

## Properties of vulcanizates based on nitrile butadiene rubber in the occurrence of halomethyl-containing compounds

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*Received April 7, 2023*

The effect of high temperature (423K) on the process of vulcanization of nitrile butadiene rubber (NBR) with the participation of hexachloro-4,4-dimethylbenzophenol (HCDMBP) was studied, which makes it possible to significantly improve the technical properties of vulcanizates. The molecular structure in the system SKN-40+HCDMBF+ZnO was determined by Fourier IR spectroscopy. Demonstrated that, from the optical densities of the absorption bands at 967, 912, and 750 cm<sup>-1</sup>, the distribution of double bonds in the NBR macromolecule was calculated. In order to confirm the data on the comparative structural activity of HXDMBF with NBR, as well as to select the effective dose of HXDMBF, the relative amount of gel formed in model mixtures based on SKN-40M at 5.0 phr presence of zinc oxide was determined by heating at 423K for 25 minutes. Demonstrated that, the density of effective row connections ( $N_c$ ) is lower in the sulphurous vulcanization group than in others.

**Keywords:** halogen-containing, butadiene-nitrile rubber, vulcanization, elastomer, plastification, spectrum, structure, gel formation

**Властивості вулканізацій на основі нітрилбутадієнового каучуку при появі галометилвмісних сполук.** Ш.М.Мамедов, Г.Г.Азізова, Г.А.Мамедова, Р.Ф.Ханкішієва, Ф.А.Аміров, І.Г.Мовлаєв, Дж.Ш.Мамедов

Досліджено вплив високої температури (423 К) на процес вулканізації бутадієн-нітрильного каучуку (БНК) за участю гексахлор-4,4-диметилбензофенолу (ГХДМБФ), що дає змогу значно покращити технічні властивості вулканізацій. Методом ІЧ-фур'є-спектроскопії визначено молекулярну структуру в системі СКН-40+НСДМБФ+ZnO. Продемонстрував, що за оптичною густиною смуг поглинання при 967, 912 і 750 см<sup>-1</sup> було розраховано розподіл подвійних зв'язків у макромолекулі NBR. Для підтвердження даних щодо порівняльної структурної активності ГХДМБФ з БНК, а також для підбору ефективної дози ГХДМБФ визначали відносну кількість гелю, що утворюється в модельних сумішах на основі СКН-40М при 5,0 м.ф. присутності оксиду цинку. шляхом нагрівання при 423 К протягом 25 хвилин. Продемонстровано, що щільність ефективних зв'язків ряду ( $N_c$ ) нижча в групі сірчаної вулканізації, ніж в інших.

### 1. Introduction

Today, obtaining solid elastomeric materials with high resistance to heat aging is one of the most important problems. Sulfur vulcanizates are characterized by high strength; however, they have a rather low heat resistance [1, 2].

The use of sulfur-free structuring systems ensures the formation of thermally stable bonds of the C-C type and allows expanding the operating temperature range of elastomeric materials significantly [1,3,4].

It is known to use phenol-formaldehyde resins, organic peroxides, etc. as structuring

agents [5]. At the same time, the resistance of vulcanizates to heat aging increases, but their tear resistance and elasticity decrease in comparison with sulfur ones. There are also instruction of the possibility of structuring elastomers with chlorine-containing organic compounds, which allows to obtain vulcanizates with high strength modulus and increased resistance to heat aging [6]. In this work, the influence of the structure of hydrogenated nitrile rubber on the resistance to aggressive environment and high temperatures was studied [7]. However, the introduction of dicumyl peroxide into the composition increases the rate of vulcanization, and ultimately the plastoelastic properties of vulcanizates deteriorate. Such special compositions based on NBR have been developed for use in diesel engines as a sealant resistant to high temperatures [8]. The authors of study the influence of the coal tar modifier on the physical and mechanical properties of butadiene-nitrile rubbers [9]. However, there is a very limited number of publications devoted to this issue both in local and foreign literature and, in particular, there are absolutely no data on the study of the structure of the SKN-26 and SKN-40M elastomer.

In this work, we studied the structuring effect of polyhalomethyl-containing compounds (PHMCC) of  $\omega$ -hexachloro-4,4-dimethylbenzophenone (HCDMBP) in elastomeric mixtures based on SKN-26 and SKN-40M.

## 2. Experimental part

The research subject was industrial nitrile butadiene rubber SKN-26 and SKN-40M, which contains chlorine-containing, epoxy and other traditional ingredients. Heat treatment of rubber compounds was carried out under pressure at 423K for 30 min [5].

Mechanical plasticization of NBR was carried out on laboratory mills in size of 160x320 mm at  $200^{\circ}\text{C} \pm 100^{\circ}\text{C}$ . Roll loading was 100 g fraction of  $f=1:2$ , and we prepared elastomeric mixture (part per hundred of rubber (phr): [1,10].

1. SKN-40M – 100; zinc oxide – 5.0, HCDMBP – 2.0, epoxy resin – 6.0, stearin – 2.0 and carbon black (P324) – 50.

2. SKN-26 – 100; zinc oxide – 5.0; epoxy resin – 6.0, stearin – 2.0, HCDMBP – 50.

3. SKN-26 – 100; zinc oxide – 5.0; epoxy resin – 6.0, stearin – 2.0, HCDMBP – 50, mass fraction of technical carbon P324 (filler).

Plasticization was carried out for 20 min. [6]. The structuring of mixtures during heating was studied in a Mooney viscometer [11]. Changes in the molecular structure of rubber SKN-26 and SKN-40M were determined by

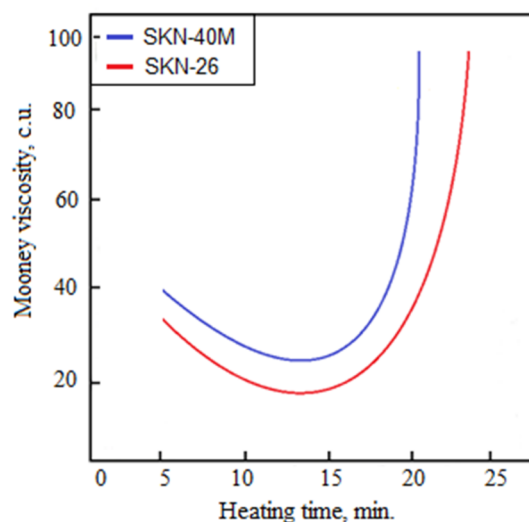


Fig. 1. Dependences of Mooney viscosity on the duration of heating at 423Kx25 min of unfilled mixtures based on: 1-SKN-40M; 2-SKN-26

IR spectroscopy [12]. Sol-gel analysis was carried out according to the method [10], while the samples were extracted with hot acetone for 24h, dried to a constant weight, and then re-extracted with cold benzene for 30h. The effective concentration of cross-links was determined by the equilibrium swelling method [9].

The physical and mechanical properties of the filled rubbers were determined in accordance with the requirements for physical and mechanical testing [13,14]. We tested reference rubbers based on SKN-40M, which are used in the rubber industry, for comparison. Filled and unfilled mixtures of the following composition were chosen for the production of molded elastomeric materials-technical products (mass fraction per 100, mass fraction of rubber):

## 3. Results and their discussion

The study of the structuring capacity of HCDMBP was carried out in unfilled systems in the activators during combining with elastomers SKN-40M and SKN-26 and epoxy resin.

As can be seen from Fig. 1, according to the change in the Mooney viscosity of model mixtures based on SKN-40M and SKN-26 containing 2.0 mass fraction of HCDMBP and 6.0 mass fraction of epoxy resin, the rate of structuring increases during heating at 423K.

Comparison of the value of the parameter  $\tau_{35}-\tau_5$  (tabl.1), which characterizes the rate of structuring (the smaller  $\tau_{35}-\tau_5$ , the higher the speed), shows that, this parameter is slightly higher for the SKN-40M elastomer (1) than for SKN-26 (2). This allows to evaluate the structuring capacity of the elastomer with the proposed vulcanizing systems.

Table 1. The effect of heating on the structuring capacity of unfilled mixtures based on rubber SKN-26 and SKN-40M (423K x 25 min)

Composition (part per hundred of rubber (phr))				Structuring start, $\tau_5$ , min		Structuring speed characteristic, $\tau_{35}-\tau_5$ , min	
1		2		1	2	1	2
SKN-40M	100	SKN-26	100	3.8	3.5	4.2	5.0
Zinc oxide	5.0	Zinc oxide	5.0				
HCDMBP	2.0	HCDMBP	2.0				
Epoxy resin ED-16	6.0	Epoxy resin ED-16	6.0				
Stearin	1.0	Stearin	2.0				
Filler P324	50	Filler P324	50				

In order to confirm the data on the structuring work of HCDMBP, an attempt was made to determine the direction of their interaction in the samples under study during combining with an elastomer. For this purpose, we studied the changes that occur in model mixtures during heating using IR spectroscopy. The obtained results are shown in Fig. 2. It can be seen that significant changes occur in the spectral region 2230 and 2320  $\text{cm}^{-1}$  [9]. The absorption band at 2240  $\text{cm}^{-1}$ , which occurs in the spectrum of SKN-40M rubber, was determined by valence vibration of the  $-\text{C}\equiv\text{N}-$  groups [12]. The occurrence of a new band in the region adjacent to 2240  $\text{cm}^{-1}$  is attributed by a number of authors to the formation of complex compounds of  $-\text{C}\equiv\text{N}-\text{C}$  groups by metal chlorides.

In the IR spectra, there is a noticeable decrease in the intensity of the absorption band at 750  $\text{cm}^{-1}$ , due to conditional vibrations of C-C bonds [9], the band at 1440  $\text{cm}^{-1}$ , which is attributed to bending vibrations of the C-H bond in the  $\text{CH}_2$  group, and also the intensities of the bands at 967  $\text{cm}^{-1}$  and 1340  $\text{cm}^{-1}$ , caused by out-of-plane and bending vibrations of the C-H bond in the group  $-\text{CH}=\text{CH}-$  trans configuration [9].

Based on the observed changes in the spectra of the SKN-26 elastomer during its joint heating with HCDMBP, it can be concluded that reactions occur with the participation of CH groups, which are bonded to nitrile groups,  $\text{CH}_2$  groups, and double bonds of elastomer molecules, during vulcanization.

In order to confirm the data on the comparative structuring work of HCDMBP with the elastomer, as well as to select the effective dosage of HCDMBP, we determined the relative amount of gel [13, 16] formed in model mixtures with the participation of zinc oxide and with various amounts of vulcanizing agents

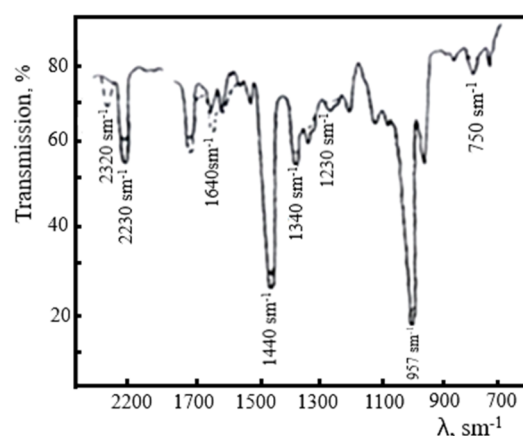


Fig. 2. Changes in the IR spectra in the SKN-40M+HCDMBP+ZnO system after heating at 423K (solid line – before heating, dotted line – after heating)

during heating at 423K for 25 min. The results are presented in Fig. 3.

As expected, the gel compound increases vividly with increasing dosage of HCDMBP. The maximum compound of gel ( $G_r$ ) in model mixtures approaches the value obtained for a standard unfilled mixture based on SKN-40M with a sulfur vulcanizing group. So, the data shown in Fig. 3 confirm that SKN-40M and SKN-26 are not inferior in structuring work to known compounds during combining with HCDMBP and other structuring systems [15,16].

The values of the effective concentration of cross-links ( $N_c$ ) for model vulcanizates are slightly lower than for a standard mixture with a sulfur vulcanizing group (Fig. 4).

This fact does not contradict the experimental data obtained by many researchers [13]. According to the results obtained in the study of vulcanization of SKN-40M and SKN-26 elastomers with help of HCDMBP, it was concluded that HCDMBP is an effective vulcanizing agent

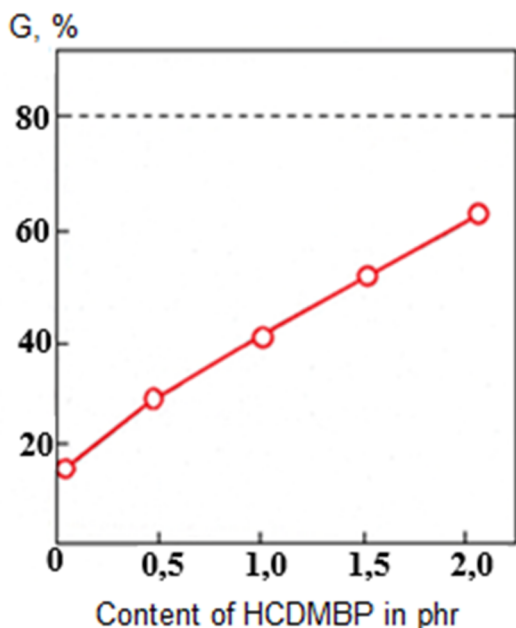


Fig. 3. Dependence of gelation in unfilled vulcanizates based on SKN-26 on the compound of HCDMBP (dotted line – the level of compound of SKN-40M gel)

for rubbers and that transverse carbon-carbon bonds are formed directly between rubber molecules in the obtained vulcanizates.

In accordance with existing views on the relationship between the structure of vulcanizates and their properties, it can be assumed that elastomers with this type of bonds should have the necessary operational qualities to work under these conditions. Extended studies of the physical and mechanical properties of elastomers were carried out to test this assumption, which allow predicting the performance of elastomer materials in aggressive liquid.

The data given in Tabl.2 allows to trace the effect of heating on a number of physical and mechanical properties of elastomers and to compare the properties of elastomer materials (EM) based on SKN-40M rubber containing HCDMBP, epoxy resin and other ingredients with the properties of commercial EM. It can be seen that vulcanizates (EM) are significantly superior to commercial [4] EMs based on the studied elastomers in terms of resistance to heating aging.

Despite the fact that the dynamic endurance indicators are somewhat lower for experimental EM than for serial ones under normal conditions, the former are distinguished by better performance characteristics at elevated temperatures due to higher coefficients of heat aging and significantly less swelling in aggressive environments.

So, from the point of view of the technological properties of elastomer mixtures, as well

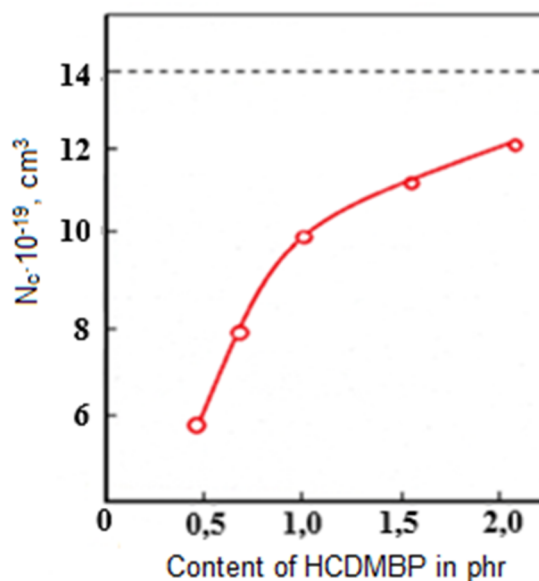


Fig. 4. Dependence of the concentration of effective cross-links ( $N_e$ ) in SKN-40M on the compound of HCDMBP (dotted line - the level of compound of effective cross-links in SKN-40M with a sulfur vulcanizing group)

as the physicochemical and physico-mechanical characteristics of vulcanizates, the results of the study presented in this paper show that HCDMBP as an organic crosslinking agent of nitrile elastomers has a significant advantage over currently used accelerators of monosulfide derivatives of 2-mercapto-becthiazole. Taking into account the kinetic features of the structuring of elastomer mixtures in the occurrence of HCDMBP, it should be recognized that this new type of polyhalomethyl containing structuring agents is of particular interest for use in the production of elastomer materials, since, compared to mercaptobenzothiazole derivatives, it meets the requirements for the development of a promising technology for the production of elastomer materials to a greater extent.

#### 4. Conclusions

The above experimental data and observations made earlier allow us to present the action of high and low molecular weight compounds as a crosslinking agent as follows, explain their distinctive features, the rate of crosslinking of SKN-26 and SKN-40M with HCDMBF in the main period, can be considered as a consequence of the formation during thermal dissociation low molecular weight products of two active fragments capable of interacting with SKN-26 and SKN-40M. According to IR spectroscopy, it was found that complex compounds of zinc chloride with nitrile groups of the elastomer are formed during the heating the systems SKN-26 + ZnO + HCDMBP.

Table 2. Comparative indicators of elastomeric materials based on SKN-40M rubber obtained in the occurrence of HCDMBP and epoxy resin after operation in sea water (I), oil-bearing (II) and clay (III) solutions. Test mode: 423K, 72 h.

Indicators	Known [3]	Suggested
	Sulfuric (C-S <sub>x</sub> -C)	-C-C- bond
Conditional tensile strength (f <sub>p</sub> ), MPA		
I	9	12
II	11	14
III	13	16
Heat aging coefficient ( I / II)		
by strength, f <sub>p</sub>	0.45/0.60	0.68/0.74
relative elongation ε <sub>p</sub>	0.57/0.72	0.81/0.78
Accumulation of residual deformation, %		
I	135	97
II	86	63
III	69	45
Mass change after swelling (mass %)		
I	135	97
II	86	63
III	63	50

It is shown that tertiary carbon atoms, which are included in the polybutadiene regions of the structures in position 1, 2, can take part in the reactions of structuring the nitrile butadiene elastomer with the help of HCDMBP. So, the decisive influence on the formation of effective cross-links is exerted by tertiary carbon atoms associated with the nitrile group.

In conclusion, we note that the developed NBR (SKN-26 and SKN-40M) based formulation can be used to obtain heat-resistant elastomer materials.

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