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# Modification of isoprene rubber with high molecular weight compounds in mixtures

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In the present work, the role of hexachloroparaxylene in modified rubbers (SKI-3) in the systems of SKI-3+SKN-40+ZnO and SKI-3+PVC+ZnO under the influence of peroxide was studied. Using physicochemical and spectral methods, the change in the molecular and spatial network of isoprene rubber SKI-3 in the presence of an accelerator for crosslinking of hexachloroparaxylene (HCPX) after peroxide crosslinking in an electric press in 423Kx40' mode is shown. Formation of carbon-carbon chemical bonds in the SKI-3 rubber macromolecule for each system under study and the increase in the crosslinking yield and cross-linking efficiency with time were investigated. The behavior of high molecular weight polyvinyl chloride (PVC) and polyvinyl acetate (PVA) has been studied, and the radical reaction mechanism by EPR crosslinking has been confirmed.

**Keywords:** isoprene, polyvinyl chloride, polyvinyl acetate, crosslinking, molecular weight, rheology, viscometer, spectroscopy.

**Модифікація ізопренового каучуку високомолекулярними сполуками в сумішах.** *С.А.Рахімова, Ф.А.Аміров, І.Г.Мовлаєв, Ш.М.Мамедов, Г.А.Мамедова, П.І.Ісмаїлова,, Р.Ф.Ханкішиєва*

Вивчено роль гексахлорпараксилолу в модифікованих каучуках (СКН-3) у системі СКІ-3+СКН-40+ZnO, СККІ-3+ПВХ+ZnO та СКІ-3+ПВА+ZnO при пероксидному впливі. За допомогою фізико-хімічного та спектрального методів показано зміну молекулярної та просторової сітки ізопренового каучуку СКН-3 у присутності прискорювача зшивання гексахлорпараксилолу (ГХПК) після пероксидного зшивання в електропресі в режимі 423Кх40′. Досліджено утворення вуглець-вуглецевих хімічних зв'язків у макромолекулі каучуку СКІ-3 для кожної досліджуваної системи та збільшення виходу зшивання та ефективності зшивання від часу. Вивчено поведінку високомолекулярного полівінілхлориду (ПВХ) та полівінілацетату (ПВА), підтверджено радикальний механізм реакції методом ЕПР зшивання.

## *1. Introduction*

On the basis of isoprene rubber, a wide range of polymeric materials can be obtained, in which increased heat resistance and resistance to aggressive environments are required. For the crosslinking of SKI-3 rubber containing double bonds and cis-trans structures in the rubber macromolecule in the presence of peroxides, the crosslinking systems based on SKI-3 rubber are resistant to thermal aging [1–5].

It is known [6, 7] that the main factor for a significant increase in bond strength in elastomercord systems is the introduction of a modifier, which leads to the formation of chemical bonds between the elastomer matrix and the cord. There is also evidence that an increase in adhesive contact in an elastomer system is achieved by introducing into the elastomer composition high-molecular and low-molecular compounds containing polar and functional groups in the molecule

that can interact with the elastomer. There is an evidence of an increase in the adhesive properties of the elastomer used in mixtures of maleimide anhydride [8, 9]. However, low-molecular-weight additives often sublimate, migrate from the composite material during operation, changing its properties. One way to increase the bond strength of an elastomeric system is to use high-molecular compounds containing various polar groups in the molecule. The purpose of this work is to study the crosslinking of the elastomeric mixtures SKI-3-SKN-40, SKI-3-PVC and SKI-3-PVA in the presence of low molecular weight compounds at various ratios.

In the course of this work, we studied the efficiency of using high-molecular-weight copolymers of butadiene-nitrile (SKN-40), polyvinyl chloride (PVC) and polyvinyl acetate (PVA) to increase the heat resistance of cord-elastomer composites. The effects of the composition and structure of isoprene SKI-3 on rheological, spatial network parameter and physical and mechanical properties of vulcanizates are considered.

## 2. Experimental

The objects of the study were elastomeric blends based on modified isoprene rubber SKI-3-SKN-40, SKI-3-PVC and SKI-3-PVA in the ratios 80:20, 90:10, 70:30. As a crosslinking agent, 4.0 wt. parts of dicumyl peroxide (PD), 3.0 wt. parts of accelerator for the crosslinking of hexachloroparaxylene (HCPX), 5.0 wt. parts of ZnO, 2.0 wt. parts of a plasticizer stearic acid, 1.5 wt. parts of softener petroleum product of bitium and 50 wt. parts of filler P324 (carbon black obtained by a furnace at 1100 K) were used.

On laboratory rollers, the specified composition was mixed at 80°C for 25 minutes and elastomer mixtures were prepared with a friction coefficient $f$ = 1:2. Then the samples were molded on an electric press in the form of plates with a thickness of 0.3 mm. Under this condition, elastomeric blends were prepared in the presence of 2.0 wt. parts of sulfur.

The structure and composition of the mixtures were confirmed by spectroscopic data.

The number of crosslinked molecules ($1/Mn_{\tau}$) and the occurrence of active network chains in the macromolecule were determined by sol-gel analysis; the calculation was carried out using the Flory-Rehner formula [10]. The change in the molecular structure of peroxide samples was observed by Fourier spectroscopy. The interpretation of the spectra was carried out in accordance with the correlation tables and guidelines [11, 12].

The rheological properties of vulcanizates were determined by capillary viscometer using an Ubbolode viscometer [12]. The change in the intrinsic viscosity of the samples was determined in a toluene solution, and the calculation was carried out according to the formulas of Mark Houwink [13].

The thermal properties of the samples were studied on a Paulik-Paulik Erden derivatorgraph (DTA), with 5 min heating rate. The physical and mechanical properties of the samples were determined by a known method [14].

## 3. Results and discussion

Modifications of isoprene rubber with high molecular weight compounds are of great importance. To determine the rheological properties, the combination of isoprene rubber with nitrile-butadiene rubber (SKN-40) and polyvinyl chloride (PVC) and polyvinyl acetate (PVA) was initially studied; the influence of the system on the structure and properties of SKI-3 was determined.

After determining the cross-linking rates for various ratios, the mass % ratio (80:20, 90:10, 70:30) of SKN-40, PVC and PVA in the composition of the elastomer was chosen. It has been established that the composition of the studied systems SKI-3-SKN-40+HCP+ZnO, SKI-3-PVC+HCP+ZnO affects the change in plasticity, stiffness and viscosity of mixtures. As a result of mechanical plasticization of mixtures, the plastoelastic properties of the elastomer can increase by a factor of 2.

A characteristic feature of the structure of quasi-systems consisting of an elastomer, chlorine- containing compounds, and metal oxides is the formation of particles of a dispersed phase and a dispersed medium. The properties of the mixtures depend on the size and internal structure of the dispersed phase particles, as well as on the intense interaction of the dispersed phase with the dispersed elastomer medium [15]. According to the colloidal chemical concept [16], in the studied elastomer mixtures, after plasticization and heating, the chemical interfacial bonds provide intensive interaction with the dispersed medium of the elastomer, which leads to structural transformation of the elastomer. This conclusion is confirmed by mechanical and thermochemical crosslinking of polymer systems of different grades at different time intervals.

Table 1. Dependence of elastomeric mixtures based on copolymers in terms of plasticity, stiffness and Mooney viscosity on the duration of mechanical plasticization

| Elastomeric mixtures | Duration of plasticization, min | Plasticity, c.u. | Stiffness, Hs | Mooney viscosity, c.u. |
|---|---|---|---|---|
| SKI-3-SKN-40 + HCPX + ZnO | 20 | 0.32 | 1400 | 40 |
| | 40 | 0.25 | 1200 | 50 |
| | 60 | 0.20 | 1000 | 60 |
| SKI-3-PVC + HCPX + ZnO | 20 | 0.27 | 1200 | 32 |
| | 40 | 0.20 | 1150 | 45 |
| | 60 | 0.17 | 900 | 50 |
| SKI-3-PVA+HCPX+ZnO | 20 | 0.24 | 1100 | 30 |
| | 40 | 0.20 | 1000 | 40 |
| | 60 | 0.13 | 900 | 50 |

As the results showed, the mechanical plasticization of quasi-systems is characterized by a change in plasticity, stiffness and viscosity with an increase in the plasticization time (Table 1). During mechanical plasticization of the quasi-systems for 20 min, a slight change in plasticity is observed, which is associated with a phase transition. An increase in the plasticization time to 30 min leads to insignificant changes in the plasticity parameters, while an increase in the plasticization time to 60 min leads to a stable value of the plasticity parameter. On the contrary, the stiffness coefficient of elastomeric mixtures decreases sharply within 30 minutes. Apparently, this phenomenon is associated with the onset of destruction of the samples. The subsequent increase in the time of mechanical plasticization of the elastomeric mixtures does not lead to a significant change in the stiffness coefficient; it remains in the range of 1100–1400 gauss.

As can be seen from Table 1, in the presence of HCPX and ZnO in mixtures, the Mooney viscosity parameter does not cause significant changes during the plasticization of elastomeric mixtures based on modified isoprene rubber (SKI-3).

Apparently, according to [17, 18], during the mechanical plasticization in the structure of SKI-3-SKN-40, SKI-3-PVC and SKI-3-PVA with low molecular weight HCPX, under the action of applied forces, polymer molecules are broken along the valence bond with the formation of free radicals, or, possibly, the resulting free radicals interact with polymer targets, forming crosslinked structures. The results of experiments show that the rate of mechanical plasticization of modified mixtures is determined by the content of polar –C≡N, C–Cl and COO groups in them, and the rate of plasticization of mixtures increases with the introduction of metal oxides (ZnO) into the composition of metal oxides.

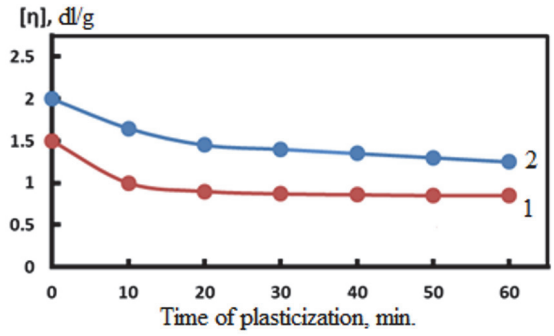


Fig. 1. Dependence of the intrinsic viscosity of solutions (toluene) on the duration of mechanical plasticization of copolymer mixtures based on SKI-3.
1. SKI-3-SKN-40 + HCPX + ZnO;
2. SKI-3-PVC + HCPX + ZnO.

The kinetics of changes in the intrinsic viscosity ($\eta_{intr.}$) of an elastomeric mixture is described by monotonically decreasing curves (Fig. 1).

At the same time, for the mixture of SKI-3-SKN-40, a higher rate of change is observed during mechanical plasticization than for the mixture with polyvinyl chloride. Based on the intrinsic viscosity data during mechanical plasticization, the molecular weight value was determined. In the elastomeric mixtures, a decrease in molecular weight from 200 thousand to 100 thousand units was observed.

As it is known, the crosslinking reaction of SKN-3 with chlorine-containing compounds occurs as a result of the decomposition of CCC and the products of their de-

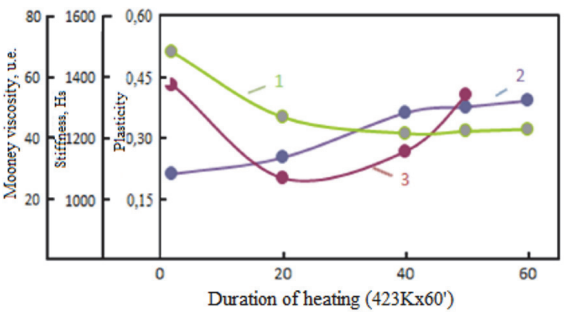


Fig. 2. Dependence of plasticity (*1*), stiffness (*2*) and Mooney viscosity (*3*) of mixtures based on copolymers SKI-3-SKN-40 + HCPX + ZnO on the duration of heating (423Kx60′).

composition [19]. Crosslinking of metal oxides plays an important role in thermochemical processes as activating compounds. The degree of dispersion and band gap width of zinc oxide have a significant effect on its activity during vulcanization [20]. The conditions for the use of oxides for crosslinking mixtures are specific.

The effect of HCPX, dicumyl peroxide and zinc oxide on the plasto-elastic properties of thermovulcanizates under thermochemical conditions was studied at a ZnO content in the mixture of 5.0 wt. parts. The obtained data (Fig. 2) indicate that plasticity in thermovulcanizates appears 45 minutes after the start of the reaction, destructive changes in thermovulcanizates are completed and then (after 60 min) plasticity monotonically increases until it reaches a constant value. On the contrary, there is a change in the value of the stiffness of thermovulcanizates.

An interesting regularity was established when considering the effect of the concentration of low molecular weight products on the properties of thermovulcanizates. In contrast to sulfur-containing structuring systems, the amount of the accelerator of crosslinking of HCPX introduced into the elastomeric blends leads not to a decrease, but to an increase in the duration of the induction period of crosslinking, which is reflected in the greater resistance of such mixtures to precure.

The most sensitive parameter of the network structure is the soluble part of the mixtures in toluene (sol fraction, S). The results of the sol-gel analysis of the investigated unfilled vulcanizates are shown in Fig. 3; it is seen that the amount of the sol fraction depends on the density of the $1/M_C$ network. A change in the amount of sol with a constant $1/M_C$ (the number of targets in the network) is observed with a change in the molecular weight distribution (MWD); obviously, this is due to the specific features of the adsorption of the elastomer on the surface of dispersed particles of HCPX. The low molecular fraction is concentrated in the volume of the elastomeric medium, so it is less crosslinked. The total amount of sol in the system is shown in Fig. 3.

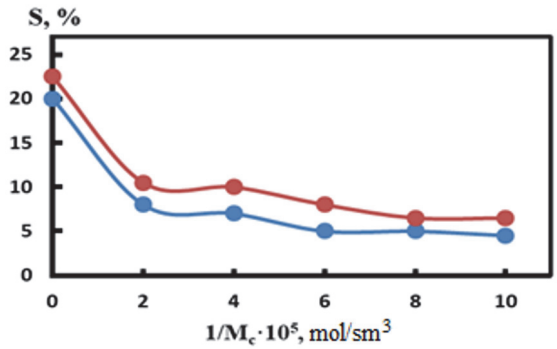


Fig. 3. Dependence of the amount of sol fraction (S) on the concentration of active chains of the network of vulcanizates
1. SKI-3-SKN-40 + DCP + HCPX + + ZnO
2. SKI-3- PVC + DCP + HCPX + ZnO

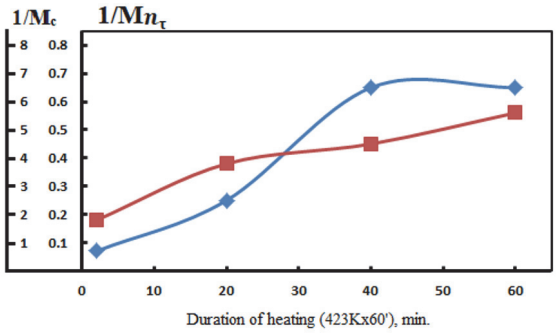


Fig. 4. Dependence of the structural parameters of the network of vulcanizates on the heating time (423x60'K) in the SKI-3-SKN-40+DCP+HCPX++ ZnO system
1. The number of crosslinked molecules
2. The number of active network chains

Naturally, the formation of a number of network targets in the system occurs actively only when the time of the crosslinking duration increases from 30 to 60 minutes, when the mixtures are crosslinked for 60 minutes. The total number of chains in the network is $11.5 \cdot 10^5$ mol/cm$^3$, and the cross-linking rate is $0.7 \cdot 10^3$ mol/cm$^3$ (Fig. 4).

The results of determination of the structural parameters of the vulcanization network by the method of sol-gel analysis, with the participation of low-molecular weight products, makes it possible to more

Table 2. Dependence of the physical and mechanical properties of vulcanizates based on copolymers (SKI-3-SKN-40) on the content of dicumyl peroxide (DCP)

| Crosslinking agent | Peroxide content, phr | Number of network chains, $1/M_C \cdot 10^5$ | Stress at 200 % elongation, $f_n$, MPa | Tensile strength | Relative elongation, ε, % |
|---|---|---|---|---|---|
| Dicumyl peroxide (DCP) | 0.5 | 0.75 | 3.7 | 11 | 650 |
| | 1.0 | 1.19 | 4.4 | 14.6 | 580 |
| | 1.5 | 2.18 | 5.71 | 16.3 | 490 |
| | 2.0 | 3.5 | 6.16 | 18.0 | 400 |
| | 3.0 | 4.1 | 8.4 | 20.5 | 370 |

fully characterize the properties of mixtures with the participation of dicumyl peroxide (DCP) based on SKN-3-SKN-40-DCP-HCPX+ZnO. The data presented in Fig. 4 describe the change in the total number of network chains and crosslinked molecules and indicate that crosslinking in these systems occurs more efficiently. A special role in the systems is played by nitrile butadiene rubber, which successfully activates crosslinking with the participation of low molecular weight compounds.

Analysis of the IR spectrum of the SKI-3-SKN-40-DCP-HCPX+ZnO structuring system shows that after heating for 30 min, a number of significant changes appear in the system.

Thus, a decrease in the intensity of the band at 1450 $cm^{-1}$ is observed, which refers to deformation vibrations of the C–H bond in the $-CH_2$ group [21], and the band at 1315 $cm^{-1}$ is caused by out-of-plane and deformation vibrations of the C–H bond in the –C=CH– group of the trans configuration [22, 23]. The absorption intensity of the 790 $cm^{-1}$ band decreases noticeably, due to vibrations of the C–C bond. This suggests that chlorine is cleaved off the HCPX molecules; as a result, apparently, the intensity of the 1230 $cm^{-1}$ bands decreases; in addition in the spectral region of 2240 $cm^{-1}$ and in the region related to SKN-40 significant events occur due to stretching vibrations in the –C≡N group [24]. The absorption intensity at a frequency of 2220 $cm^{-1}$ is related to the formed complex compounds of the –C≡N group. Taking into account these changes, it can be assumed that in mixtures of SKI-3-SKN-40 with HCPX, the crosslinking reaction proceeds with the participation of the –CH– group associated with nitrile groups and double bonds of polymer molecules.

In conclusion, according to the data of IR spectroscopy, the crosslinking of the SKI-3-SKN-40-DCP-HCPX+ZnO systems for 20–30 min proceeds with the following changes: the intensity of the bands at 978 $cm^{-1}$ and 1370 $cm^{-1}$ decreases due to the deformation vibrations of the C–H bond in the –CH = CH– group. From the optical densities of the absorption bands at 978 $cm^{-1}$ of double bonds (1.4 trans) and at 928 $cm^{-1}$ of double bonds (1.2), the distribution of double bonds was calculated for the polymer system SKI-3-SKN-40-DCP-HCPX+ZnO: 20 % are 1.2 bonds, 60 % are 1.4-trans bonds, and 20 % are 1.4-cis bonds.

Crosslinking of polymer systems in the presence of a crosslinking agent of dicumyl peroxide occurs with the simultaneous formation of vulcanization structures by the formation of C–C bonds, which increases the resistance to rupture of vulcanizates depending on the crosslinking agent of dicumyl peroxide (Table 2). It should be noted that when the number of crosslinked molecules in the elastomeric system becomes significant, the strength of the vulcanizates decreases.

Indeed, as can be seen from Table 2, a decrease in the tensile strength occurs when the formed chemical bond of C–C becomes unchanged, and its relative elongation decreases; as a result, a monotonic increase in the concentration of active chains is observed.

The composition of mixtures with the participation of DCP is given in the methodology on glava 2.

## 4. Conclusion

The above experimental data and earlier observations make it possible to show the influence of high and low molecular weight compounds as a structuring agent and explain their distinctive features. The rate of crosslinking of DCP and HCPX with copolymers in the main period may be due to the formation of low molecular weight products during thermal dis-

sociation of two active fragments capable of interacting with the elastomer.

The density of vulcanization networks obtained under the action of DCP and HCPX is due to a structuring effect of the used dicumyl peroxide (DCP) and HCPX, which leads to the appearance of cross C–C links between elastomer molecules.

When crosslinking copolymers based on isoprene rubber SKI-3 with high and low molecular weight compounds (PD, HCP, ZnO), the molecular weight of the elastomeric mixture increases. As a result of crosslinking with particles of the dispersed phase, an increase in the number of active chains of the network ($1/M_s$) is noted.

Based on the foregoing and experimental data, we tried to explain the position of the studied crosslinking agents in relation to copolymers. When cross-linking SKI-3 using DCP, HCPX, and ZnO at 423 K for 20–40 min, HCPX decomposes by eliminating chlorine from both trichloromethyl groups, and the resulting diradical accepts hydrogen from elastomer macromolecules. The introduction of high and low molecular weight compounds into rubber macromolecules leads to a change in the structure of elastomer systems. As a result of a chemical reaction in the quasi-systems, chemical C–C bonds are formed in the rubber molecule. A change in the molecular structure and the appearance of new active cross-links leads to a change in the plastoelastic and physical-mechanical properties. For each mixture under study, as a result of heating at 150°C for 40 min, different changes in viscosity (molecular weight) are observed. As a result of changing the molecular weight with modifying additives, a change in these properties is observed.

In conclusion, it should be noted that the developed formulation based on copolymers can be used in the elastomeric industry to obtain heat-resistant elastomeric materials.

## References


1. Sh.M.Mammadov, Fundamentals of Technology for the Synthesis, Processing and Vulcanization of NBR, Lap Lambert Academic Publishing, Germany (2015).
2. Sh.M.Mammadov, F.I.Yadreev, Nitrile Butadiene Rubber and Rubber Based on Them, Elm, Baku (2001).
3. A.S.Kuzminskii, S.M.Kavun, V.P.Kirpichev, Physical and Chemical Principles of Processing and Application of Elastomers, Khimiya, Moscow (1976).
4. P.J.Feory, Rehman, *J.Chem.Phys.*, **11**, 312 (1968).
5. N.I.Avvakumova, L.A.Budarina, S.M.Divgun et al., Workshop on Chemistry and Physics of Polymers, Chemistry, Moscow (2007) [in Russian].
6. V.O.Reikhsfeld, L.N.Erkova, V.L.Ruban, Laboratory Workshop on Synthetic Rubbers, Chemistry, Moscow (1967) [in Russian].
7. N.D.Zakharov, N.V.Belozerov, Main Properties of Rubbers and Methods for Their Determination, Chemistry, Moscow (2006) [in Russian].
8. K.V.Nelson, Vibrational Spectra and Molecular Processes in Rubbers, Khimiya, Moscow (1989) [in Russian].
9. L.Bellamy, Infrared Spectra of Complex Molecules, Chemistry, Moscow (2000) [in Russian].
10. Ya.S.Lipatov, Physics-Chemistry of Multicomponent Systems, Naukova Dumka, Kyiv (2006).
11. D.Ingrad, Electron Paramagnetic Resonance in Free Organic Radicals, Chemistry, Moscow (1998).
12. K.A.Chernkov, *Rubber and Rubber*, 45 (2005).
13. M.E.Tsyganova, *Vysokomol.Comm.*, **4**, 145 (2012).
14. I.N.Pugacheva, N.S.Nikulina, S.S.Nikulin, *Chemistry for Sustainable Development,* **5**, 641 (2016).
15. I.A.Tutorsky, E.E.Potapov, A.G.Schwartz, Chemical Modification of Elastomers, Chemistry, Moscow (2003) [in Russian].
16. Z.V.Onishchenko, *Kauchuk i Rezina*, **4**, 23 (2008).
17. B.C.Grishin, *Kauntsch.and Gummi.Kustst.*, **3**, 222 (1993).
18. B.A.Dogadkin, A.A.Dontsov, V.A.Shershnev, Chemistry of Elastomers Chemistry, Moscow (1981) [in Eussian].
19. A.C.Estrin, JI.M.Kogan, V.A.Kroll, Modified Diene Elastomers. Synthetic Rubber, Chemistry, Leningrad (1983).
20. T.Guillaume, B.Bernard, A.Bruno, *J.Progress in Polymer Science*, **36**, 191 (2011).
21. D.Feldman, A.Barbalata, Synthetic Polymers: Technology, Properties, Applications; Chapman & Hall, London (1996).
22. Klinkender, C.R.Handbook of Specialty Elastomers, CRC Press (2008).
23. J.George, K.T.Varguhese, S.Thomas, *Polym.*, **41**, 1507 (2000).
24. F.W.Barlow, Rubber Compounding: Principles, Materials and Techniques Rubber, Ed. Marcel Dekkar, New York (1993).