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Investigation of the rheological structural parameters of a network of NBRbased vulcanizates with the participation of chlorine-containing

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Abstract

A new class of active organic crosslinking agents for the vulcanization of NBR on the basis of chlorine-containing compounds (CCAC) has been found, allowing to improve significantly the rheological and structural parameters of NBR. Gel content and Mooney viscosity in binary systems after plastification on rollers were studied. The sol fraction of crosslinked NBR (SKN-40+CCAC) was found to be characterized by a bimodal MWD. Abnormally high value of M_w/M_{n_s} of sol fractions is associated with the bimodal nature of their MWD and indicates the presence of gel in the elastomer. The value of M_η of the sol fractions in cross-linked NBR was found to be insignificant. The sol fraction of cross-linked HCPX elastomer was shown to have lower values of the specified parameters and lower content of high-molecular weight fractions. The branching density ρ of macromolecules of sol fraction of cross-linked NBR was $1.90\text{-}2.3\cdot10^{-3}$, i.e. on average corresponded to one monomer unit and two hundred branching nodes per molecule.

Keywords: nitrile butadiene rubber, hexachloroparaxylene, Mooney viscosity, sol fraction, rheology, crosslinking, vulcanization, gel, plasticity, dispersion

1. Introduction

In order to obtain homogeneous mixtures with additive properties, it is necessary to have: elastomers with close compatibility features, giving mixtures with one glasstransition point; elastomers with similar viscosities, elastomers with similar vulcanization characteristics, the possibility of some variation in the plasticity of blended elastomers in order to overcome small differences and viscosities in compatibility features [1-3]. It is necessary to use a method for displacement that promotes their uniform distribution in elastomers.

The cross-linking of nitrile butadiene rubber (NBR) with chlorine-containing aromatic compounds (CCAC) generally consists of components of different structures. In principle, any technological characteristic of NBR will obviously be a function of the relative content of features in the structure of each of the components.

In this regard, one of the most important rheological characteristics of NBR was studied –the ability to plasticize on rollers and the effect of heating on the structural parameters of the spatial network of NBR polymer systems (SKI-40 + CCAC) cross-linked after heating in an electric press at a mode of 423K x 30 min.

Previously [4-6], the kinetics of thermochemical structuring of nitrile butadiene rubber (NBR) in the presence of aromatic halogen compounds was studied. The elastomers formed in this process may contain a variety of cross-links of different energies. In addition, chlorine-containing substances are often introduced into the composition of the elastomer as an elastomer crosslinking accelerator, which allows achieving optimal properties of elastic materials with less heating. However, at present, the role of chlorine-containing aromatic compounds as an accelerator of NBR crosslinking during heating has not been adequately studied. The known data are fragmented and incomplete.

2. Experimental part

The objects of study were nitrile butadiene rubber (NBR) brand SKN-40M and organic crosslinking agents (OCA) - the chlorine-containing aromatic compounds (CCAC), hexachlorparaxylene (HCPX), ω-octachlor-4.4dimethyl diphenylmethane (OCDMDPM) and ωdecachlor-4.4-dimethyl-1.4-dibenzylbenzene (DCDMDB) [7, 8].

Mechanical (cold) plastification of NBR was carried out on laboratory rollers with the size of 160×320 mm at 203 K ± 283K. The rollers load was 100g with a fraction f=1:2, elastomer mixtures (wt.% per 100 wt.% of rubber) were prepared with the following composition.

1.SKN-40M-100 + HCPX – 3.0;
2.SKN-40M-100 + OCDMDPM – 3.0;
3.SKN-40M-100 +DCDMDB-3.0

After mechanical plastification on rollers, it was vulcanized in an electric press at 423K×40 min. Plastoelastic properties of mixtures were determined according to GOST 415-92, 10722-87. Rheological properties of the samples were determined on an Ubbelohde capillary viscometer [9] in toluene at 293 K; the calculation was carried out according to Mark–Houwink equation at value of solution constant K = 1.16×10 and α = 0.7 [10].

Molecular characteristics of the elastomer cross-linked by different OCAs were determined by sol-gel analysis [6], equilibrium swelling [7], molecular sieve chromatography [8], and viscometry [9]. The content of sol fraction S in the elastomer, macrogel G, its degree of equilibrium swelling Q_e, number average molecular weight of the chain segment between cross-links ¯$_c$, resistance of the macrogel to shear deformations θ [6], the number average ¯n$_s$, $_n$mass average ¯$_w$ and viscosity average ¯$_η$ molecular weights, degree of polydispersity, ¯$_n$, MWD and branching density ρ of the sol fraction macromolecules have been estimated.

The value of ¯$_c$ was calculated using nomograms obtained by graphical solution of the Flory-Rehner equation [10], and the values of ¯n$_s$ and ρ were calculated from the known relations of sol-gel analysis [11].

The MWD of sol fractions was determined by molecular sieve chromatography [8]. This method allows to simultaneously separate elastomer into fractions and to relatively quickly determine their molecular characteristics. The analysis of cross-linked elastomer by molecular sieve chromatography was performed using a glass column with a length of 800 mm and a diameter of 8 mm. A modified silochrome S-2 with a grain size of 0.16-0.25 mm was used as a nozzle. The flow rate of eluent (carbon tetrachloride) was 1 ml/min. The detector was an ITR-2 interferometer. The column was calibrated using narrow fractions of NBR with¯$_w$/M ‾$_n$ ≤ 1.1.

3. Results and discussion

The experiments have shown that plastification on cold rolls (293-300 K) has significantly higher effect on noncross-linked elastomers than on cross-linked ones. Thus, the Mooney viscosity of non-cross-linked SKN-40 decreases by 50 and 70 % respectively after 20 minutes of plastification, and the viscosity of elastomers cross-linked with TCMCC by 18 and 30 % of the initial viscosity (Fig.1).

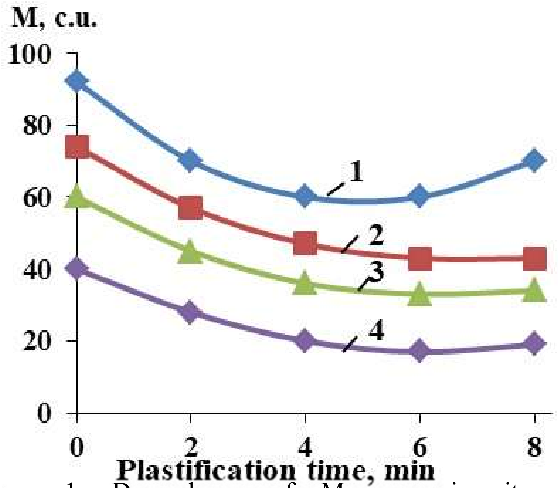

Figure 1. Dependence of Mooney viscosity on plastification time
1. SKN-40M + DCDMDB;
2. SKN-40M + OCDMDPM;
3. SKN-40M + HCPX;
4. SKN-40M

The data in Table 1 below show that all the mixtures containing CCAC in their composition have a high content of dense gel in SKN-40, while those without organic crosslinking agents (OCA) do not.

The quasi-binary system (SKN-40-CCAC+ZnO) has higher viscosity than the binary mixtures. The gel content during mechanical plastification of cross-linked NBR also decreases slightly and even after plastification for 30 min it becomes 50 %.

A less drastic change in the properties of cross-linked NBR during plastification can be explained by the presence of labile cross-links in them, which easily break down with the formation of active fragments, which then recombine again, creating new cross-links. [12].

Table 1: Changes in gel content, density of binary and quasi-systems and viscosity after plastification on rolls

Composition	Gel content, G%	Gel density, g/cm^3	Mooney viscosity, c.u.
SKN-40M	78	-	25
SKN-40M + HCPX	78	3.8	43
SKN-40M + OCDMDPM	84	4.4	46
SKN-40M + DCDMDB	87	4.5	49
SKN-40M + HCPX + ZnO	85	4.1	53
SKN-40M +OCDMDPM+ZnO	90	4.7	56
SKN-40M + DCDMDB + ZnO	92	4.8	60

The destruction of the main polymer chains obviously occurs during mechanical plastification of non-cross-linked NBR, as evidenced by a decrease in the intrinsic viscosity of the toluene solution of the polymer (Fig. 2)

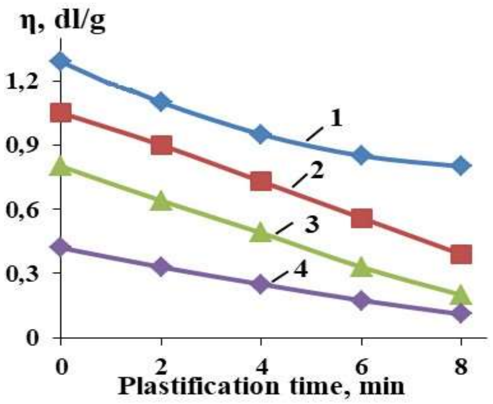

Figure 2. Dependence of intrinsic viscosity on plastification time

1. SKN-40M + DCDMDB;
2. SKN-40M + OCDMDPM;
3. SKN-40M + HCPX;
4. SKN-40M

The observed decrease in the intrinsic viscosity of NBR polymer systems during their mechanical plastification indicates chain degradation in the samples.

Thus, the behavior of polymer systems (SKN-40M + CCAC) during processing on rollers has different rheological properties.

It was natural to expect that the nature of the interaction of binary mixtures containing chlorinecontaining compounds with zinc oxide would be different.

Indeed, the introduction of carbon black P324 drastically increases the Mooney viscosity of the binary mixture during heating at 423 K (Fig.3).

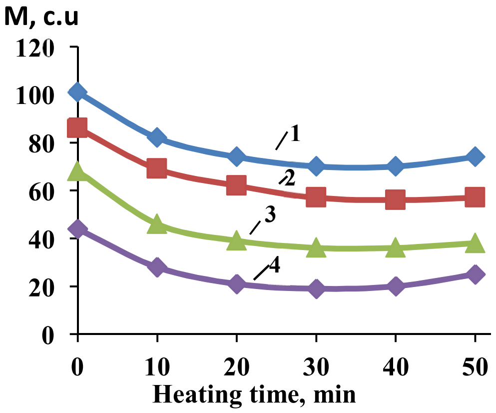

Figure 3. Dependence of Mooney viscosity on the heating time

1. SKN-40M + DCDMDB; 2. SKN-40M + OCDMDPM;

3. SKN-40M + HCPX; 4. SKN-40M

Consequently, the introduction of carbon black in binary elastomeric mixtures creates strong bonds between the polymer and the carbon black as a result of the interaction of the carbon black particles with the active polymer fragments that form cross-links in the elastomer.

The introduction of carbon black into the binary mixtures seems to result only in a weak physical interaction of the binary mixtures with the carbon black [2]. The radicals, arising during the destruction of the main polymer chains, probably cannot react with the carbon black because SKN-40-P324 does not form carbon in the elastomeric gel, although the destruction of its molecular chains does occur (Table 2).

Table 2: Effect of carbon black (P 324) on Mooney viscosity and formation of carbon elastomer gel

Indicators	NBR + P324	NBR+ HCPX+ P324	NBR+ OCDMDPM + P324	NBR + DCDMDB + P324
Color of the mixture	Dark	Dark	Dark	Dark
Amount of carbon elastomeric gel,%				
At 298 K	32	75	90	86
At 343 K	22	53	69	72
Increase in Mooney viscosity of the mixture with participation carbon black (P 324)				
At 298 K	12	22	75	81
At 343 K	12	28	35	31

The physical nature of the interaction of elastomers with carbon black is confirmed by equal values of the Mooney viscosity of the SKN-40M elastomer and its carbon mixture at temperatures above 343 K, when weak intermolecular interaction between the elastomer and carbon black is eliminated. At the same time, the Mooney viscosity of SKN-40M + CCAC and its carbon mixture at all studied temperatures differ significantly (Table 2).

Thus, when using CCAC as an organic crosslinking agent (OCA) for crosslinking NBR, binary and quasibinary vulcanized samples are characterized by significantly better processing properties than non-cross-linked elastomer mixtures.

The presence of cross-links (C-C, C-Cl) in the NBR structure helps to reduce its destruction during plastification on rollers and improve the interaction of the polymer with carbon black, which leads to an increase in the viscosity of raw binary and quasi-binary cross-linked vulcanizates. Molecular weight distribution (MWD) parameters of sol fractions were established by molecular sieve chromatography [8]. This method allows simultaneous separation of elastomer into fractions and relatively fast determination of their molecular characteristics. Analysis of cross-linked elastomer by molecular chromatography was performed using a glass column for narrow fractions of NBR with M_n/M_n. It has been found that the sol fractions of NBR cross-linked with various CCAC C are characterized by a bimodal MWD (Fig. 1). This agrees with the results obtained for crosslinked elastomers by nephelometric titration [6]. At the same time, fractions with relatively high molecular weights (≤ $3.8 \cdot 10^5$) prevail in the NBR sol fractions. At the same time, the sol-fractions of the cross-linked NBR, especially

SKN-40, contain more fractions compared to the standard NBR with low molecular weights (≤ $3.0\text{-}10^4$). The anomalously large value of $\bar{M}_w/\bar{M}_{n_s}$, of the sol fractions of NBR cross-linked by various OCAs (Table 3) is associated with the bimodal nature of their MWD and indicates the presence of a macrogel in the elastomer [13].

Table 3 shows the values of the structural parameters of macrogels of NBR cross-linked with chlorine-containing aromatic compounds, obtained from the data of equilibrium swelling, as well as by calculation using the equations of sol-gel analysis and molecular sieve chromatography.

Cross-linked NBR - SKN-40M + OCDMDPM and SKN - 40M + DCDMDB - is characterized by the highest content of macrogel G and a lower degree of its equilibrium swelling Q_e compared to SKN-40M + HCPX. The θ value of cross-linked elastomer macrogels of various compositions was 1.0, which indicates a high strength of the macrogel [14].

Due to the inhomogeneity of cross-linked elastomer (NBR) macrogels of different compositions [15-17], the estimation of $\bar{M}$ using the Flory-Rehner equation is only rational in the case of densely cross -linked macrogels, i.e., when the number of bonds within particles is so much greater than the number of bonds between them that the latter can be neglected.

The M_c values of the macrogels cross-linked with different chlorine-containing aromatic compounds of NBR calculated by the sol -gel analysis formulas using molecular sieve chromatography data and the Flory -Rehner equation correlate satisfactorily with each other.

Based on the obtained data, a macrogel in a crosslinked elastomer can be schematically represented as consisting of large aggregates of highly cross-linked microgel particles.

Table 3: Molecular characteristics of the sol fractions of the cross-linked NBR

Composition	S, %	$\bar{M}_\eta \cdot 10^{-4}$	$\bar{M}_{n_s} \cdot 10^{-4}$	$\bar{M}_w \cdot 10^{-4}$	$\bar{M}_w/\bar{M}_{n_s}$	$\rho \cdot 10^3$	G, %	Q_e, %	θ	$\bar{M}_c \cdot 10^{-4}$	$\bar{M}_{c^*} \cdot 10^{-4}$
SKN-40M+ HCPX	14	12.1	3.5	16.2	4.2	1.9	86.0	21	1	8.7	6.80
SKN-40M+ OCDMDPM	9.7	15.0	3.4	18.0	5.3	2.1	90.3	17.3	1	5.5	4.85
SKN-40M+ DCDMDB	5.8	16.1	3.2	19.5	6.0						

The values of $\bar{M}_\eta$ of the sol-fractions of the studied NBR cross-linked with chlorine-containing aromatic compounds differed insignificantly.

Molecular parameters of sol fractions of cross-linked NBR by HCPX, OCDMDPM and DCDMDB systems were similar due to the same way of their preparation. The sol fraction of elastomer cross-linked with hexachloroparaxylene had lower values of the above parameters and lower content of high-molecular weight fractions. This explains the relatively low degree of polydispersity.

The branching density p of the macromolecules of the sol fractions of the cross-linked NBR was $1.90 \cdot 10^{-3}$; $2.1 \div 2.3 \cdot 10^{-3}$, i.e. on average, one link out of two hundred was cross-linked. This corresponded to the presence of about two hundred branching nodes per macromolecule in the elastomer. The obtained data correlate satisfactorily with the results of viscometric measurements available in the literature [18-20].

In this case, the number of bonds between particles and individual agglomerates is negligible. The macrogel in the these rubbers is formed directly during processing by the mechanism considered in the theory of gel formation, which seems to be close to the continuous cross-linking of macromolecules in an unbounded isotropic system. The results of the study show that molecular sieve chromatography is a promising method for determining the molecular parameters of the cross-linked CCAC elastomer. This method can be used in conjunction with other methods to directly control the molecular characteristics of nitrile elastomers in order to assess their standardity under production conditions.

Thus, the sol fractions of the investigated cross-linked NBR are characterized by a bimodal MWD, high values of $\overline{M}_w/\overline{M}_{n_s}$ and ρ, indicating the presence of a gel in it. The macrogel in the investigated cross-linked NBR has greater resistance to shear de-formations.

4. Conclusion

Based on the above and based on experimental data, we will try to explain the position of the crosslinking agents CCAC we studied with respect to SKN-40M. In the process of plastification at 343K, a decrease in the intrinsic viscosity of the sol fraction of NBR during their mechanical plastification indicates the destruction of the main chains. The introduction of carbon black into the system SKN-40M+CCAC+P324 causes apparently weak physical interaction of the elastomer with the carbon black. It is likely that the radicals arising from the degradation of the basic polymer are not capable of reacting with the carbon black.

Crosslinking of NBR with CCAC at 423K×30 min occurs as a result of decomposition of CCAC with elimination of chlorine from both trichloromethyl groups and the resulting biradical accentuates the hydrogen of NBR macromolecules.

The molecular parameters of sol fractions of NBR cross-linked with CCAC systems are similar, which is due to the same way of their preparation. Cross-linked NBR is characterized by the highest macrogel G content and a lower degree of its equilibrium swelling Q_e as compared to SKN-40M+HCPX. Due to the inhomogeneity of macrogels of cross-linked NBR of different compositions, the values of M_s were estimated.

The large M_w/M_n value of the sol fractions cross-linked with various CCAC is associated with the bimodal nature of their MWD and indicates the presence of a microgel in the elastomer.

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