

# Rubber devulcanization in the planetary extruder – processing and structure

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**Abstract:** Thermo-mechanical devulcanization process of ground tire rubber (GTR) in a planetary extruder was investigated. The rheological properties of reclaimed rubber (rGTR) were studied using a Mooney viscometer and a rubber processing analyzer (RPA). Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) were used to determine reclaimed rubber structure. Increasing the scale of the devulcanization process (from 0.5 to 4 kg/h) resulted in a deterioration of the processing properties, which in the case of partially devulcanized rubber can only be determined using an RPA rheometer.

**Keywords:** waste tires, recycling, devulcanization, planetary extruder, rheological properties.

## Dewulkanizacja gumy w wyciarkarce planetarnej – właściwości przetwórcze i struktura

**Streszczenie:** Zbadano proces termo-mechanicznej dewulkanizacji zmielonych opon samochodowych (GTR) w wyciarkarce planetarnej. Właściwości reologiczne regeneratu gumowego (rGTR) oznaczono za pomocą wiskozymetru Mooney'a i reometru bezrotorowego (RPA). Do oceny struktury regeneratu gumowego stosowano spektroskopię w podczerwieni z transformacją Fouriera (FT-IR) i skaningową mikroskopię elektronową (SEM). Zwiększanie skali procesu dewulkanizacji (z 0,5 do 4 kg/h) skutkowało pogorszeniem właściwości przetwórczych rGTR, które w przypadku częściowo zdewulkanizowanej gumy można oznaczyć jedynie za pomocą reometru RPA.

**Słowa kluczowe:** zużyte opony, recykling, dewulkanizacja, wyciarkarka planetarna, właściwości reologiczne.

Waste tires generation in China presented a growing trend and reached around 14.6 mln tons in 2018, which was about 3.2 times higher than the amount in generated in the European Union [1]. On the other hand, recycling level of waste tires in China is low, approx. 47% [2], which is due to the lack of a normative and efficient recycling technology.

Similar trends and problems with recycling of used tires, although on a much smaller scale, are also observed in Poland. In 2021, 252,600 tons of waste tires generated in Poland were recycled – 45%, energy recovery – 30%

and unknown/stock disposal – 25% [3], which is the highest level in the European Union. This is due to the limited number of Polish companies dealing with waste tire management and recycling.

Increasing number of illegally dumped or stockpiled waste tires is a serious threat to the natural environment and human health, mostly due to the higher risk of their uncontrolled combustion and emission of toxic substances [4].

Law regulations, limited petroleum sources and increasing awareness of consumers resulted in the sustainable development of waste tires recycling technologies [5]. In 2021, European Tire and Rubber Manufacturers' Association and the European Recycling Industries' Confederation opened a call for the development of harmonized end-of-waste criteria for waste tires for safety and quality criteria. This strategy allows increasing the content of waste tire rubber during manufacturing of rubber goods and promotes the circular economy in the European Union [6].

Development of rubber devulcanization technologies is a step forward to further developing rubber recycling

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and upcycling technologies. Considering environmental and economic aspects, reactive extrusion is the most promising method for rubber devulcanization [7, 8], which makes the production less complex, more flexible, and easier for upscaling [9].

The first attempts to devulcanize rubber using a twin-screw extruder were made by Toyota Motor Corp, Toyoda Gosei Co. Ltd., Toyota Central R&D Labs Inc. [10, 11], and currently this technology is being developed and optimized by academia and industry [12, 13]. In this field of research, rubber recycling using a planetary extruder is an innovative approach and an interesting alternative for twin screw extruders, which allows designing closed-loop processes in the rubber industry [14].

The aim of the research was to investigate the effect of output of ground tire rubber (GTR) devulcanization carried out in a planetary extruder on rheological properties and structure of the obtained reclaimed rubber (rGTR).

## EXPERIMENTAL PART

### Materials

Ground tire rubber with particle size up to 0.6 mm obtained from a mixture of passenger and truck tires was supplied by Grupa Recykl S.A. (Śrem, Poland). According to the technical data sheet, GTR particle size distribution determined by percentage of rubber powder remaining on the sieve is: <0.6 mm – 0.4%; 0.6 mm – 2.5%; 0.5 mm – 33.0%; 0.4 mm – 28.4%; 0.3 mm – 19.0%; 0.2mm – 15.5% and 0.1 mm – 1.2%. GTR particles size was selected based on preliminary tests and literature data, which indicated that a smaller GTR particle size results in higher devulcanization degree and easier processing [15]. Thermogravimetric

analysis (TGA) performed according to the ASTM D6370 standard was used to determine GTR composition, which showed that organic substances (rubber and additives) – 63.7 wt%, carbon black – 29 wt% and ash – 7.3 wt%. TGA curves showed two peaks at 390.9°C and 447.4°C, which corresponded to the presence of natural rubber and synthetic rubber (styrene-butadiene rubber and butadiene rubber) commonly used in tire industry [16].

### Rubber devulcanization in the planetary extruder

Laboratory planetary extruder model PLATEX 80 produced by Takimsan Disli Kesici Ltd. Sti. (Istanbul, Türkiye) was used for thermo-mechanical devulcanization of GTR. The process was carried out at 200°C and a screw rotation speed of 15 rpm with variable output: 0.5; 1.0; 2.0 and 4.0 kg/h. The obtained GTR samples were named as rGTR<sub>0.5</sub>; rGTR<sub>1</sub>; rGTR<sub>2</sub> and rGTR<sub>4</sub>, respectively. Figure 1 shows the appearance of the obtained products as a function of devulcanization output. The higher devulcanization output resulted in the GTR particles not sticking together and there were fewer agglomerates. The samples were passed through a two-roll mill, sufficient to combine the rubber particles/agglomerates and obtain rubber sheets. However, in the case of GTR<sub>4</sub> the rubber sheet was not as consistent as in the other samples.

### Characterization

Mooney viscosity of reclaimed rubber was measured at 100°C according to ISO 289-1 standard using a Mooney viscometer MV2000 (Alpha Technologies, Akron, OH, USA). Processability and flow properties were characterized based on ASTM D6204 standard using Premier

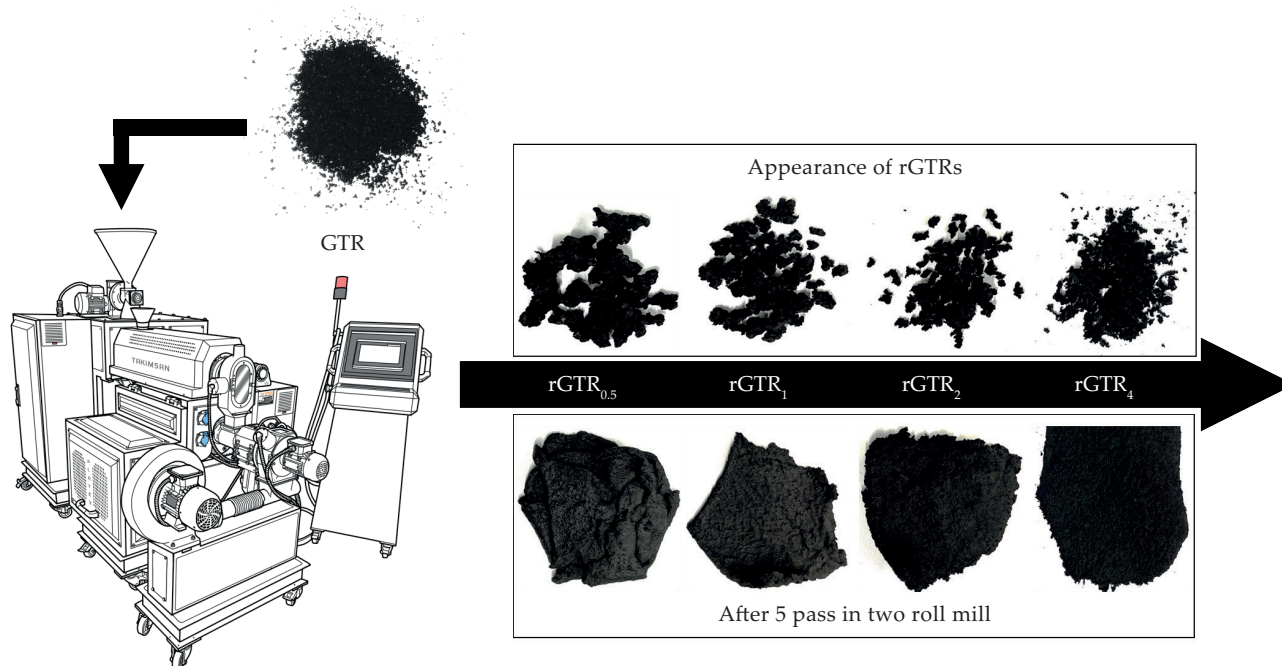


Fig. 1. Scheme of sample preparation and appearance of rGTR after devulcanization in a planetary extruder and rolling in a two-roll mill

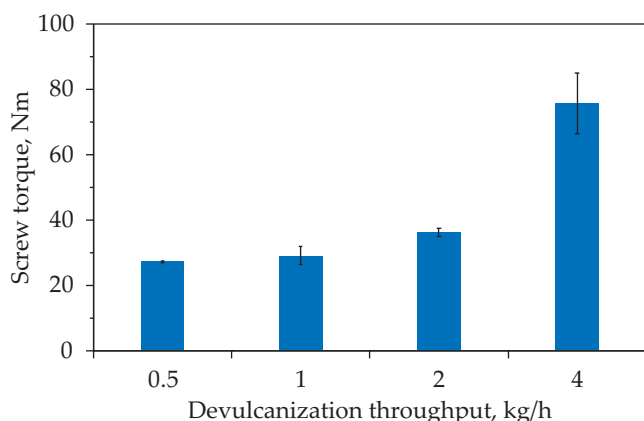


Fig. 2. Effect of devulcanization output on screw torque

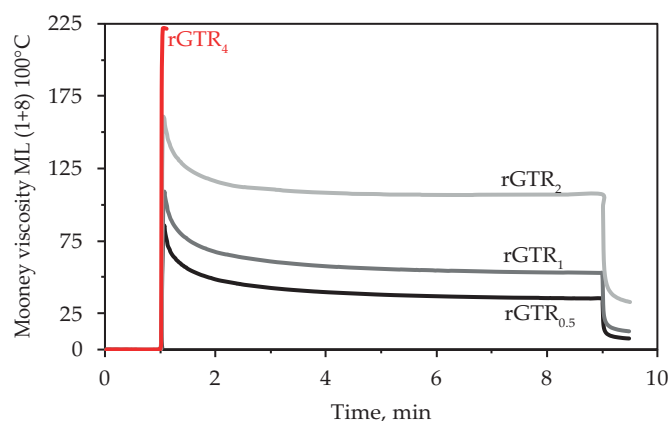


Fig. 3. Effect of devulcanization output on Mooney viscosity

RPA Rheometer (Alpha Technologies, Akron, OH, USA). Method A (low strain frequency sweep) was used. The measurements were carried out at 100°C, and the conditioning step included a deformation of 2.8%, a frequency of 5 Hz and a time of 5 minutes. A three-point frequency sweep was performed at ±7% distortion and at three frequencies: 0.1; 2.0 and 20 Hz. Fourier transform infrared spectroscopy (FT-IR) analysis was performed using an IRTracer-100 from Shimadzu (Kyoto, Japan) equipped with a single-reflection ATR accessory with a prism made from germanium crystal. Measurements were performed in an attenuated total reflectance mode at 4 cm<sup>-1</sup> resolution and 32 scans in the wavelengths range of 4000–500 cm<sup>-1</sup>. The morphology was evaluated using a FlexSEM 1000 II scanning electron microscope from Hitachi (Tokyo, Japan). The electron beam accelerating voltage was 20 kV. The samples were coated with a thin gold layer to increase their conductivity in the vacuum chamber using a 108 Auto Sputter Coater from Cressington (Watford, UK).

## RESULTS AND DISCUSSION

Monitoring screw torque during extrusion is a good indicator of process progress, allowing for a better understanding of process dynamics and stability [17]. Fig. 2 shows the correlation between screw torque and devulcanization efficiency. As expected, increasing the efficiency of the rubber devulcanization process resulted in

greater screw torque, but this correlation is not linear. The torque for the rGTR<sub>4</sub> devulcanization process was almost 2.8 times higher than for rGTR<sub>0.5</sub>. Moreover, the small standard deviation of the screw torque indicates that thermo-mechanical devulcanization in the planetary extruder is a stable process.

The appearance and behavior during passing through a two-roll mill (Fig. 1) clearly indicates that obtained rGTR samples are characterized by different devulcanization levels which affect their flowability and processing properties. Mooney viscosity is a parameter commonly used for rubber devulcanization process assessment. It was found that the Mooney viscosity increases with the increase in the output of the devulcanization process (Fig. 3) and is in the range of 38–106, which is close to the values described in the literature for commercial reclaimed rubbers, usually in the range of 65–90 [18]. For the rGTR<sub>4</sub> sample, which was only partially devulcanized, the Mooney viscosity could not be measured. In this case, the viscoelastic properties were determined using a rubber process analyzer (RPA) and the obtained results are summarized in Table 1.

The storage modulus ( $G'$ ), loss modulus ( $G''$ ) and dynamic complex viscosity ( $\eta^*$ ) increase with the increase in devulcanization efficiency, and the relationship is almost linear. This is due to the limited flowability of rGTR, which is associated with a lower devulcanization output. As could be expected frequency has a significant impact on the viscoelastic properties. Lower  $G'$ ,  $G''$  and  $\eta^*$  were obtained at higher frequency. For example, the

Table 1. Mooney viscosity and viscoelastic properties of rGTR

Sample	Mooney viscosity ML (1+4) 100°C	$\eta^*$	$G'$	$G''$	$\tan\delta$	$\eta^*$	$G'$	$G''$	$\tan\delta$	$\eta^*$	$G'$	$G''$	$\tan\delta$
		Pa·s	kPa	kPa		Pa·s	kPa	kPa		Pa·s	kPa	kPa	
		20 Hz				2 Hz				0.1 Hz			
rGTR <sub>0.5</sub>	37.8±0.5	1929 ±167	236.6 ±20.8	68.7 ±4.8	0.291 ±0.005	13971 ±1362	170.8 ±16.9	42.0 ±3.2	0.246 ±0.006	244369 ±28153	124.9 ±14.8	27.7 ±1.6	0.223 ±0.014
rGTR <sub>1</sub>	56.4±0.7	2768 ±284	341.2 ±35.7	92.6 ±7.2	0.272 ±0.008	20635 ±2325	252.5 ±28.4	60.6 ±6.9	0.240 ±0.000	371532 ±44888	189.9 ±22.7	42.3 ±6.3	0.223 ±0.006
rGTR <sub>2</sub>	106.2±1.3	3929 ±397	488.8 ±50.6	96.0 ±17.7	0.232 ±0.011	30818 ±3468	379.8 ±43.2	78.8 ±6.7	0.208 ±0.006	583030 ±70311	299.6 ±36.3	58.6 ±6.0	0.196 ±0.003
rGTR <sub>4</sub>	-	6248 ±313	785.0 ±39.0	142.8 ±8.8	0.182 ±0.002	51813 ±2424	642.7 ±29.9	110.7 ±5.9	0.172 ±0.001	1030119 ±48268	532.3 ±24.8	87.3 ±4.7	0.164 ±0.001

dynamic complex viscosity for the  $rGTR_{0.5}$  was in the range of 1929–244369 Pa·s, while for sample  $rGTR_4$  was in the range: 6248–1030119 Pa·s. Furthermore, regardless of the frequency, the loss factor ( $\tan\delta$ ) decreases with the increase in the devulcanization process output, which can be explained by better carbon black migration [19].

For better understanding of this phenomena and the structure of reclaimed rubbers, the samples were examined using FT-IR and SEM techniques. Figure 4 shows FT-IR spectra which provide information about functional groups present on the surface of untreated GTR and  $rGTR$ . The absorbance maxima at  $1375\text{ cm}^{-1}$  (peak g) and  $820\text{ cm}^{-1}$  (peak l) are related to the vibrations of  $\text{CH}_3$  groups and to  $-\text{CH}=\text{CH}-$  bonds vibrations present in the natural rubber. Absorbance peaks at  $966\text{ cm}^{-1}$  (peak j),  $910\text{ cm}^{-1}$  (peak k) and  $699\text{ cm}^{-1}$  (peak m) are attributed to vibration of  $=\text{CH}_2$  in polybutadiene and C-H in benzene ring, which confirm the presence of butadiene rubber and styrene-butadiene rubber in GTR [20]. The presence of natural rubber and styrene-butadiene rubber in GTR and reclaimed GTR confirms that waste tires were used during GTR manufacturing.

The results of FT-IR analysis showed that the chemical structure of GTR and  $rGTR$  is similar. The absorbance bands at  $1650\text{--}1600\text{ cm}^{-1}$  (signal d) correspond to  $\text{C}=\text{C}$  stretching vibrations, while at a wavelength of  $1537\text{ cm}^{-1}$  (signal e) they are related to the presence of zinc stearate, commonly used in the rubber industry [21]. The absorbance at  $3300\text{ cm}^{-1}$  (signal a) is assigned to  $-\text{OH}$  groups, while the bands at wavenumber  $1300\text{ cm}^{-1}$  (signal h) and  $1090\text{ cm}^{-1}$  (signal i) correspond to the stretching of C-O and C-O-C bonds. The strongest absorbance bands associated with C-H stretching vibrations at  $3000\text{--}2800\text{ cm}^{-1}$  (peaks b and c) and  $-\text{CH}_2$  strain at  $1445\text{ cm}^{-1}$  (peak f) showed no significant differences between GTR and  $rGTR$  spectra. This suggests that the GTR hydrocarbon skeleton was not degraded even for the  $rGTR_{0.5}$  sample characterized by a high degree of devulcanization (low Mooney viscosity), which is consistent with the literature [22, 23]. FT-IR analysis indicates limited oxidation of GTR and high selectivity of thermo-mechanical devulcanization carried out in a planetary extruder.

SEM images of untreated GTR,  $rGTR_{0.5}$  and  $rGTR_4$  samples are presented in Fig. 5. It was observed that higher

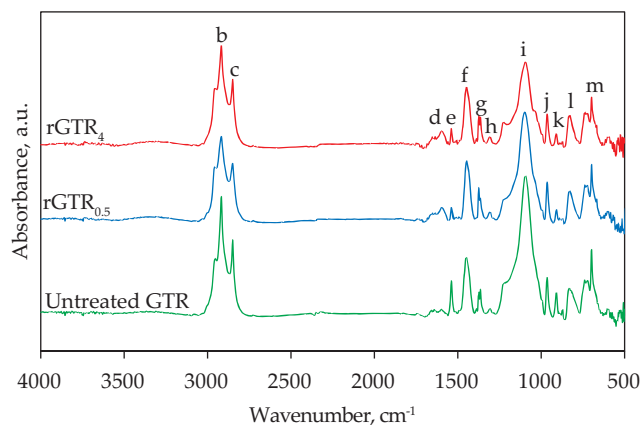


Fig. 4. FT-IR spectra of GTR,  $rGTR_{0.5}$  and  $rGTR_4$

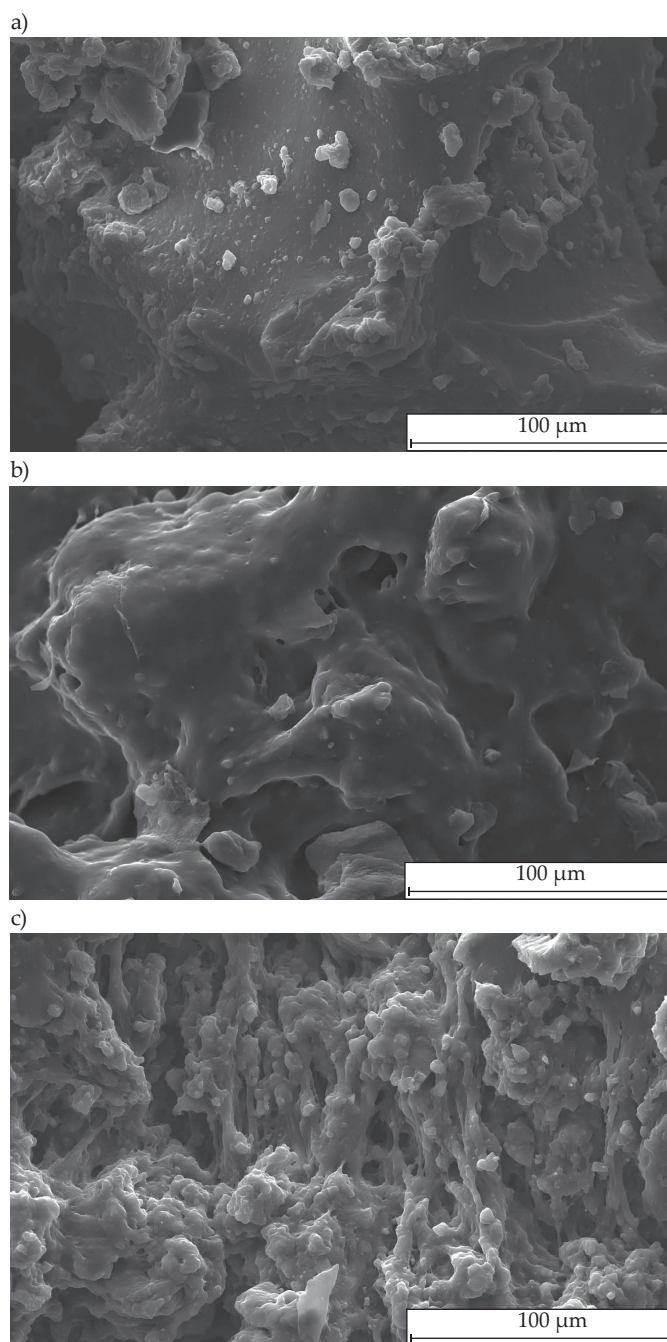


Fig. 5. SEM images: a) untreated GTR, b)  $rGTR_{0.5}$ , c)  $rGTR_4$ ; 500× magnification

output of the process resulted in lower devulcanization degree. Therefore, the smoother surface and melted area related to degradation of three-dimensional network present in cross-linked GTR was less efficient for  $rGTR_4$  comparing to  $rGTR_{0.5}$ . The observations of structure for studied materials corresponded with their processing properties assessment.

## CONCLUSIONS

In this work, GTR was devulcanized in a planetary extruder. Increasing the output of the devulcanization process (0.5–4 kg/h) resulted in a higher screw torque,

which was associated with higher viscosity and poorer flowability. Unlike the Mooney viscometer, the rubber process analyzer made it possible to determine the viscoelastic properties of all tested samples. FT-IR analysis confirmed the high selectivity of GTR devulcanization in the planetary extruder. SEM showed that the higher devulcanization process output resulted in a smoother surface and a larger remelting area of rGTR. The authors confirmed the high potential of planetary extrusion and rubber process analyzer for rubber devulcanization to develop and scale up new products based on waste tire rubber.

#### Authors contribution

J.Z. – testing, data curation, investigation, visualization, writing; M.K. – testing, data curation, investigation, visualization, writing; S.W. – data curation, formal analysis, writing; K.F. – research concept, methodology, testing, data curation, formal analysis, investigation, validation, visualization, writing.

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#### Conflict of interest

The authors declare no conflict of interest.

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