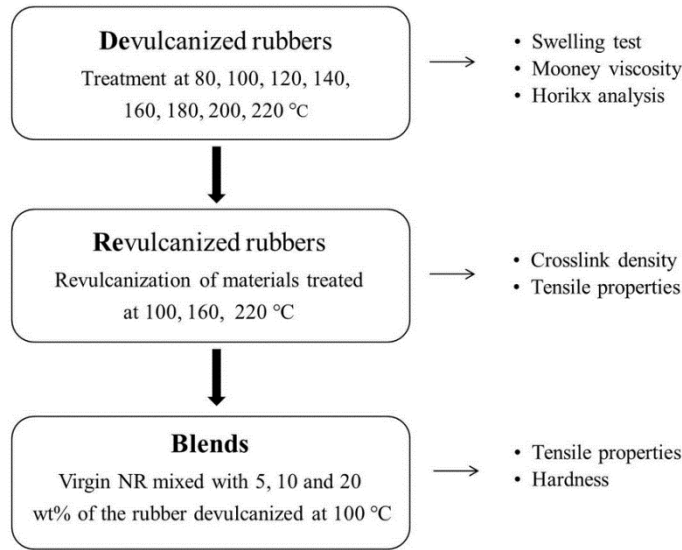


Fig. 2. Experimental procedure

2.4. Characterization of reclaimed rubber

2.4.1. Degree of devulcanization

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

The soluble fraction was given by equation (1):

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

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

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

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

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

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

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

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

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

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

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

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

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

2.4.2. Horikx diagram

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

2.4.3. Mooney viscosity

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

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

2.4.4. Hardness Shore A

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

2.4.5. Mechanical properties

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

3. Results and discussions

3.1. Waste material characterization

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

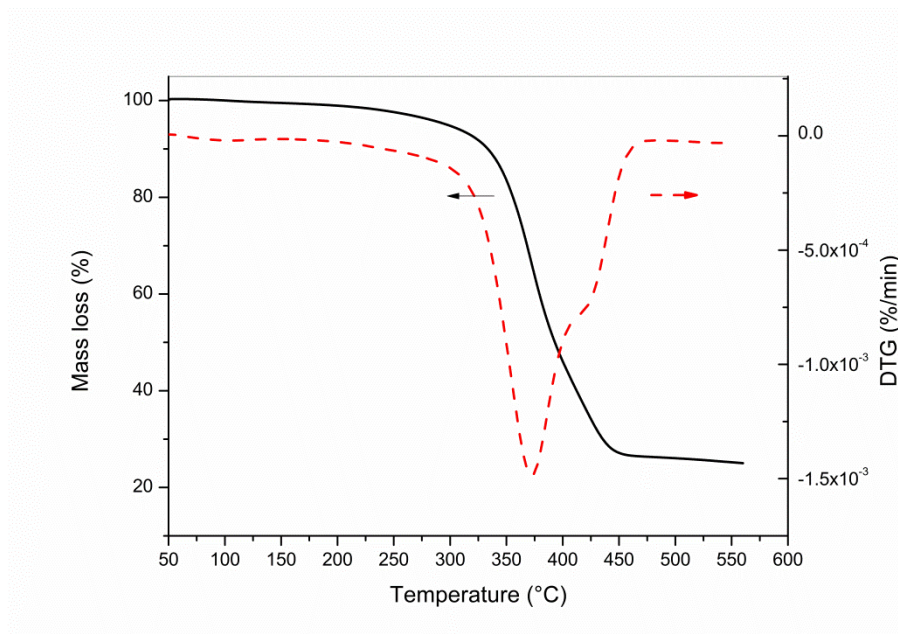


Fig. 3. NR mass loss and its derivative (DTG) as a function of temperature

3.2. Devulcanization analyzes

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

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

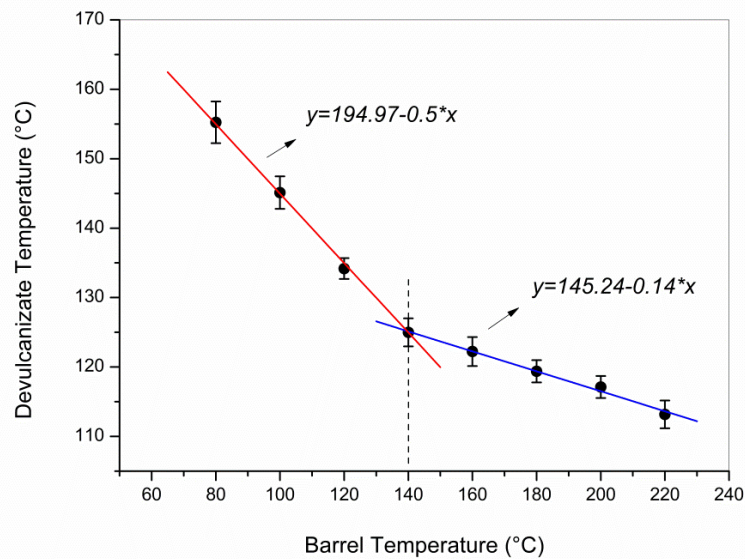


Fig. 4. Temperature of the material at the exit of the extruder die as a function of the barrel temperature (3 measurements were done in each condition)

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

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

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

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

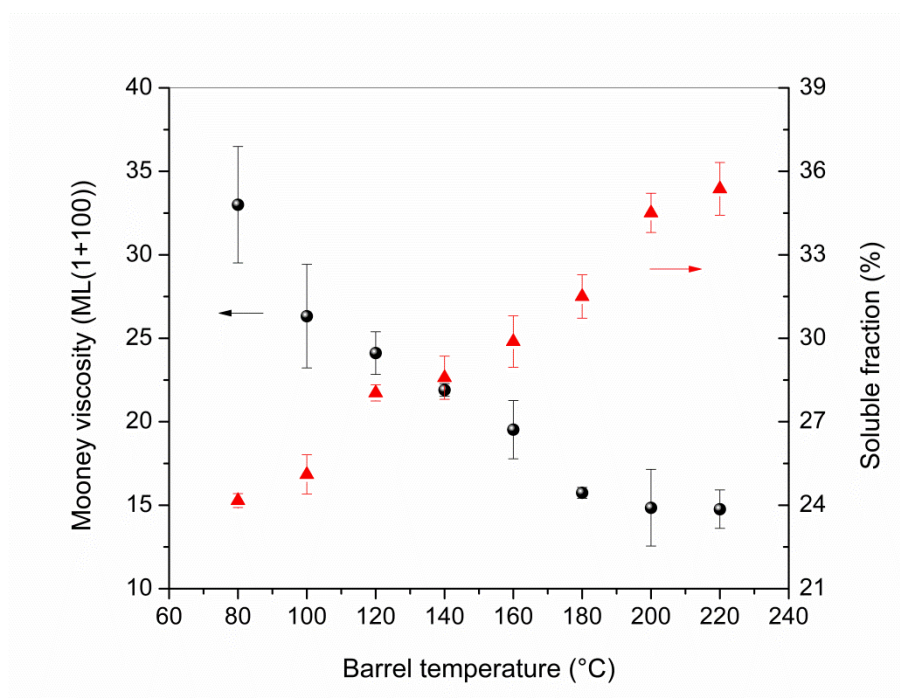


Fig. 5. Mooney viscosity and soluble fraction of the devulcanized NR as a function of the barrel temperature (3 samples were tested in each condition)

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

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

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

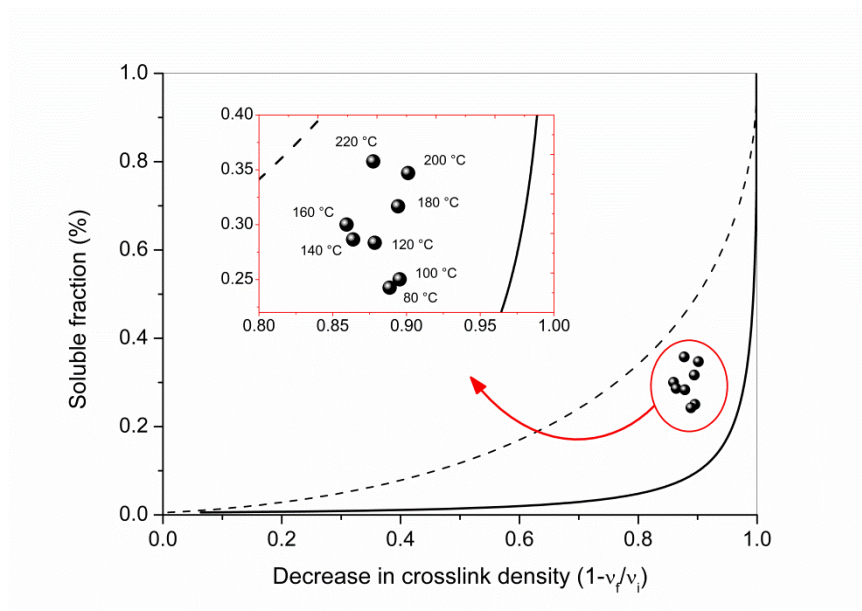


Fig. 6. Soluble fraction of devulcanized NR against relative decrease in crosslink density

3.3. Revulcanized materials properties

3.3.1. Revulcanized materials based entirely on recycled rubbers

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

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

Table 3

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

Material/ Property	Soluble fraction [%]	Crosslink density [x 10 ⁻⁴ mol/cm ³]	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

3.3.2. Revulcanized blends with virgin rubber

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

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

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

Table 4

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

4. Conclusion

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

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

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