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The properties of rubber based on a combination of butadiene nitrile NBR 4045 and halobutyl CIIR and BIIR caoutchoucs

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ABSTRACT

The influence of chlorinated butyl rubber (CIIR) and bromobutyl rubber (BIIR) in combination with nitrile butadiene rubber NBR 4045 on the rheometric characteristics of the rubber compound, physico-mechanical, performance and dynamic properties of rubber is examinated. Along with rubber, the rubber compound contained a vulcanizing agent (sulfur), vulcanization accelerators (2,2′-dibenzthiazole disulfide, diphenylguanidine), vulcanization activators (zinc white, stearic acid), stabilizer (naphtham-2), softeners (rosin, SMPlast resin, bitumen petroleum, industrial oil I-12A), fillers (carbon blacks P 514 and P 803, natural chalk, trans-polynorbornene) and other ingredients. It has been established that the nature of halobutyl rubbers in combination with NBR 4045 rubber has virtually no effect on the maximum and minimum torques, and BIIR promotes a higher rate of vulcanization of the rubber mixture. Vulcanizates containing combinations of NBR 4045 rubber with halobutyl rubbers are characterized by almost identical physical and mechanical properties and, after exposure to sea water, their masses change slightly. Vulcanizate based on a combination of rubbers NBR 4045: BIIR = 75:25 parts per hundred parts of rubber (phr) has the least changes in physical and mechanical properties in sea water and advanced dynamic properties.

KEYWORDS

physico-mechanical performance and dynamic properties • butadiene-nitrile rubber • halobutyl rubber vulcanized rubber • rheometric •

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Introduction

It is known [1–6] that vulcanized rubber, due to its elastic elastic structure, has higher dynamic properties compared to other materials. To improve the dynamic (vibration damping) properties of rubbers, special ingredients are introduced into them (for example, diatomite [7], various grades of carbon black N 110, N 330, N 550, and N 990 [8], graphene nanoplatelets [9], zeolite [10], organic montmorillonite [11], silicon dioxide Silica Perkasil KS-408 [12], organically modified nanoclay Cloisite 30B as a nanoscale anisotropic additive in combination with carbon black [13]. In [14–16], *trans*-polynorbornene [14,15] and various dispersed fillers (diatomites NDP-D-400 and NDP-230, microquartz and magnesium hydrosilicate) [16] were used as such ingredients. In [14,15], it was shown the prospects of using *trans*-polynorbornene as a functional ingredient of targeted action for a rubber mixture based on general rubbers (butadiene-methylstyrene SKMS-30 ARK, butadiene SKD and isoprene SKI-3) and special (butadiene-nitrile NBR 6280) rubbers for the manufacture of gaskets for rail fastenings. Using the method of dynamic mechanical analysis, it was established that the introduction of trans-polynorbornene into the rubber mixture helps to improve the vibration-damping properties of vulcanizates. In [16], the influence of dispersed fillers on the dynamic characteristics of rubber based on general and special purpose rubbers for railway under-rail pads was studied. It has been shown that rubber containing diatomite NDP-D-400 has increased damping properties.

In [17–26], it was shown that the use of combinations of rubbers of different nature (nitrile butadiene [17], butadiene rubber and ethylene vinyl acetate [18], siloxane rubber [19], urethane rubber and epoxy resin [20], natural rubber and epoxidized natural rubber [21], natural and nitrile butadiene rubbers [22], nitrile butadiene rubber and polyvinyl chloride [23], natural and styrene butadiene rubbers [24], chlorobutyl rubber [25], ethylene propylene diene and epoxidized natural rubbers [26]) is one of the promising ways of creating rubbers with improved dynamic properties. In [27,28], it is shown that the use of a combination of rubbers of different polarities (polar butadiene-nitrile NBR 4065 and non-polar butadiene-methylstyrene SKMS-30ARK and butyl rubber BK-1675) with the addition of *trans*-polynorbornene, sevilene 11808-340 [27] and polyisobutylene P-200 or sevilene 11808-340 [28] leads to an increase in the dynamic parameters of rubbers for products operating under conditions of exposure to sea water. In this regard, the purpose of the work was to study the influence of a combination of halobutyl caoutchoucs (chlorinated butyl rubber (CIIR) and bromobutyl rubber (BIIR)) with butadiene-nitrile rubber NBR 4045 on the properties of rubber used to manufacture products used in sea water. To achieve this goal, the following tasks were solved: rheometric characteristics of a rubber compound containing different combinations of rubbers were studied, physico-mechanical, performance and dynamic properties of vulcanizates obtained on the basis of this rubber compound were determined and analyzed.

Materials and Method

The rubber compound based on CIIR and BIIR with a Mooney viscosity ML_{1+8} (125 °C) of 39 and 32, mass fraction of chlorine (bromine) of 1.20 and 1.74 %, respectively (Nizhnekamskneftekhim, Russia), in combination with nitrile butadiene rubber NBR 4045 with a mass fraction of acrylic acid nitrile 36-40 wt. %, Mooney viscosity ML_{1+4} (100 °C) 42–48 (Sibur, Russia) contained the following ingredients: vulcanizing agent (sulfur (Kaspiygaz, Russia)), vulcanization accelerators (2,2′-dibenzthiazole disulfide Vulkacit DM (Lanxess, Germany), diphenylguanidine (Khimprom, Russia)), vulcanization activators (zinc oxide (Empils-zinc, Russia), stearic acid (RossPolymer, Russia)), antioxidant (naphtham-2 (Bina Grupp, Russia)), softeners (rosin (Sibles, Russia), SMPlast resin (Region-NK, Russia), petroleum bitumen (TAIF-NK, Russia), factis (Alphaplastic, Russia) and industrial oil I-12A (Necton Sea, Russia)), fillers (carbon black P 514 (Ivanovskii Tekhuglerod i Rezina, Russia), carbon black P 803 (Ivanovskii Tekhuglerod i Rezina, Russia), natural chalk (Melstrom, Russia), trans-polynorbornene (Astron Industriebeteiligungs GmbH, Austria)). The rubber mixture was prepared on laboratory rollers LB 320 160/160 (Polimermash group, Russia) at a roller temperature of 60–70 °C for 25 min. The rheometric characteristics of the rubber compound were studied on a MDR 3000 Basic rheometer from Mon Tech (Buchen, Germany) at 150 °C for 30 min in accordance with ASTM D2084-79. Standard samples for determining physico-mechanical properties were vulcanized at a temperature of 150 °C for 30 min in a P-V-100-3RT-2-

PCD vulcanization press (Pan Stone Hydraulic Industries Co., Ltd., Taiwan). The main characteristics of vulcanizates were determined according to the standards in force in the rubber industry: elastic strength properties were determined according to Russian State Standard GOST 270-75 "Rubber. Method of the determination elastic and tensile stress-strain properties", Shore A hardness was measured in accordance with Russian State Standard GOST 263-75 "Rubber. Method for the determination of Shore A hardness", tear resistance was found according to Russian State Standard GOST 262-93 "Rubber, vulcanized. Determination of tear strength (trouser, angle and crescent test pieces)", the change in conditional tensile strength, relative elongation at break and hardness after exposure to sea water (8 % aqueous solution of sea salt) was determined according to Russian State Standard GOST 9.030-74 (method B) "Unified system of corrosion and ageing protection. Vulcanized rubbers. Method of testing resistance to attack by corrosive media in limp state", the change in mass after exposure to sea water was found according to Russian State Standard GOST 9.030-74 (method A) "Unified system of corrosion and ageing protection. Vulcanized rubbers. Method of testing resistance to attack by corrosive media in limp state". The dynamic parameters (mechanical loss tangent) of vulcanizates of various variants of the rubber compound were studied at a temperature of 30 °C on a Metravib VHF 104 dynamic mechanical analyzer (France) in the "tension-compression" deformation mode (degree of deformation 0.01%) and a frequency of 1000 Hz.

Results and Discussion

The effectiveness of using the combination of SKN-4045 with CIIR and BIIR was assessed by the rheometric properties of the rubber compound, physico-mechanical properties, and changes in these indicators after exposure to sea water, as well as the dynamic properties of vulcanizates. Variants of the studied rubber compound containing NBR 4045, CIIR and BIIR in various proportions are shown in Table 1. Figure 1 and Table 1 show the obtained vulcanization curves and the following values of the rheometric parameters of the rubber compound respectively.

Table 1. Variants and rheometric properties of the rubber compound

Caoutchoucs	Variants of the rubber compound						
	1	2	3	4	5	6	7
CIIR, phr*	25.0	–	20.0	–	–	100.0	–
BIIR, phr	–	25.0	–	20.0	–	–	100.0
NBR 4045, phr	75.0	75.0	80.0	80.0	100.0	–	–
Rheometric properties of the rubber compound at 150 °C							
M_H, dN·m	9.00	8.99	8.46	8.28	6.37	5.43	5.05
M_L, dN·m	0.83	0.87	0.78	0.80	0.70	1.01	0.94
t_s, min	3.15	2.76	3.24	2.87	5.37	8.09	5.78
t_{90}, min	20.04	18.11	19.79	18.31	22.39	22.94	15.64

Note: M_H is the maximum torque; M_L is the minimum torque; t_s is the curing scorch time; t_{90} is the optimum curing time.
*phr (parts per hundred parts of rubber)

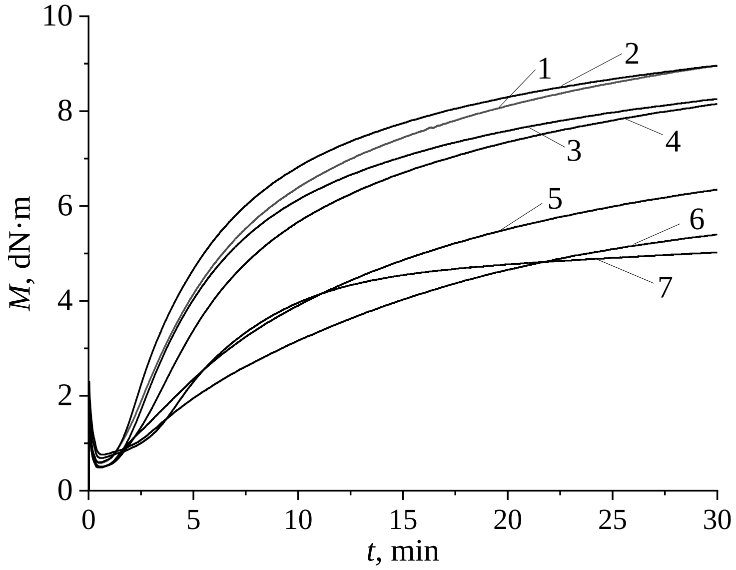

Fig. 1. Rubber compound vulcanization curves
(curve numbers correspond to rubber compound variant numbers)

As can be seen from Fig. 1 and Table 1, replacing CIIR with BIIR (variants 1–4) has virtually no effect on the maximum and minimum torques of the rubber compound. At the same time, BIIR helps to reduce the start and optimum times of vulcanization of the rubber compound. Such a change in the curing scorch time and optimum curing time is due to the increased reactivity of bromobutyl rubber due to the lower energy of the C–Br bond compared to the C–Cl bond and the higher rate of vulcanization of the rubber compound containing bromobutyl rubber [29–32]. Variants 5–7 of the rubber compound are characterized by lower values of the maximum torque and longer times for the onset and optimum of vulcanization compared to the rubber compound options containing combinations of nitrile-butadiene and halobutyl rubbers.

Table 2. Physico-mechanical and performance properties of vulcanizates

Indicators	Variants of the rubber compound						
	1	2	3	4	5	6	7
Physico-mechanical properties of vulcanizates							
f_p, MPa	5.4±0.2	5.6±0.2	4.2±0.2	4.4±0.2	3.8±0.2	4.0±0.2	3.7±0.1
ε_p, %	510±20	510±18	420±16	410±15	490±19	500±21	520±20
H, units Shore A	60±1	63±1	64±1	68±1	51±1	57±1	53±1
B, kN/m	29±2	30±2	28±2	26±2	24±2	22±2	22±2
Changes in the physical and mechanical properties of vulcanizates after exposure to sea water at 23 °C for 24							
Δf_p, %	+6.2±0.2	+4.9±0.2	+5.2±0.2	+5.4±0.2	+10.8±0.4	-14.4±0.6	-16.2±0.6
$\Delta \varepsilon_p$, %	-2.6±0.1	-1.9±0.1	-5.8±0.2	-6.3±0.2	-2.0±0.1	-10.2±0.4	-9.6±0.4
Δ*H*, units Shore A	+3±1	+2±1	+2±1	+3±1	+6±1	+6±1	+7±1
Change in the mass of vulcanizates after exposure to sea water at 23 °C for 7 days							
Δ*m*, %	0.68±0.01	0.64±0.01	0.62±0.01	0.59±0.01	0.15±0.01	0.43±0.01	0.39±0.01
Note: f_p is the tensile strength; ε_p is the elongation at break; *H* is the hardness; *B* is the tear resistance; Δf_p, $\Delta \varepsilon_p$, Δ*m* are relative changes in tensile strength, elongation at break and mass after exposure of rubber to sea water; ΔH is the difference in hardness after and before aging in sea water.							

The results of studies of physico-mechanical properties (Table 2) show that vulcanizates containing combinations of NBR 4045 rubber and halobutyl rubbers are characterized by almost identical elastic-strength properties, hardness and tear resistance (variants 1-4).

Moreover, an increase in the proportion of halobutyl rubbers in combination with NBR 4045 leads to an increase in the elastic-strength properties of rubber. Vulcanizates of variants 5–7, containing separately only each of the rubbers used, have lower physical and mechanical properties. It also follows from Table 2 that the smallest change in elastic-strength properties after daily exposure to sea water is characterized by rubber that includes the rubber combination SKN-4045: BIIR = 75:25 phr. The mass of vulcanizates based on a combination of nitrile butadiene and halobutyl rubbers changes slightly after a week's exposure to sea water.

Subsequently, the values of the mechanical loss tangent tanδ were determined for different variants of vulcanizates (see Fig. 2).

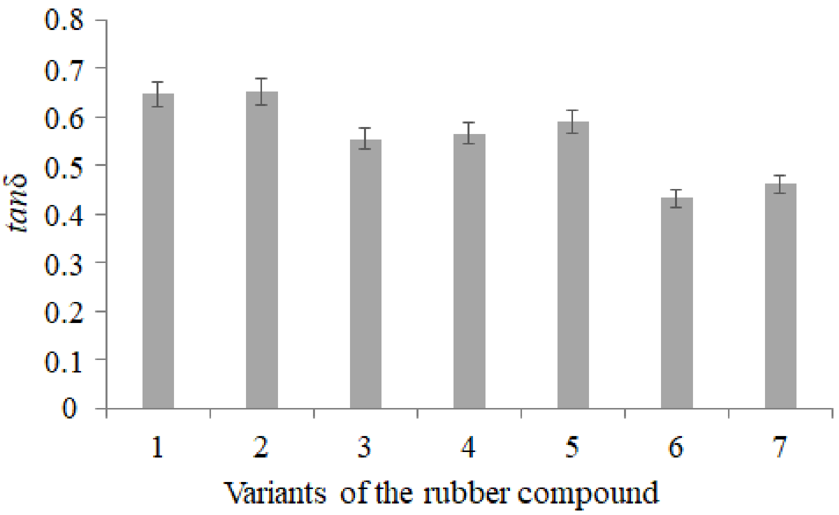

Fig. 2. The mechanical loss factor of vulcanizates

According to [33–36], materials (polymers) with high *tan*δ values have good dynamic properties. As can be seen from Fig. 2, an increase in the content of halobutyl rubbers leads to an increase in *tan*δ. Vulcanizates of options 1 and 2 have almost equally high *tan*δ values, and, therefore, they are characterized by better dynamic properties.

Conclusions

1. The effect of halobutyl rubbers (CIIR and BIIR) in combination with nitrile butadiene rubber NBR 4045 on the rheometric properties of the rubber compound, physico-mechanical, performance and dynamic properties of the vulcanizates was studied.
2. It was shown that equal-mass replacement of CIIR with BIIR has virtually no effect on the rheometric characteristics (maximum and minimum torques) of the rubber compound. At the same time, BIIR helps to reduce the onset and optimum times of vulcanization (higher vulcanization rate) of the rubber compound.

3. It was established that the vulcanizate of the rubber compound based on a combination of NBR 4045:BIIR rubbers at a ratio of 75:25 phr has increased physico-mechanical properties; their smallest changes after exposure to sea water; better dynamic properties (high value of the mechanical loss factor).

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