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The influence of brombutyl and divinylstyrene caoutchoucs, sevilen on the properties of seawater-resistant rubber

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ABSTRACT

The effect of bromobutyl caoutchouc BBK-232, sevilene 11808-340, divinylstyrene caoutchoucs DSSK-628V and SKMS-30ARK on the rheometric characteristics of the rubber mixture, physical, mechanical, operational and dynamic properties of rubber used for the manufacture of seawater-resistant products are studied. Along with the listed ingredients, the rubber mixture contained a vulcanizing agent - sulfur; vulcanization accelerators - 2,2'-dibenzothiazole disulfide, diphenylguanidine; vulcanization activators - zinc white, stearin; antioxidant - naphtham-2; fillers - technical carbons P 514 and P 803, natural chalk; polymer filler - trans-polynorbornene; softeners - rosin, petroleum polymer resin "Shinplast", factice; plasticizer - petroleum bitumen. It was found that rubber based on DSSK-628V and BBK-232 couutchoucs with their mass ratio of 75:25 not containing sevilen 11808-340 has better rheometric, physical-mechanical, dynamic properties and resistance to sea water.

KEYWORDS

physical-mechanical, operational and dynamic properties • bromobutyl caoutchouc • sevilen • rubber divinylstyrene caoutchous • rheometric • sea water

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Introduction

In industrial production, rubber is one of the widely used polymeric materials that underlie the manufacture of products used in various fields of activity, including products with high dynamic properties. Special requirements are imposed on such rubbers, since they must have good dynamic properties and be resistant to the effects of sea water. Such rubbers are usually prepared on the basis of general-purpose and special-purpose caoutchoucs [1–3]. In [4–14], it was established that the use of combinations of caoutchoucs of different nature is one of the promising ways to create rubbers with improved dynamic properties. In [15,16], it was shown that rubbers based on combinations of caoutchoucs of different polarity (polar butadiene-nitrile SKN 4065 and non-polar butadiene-methylstyrene SKMS-30ARK and butyl rubber BK-1675) with additives of trans-polynorbornene, sevilene 11808-340 [15], polyisobutylene P-200 with sevilene 11808-340 [16], as well as rubbers containing polyisobutylene [17–20], sevilene [21–27] and based on halobutyl caoutchoucs [28–33], are characterized by fairly high dynamic properties. In this regard, the aim of this work is to study the influence of bromobutyl caoutchouc BBK-232 and sevilene 11808-340, as well as divinylstyrene caoutchoucs DSSK-628V and SKMS-30ARK on the properties of rubber used for the manufacture of products used in sea water.

Materials and Method

The rubber mixture under study included the following caoutchoucs and ingredients: SKMS-30 ARK, DSSK-628V and BBK-232 caoutchoucs; sevilen 11808-340; vulcanizing agent - sulfur; vulcanization accelerators - 2,2′-dibenzothiazole disulfide, diphenylguanidine; vulcanization activators - zinc white, stearic acid; antioxidant - naphtham-2; fillers - carbon black P 514, carbon black P 803, natural chalk; polymer filler - trans-polynorbornene; softeners - rosin, Shinplast petroleum polymer resin, factis, petroleum bitumen. The rubber mixture was prepared on a laboratory mill LB 320 160/160 at a roll temperature of 60–70 °C for 25 min. The rheometric characteristics of the rubber mixture were studied on a rheometer MDR 3000 Basic by Mon Tech at 150 °C for 30 min in accordance with ASTM D2084-79. Standard samples for determining the physical and mechanical properties were vulcanized at a temperature of 150 °C for 30 min in a vulcanization press type P-V-100-3RT-2-PCD. The main characteristics of the vulcanizates were determined in accordance with the standards current in the rubber industry: elastic-strength properties were determined according to GOST 270-75; Shore A hardness - according to GOST 263-75; tear resistance - according to GOST 262-93; change in conventional tensile strength, relative elongation at break and hardness after exposure to sea water (8 % aqueous solution of sea salt) - according to GOST 9.030-74 (method B); change in mass after exposure to sea water - according to GOST 9.030-74 (method A). Dynamic parameters (tangent of the angle of mechanical losses) of vulcanizates of different variants of rubber compound were studied at a temperature of 30 °C on a Metravib VHF 104 dynamic mechanical analyzer in the "tension-compression" deformation mode (degree of deformation 0.01 %) and a frequency of 1000 Hz.

Results and Discussion

The efficiency of using bromobutyl caoutchoc BBK-232, sevilen 11808-340, divinylstyrene caoutchocs DSSK-628V and SKMS-30ARK was assessed by the kinetic (rheometric) properties of the rubber mixture, physical and mechanical properties and changes in these parameters after exposure to sea water, as well as the dynamic properties of the vulcanizates. The variants of the studied rubber mixture containing caoutchocs SKN-4045, DSSK-628V, BBK-232 and sevilen in different quantities are given in Table 1. Figure 1 shows the vulcanization curves for different rubber compound variants.

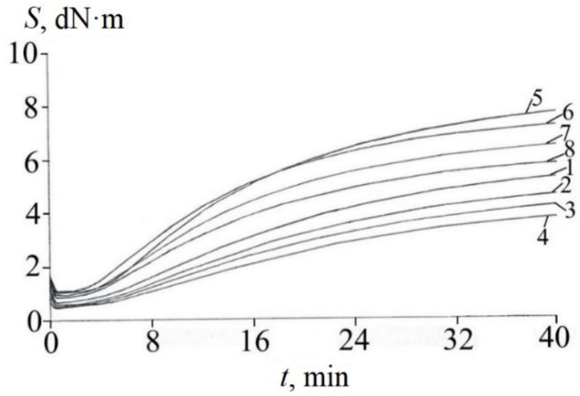

Fig. 1. Vulcanization curves of rubber compound (curve numbers correspond to variant numbers)

Table 1. Variants and rheometric properties of rubber mixture

Caoutchoucs, sevilen, indicators	Variants							
	1	2	3	4	5	6	7	8
BBK-232, mass parts	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
SKMS-30ARK, mass parts	75.0	75.0	75.0	75.0	-	-	-	-
DSSK-628V, mass parts	-	-	-	-	75.0	75.0	75.0	75.0
Sevilen 11808-340, mass parts	-	5.0	10.0	15.0	-	5.0	10.0	15.0
Rheometric properties								
S_{max}, dN·m	5.27	4.62	4.21	3.80	7.69	7.20	6.46	5.79
S_{min}, dN·m	0.86	0.74	0.69	0.63	1.33	1.34	1.18	1.09
t_s, min	13.46	15.31	16.91	19.48	9.13	8.38	9.54	10.71
t_{90}, min	31.09	31.41	31.60	32.21	29.75	27.64	28.77	29.18

Note: S_{max} and S_{min} are the maximum and minimum torques; t_s and t_{90} are the start and optimum times of vulcanization.

Table 1 shows the results of studies of rheometric parameters for different variants of the rubber compound, as shown in Fig. 1. As can be seen, an increase in the content of sevilene 11808-340 in variants 1–4 of the rubber compound based on SKMS-30ARK caoutchouc and variants 5–8 of the rubber compound based on DSSK-628V caoutchouc leads to a decrease in the maximum and minimum torques, while the times of the onset and achievement of the vulcanization optimum increase. Equal-mass replacement of SKMS-30ARK (variants 1–4) with DSSK-628V (variants 5–8) leads to an improvement in the rheometric, and, consequently, technological properties of the rubber compound.

The results of studies of the physical and mechanical properties of the vulcanizates of the rubber compound are shown in Table 2. It follows from the data in Table 2 that with equal-mass replacement of SKMS-30ARK with DSSK-628V, there is an increase in the conventional tensile strength, hardness and tear resistance, a decrease in the values of relative elongation at break and rebound elasticity of vulcanizates. An increase in the content of sevilen leads to a decrease in the values of conventional tensile strength, hardness and tear resistance, an increase in the values of relative elongation at break and rebound elasticity of vulcanizates. The best physical and mechanical properties are possessed by the vulcanizate of variant 5 of the rubber mixture containing a combination of DSSK-628V and BBK-232 caoutchoucs in a mass ratio of 75:25.

The results of the study of rubber resistance to the effects of sea water are also presented in Table 2, from which it follows: changes of the physical and mechanical properties and the degree of swelling of vulcanizates based on DSSK-628V caoutchouc are less than those based on SKMS-30ARK caoutchouc; an increase in the content of sevilene leads to an increase in these indicators of vulcanizates; which are generally small and do not exceed 6 % for physical and mechanical indicators and 0.6 % for the degree of swelling. From the results of studies of the dynamic properties of vulcanizates presented in Table 2 it follows: vulcanizates based on DSSK-628 caoutchouc, in comparison with vulcanizates based on SKMS-30ARK caoutchouc, have higher values of the tangent of the angle of mechanical losses and lower values of the modulus of elasticity; the introduction of sevilene leads to a decrease in the tangent of the angle of mechanical losses and an increase in the modulus of elasticity; The best dynamic properties are possessed by the vulcanizate of variant 5 of the rubber mixture, based on DSSK-628V and BBK-232 caoutchoucs with their mass ratio of 75:25.

Table 2. Physical, mechanical and dynamic properties of vulcanizates

Indicators	Variants							
	1	2	3	4	5	6	7	8
f_p, MPa	5.2	5.0	4.7	4.3	5.0	5.2	5.1	4.9
ε_p, %	560	580	590	620	400	410	420	440
H, units Shore A	54	52	51	50	55	56	54	52
B, kN/m	27	26	25	22	25	32	29	26
S, %	31	30	29	27	16	21	20	19
Changes in physical and mechanical properties of vulcanizates after exposure to sea water at 23°C for 30 days								
Δf_p, %	+1.9	+2	+2.4	+2.6	+1.7	+1.6	+1.9	+2.2
$\Delta\varepsilon_p$, %	-3.6	-3.9	-4.5	-5.3	-3.2	-3.5	-4.7	-5.6
ΔH, units Shore A	+4	+3	+3	+1	+4	+4	+3	+2
Degree of swelling of vulcanizates after exposure to an 8 % aqueous solution of sea salt at 23 °C for 7 days								
Δm, %	0.50	0.46	0.53	0.54	0.26	0.24	0.27	0.30
Dynamic properties of vulcanizates of rubber compound								
$E'\cdot10^{-7}$, Pa	2.18	2.26	2.25	2.14	2.32	2.78	2.81	2.8
tgδ	0.304	0.292	0.284	0.282	0.555	0.476	0.454	0.442

Note: f_p is a conventional tensile strength, ε_p is a relative elongation at break, *H* is hardness, *B* is a tear resistance, Δf_p, $\Delta\varepsilon_p$, Δm are relative changes in conventional tensile strength, relative elongation at break and weight after keeping rubber in sea water, ΔH is a difference in rubber hardness before and after keeping in sea water, E' is the elastic modulus, tgδ is a tangent of mechanical loss angle.

Conclusions

The influence of bromobutyl caoutchouc BBK-232, sevilen 11808-340, divinylstyrene caoutchoucs SKMS-30ARK and DSSK-628V on the rheometric, physical-mechanical, operational and dynamic properties of rubber was studied. It was found that the best rheometric, physical-mechanical, dynamic properties and stability in sea water are possessed by rubber based on a combination of caoutchoucs DSSK-628V (75.0 parts by weight) and BBK-232 (25.0 parts by weight), not containing sevilen 11808-340.

CRediT authorship contribution statement

Evgeniy N. Egorov iD Sc: writing – review & editing, writing – original draft, conceptualization, investigation; **Nikolay I. Kol'tsov** iD Sc: writing – review & editing, writing – original draft, conceptualization, supervision, data curation.

Conflict of interest

The authors declare that they have no conflict of interest.

References

1. Nafeesa MS, Azura AR. The Influence of Different Types of Rubber on Curing Behaviour and Dynamic Properties of Rubber Compound. *Journal of Physics: Conference Series*. 2018;1082: 012010.
2. Nobari Azar FA, Karimzadeh Naghshineh A, Sen M. Preparation and characterization of natural rubber–based new elastomers for high-damping base isolation systems. *Journal of Elastomers and Plastics*. 2022;54(6): 959–974.
3. Lei T, Zhang Y-W, Kuang D-L, Yang Y-R. Preparation and Properties of Rubber Blends for High-Damping-Isolation Bearings. *Polymers*. 2019;11(8): 1374.
4. Qin R, Huang R, Lu X. Use of gradient laminating to prepare NR/ENR composites with excellent damping performance. *Materials and Design*. 2018; 149: 43–50.
5. Zhao X, Yang J, Zhao D, Lu Y, Wang W, Zhang L, Nishi T. Natural rubber/nitrile butadiene rubber/hindered phenol composites with high-damping properties. *International Journal of Smart and Nano Materials*. 2015;6(4): 239–250.
6. Dharmaraj MM, Chakraborty BC, Begum S. The effect of graphene and nanoclay on properties of nitrile rubber/polyvinyl chloride blend with a potential approach in shock and vibration damping applications. *Iranian Polymer Journal*. 2022;31: 1129–1145.
7. Akyüz S, Darı ME, Esiyok YE, Ermeydan MA. Effects of NR/SBR ratio on mechanical properties and artificial mechanical performance of anti-vibration bushings. *Iranian Polymer Journal*. 2021;30: 1317–1328.
8. Lu X, Huang R, Li H, Long J, Jiang Z. Preparation of an elastomer with broad damping temperature range based on EPDM/ENR blend. *Journal of Elastomers and Plastics*. 2017;49(8): 758–773.
9. Egorov EN, Kol'tsov NI. Influence of glass fibers on the physico-mechanical and performance properties of rubber based on general and special purpose caoutchoucs. *Materials Physics and Mechanics*. 2024;52(1): 126–131.
10. Egorov EN, Sandalov SI, Kol'tsov NI. Study of the influence of dispersed fillers on properties of rubber for gaskets of rail fastening. *Materials Physics and Mechanics*. 2023;51(6): 119–126.
11. Nabil H, Ismail H, Ratnam CT. (2014). Simultaneous Enhancement of Mechanical and Dynamic Mechanical Properties of Natural Rubber/Recycled Ethylene-Propylene-Diene Rubber Blends by Electron Beam Irradiation. *International Journal of Polymer Analysis and Characterization*. 2014;19(3): 272–285.
12. Nabil H, Ismail, H, Azura AR. Optimization of accelerators on curing characteristics, tensile, and dynamic mechanical properties of (natural rubber)/(recycled ethylene-propylene-diene-monomer) blends. *Journal of Vinyl and Additive Technology*. 2014;21(2): 79–88.
13. Marzocca AJ, Mansilla MA. Dynamic mechanical properties in natural rubber/styrene-butadiene rubber blends: The local strain behavior in the glass transition region. *Polymer Engineering and Science*. 2023;63(5): 1471–1480.
14. Egorov EN, Salomatina EV, Vassilyev VR, Bannov AG, Sandalov SI. Effect of Polynorbornene on Physico-Mechanical, Dynamic, and Dielectric Properties of Vulcanizates Based on Isoprene, α-Methylstyrene-Butadiene, and Nitrile-Butadiene Rubbers for Rail Fasteners Pads. *Journal of Composites Science*. 2023;7(8): 334.
15. Egorov EN, Ushmarin NF, Sandalov SI, Kol'tsov NI. Research of operational and dynamic properties of rubber for products working in sea water. *ChemChemTech*. 2020;63(11): 96–102. (In Russian)
16. Egorov EN, Ushmarin NF, Sandalov SI, Kol'tsov NI, Voronchikhin VD. Investigation of the dynamic properties of seawater-resistant rubber. *Journal of Siberian Federal University. Chemistry*. 2021;14(1): 38–44.
17. Egorov EN, Ushmarin NF, Salomatina EV, Matyunin AN. The effect of polyisobutylene on physical-mechanical, operational, dielectric and dynamic properties of rubber for laying rail fasteners. *ChemChemTech*. 2022;65(5): 94–102. (In Russian)
18. Xia L, Li C, Zhang X, Wang J, Wu H, Guo S. Effect of chain length of polyisobutylene oligomers on the molecular motion modes of butyl rubber: Damping property. *Polymer*. 2018;141: 70–78.
19. Wu J, Huang G, Wang X, He X, Zheng J. Detecting different modes of molecular motion in polyisobutylene and chlorinated butyl rubber by using dielectric probes. *Soft Matter*. 2011;7(19): 9224–9230.
20. Giller CB, Roland CM. Strength Enhancement in Miscible Blends of Butyl Rubber and Polyisobutylene. *Macromolecules*. 2013;46(7): 2818–2822.
21. He X, Qu M, Shi X. Damping properties of ethylene-vinyl acetate rubber/polylactic acid blends. *Journal of Materials Science and Chemical Engineering*. 2016;4(3): 15.
22. Yu Z, Wang C, Zhang X, Zhao Y, Wen S, Zhang ZX. Controlled damping ethylene-vinyl acetate copolymer/styrene ethylene butylene styrene foam in wide temperature range prepared by supercritical nitrogen. *Polymer Engineering and Science*. 2023;63(10): 3429–3432.

23. Raksaksri L, Chuayjuljit S, Chaiwutthinan P, Boonmahitthisud A. Vinyl acetate ethylene copolymer and nanosilica reinforced epoxidized natural rubber: Effects of sulfur curing systems on cure characteristics, tensile properties, thermal stability, dynamic mechanical properties and oil resistance. *Journal of Vinyl and Additive Technology*. 2019;25(s2): E28–E38.
24. Nadal A, Segura J, Juliá E, Gadea JM, Montava I. Evaluation of acoustic and dynamic behaviour of ethylene vinyl acetate panels. *Materials Science and Engineering Technology*. 2019;50(1): 14–24.
25. Singla RK, Zafar MT, Maiti SN, Ghosh AK. Physical blends of PLA with high vinyl acetate containing EVA and their rheological, thermo-mechanical and morphological responses. *Polymer Testing*. 2017;63: 398–406.
26. Zia-ul-Haq M, Wu J, Haq ZU, Peng Z, Zhang Y. Enhanced mechanical, thermal performance and kinetics of thermal degradation of silicone rubber/ethylene–vinyl acetate copolymer/halloysite nanoclay nanocomposites compatibilized by ethylene–acrylic acid copolymer. *Journal of Polymer Research*. 2023;30: 306.
27. Sadeghi-Askari A, Tavakoli M. Optimization of mechanical and dynamic-mechanical properties of electron beam irradiation of reclaimed tire rubber/poly (ethylene-co-vinyl acetate) nanocomposite by design of experiment. *Iranian Polymer Journal*. 2023;32: 417–431.
28. Cao R, Zhao X, Zhao X, Wu X, Li X, Zhang L. Bromination modification of butyl rubber and its structure, properties and application. *Industrial and Engineering Chemistry Research*. 2019;58(36): 16645–16653.
29. Chen B, Dai J, Song T, Guan Q. Research and Development of High-Performance High-Damping Rubber Materials for High-Damping Rubber Isolation Bearings: A Review. *Polymers*. 2022;14(12): 2427.
30. Behera PK, Kumar A, Mohanty S, Gupta VK. Overview on Post-Polymerization Functionalization of Butyl Rubber and Properties. *Industrial and Engineering Chemistry Research*. 2022;61(46): 16910–16923.
31. Chen J, Wang J, Li S, Xiang K, Song S. Pyridine terminated polyurethane dendrimer/chlorinated butyl rubber nanocomposites with excellent mechanical and damping properties. *Chinese Journal of Chemical Engineering*. 2023;53: 211–221
32. Pan Y, Wang J, Yang S. Preparation of novel damping layered silicates and its application in chlorinated butyl rubber (CIIR) composites. *Polymer-Plastics Technology and Materials*. 2019;59(4): 385–397.
33. Liu Z, Wang K, Wu Y, Zhang H, Hao T, Qi H, Liu B. A Novel Method to Characterize the Damping Capacity of EPDM/CIIR Blends Using Vibrating Rubber Balls. *Polymers*. 2024;16(11): 1447.