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Influence Nanopowders Metal Oxide on the Rheological and Structural Properties of Vulcanizates

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Abstract Method viscometry and rheological studied the kinetics of crosslinking (vulcanization) of the unsaturated nitrile-butadiene elastomers (NBR) in the presence of nanosized metal oxide powders (ZnO, Al_2O_3, ZrO_2). The activating ability of nanoscale metal oxide powders depends not only on particle size but also on the type of elastomer used, as well as on the type of crosslinking agent disulfochloridebenzene (DSCB). Therefore, it was of interest to elucidate the role of nanosized metal oxide powders that differ in activity by crosslinking NBR elastomer with DSCB. It has been shown that crosslinking NBR with DSCB activating effect of metal oxides is accomplished by comparing the crosslinking defined by a change in the Mooney viscosity and the number of cross-linking and change of carbon elastomeric gel. It was found that, the properties of vulcanizates based on designed mixtures NBR, when applying the radiation-chemical technology allows obtaining a vulcanizate containing sulfide, sulfur and carbon-carbon bonds provides elastomer with high strength and dynamic characteristics.

Keywords Butadiene nitrile, Nanocomposite, Elastomer, Vulcanisation, Radiation, Disulfochloridebenzene

1. Introduction

It is known [1-6] on the rate of radiation crosslinking and properties of the elastomer affects the type of metal oxide used. This is particularly evident in the cross-linking of unsaturated elastomers, acrylic compounds where the role of the oxide is reduced mainly to the formation of additional bonds vulcanizates adsorption type, contributes to the molecular weight and dynamic properties. The share of these bonds is higher, the greater the specific surface area of the metal oxide.

Currently, the industry produces a large range of materials from butadiene nitrile rubbers, [7] which can operate in the oil and engineering industries, have high oil and petrol-resistant. Due to the increasing demand for these elastomeric materials works are underway to improve their performance.

The main components of butadiene-nitrile formulations are NBR, carbon black, crosslinking agent (sulfur accelerator (thiuram, kaptax)). Additionally, the formulations used heat stabilizers, which are usually metal oxides used. It is also known, sizes of less than 100 nm (nanoparticles) confer new properties of the material. [8, 9]

NBR, materially differ greater tendency to crosslinking than other diene rubbers. Since it is cured by heating even without the addition of excipients, and in the presence of metal oxide nanoparticles may be prepared technical valuable elastomeric materials.

One can assume that, during thermal vulcanization and thermo-radiation of NBR with DSCB and also presence of oxide nanopowder, will also effects on the rate of vulcanization blends and properties of the resulting elastomer.

Likely role nanosize metal oxide powder in the system more diverse: in the first, it can activate double bond in the elastomer and also crosslinker, [10] secondly, as in the above described systems; it may be involved in the formation of bonds adsorption character. Furthermore, the nanoparticles can be reacted with hydrogen chloride released during the vulcanization of unsaturated elastomers. It takes into account the absorption capacity of oxides, which is associated with a specific surface area [11].

The influence on the properties of nanoscale powders NBR as a whole has not been known yet-sufficient. One reason for this is the complexity of the production of nanopowders.

This paper presents a study the impact of nano-sized powder of metals oxide on vulcanizates, obtained from the joint application of disulfide chloride benzene (DSCB) and carbon black (P 321), which is characterized by an active effect on the initial stage of curing, and is the cross linkers in thermal and radiation vulcanization.

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2. Methodology and Research Facility

The rubber was used as the nitrile rubber (NBR), with high acrylonitrile content. NBR turns together with coagulation of the nitrile-butadiene latex in the ratio of 60:40. According to a study by IR - spectroscopy in the butadiene portion of the polymer at 30°C polymerization of the isomeric composition of the double bonds in the polymer was investigated 1,2-isomer of 14.3% 1,4-isomers 70.9%.

To study the effect of nano-sized metal oxide powder in the curing rate and the properties of NBR were prepared mixture containing 100 mass parts elastomer.

The physical and chemical properties of nanooxides seen on table 1.

Table 1. The physical and chemical properties of nanooxides

Characterics	Nanooxides		
	ZnO	Al_2O_3	ZrO_2
Molecular weight (g/mol)	81.4	101.96	123.2
Particle size (nm)	20-25	40-50	30-35
Specific surface (m^2/g)	250	180	160
True Density (g/sm^3)	5.606	2.9	5.89
Nanoparticles purity (%)	>99.2	>99.9	>99.9

The nanomaterials had been obtained from the Inc. Houston, TX, USA Elastomeric compositions produced based of NBR in laboratory mill (316 x 316) with a fraction f = 1: 2 with vigorous stirring for 7 min. Then, samples were formed in hydraulic press (a pressure of 250 atm) at 353-358K and 423K, with a thickness of 0,2 mm for vulcanization. The compositions of the systems studied are shown in Table 2.

Raw plates intended for radiation curing, and the containers were placed in a vial. Radiation vulcanization performed on the source Co^{60} γ-radiation at a power of 6.7 Gy / sec, in air at 293K.

The absorbed dose in the samples was calculated by comparing the density of electronic test and dosimetric systems. Radiation-thermal vulcanizates obtained by preheating a press 180°C for 5-7 minutes and then irradiated in air.

The intrinsic viscosity of the samples was determined in toluene at 293 K in a known manner [12] on capillary viscometer type Ubbelohde.

The calculation was performed by the Mark-Houwink $[\eta] = KM^{\alpha}$ constant value of $K = 1.9 \times 10^4$ and $\alpha = 0.64$ (for toluene).

The nature of the interaction of nano-sized metal oxide powder and DSCB elastomer tried to change the output number of cross-linking ($\grave{n}_C$) is not filled in the thermal radiation and thermo-radiation vulcanizates, which was calculated from the results obtained by the equilibrium swelling in toluene [12].

The number of crosslinked molecules ($1/\,M_{n_\tau}$) was determined by a sol-gel analysis. Calculation of the spatial grid parameters of thermal, radiation samples were determined according to the formula of Flory-Rehner [13]. The change of the molecular structure of cross-linked elastomer was determined by the method of Fourier spectroscopy. Identification of the spectra was performed according to the correlation table. [14-16]. Assessment of the impact of nano-sized metal oxide powder, crosslinking additives and carbon black in the mechanical and dynamic properties were performed on the following parameters: tensile strength, elongation after fracture, stress relaxation and conditional equilibrium modulus.

Rheological plasticity and nanocomposites were determined on a Mooney viscometer (VM-2004 firm Cibitre Sri-Instruments) and PSM-2 Rheometer (Germany).

3. Results and Discussion

Effect of additive metal oxide nanopowder NBR structured rheology. Structured NBR, obtained with using activating nanoparticles, contains, as a rule, of two or three components of different structure.

In principle, any technical characteristics of these elastomers, obviously, will be a function of the content and structure of the characteristics and size of the particles of each of the components.

One of the most important characteristics of the elastomer plasticizing ability was investigated on the rollers. It was studied the properties of composites with metal oxide nanopowders: heterogeneous and quasi systems, that differs by a combination of gel structure, plasticity and Mooney Viscosity.

Table 2. Composition of the systems studied

Polymer systems	Contents, weight/h in 100 weight/h of elastomer											
	1	2	3	4	5	6	7	8	9	10	11	12
NBR	100	100	100	100	100	100	100	100	100	100	100	100
Sulfur	-	-	2.0	2.0	-	-	2.0	2.0	-	-	2.0	2.0
DSCB	-	4.0	4.0	4.0	-	6.0	6.0	6.0	-	6.0	6.0	6.0
ZnO	5.0	5.0	5.0	5.0	-	-	-	-	-	-	-	-
Al_2O_3	-	-	-	-	8.0	8.0	8.0	8.0	-	-	-	-
ZrO_2	-	-	-	-	-	-	-	-	7.0	7.0	7.0	7.0
P-324	-	-	-	5.0	-	-	-	5.0	-	-	-	5.0

Table 3. Characteristics of the test samples

System oxides	The duration of masti-cation, (min.)	Content, gel elasto-mer, (%)	The degree of Swelling in toluene	The molecular weight of the sol fraction x10^4	Mooney viscosity (MU)	Plasti-city index, (%)	Stif-fness, (gs)
1.NBR+ZnO	3	57,1	48,4	19	50	0,29	1310
2.NBR+DSCB+ZnO	5	65,8	44,1	17	50	0,25	1100
3.NBR+DSCB+ZnO+S	7	72,7	40,0	16	65	0,21	1000
4.NBR+DSCB+ZnO+S+P324	10	81,3	31,3	12	68	0,20	800
5.NBR+Al_2O_3	5	45,2	61,6	9	40	0,32	1400
6.NBR+DSCB+Al_2O_3	8	54,0	58,4	10	49	0,30	1250
7.NBR+DSCB+Al_2O_3+S	12	58,6	50,2	12	61	0,27	1100
8.NBR+DSCB+Al_2O_3+S+P324	14	62,3	45,3	13	63	0,23	1000
9.NBR+ZrO_2	7	42,3	65	7	35	0,30	1350
10.NBR+DSCB+ZrO_2	10	49,7	62	6	42	0,27	1120
11.NBR+DSCB+ZrO_2+S	12	54,3	59	6	50	0,25	1050
12.NBR+DSCB+ZrO_2+S+P324	15	59,9	57	5	55	0,22	900

For the interpretation of the studied factors are analyzed the results. Changes in the structure and properties of NBR with nanoparticles of metal oxides in binary and quasi systems obtained at low temperature (423 K) mastication on a mill, shown in Table 3.

As can be seen from the results (Table 3, samples 1, 5, 9) introduction of nano metal oxide has a significant impact on the rate of plasticizing systems. The nature, of their actions is largely determined by the gel content. So, if the molecular weight of the sol fraction is slowed down in the presence of Al_2O_3 and ZrO_2, the noticeable acceleration of the process is observed when administered in a mixture of ZnO NBR.

For the interpretation of the factors studied to analyze the results. Changes in the structure and properties of NBR nanoparticulate metal oxides and binary quasi systems at low temperature (423 K) mastication on a mill shown in Table 3.

As can be seen from the results (Table 3, samples 1, 5, 9) introduction of nano metal oxide has a significant impact on the rate of plasticizing systems. The nature, of their actions is largely determined by the gel content. Thus, if in the presence of ZrO_2 and Al_2O_3 the molecular weight of the sol fraction is slowed, but when administered ZnO in a mixture of NBR observed noticeable acceleration of process.

In the process the low molecular weight plasticizing NBR-oxide nanopowders can distinguish two stages:

1. Structuring elastomer. In this step, patterning predominates over destruction. In table 3, samples 1, 5, 9 observe an increase in the molecular weight of the sol fraction, Mooney viscosity and decrease ductility, stiffness of elastomer blends.
2. Gelling. There has been a rapid increase in the gel content to a substantially constant value. The molecular weight of the sol fraction of the elastomer is sharply reduced and Mooney viscosity, passing through a maximum increases.

The changes caused by thermal oxidation of the elastomer. This is confirmed by data showing that mechanical degradation under the experimental conditions does not occur.

Based on the comparison of the value of the parameter characterizing the rate of mastication τ (Table 3, samples 4, 5, 9), to draw up a row of activity of metal oxide nanopowders in the vulcanization of NBR.

$$ZrO_2 < Al_2O_3 < ZnO$$

The practical interest is the expansion of the application of low-molecular DSCB at mastication and asking his influence in particular on reservoir elastic properties of elastomers. To this end the elastomeric mixtures were prepared by NBR (Table 3, samples 2, 6, 10) comprising nano metal oxides at varying doses.

The presented table 3, samples 2, 6, 10 shows that the introduction of DSCB in, has a significant impact on the rate of patterning compounds. Exhibits an effective plasticizing effect, greatly increases the Mooney viscosity and gel content.

As is known, [7] sulfuric vulcanization of NBR using low molecular weight compounds allows to obtain elastomers with high molecular weight.

From the presented in Table 3, Samples 3, 7, 11 during mastication in the presence of oxide nanopowders.

DSCB and sulfur provides improved reservoir elastic properties of mixtures. With the introduction of sulfur in the mixture does not change the stiffness of the elastomer, observed increases molecular weight sol fraction at mastication duration for 7-12 min.

Evaluation of the effect of the fillers according to the following exponents-lam: hardness, ductility and toughness Mooney. As can be seen from Table 3, Samples 4, 8, 12 its optimal content is 50.0 weights by parts wherein the compositions have the maximum hardness after plasticization decreases the ductility, the Mooney viscosity increases.

Tests have shown that the ability of the activating metal oxides influences the particle size of powders and the specific surface area. Since, in spite of their identical polarizing ability, ZnO offers greater speed acceleration the formation of the structure of the mixtures in comparison with Al_2O_3 and ZrO_2, Most likely this is due to the particle size of the nanoscale powders and the specific surface area of ZnO. Aluminum oxide is an insulator in this case is characterized by low activity [17-21].

Thus, the best reservoir elastic performance elastomer based on NBR during mastication DSCB-th ensured in the presence of nanosized zinc oxide powders. This is the highest degree of structuring to form a gel adsorption character.

According to researchers in the relationship of the mechanism of me-metal oxides are rather contradictory. However, most authors tend to believe [22, 23] that their main role is to bind the hydrogen chloride produced during the interaction with the elastomer DSCB. In this regard there was a need to study the effect of nanosized metal oxide powders with NBR vulcanized with DSCB.

To study the effect of metal oxide powders on properties of elastomers NBR elastomers were vulcanized mixture (Table 3 samples 2, 6, 10). The technology of thermal and radiation vulcanizates test samples were cured in a machine for (423K × 40') and on the source of Co^{60} γ in air at 100-500 kGy absorbed dose.

The results showed that a crosslinking NBR with DSCB in the absence of metal oxide proceeds slowly. (Fig.1.)

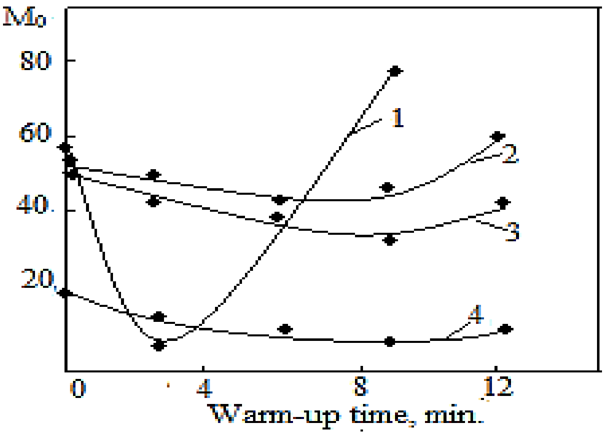


Figure 1. The kinetics of change of viscosity mixtures based on NBR with DSCB and various metal oxides during heating at 423K x 60 min. 1-NBR+DSCB+ZnO, 2-NBR+DSCB+Al_2O_3, 3-NBR+DSCB+ZrO_2, 4-NBR+DSCB (without oxides)

It accelerates the process of vulcanization of the elastomer is observed only in the presence of nanosized zinc oxide, characterized by the highest reactivity. The introduction of aluminum and zirconium oxide has little influence on the process of structuring the elastomer.

A similar pattern is observed for radiation vulcanizates. (Fig. 2.)

Application of viscos metric method for evaluating the effectiveness of DSCB and metal oxide powders to change the molecular weight of the polymer, allows to obtained more in-depth information about the processes occurring in the elastomer during vulcanization heat and radiation dose.

In Fig. 3 shows the dependence of the intrinsic viscosity and NBR crosslinking chlorinated compounds DSCB with nanoscale metal oxides on the duration of heating in toluene. The change in viscosity with the required level does not result in a significant change in the molecular weight of the elastomer. The most intensive growth of the molecular weight is different in the NBR+DSCB+ZnO. With increasing duration of warm-up increases monotonically solution viscosity (Fig. 3.-Curve 1).

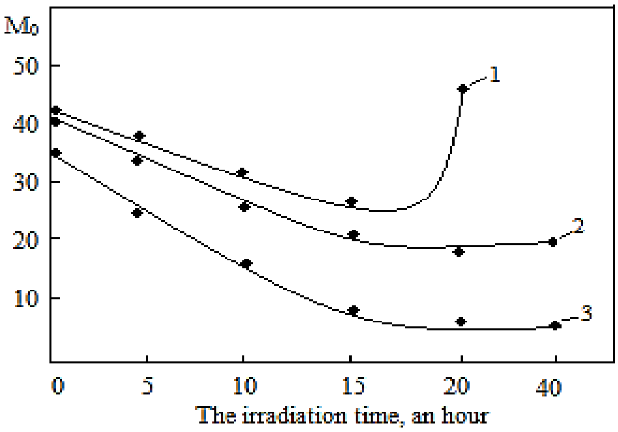


Figure 2. Kinetics of change in the Mooney viscosity mixtures based on NBR with DSCB and various nanoscale metal oxide on the length of exposure time (D = 500 kGy, τ = 20 h.) 1-NBR+DSCB+ZnO, 2-NBR+DSCB+Al_2O_3, 3-NBR+DSCB+ZrO_2

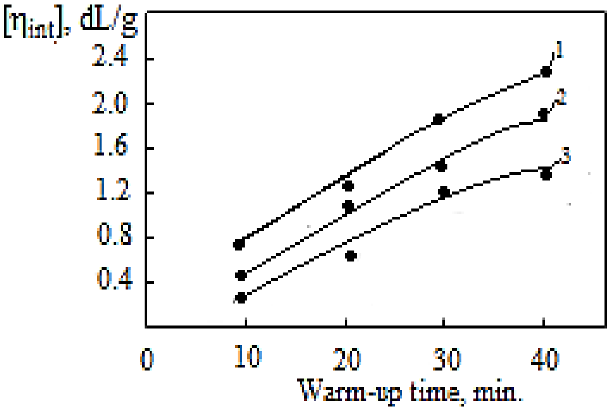


Figure 3. The dependence of the intrinsic viscosity of NBR with DSCB and various nano-sized metal oxides on the duration of heating at 423K. 1-NBR+DSCB+ZnO, 2-NBR+DSCB+Al_2O_3,3-NBR+DSCB+ZrO_2

Increase in DSCB content above 6.0 weights by part does not cause significant changes in the nature of the elastomer.

To understand the laws governing the formation of chemical bonds (C-C) in the investigated polymer system, at different absorbed dose (kGy 100-500); consider the growth curves of molecular weight (MW), in the initial stage of crosslinking. At Figure 4 shows data changes in the intrinsic viscosity unfilled vulcanizates depending on the radiation dose. From Figure 4 it can be seen, nanopowder oxides except zirconium oxide in the elastomeric composition has an activating of action, with increasing absorbed dose causes acceleration of process of crosslinking NBR. Intrinsic viscosity (Table 2, sample 2) increased from 0.3 to 2.2. With the increase of the absorbed dose of higher 400 kGy, intrinsic viscosity decreases. (Fig 4., Curve 1)

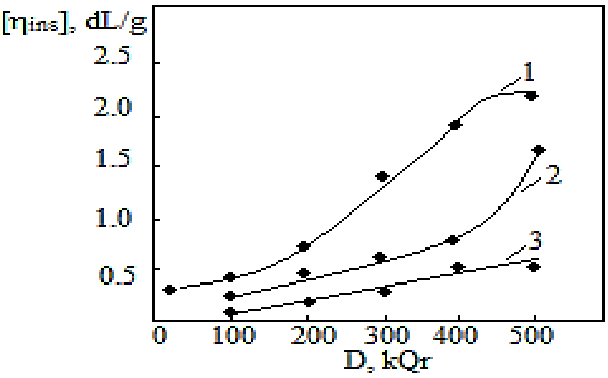


Figure 4. The dependence of the intrinsic viscosity of the mixtures on the basis of NBR with DSCB nano sized oxides with different depending on the radiation dose. 1-NBR+DSCB+ZnO, 2-NBR+DSCB+Al_2O_3, 3-NBR+DSCB+ZrO_2

As a result, degradation of the main polymer chain decreases molecular weight of the elastomer. Increasing the viscosity of the absorbed dose in 400-500 kGy values, may be associated, with the formation of spatial structures, in consequence of reactions within the molecular crosslinking. When studying the molecular characteristics NBR has been found that the duration of irradiation with increasing improves gel fraction greater vulcanized blends 2 and 6.

Number sol fraction soluble even at doses 100 kGy age is 15% and after irradiation with 400-500 kGy, the polymer becomes completely insoluble, indicating that crosslinking of the molecules of the polymer chains with DSCB.

It is known that the solubility of substances in mixtures vulcanizing elastomers may differ from its solubility and strongly influence the kinetics of crosslinking (vulcanization) mixtures and the properties of the vulcanizates.

Previously, [24-26] we investigated the changes in the properties of vulcanizates from blends of polar elastomers, when applying sulfur halide vulcanizing. It has been shown that the thermal radiation crosslinking and 2,4-dichloro 6-diethylamino-triazines (DSCB) with sulfur provides a vulcanizate comprising polysulphide sulfur bonds and additional carbon-carbon bonds (C-S-C, C-C) conditionality self-crosslinking action DSCB, a set of cross-linking is a way to achieve optimal properties of vulcanizates.

First of all, it was of interest to investigate the influence of the main components of the crosslinking group at its vulcanization activity in said mixture of elastomers. (Table 4)

Given the effective action of zinc oxide nanopowder by crosslinking DSCB. We investigated its combination with nanopowders oxide and zirconium oxide as a crosslinking activator NBR DSCB with sulfur. (Table 2 samples 3, 7, 11) To do this, we have been subjected to scrutiny parameter space grids, estimated inhomogeneous structure vulcanizates.

Analysis of the parameters n_c' shows that the density of spatial grid vulcanizates (Table 2, sample 3) received more than a combination of nano-sized powder of zirconium oxide. Because of the combination of nano-powders obtained the lowest degree of cross-linking system provides DSCB+S+ZnO+ZrO_2.

At the curing temperature 433 K contributes to the formation of poly-sulphide bonds. High temperature (433K) vulcanizates have a low content of the sol fraction of the great figures of effective crosslinking yield. One of the important molecular characteristics of the elastomer, determining its characteristics is the effect of the crosslinking agent (DSCB) and nano metal oxide on the physico-mechanical properties of the vulcanizates. From the presented data (Table 4) that the strength relative residual elongation (ε, ε') of the elastomer vulcanized at 433 K nearly equal. The share of active circuits Vr, changed slightly, averaging 0,62.

Table 4. Effect of nanooxides on the structural parameters of vulcanizates based on NBR

Regime of vulcanization	Elostomer systems	Sectors structural parameters of a spatial grid			Physical and mechanical properties			Chemical cross-linking
		V_r	S, %	$n`_c \cdot 10^{-19}$, sm^3	σ_z, *MPa*	ε,%	έ, %	
(423-40`) System 1	DSCB+S+ZnO+Al_2O_3	0.85	0,72	10	14	550	20	C-S-C
System 2	DSCB+S+ZnO+ZrO_2	0.76	0,54	8	12	620	14	C-S-C
(D=500 kGy) System 3	DSCB+S+ZnO+Al_2O_3	0,58	0,46	6	10	730	6	C-C
System 4	DSCB+S+ZnO+ZrO_2	0,49	0,40	3	8	780	8	C-C

Effect of cross-linking agent (DSCB) and nanoscale metal oxide powders for radiation crosslinking NBR can be traced by comparing the performance parameters of the spatial grid with a vulcanizate obtained by thermochemical methods. On the nature of a combination of nanoscale metal oxide powders was judged by the change in the number of cross-links in the elastomer.

Calculation of radiation-chemical yield a concentration of cross-linking (G_{nc}) showed that the system 7, the number of cross-links are in $1cm^3$ vulcanizate at 500 kGy it is $5,0 \cdot 10^{-19}$ ties, and for the system $11,3 \cdot 10^{-19} cm^3$.

It was found that the combination of zinc oxide nanopowder with aluminum oxide significantly influences the proportion of active circuits (V_r). It should be noted that irradiation of the images combined with nano zinc oxide with zirconium oxide yield crosslinks two times smaller.

Upon irradiation with 7 and 11 to a dose of 500 kGy maintains the tensile strength of the elastomer. With further increase of the dose (above 500 kGy) does not affect the process of structuring NBR. Sharply reduced elasticity of the samples.

According to the existing presentation, a necessary condition for amplification is the formation of structural mesh (chain structures) of carbon black (filler), which adsorbs and orients the molecular chain of the elastomer polymer formed spatial grid of polymer. [18, 27, 28]

Physical and mechanical properties of the elastomer depends, ultimately on the properties of both spacecraft structural grids, and the interaction of these nets that amount of filler elastomer linkages and their strength.

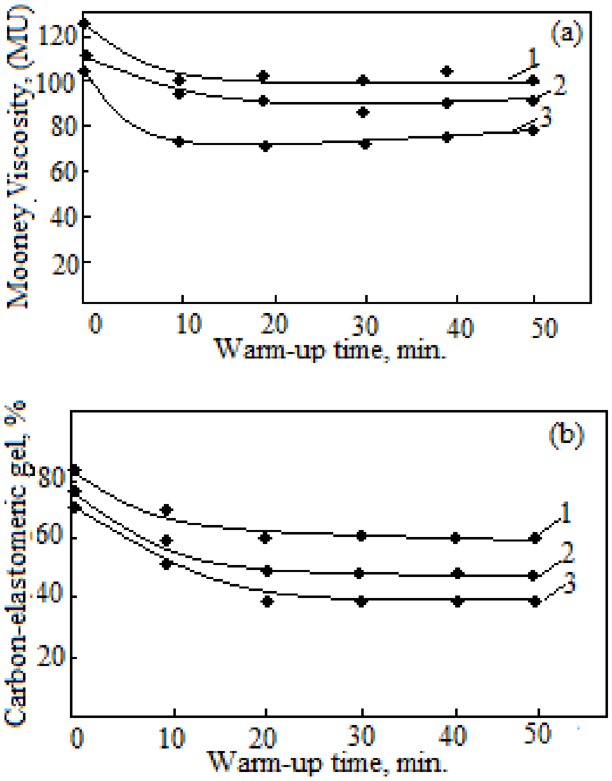
One way to impact on the structure filled with an elastomer to modify their properties is the use of a filler. In a joint application with filler nanoscale metal oxides differing, for physico-chemical properties, therefore, the presence of nano-sized particles may change the structure of the polymer network. Therefore, it was of interest to investigate the effect of filler combinations with a metal oxide nanopowder on the structure and mechanical properties of the elastomer (Table 2, Samples 4, 8, 12).

Interaction filled elastomer evaluated by a carbon elastomer gel (CEG).The results showed that the behavior of the combination of nano metal oxide with a filler in mixtures on the basis of NBR is different. For mixtures obtained upon heating investigated combinations nanopowders containing metal oxides, an increase in viscosity and CEG compared mixtures obtained without the addition of carbon black (Figure 5).

One of the reasons for increasing the viscosity of mixtures with combinations of a metal oxide nanopowder may presence of a strong bond between the carbon structures.

The formation of various less carbon structure increases the contact surface of the elastomer with the filler, the effect of increased interaction between the elastomer and filler, ultimately, to increase the viscosity of the mixtures.

When, radiation structuring elastomers (NBR) with the participation of the orientation of the filler increases the ability to cross-linking. As a result of the irradiation 1500 kGy is less reflected in the UEG and the change of Mooney viscosity, which is largely determined by the actions of the reinforcing filler.



1. A mixture with the filler and nanopowders of ZnO
2. A mixture with the filler and nanopowders of Al_2O_3
3. A mixture with the filler and nanopowders of ZrO_2

Figure 5. (a) Dependence the Mooney viscosity and **(b)** Carbon elastomeric gel (CEG) mixtures from the filler and nanopowders of metal oxides

Changes in the structure of the elastomer made combinations of nano metal oxides in the presence of the filler can greatly affect the properties of the elastomer. The mechanical property of the elastomer varies depending on the content of the filler. (50 wt. h.) In the combinations in accordance with the above structure changes mixtures (Fig. 5).

Tensile strength, modules, elongation at vulcanizates based mixtures NBR retains satisfactory operation requirement. Physical and mechanical properties of filled vulcanizates (Table 2 Sample 8), based on NBR are presented in Table 4.

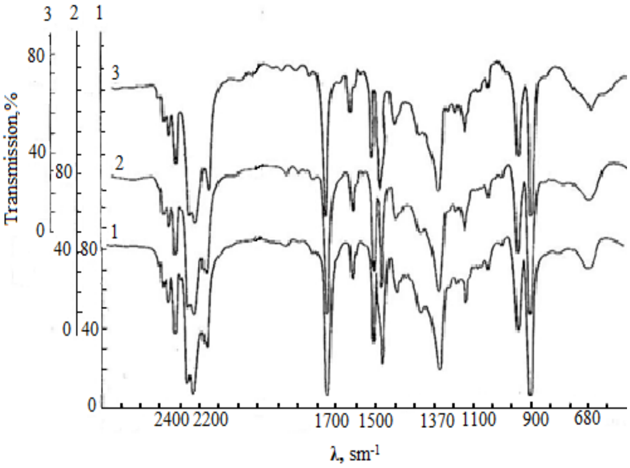
It is seen that the radiation yield vulcanizates of thermal strength properties, but the superior for thermal heat aging and solvent. In general, the level of physical and mechanical properties of vulcanizates of radiation closes to the thermal properties of levels.

This means that the use of low molecular weight additives DSCB involving on-metal oxide nanopowders leading to the formation of C-S-C and C-C chemical bonds, effectively participate in the formation of cross-links in the mesh radiation vulcanizates.

Thus, better mechanical performance, based elastomer

NBR DSCB provided by crosslinking in the presence of a combination of nano-sized powders of zinc oxide with alumina. This is due to the highest degree of crosslinking and the formation of relationships in the vulcanizates adsorption character of the radiation curing.

Character interaction with elastomers DSCB tried to change the Fourier Spectra (Figure 6).



1-NBR+DSCB+ZnO+S,
2-NBR+DSCB+Al_2O_3+S,
3-NBR+DSCB+ZrO_2+S

Figure 6. Fourier Spectra system of nanocomposite

After the heat treatment of the films (Table 1, Sample 3, 7, 11) decrease intensity absorption bands at 1380, 1195 and 1170 cm^{-1} characteristic for $-SO_2Cl$ groups, as well as the appearance of a new band at 1150 cm^{-1} attributable to the sulfone group $-SO_2$. [29-32]

Influenced DSCB observed cis and trans configurations and a reduction absorbance of the band at 967 cm^{-1} characteristic for the groups -CH2, cis position.

Based on IR spectrum, we can conclude that with heating systems NBR+DSCB+ZnO+S by cleavage of active chlorine from aromatic ring happens a chemical interaction between the vulcanizing agent- sulfur with the double bonds of the polymer.

Thus formed cross-links contain sulfonic groups. In favor of these assumptions, evidences data of elemental analysis of the samples.

After 40 min. warming at 423 K, virtually all of the sulfur contained in the curing agent DSCB remains within the elastomer, the amount of chlorine is significantly reduced, and it is in vulcanizates 34.2% with DSCB. Reducing the amount of chlorine associated with the system dehydrochlorination.

The optical density of the bands at 2230 cm^{-1} relating to a combination of groups -C≡N, when heating NBR with DSCB does not change. [33]

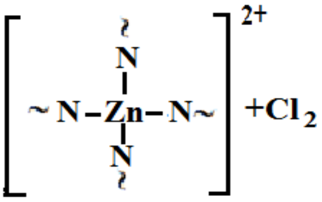
This indicates that in the crosslinking reaction of these groups do not participate directly. However there is the assumption that the nitrile groups may activate an adjacent tertiary carbon atom, thereby enhance the degree of the number of crosslinked polymer molecules. Obviously, when crosslinking NBR, powdered of nano zinc oxide acts as the acceptor of hydrogen chloride that is released during the interaction of elastomer and a curing agent DSCB. (Table 5)

Table 5. Changes in the content of zinc chloride NBR with DSCB

The vulcanization time, min	10	20	30	40
The content of $ZnCl_2$ in the polymer with %	0.57	0.70	0.78	0.72

Confirming this it is the formation of zinc chloride in sample, while warming up the mixture.

Removal of hydrogen chloride from the reaction shifts in the direction of the last stitching and is one of the reasons for the formation of cross-links in the system. Zirconium oxide, reactions-breaking capacity is small, has no influence on this process. The resulting zinc chloride is capable of catalyzing polymerization processes butadiene elastomer. This produces a strong carbon-carbon bond. Moreover, one would expect that the resulting system zinc chloride will participate in the formation of labile coordinating crosslinking type.



$$\left[\sim N-\overset{\overset{\wr}{N}}{\underset{\underset{\wr}{N}}{Zn}}-N\sim\right]^{2+}+Cl_2$$

Scheme 1. Creating complex combinaton

The presence of the labile bonds in the elastomer with nano powders of metal oxides can be judged by a marked drop in the number of crosslinks when swollen in its solvent.

In vulcanizates without oxide zinc and with oxides alumina or zirconia, this phenomenon is not observed practically. Obviously, such a set of cross-linking provides high strength and dynamic performance elastomer with nano-sized zinc oxide powder.

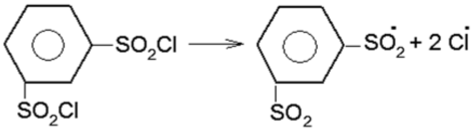
Indeed, in the IR spectra of NBR+ZnO+DSCB after warm bar appears in 2242 cm^{-1} (see. Figure 6) that can be linked to form a complex between the zinc chloride and nitrogen lone pair of electrons [37]. The presence of the labile bonds in the elastomer to the metal oxide can be judged by a marked drop in the number of crosslinks in their swelling in a solvent. In vulcanizates without oxides of alumina and zirconia is a phenomenon not observed practically. (Table 6)

Table 6. Change of number of cross-linking at the using of different swelling agents

Swlling agent	m-Xylol	Benzine-Benzene
ZnO	22,3	16,0
Al_2O_3	15,1	14,2
ZrO_2	12,8	11,9

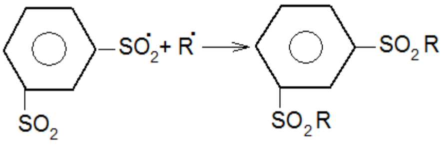
Obviously, such a set of cross-linking provides high strength and dynamic performance elastomer with nano-sized zinc oxide powder. Vulcanizates without nanooxide alumina and zirconia, wherein the labile communication such missing, and have a low resistance and low dynamic endurance strength.

Thus, on the basis of these studies suggest the following reaction scheme crosslinking NBR with DSCB.



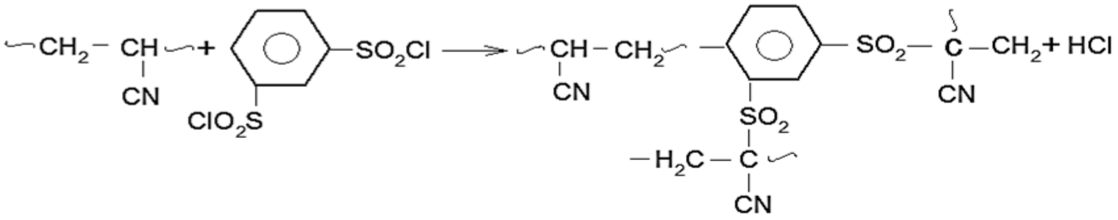
RH- is macromolecule of rubber

$RH + \dot{Cl} \rightarrow \dot{R} + HCl$



Scheme 2. Crosslinking reaction NBR with DSCB-th

$\dot{R} + \dot{R} \rightarrow R-R$



4. Conclusions

The first time the chemical interaction disulfide chloride benzene (DSCB) compounds with nitrile-butadiene rubber (NBR) in the presence of nanoscale metal oxide powders.

Considered in general terms the impact of nano zinc oxide, alumina and zirconia during thermal and radiation crosslinking to influence the rheological properties of the vulcanizates.

It is shown that using disulfide chloride benzene (DSCB) allows you to get the maximum growth of the elastomer molecular weight, with increased density in the quasi-system grid vulcanizates. Fast mixing at 433K is increased with the combination of nano zinc oxide with aluminum oxide.

Staple NBR, DSCB activated largely nano-sized zinc oxide powder, which acts as a scavenger of hydrogen chloride released during the reaction of the elastomer and cross-linking agent to form an effective cross-linking of the resulting zinc chloride is able to activate the crosslinking in the elastomer and to participate in creating a focal cross ties.

Studied polymeric systems are reticulated macromolecular structures in which a low molecular weight benzene disulfide chloride benzene (DSCB) enters into a chemical crosslinking initiator active nano powders together with sulfur and a filler. Additives, metal oxide nanopowders cause a change in the molecular chain of the elastomer and curing kinetics contributes to the formation of the chemical structure (C-S-C; C-C) and the properties of crosslinked elastomers. With the introduction of fine particulate filler (F 324) is enhanced thermal and radiation vulcanizates; significantly improved physical, mechanical and heat aging resistance.

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