

Investigating the combined impact of plasticizer and shear force on the efficiency of low temperature reclaiming of ground tire rubber (GTR)

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Abstract

In the present work, ground tire rubber (GTR) was mechano-chemically reclaimed at ambient temperature using two-roll mills. Road bitumen and styrene-butadiene-styrene (SBS)-modified bitumen at variable content (in range: 2.5-20 phr) were applied as reactive plasticizers to enhance reclaiming of GTR. For better understanding the plasticizing effect of bitumen on the quality of obtained reclaimed rubber, mechano-chemically reclaimed GTR has been compared with GTR after thermo-mechanical reclaiming *via* low temperature extrusion (120°C), which allows generation of high shear forces on GTR. Reclaiming process was evaluated by oscillating disc rheometer measurements, followed by mechanical, physical, thermal, and morphological properties analyses performed on vulcanized reclaimed rubber. The obtained results showed that application of bitumen during mechano-chemical reclaiming of GTR improves processing and prevents oxidation of reclaimed GTR through enhancement of physical and chemical interactions between GTR and bitumen. On the other hand, high shear forces acting on GTR during thermo-mechanical reclaiming caused effective scission of cross-linking bonds, while at the same time an adverse oxidative degradation of GTR occurs. Noticeably, the type of bitumen strongly affected the nature of the interfacial interactions between GTR and bitumen. Plasticization/partial reclaiming of GTR (road bitumen, SBS-

1 modified bitumen) and encapsulation of GTR (SBS modified bitumen) were confirmed by
2 mechanical properties, FTIR, TGA and SEM measurements.

3
4 **Keywords:** Recycling; Ground tire rubber; Reclaiming; Bitumen; Low temperature
5 processing

6 7 **1. Introduction**

8 Dynamic development of the automotive industry is responsible for the increase of
9 waste rubber, especially used tires, which are a serious threat to the natural environment.
10 Legal regulations as well as economic and ecological factors contribute to heightened interest
11 in the technologies based on recycling of the used tires [1]. At present, grinding is one of the
12 most commonly used methods of waste tires recycling [2]. During this operation, used tires
13 are mechanically disintegrated until the required particle size is reached. Ground tire rubber
14 (GTR) without additives can be processed through reactive sintering under high pressure and
15 at high temperature [3]. However, the cross-linked structure of GTR limits the application of
16 this method to production of low-cost products with simple shapes and low quality
17 requirements. Therefore, studies conducted in this field are mainly focused on application of
18 GTR as fillers or modifiers in polymer compositions [4, 5], bitumen [6] and concrete [7].
19 Moreover, GTR has been applied as a component in pyrolysis [8] and in the
20 reclaiming/devulcanization process [9].

21 During the reclaiming process, three-dimensional network of a cross-linked rubber is
22 destroyed by means of thermal, mechanical or chemical energy. The resulting product is
23 commonly called reclaimed rubber. In contrast to GTR, reclaimed rubber can be easily
24 processed, shaped and vulcanized. Reclaimed rubber is used as a cheap substitute of fresh
25 rubber during manufacture of new rubber compounds. Reclaiming/devulcanization is usually
26 performed at a high temperature (180-300°C), high shear force and with the usage of
27 chemical additives (e.g. disulfide, peroxides, plasticizers etc.). These specific conditions are
28 necessary to scission of cross-linking bonds presented in rubber, leading to easier processing
29 of GTR and at the same time higher quality of the obtained reclaimed rubber [10, 11].

30 Recently, Saiwari et al. [12] examined the effect of the most crucial thermo-
31 mechanical parameters on the efficiency of reclaiming of different unfilled elastomers -
32 commonly used in tire industry (styrene-butadiene rubber, butadiene rubber, natural rubber,
33 chlorinated butyl rubber). They indicated that temperature is the main parameter affecting the
34 reclaiming efficiency and that GTR reclaiming should be performed at a reasonably low

1 temperature. Accordingly, it was confirmed that low temperature reclaiming of GTR allows
2 for selective scission of cross-linked bonds instead of the main chain scission, thereby
3 enhances the mechanical properties of the obtained reclaimed rubber. Further advantages of
4 low temperature reclaiming of GTR are: intensification of shear forces acting on GTR,
5 limitation of secondary cross-linking, reduction of energetic costs and reduction of the
6 amount of gases generated during reclamation. Similar observations were also described
7 elsewhere [13-15]. On the other hand, low temperature reclaiming has a negative influence
8 toward processing of GTR [16].

9 Application of plasticizers, as low molecular weight compounds, causes increase of
10 flexibility, workability or distensibility of the processed material, through which enhances
11 GTR processability during low temperature reclaiming. Xu et al. [17] used treated distillate
12 aromatic extract (TDAE), naphthenic oil, wood tar, shea butter and recycled cooking oil as
13 plasticizers during thermo-mechanical reclaiming of GTR. They also studied the effect of
14 type and content of plasticizer on the efficiency of GTR reclaiming. The best mechanical
15 properties were received for GTR reclaimed with wood tar, which was related to the low
16 degree of reclaimed rubber (the highest cross-link density).

17 In a previous work [18] we applied heavy oils from pyrolysis of tires as plasticizers
18 during low temperature reclaiming of GTR. Obtained results indicate that plasticization of
19 GTR with heavy oils allows selective scission of cross-linked bonds, which has beneficial
20 influence on reclaiming efficiency of GTR. Alternative solutions are bitumens, which could
21 be applied as a low-cost and effective plasticizers for reclaiming of GTR. Swelling and partial
22 reclaiming/devulcanization of GTR particles with bitumen enable exchange of components
23 between GTR and bitumen phase, which facilitates release of the rubber degradation products
24 to bitumen phase and diffusion of some bitumen compounds into the GTR phase [19, 20].
25 Grigoryeva et al. [21] and Zhang et al. [22, 23] proposed application of GTR/bitumen blends
26 in thermoplastic elastomers. GTR/bitumen blends were prepared at elevated temperatures
27 using two-roll mills or extruder. Recently, Singh et al. [24] applied thermo-mechanically
28 reclaimed GTR in modification of bitumen. Authors proved that reclaimed GTR has the
29 potential to chemically interact with bitumen, possibly as a result of co-vulcanization of
30 reclaimed rubber and asphaltene phase presented in bitumen. Furthermore, it should be
31 mentioned that sulfur and vulcanization accelerators from GTR as well as sulfur compounds
32 present in bitumen may also affect curing and mechanical properties of reclaimed rubber and
33 rubber compounds. However, to the best of our knowledge, this phenomenon is poorly
34 described in the literature.

In the present work, reclaiming of GTR was conducted at ambient temperature using a two-roll mills, which allowed for generation of suitable shear forces on GTR and reduction of energy cost during the process. In the light of above mentioned studies, we aimed to examine the effects of the bitumen type and content on curing characteristics, physical and mechanical properties of obtained reclaimed rubber. Two types of commonly used bitumens (bitumen 160/220 and styrene-butadiene-styrene (SBS)-modified Modbit 25/55-60) at variable content (ranging from 2.5 phr to 20 phr based on 100 parts of GTR) were applied as reactive plasticizers during reclaiming of GTR. Curing characteristics, chemical structure (FTIR analysis), static mechanical properties (tensile strength, elongation at break, hardness), physical properties (density, cross-link density, sol fraction), thermal properties (TGA-DSC-FTIR analysis) and morphology (SEM) of vulcanized reclaimed GTR were determined for comprehensive structure-properties relationships assessment. The presented work is a continuation of the authors' research about recycling of the used car tires [25-27].

2. Experimental

2.1. Materials

Ground tire rubber (GTR) with particles size below 0.8 mm was received from Orzeł S.A. (Poland). GTR was obtained during ambient grinding of the used tires (mix of passenger car tires and truck tires). Road bitumen 160/220 and polymer modified bitumen Modbit 25/55-60 were received from Lotos Asfalt Sp. z o.o. (Poland). Characteristics of the used bitumen is presented in Table 1.

Table 1. Characteristics of bitumens

Item	Bitumen 160/220	Modbit 25/55-60	Standard
Penetration at 25°C (1/10 mm)	170-210	25-55	PN-EN 1426
Softening point (°C)	35-43	≥60	PN-EN 1427
Frass breaking point (°C)	≥-15	≤-10	PN-EN 12593
Flash point (°C)	220	≥ 235	PN-EN 13398

2.2. Reclaiming of GTR

Mechano-chemical reclaiming of GTR was conducted at ambient temperature using a two-roll mills from Buzuluk (Czech Republic). GTR was masticated in small gap (high shear forces) for 30 minutes. In order to improve the GTR processing during mechano-chemical reclaiming, different amounts (2.5, 5, 10 and 20 phr) of bitumen were applied as reactive plasticizer. Selected bitumen's were characterized by different values of different penetration and softening point (see Table 1), which is related to their viscosity. Modbit 25/55-60 is a bitumen modified with SBS and has higher viscosity than the conventional road bitumen

1 160/220. For better understanding the influence of reclaiming conditions on the quality of
2 obtained reclaimed rubber, the properties of GTR reclaimed *via* two-roll milling was
3 compared with GTR after thermo-mechanical treatment *via* extrusion. Thermo-mechanical
4 reclaiming of GTR was conducted in a co-rotating twin screw extruder EHP 2x20 from
5 Zamak Mercator (Poland). The extruder had eleven heating/cooling zones with a screw
6 diameter of 20 mm and L/d ratio of 40. Barrel temperature during reclaiming was 120°C. The
7 screw rotation speed was set constant at 600 rpm. Low temperature extrusion conditions
8 allows generation of high shear forces on GTR.

9 10 **2.3. Curing of reclaimed GTR**

11 Obtained reclaimed GTR (rGTR) was mixed with sulfur curing system and processed
12 using two-roll mills from Buzuluk (Czech Republic). Composition of tested compounds is
13 presented in Table 2. Tested compounds were formed in sheets with 2 mm thickness and then
14 cured in electric heated press at 150°C under the pressure of 4.9 MPa for the optimum
15 vulcanization time determined according to ISO 3417 standard.

16 17 18 **2.3. Measurements**

19 Vulcanization process was investigated according to ISO 3417 at 150°C, using
20 Monsanto R100S rheometer with oscillating rotor (USA). Oscillation angle was 1° and torque
21 range 0-100 dNm. Cure rate index (CRI) values were calculated in accordance with the
22 formula [28] (1):

$$23 \quad \text{CRI} = \frac{100}{t_{90} - t_2} \quad (1)$$

24 where: t_{90} – optimum vulcanization time, min; t_2 – scorch time, min.

25
26 To investigate the aging resistance of vulcanizates at elevated temperatures, R_{300}
27 parameter was determined [29]. R_{300} is the percentage of reversion degree after a period of
28 300 s calculated from the time at which torque has the maximum value (M_H). R_{300} was
29 calculated in accordance with the formula (2):

$$30 \quad R_{300} = \frac{M_{\max.} - M_{300s}}{M_{\max.}} \times 100 \% \quad (2)$$

31 where: $M_{\max.}$ – maximum torque; M_{300s} – torque 300 s after maximum torque.

32 Chemical structure of the vulcanizate samples was determined using Fourier transform
33 infrared spectroscopy (FTIR) analysis performed by means of a Nicolet iS10 spectrometer

- 1 from Thermo Scientific (USA). The device had an ATR attachment with a diamond crystal.
 2 Measurements were performed with 1 cm^{-1} resolution in the range $650\text{-}4000\text{ cm}^{-1}$.
 3
 4 Table 2. Composition, curing characteristics, mechanical and physical properties of tested
 5 compounds

Component*	Sample name									
rGTR <i>via</i> milling	100	100	100	100	100	100	100	100	100	-
rGTR <i>via</i> extrusion at 120°C										100
Bitumen 160/220		2.5	5	10	20					
Modbit 25/55-60						2.5	5	10	20	
Curing characteristics at 150°C										
Minimal torque (dNm)	35.1	32.3	31.7	28.3	21.4	31.8	30.7	30.5	22.8	6.6
Maximal torque (dNm)	52.5	47.4	46.8	42.3	32.4	50.1	49.4	44.4	34.6	28.7
ΔM (dNm)	17.4	15.1	15.1	14.0	11.0	18.3	18.6	13.9	11.8	22.1
Scorch time (t_2 , min)	3.0	3.1	3.1	3.2	3.3	2.8	2.7	2.8	3.4	3.1
Optimum cure time (t_{90} , min)	7.3	6.7	6.7	6.9	6.8	7.3	7.2	7.1	7.4	9.8
Cure rate index (CRI, min^{-1})	23.0	27.9	27.6	27.0	28.2	22.3	22.2	23.4	24.8	15.0
Thermal aging resistance (R_{300} ,%)	0.0	0.4	0.5	0.6	0.8	0.6	0.7	0.9	0.9	1.1
Mechanical properties										
Tensile strength (MPa)	5.5 ± 0.2	4.6 ± 0.4	4.5 ± 0.3	4.5 ± 0.1	3.3 ± 0.2	5.0 ± 0.3	5.1 ± 0.1	4.5 ± 0.1	3.7 ± 0.1	5.3 ± 0.3
Elongation at break (%)	178 ± 7	162 ± 13	190 ± 13	184 ± 8	194 ± 9	164 ± 11	154 ± 15	177 ± 7	194 ± 7	192 ± 13
Hardness ($^{\circ}\text{Sh A}$)	70	69	68	68	61	67	66	65	64	57
Physical properties										
Density at 25°C (g/cm^3)	1.20	1.19	1.18	1.18	1.16	1.19	1.19	1.18	1.16	1.20
Cross-link density ($\text{mol}/\text{cm}^3 \times 10^{-4}$)	2.53	2.42	2.33	2.35	1.91	2.39	2.39	2.13	1.72	1.89
Sol fraction (%)	6.1	7.6	10.6	13.0	19.1	7.8	9.0	11.8	17.8	9.3
Corrected sol fraction (%)**	-	7.4	9.6	12.4	15.9	7.6	8.6	10.8	14.8	-
Theoretical sol fraction (%)***	-	8.6	10.9	15.2	22.8	8.6	10.9	15.2	22.8	-

6 *For all samples the same curing system samples was used. The curing system composition (phr): stearic acid
 7 1.0; zinc oxide 2.5; TBBS (N-tert-butyl-2-benzothiazole sulfenamide) 0.35; sulfur 1.5

8 **Presented calculation assumes that the whole bitumen in GTR/bitumen composition was dissolved in toluene

9 ***Presented calculation based on the additivity principle and lack of physical/chemical interactions between
 10 milled rGTR and bitumen

11

12 The tensile strength and elongation at break were estimated in accordance with ISO
 13 37. Tensile tests was performed on the Zwick Z020 machine (Germany) at a constant speed of
 14 500 mm/min. Shore hardness type A was estimated using Zwick 3130 durometer (Germany)
 15 in accordance with ISO 7619-1.

16 The density of the samples was measured based on the Archimedes method, as
 17 described in ISO 2781. Accordingly, all measurements were carried out at room temperature
 18 in methanol medium.

1 Sol fraction was determined as mass difference of vulcanizate samples before swelling
2 (W_1) and after extraction (W_2), according to equation (3):

$$3 \text{ Sol fraction} = \frac{W_1 - W_2}{W_1} \times 100 \% \quad (3)$$

4 Cross-link density of the vulcanizate was determined by equilibrium swelling in toluene
5 (room temperature, 72 h), according to the Flory-Rehner equation [30] (4):

$$6 v_e = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{[V_1(V_r^{1/3} - V_r/2)]} \quad (4)$$

7 where: v_e – cross-link density, mol/cm³; V_r – gel volume in the swollen sample; V_1 – solvent
8 molar volume (toluene = 106.2, cm³/mol [31]); χ – polymer-solvent interaction parameter (in
9 the calculations, it was assumed to be 0.391 [32]).

10 The Flory-Rehner equation can be applied for non-filled compounds, while studied rGTR was
11 filled with ~34 wt. % of carbon black, which is an active filler commonly applied in tire
12 industry. Therefore, the Kraus correction for filled compounds [33] was applied to calculate
13 the actual remaining cross-link density. In its simplified form, the cross-link density with
14 Kraus correction is calculated according equations [34] (5) and (6):

$$15 v_{\text{after correction}} = \frac{v_e}{1 + K + \Phi} \quad (5)$$

$$16 \Phi = \frac{\phi_f \times \rho_r \times m_0}{\rho_f \times m_{\text{dry}}} \quad (6)$$

17 where: v_e – the measured chemical cross-link density, mol/cm³; $v_{\text{after correction}}$ – the actual
18 chemical cross-link density, mol/cm³; K – constant characteristic of the filler independent of
19 the solvent; ϕ_f – the volume fraction of filler in the sample which is calculated; ρ_r – the
20 density of the studied compound, g/cm³; m_0 – the weight of sample before extraction, g; ρ_f –
21 the density of filler, g/cm³; m_{dry} – the weight of sample after extraction, g.

22 During calculations, the density of carbon black was chosen equal to 1.85 g/cm³ and the K
23 constant was chosen to be 1.17 [35].

24
25 The thermal analysis of vulcanizate samples was performed using the simultaneous
26 TGA/DSC model Q600 from TA Instruments (USA). Samples of vulcanizate weighing
27 approximately 10 mg were placed in a corundum dish. The study was conducted in an inert
28 gas atmosphere - nitrogen (flow rate 100 ml/min) in the range from 25 to 800°C with a
29 temperature increase rate of 20°C/min. Volatile products from thermal degradation of
30 vulcanizate samples were also evaluated using a Fourier transform infrared spectroscopy

1 (FTIR). During TGA/DSC measurements volatile degradation products were directed (using
2 heated transfer line with temperature 220°C) to Nicolet iS10 spectrometer from Thermo
3 Scientific (USA). Presented solution allows “on-line” characterization of volatile products
4 during TGA/DSC measurements. The timing offset of FTIR spectra comparing to TGA
5 curves is related to a volume of thermogravimetric apparatus chamber.

6 The morphology of the vulcanized reclaimed GTR after extraction in toluene (at
7 room temperature, 72 h) was observed with a JEOL 5610 scanning electron microscope.
8 Before measurement the samples were covered with a fine gold-palladium layer in order to
9 increase their conductivity in a vacuum chamber.

11 3. Results and discussion

12 3.1. Curing characteristics

13 The effect of the applied GTR reclaiming method on curing characteristics of
14 reclaimed GTR is shown in Table 2 and Figure 1. The rGTR obtained *via* extrusion at 120°C
15 was characterized by its minimum torque value (~ 7 dNm), the lowest value among studied
16 samples. This indicated that high shear forces and elevated temperature acting on GTR during
17 extrusion enhanced scission of cross-linking bonds and caused partial degradation of polymer
18 chains. For products of mechano-chemical reclaiming of GTR conducted at ambient
19 temperature using a two-roll mills, minimal torque decreased with higher content of bitumen,
20 from ~ 35 dNm for sample without bitumen to ~ 22 dNm for rGTR modified with 20 phr of
21 bitumen. This suggests better processing of GTR reclaimed in the presence of bitumen, due to
22 plasticizing and partial reclaiming of rGTR. It was noticed that the type of used bitumen has
23 slight influence on minimal torque. Maximal torque values correspond with stiffness and
24 shear modulus of vulcanized samples. The lowest value (~ 22 dNm) of maximal torque was
25 determined for GTR reclaimed *via* extrusion at 120°C, which is related to its minimal torque.
26 It was realized that maximal torque values decreased with increasing content of bitumen
27 during mechano-chemical reclaiming of GTR, from ~ 53 dNm for sample without bitumen to
28 ~ 34 dNm for GTR modified with 20 phr of bitumen. It was also observed that GTR reclaimed
29 in presence of Modbit 25/55-60 (bitumen modified with SBS copolymer) take a slightly
30 higher maximal torque value compared to GTR reclaimed with bitumen 160/220, which may
31 be due to different composition and physical properties of the used bitumens (see Table 1).
32 Torque increment (ΔM) is correlated with the cross-link density of the obtained
33 revulcanizates [36]. The highest value of ΔM (~ 22 dNm) was observed for the reclaimed
34 GTR obtained *via* extrusion at 120°C. This suggests better diffusion conditions of curing

1 additive to the curing site in rGTR obtained *via* extrusion at 120°C in comparison with rGTR
 2 obtained *via* milling at ambient temperature. This may be due to the significant difference in
 3 their processing properties (minimal torque values). Furthermore, this phenomenon could be
 4 explained by higher degradation of vulcanization accelerators and activators residues present
 5 in rGTR. It was noticed that higher content of bitumen applied during mechano-chemical
 6 reclaiming of GTR caused a decrease in ΔM . This indicates that cross-link density of rGTR
 7 vulcanizate modified with bitumen is decreased, which is related to its partial plasticizing
 8 with bitumen. Furthermore, in case of rGTR obtained *via* extrusion and rGTR modified with
 9 bitumen, increasing the mobility of main chains caused their lower thermal resistance aging,
 10 as evaluated by the R_{300} parameter. It was observed that reclaiming method of GTR affects
 11 also the optimal vulcanization time (t_{90}) and CRI, however it has an insignificant influence on
 12 the scorch time (t_2). In addition, the type of the used bitumen influenced on the t_{90} and CRI
 13 parameters, possibly due to reactions between sulfur curing system and bitumen components.
 14 Namely, the unsaturated components of bitumen and SBS copolymer present in Modbit
 15 25/55-60 might react with sulfur curing system, leading to enhanced physical and chemical
 16 interactions between rGTR and bitumen. It was noticed that bitumen content during mechano-
 17 chemical reclaiming of GTR had insignificant influence on t_{90} and CRI, while the slight
 18 difference between values of these parameters may be due to diverse composition of GTR
 19 obtained from waste tire (mix of passenger and truck tires). For better presentation of such
 20 differences during vulcanization of obtained reclaimed GTR, selected curing curves are
 21 shown in the Figure 1.

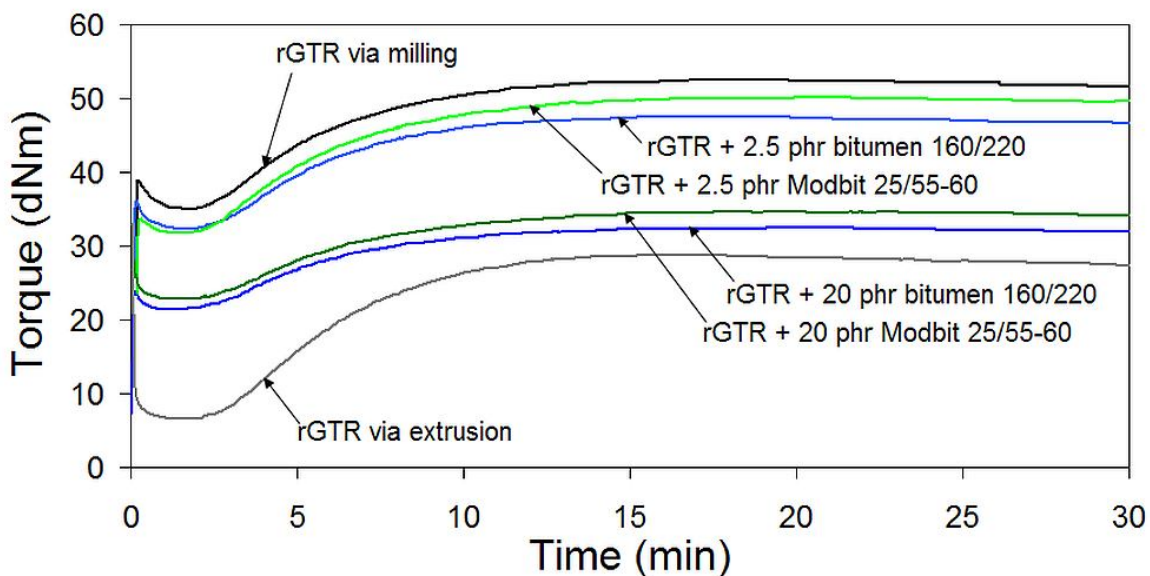


Figure 1. Curing curves for reclaimed GTR

22
 23
 24

3.2. FTIR analysis

FTIR spectra obtained for vulcanized rGTR are presented in Figure 2. The significant differences in FTIR spectra indicate that reclaiming method applied to GTR strongly affects the chemical structure of the obtained vulcanized rGTR. Weak absorption of samples is related to the presence of carbon black in reclaimed rubber. The absorbance maxima at 2965 cm^{-1} is assigned to the aromatic C-H bonds vibrations (e.g. carbon black), while 2915 and 2850 cm^{-1} is corresponded to the C-H vibrations of CH_2 groups in aliphatic chains of elastomers. The peaks in the range between 1540 cm^{-1} and 670 cm^{-1} are attributed to the C=C bond in benzene, characteristic for e.g. styrene butadiene rubber, which is commonly applied in tire industry. The absorbance maxima at 1377 cm^{-1} is attributed to the vibrations of CH_3 groups, which confirms the presence of natural rubber in the examined rGTR. The signals at 3560 cm^{-1} and 3410 cm^{-1} suggest the presence of hydroxyl groups (-OH), which is associated with the degradation of vulcanized reclaimed rubber observed especially in sample rGTR obtained *via* extrusion at 120°C and sample rGTR reclaimed *via* milling (without bitumen). The presence of two maxima in this wavenumber range may be the result of the diversity of oxidation products, which are mixture of aliphatic and aromatic compounds [37]. The absorbance maxima at 1115 cm^{-1} , characteristic for the valence vibrations of C-O bonds, also indicates the presence of -OH groups. Furthermore, in sample rGTR obtained *via* extrusion at 120°C and sample rGTR reclaimed *via* milling (without bitumen) small peak at 1690 cm^{-1} from carbonyl groups (C=O) was observed. Presented results confirm partial oxidation of main chain during reclamation of GTR (sample rGTR prepared *via* extrusion) and vulcanization of reclaimed rubber (sample rGTR *via* milling). Addition of bitumen 160/220 and Modbit 25/55-60 during reclamation of GTR, limited oxidation during reclaiming and vulcanization of reclaimed rubber, which may be related to its plasticizing effect (easier processing of GTR). However, in case of GTR reclaimed with higher content of Modbit 25/55-60, higher intensity of absorbance maxima at 1115 cm^{-1} was observed, which suggests partial oxidation of this sample. This indicates that bitumen modified with SBS copolymer has slightly lower resistance for oxidation comparing to pure bitumen. This phenomenon is the result of C=C bonds presence in the structure of SBS copolymer [38, 39].

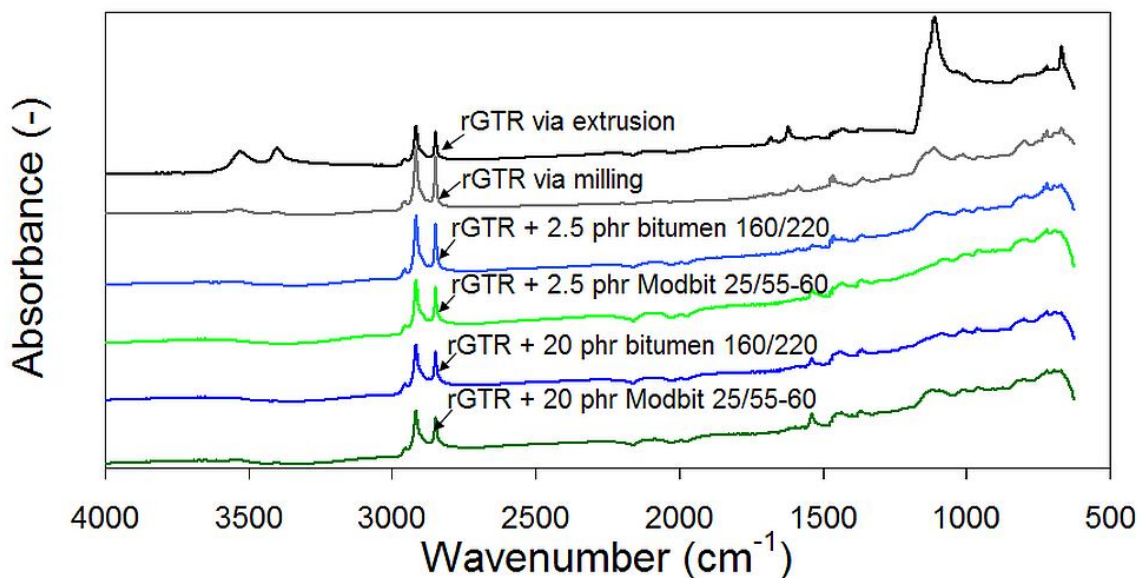


Figure 2. FTIR of vulcanized reclaimed GTR

3.3. Mechanical and physical properties of vulcanized rGTR

The results of static mechanical properties of rGTR vulcanizates are presented in Table 2. Significant differences in mechanical properties were observed in case of rGTR with 20 phr bitumen. Addition of 20 phr of bitumen, regardless of bitumen type, caused the decrease of tensile strength and hardness, while elongation at break has increased. This confirmed plasticization effect of bitumen, mentioned previously in curing characteristics section. Reclaiming method used during this study - extrusion at 120°C or milling at ambient temperature, has small influence on mechanical properties of obtained reclaimed rubber vulcanizates. The reclaimed samples were characterized by similar tensile strength and elongation at break, ~ 4.5-5 MPa and ~162-194 % respectively. For better presentation of tensile properties, selected stress-strain curves for reclaimed GTR vulcanizates are presented in the Figure 3. On the other hand, reclaiming method had strong influence on hardness of reclaimed GTR vulcanizates, which corresponded with their processing properties (minimal torque value).

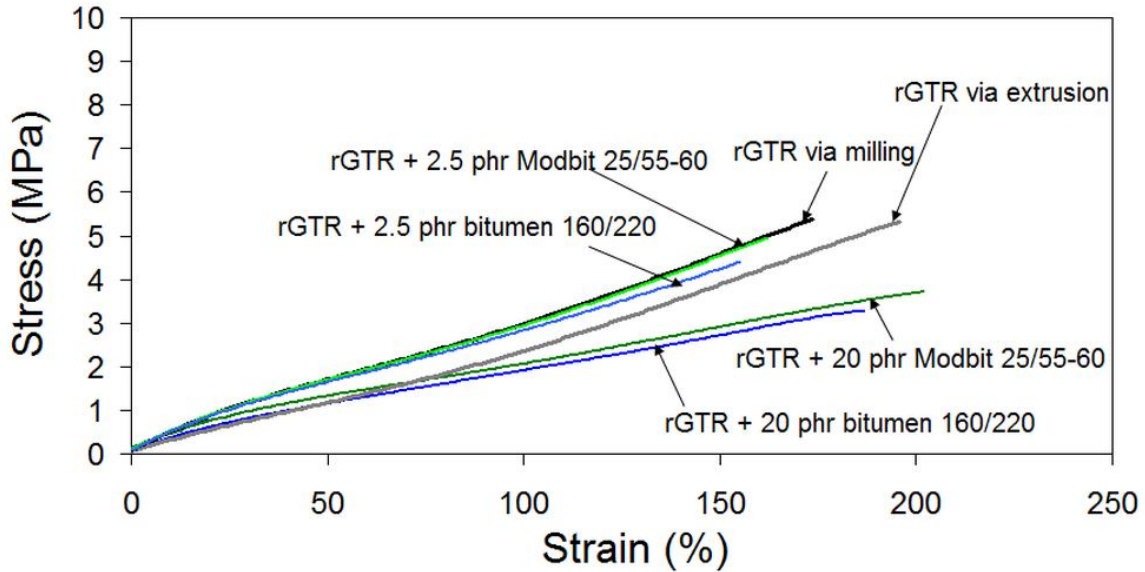


Figure 3. Stress-strain curves determined for vulcanized reclaimed GTR

Physical properties of vulcanized reclaimed GTR are presented in Table 2. It was observed that reclaiming method – extrusion/milling – had small influence on density of rGTR vulcanizates. On the other hand, the GTR samples reclaimed with bitumen were characterized by lower density, which was related to density of pure bitumen (~1.02 at 25°C). Type of bitumen had insignificant influence on density of obtained revulcanizates. Cross-link density and sol fraction give valuable information about reclaiming efficiency. It was noticed that reclaiming method had significant influence on cross-link density and sol fraction of reclaimed GTR vulcanizates. Scission of sulfur-sulfur, carbon-sulfur and carbon-carbon bonds during reclaiming of GTR caused the decrease of its cross-link density, which enhanced polymer chains' mobility confirmed by increasing sol fraction. Reclaiming of GTR with 20 phr of bitumen caused significant decrease of cross-link density and increase of sol fraction, which corresponded with mechanical properties of reclaimed GTR vulcanizates (see Table 2). It is well known that bitumen is soluble in toluene, which was used as a solvent during extraction. Therefore, corrected sol fraction was calculated based on GTR content, assuming that whole bitumen applied during reclaiming was dissolved during extraction. Moreover, theoretical sol fraction was calculated based on the additivity principle and lack of physical/chemical interactions between rGTR obtained *via* milling and bitumen. Presented sol fraction results indicate that during extraction bitumen was only partially removed from GTR matrix, which confirmed enhanced physical and chemical interactions (co-vulcanization) between GTR and bitumen phase. As mentioned before, this phenomenon was also recently suggested by Singh et al. [24].

3.4. TGA/DSC/FTIR results

Thermogravimetric analysis was applied for determination of change in chemical structure of reclaimed rubber. This methodology was previously described by Kleps et al. [40] and Scuracchio et al. [41], which used TGA for evaluation of GTR reclaiming efficiency. During present research, this methodology was expanded using TGA conjugated with DSC and FTIR (TGA/DSC/FTIR), which allowed for better characterization of changes in chemical structure of reclaimed GTR vulcanizates. The results of TGA are presented in Figure 4 and in Table 3. It was recognized, regardless of applied reclaiming method of GTR, that all TGA curves determined for vulcanized reclaimed GTR show similar trends. On the other hand, significant differences in char residue values (from 36.9 % to 32.2% wt.) were observed. High values of char residue are due to content of carbon black and SiO₂ in GTR, usually ~ 34 % wt. Presented TGA results indicate a different structure of the studied vulcanized reclaimed GTR, which was meanwhile confirmed by the FTIR analysis (see Figure 2). As mentioned in curing characteristics and physical properties section, combination of high shear forces and temperature during GTR extrusion causes effective scission of cross-linking bonds and partial degradation of polymer chains. It should be mentioned that cross-link density has significant influence on thermal stability of rubber compounds [42]. Therefore, sample rGTR obtained *via* extrusion (cross-link density: $1.89 \text{ mol/cm}^3 \times 10^{-4}$) was characterized by lower thermal stability compared to rGTR obtained *via* milling (cross-link density: $2.53 \text{ mol/cm}^3 \times 10^{-4}$). Furthermore, it was observed that increase of bitumen content during reclaiming of GTR causes increase of T_{-2%}, T_{-5%}, T_{-10%} temperatures, which corresponded with 2, 5 and 10 % weight loss. This could be somehow confusing because increasing the content of bitumen caused a fall in cross-link density. This phenomenon is related to evaporation/decomposition of two types of low molecular compounds. The first type contains low molecular resins, oils and other low molecular compounds, whereas the second type comprises low molecular compounds, which could be evaporated/decomposed through thermal degradation; among which are plasticizers, accelerators and other additives present in GTR [43].

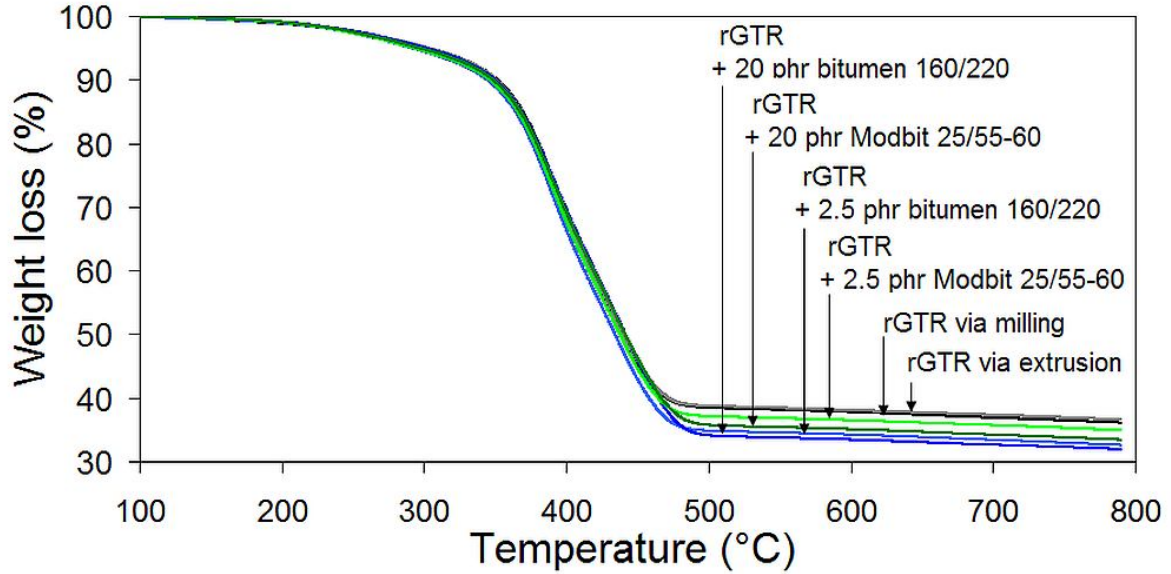


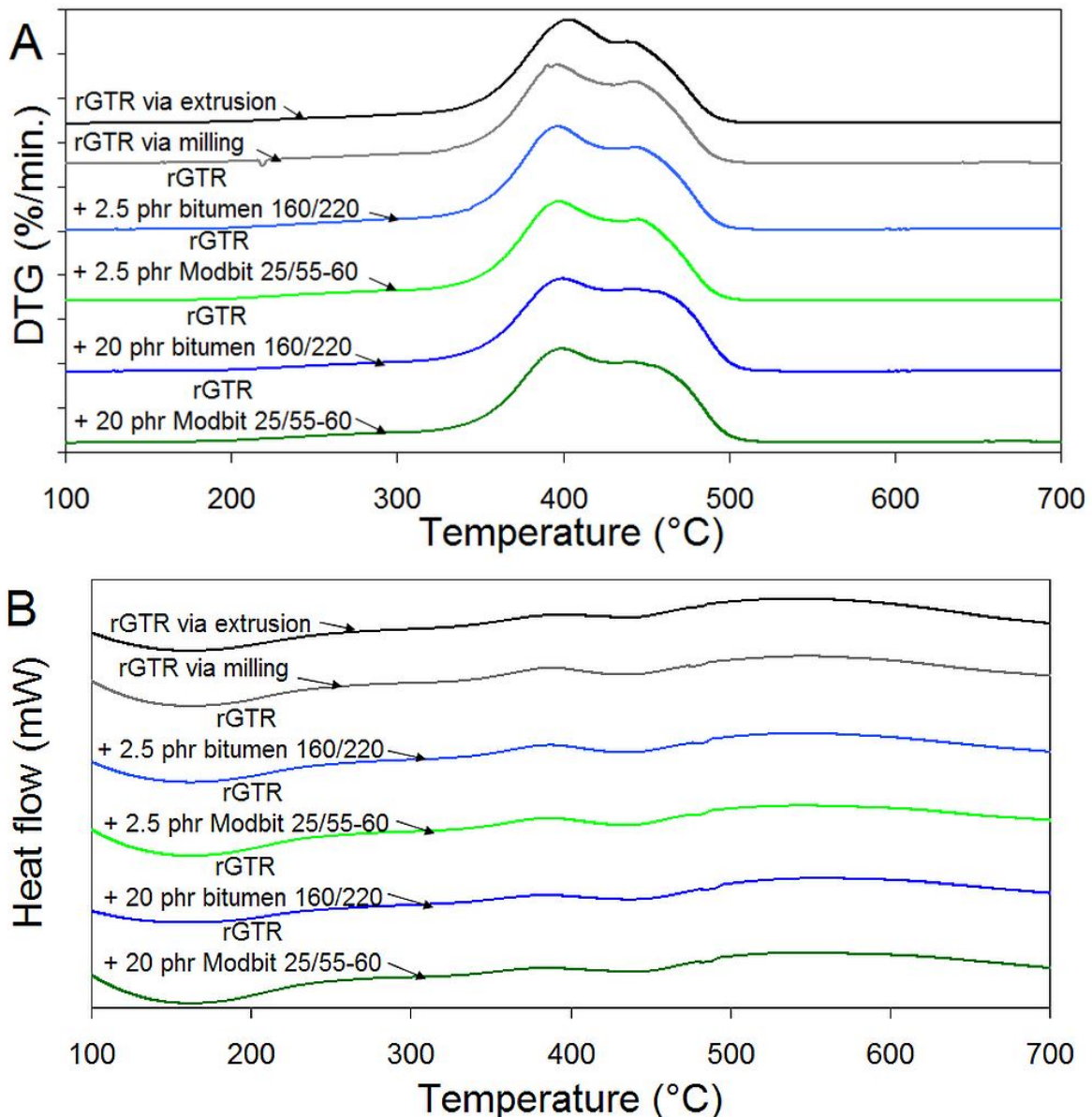
Figure 4. TGA curves of vulcanized reclaimed GTR

Table 3. Thermal decomposition characteristics of vulcanized reclaimed GTR estimated from TGA data

Sample	T _{-2%} (°C)	T _{-5%} (°C)	T _{-10%} (°C)	T _{-50%} (°C)	Char residues at 750°C
rGTR <i>via</i> extrusion	232.6	300.6	351.3	438.6	36.5
rGTR <i>via</i> milling	239.9	302.5	350.9	440.3	36.9
rGTR + 2.5 phr bitumen 160/220	232.8	291.3	344.4	434.3	32.9
rGTR + 2.5 phr Modbit 25/55-60	233.8	292.3	346.3	437.7	35.3
rGTR + 20 phr bitumen 160/220	240.0	300.7	349.6	441.6	32.2
rGTR + 20 phr Modbit 25/55-60	237.5	296.3	348.5	441.5	33.8

The curves of derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) are presented in Figure 5. Three peaks of maximal rate of thermal degradation were observed on DTG curves (Figure 5A). First step of thermal degradation with $T_{max1} \sim 250^{\circ}\text{C}$ of vulcanized reclaimed GTR is volatilization/decomposition of plasticizers, accelerators residues and other low molecular additives present in GTR. Another two peaks from DTG curves are related to the temperatures of maximum rate of thermal degradation of natural rubber ($T_{max2} \sim 400^{\circ}\text{C}$) and styrene-butadiene rubber ($T_{max3} \sim 450^{\circ}\text{C}$). Those rubbers are the main compounds used in car tires manufacturing [44]. It was observed that higher content of bitumen shifted T_{max3} towards higher temperatures, while T_{max2} shifted towards lower temperatures. This phenomenon suggests that aromatic components of bitumen enhanced

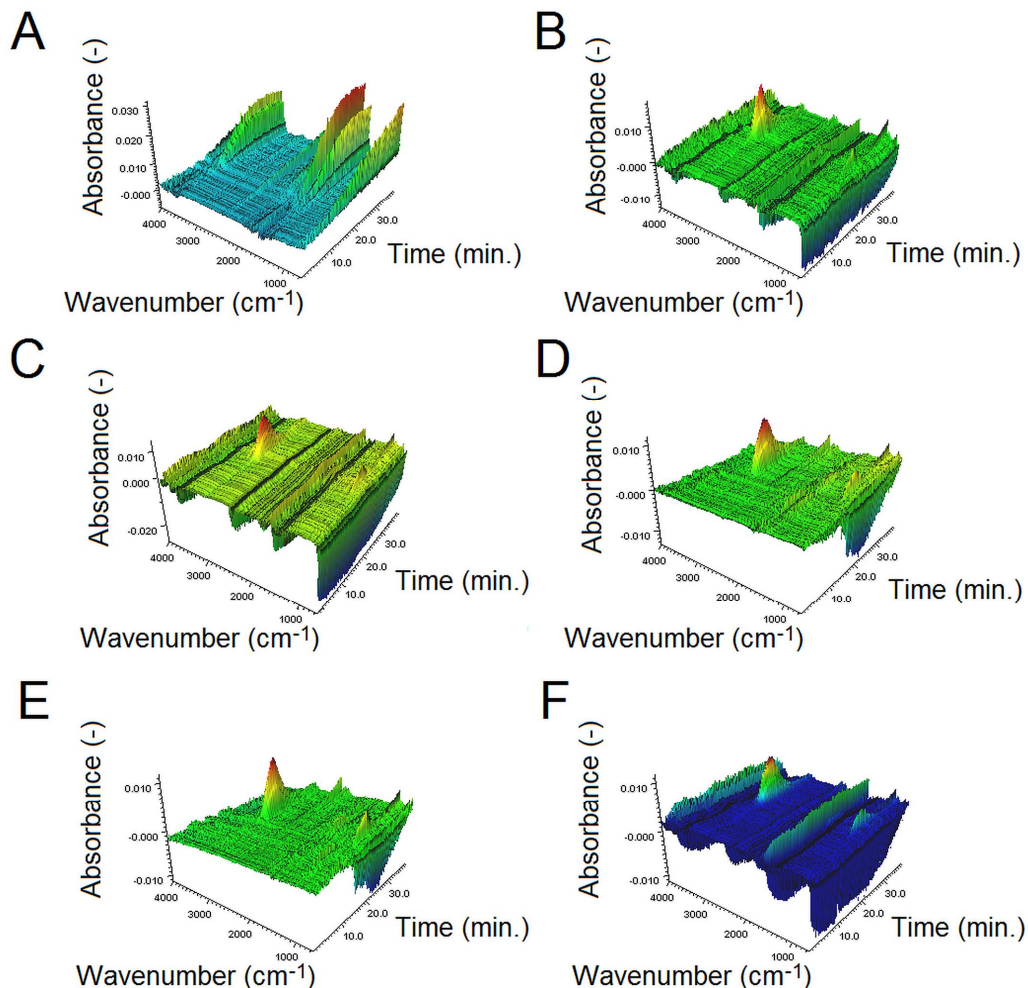
1 reclaiming of styrene-butadiene rubber compared to natural rubber. Furthermore, samples
 2 with higher content of bitumen were characterized by higher char residue (carbon black)
 3 content. Recently, Garcia et al. [45] indicate that carbon black present in the reclaimed rubber
 4 could adsorb low molecular volatile products formed during thermal degradation (barrier
 5 effect), which improved thermal stability of reclaimed GTR. Presented DSC curves (Figure
 6 5B) corresponded with described above three steps of thermal degradation of vulcanized
 7 reclaimed GTR.



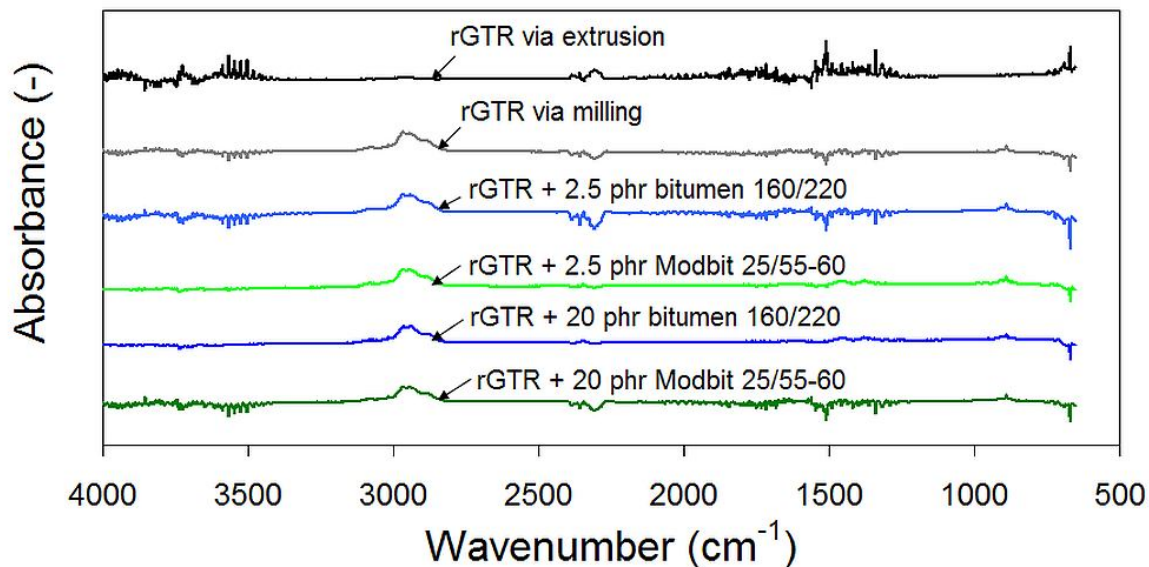
9
 10 Figure 5. A – DTG and B – DSC curves of vulcanized reclaimed GTR

11
 12 FTIR spectra determined for volatile products emitted during thermal decomposition of
 13 vulcanized reclaimed GTR, are presented in Figures 6 and 7. As could be expected, thermal
 14 degradation products were characterized by different chemical structures compared to

1 vulcanized rGTR (see Figure 2). Regardless of reclaiming method, in all samples absorbance
 2 peak in the region of 2320 cm^{-1} was observed, which is attributed to carbon dioxide formed
 3 during thermal degradation [46]. Absorbance maxima at 2970 and 2900 cm^{-1} were present
 4 only in samples of vulcanizates based on reclaimed rubber obtained *via* milling (without and
 5 with bitumen), which confirms lower degradation of GTR during reclaiming *via* milling,
 6 comparing to rGTR obtained through extrusion. Furthermore, in case of samples: rGTR *via*
 7 extrusion (Figure 6A), rGTR by milling (Figure 6B), rGTR + 2.5 phr bitumen 160/220
 8 (Figure 6C) and rGTR + 20 phr Modbit 25/55-60 (Figure 6F) the presence of absorbance peak
 9 at $3500\text{-}4000\text{ cm}^{-1}$ assigned to hydroxyl group (-OH), was observed. This indicates partial
 10 degradation by oxidation of GTR during reclaiming, which was also confirmed by FTIR
 11 analysis of reclaimed GTR vulcanizates (section 3.2). Possible degradation products formed
 12 during thermal degradation of GTR are described in details in the literature [37, 47].



13
 14 Figure 6. TGA-FTIR plots determined for volatile products emitted during thermal
 15 decomposition of vulcanized reclaimed GTR: A – rGTR *via* extrusion; B – rGTR *via* milling;
 16 C – rGTR + 2.5 phr bitumen 160/220; D – rGTR + 20 phr bitumen 160/220;
 17 E – rGTR + 2.5 phr Modbit 25/55-60; F – rGTR + 20 phr Modbit 25/55-60



1
2 Figure 7. FTIR spectra at maximal intensity determined for volatile products emitted during
3 thermal decomposition of vulcanized reclaimed GTR
4

5 3.5. Morphology assessment

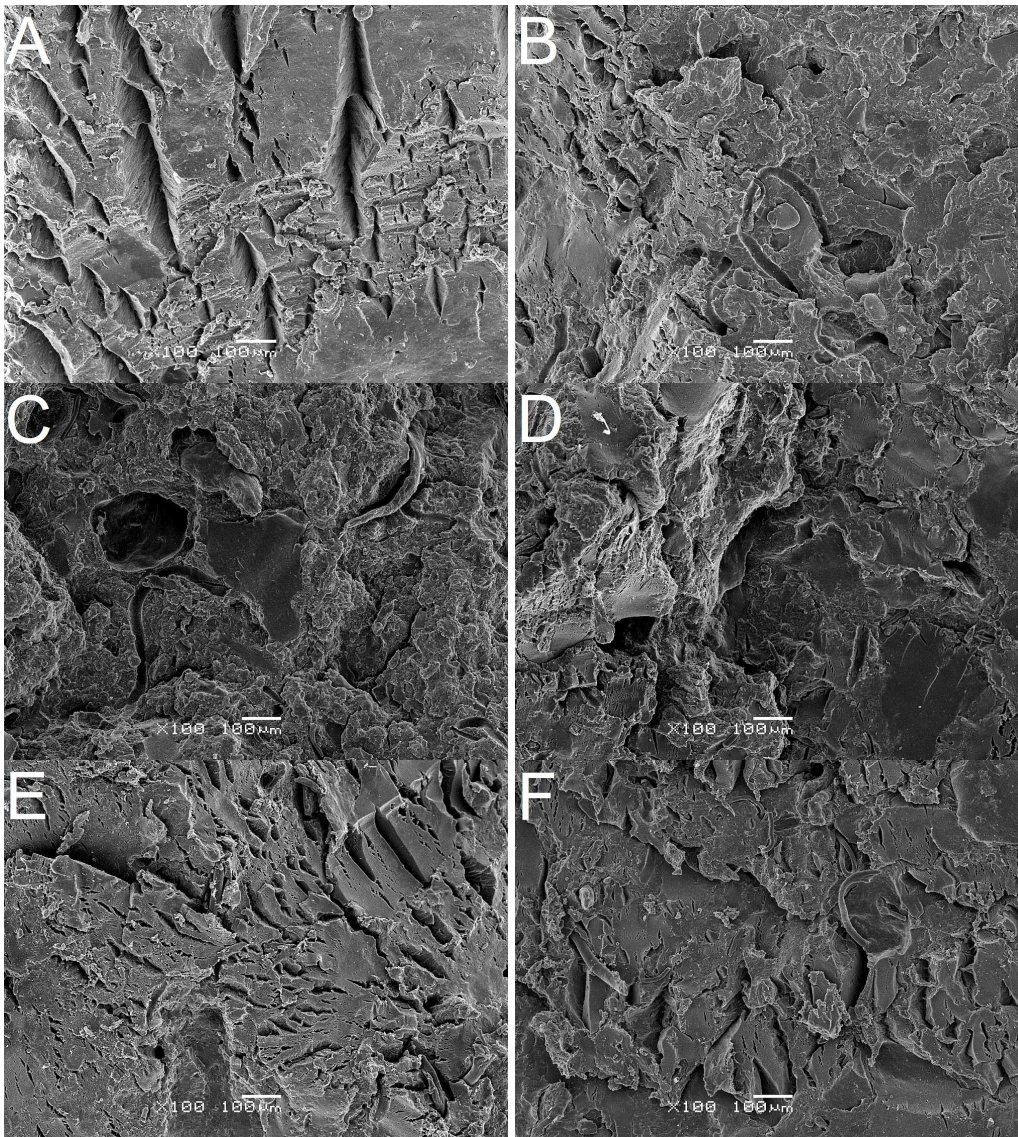
6 The morphology of the vulcanized reclaimed rubber samples is presented in the
7 Figures 8 and 9. Micrographs show the surface of samples previously subjected to extraction
8 in toluene (at room temperature, 72 h). It can be observed that reclaiming method has
9 significant influence on the morphology of studied samples. For sample rGTR obtained *via*
10 extrusion, some gaps have been observed in the microstructure after the extraction. This
11 indicates that low molecular compounds, formed during thermo-mechanical reclaiming and
12 partial oxidation of GTR, were dissolved during extraction. Low molecular products of GTR
13 degradation function like plasticizers of obtained reclaimed rubber, which enhances its further
14 processing (see Figure 1). On the other hand, surface of the sample rGTR obtained *via* milling
15 appears smooth, which suggests lower degradation during reclaiming. This is in agreement
16 with minimal torque, sol fraction and cross-link density measurements. It was noticed that the
17 type of bitumen applied during GTR reclaiming strongly affected the morphology of
18 vulcanized rGTR. For samples of rGTR reclaimed with Modbit 25/55-60, after the extraction,
19 gaps similar to those observed in case of rGTR obtained by extrusion have been observed. On
20 the other hand, the surface of rGTR reclaimed with bitumen 160/220 samples was clearly
21 smoother and similar to the surface of sample rGTR obtained *via* milling. For better
22 characterization and confirmation of these results, morphology of samples rGTR + 20 phr
23 bitumen 160/220 and rGTR + 20 phr Modbit 25/55-60 were observed at a higher
24 magnification in comparison to Figure 8, which is shown in Figure 9. It is clearly visible that

1 the gaps present in the structure of sample rGTR + 20 phr bitumen 160/220 sample have on
2 average a smaller size, when they compared with the surface of rGTR + 20 phr Modbit 25/55-
3 60 sample. This phenomenon is due to the presence of SBS copolymer in the modified
4 bitumen Modbit 25/55-60. These results suggest that GTR particles are encapsulated by the
5 SBS phase, which is partially miscible with the bitumen phase. In agreement with this, the
6 swelling of SBS was observed during extraction of vulcanized rGTR with toluene, which
7 created cracks in the vulcanized reclaimed rubber and thereby gaps in the structure after
8 extraction. The schematic path of a mechanism that probably appears during GTR reclaiming
9 using bitumen and bitumen modified with SBS is presented in Figure 10. It should be
10 mentioned that phenomenon of GTR encapsulation with elastomers, e.g. styrene-butadiene-
11 styrene copolymer [27, 48], ethylene-propylene-diene-monomer rubber [49], butyl rubber
12 [50], ethylene-octene copolymer [51], trans-polyoctylene rubber [52] or ethylene-vinyl acetate
13 copolymer [53], was also observed and described by several independent research groups.

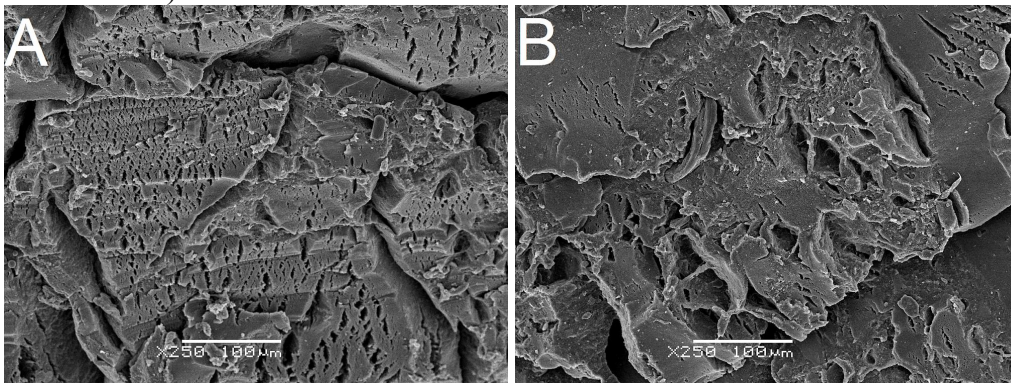
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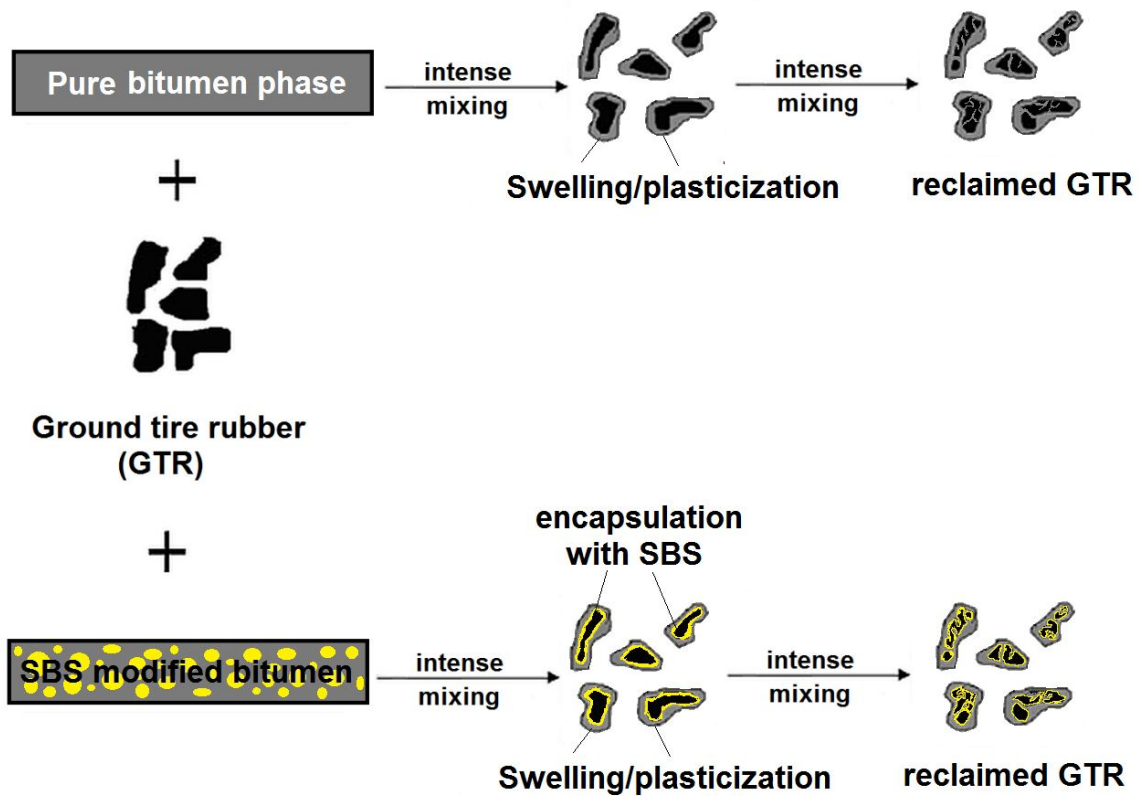
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1 Figure 8. SEM images of vulcanized reclaimed GTR. A – rGTR *via* extrusion;
 2 B – rGTR *via* milling; C – rGTR + 2.5 phr bitumen 160/220; D – rGTR + 20 phr bitumen
 3 160/220; E – rGTR + 2.5 phr Modbit 25/55-60; F – rGTR + 20 phr Modbit 25/55-60
 4 (magnification x100)



5
 6 Figure 9. SEM images of vulcanized reclaimed GTR. A – rGTR + 20 phr bitumen 160/220
 7 and B – rGTR + 20 phr Modbit 25/55-60 (magnification x250)



8
 9 Figure 10. Schematic illustration of GTR reclaiming using bitumen and bitumen modified
 10 with SBS
 11

12 4. Conclusions

13 GTR has been reclaimed at low temperature applying two methods: thermo-
 14 mechanical reclaiming *via* extrusion and mechano-chemical *via* milling in presence of two
 15 types of bitumen (road bitumen 160/220 and styrene-butadiene-styrene copolymer modified
 16 Modbit 25/55-60) as reactive plasticizers (in range: 2.5-20 phr). The effects of plasticization
 17 and shear forces during reclaiming of GTR on quality of reclaimed rubber were studied. The

1 obtained results indicated that method of GTR reclaiming (mechano-chemical or thermo-
2 mechanical) strongly affects the processing, chemical structure, thermal and morphological
3 properties of vulcanized reclaimed rubber, while its influence on mechanical properties was
4 negligible. High shear forces acting on GTR during thermo-mechanical reclaiming *via*
5 extrusion, improved processing of the obtained reclaimed rubber due to its partial oxidative
6 degradation. This was confirmed by FTIR analysis, processing characteristics (minimal
7 torque, torque increment) and cross-link density evaluation. It was observed that application
8 of bitumen as reactive plasticizers during mechano-chemical reclaiming of GTR, prevents
9 oxidation of reclaimed GTR and enhanced its processing, which can be explained in view of
10 enhanced interfacial interaction between GTR and bitumen. Increased bitumen content,
11 during GTR reclaiming process, deteriorated the mechanical properties and cross-link density
12 of vulcanized reclaimed rubber, which is due to plasticizing effect of bitumen. Furthermore, it
13 was demonstrated that chemical composition of the used bitumen has significant influence on
14 structural, mechanical, thermal and morphological properties of vulcanized reclaimed rubber.
15 Bitumen 160/220 and SBS-modified bitumen (Modbit 25/55-60) both enhanced
16 plasticization/partial reclaiming of GTR particles, while SBS-modified bitumen also caused
17 encapsulation of GTR particles within the SBS elastomer phase. This phenomenon had a
18 significant influence on improving the physical and chemical interactions between GTR and
19 bitumen phases. Based on presented results, further research in this field should focus on two
20 directions: i) optimization of reclaiming process conducted at lower temperatures, for
21 example reducing time during mechano-chemical reclaiming *via* milling, to achieve effective
22 and energy-saving process parameters; ii) application of other chemical additives, which
23 affect on the processability (e.g. peptizators, peroxides, vulcanization accelerators, etc.) and
24 mechanical properties (e.g. thermoplastic elastomers) of the obtained reclaimed rubber.

25

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4

5 **Figure captions**

6 Figure 1. Curing curves for reclaimed GTR

7 Figure 2. FTIR of vulcanized reclaimed GTR

8 Figure 3. Stress-strain curves determined for vulcanized reclaimed GTR

9 Figure 4. TGA curves of vulcanized reclaimed GTR

10 Figure 5. A – DTG and B – DSC curves of vulcanized reclaimed GTR

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13 C – rGTR + 2.5 phr bitumen 160/220; D – rGTR + 20 phr bitumen 160/220;
14 E – rGTR + 2.5 phr Modbit 25/55-60; F – rGTR + 20 phr Modbit 25/55-60

15 Figure 7. FTIR spectra at maximal intensity determined for volatile products emitted during
16 thermal decomposition of vulcanized reclaimed GTR

17 Figure 8. SEM images of vulcanized reclaimed GTR. A – rGTR *via* extrusion;
18 B – rGTR *via* milling; C – rGTR + 2.5 phr bitumen 160/220; D – rGTR + 20 phr bitumen
19 160/220; E – rGTR + 2.5 phr Modbit 25/55-60; F – rGTR + 20 phr Modbit 25/55-60
20 (magnification x100)

21 Figure 9. SEM images of vulcanized reclaimed GTR. A – rGTR + 20 phr bitumen 160/220
22 and B – rGTR + 20 phr Modbit 25/55-60 (magnification x250)

23 Figure 10. Schematic illustration of GTR reclaiming using bitumen and bitumen modified
24 with SBS

25 **Table captions**

26 Table 1. Characteristics of bitumens

27 Table 2. Composition, curing characteristics, mechanical and physical properties of tested
28 compounds

29 Table 3. Thermal decomposition characteristics of vulcanized reclaimed GTR estimated from
30 TGA data

31