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The effect of functional groups of carbon black on rubber properties

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Abstract

The effect of functional groups of oxidized carbon black N326 on technological, technical and functional properties of butyl rubbers was studied. It was found that the introduction of oxidized carbon black N326 into rubber delays scorching of rubber mixes and reduces their gas transmittivity.

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Keywords: carbon black, oxidation, functional groups, butyl rubber, rubber mix, scorching time, vulcanizates, strength, gas transmittivity

1. Introduction

The production of some mechanical rubber goods requires rubbers with multifunctional properties such as strength, electroconductivity, barrier properties, elasticity, resistance to oxidative ageing and others. The distinctive features of such rubbers are their compositional homogeneity created by mixing ingredients, and a low rate of vulcanization. Until 2006, many of the listed properties were ensured by compounding with channel carbon black K354 (GOST 7886), which retarded vulcanization of rubber mixes and increased the strength of resulting rubbers [1]. Its production was stopped to prevent environmental contamination [2], so it became necessary to find a substituent. However, an analog of channel carbon black K354 is absent among furnace grades. Some compositions

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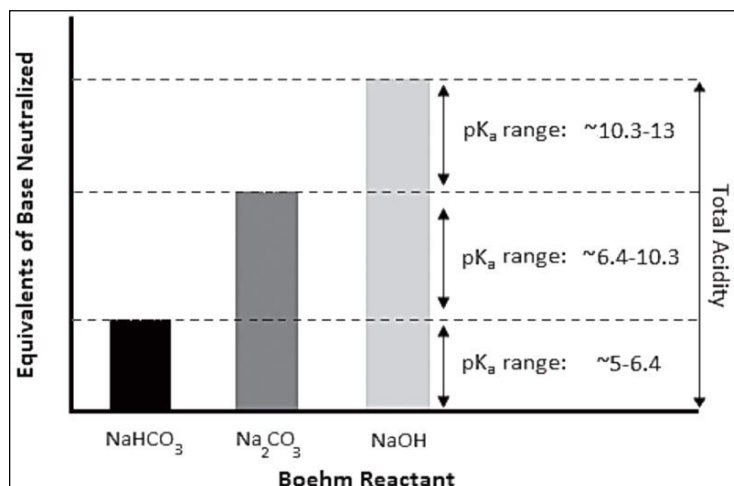


Fig. 3. A scheme for calculation of the concentration of protonogenic functional groups with different pKa, which is used for their selective neutralization by the Boehm method [7].

The effect of protonogenic groups of a carbon filler on the rubber properties remains poorly understood. It is believed that the presence of functional groups on the surface of carbon fillers facilitates strengthening of rubber and improves gas barrier properties of a polymeric composite [8]. Thus, a comparison of the properties of natural, butadiene and polymethylsiloxane rubbers compounded with carbon nanotubes, carbon black or graphene oxide showed that the most important property of the filler used to improve gas barrier properties of rubbers is its ability to a complete dispersion, which is facilitated by the functional groups on its end atoms. At a complete dispersion of carbon filler, the interphase surface area and the crooked path of gas in the composite reach their limiting values. Gas transmittivity is affected also by the concentration of chemical bonds between functional groups of the carbon material and macromolecules of the polymer [5]. However, the effect exerted by individual functional groups of carbon fillers on gas barrier and other properties of rubbers is not quite clear.

An increase in the oxidation degree of a carbon filler increases the modulus of elasticity E' for methylstyrene rubbers at different temperatures [9] and intensity of the interaction with butyl rubber [10-12]. The observed increase in the modulus of elasticity E' for rubbers is caused by the growth of the average molecular weight of rubber in the matrix filled with the oxidized carbon black. It was found that all functional groups on the surface of disperse carbon exert a pronounced effect on the adsorption processes in a polymeric medium and change the molecular composition of adsorption layers and, accordingly, their extent. The presence of functional groups raises the activation energy of polyisoprene rubber adsorption and enriches the adsorption layers with low-molecular fractions of the polymer [13].

In this connection, studies on the interaction of rubbers with functionalized carbon black are in progress.

The goal of the work was to compare the effect of protonogenic functional groups located on the surface of carbon black N326 on the properties of rubber mixes and their butyl rubber vulcanizates.

2. Study subject

Subjects of study were the samples of furnace carbon black N326 (Omsktekhuglerod Ltd.) oxidized under laboratory conditions at standard temperature for 15 min by various oxidants: a 2% aqueous solution of hydrogen peroxide (a liquid-to-solid weight ratio of 1:1) in the air activated by ozone (sample 1), a 2% solution of hydrogen peroxide (a liquid-to-solid weight ratio of 1:1) in the air activated by singlet oxygen (sample 2), only the singlet oxygen 1O_2 (sample 3), only the ozone (sample 4), and only the 30% solution of hydrogen peroxide (a liquid-to-solid weight ratio of 1:1) (sample 5). Rubber mixes were represented by a commercial mix with channel carbon black K354 (Khazarsk chemical plant, Republic of Turkmenistan) and experimental mixes with the samples of

oxidized carbon black N326. Carbon black samples were employed as fillers of butyl rubber mixes that are used in the production of sealing chambers. The basic composition of rubber mixes is listed in Table 1.

Table 1. Basic composition of rubber mixes.

Material	commercial	1	2	3	4	5
	Content per 100 weight fractions of rubber					
Synthetic rubber BK-1675N	100.0	100.0	100.0	100.0	100.0	100.0
Carbon black K354	60.0	-	-	-	-	-
Carbon black N326 oxidized by 2% H ₂ O ₂ and O ₃ ozone	-	60.0	-	-	-	-
Carbon black N326 oxidized by 2% H ₂ O ₂ and singlet ¹ O ₂	-	-	60.0	-	-	-
Carbon black N326 oxidized by singlet ¹ O ₂	-	-	-	60.0	-	-
Carbon black N326 oxidized by O ₃ ozone	-	-	-	-	60.0	-
Carbon black N326 oxidized by 30% H ₂ O ₂	-	-	-	-	-	60.0
Sulfur vulcanizing system		3.3 3.3	3.3	3.3	3.3	3.3

The study was performed with butyl rubber BK 1675N (Tolyattikauchuk Ltd., Tolyatti).

3. Methods

Rubber mixes were prepared in a lab-scale rubber mixer R/S 4,5/20-140 with two-bladed rotors and a 2.5 dm³ mixing chamber using a two-step mixing mode. At the first step, mixing was carried out for 4 min at a rotor rate of 40 rpm and a temperature of 80 °C; and at the second step, for 2 min at 30 rpm and 60 °C. After the second step, the rubber mix was treated on the lab-scale rollers LB 350 150/150 at a controllable temperature of 65°C and roller friction of 1:1.25. Vulcanization of the rubber mixes was performed using a lab-scale hydraulic press PKMV-160.

Functional groups on the surface of carbon black samples were detected by the Boehm method [12]. Precision of the method upon repetition was 7%. The start of scorching was determined in compliance with GOST 54552-2011 using an MV 2000 viscometer (Alpha Technologies, USA). Physical-mechanical characteristics of rubbers were assessed according to GOST 270-75. The rate of gas transmission (99.9% pure nitrogen) through the rubber was measured manometrically at standard temperature and a pressure drop from atmospheric to 10 Pa according to the China GB 1038 standard on a VAC-V2 (Labchink Instruments, China) instrument.

A relative fraction of the filler particles with the size up to 5 μm in rubber was determined on a disperGRADER αview 660 AAD 1090 (Alpha Technologies, USA) instrument by processing the images of rubber sections illuminated at an angle of 30°.

4. Results and discussion

The oxidized samples of carbon black had different functional composition (Table 2).

Table 2. Content of functional groups on the surface of carbon black samples.

Functional groups	K354 Q, mg-eq/g	Content of groups Q, mg-eq/g, in N326 samples				
		1	2	3	4	5
Phenol PhG	0.050	0.018	0.014	0.014	0.001	0.020
Lactone LG	0.045	0.003	0.006	0.028	0.013	0.042
Carboxyl CG	0.046	0.012	0.013	0.006	0.01	0.035

Technological and physico-mechanical properties of commercial rubber compounded with K354 and experimental rubbers compounded with oxidized N326 are listed in Table 3.

Table 3 Technological and physico-mechanical characteristics of rubbers.

Characteristics	commercial	Values for experimental rubbers				
		1	2	3	4	5
Start of rubber mix scorching at 130 °C, τ_5 , min	9.75	14.92	14.28	17.32	15.82	12.30
Engineering stress at a 300 % extension, MPa	7.01	6.93	6.79	7.18	7.12	5.95
Engineering tensile strength (fp), MPa	17.3	15.6	14.2	16.2	16.7	17.7
Relative extension at rupture (ep), %	530	520	480	530	540	590
Relative residual deformation after rupture, %	29	36	40	36	40	40
True strength (σ_p), MPa	109	96.7	82.4	102	106.9	122.1
Nitrogen transmission rate (GTR), $\text{cm}^3/\text{m}^2 \cdot 24\text{h} \cdot 0.1\text{MPa}$	87.051	58.247	72.012	77.564	73.391	54.662
Nitrogen diffusivity, cm^2/s	$3.058 \cdot 10^{-5}$	$1.539 \cdot 10^{-5}$	$5.887 \cdot 10^{-5}$	$2.883 \cdot 10^{-4}$	$2.895 \cdot 10^{-5}$	$1.790 \cdot 10^{-5}$
Nitrogen transmittivity index, $\text{cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cm mm Hg}$	$1.343 \cdot 10^{-10}$	$8.498 \cdot 10^{-11}$	$3.229 \cdot 10^{-11}$	$1.149 \cdot 10^{-10}$	$3.394 \cdot 10^{-11}$	$8.422 \cdot 10^{-11}$

As follows from Table 3, all the experimental samples under consideration exert a beneficial effect on τ_5 , and their efficiency exceeds that of K354. This may be caused by their higher dispersion, which is illustrated on Fig. 4.

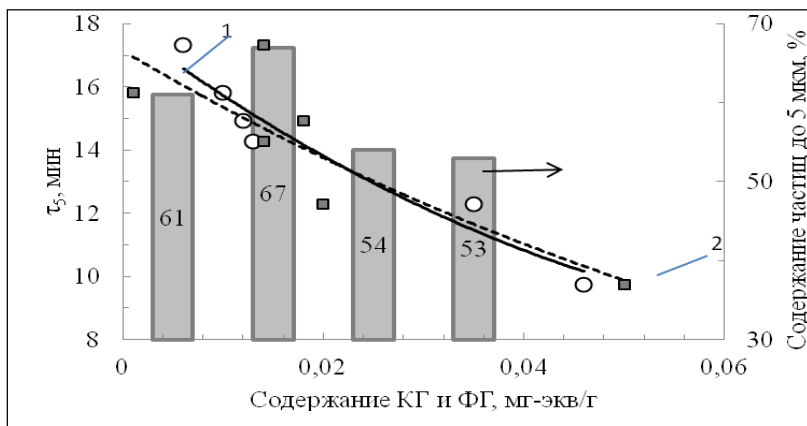


Fig. 4. The effect of carboxyl (1) and phenol (2) functional groups of carbon black on scorching of rubber mixes.

Functional groups of carbon black affect the tensile elasticity and strength of rubbers. An increase in the content of protonogenic groups on a carbon filler is accompanied by a decrease in the stress of tested rubbers at a 300% extension (Fig. 5).

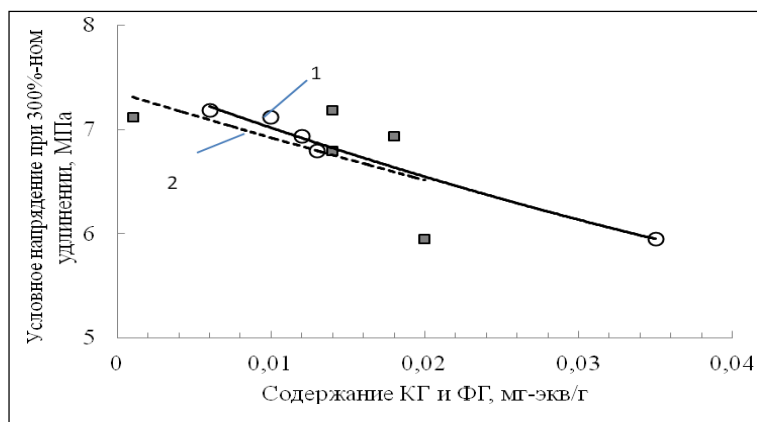


Fig. 5. The effect of carboxyl (1) and phenol (2) functional groups of carbon black on the engineering stress at a 300% extension of experimental rubbers.

Since the most important operational property of butyl rubbers is their low gas transmittivity, it was interesting to compare the rates of gas transmission in experimental rubbers. The formation of bound rubber irrespective of its functionality with carbon black [10] as well as the weakly base nature of butyl rubber [14] give grounds to expect binding of butyl rubber macromolecules to acidic regions of the carbon black surface.

Fig. 6 displays gas transmittivity index of experimental rubbers versus the content of protonogenic phenol and carboxyl oxygen-containing groups in carbon black. The dependences of gas transmission rate on the content of lactone groups on the carbon surface have a similar shape, but with a smaller slope.

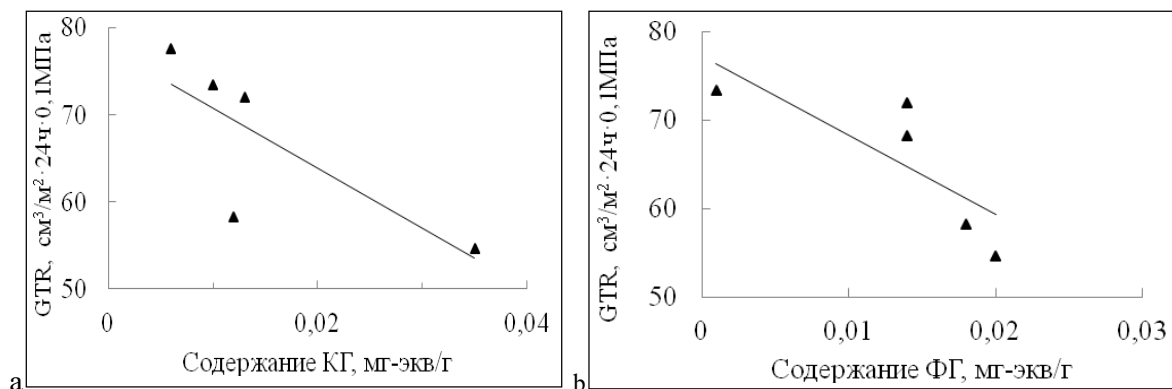


Fig. 6. Nitrogen GTR transmission rate of experimental rubbers compounded with carbon black versus the content of carboxyl (a) and phenol (b) groups.

A decrease in gas transmittivity of experimental rubbers confirms that protonogenic groups interact with butyl rubber macromolecules [10] and thus participate in the formation of quite a dense and extended interphase layer [13]. Overall, this enhances the gas barrier properties of rubbers.

5. Conclusion

Functional groups of oxidized carbon black N326 exert an effect on technological, technical and functional properties of butyl rubbers. The application of oxidized carbon black N326 in the rubber composition makes it possible to delay rubber mixes scorching and decrease their gas transmittivity.

References

- [1] Encyclopedia of Polymers (Eds. V.A. Kargin et al.), Vol. 1. Sovetskaya Entsiklopediya, Moscow, 1972. 1196 p.
- [2] Analysis of economical efficiency of alternative ways of natural gas utilization [Text]. Institute of Financial Research, Moscow, 2007. 40 p.
- [3] Prodotti, N. Nuovi tipi di nerofumo [Text] / N. Prodotti // Materie Plastiche ed Elastomeri, 1974, No. 6, p. 523.
- [4] Na Li, Xiaoliang M, Qingfang Zha, Kyungsoo Kim, et al., Maximizing the number of oxygen-containing functional groups on activated carbon by using ammonium persulfate and improving the temperature-programmed desorption characterization of carbon surface chemistry// Carbon 2011, V. 49, No. 15, p. 5002-5013.
- [5] K.A. Pechkovskaya, Soot as a Rubber Booster. Khimiya, Moscow, 1968. 418 p.
- [6] G.I. Razdyakonova, O.A. Kokhanovskaya, V.A. Likhonov, Influence of Environmental Conditions on Carbon Black Oxidation by Reactive Oxygen Intermediates, Procedia Engineering, 2015, Vol. 113, pp.43-50.
- [7] R.B. Fidel, D. A. Laird, M.L. Thompson, Evaluation of Modified Boehm Titration Methods for Use with Biochars // J. Environ. Qual, 2013, No. 42, pp. 1771–1778.
- [8] B. Ozbas, C.D. O'Neill, R.A. Register, I.A. Aksay, R.K. Prud' Homme, D.H. Adamson, Multifunctional Elastomer Nanocomposites with Functional Graphene Single Sheets, Journal of Polymer Science Part B: Polymer Physics, 2012, Vol. 50, pp. 910-916.
- [9] G.I. Razdyakonova, E.A. Strizhak, N.S. Mitryaeva, M.N. Nagornaya, The effect of N326 carbon black oxidation on rubber properties., Omsk Scientific Bulletin, 2015, No. 3 (143), pp. 364-367.
- [10] A. Roychoudhury, P.P. De, Elastomer-carbon black interaction: Influence of elastomer chemical structure and carbon black surface chemistry on bound rubber formation, J. Appl. Polym. Sci, 1995, Vol. 55. – No. 1, pp. 9-15.
- [11] J.A. Ayala, W.M. Hess, A.O. Dotson, G.A. Joyce, Rubber Chem. and Technol., 1990, Vol. 63. – No. 5, pp. 747-778.
- [12] H. P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon 1994, Vol. 32(5), pp. 759–69.
- [13] G.I. Razdyakonova, E.A. Kiseleva, The effect of functional composition of carbon black on interphase layers in a rubber medium, Kauchuk I Rezina (Elastomer and Rubber), 2013, No. 3, pp. 40-43.
- [14] I.A. Starostina, O.V. Stoyanov, The development of methods for assessment of surface acid-base properties of polymeric materials, Bulletin of Kazan Technological University, 2010, No. 4, pp. 58-68.