Efficiency of thermomechanical reclaiming of ground tire rubber conducted in counter-rotating and co-rotating twin screw extruder

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Abstract: In this article the results of research on a continuous thermomechanical reclaiming process of ground tire rubber (GTR) conducted in a twin screw extruder are presented. The effects of the rotation direction (co-rotating/counter-rotating), design of co-rotating plasticizing units and the rotational speed of the screws on the extruder working parameters, sol fraction and the degree of reclaiming in the obtained products were described. The influence of secondary vulcanization on cure characteristics as well as mechanical properties of revulcanizates, and blends of reclaimed rubber and styrene-butadiene rubber (SBR) were determined. Based on the obtained results, it was concluded that the application of counter-rotating plasticizing system (i.e. screw profile A), consisting mainly of transport elements with different pitch, increases the time during which ground tire rubber is exposed to the barrel temperature. The use of co-rotating plasticizing system, equipped with kneading elements and characterized by constant pitch, causes that the retention time of ground tire rubber in the extruder barrel is much shorter. In the case of co-rotating plasticizing system, it is also higher shear forces (then in counter-rotating screw configuration), besides temperature, acts on ground tire rubber, and converts mechanical energy into heat. Testing of styrene-butadiene rubber-ground tire rubber/reclaimed ground tire rubber (SBR-GTR/dGTR) compounds confirmed that the reclaiming process has positive influence on properties of obtained products.

Keywords: material recycling, ground tire rubber, reclaiming, twin screw extruder, screw configuration.

Efektywność procesów termomechanicznej regeneracji miału gumowego, prowadzonych w przeciwbieżnej lub współbieżnej wytłaczarce dwuślimakowej

Streszczenie: Badano proces termomechanicznej regeneracji ciągłej miału gumowego, prowadzony przy użyciu wytłaczarki dwuślimakowej. Scharakteryzowano wpływ kierunku obrotów ślimaków (przeciwbieżny/współbieżny), konstrukcji współbieżnego układu uplastyczniającego oraz prędkości obrotowej ślimaków na przebieg procesu regeneracji, zawartość frakcji zolowej, stopień regeneracji uzyskanych produktów. Określono wpływ wtórnej wulkanizacji otrzymanych regeneratów na przebieg krzywych wulkametrycznych oraz właściwości mechaniczne rewulkanizatów oraz mieszanin otrzymanego regeneratu gumowego z kauczukiem butadienowo-styrenowym. Na podstawie uzyskanych wyników stwierdzono, że zastosowanie przeciwbieżnego układu uplastyczniającego (ślimak A), zawierającego głównie elementy transportowe o różnym skoku, wydłuża czas oddziaływania temperatury cylindra na miał gumowy. Wykorzystanie do regeneracji termomechanicznej współbieżnego układu uplastyczniającego, zawierającego elementy rozcierające oraz elementy transportowe o stałym skoku, znacznie skraca czas przebywania miału gumowego w cylindrze wytłaczarki. W przypadku współbieżnego układu uplastyczniającego na miał gumowy, oprócz temperatury cylindra, oddziaływają również siły ścinające, w wyniku których energia mechaniczna jest zamieniana w energię cieplną. Badania mieszanin kauczuku butadienowo-styrenowego z miałem gumowym oraz regeneratem gumowym (SBR-GTR/dGTR) potwierdziły korzystny wpływ procesu regeneracji na właściwości otrzymanych produktów.

Słowa kluczowe: recykling materiałowy, odpady gumowe, regeneracja, wytłaczarka dwuślimakowa, konfiguracja ślimaków.

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End-of-life tires and other waste rubber, originally made of high quality rubber, are a valuable source of recycled materials. It has been estimated that over 17 million tons of used tires are generated each year worldwide, including 3.3 million tons in the EU [1]. Material recycling of waste rubber, which is still conducted on a small-scale, should be considered as an alternative to energy recovery that uses tires as fuel. Burning of scrap tires in cement factories and electric power stations allows for recovery only ca. 37 % of energy used for their production [2]. Therefore, at present, searching for novel, alternative and economically justified ways of waste rubber recycling remains a primary interest of many scientific centers and manufacturers worldwide.

Reclaiming is one of the material recycling methods applied to waste rubber. Reclaiming is a process which transforms production scrap rubber and waste rubber by using thermal, mechanical or chemical energy in the products that can be processed and vulcanized again. Despite the fact that a number of reclaiming methods have been described in detail [3—5], reclaiming is still used on a small scale, mainly due to high production costs of reclaimed rubber resulting from high energy consumption (i.e. high temperature and long production time) and stringent environmental laws. Moreover, profitability of reclaimed rubber production is affected by the expectations of high quality of rubber products and reclaimed rubber as well as an on-going replacement of cross-linked elastomers with other materials such as, thermoplastic elastomers.

Developed by Toyota R&D a continuous reclaiming conducted in co-rotating twin screw extruder is a relatively new form of material recycling applied to waste rubber [6, 7].

Si et al. [8] investigated the effect of strong shear force on the properties of ground tire rubber and thermoplastic elastomer (EPDM or POE) blends. The obtained results suggests that increased temperature generated by the extruder barrel and strong shearing of the processed material, causes secondary cross-linking in the final product. This conclusion has also been reached in work of Yazdani et al. [9] and in our earlier studies [10, 11].

Maridass and Gupta [12—15] conducted research on the effect of barrel temperature and the screw rotational speed in a counter-rotating twin screw extruder on reclaiming of waste rubber and the properties of revulcanizates.

Difference between influence of counter-rotating and co-rotating twin screw extruder on thermomechanical reclaiming of ground tire rubber is unknown in above presented state of knowledge. Characteristic of correlation between the type of used extruder its useful data for companies which intend to began operations based on material recycling of rubber.

In the present work thermomechanical reclaiming of ground tire rubber was conducted in two types of extruder: counter-rotating and co-rotating. Two different plasticizing system for co-rotating extruder was used, to comparison the effect of different shear force acting on ground tire rubber. The effect of screw speed on quality of obtained products was also described. Reclaimed rubber was evaluated by percent of reclaiming, sol fraction and mechanical properties of prepared revulcanizated rubber.

After compounding of ground tire rubber (without reclaiming) and reclaimed rubber with virgin styrene-butadiene rubber in different weight ratio, cure characteristics and mechanical properties of obtained vulcanizates were determined.

EXPERIMENTAL PART

Materials

Ground tire rubber (GTR), 1.5 mm fraction was prepared by ABC Recykling (Poland). GTR were obtained from whole used tires (passenger tires and truck tires in ca. 50:50 ratio) in ambient mechanical grinding process. The characteristics of ground tire rubber are presented in Table 1. Solvent used for chemical analyses and the curing agents for vulcanization were obtained from POCH S.A. and STANDARD Sp. z o.o. (Poland). Styrene-butadiene rubber Ker 1502 (Mooney viscosity *ML*(1+4), 100 °C: 45—54) was obtained from Synthos S.A. (Poland).

Table 1. Characteristics of ground tire rubber

Properties	Mass content, %	Methods
Rubber additives	15.3	TGA
Rubber (SBR, NR)	48.7	TGA
Carbon black	32.7	TGA
Mineral components	3.3	TGA
Sulfur content	2.0	Elemental analysis

Sample preparation

Thermomechanical reclaiming of ground tire rubber was conducted by using a Leistritz ZSE 27HP twin screw extruder ($d = 27$, $L/d = 28$, Germany) equipped with a gear box which allows changing the direction of screw rotation. The design of plasticizing systems, i.e. counter-rotating (screw profile A) and co-rotating (screw profile B and screw profile C) is presented in Fig. 1. Ground tire rubber was being added gravimetrically at a flow rate of 5 kg/h. Barrel temperature was 180 °C, while on the first zone after feed hooper temperature had been set at 80 °C. Rotational speed of the screws was set at the following values: 50, 100, 150, 200 and 250 rpm. The obtained reclaimed rubber and its blend with SBR (see Tables 2 and 3 for the blend composition) were vulcanized at 150 °C/160 °C (respectively: reclaimed rubber/SBR blends) and under a pressure of 4.9 MPa for the determined optimal time. Compounds of SBR filled with ground rubber which has not been reclaimed (GTR) were used as a reference material.

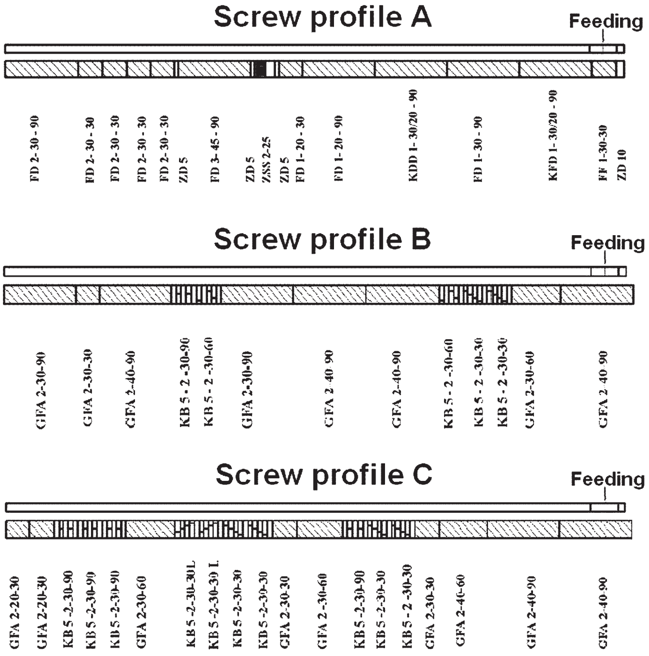

Fig. 1. Schematic view of screw configuration

Table 2. Compounding formulation of revulcanized rubber (phr)

Reclaimed rubber (dGTR)	100.0
Stearic acid	1.0
ZnO	2.5
TBBS	0.35
Sulfur	1.5

Table 3. Compounding formulation of styrene-butadiene rubber-GTR/dGTR blends (phr)

Sample	P1	P2	P3	P4	P5	P6	P7
SBR	100	100	100	100	100	100	100
GTR	0	10	30	50	-	-	-
dGTR*	-	-	-	-	10	30	50
Stearic acid	3.0	3.0	3.0	3.0	3.0	3.0	3.0
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0
MBT	0.65	0.65	0.65	0.65	0.65	0.65	0.65
TMTD	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	2.0

* Sample D10 of reclaimed ground tire rubber was used.

Methods of testing

The resulting reclaimed rubber was subjected to a preliminary extraction with acetone (at room temperature for 48 h followed by drying to a constant mass at 70 °C) in order to remove low molecular weight substances.

The crosslinking density of the obtained samples was determined by equilibrium swelling in toluene (at room temperature for 72 h; drying to constant weight at 70 °C), according to the Flory-Rehner equation [16] without Kraus correction (based on ASTM D 6814) (1):

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

where: V_e — crosslinking density, mol/cm^3; V_r — means volume fraction of rubber hydrocarbon in swollen sample; V_1 — solvent molar volume (toluene = 106.2 cm^3/mol [17]); χ — polymer-solvent interaction parameter (in the calculations, it was assumed to be 0.391 [18]).

V_r was determined, according to equation (2):

$$V_r = \frac{\dfrac{m_r}{\rho_r}}{\dfrac{m_r}{\rho_r}+\dfrac{m_s}{\rho_s}} \tag{2}$$

where: m_r — mass of dry rubber sample, g; ρ_r — density of dry rubber, g/cm^3; m_s — mass of solvent absorbed by sample, g; ρ_s — density of solvent, g/cm^3.

The degree of reclaiming was determined on the basis of changes in the crosslinking density of the reclaimed material (ν_2) compared to the ground tire rubber without reclaiming (ν_1), according to equation (3):

$$\text{Degree of reclaiming} = \frac{\nu_1-\nu_2}{\nu_1}\,100\ \% \tag{3}$$

Sol fraction was determined as mass difference between reclaimed ground tire rubber samples before swelling (W_1) and after solvent evaporation (W_2), according to equation (4):

$$\text{Sol fraction} = \frac{W_1-W_2}{W_1}\,100\ \% \tag{4}$$

The vulcanization process was studied at 150 °C according to PN-ISO 3417:1994 standard. The measurements were performed using a Monsanto R100S vulcameter (USA) with an oscillating rotor. The rotor oscillation angle was 3°, while torque ranged between 0 and 100 dNm.

Tensile strength and elongation at break of the obtained vulcanizates were tested according to PN-ISO 37 standard by using a Zwick Z020 testing machine (Germany). Shore A hardness was determined for each sample with a Zwick 3130 durometer (Germany) in accordance with ISO 7619-1. For all samples, abrasion resistance was measured with an abrasion tester from Gibitre Instruments (Italy) according to ISO 4649 standard. The rebound resilience determination was performed using the Schob pendulum from Gibitre Instruments (Italy) according to ISO 4662. The reported results are the means of 5 measurements per sample.

RESULTS AND DISCUSSION

Reclaiming process

The names of samples obtained in different screw configuration and screw speed, the values of screw torque, crosslink density and the degree of reclaiming measured in the obtained rubber reclaimed are presented in Table 4. Samples D1—D5 were prepared by using counter-rota-

Table 4. The effect of rotational direction of the screws, screw configuration and screw (rotor) speed on reclaiming of GTR

Sample	Rotor speed rpm	Screw configuration	Rotational direction of the screws	Screw torque Nm	Cross-link density 10^{-4}·mol/cm^3	Degree of reclaiming, %
D1	50	Screw profile A	Counter-rotating	30	4.31	46
D2	100			25	4.34	45
D3	150			22	4.68	41
D4	200			19	4.09	48
D5	250			17	4.61	42
D6	50	Screw profile B	Co-rotating	30	4.21	47
D7	100			22	4.05	49
D8	150			19	3.66	54
D9	200			17	3.68	54
D10	250			17	3.76	53
D11	100	Screw profile C	Co-rotating	95	3.37	58
D12	150			78	3.22	59
D13	200			69	3.13	61
D14	250			62	2.92	63
Ground tire rubber				–	7.94	0

ting screw profile A. Samples obtained by co-rotating extrusion were D6—D10 (screw profile B) and D11—D14 (screw profile C). Increasing number of sample correspond to increase of screw speed.

The screw torque and crosslink density of reclaimed rubber decreased with increasing rotational speed of the screws. This confirms scission of cross-links of ground tire rubber and degradation of rubber main chain during thermomechanical reclaiming. The values of screw torque for both counter-rotating (screw profile A) and co-rotating (screw profile B) plasticizing systems were similar. The use of a higher number of kneading elements in screw profile C resulted in a significant increase in screw torque, which made it impossible to generate a sample of reclaimed rubber at a rotational speed of 50 rpm. In the case of screw profile C, the increased shear force acting on ground tire rubber caused a ca. 20 % increase in the degree of reclaiming of the obtained products, and was accompanied by a significant rise in the values of screw torque.

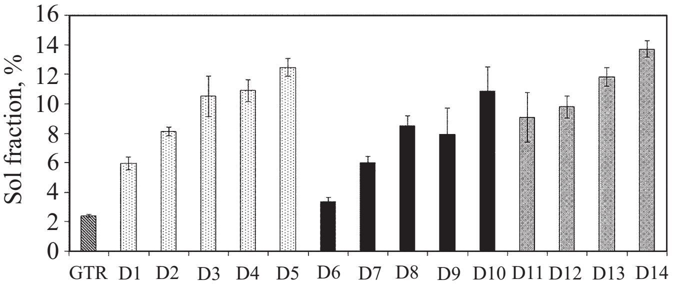

Fig. 2. Sol fraction of reclaimed ground tire rubber; explanations of symbols D1—D14 see text

In Fig. 2 the determinations of sol fraction in the obtained reclaimed rubber are presented. A visible influence of the direction of screw rotation (counter-rotation/co-rotation), design of co-rotating plasticizing system and the screw rotational speed on sol fraction was noted. All the obtained reclaimed samples were characterized by higher sol fraction compared to ground tire rubber, which confirms the partial degradation of the processed material. Sol fraction as well as the degree of reclaiming of obtained samples increased with increasing rotational speed of the screws during thermomechanical reclaiming in a twin screw extruder. The values of sol content for the screw profiles A and C were slightly larger than those for screw profile B, which confirms the critical effect of temperature, originating from the extruder barrel and shear forces in ground tire rubber, on the reclaiming process [19].

In order to specify difference between main-chain scission and cross-link scission during reclaiming, Horikx's theory [20] was applied. Horikx's theory based on the relationship between sol fraction and changes in crosslinking density after the degradation of cross-links. Frequently, breaking of cross-links is accompanied by main-chain degradation of a polymer, which can be described by equation (5):

$$1-\frac{\nu_2}{\nu_1} = 1-\frac{(1-S_2^{1/2})^2}{(1-S_1^{1/2})^2} \tag{5}$$

where: ν_1, ν_2 — crosslinking density before (1) and after (2) reclaiming, mol/cm^3; S_1, S_2 — content of sol fraction before (1) and after (2) reclaiming, %.

Based on equation (5), a theoretical curve was plotted to which experimental data points were added (Fig. 3). In this study S_1 was 2,3 %. According to Horikx's theory, the presence of data points below the theoretical curve indi-

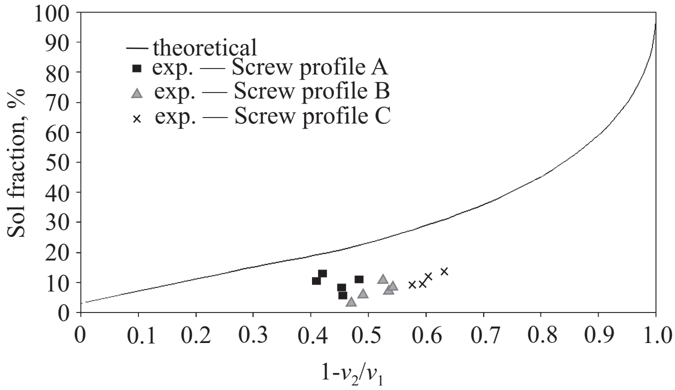

Fig. 3. Percentage of sol fraction versus the relative decrease in crosslink density, according to Horikx theory

cates that the selective degradation of cross-links, mainly S-S and C-S bonds, has taken place during reclaiming. The results show that cross-link bonds of ground tire rubber are broken selectively during thermo-mechanical reclaiming process conducted in co-rotating twin screw extruder. However, it should be mentioned that used theory has limitations which do not include the intermediate case between cross-links bonds scission and main chain degradation.

Revulcanization process

The effect of reclaiming conditions on secondary vulcanization of reclaimed rubber is presented in Table 5 and Fig. 4. The vulcametric curves for samples obtained in different screw profiles and screw rotation speed (Fig. 4) demonstrate that the studied reclaiming conditions have a influence on the vulcanization process. It was observed that during reclaiming of ground tire rubber the minimum and maximum values of torque decreased with increasing rotational speed of the screws. A noticeable drop in ΔM confirms a decrease in crosslinking density of the obtained revulcanizates [21]. Lower ΔM values are also associated with decreased crosslinking density of reclaiming rubber in response to increasing rotational speed. Scorch time and the optimal vulcanization time for specific blends were constant, which confirmed small influence of reclaiming conditions on both these parameters [10].

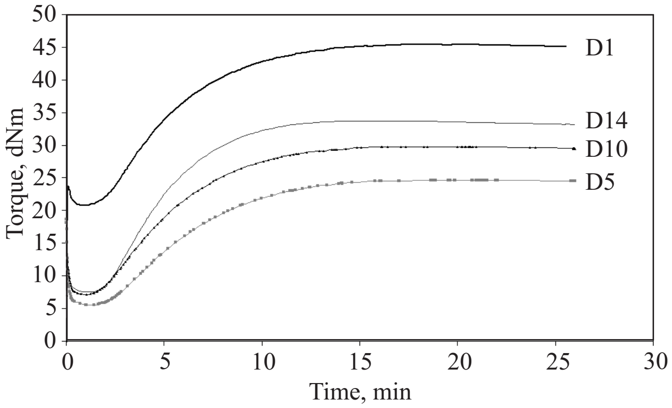

Fig. 4. Curing curves for D1, D5, D10 and D14 samples

Table 5. Reclaimed rubber vulcanized at 150 °C — curing characteristics

Sample	Parameters of vulcanization				
	Torque rheometer		ΔM	t_2, min	t_{90}, min
	M_L, dNm	M_H, dNm			
D1	20.8	45.4	24.8	2.2	10.3
D2	14.3	38.8	24.5	2.4	10.6
D3	9.3	32.0	22.7	2.6	10.8
D4	7.5	28.8	21.3	2.9	11.0
D5	5.6	24.7	19.1	2.8	11.1
D6	24.0	54.2	30.2	2.0	10.9
D7	16.1	46.7	30.6	1.9	8.8
D8	9.4	37.0	27.6	2.1	9.8
D9	11.2	39.3	28.1	1.9	9.5
D10	7.2	29.8	22.6	2.2	10.1
D11	9.4	36.6	27.2	2.2	10.5
D12	12.8	42.4	29.6	2.2	10.3
D13	8.0	35.5	27.5	2.2	9.1
D14	7.5	33.7	26.2	2.3	8.9

Mechanical properties of revulcanized rubber

In Figures 5—9 the mechanical properties of the obtained revulcanizates are presented. It was noted that ten-

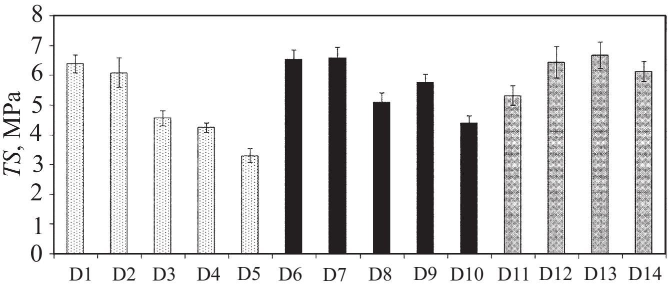

Fig. 5. Tensile strength of revulcanized rubber

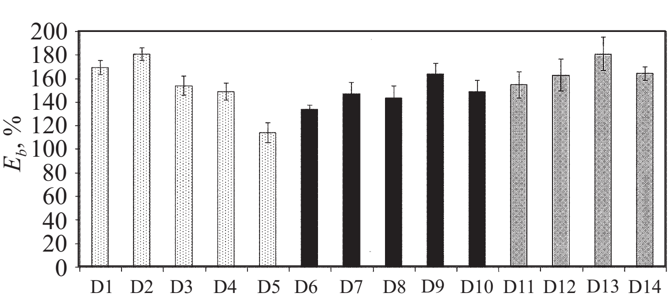

Fig. 6. Elongation at break of revulcanized rubber

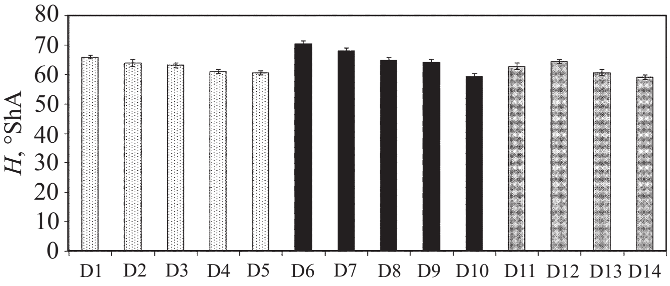

Fig. 7. Hardness of revulcanized rubber

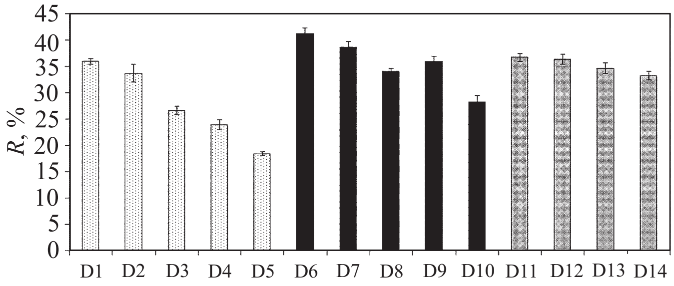

Fig. 8. Resilience of revulcanized rubber

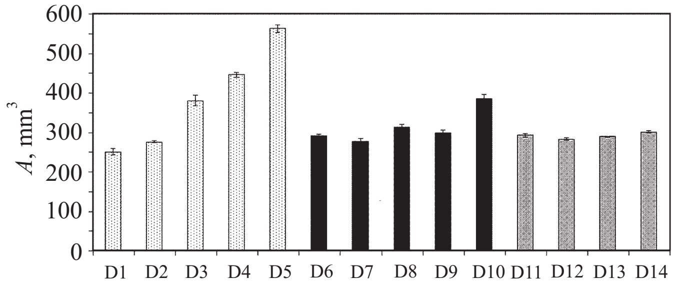

Fig. 9. Abrasion resistance of revulcanized rubber

sile strength, elongation at break, hardness and rebound resilience decreased with increasing rotational speed and the degree of reclaiming. Low values of elongation at break can be due to small degree of reclaiming of obtained samples and oxidation reactions of ground tire rubber during thermomechanical reclaiming.

Abrasion resistance slightly increased with increasing rotational speed and the degree of reclaiming. The lowest values of the aforementioned parameters were determined in the samples of reclaimed rubber prepared at higher rotational speeds by using screw profile A. A significant drop in the values of mechanical properties resulted from the partial main-chain degradation. In the case of co-rotating screw profile B, increased rotational speed caused lower main-chain degradation. Decrease in tensile strength, hardness and rebound resilience was observed for samples D6—D10, while abrasion resistance and elongation at break increased only slightly with increasing rotational screw speed. The increased rotational speed of screw profile C did not affect the mechanical properties of revulcanizates in a significant way.

Cure characteristics of SBR-GTR and SBR-dGTR blends

In order to compare the obtained reclaimed ground tire rubber (dGTR) to ground tire rubber without reclaiming (GTR), rubber blends have been prepared as listed in Table 3. Sample D10 was selected for further investigation after analyzing the values of screw torque, the degree of reclaiming, sol fraction and mechanical properties in relation to rotational speed of the screws, which affects the extruder's efficiency.

Table 6. Curing characteristics of SBR-GTR/dGTR blends at 160 °C

Sample	P1	P2	P3	P4	P5	P6	P7
M_L, dNm	3.6	4.0	5.2	6.6	3.5	3.8	4.2
M_H, dNm	33.3	32.0	30.9	30.5	30.3	28.5	24.7
ΔM, dNm	29.7	28.0	25.7	23.9	26.8	24.7	20.5
t_2, min	3.3	2.9	2.4	2.1	2.8	2.2	2.1
t_{90}, min	7.1	5.7	5.3	4.6	5.7	5.1	3.3

The effect of the contents of ground tire rubber and reclaimed rubber on curing characteristics of SBR-GTR/dGTR blends is presented in Table 6 and Fig. 10. The addition of ground tire rubber or obtained reclaimed rubber resulted in decreasing of scorch time and the optimal vulcanization time compared to the reference sample. This finding can be explained by the action of the residues of vulcanization accelerators which are present in ground tire rubber [22, 23]. Decrease in the torque values of the tested blends most likely resulted from the partial reclaiming of ground tire rubber and used reclaimed rubber under the influence of the vulcanization accelerator TMTD during the processing of rubber blends. Accelerator TMTD can act also as reclaiming agent [24—26]. This conclusion is supported by the results of the study on SBR/reclaimed rubber blends vulcanized with the use of sulfur system containing the vulcanization accelerator TBBS (*N-tert*-butyl-2-benzothiazyl sul-

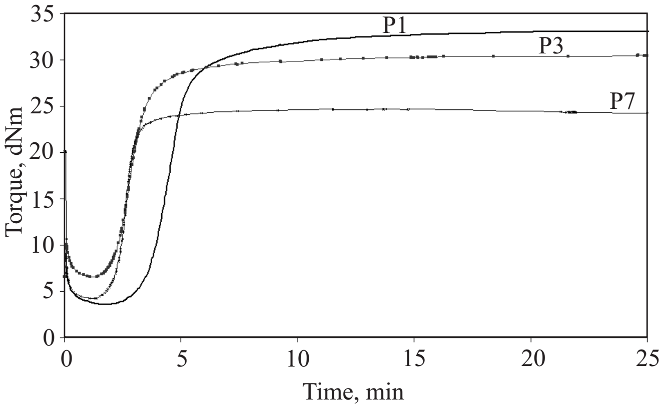

Fig. 10. Curing curves for P1, P4 and P7 samples

fenamide) where ΔM increased with increasing content of reclaimed rubber [27]. ΔM for reclaimed rubber was lower than for ground tire rubber due to lower crosslinking density of the reclaimed rubber.

Mechanical properties of SBR-GTR and SBR-dGTR vulcanizates

The effects of the contents of ground tire rubber and reclaimed rubber on mechanical properties of the obtained vulcanizates are graphically depicted in Figs. 11—15. The use of the produced reclaimed rubber in rubber blends allowed to improve mechanical properties of the final products in a significant way. A visible increase in tensile strength from 1.70 MPa (reference sample) to 2.76 MPa (sample containing 50 phr of reclaimed rubber) was observed. Elongation at break increased from 201 % in the reference sample to 325 % in the sample containing 50 phr of reclaimed rubber. The addition of ground tire rubber did not result in such large increase of the tensile properties. The hardness value of the reference sample reached 49 °ShA, which was three-fold higher compared to the sample containing 50 phr of reclaimed rubber (16 °ShA). Due to crosslinked structure of ground tire rubber, samples containing ground tire rubber were characterized by slightly higher hardness than samples containing reclaimed rubber. The higher content of ground tire rubber and reclaimed rubber in SBR-based blends resulted in visibly decreased abrasion resistance and rebound resilience. For larger contents of GTR/dGTR, i.e. 30 phr and 50 phr, the values of abrasion resistance and rebound resilience were similar. The presented results confirm that reclaiming of waste rubber has a positive effect on the properties of polymer compositions prepared with the use of reclaimed rubber [28—30].

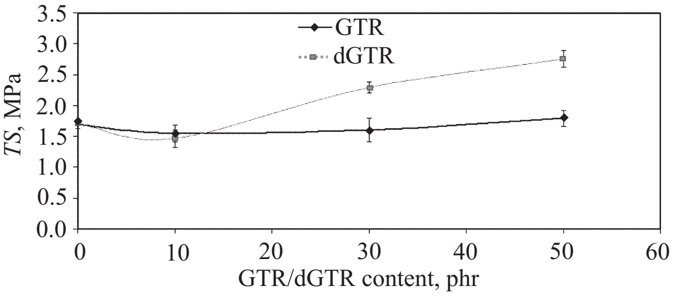

Fig. 11. Tensile strength of SBR-GTR/dGTR vulcanizates

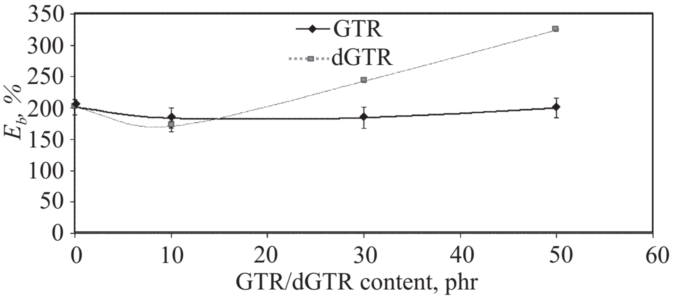

Fig. 12. Elongation at break of SBR-GTR/dGTR vulcanizates

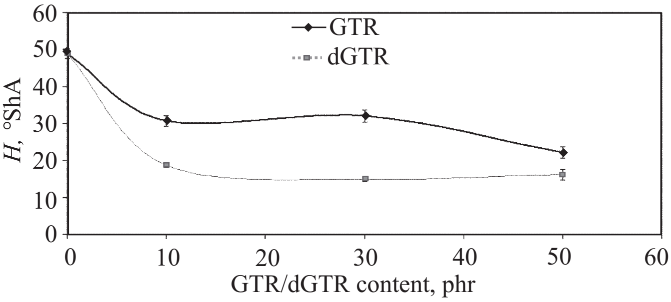

Fig. 13. Hardness of SBR-GTR/dGTR vulcanizates

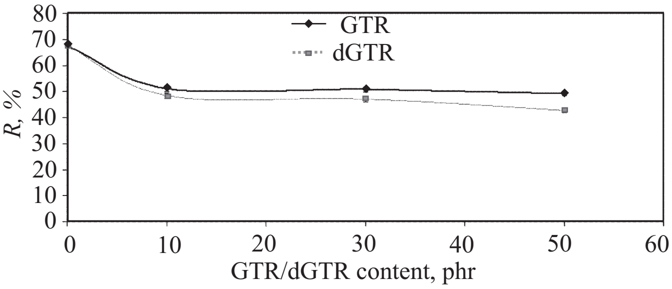

Fig. 14. Resilience of SBR-GTR/dGTR vulcanizates

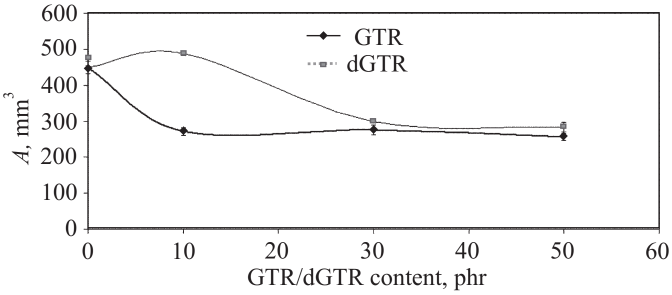

Fig. 15. Abrasion resistance of SBR-GTR/dGTR vulcanizates

CONCLUSIONS

The presented results confirmed that the direction of screw rotation, design of plasticizing system and the value of shear force controlled by rotational speed of the screws have a significant effect on the properties of the obtained reclaimed rubber. The increased rotational speed of the screws (i.e. larger shear force) resulted in lower crosslinking density (higher degree of reclaiming) of the produced reclaimed rubber. The use of counter-rotating plasticizing system, which mainly consists of transport elements with variable pitch, caused that ground tire rubber was basically exposed to the barrel temperature due to longer retention time of the material in the barrel. On the other hand, the application of co-rotating plasticizing unit containing kneading and transporting elements with constant pitch resulted in much shorter retention time of ground rubber in the extruder barrel. Besides barrel temperature, ground tire rubber in a co-rotating plasticizing system was subjected to shear forces, whose mechanical energy got converted into heat. A comparison of the properties of SBR/GTR and SBR/dGTR blends demonstrated that the reclaiming process has a positive effect on the mechanical properties of obtained products.

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