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APPLICATION OF SILICEOUS COMPOUNDS IN RECYCLING OF VULCANIZED WASTES BASED ON NITRILE RUBBER

The possibility of application of siliceous compounds: Perkasil and silan, as modification agents is studied for support of rational using of rubbertechnical articles production wastes based on butadienenitrile rubber. The main technological and exploitation characteristics of elastomeric compositions filed by untreated and treated ground vulcanizate are researched. It's shown that surface modification of ground vulcanizate based on BNKS-18 A by siliceous compounds allows get satisfactory properties of rudders even with the high contamination of modified wastes in elastomeric composition.

Introduction. Issue of rubber products (RTI) promotes the formation of large quantities of waste, the use of which in particulate form allows them back into production. It should be noted that the use of waste in such state in the formulation of similar elastomeric compositions allows obtaining vulcanizates that are not inferior in strength properties of the original rubber [1].

Adding such mixture of ground vulcanizate (GV) leads to increased production efficiency by improving RTI ecology, reduce production costs, the main raw material savings.

It is known [2] that the increase in the content of ground vulcanizate in each formulation is possible only up to the point when technical properties of the elastomer composition correspond to normalized values. In this regard, the constant search of prescription and technological tricks to increase the dosage of ground vulcanizate in elastomeric compositions while maintaining high physical and mechanical properties.

To achieve this, a lot of work carried out in the mechanochemical treatment of GV. Mechanical properties of the composites obtained using the modified ground vulcanizate properties superior to similar material containing untreated particles shredded vulcanizate. Increased adhesion to polymers modified GV significantly increases its content in polymer blends [1]. It is well known [3, 4], that the introduction of the modified ground vulcanized in a matrix in an amount of 20 wt %. Produces rubber satisfactory set of properties. However, in the case of each specific elastomeric composition is necessary to establish the optimum dosage pulverized vulcanizate as well as its modes of modification.

One area of development in the modification modes is the use of shredded vulcanizate its mechanical activation which can prevent agglomeration of particles, to increase surface activity, and also more evenly distribute the particles in the pulverized vulcanized elastomeric matrix. [4]

In addition, works on chemical modification of the surface of GV. To ensure an improved interac-

tion between the elastomer matrix and pulverized vulcanizate as modifying agents used are plasticizers, etc. nitroincluded compound [5].

Main part. The aim of this work is to investigate the possibility of applying for the surface modification of vulcanized rubber ground Perkasil silicon compounds and silane.

To achieve this goal tests for determining cure characteristics and basic mechanical will be conducted and operational performance elastomeric composition will be investigated.

As objects of study were used rubber mixture based BNKS A-18 and ground vulcanizate on the basis of the elastomeric composition. GV was obtained by crushing rollers and pre-mixing was before mechanochemical activation by grinding in a planetary mill "Pulverisette 6" firm "FRITCH" jointly with organosilicon compounds and silane Perkasil in two combinations: 1) GV + Perkasil; 2) GV + Perkasil + silane.

Perkasil relates to a class of amorphous precipitated silicates. Active ingredient improves the wear resistance and tensile strength, the dimensional stability, and imparts a high resistance to abrasion, cracks and cuts as well as improves the adhesion of metal to rubber and rubber to the base fabric, is applied to the footwear industry and the manufacture of rubber articles for industrial use [5].

Application of silane due to its ability to serve as a coupling agent is under investigation. Organosilicon coupling agents have been used successfully to improve the physical properties of a number of inorganic fillers including calcium silicate, kaolin, mica, silicic acid and talc. The reaction between the bifunctional organosilanes, and the silica or silicate particle occurs via a hydrophobic interaction of the silane alkoxy groups and silanol groups on the surface of silica or a silicate, followed by reaction of the sulfur-containing functional group of the silane with an olefinic elastomer to form a group of covalently bound structure [6].

Acceptable mode of mechanical activation was chosen on the basis of published data [4]. Milling was carried out for 3 minutes at room temperature

led speed – 400 min⁻¹, the number of balls – 5, the size of the balls – 20 mm. GV obtained particles had a size of not more than 0.5 mm. GV thus modified elastomer composition is administered in different doses (10, 30 and 50 phr). As reference samples were used, containing no GV in rubber composition, mixtures with ground vulcanizate were not subjected to modification.

The initial stage of research was to determine the basic parameters of the kinetics of isothermal curing. Results are presented in Table 1. From these data it is evident that the elastomeric compositions, the unmodified filled shredded vulcanizate and GV modified Perkasil, decreases with increasing dosage of time to achieve the optimum degree of vulcanization compared with the original rubber compound. Thus, for compositions that contain unmodified GV maximum reduction of this indicator is 18.6% at a dose of 50 phr, and for compositions GV Perkasil modified at a dose of 50 phr –

28,5%. Time to reach an optimal degree of vulcanization of rubber mixtures which contain the shredded vulcanizate modified Perkasil silane, when dosages of 10 and 30 phr remains at the initial rubber mixture, and at 50 phr increases from 8.48 to 11.71 dH·m.

Consequently, it can be assumed that modification and combination Perkasil silane produces additional crosslink that can not be formed between the elastomeric matrix and unmodified GV and pulverized vulcanizate having undergone modification only Perkasil.

In the next step identifies the main physical and mechanical properties of the elastomeric compositions and rubber resistance to heat aging (Table 2). Found that the introduction of ground vulcanized rubber in all studied doses in rubber mixtures based on BNKS A-18 leads to a decrease Tensile strength at 19–36%, and the elongation at break – by 31–47%.

Table 1

The test results on the vulcanization kinetics of rubber mixtures

Figure	Without additive	Dosage of ground vulcanizate, phr								
		Unmodified GV			Perkasil			Perkasil + silane		
		10	30	50	10	30	50	10	30	50
M_{\min}	5.82	8.40	11.79	15.4	8.81	12.92	17.53	10.19	12.08	18.59
M_{\max}	52.92	53.49	52.92	53.08	54.83	55.59	54.79	59.23	55.65	61.34
τ_{50}	5.95	5.26	4.74	4.12	5.35	4.34	3.96	5.15	4.71	4.09
τ_{90}	8.48	7.98	7.55	6.9	7.85	6.60	6.06	8.24	8.88	11.71
τ_{\max}	5.93	5.15	4.56	3.96	5.31	4.27	3.87	5.02	4.50	3.73
R_S	13.06	12.30	11.95	12.00	12.89	13.28	12.60	13.41	12.36	12.25

Note. M_{\min} – minimal torque moment, dN · m; M_{\max} – maximal torque moment, dN · m; τ_{50} – time of achievement of adjusted vulcanisation, min; τ_{90} – time of achievement of optimum vulcanisation, min; τ_{\max} – time of achievement of maximal cure rate, min; R_S – cure rate, dN · m/min.

Table 2

Physical-mechanical properties of experimental rubbers

Dosage of ground vulcanizate, phr	Before aging		After aging in air during 72 h at 100°C		Aging coefficients by tensile strength
	Elongation at break, %	Tensile strength, MPa	Elongation at break, %	Tensile strength, MPa	
Without additive	190	12.6	165	10.5	0.83
Unmodified GV					
10	130	9.0	90	5.1	0.56
30	120	8.5	80	4.8	0.56
50	120	8.1	80	4.6	0.57
GV modified by Perkasil					
10	130	8.5	70	5.1	0.60
30	120	9.3	90	5.2	0.56
50	110	9.0	90	5.1	0.56
GV modified by Perkasil and silane					
10	130	10.2	90	5.4	0.53
30	110	10.2	80	4.8	0.47
50	100	9.9	70	5.2	0.53

Table 3

**Values of relative residual compressive deformation (RRCD),
concentration of crosslinks and change of sample weight after ASTM No. 3 act of experimental rubber**

Dosage of GV, phr	RRCD, %	Concentration of crosslinks	Change of sample weight after ASTM No. 3 act, %
Without additive	16.0	$2.49 \cdot 10^{-4}$	2.68
Unmodified GV			
10	18.5	$2.44 \cdot 10^{-4}$	2.25
30	19.1	$2.37 \cdot 10^{-4}$	1.68
50	22.8	$2.17 \cdot 10^{-4}$	1.75
GV modified by Perkasil			
10	22.3	$2.10 \cdot 10^{-4}$	1.67
30	18.8	$2.30 \cdot 10^{-4}$	1.30
50	23.1	$1.90 \cdot 10^{-4}$	0.69
GV modified by Perkasil and silane			
10	20.6	$2.30 \cdot 10^{-4}$	0.30
30	17.2	$2.44 \cdot 10^{-4}$	0.72
50	16.7	$2.53 \cdot 10^{-4}$	1.09

Thus elastomeric composition contains shredded vulcanizate unmodified and crumb rubber modified Perkasil, reduction of strength properties is 28–35%. Tensile strength of samples of rubber filled with rubber crumb, modified Perkasil and silane is reduced by 20%. It should be noted that increasing the dosage of GV current has virtually no effect on the conventional change of the tensile strength.

This suggests the possibility of stronger crosslinks that connect the elastomeric matrix with particles of ground vulcanized using a combination of double-modifying agents.

To evaluate resistance to thermal aging of the rubber specimens were exposed to elevated temperature (100°C) in air for 72 hours. The results showed that for all experimental compositions is a reduction relative to the original as rubber Tensile strength (at 48–51%) and the elongation at break (at 45–57%).

Investigated elastomeric compositions containing shredded vulcanizate have approximately the same resistance to temperature and oxygen in the air, as indicated by calculated coefficients aging Tensile strength. It should be noted that the increase in dosage ground vulcanizate has almost no effect on the change of heat-resistant rubber.

Elastomer composition, based on BNKS A-18, is widely used for manufacture of sealing products, operating in hostile environments and under the influence of static loads. So the next step was to determine the relative compression set (RRCD) after thermal aging in air, as well as the degree of swelling. The test results are shown in Table 3.

RRCD after thermal aging in air for 24 hours at a temperature of 100°C for the experimental rubbers increases in comparison with the original.

However, it should be noted that with increasing content of comminuted vulcanized rubber, and silane-modified Perkasil, elastomeric compositions have increased resistance to the accumulation of residual deformation. Thus, for these compositions GV at a dosage of 10 phr, RRCD is higher than the initial rubber by 28.5% but at 50 phr – only 4.4%.

All investigated elastomer compositions comprising GV have greater resistance to aggressive environments than the original tires. Thus, for compositions filled shredded vulcanizate unmodified, weight change after standing in the solvent ASTM № 3 16–37% lower than that of rubber additives without GV, and the samples containing the shredded vulcanizate Perkasil modified silane, at a dosage of 10 phr decrease in this indicator reaches 88.8%.

The concentration of cross-linking was calculated on the basis of tests of resistance to aggressive environments. Maximum concentration of cross-linking is observed for samples containing 30 phr of crumb combined with Perkasil, and 50 phr of crumbs for samples combined with Perkasil silane. For these samples minimum values of RRCD are observed.

Conclusion. Surface modification of pulverized vulcanizate based BNKS A-18 using silicon containing compounds improves its compatibility with the elastomeric matrix, as evidenced by the results of studies, and thus allows to make a conclusion on the possibility of applying Perkasil silane as modifying agents.

It should be noted that the use of silane and Perkasil modifying shredded vulcanizate better effect than using only Perkasil. In the case of only Perkasil conventional tensile strength is reduced by 26–35%, 17–45% RRCD on, and using application

Perkasil silane and these figures are reduced by 19–21% and 4–28%, respectively. Thus, the use of combinations of substances and silane Perkasil allows to obtain satisfactory properties even when the rubber-modified high particulate content in the elastomeric vulcanizate composition.

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