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Physical modification of filler of elastomer compositions

***Abstract:** Element-based coatings (E=Cr, Mo) deposited on carbon P-324 by means of self-ion assisted deposition (SIAD) technique exhibit some advanced properties such as specific surface area. The SIAD modified surfaces of carbon were examined using investigation of the surface area and porosity by High Speed Gas Sorption Analyzer NOVA 2200 (Quantachrome Corp. USA). Introduction of the modified filling compound was increased physico-mechanical properties of elastomer composition.*

Streszczenie.** Powłoka (E=Cr, Mo) naniesiona na węgiel P-324 metodą self-ion assisted deposition (SIAD) wykazuje pewne specjalne właściwości. Modyfikowana w ten sposób powierzchnia była badana pod względem porowatości przy użyciu analizatora sorpcyjnego o dużej szybkości gazu High Speed Gas Sorption Analyzer NOVA 2200 (Quantachrome Corp. USA). Wprowadzenie zmodyfikowanego wypełniacza skutkowało poprawą właściwości fizyko-mechanicznych kompozytu. **(Modyfikacja fizycznych właściwości wypełniacza kompozytu elastomerowego).

Keywords: filler of elastomer, carbon, physical-mechanical properties.
Słowa kluczowe: elastomer, kompozyty, węgiel.

1. Introduction

At present, there is a great deal of the facts confirming an essential role of a surface activity of carbon black in its influence on properties of rubbers [1]. Representations about character of the active centers, and about interrelation between structure of chemical groupings on the surface of carbon black and properties of rubbers allow to draw a conclusion about the influence of modified carbon filler on physicomechanical characteristics of rubbers due to introduction (physically or chemically) of various functional groups on its surface.

Firstly, attempts have been undertaken to increase vulcanizate durability due to updating of carbon black by polymers. However, the inoculation of polystyrene and polyisoprene on the surface of carbon black has not led to desirable result. On the contrary, decrease in strengthening ability of filler was observed in isoprene rubbers that are connected to deactivation of inoculation of unsaturated polyisoprene because of its oxidation during preparation of a sample.

Application of surface-active substances (cetyl-methylammonium-bromide and aerosol OT) on a surface of oven carbon black also improved dispersive ability, but reduced strengthening effect and resistance to tear and abrasion, and also the module of vulcanizates.

Processing of channel carbon black by surface-active substances removed the typical effect of cure retarding of rubbers and increased their strength characteristics. In the foreign and domestic literature, there are data on the usage of chlorinated carbon black to improve of adhesive properties of elastomers and increase of efficiency of pitch vulcanization. However, chlorinated carbon black considerably raises rubbers scorchiness and reduces radiation resistance of vulcanizates.

Carbon black which surface is modified by silicon dioxide increases the elastic module and reduces wear resistance of rubbers. Oxidized carbon black retards vulcanization of rubber mixes and reduces modules; increases tear resistance and dynamic fatigue of vulcanizates. The literary data show a basic opportunity to provide rubbers with the certain properties by the usage of modified carbon black at corresponding selection of chemical agents, and perspectives of its application for production of rubber technical articles.

2. Experimental

We had started works on modifying of the surface of carbon black by SIAD in conditions of self-radiation by metals (chromium, molybdenum).

Technical carbon P - 324 has been chosen as object of research. The choice of metals has been caused by the greatest level of adhesion of these metals to rubber surfaces [2].

This type of an ionic source with the electrodes made of a material of the rendered covering (chromium, molybdenum), allows to receive adjustable streams of metal ions with density I (2) and neutral atoms with density A (3), see the fig. 1. The neutral fraction of the required material (or materials) evaporates in different directions, being besieged, including, on particles of filler 4.

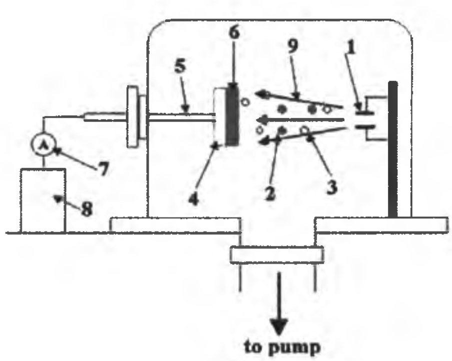

Fig. 1. Schematic representation of self ion-assisted deposition: 1 – vacuum arc ion source, 2 – ionized fraction, 3 – neutral fraction, 4 – target, 5 – target holder, 6 – modified surface, 7 – current integrator, 8 – high voltage power supply, 9 – electric field

Under the action of a potential difference between a high-voltage electrode 5 on which the substrate is placed, and a source of ions 1 generated ions are extended from a digit interval and according to direction of intensity of an electrostatic field 8 direct to a target, taking root in its surface. As a result of it the modified surface of a target 6 is formed.

The control over the process of covering drawing on a product and its simultaneous irradiation is carried out by change of an operating mode of an ionic source 1 at integration of the current of ions by corresponding devices 7. Energy of assisting ions in experiments was within the limits of 3 kV and the vacuum was 10^{-2} Pa.

The researches of influence of the modified technical carbon on properties of elastomer compositions were carried out using the unfilled standard rubber mixes based on rubber SKI-3 and SRMS-30 ARKM-15, Tables 1, 2. With the use of device NOVA 2200 (USA) in research laboratory of BGTU the specific surface of carbon.

Technical carbon (initial and modified) was entered in quantities of one, three and five mass parts as the modifying additive.

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Table 1. Compounding of a rubber mix based on SKI-3 in accordance with GOST 14925-73

Components	The contents of components, weights part on 100 weight parts rubber
SKI-3	100
Sulfur	1,0
Altax	0,6
Diphenylguanidine	3,0
Zinc oxide	5,0
Stearin	1,0
In total	110,6

Technical carbon (initial and modified) was entered in quantities of one, three and five mass parts as the modifying additive.

Table 2. Compounding of a rubber mix based on SRMS-30 ARKM-15 in accordance with GOST 11138-72

Components	The contents of components, weights part on 100 weight parts rubber
SRMS-30 ARKM-15	100
Sulfur	2,0
Altax	1,5
Diphenylguanidine	0,3
Zinc oxide	5,0
Stearin	2,0
In total	110,8

The results of researches shown that introduction of the modified technical carbon in various dosages results in increase of strengthening parameters in unfilled rubber mixes based on crystallizing and noncrystallizing rubbers, see Tables 3, 4. Introduction of strengthening fillers renders various influences on rubbers in view of features of a structure of rubber.

Table 3. Physicomechanical parameters of rubber mixes based on SKI-3

The name of a parameter	The contents of additives in a rubber mix based on SKI-3			
	0	1	3	5
additives of technical carbon P-324				
Tensile strength, MPa	20,8	-	-	21,8
Percentage elongation, %	715	-	-	700
additives of the modified technical carbon (Cr)				
Tensile strength, MPa	20,8	19,6	22	22,2
Percentage elongation, %	715	730	714	684
additives of the modified technical carbon (Mo)				
Tensile strength, MPa	20,8	23,5	23,2	23
Percentage elongation, %	715	774	682	644

The rubber SKI-3 has a regular structure and is capable to crystallization therefore Introduction of strengthening fillers influences on strength characteristics of rubbers based on this rubber. From Table 3 it is visible, that rubbers based on SKI-3 without filler have tensile strength of 20,8 MPa and percentage elongation of 715%. Introduction of technical carbon P-324 results in increase in tensile strength of 21,8 MPa, percentage elongation of 700%. Introduction of technical carbon modified by chromium increase in tensile strength up to 23 MPa.

Thus, it is possible to draw a conclusion that at increase in the contents of the modified technical carbon tensile strength of vulcanizates based on SKI-3 is increased a little.

In a case of introduction of strengthening fillers in rubber mixes on a basis of no crystallizing rubbers strength characteristics of rubbers grow in some times. In Table 4 the results of research of the basic physicomechanical parameters of rubbers based on SRMS-30 ARKM-15 with various dosages of filler are presented.

In case of application of the modified types of technical carbon in a dosage of 5 weight parts also the increase in tensile strength is observed. So, rubbers based on SRMS not containing filler have tensile strength of 2,38 MPa, and for the rubbers containing 5 weights parts of the modified technical carbon (Cr) the given parameter makes 3,31 MPa.

Table 4. Physicomechanical parameters of rubber mixes based on SRMS-30 ARKM-15

The name of a parameter	The contents of additives in a rubber mix based on SRMS-30 ARKM-15			
	0	1	3	5
additives of technical carbon P-324				
Tensile strength, MPa	2,38	-	-	3,0
Percentage elongation, %	472	-	-	616
additives of the modified technical carbon (Cr)				
Tensile strength, MPa	2,38	1,91	2,53	3,31
Percentage elongation, %	472	567	590	638
additives of the modified technical carbon (Mo)				
Tensile strength, MPa	2,38	1,23	2,34	3,21
Percentage elongation, %	472	498	522	650

The results of researches have shown, that introduction of the modified types of technical carbon in various dosages results in increase of strength parameters in unfilled rubber mixes based on crystallizing and noncrystallizing rubbers.

At introduction of the modified technical carbon, hardness of rubbers practically does not change in comparison with the rubbers containing initial technical carbon P-324.

Rubber is a multicomponent system, and an introduction of even insignificant dosage of components is capable to speed up or slow down process of vulcanization.

It was interesting to investigate influence of the modified technical carbon on vulcanization kinetic of tread rubber. A corresponding industrial rubber mix without additives is accepted as compared samples.

At introduction of researched additives in industrial tire rubber mixes insignificant decrease is observed in optimum time of vulcanization, hence, process of vulcanization is intensified a little. In mixes at addition of the modified technical carbon there is a decrease in optimum time of vulcanization to 11,20 minutes that corresponds to a dosage of filler of 5 weight parts, see Table 5.

Thus, in researched tire mixes with introduction of modified filler there is a decrease in optimum time of vulcanization that promotes an intensification of process of vulcanization. Speed of vulcanization practically does not change.

Table 5. Results of tests of tire rubber mix on reometer ODR-2000

The name of a parameter	The maintenance of additives of modified carbon black in the rubber mix, weight parts			
	initial	1	3	5
The minimal twisting moment, dN·m	6,50	3,76	3,49	4,38
The maximal twisting moment, dN·m	40,17	36,16	35,69	39,46
Time necessary for increase of the twisting moment on 2 units in comparison with the minimal twisting moment, minutes	6,24	5,98	6,06	5,75
Time of achievement of the set degree of vulcanization, minutes	8,60	8,22	8,31	8,03
Optimum time of vulcanization, minutes	12,14	11,57	11,41	11,20
Speed of vulcanization, dN·m /minutes	8,08	8,00	8,04	8,77
Time of achievement of the maximal speed of vulcanization, minutes	8,10	7,70	7,91	7,51

From Table 6 in which results of definition of physicomechanical parameters of researched rubbers are specified, it is visible, that at addition of various dosages of modified filler in tire rubber mixes percentage elongation changes, but these changes are within the limits of an allowable error in accordance with GOST. In a case with conditional tensile strength, various laws are observed.

So, for a sample with initial carbon black tensile strength is equal 22,46 MPa. At addition of modified filler in a dosage of 1 weight part tensile strength is equal 23,38 MPa. At a dosage of 3 weight part the given parameter is reduced up to 23,30 MPa (on 9,5% below a sample of comparison), at a dosage 5 weight part – up to 21,26 MPa, that below previous value, and also is lower, than for a sample of comparison.

Table 6. Physico-mechanical parameters of tire rubber mixes

The maintenance of additives of modified carbon black in the rubber mix, weight parts	Percentage elongation, %	Tensile strength, MPa
initial	480	22,46
1	560	23,38
3	550	23,30
5	530	21,26

Analyzing the received data, it is possible to draw a conclusion, that at introduction of modified filler in tread rubber mixes, which compoundings contain active filler, the increase in tensile strength is observed all over again at a stretching, and then at a filler dosage of 5 weight part decrease in the given parameter is observed. The parameter of percentage elongation is increased at introduction of modified filler in tire rubber mixes.

The results of definition of tire rubbers abrasion are resulted in Table 7. The given researches were carried out on a protector – racing rubber.

From the received results follows, that in tire rubbers the abrasion decrease is observed at introduction of the modified technical carbon. The minimal value of $2{,}6\times10^{-2}$ sm^3/J corresponds to 5 weight part of additives.

Rubber abrasion without additives it is equal $4{,}3\times10^{-2}$ sm^3/J. Resistance to abrasion, accordingly, increases and at a dosage of the modified technical carbon of 5 weight part and is equal 38,6, that is higher than that of compared sample. Hence, at introduction of the modified technical carbon in tire rubbers there is a reduction of abrasion and increase in resistance to abrasion. In this case, an optimum dosage is 5-weight part.

Table 7. The results of definition of tire rubber abrasion

The maintenance of additives of modified carbon black in the rubber mix, weight parts	Abrasion, sm^3/J×10^4	Abrasion resistance, J/mm^3
initial	4,3	22,8
1	4,2	23,7
3	3,5	28,0
5	2,6	38,6

There is a lot and other more specific methods of laboratory and bench tests of rubber. Laboratory researches of the simple, specially prepared samples cannot to reflect real conditions of operation, but allow to regulate and simplify strictly conditions of deformation and to receive well-reproduced results as against results of operational tests. Therefore, laboratory researches of simple samples are the first and basic stage by development of new or quality assurance of existing kinds of rubber articles. The knowledge of the general laws of behavior of rubber in various conditions helps to establish connection between laboratory and operational characteristics of a product.

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