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Zh. S. Shashok, E. P. Uss, A. V. Kasperovich
Belarusian State Technological University

RESEARCH OF INFLUENCE OF VARIOUS CARBON BLACK TYPES ON TECHNICAL PROPERTIES OF RUBBERS

The influence of carbon black types P-803 and S800 on elastic, strength and deformation properties of rubbers intended for production of molded rubber products has been studied. As objects of research the rubber mixtures based on combination of general purpose rubber SRI-3+SRD and special purpose rubber BNRS-18AMN were used. The studies of chemical composition of the surface of various carbon black types revealed that the surface of carbon black type S800 contains a large amount of sulfur and a minimal amount of oxygen, the presence of which may influence the curing process, and consequently on the elastic and mechanical properties of rubbers. It was established that P-803 carbon black type substitution by S800 type leads to increase in strength characteristics, Shore A hardness and to decrease in relative compression set of vulcanizates based on BNRS-18AMN. In rubber based on combination of rubbers SRI-3+SRD with carbon black type S800 revealed decrease resistance against growth tears and increase Shore A hardness of vulcanizates, compared with samples of rubber with carbon black type P-803. The character of changes in rubber properties may be due to the influence of the carbon black type on the structure and density of curing grid.

Key words: rubber, elastomeric composition, filler, technical carbon, physical and mechanical characteristics.

Introduction. Higher requirements for the operational properties of elastomer materials and expanding their application determine the need to find new ways to produce elastomeric materials and products based on them. Fillers and especially, carbon black, which is widely used in rubber, have greater impact on changing properties of elastomeric materials.

Filled elastomer composition is microheterogeneous, heterophase system, basic filler is carbon black. The addition of fillers improves the physical-mechanical and technological properties of polymers and increases the volume of material, i.e. decreases its cost. The efficiency of filler is determined by many factors: particle shape and size, feature of adsorption interaction at the interface between polymer filler phases, amount of filler and others [1].

Regarding this, proper selection of carbon black type that meets customer requirements determines the regulation of important processing properties of rubber compounds and ensures properties of complex operational properties of finished articles.

Main part. The aim of the work was to study the effect of different types of carbon black on the technical properties of elastomeric materials based on special purpose rubber BNKS-18AMN and combination of general purpose rubber SKI-3 + + SKD to manufacture molded rubber articles. These rubber compounds were added to various types of carbon black in equal amounts: industrial type P-803 and investigated OMCARB ™ S800 (manufacturer Ltd. "Omsktehuglerod").

Carbon black type P-803 produced by a furnace method with thermo-oxidative decomposition of liquid hydrocarbon raw material shows a low dispersion and average structure properties. Technical type of carbon filler S800 is modified to reduce the curing speed; it has high purity and good dispersion in rubber compounds; it also imparts high electrical resistance and excellent surface smoothness to rubber articles.

The chemical composition and structure of carbon black surface of various types was investigated by the scanning electron microscope JSM-5610 Jeol LV. Determination of elastic-strength characteristics of rubber at tensile strength was carried out according to GOST (National Standard) 270-75. Testing rubber to resist crack propagation under multiple bending was performed on samples with a puncture at 70° at Con De Mattia Flex Testing according to GOST (National Standard) 9983-74.

The relative residual compression deformation of rubber after aging for 24 hours at 100°C was determined according to GOST (National Standard) 9.029-74. Hardness Shore A of vulcanizate was measured at DIGI-TEST Automatic device according to GOST (National Standard) 263-75.

The chemical composition of carbon black can vary greatly depending on the conditions of its production and the hydrocarbons type. The main chemical components of carbon particles are carbon, oxygen and hydrogen [2].

The surface functional groups of carbon black can have both positive and negative effects on properties of rubbers. Thus, a large number of carboxylic acid groups results in slow curing of rubber compounds. Regarding this, carbon black for rubber manufacture specifies the pH standard for aqueous solution. For coloring carbon types the oxygen-containing groups' availability is not only useful, but necessary. Therefore, to produce the most valuable types of colorant carbon black the dispersed carbon black obtained in the reactor is subjected to further oxidation, including the effects of strong oxidants such as nitric acid, ozone and others [3].

Conventional furnace carbon black, that is not specially treated, has 95–99.5% carbon content, 0.2–0.5% hydrogen, and 0.2–1.3% oxygen. Intentionally oxidized carbon black may contain more than 10% oxygen. There are small amounts of sulfur (0.1–1.0%) and minerals (to 0.5%) in the product [2].

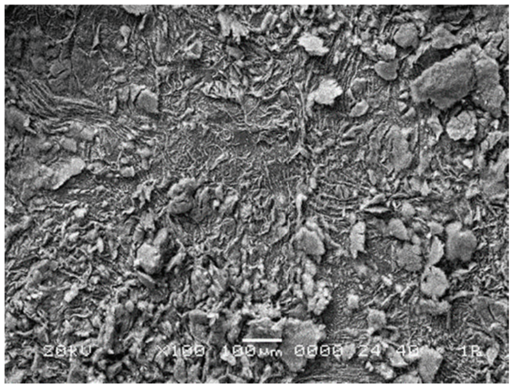
Oxygen and minerals are preferably present in the surface layer. Oxygen binds carbon particles that are formed in the oxidation process and move in the stream of reaction gases; mineral particles may fall on the surface of carbon black from the industrial water used for cooling high temperature gas stream in the production reactor. The amount of oxygen in the product under equal conditions depends on the dispersion of the latter. More dispersed product contains more oxygen. Oxygen is a member of carbonyl, hydroxyl and carboxyl groups of the carbon particles on the surface layer [4].

Sulfur is extracted from raw material and can be presented in the form of elemental sulfur or inorganic sulfate, and organosulfur compounds. Sulfur in carbon black impacts on rubber vulcanization processes and their properties [5]. Therefore, there is feasible sulfur content of standardized specifications for all carbon blacks. The amount of sulfur in the carbon black depends on its absolute content in the feedstock, the carbon black type, and the output [6].

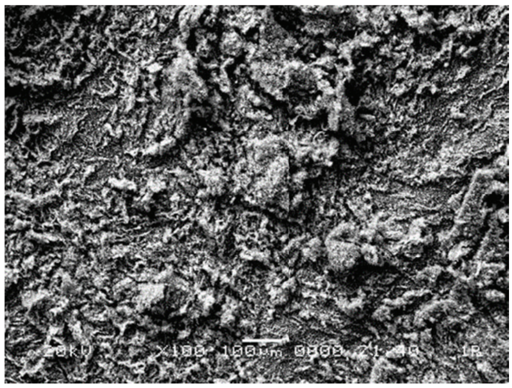
Fig. 1 shows images of surfaces of carbon black types P-803 and S800, respectively.

Table 1 shows the chemical composition of the surface of the carbon black types P-803 and S800.

As it can be seen from the presented data, the surface of carbon black type S800 contains greater amount of sulfur and less oxygen amount if compared to carbon black type P-803. Such differences in the content of components on the surface can be related to the composition constituents, as in the course of preparation carbon black type S800 is deposited on the metal channels, along with sulfur, which is obtained from the raw material and the carbon black P-803 is extracted from the reactor aerosol, which may be further purified by several elements.



a



b

Fig. 1. Electron micrographs of the surfaces of carbon samples:
a – type P-803; *b* – type S800

Table 1

The elemental composition of the surface of the researched carbon black types

Element	The content of the chemical element (%) on the surface of the technical carbon	
	P-803	S800
Oxygen	61.05	38.61
Silicon	2.65	3.91
Sulfur	13.42	32.83
Titan	22.88	24.65

Thus, on the surface of carbon black types P-803 and S800 contains a different amount of sulfur and oxygen elements, which can lead to functionalization of surfaces while contacting the environment. The presence of the filler on the surface functional groups of different nature can influence the kinetics of the process of curing rubber mixtures as well as structure and density of the resulting three-dimensional network of vulcanizate, which in turn will affect the elastic-strength and elastic-dynamic properties of rubber. Thus, increasing oxygen content in the carbon black decreases conventional stress at a given elongation of vulcanizate (oxygen can interact with ingredients of curing system and cause some reduction in the concentration of cross-linking bonds). Tensile strength increases with increase of oxygen content in carbon black. [1] The carboxyl groups cause the acidity of carbon black and the adsorption of bases. This leads to reducing activity of curing accelerators and slows down the curing process. The hydroxyl groups of phenolic compounds in the surface rubbers slow down the aging process [3].

Increased sulfur contents can lead to the formation of additional cross-links, which in turn impacts not only on strength properties of vulcanizates, but also on their hardness and heat production.

In operation, rubber products typically are not subjected to large deformations similar to destructive ones, but in laboratory practice rubber tensile test is widely used, since under these conditions its specific properties are manifested most clearly.

Table 2 shows the results of investigation of elastic-strength characteristics of rubbers.

Table 2

The elastic-strength characteristics of rubbers, containing various carbon black types

Carbon black type	Conventional stress at 100% elongation, MPa	Elongation at break, %	Tensile strength, MPa
Rubber based on SKI-3+SKD			
P-803	1.1	680	18.0
S800	1.1	645	18.0
Rubber based on BNKS-18AMN			
P-803	3.9	275	8.8
S800	4.3	215	11.6

The above data show that the replacement of carbon black type P-803 by type S800 in the rubber composition based on combination of rubbers SKI-3+SKD has no effect on the strength characteristics of the vulcanizates: conventional stress at 100% elongation for the investigated rubbers was 1.1 MPa, tensile strength – 18.0 MPa. Change in elongation at break is within the error range allowed by GOST (National Standard) for this measurement.

The replacement of furnace carbon black of type P-803 by S800 leads to some increase in strength characteristics of vulcanizates based on BNKS-18AMN. Thus, the conventional tensile strength is increased by 24% (for rubber samples of type P-803 – 8.8 MPa, and type S800 – 11.6 MPa) the conventional stress at 100% elongation is increased by 10%. However, it should be noted that this replacement of carbon black is decreased in elongation at break by 28%. Changing the elastic-strength properties of rubber is, probably, due to differences in vulcanizates structures containing different types of carbon black.

Dynamic loading of the material leads to changes in its physical and mechanical properties and the accumulation of microdefects in its structure. This process is called fatigue fracture of the material, and the material's ability to resist fracture under dynamic loading is called fatigue endurance. Typically, the rubber has high fatigue endurance, if it has high strength and low internal friction upon exposure to cyclic strain.

The results of tests of rubber samples based on a combination of rubber SKI-3+SKD upon crack growth during bending are shown in Fig. 2.

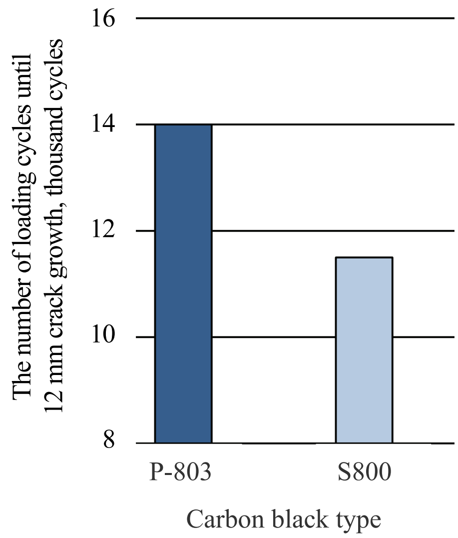


Fig. 2. Change in the crack growth resistance at bending of rubber depends on the carbon black type

Studies of rubber properties at temperature of 70°C have shown that the best resistance to crack growth under alternating bending has the rubber containing carbon black type P-803. According to elemental analysis of carbon black surface researching types obtained by scanning electron microscope on the surface of carbon black type S800 contains a significant amount of sulfur in comparison with type P-803. In this regard, one can assume that using carbon black type S800 at curing can form the additional cross-linking, and consequently, increased heat buildup during repeated deformations due to internal friction segments when exposed to cyclic loads.

Due to the fact that products based on butadiene-nitrile rubber used as sealing material, it was of interest to investigate the influence of carbon black on the heat resistance of the rubber in compression (Fig. 3). It is known [7] that prolonged exposure to stress and high temperature transformation of structure of elastomeric matrix can occur and deterioration of physical and mechanical properties. In this connection, a significant influence on the heat resistance in compression of rubbers based on butadiene-nitrile rubbers will have the structure and density of curing network, and the ratio of different types of cross-linking bonds. The most preferred are vulcanizates containing monosulfide and carbon-carbon bonds. Release of tension of sulfur vulcanizates based on unsaturated rubber is mainly due to break of polysulfide bonds. The increase in the degree of cure typically increases thermal stability under compression [8].

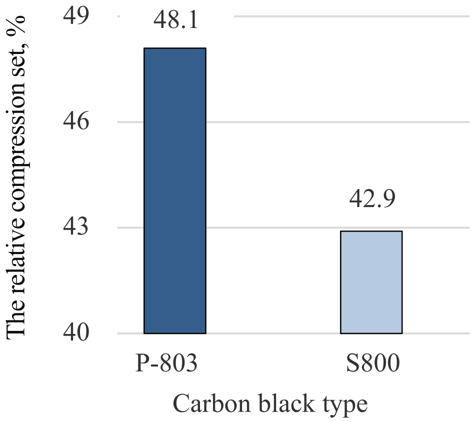


Fig. 3. Changing the relative compression set of the vulcanizate based on BNKS-18AMN depending on type of carbon black

As a result of studies to determine the resistance to aging under static compressive strain of rubber based on BNKS-18AMN revealed that the smallest value of the relative compression setis observed for rubber with carbon black type S800. So, when introduced into rubbercompound carbon black type P-803 value of the relative compression set of vulcanizates samples is 48.1%, which is 11.0% more than the value of this indicator for samples containing carbon black type S800 (42.9%). These changes may be associated with the peculiarities of the nature of crosslinking of rubber curing network in case of replacement of carbon black type P-803 to exploring type S800.

Hardness – one of the most important physical and performance characteristics. It is indicated in most of the guests and technical specifications for rubber products. Hardness is widely used for quality control of rubber products, because the amount depends on properties of rubber and compliance with the dosage of curing group, fillers and plasticizers by mixing [1]. The results are shown in Table. 3.

Table 3

The hardness of the rubber containing various types of carbon black

Elastomeric base of carbon black	Type of carbon black	Hardness, cond. units Shore A
SKI-3+SKD	P-803	52.8
	S 800	54.9
BNKS-18AMN	P-803	67.4
	S800	70.6

The presented data show that the replacement of carbon black type P-803 BY type S800 increases Shore A hardness for vulcanizate based on a combination of common rubbers SKI-3+SKD, and to vulcanizates based on rubber BNKS-18AMN. Thus, for the sample based on SKI-3+SKD Shore A hardness is increased by 4%, while for the sample based on BNKS-18AMN by 4.7%. These changes of properties are, probably, due to the structure of the resulting cross-linking bonds during vulcanization, as well as the influence on process of structuring functional groups and structure of the used carbon black.

Conclusion. Thus, the results of the research of the effect of carbon black of various types in the properties of rubber have shown that the use of carbon black S800 type instead of the type P-803 has the greatest influence on the elastic-strength and elastic-deformation properties of vulcanizates based on rubber BNKS-18AMN. In this case, the introduction of carbon black type S800 increases tensile strength by 1.32 times, hardness by 3 cond. units, and decreases relative deformation compression by 11%. The studies found out that it is advisable for common rubber to use carbon black S800 type in rubber products, used in static conditions, due to the deterioration of the dynamic properties of vulcanizates by replacing carbon black S800 type by type P-803.

References

1. Kornev A. Ye. *Tekhnologiya elastomernykh materialov: uchebnik* [Technology of elastomeric materials: Textbook]. Moscow, ISTEK Publ., 2009. 502 p.

2. Orlov V. Yu., Komarov A. M., Lyapina L. A. *Proizvodstvo i ispol'zovanie tekhnicheskogo ugleroda dlya rezin* [Production and use of technical carbon for rubbers]. Yaroslavl', Alexander Rutman Publ., 2002. 512 p.

3. Ivanovskiy V. I. *Tekhnicheskiy uglerod. Protsessy i apparaty* [Carbon black. Processes and devices]. Omsk, OAO "Tehuglerod", 2004. 228 p.

4. Shutilin Yu. F. *Spravochnoe posobie po svoystvam i primeneniyu elastomerov* [The handbook on properties and application of elastomers]. Voronezh, Voronezh State Technol. Akad. Publ., 2003. 871 p.

5. Gyul'misaryan T. G., Gilyazetdinov L. P. *Syr'e dlya proizvodstva uglerodnykh pechnykh sazh* [Raw materials for production of oven carbon]. Moscow, Chemistry Publ., 1975. 159 p.

6. Tsekhanovich M. S. Production of technical carbon and environmental protection. *Sbornik materialov Vsesoyuznogo soveshchaniya* [Collection of materials of all-Union meeting]. Moscow, TSNIITEneftekhim Publ., 1987, pp. 20–23 (In Russian).

7. Dontsov A. A. *Protsessy strukturirovaniya elastomerov* [Process of structuring elastomers]. Moscow, Khimiya Publ., 1978. 288 p.

8. Fedyukin D. L., Makhlis F. A. *Tekhnicheskie i tekhnologicheskie svoystva rezin* [Technical and technological properties of rubbers]. Moscow, Chemistry Publ., 1985. 240 p.

Information about the authors

Shashok Zhanna Stanislavovna – PhD (Engineering), Assistant Professor, the Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: shashok@belstu.by

Uss Elena Petrovna – PhD (Engineering), assistant lecturer, the Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: uss@belstu.by

Kasperovich Andrey Victorovich – PhD (Engineering), Assistant Professor, Head of the Department of Technology of Petrochemical Synthesis and Polymer Materials Processing. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: andkasp@belstu.by

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