KRZYSZTOF FORMELA[1), *)], MAGDALENA CYSEWSKA[1)], JÓZEF HAPONIUK[1)], ANDRZEJ STASIEK[2)]

The influence of feed rate and shear forces on the devulcanization process of ground tire rubber (GTR) conducted in a co-rotating twin screw extruder

Summary — The search for new ways to recycling of rubber waste has been the aim of many studies conducted by research centers and companies worldwide. The results of our investigations on the process of continuous thermomechanical devulcanization of ground tire rubber using a twin screw extruder are presented. We used a co-rotating twin screw extruder with a special configuration of plasticizing unit, enabling generation of considerable shear forces. Various properties were characterized, such as the influence of the ground tire rubber feed rate and screw speed (shear forces) on the screw torque, acetone extract, sol fraction, and the degree of devulcanization in the resulting products. The effect of a secondary vulcanization on the vulcametric curves was determined, and the mechanical properties (tensile strength, elongation at break, hardness, resilience and abrasion resistance) of the revulcanized material were studied. It has been determined that the devulcanization process depends on the values of shear force and residence time acting on ground tire rubber. The devulcanization degree increases with increasing screw speed and feed rate. The results of repeatability of continuous devulcanization process of ground tire rubber were also determined. Obtained products possess the quality comparable to that of reclaim rubber available on the market.

Keywords: recycling, rubber waste, devulcanization, twin screw extruder, revulcanization.

WPŁYW SZYBKOŚCI DOZOWANIA ORAZ SIŁ ŚCINAJĄCYCH NA PROCES DEWULKANIZACJI ROZDROBNIONYCH ODPADÓW GUMOWYCH PROWADZONY PRZY UŻYCIU WYTŁACZARKI DWUŚLIMAKOWEJ WSPÓŁBIEŻNEJ

Streszczenie — Przedstawiono wyniki badań procesu termomechanicznej dewulkanizacji ciągłej rozdrobnionych odpadów gumowych, prowadzonej przy użyciu wytłaczarki dwuślimakowej współbieżnej. Zastosowano układ uplastyczniający umożliwiający generowanie znacznych sił ścinających. Scharakteryzowano wpływ szybkości dozowania miału gumowego oraz prędkości obrotowej ślimaków (sił ścinających) na moment obrotowy ślimaków, zawartość ekstraktu acetonowego, zawartość frakcji zolu oraz stopień dewulkanizacji otrzymanych produktów. Określono wpływ wtórnej wulkanizacji na krzywe wulkametryczne oraz właściwości mechaniczne otrzymanych rewulkanizatów. Zaprezentowano również wyniki badań powtarzalności procesu ciągłej dewulkanizacji miału gumowego. Otrzymane produkty charakteryzowały się jakością zbliżoną do jakości regeneratów gumowych dostępnych na rynku.

Słowa kluczowe: recykling, odpady gumowe, dewulkanizacja, wytłaczarka dwuślimakowa, rewulkanizacja.

INTRODUCTION

Reclaiming of rubber waste accompanied by devulcanization is defined as processing of postproduction rubber scrap and end-of-life rubber products, using thermal, mechanical or chemical energy, into the products which can be again reprocessed and vulcanized. At present, a number of methods for devulcanization of rubber waste are available; they have been extensively described in review papers [1, 2]. A continuous thermomechanical devulcanization by using a twin extruder is a relatively new method of material recycling, which requires determining the relationship between the processing parameters and the properties of the resulting devulcanizated/reclaimed rubber. The first reports on continuous devulcanization using twin screw extruders appeared in

[1)] Gdansk University of Technology, Chemical Faculty, Department of Polymers Technology, G. Narutowicza Street 11/12, 80-233 Gdansk, Poland.

[2)] Institute for Engineering of Polymer Materials & Dyes, M. Sklodowskiej-Curie Street 55, 87-100 Torun, Poland.

[*)] Author for correspondence; e-mail: kformela@urethan.chem.pg.gda.pl

the late 1990s, when a research team at Toyota developed an innovative method for the continuous devulcanization of sulfur vulcanized EPDM rubber materials [3]. Based on the studies of Mouri *et al.*, they proved that the configuration and geometry of the plasticizing system are essential factors during devulcanization, which together with the processing parameters allow obtaining regenerated materials with the desired properties. Fukumori and Matsushita [4] presented a model for the selective degradation of the sulfide cross-linking bonds under the influence of shear forces. The model is based on clear differences in the bond energy and the elastic constants between the carbon-carbon bond and the sulfur-sulfur bond. The authors of this theory suggest that it is possible to selectively break the sulfide cross-linking bonds with the adequate values of shear force, which can be obtained by the proper configuration of the extruder's plasticizing system. Sutanto *et al.* [5] pointed out, that according to the described model, the selective breakage of sulfide bonds is only possible if the number of C-C bonds is equivalent to the number of C-S and S-S bonds. In practice, the manufactured rubber products include a larger number of C-C bonds than C-S or S-S bonds therefore the probability of stretching and breaking C-C bonds is much larger than for the S-S bonds. Fukumori *et al.* [6, 7] presented the possibility of using the products of the continuous devulcanization of waste rubber powder from used car tires. It was determined that the addition of 30 wt. % of the devulcanized product to conventional mixtures barely affects mechanical properties of the revulcanized material. In 2001, Yokohama Rubber Co., Ltd. licensed from Toyota the technology for the continuous devulcanization of waste from discarded tires.

Maridass and Gupta [8—11] characterized the effect of the working parameters of a counter-rotating twin screw extruder on devulcanization process of ground tire rubber. Yazadani *et al.* [12] studied the influence of temperature and the extruder screw speed on the quality of the produced devulcanized materials obtained in co-rotating twin screw extruder. The results showed a clear impact of screw speed on the degree of devulcanization carried out at temperatures between 220 and 280 °C.

In Poland, Parasiewicz *et al.* [13] investigated the influence of temperature distribution in the cylinder on the process of rubber powder devulcanization. Pilot-scale tests were conducted on a co-rotating twin screw extruder prototype built at the Institute for Engineering of Polymer Materials & Dyes in Torun, Poland. The devulcanized material with the best properties was obtained by applying the following temperature profile: 170/180/185/190/130/110/90 °C.

The above presented review of knowledge on continuous devulcanization, using a twin extruder does not contain any information about the relationship between devulcanization efficiency and the quality of the produced devulcanizates, the latter being extremely important when dealing with scaling the production up from

the laboratory conditions to semi-technical or industrial level. The application of specifically designed plasticizing system, which allows strong shearing of ground rubber, resulted in lowered devulcanization temperature, namely 180 °C. The remaining thermal energy, which is necessary for conducting the devulcanization process, originates from shear forces and mixing (friction *via* mixing) of cross-linked ground tire rubber. Lowering the input of thermal energy from outside of the system is beneficial for the environment, and reduces the production costs. The results obtained in this study were compared with those from our previous investigations therefore we were able to assess the repeatability of a continuous thermomechanical devulcanization process.

The aim of our study was to determine the impact of the ground tire rubber feed rate and screw speed on the quality of the obtained devulcanized products. In the presented study the screw torque, the content of acetone extract, the sol fraction and the degree of devulcanization were measured. The effect of a vulcanization of reclaimed rubber on the vulcametric curves was determined, and the mechanical properties of the obtained revulcanized materials were studied.

EXPERIMENTAL

Materials

Ground tire rubber (GTR) (1.5 mm fraction) from whole used tires (mix of passenger and truck tires in 50:50 ratio) was prepared by ABC Recykling (Poland). The characteristics of ground tire rubber are presented in Table 1.

T a b l e 1. Characteristics of ground tire rubber

Properties	Mass contents, %	Methods
Acetone extract	8.7	PN-92/C-04219
Rubber additives	15.3	TGA
Rubber (SBR, NR)	48.7	TGA
Carbon black	32.7	TGA

Solvent (acetone, toluene) used for chemical analyses and the curing agents (stearic acid, sulfur, zinc oxide, TBBS: *N*-tertbutyl-2-benzothiazole sulfonamide) for vulcanization were obtained from POCH S.A. and „STANDARD" Sp. z o.o. (Poland).

Sample preparation

The thermomechanical devulcanization of the ground tire rubber was performed using a Bühler's twin screw extruder (model BTSK 20/40) with a special screw design that is able to generate large shear forces as presented in Figure 1. The ground tire rubber was fed *via* a volumetric
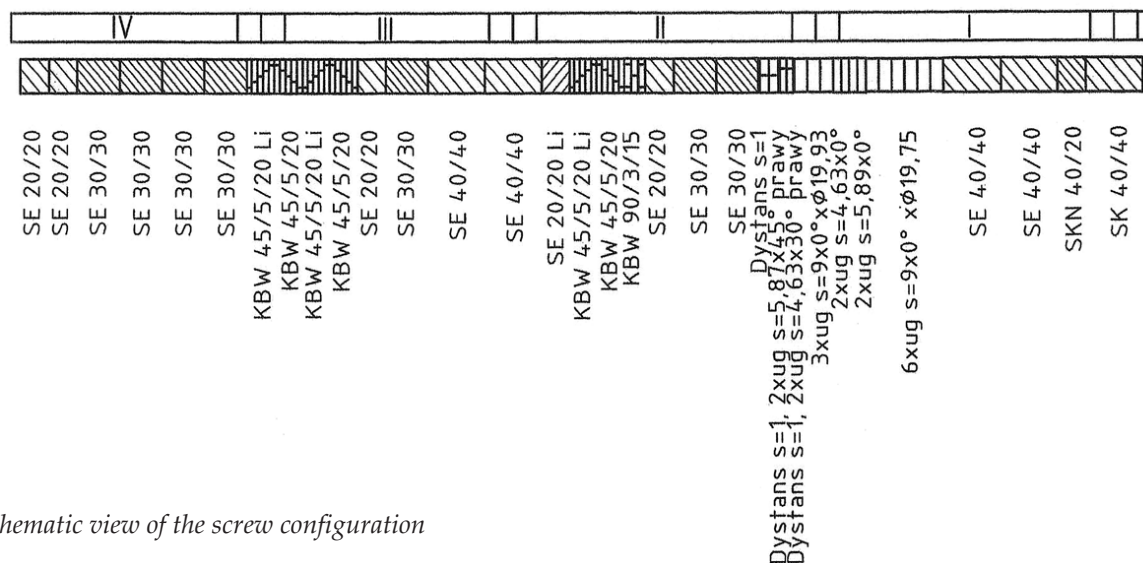
Fig. 1. Schematic view of the screw configuration

screw feeder at various rates, namely 0.54, 1.08, 1.62 and 2.16 kg/h. Screw speed (shear forces) was the second variable which had been set at 200, 300, 400, 500 and 600 rpm. The process temperature remained constant at 180 °C.

The resulting devulcanized rubber underwent a vulcanization. The mixture composition (parts by wt.) was as follows: 100.0 devulcanized rubber, 2.5 ZnO; 1.0 stearic acid; 1.5 sulfur; and 0.35 TBBS. The rubber compound was vulcanized according to the optimal time at 150 °C under the pressure of 4.9 MPa. Samples of commercially available reclaimed rubber, in the form of cylindrical blocks (PW) and sheets (PP) (from different manufacturer/importer), were used as reference materials; reference samples were vulcanized under conditions identical with those used for other samples.

Methods of testing

In order to control the conditions of devulcanization, we determined the impact of the feed rate and screw speed on screw torque. The resulting devulcanized rubber was subjected to a preliminary extraction with acetone (at the room temperature for 48 h followed by drying to a solid mass at 70 °C) in order to remove low molecular weight substances.

— The cross-linking density of the obtained samples was determined by equilibrium swelling in toluene (at the room temperature for 72 h; drying to constant weight at 70 °C), according to the Flory-Rehner equation [14] (based on ASTM D 6814) (1):

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

where: ν_e — *cross-linking density, mol/cm³; V_r — gel volume in the swollen sample, cm³; V_1 — solvent molar volume (toluene = 106.2 cm³/mol [15]); χ — polymer-solvent interaction parameter (in the calculations, it was assumed to be 0.391 [16]).*

— The degree of devulcanization was determined on the basis of changes in the cross-linking density of the devulcanized rubber compared to the ground tire rubber without devulcanization.

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

— Tensile strength and elongation at break of the obtained vulcanizates were tested according to the standard PN-ISO 37 by using a Zwick Z020 testing machine; five measurements were performed for each sample.

— Shore A hardness was determined for each sample with a Zwick 3130 durometer in accordance with the standard ISO 7619-1.

— For all samples, abrasion resistance was measured according to the standard ISO 4649.

— The rebound resilience determination was performed using the Schob pendulum according to the standard ISO 4662.

A comparative analysis of the devulcanized rubber materials obtained in this study and the products obtained during the implementation of earlier works [17, 18] was performed. The devulcanization process was carried out under identical conditions regarding the cylinder temperature (180 °C), speed (200, 300, 400 and 500 rpm), screw configuration and feed rate (1.62 kg/h). The obtained devulcanized products were vulcanized under identical conditions with respect to cross-linking agents, temperature and the pressure of the vulcanization press. The second series of devulcanized materials was obtained about half a year after finalizing the analysis of the first batch of samples.

RESULTS AND DISCUSSION

Figure 2 presents the effect of screw speed on torque in dependence on the determined feed rate of ground tire
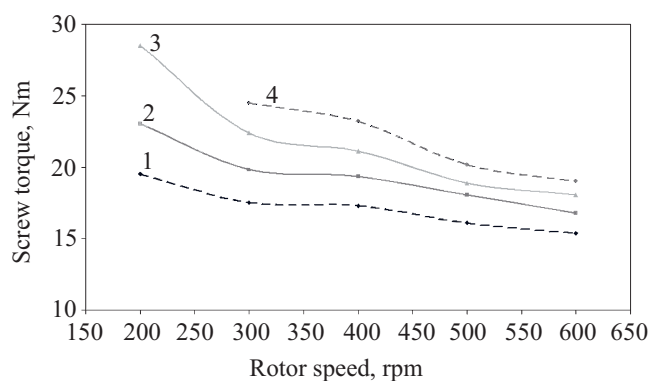
Fig. 2. Relationship between the screw (rotor) speed and torque at various feed rates: 1 — 0.54 kg/h; 2 — 1.08 kg/h; 3 — 1.62 kg/h; 4 — 2.16 kg/h

rubber. The tests have shown a significant decrease in torque with increasing screw speed and the decreasing feed rate of rubber powder, which is related to the ongoing process of devulcanization. During the devulcanization process the cross-linked molecules of ground rubber become more plastic which allows partial flow of the blend and, at the same time, lowers the screw torque (an equivalent to friction in the plasticizing system). The increased efficiency resulted in the increased screw torque values; this remains in agreement with the general rules of extrusion and is due to better filling of the screw channel with the fed material.

The use of a too high feed rate (2.16 kg/h) at low screw speed resulted in exceeding the maximum torque, and ultimately stopping the machine making it impossible to obtain a sample at the speed of 200 rpm. A comparative analysis of the results obtained for the new kneading segments marked as KBW 45/5/20 Li (with five kneading discs tilted 45°) with those obtained during our previous study on the devulcanization process [19], where at the speed of 600 rpm an apparent increase in torque had been observed — suggests increased consumption of the plasticizing system.

The values of cross-linking density and the degree of devulcanization of the devulcanized products are presented in Table 2. A slight increase of the acetone extract content obtained for the devulcanized material is comparable to the values obtained for ground tire rubber without devulcanization (Table 1), which suggests only a partial degradation of the main chain. The sol fraction content and the degree of devulcanization increase with increasing feed rate and screw speed under the studied conditions. A decrease in cross-linking density of the devulcanized material confirms the breaking of cross-linking bonds during thermomechanical devulcanization of rubber powder. The obtained devulcanizates were characterized by lower contents of acetone extract and sol fraction, and decreased cross-linking density as compared to commercially available reclaimed rubber, produced with the batch method and has a higher degree of devulcanization. The obtained results indicate that a par-

tially selective scission of cross-linking sulfide bonds took place. This phenomenon can be explained by the model proposed by Fukumori and Matsushita [2] (see Fig. 3).

T a b l e 2. The effect of feed rate and screw (rotor) speed on GTR devulcanization

Sample	Rotor speed rpm	Feed rate kg/h	Acetone extract %	Sol fraction %	Cross-linking density mol/cm^3 × 10^{-4}	Degree of devulcanization %
P1	200		9.2	11.6	4.42	44
P2	300		9.3	12.8	5.50	31
P3	400	0.54	9.3	13.1	4.53	43
P4	500		9.8	13.3	4.60	42
P5	600		9.7	13.7	4.58	42
P6	200		9.3	11.3	5.12	36
P7	300		9.3	12.7	4.04	49
P8	400	1.08	9.4	12.7	4.60	42
P9	500		9.8	13.4	3.91	51
P10	600		9.8	13.4	4.28	46
P11	200		9.6	11.8	3.98	50
P12	300		9.2	13.1	4.46	44
P13	400	1.62	8.2	14.4	3.89	51
P14	500		8.0	15.5	3.80	52
P15	600		9.0	15.0	3.80	52
P16	300		8.9	13.4	3.49	56
P17	400	2.16	7.8	15.2	2.91	63
P18	500		8.8	15.2	3.38	57
P19	600		8.6	15.5	3.15	60
PW	commercial reclaim rubber A		13.1	19.7	2.74	66
PP	commercial reclaim rubber B		12.4	10.2	1.62	80

The effect of the feed rate and screw speed on the process of vulcanization of the devulcanized rubber is presented in Table 3 and Figures 4—6. It was observed that an increase in the feed rate and screw speed during devulcanization of waste rubber is followed by a clear decrease in the minimum and maximum torque, which has been confirmed by decreased cross-linking density of the obtained revulcanizates. However, the effect of the studied devulcanization conditions on the optimal time of vulcanization is negligible which has already been confirmed by previous studies [18]. In Fig. 4 the vulcametric curves for sample P1 with and without the sulfur curing system are presented. The cross-linking agents present in ground tire rubber after devulcanization are a proof that secondary vulcanization of GTR has been completed. The vulcametric curves for samples P1—P5 (Fig. 5) demonstrate that the studied devulcanization conditions did not have any significant effect on the vulcanization process.
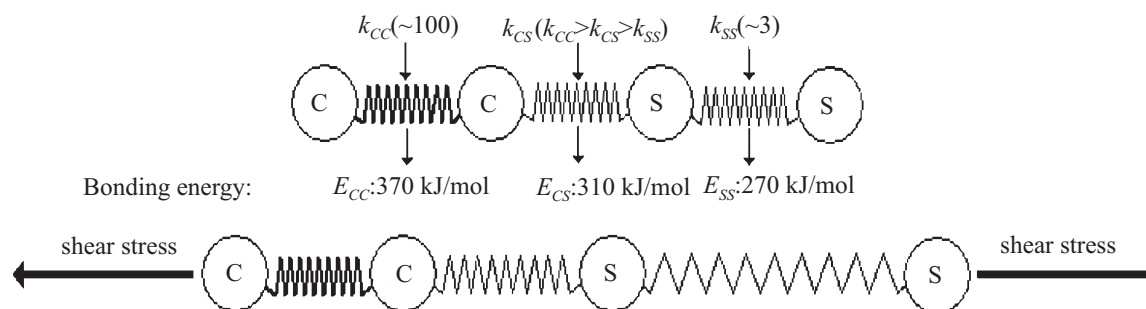
Fig. 3. Scheme of decomposition of sulfur cross-linking bonds under a shear field [2]

In Fig. 6 the vulcametric curves for devulcanizate P1 and the samples of commercially available reclaimed rubber are contrasted. The plotted curves indicate that the revulcanization process in the investigated devulcanizates are different from curves of commercial regenerated rubber. The difference is connected to the varying degree of devulcanization and the degradation level of the main chain caused by applying different methods of rubber waste reclaiming.
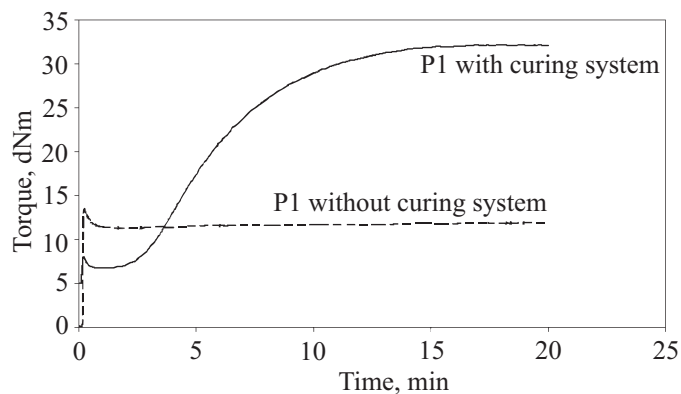

Fig. 4. Vulcametric curves for sample P1 with and without sulfur curing system at 150 °C

T a b l e 3. Curing characteristics of devulcanized rubber at 150 °C

Sample	Torque rheometer		ΔM	t_2 min/s	t_{90} min/s
	$M_{min,}$ dNm	$M_{max.,}$ dNm			
P1	5.0	32.2	27.2	2:10	10:01
P2	5.8	30.3	24.7	2:56	10:52
P3	6.2	29.9	23.7	2:57	11:26
P4	5.0	28.0	23.0	3:14	11:06
P5	4.7	28.6	23.9	3:06	11:18
P6	7.8	29.6	21.8	3:09	10:47
P7	4.9	31.6	26.7	2:10	10:17
P8	5.5	29.6	24.1	2:58	10:19
P9	5.2	28.8	23.6	2:58	11:01
P10	4.8	27.7	22.9	2:58	11:12
P11	7.7	36.5	28.8	2:54	9:27
P12	6.3	30.9	24.6	2:56	10:25
P13	4.6	33.3	28.7	2:10	10:38
P14	6.2	29.2	23.0	3:01	10:20
P15	5.9	27.8	21.9	3:13	10:04
P16	7.7	29.0	21.3	3:02	10:34
P17	6.9	31.8	24.9	2:58	10:41
P18	5.7	28.4	22.7	3:02	10:50
P19	5.3	29.2	23.9	2:51	10:58
PW	4.6	21.2	16.2	5:01	14:37
PP	2.5	25.7	23.2	4:01	12:51

Fig. 5. Vulcametric curves for samples P1—P5 at 150 °C

Fig. 6. Comparison of vulcametric curves for sample P1 and samples of commercial reclaim rubber PW and PP at 150 °C

The mechanical properties of revulcanizated rubber are showed in Table 4. Increased feed rate and screw speed adversely affect the mechanical properties of the produced revulcanized materials. The high degree of
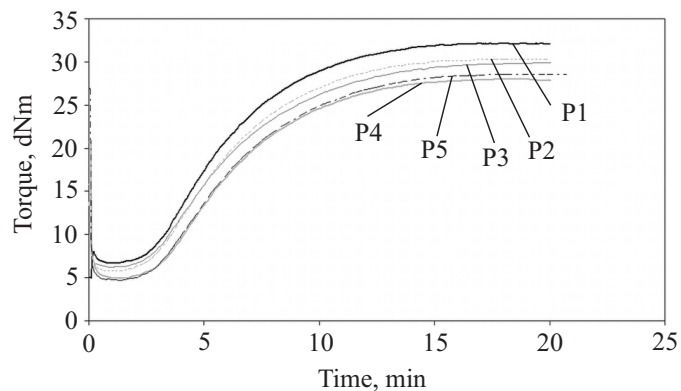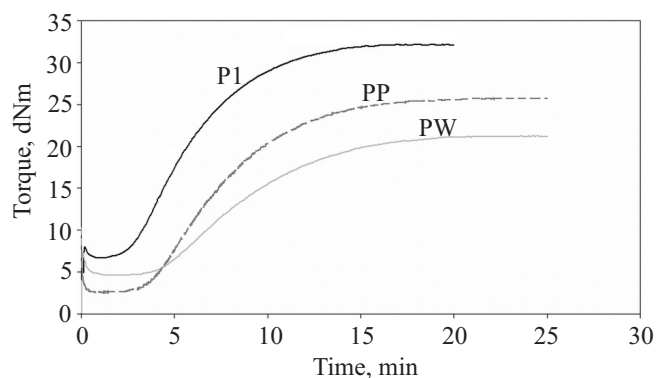
T a b l e 4. **Physical properties of revulcanized rubber**

Sample	Rotor speed, rpm	Feed rate, kg/h	TS, MPa	E_b, %	H, °Sh A	R, %	A, mm^3
P1	200		6.89±0.20	168±5	57	16	167
P2	300		6.05±0.28	167±4	58	16	171
P3	400	0.54	5.85±0.19	152±5	57	16	192
P4	500		5.27±0.35	144±7	57	16	195
P5	600		5.67±0.11	153±4	57	14	213
P6	200		6.66±0.34	170±9	58	18	154
P7	300		6.15±0.26	163±8	58	16	151
P8	400	1.08	6.21±0.34	168±4	57	16	174
P9	500		6.27±0.22	168±4	57	16	161
P10	600		5.79±0.08	162±6	56	16	161
P11	200		7.24±0.37	164±6	61	18	145
P12	300		6.82±0.35	173±7	58	16	155
P13	400	1.62	6.54±0.05	167±3	58	16	162
P14	500		6.43±0.18	177±3	56	16	179
P15	600		5.41±0.51	164±8	55	16	196
P16	300		6.14±0.65	167±7	59	18	178
P17	400	2.16	6.49±0.59	157±6	60	16	178
P18	500		5.99±0.41	174±8	58	16	228
P19	600		6.05±0.40	167±7	57	16	170
PW	commercial reclaim rubber A		8.79±0.33	364±12	50	19	218
PP	commercial reclaim rubber B		3.62±0.13	210±10	57	21	94

TS — tensile strength, E_b — elongation at break, H — hardness, R — resilience, A — abrasion resistance.

T a b l e 5. **Characterization of the process repeatability based on the working parameters of the extruder, acetone extract, sol fraction and the degree of devulcanization (series 1 according to [17])**

Sample	Rotor speed rpm	Screw torque, Nm		Energy consumption, kJ/kg		Acetone extract, %		Sol fraction, %		Percentage of devulcanization, %	
		series		series		series		series		series	
		1	2	1	2	1	2	1	2	1	2
1	200	30.2	28.5	2572	2378	9.2	9.6	11.4	11.8	37	50
2	300	24.2	22.4	3278	3022	9.2	9.3	13.3	13.1	32	44
3	400	21.6	21.2	3928	3867	8.2	9.6	13.6	14.4	39	51
4	500	20.3	18.9	4601	4311	8.0	9.4	14.4	15.5	49	52

devulcanization, obtained during the high shear (by increasing rotational speed of the screws) of rubber powder, caused a decrease in tensile strength (TS), elongation at break (E_b), hardness (H), resilience (R) and resistance to abrasion (A), which is associated with the degradation of the rubber hydrocarbon main chain.

In Tables 5 and 6 the results of the comparison between the devulcanization process and the devulcanized products obtained in the two series of samples, separated by about half a year, are summarized. The two series of samples were generated under identical laboratory conditions, *i.e.* with a Bühler's twin screw extruder (model BTSK 20/40) and under identical devulcanization conditions (temperature, rotational speed of the screw, efficiency and the plasticizing system design). The devulcanization process was supervised by two research teams consisting of different persons. Based on the analysis of data in Table 4, a significant decrease in torque and the power consumption of the screw drive was noted. This has confirmed earlier suppositions regarding the consumption of the plasticizing system, in particular novel kneading segments marked as KBW 45/5/20 and the entire barrel. Under the studied devulcanization conditions, the plasticizing system consumption resulted in a slight increase in the mass of acetone extract and the content of sol fraction, and in a pronounced increase in the degree of devulcanization which can be related to the prolonged processing time of rubber powder in the plasticizing system.

The results presented in Table 5 indicate a slight decrease in the optimal time of vulcanization, and a similar trend of reduction in mechanical properties with increas-

T a b l e 6. The effect of the process repeatability on the curing characteristics and mechanical properties (series 1 according to [18])

Sample	Rotor speed rpm	t_{90}, min/s		TS, MPa		E_b, %		H, °Sh A		R, %		A, mm³	
		series		series		series		series		series		series	
		1	2	1	2	1	2	1	2	1	2	1	2
1	200	12:23	9:27	6.50±0.17	7.24±0.37	194±10	164±6	60	61	19	18	88	145
2	300	12:01	10:25	6.26±0.31	6.82±0.35	188±1	173±7	59	58	19	16	115	155
3	400	11:26	10:38	5.77±0.20	6.54±0.05	178±6	167±3	59	58	18	16	133	162
4	500	10:53	10:20	5.55±0.20	6.43±0.18	170±5	177±3	58	56	18	16	149	179

t_{90} — optimum vulcanization time, TS — tensile strength, E_b — elongation at break, H — hardness, R — resilience, A — abrasion resistance.

ing speed. Much greater differences in the degree of de-vulcanization, and slight differences in the processing and mechanical properties (except for abrasion) of the samples probably resulted from the complex composition of rubber powder obtained from waste tires. However this hypothesis needs to be confirmed by further studies.

CONCLUSIONS

In this paper we determined the influence of feed rate and screw speed on the quality of the devulcanized rubber obtained by continuous thermomechanical devulcanization in a twin screw extruder with a special screw design. Based on the obtained results, it has been concluded that the application of plasticizing system, which allows generating a strong shearing force acting on ground rubber, resulted in the lowered devulcanization temperature, namely, 180 °C. This should be considered extremely significant when technological processes are planned because of environmental protection and economic issues. Increased rotation speed of the screws resulted in the increased degree of devulcanization and decreased torque values both being an effect of increasingly stronger shear forces acting on the cross-linked ground tire rubber. Shearing caused a partially selective breaking of cross-linking bonds. These results were confirmed by the measured contents of acetone extract and sol fraction which were much lower than those determined in commercial regenerated rubber that is produced by batch method. A comparative analysis of thermomechanical devulcanization of waste rubber, conducted at different time intervals, confirmed the repeatability of this process. The cross-linked devulcanizates were characterized by mechanical properties similar to those displayed by commercial reclaimed rubber.

REFERENCES

1. Adhikari B., De D., Maiti S.: *Prog. Polym. Sci.* 2000, **25**, 909.
2. Rajan V. V., Dierkes W. K., Joseph R., Noordermeer J. W. M.: *Prog. Polym. Sci.* 2006, **31**, 811.
3. Mouri M., Sato N., Okamoto H., Matsushita M., Fukumori K., *et al.*: *Proc. Int. Symp. Feedstock Recycl. Plast.* 1999, **22**, 269.
4. Fukumori K., Matsushita M.: *R&D Review of Toyota CRDL* 2003, **38**, 39.
5. Sutanto P., Laksmana F. L., Picchioni F., Janssen L. P. B. M.: *Chem. Eng. Sci.* 2006, **61**, 6442.
6. Fukumori K., Matsushita M., Okamoto H., Norio S., Suzuki Y., Takeuchi K.: *JSAE Rev.* 2002, **23**, 259.
7. Fukumori K., Matsushita M., Mouri M., Okamoto H., Sato N., Takeuchi K., Suzuki Y.: *Kaut. Gummi Kunstst.* 2006, **59**, 405.
8. Maridass B., Gupta B. R.: *Polimery* 2007, **52**, 456.
9. Maridass B., Gupta B. R.: *Polym. Test.* 2004, **23**, 377.
10. Maridass B., Gupta B. R.: *Kaut. Gummi Kunstst.* 2003, **56**, 232.
11. Maridass B., Gupta B. R.: *Polym. Compos.* 2008, **29**, 1350.
12. Yazdani H., Karrabi M., Ghasmi I., Azizi H., Bakhshandeh G. H.: *J. Vinyl Addit. Technol.* 2011, **17**, 64.
13. Parasiewicz W., Mężyński J., Niciński K., Ostaszewska U.: *Elastomery* 2011, **15**, 16.
14. Flory P. J., Rehner J.: *J. Chem. Phys.* 1943, **11**, 512.
15. Baeta D. A., Zattera J. A., Oliveira M. G., Oliveira P. J.: *Braz. J. Chem. Eng.* 2009, **26**, 23.
16. Marzocca A. J.: *Eur. Polym. J.* 2007, **43**, 2682.
17. Formela K., Kołacka K., Stankiewicz P., Haponiuk J., Stasiek A.: „Optimization of continuous devulcanization of rubber waste" (in Polish), in: „Modification of polymers — present state and perspectives", (Ed. Steller R.), Tempo s.c., Wrocław 2011.
18. Formela K., Kołacka K., Stankiewicz P., Haponiuk J., Stasiek A..: *Przem. Chem.* 2012, **91**, 1770.
19. Formela K., Haponiuk J., Stankiewicz P., Stasiek A.: *Przem. Chem.* 2011, **90**, 2175.