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Study on structural analysis of composite based on isoprene rubber with the participation of butadiene-nitrile rubber

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Abstract

The molecular weight distribution (MWD) of cross-linked elastomers has been studied by sol-gel permeation chromatography. The value of the number average molecular weight M_n *of the samples decreases from* $500•10^3$ *to* $150-200•10^3$*, and the value of* M_w *is reached from* $2000•10^3$ *to* $1000•10^3$*. It has been shown that the mixture is characterized by a relation between the plasticity and the molecular weight of the samples, and the plasticity of the required group can be obtained by adjusting the molecular weight distribution of growing chains. The kinetics of metal oxide vulcanization of isoprene mixtures with NBR has been investigated by exposing to high temperature. The calculation showed that cis - unsaturation is 4% in the change mode. It has been found that the yield of the number of cross-links during metal oxide vulcanization increases 1.5 times. In order to accelerate the degree of cross-linking and optimal properties of vulcanizates, hexachloroparaxylene was introduced into quasi-systems as an accelerator. It is assumed that these changes are associated with the occurrence of mechanochemical processes leading to the formation and increase of the concentration of cross-links* n_c*.*

Keywords: kinetics vulcanization; structures; isoprene; rheology; crosslinking; viscosity; gel-fraction, elasticity

1. Introduction

One of the effective ways to change the properties and expand the application areas of isoprene rubbers is the use of various classes of high molecular weight compounds. This direction began to develop successfully after establishing a connection between the properties of an elastomer and the parameters of their vulcanization structure, taking into account not only the representations of their vulcanization structure and the static theory of networks [1-3], but also the regularities of physicochemical processes, occurring during the modification of elastomers by high-molecular compounds (features of their dispersion and sorption, chemical transformations during modification, effects of microstate and association of polar functional groups, etc.), leading to the formation of complex vulcanization structures [4-10].

The patterns of behavior of high-molecular compounds in elastomers have been studied in detail using the sample of butadiene-styrene, ethylene-propylene, chloroprene, fluoroelastomers. The combination of elastomers with various unsaturated elastomers is the course of chemical reactions in the structure, causing the transformation of elastomers and their chemical interaction with each other during vulcanization. As a result of these processes, microparticles of a dispersed phase are formed, consisting of a grafted polymer chemically bonded to elastomers, and the properties of the obtained elastomers depend on the structure and size of particles, dispersed phase, and the number of interfacial chemical bonds.

This method allows, at the stage of obtaining elastomeric compositions, to carry out targeted controlled properties of the vulcanizer by combining high molecular weight isoprene and NBR with different unsaturation [11-17].

Isoprene and nitrile butadiene rubber (NBR) are known to have a significantly higher crosslinking tendency than other diene elastomers. Thus, it is vulcanized by a high temperature of additives, auxiliary substances, and in the presence of metal oxides, commercially valuable vulcanizates can be obtained. The mechanism of crosslinking of isopropene mixture (SKI-3) with NBR during metal oxide vulcanization is still insufficiently studied.

This work is devoted to the study of the structural parameters of the network and the kinetics of crosslinking of isoprene mixture with a butadiene-nitrile elastomer in the presence and absence of metal oxides.

2. Object and methods of the research

The object of the study was isoprene mixture with nitrile butadiene rubber. Synthetic isoprene rubbers (SKI-3 Russia) are obtained in the solution based on methyl alkyl catalysts and provide the predominant formation of structures of cis-1.4 unit up to 93%. Lithium polyisoprene crystallizes in an undeformed state. It is characterized by a very low crystallization capacity.

Polyisoprene expands (SKI-3) without plasticizer at 303K, after 8 minutes of plasticization, nitrile butadiene rubber (NBR) of SKN-40 brand is introduced in a ratio of 80:20 wt. parts. The obtained mixture is expanded for 15-20 minutes at 313K, after which the sample is pressed at 423K. The duration of vulcanization was varied from 0-60 minutes.

The spatial network and kinetics of heterogeneous vulcanization were determined by the maximum swelling of the sample in solvent chloroform. The calculation was carried out according to the Flory-Rehner equation [4] derived for static networks. The validity of the extension of this method to heterogeneous networks is confirmed by the results of determining the concentration of cross-links by two independent methods. The apparent activation energy E was calculated graphically using the Arrhenius equation [18, 19]. Sol-gel analysis was determined using the method [4, 20, 21]. The parameter of the spatial network and the number of cross-links and physical and mechanical properties were determined by a known method [22-24].

3. Results and discussion

From the data presented in Fig. 1, it can be seen that with an increased duration of heating, the gel fraction in the heterogeneous mixture SKI-3-SKN-40 monotonically increases up to 40%. The introduction of zinc oxide into the composition sharply increases the gel fraction in the samples and reaches the maximum number (60). When SKI-3 rubber contains 10% NBR, the rubber mixture after heating has a low gel fraction, which was determined by nc (Table 3). The results of the study of the gel fraction by the gel chromatogram analysis are shown in Fig. 2.

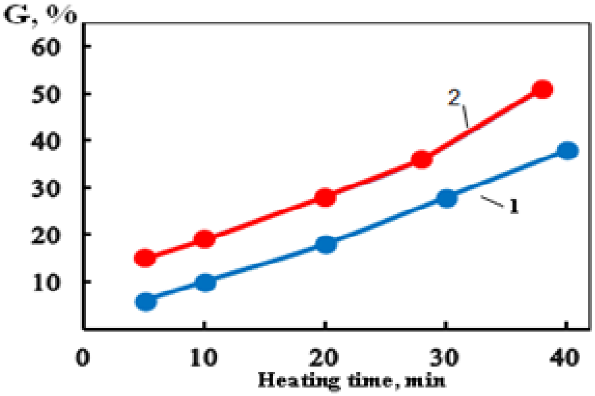

Figure 1. Dependence of the yield of the gel fraction on the duration of heating, min. 1-Mixture SKI-3-SKN-40 2. Mixture SKI-3-SKN-40+ZnO

According to the obtained data, the samples with the participation of zinc oxide, in contrast to those without zinc oxides, are characterized by highly mobile MWD of the sol fraction. Molecular weight regulation after radiation crosslinking allows obtaining elastomers with different MWDs. When regulating the molecular weight distribution (MWD), the value of the number average molecular weight (Mn) decreases up to $150\text{-}200 \cdot 10^3$, and the values of MW - from $2000 \cdot 10^3$ to $1000 \cdot 10^3$.

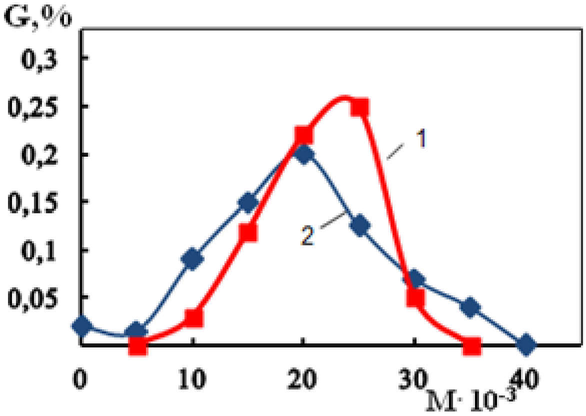

Figure 2. Normalized gel chromatogram of the mixture SKI-3-SKN-40
1-Sample of the mixture SKI-3-SKN-40 (80:20)
2-Sample of the mixture SKI-3-SKN-40 +ZnO

Considering the main visco-elastic characteristics of isoprene-nitrile rubber with NBR (SKI-3-SKN-40-ZnO), viscosity, plasticity and elastic recovery, there is found a stable difference between crosslinked and uncrosslinked SKI-3. It has been shown that, with the same plasticity, crosslinked SKI-3 has elastic recovery (Fig. 3).

In order to identify the reasons for the observed difference, let us compare the data on the molecular structure of typical samples of crosslinked and uncrosslinked isoprene mixtures shown in Table 1.

The results of the study again confirm that the plastic-elastic properties of modified isoprene with NBR are mainly determined by the composition of the microgel included in the elastomer, while the influence of the MWD of the sol fraction is not detected. Crosslinked SKI-3 is characterized by a relation between plasticity and the molecular weight of the samples, since this elastomer is helium-free, which apparently determines its significantly higher plasticity.

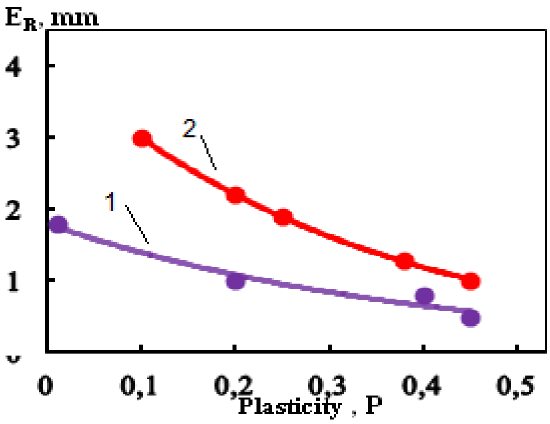

Figure 3. Dependence of elastic recovery (E_R) of a crosslinked and uncrosslinked mixture of isoprene with NBR (80:20) on their plasticity 1-SKI-3-SKN-40 (uncrosslinking) 2-SKI-3-SKN-40 (crosslinking)

The observed correlation between the structure and properties of elastomers is consistent with modern theoretical concepts on the relation of the viscoelastic behavior of elastomers with the molecular weight and structure of the chain. As it is known, crosslinked macromolecules of amorphous polymers form loose tangles in weight and penetrating each other, create mutually overlapping chains. The mechanical response of such a system to an external influence depends on its duration *t*. At $t<\tau_1$ (where τ_1 is the maximum relaxation time), when the polymer chains are still entangled, the system behaves like an elastic network, while at $t>\tau_1$, the system goes into a viscous flow regime. The value of τ_1, which determines the transition from one behavior mode to another, depends on the nature of the polymer and increases with an increase in the molecular weight of the chains. This position of theory is manifested when observed for crosslinked isoprene-nitrile elastomer (INE). The plasticity index depends on the molecular weight, since when measuring it, the duration of load application (3 min) is commensurate with the maximum relaxation time of long elastomer chains (at $n=10^4$, τ_1 is 10 with 14). Thus, it was established that the crosslinked isoprene-nitrile copolymer is characterized by a different molecular structure compared to uncrosslinked ones and has a mobile MWD. By adjusting the MWD of the growing chains, a crosslinked elastomer of the desired plasticity group can be obtained.

Table1: Molecular parameters and visco-elastic properties of mixtures of SKI-3-SKN-40 + ZnO

Crosslinked composite						Uncrosslinked composite					
Mooney viscosity at 373 K	Plasticity, conv. unit	Elastic recovery, mm	Sol fraction S %			Mooney viscosity at 373 K	Plasticity, conv. unit	Elastic recovery, mm	Sol fraction S %		
			$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	$\frac{Mw}{Mn}$				$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	$\frac{Mw}{Mn}$
59	0.25	1.15	240	970	4.8	69	0.38	1.30	200	930	3.9

For the vulcanization of isoprene mixtures (SKI-3-SKN-40) ZnO 5.0 parts by weight were used. The time interval for vulcanization was established for each composition of mixtures (Table 2).

Table 2: Intervals of vulcanization of a mixture of isoprene rubber with NBR in the presence of zinc oxide

Vulcanizing agents, wt. parts. per 100 wt. parts elastomer	Vulcanization interval, 423 K, min
Vulcanizates (oxide free)	90 min
SKI-3-SKN-40+ZnO (90:10) SKI-3-SKN-40+ZnO (80:20) SKI-3-SKN-40+ZnO (70:30)	50 min 30 min 30 min

According to the views established in the literature [14–20], it is assumed that the crosslinking of isoprene mixture with NBR during metal oxide vulcanization occurs due to double bonds. Changes in the content of double bonds were assessed by the yield of effective crosslinks when the same network density was achieved.

The kinetics of vulcanization of isoprene mixture with NBR (80:20) without additives *E* in the first part is equal to - 17.4, with additives of metal oxides - 29.3 kcal/mol. This phenomenon is obviously associated with the presence of two crosslinking mechanisms. Probably, initially, the kinetics of crosslinking is influenced by valuable oxidative processes that develop in elastic media due to the presence of traces of oxygen, which can lead to additional crosslinking. Therefore, although *E* increases, the process is accelerated, since the kinetics of crosslinking in this area is limited by the kinetics of the occurrence of an active medium by reactions of their addition to rubber. The kinetics of vulcanization was investigated by the change in the number of crosslinks n_c and the apparent energies are shown (Table 3).

Table 3: Apparent activation energies and limiting degrees of crosslinking during vulcanization of isoprene mixture with NBR (423 K x 40′)

Vulcanizing agents, wt. parts. per 100 wt. parts elastomer	E, kcal/mol	Number of cross-links $n_c' \cdot 10^{-19}$, cm^{-3}
SKI-3-SKN-40	17.4	0.9
SKI-3-SKN-40+ZnO (80:20)	29.3	3.7

A slight increase in n_c' in the presence of metal oxides compared to vulcanizates without oxide (Table 3) and values of n_c' close to the calculated ones make it possible to suggest that in the presence of metal oxides, vulcanization occurs due to the formation of active centers, which are suppressed by metal oxides or their transformation products. A satisfactory confirmation of this assumption is that the studied elastomers have very close values *E* at metal oxide vulcanization. It has been observed a change in the absorption bands 730 cm^{-1}, corresponding to double bonds in the 1.4-cis configuration. The calculation showed that crosslinking leads to a decrease in cis-unsaturation by 4%, of which 3% goes to isomerization and 1% is consumed. An increase in the heating time leads to a decrease in cis-unsaturation by 9%, of which 5% goes to isomerization, and 4% is consumed.

Thus, an increase in the duration of heating leads to a decrease in the ability to crystallize, contributes to a significant drop in unsaturation, at the same time, the yield of crosslinks increases sharply.

Heat crosslinking and metal oxide vulcanization would be expected to cure at a similar rate and with the same degree of crosslinking, which is not actually observed.

The investigated elastomers have different rates of vulcanization, which is shown by the example of samples at 423K x 40΄ (Fig. 4). The limiting values of n_c΄ crosslink yield are also different.

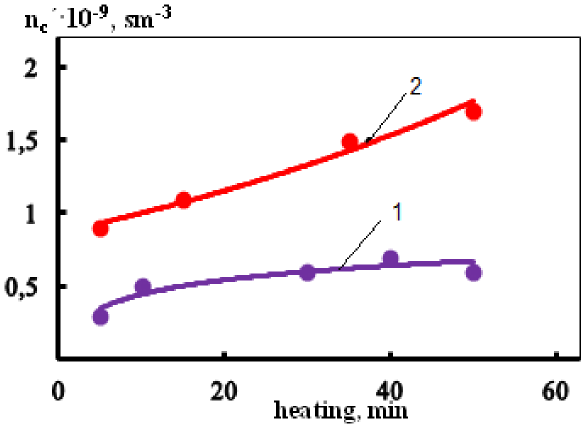

Figure 4. Kinetics of cross-linking (n_c΄) upon vulcanization of isoprene mixture with NBR (80:20) in the presence of in the presence of metal oxides and hexaachloroparaxylene (HCPX)

The simplest calculations show that with the indicated amount, the decrease in unsaturation (4%) can reach the yield value of 0.4-0.8·$10^{19}$$cm^{-3}$, provided that a cross-link is formed during the intermolecular reaction. In the presence of metal oxides, the yield of cross-linking n_c 'is 0.8-1.8·$10^{19}$$cm^{-3}$. Consequently, crosslinking is carried out not only due to double bonds, apparently some more mobile reactive centers are involved in crosslinking, which possibly, appear during the vulcanization process, since the kinetics without oxide vulcanizates is described by a zero-order equation, and the limiting degree of crosslinking is not achieved.

The interaction of elastomers with low molecular weight monomers is an important issue in the crosslinking of elastomers, since vulcanizates based on pure and binary mixtures do not have the necessary complex due to their practical application. To study the acceleration of the crosslinking yield, 3.0 wt. parts per 100 wt. parts of elastomer of hexachloroparaxylene (HCPX) was used. In the presence of HCPX, the rate and degree of crosslinking at 423Kx40΄ practically does not decrease in the presence of metal oxides. Moreover, the initial crosslinking period is accelerated. This can be seen from the kinetic curve of cross-linking in the mode 423Kx40΄ (Fig. 5). According to the literature data [1, 5], the acceleration of crosslinking is due to the conjugated bonds of the accelerator molecule, and intermolecular transfer of electronic excitation energy in an elastic medium is possible.

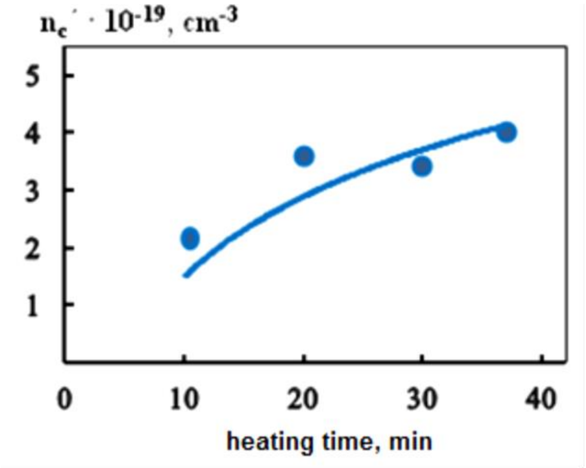

Figure 5. Kinetics of cross-linking n_c΄ during vulcanization of isoprene mixture with NBR (423Kx50΄) 1-SKI-3-SKN-40; 2-SKI-3-SKN-40+ZnO

4. Conclusion

In this work, using physicochemical methods, it was possible to establish a correlation between some of the main parameters of a crosslinked mixture of isoprene with butadiene-nitrile elastomer and the characteristic features of the morphology of the structural parameters of the network using the samples of three types of elastomer composition, differing in structure and their effect on the kinetics of vulcanization with the participation of oxides metals and accelerators. One of the results can be considered the proof of the decisive effect of heating on the structure and composition of the isoprene mixture with NBR is characterized by a significantly greater tendency to crosslinking.

Here are some examples from the obtained results, the reason for the dependence of the molecular weight distribution (MWD) of sol fraction without the introduction of low molecular weight metal oxides during vulcanization allows to obtain elastomers with different MWD. The value of M_n when adjusting the MWD decreases to 150-200·10^3, and the values M_w from 2000·10^3 to 1000·10^3. Examination of the rheological characteristics of the elastomer, Mooney viscosity, plasticity and elastic recovery reveals a stable difference between cross-linked and non-cross-linked elastomers, consisting in that crosslinked INR has lower Mooney viscosity and elastic recovery.

Analysis of the state of scientific and applied research in the field of vulcanization kinetics shows that the studied mixture of elastomers has different crosslinking rates, which is shown by an example at 423Kx40΄. In the proposed mixture in the presence of metal oxides activates the rate and yield of cross-links, which is associated with an increase in the molecular weight of vulcanizates. An important role in crosslinking is played by the use of polyfunctional monomers with different polar groups in systems, which accelerates the vulcanization process. The introduction of HCPX into systems has a positive effect that accelerates the formation of the degree of crosslinking and changes in rheological properties.

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