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Investigation of the Influence of Technological Additives on the Properties of Thermo-Aggressive Resistant Rubber

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Abstract

The influence of various technological additives on the plastic and rheometric properties of a rubber mixture is investigated, physical-mechanical and performance characteristics of rubber based on a combination of SKN 4055 nitrile butadiene caoutchouc and Therban 3406 hydrogenated nitrile butadiene caoutchouc are assessed. The rubber mixture included SKN 4055 and Therban 3406, curing agent Luperox F-40P, antioxidant Diaphene FP, fillers: burnt magnesia, carbon black T 900 and P 514, oligoester acrylates TGM-3, MGF-9, and other ingredients. We used Z-50, Z-60, Struktol WB-222, Kvalistrol A-100, B-70 and B-70-20 as technological additives. The rubber mixture was made on laboratory rolls LB 320 160/160, then vulcanized at 150 °C for 60 min and thermostated at 160 °C for 3 h. Studies of the plastic and rheometric properties of the rubber compound, the physical and mechanical properties of vulcanizates were carried out in accordance with the standards existing for rubber industry. The study of thermo-aggressive resistance of vulcanizates was carried out by determining the change in their physical-mechanical parameters after 1 day exposure to air and standard liquid SZhR-1 at a temperature of 150 °C. It is found that the introduction of technological additives leads to improvement in the distribution of ingredients, as well as in the plastoelastic and rheometric properties of the rubber mixture. Rubber containing Kvalistrol B-70-20 has increased physical and mechanical properties, exhibiting the least changes after exposure to aggressive media.

Keywords: technological additives, rubber mixture, vulcanizates, plastoelastic and rheometric properties, physical-mechanical properties, thermo-aggressive resistance

INTRODUCTION

Currently, the demand for thermo-aggressive resistant rubber products that can withstand harsh operating conditions is high enough. For these purposes, rubbers based on butadiene-nitrile (NBR) [1, 2] and hydrogenated butadiene-nitrile (HBNR) [3, 4] caoutchoucs are mainly used. Technological additives (TA) are introduced into rubber mixtures to regulate the technological parameters of processing and increase the operational properties [5–11]. The effectiveness of TA is determined by their ability to reduce the surface tension of rubber compounds, concentrating on the boundaries of contact of caoutchouc with fillers and powdery ingredients. This makes it possible to improve the degree of dispersion of powdery ingredients in the caoutchouc matrix, the technological properties of rubber mixture and, as a consequence, to increase the physical-mechanical properties of vulcanizates. In [12, 13], the effect of technological additives Oxanol TsS-100, KD-6, Lubstab-01, Zincolet BB 222, dispersant FL Plus and MA-L22 on technological, physical-mechanical and operational properties of rubbers based on various grades of nitrile butadiene caoutchoucs was investigated. It has been found that for rubbers based on caoutchoucs BNKS-18AMN, BNKS-28AMN and BNKS-40AMN the effective TA are Oxanol TsS-100, Zincolet BB 222 and MA-L22, respectively. Since rubbers based on HBNR, in comparison with rubbers based on BNR, have increased thermo-aggressive resistance, it is of interest to study the effect of TA on the properties of rubber based on a combination of BNR with HBNK. In this regard, we investigated the effect of various technological additives on the properties of rubber based on a combination of SKN 4055 and Therban 3406 caoutchoucs.

EXPERIMENTAL

The rubber mixture contained (mass %): caoutchoucs SKN 4055 (20.0) and Therban 3406 (80.0); vulcanizing agent Luperox F-40P (4.0); antioxidant Diaphene FP (2.0); fillers – burnt magnesia (4.0), technical carbons T 900 (20.0) and P 514 (40.0); vulcanization coagents – oligoetheracrylates TGM-3 (7.0), MGF-9 (7.0) and other ingredients. The rubber mixture was prepared on laboratory rollers LB 320 160/160 by mixing caoutchoucs with ingredients in two stages. At the first stage the masterbatch was made by mixing caoutchoucs with Diaphene FP, burnt magnesia, technical carbons P 514 (1/2 of its total amount) and T 900 (1/2 of its total amount) at a temperature of 60–70 °C for 20 min. After that, the masterbatch was cooled at room temperature on a metal table for 2 h. The second stage proceeded at a temperature of 60–70 °C for 8 min. Technical carbons P 514 (1/2 of the total amount) and T 900 (1/2 of the total amount), TGM-3 and MGF-9 oligoetheracrylates, technological additives, Luperox F-40P and others were introduced into the masterbatch ingredients. After preparation, the rubber mixture was cooled on a metal table, vulcanized in a press at 150 °C for 60 min, and thermostated at 160 °C for 3 h.

The plastoelastic properties of the rubber mixture were studied on an MV 3000 Basic viscometer at a temperature of 120 °C in accordance with GOST 10722-76. The vulcanization characteristics of the rubber mixture were studied on a Mon Tech MDR 3000 Basic rheometer at 150 °C for 40 min in accordance with GOST 12535-84. Standard samples for determining physical and mechanical properties were vulcanized at a temperature of 150 °C for 30 min in a P-V-100-3RT-2-PCD type vulcanizing press. The main characteristics of the vulcanizates were determined according to the strength standards in rubber industry: the nominal tensile strength and relative elongation at break were determined according to GOST 270-75; Shore A hardness – according to GOST 263-75; rebound elasticity – according to GOST 27110-86; tear resistance – according to GOST 262-79. Changes in conditional tensile strength, relative elongation at break and hardness after aging in air were determined according to GOST 9.024-74; changes in conditional tensile strength, relative elongation at break and hardness after exposure to aggressive hydrocarbon media – according to GOST 9.030-74, method B. The dynamic parameters (modulus of elasticity, mechanical loss tangent) of vulcanizates of various types of the rubber mixture were studied at room temperature on a Metravib VHF 104 dynamic mechanical analyzer at a degree of deformation of 0.01 % and a frequency of 1000 Hz according to GOST 23326-78.

Using TA (CD-12, Z-50, Z-60, Struktol WB-222, Kvalistrol A-100, B-70 and B-70-20) in quantities of 2.0 mass parts per 100.0 mass parts of rubbers, several versions of the rubber mixture were prepared. Table 1 shows the variants for a rubber mixture with different TA.

TABLE 1

Content of technological additives in various options of the rubber mixture, mass %

Technological additives	Variant							
	1	2	3	4	5	6	7	8
CD-12	–	2.0	–	–	–	–	–	–
Z-50	–	–	2.0	–	–	–	–	–
Z-60	–	–	–	2.0	-	–	–	–
Struktol WB-222	–	–	–	–	2.0	–	–	–
Kvalistrol A-100	–	–	–	–	–	2.0	–	–
Kvalistrol B-70	–	–	–	–	–	–	2.0	–
Kvalistrol B-70-20	–	–	–	–	–	–	–	2.0

RESULTS AND DISCUSSION

The efficiency of using TA for each variant of the rubber mixture was assessed by the plastoelastic, rheological properties, as well as the

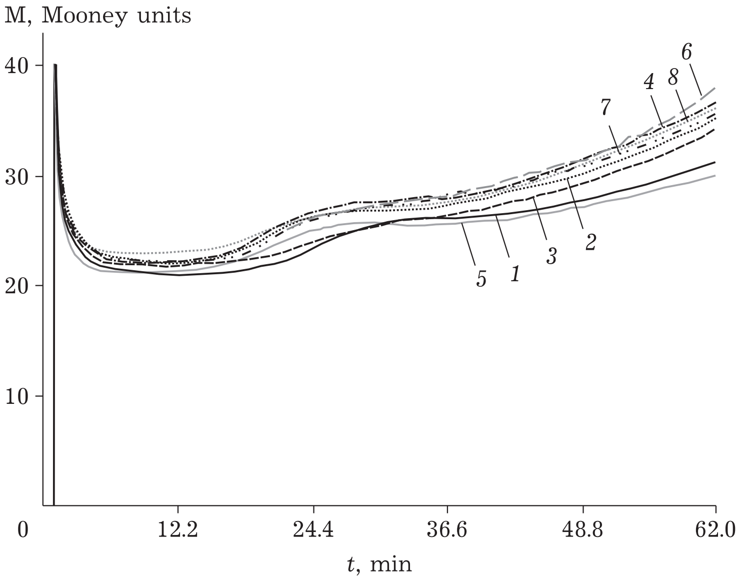

Fig. 1. Dependences of Mooney viscosity on time for a rubber mixture (curve numbers correspond to variant numbers).

physical-mechanical parameters of vulcanizates and changes in these parameters after thermal aging in air and exposure to aggressive media.

The time dependences of viscosity for different variants of the rubber mixture at 120 °C are shown in Fig. 1.

Based on the data (see Fig. 1), the plastic properties of different variants of the rubber mixture were determined (Table 2).

It can be seen that the introduction of TA into the rubber compound leads to a decrease in the maximum viscosity by 12.2 % and an increase in the minimum viscosity by 8.7 %, which is apparently associated with the melting points of the TA. These data indicate that the plastoelastic properties of the rubber compound containing TA change within acceptable limits.

The rheometric curves for different variants of the rubber mixture taken at 150 °C are presented in Fig. 2.

Table 3 shows the rheometric properties of these rubber compounds. From the presented data it follows that the addition of TA improves the rheometric properties of the rubber mixture. Moreover, the introduction of Kvalistrol B-70-20 into the rubber compound leads to the greatest increase in the maximum torque (18.8 %) and the difference between the maximum and minimum torques (9.54 dN · m), and, consequently, the degree of crosslinking of the rubber compound at its vulcanization, and improves the physical and mechanical properties of rubber.

Table 4 shows the results of the study of the physical-mechanical properties of vulcanizates for different variants of the rubber mixture.

From the presented data it follows that the vulcanizate of the 8th variant with TA Kvalistrol B-70-20 is characterized by increased physical and mechanical properties (in comparison with the vulcanizate of the first variant, there is an increase in the conditional stress at 100 % elongation by 20 %, the conditional tensile strength by 4.9 %, hardness by 12.1 %, and tear resistance by 17.4 %). This is a confirmation of the previously noted assumption that the 8th variant of the rubber compound, which has the largest difference

TABLE 2

Plastic properties of the rubber mixture

Indicators, Mooney units	Variant							
	1	2	3	4	5	6	7	8
M_{max}	39.24	36.22	34.46	38.17	35.53	40.22	38.67	37.56
M_{min}	20.94	21.87	21.16	22.77	21.69	21.75	22.27	22.15

Note. M_{max} и M_{min} – maximum and minimum viscosities.

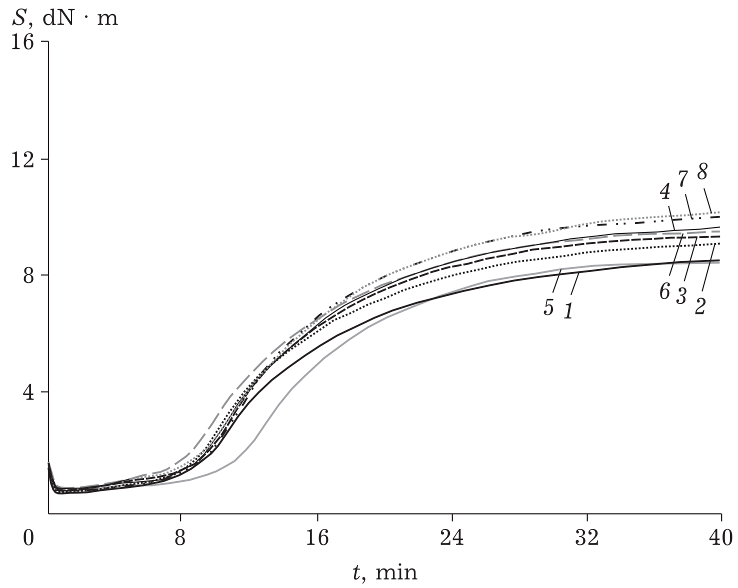

Fig. 2. Dependences of torque on time for a rubber mixture (curve numbers correspond to variant numbers).

between the maximum and minimum torques, should be characterized by increased physical and mechanical properties.

For the obtained vulcanizates, changes in physical-mechanical parameters and hardness were determined after thermal aging in air and in SZhR-1 at a temperature of 150 °C for 24 h. The results of the investigation are presented in Table 5.

It follows from the data obtained that the smallest changes in physical and mechanical properties after aging in air and in SZHR-1 are characteristic of the vulcanizate of the 8th variant

TABLE 3

Rheometric parameters of the rubber mixture at 150 °C

Parameter	Variant							
	1	2	3	4	5	6	7	8
S_{max}, dN · m	8.73	9.31	9.60	9.89	8.67	9.81	10.25	10.37
S_{min}, dN · m	0.67	0.76	0.77	0.75	0.76	0.85	0.89	0.83
t_s, min	10.33	9.83	10.11	10.09	12.43	9.34	10.50	10.36
t_{90}, min	27.01	26.22	25.82	26.33	25.86	25.99	25.98	26.66
V_{max}, (dN · m)/min	1.62	1.61	1.58	1.55	1.71	1.64	1.86	1.81

Note. S_{max} – maximum torque; S_{min} – minimum torque; t_s – start time of vulcanization; t_{90} – optimal vulcanization time; V_{max} – maximum vulcanization rate.

TABLE 4

Physical-mechanical properties of rubber

Parameter	Variant							
	1	2	3	4	5	6	7	8
f_{100}, MPa	2.5	2.6	2.7	2.8	2.8	2.9	2.9	3.0
f_p, MPa	14.4	14.5	14.7	14.3	13.7	14.4	14.8	15.1
ε_p, %	490	460	450	480	510	500	510	500
H, Shore A units	66	70	71	70	67	72	73	74
B, kN/m	46	47	46	46	47	48	50	54

Note. f_{100} – conditional stress at 100 % stretching; f_p – conditional tensile strength; ε_p – elongation at break; H – hardness; B – tear resistance.

TABLE 5

Changes in the physical-mechanical parameters and hardness of vulcanizates after heat exposure to aggressive media

Parameter	Variant							
	1	2	3	4	5	6	7	8
After aging in air (150 °C, 24 h)								
Δf_p, %	−13.8	−12.4	−14.1	−17.9	−15.8	−19.1	−12.3	−9.1
$\Delta \varepsilon_p$, %	−18.6	−19.7	−17.7	−19.6	−20.2	−21.6	−14.2	−12.1
ΔH, Shore A units	+1	+1	+2	+2	+2	+1	+1	+1
After exposure in SZhR-1 (150 °C, 24 h)								
Δf_p, %	−17.1	−18.3	−19.2	−20.9	−19.6	−17.9	−14.5	−12.1
$\Delta \varepsilon_p$, %	−15.9	−16.7	−19.5	−21.4	−22.1	−18.7	−13.2	−10.8
ΔH, Shore A units	−4	−3	−4	−3	−5	−4	−4	−2

Note. Δf_p и $\Delta \varepsilon_p$ – relative change in tensile strength and elongation at break, respectively; ΔH – change in hardness.

of the rubber mixture (for this variant, in comparison with the vulcanizate of the first variant, after thermal-oxidative aging in air, a decrease in the relative tensile strength and elongation at break is 34.0 and 34.9 %, respectively, and after exposure to SZHR-1, by 29.2 and 32.0 %, respectively). Thus, the introduction of Kvalistrol B-70-20 into the studied rubber mixture contributes to a better preservation of the resistance of vulcanizates to the thermal effects of aggressive media.

CONCLUSION

A rubber mixture based on a combination of caoutchoucs SKN 4055 and Therban 3406, containing TA Kvalistrol B-70-20, is characterized by improved processability. Compared to the TA-free rubber compound, it is characterized by an increase in the maximum torque by 18.8 % and the difference between the maximum and minimum torques by the 9.54 dN · m. The vulcanizate with TA Kvalistrol B-70-20, compared to the vulcanizate without TA, has improved physical and mechanical properties and is characterized by an increase in nominal stress at 100 % elongation by 20.0 %, nominal tensile strength by 4.9 %, hardness by 12.1 %, and tear resistance by 17.4 %. The introduction of Kvalistrol B-70-20 into the rubber mixture leads to an increase in the resistance of rubber to the thermal effects of aggressive media. Compared to the TA-free vulcanizate, the vulcanizate with Kvalistrol B-70-20 exhibits a smaller decrease in physical and mechanical properties after thermal aging in air by 34.0 % and after exposure to SZHR-1 by 29.2 %.

As a result of the investigation, it is found that the use of technological additives improves the plastoelastic and rheometric properties of the rubber mixture based on SKN 4055 and Therban 3406 caoutchoucs. The vulcanizate with TA Kvalistrol B-70-20 has improved physical and mechanical properties and exhibits their least changes after thermal aging in air and in SZHR-1. Thus, it is recommended to use Kvalistrol B-70-20 as a technological additive to manufacture heat-resistant rubber sealing elements.

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