

EFFECT OF NANO-DIMENSIONAL POWDERS OF METAL OXIDES ON THE PHYSICO MECHANICAL PROPERTIES OF VULCANIZED NITRILE RUBBER

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Abstract. The crosslinking activation ability of nanoscale metal oxides depends not only on the type of crosslinking agent, but also on the type of rubber used. Therefore, it was of interest to clarify the role of nano-sized metal oxides, which differ in activity when nitrile-butadiene rubber (NBR) is crosslinked with with benzene-1,3-disulfonyl chloride (DSCB). Nanocomposites were irradiated in evacuated ampoules by gamma radiation from a Co60 source to various doses (D) from 100 to 500 kGy and the results of irradiated simples, compared to non-irradiated samples (D = 0). Based on results of FTIR analysis characterization it was assessed that in the γ -radiation crosslinking of NBR with DSCB, nano-sized zinc oxide is activated. Using the activating action of nanoscale metal oxides one of the prospective ways of influencing the radiation-chemical processes of formation of nanoscale metal oxides and controlling the physicochemical and mechanical properties of polymer nanoscale composites. Thus, analysis of the investigations conducted makes it possible to conclude that low-molecular-weight additives and nanoscale metal oxides can be effectively used in the radiation vulcanisation and radiation protection of NBR-based elastomers.

Keywords: butadiene-nitrile rubber, nanocomposite, crosslinking, gamma-radiation

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Manuscript received: 15 February 2018

1. Introduction

The use of technological additives opens up new possibilities for improving the formulation and the process of making rubber compounds: the number of softeners in formulations is reduced while preserving or shortening the duration of the mixing cycle (Mammadov, 2015), the quality of mixing is increased, the difficulties associated with the manufacture and processing of high-filled rubbers are eliminated (Lituri & Deforte, 2005), the operating conditions of the equipment are improved, which allows increasing the productivity.

The use of technological additives allows to increase the uniformity and stability of rubber compounds and vulcanizates, and, ultimately, to improve the quality of the finished product (Viet, 2008). Vulcanization activators - are components of the cure system, which enhance the effectiveness of the accelerator, typically used inorganic and organic activators. The most common activators are metal oxides and long-chain fatty acids (Mammadov *et al.*, 2016).

The action of these modifiers is often due to their influence on the process crosslinking of polymers, including the ability to form a chemical bond (Mammadov, 2012). The highly developed surface, as well as the proximity of the nanoparticle size to the size of the macromolecules leads to forming nanocomposites unique electronic, electro-mechanical and physical properties are very promising for the creation of new constructional materials (Pomogaylo *et al.*, 2002; Przybyszewska & Zaborski, 2009; Tian *et al.*, 2006) used for new equipment, solid and elastic defense materials. Significantly, the desired effect is achieved by introducing a small amount of modifier.

In view of the fact that, during the cross linking process, zinc oxide reacts with the carboxylic groups of the elastomer, which leads to the formation of carboxylic salts (ionic crosslinks), the most important parameters influencing the activity of zinc oxide are its surface area, particle size, and morphology. These parameters determine the size of the interphase between the cross linking agent and elastomer chains (Maiti *et al.*, 2008).

However, to crosslink NBR, high radiation doses are required to reach the desired crosslink density. But at high radiation doses, the mechanical properties are adversely affected due to the degradation induced by radiation (Zhang et al, 2009; Sahoo & Bhowmick, 2007).

The effect of radiation dose on the mechanical properties of NR/BR blending system was studied (Feldman, 2012). A comparison was made between sulfur vulcanization and radiation vulcanization for an optimal nature rubber (NR)/ butyl rubber (BR) blending ratio (60/40) at the dose range from 10 to 150kGy. The result shows that the mechanical properties, especially, tensile strength, elongation at break, and tear strength have been improved significantly by radiation–vulcanization.

The nitrile butadiene rubber is a family of unsaturated copolymers of 2propenenitrile and butadiene monomers (1,3-butadiene or 1,2-butadiene). The information available in the literature on the mechanism of crossling in the presence of nanopowder oxides is quite contradictory. This is especially clear for the cross-linking of unsaturated rubbers based on acrylic compounds, where the role of the oxide is reduced, the main images in the formation in space of elastomers of additional bonds of adsorption character, enhancing the mechanical properties. Moreover, the proportion of these bonds is the higher, the greater the specific surface area and the size of the powder of metal oxides.

It can be assumed that when cross-linking the NBR with benzenedisulfonyl chloride (DSCB), the type of used nano-oxide will also affect the crosslinking speed of polymer mixtures and the final properties of obtained elastomeric material. The role of nanopowders in this system is even more diverse, firstly, it can cause activation of the double bond of both rubber and the cross-linking agent (Hamed & Hua, 2004) in the second, it is possible that it participates in the formation of adsorption bonds, in addition, nano-oxides of metals can interact with hydrogen chloride, which is released when cross-linking unsaturated rubbers (Chen *et al.*, 2009). The resulting metal chlorides are catalysts for the crosslinking process. This is particularly true for crosslinking of chlorine-containing aromatic compounds.

However, in the crosslinking of NBR, the role of metal oxide nanopowders in is more complex, since some of the chlorides formed can react with the nitrile group Omrani *et al.*, 2009). At present, the most urgent problem is the production of cheap and high-quality elastomeric materials (Luther & Bachmann, 2008). The use of metal oxide nanopowders can reduce the consumption of rubber and have a direct effect on the properties of the resulting materials, the most common nanopowder in elastomer technology is metal oxides (Depew, 1933).

Nowadays, the use of new types of nano-sized powders aimed at improving the technological properties of elastomeric mixtures and providing the necessary complex of properties of elastomeric materials is an urgent task (Woods & Pikaev, 1994).

In this connection, it became necessary to study the effect of nano-sized metal oxide powders when cross-linking the butadiene-nitrile rubber (NBR) with disulfochloride benzene (DSCB).

2. Experimental part

For elastomeric materials preparation, nitrile butadiene rubber with a 36 - 40 content of acrylonitrile (SKN-40, Russia) was used. It was synthesized with cocoagulation of butadiene-nitrile latex in a ratio of 60:40.

As a rubber, butadiene-nitrile rubber with a high content of acrylonitrile (SKN-40, Russia) was used. It is obtained with co-coagulation of butadiene-nitrile latex in a ratio of 60:40.



Scheme 1. Chemical structure of NBR

As the crosslinking agent disulphochloride benzene (DSCB) aromatic compounds, which react readily with macromolecules NBR. It is a colourless viscous oil that dissolves in organic solvents, but reacts with compounds containing reactive N-H and O-H bonds. Chemical structure of DSCB is shown in scheme 2.



Scheme 2. Chemical structure of DSCB

In order to clarify the role of nanopowders on the crosslinking of NBR by disulfochloride-benzenes, oxides with different reactivity with hydrogen chloride, Al2O3 and ZnO, were taken. The nanomaterials had been obtained from the Inc. Houston, TX, USA. The physical and chemical properties of nanopowders are summarized in the table 1.

Characterics	Nanooxi	Nanooxides		
	ZnO	Al ₂ O ₃		
Molecular weight (g/mol)	81.4	101.96		
Particle size (nm)	20-25	40-50		
Specific surface (m^2/g)	250	180		
True Density (g/sm ³)	5.606	2.9		
Nanoparticles purity (%)	>99.2	>99.9		

Table 1. The physical and chemical properties of nanooxides

To determine the concentration of nano particles of zinc oxide and aluminum, we introduced the formula - $C=0,1e^n$, Where C is the content of zinc and aluminum oxides in the mixture, wt. part.

To study the effect of ZnO and Al_2O_3 nanopowders on the properties of mixtures from NBR, mixtures containing 100 wt. part. Composition of the NBR-based rubber compounds [phr]:

1. NBR-100 + 4.1 ZnO + 3.0 DSCB; 2. NBR-100 + 5.7Al₂O₃ + 3.0 DSCB.

The comparison was carried out with the mixtures with standard oxides.

Nanocomposites based on NBR were prepared on two roll-mixing mills (outside diameter 470 mm, working distance 300 mm, a speed of slow roll 24 rpm and friction ratio of (1:1.4) in accordance with ASTM D3182-07. First, NBR (100 phr) was masticated for 2 min followed by the addition of nanopowders and DSCB.

Compounds were finally sheeted again in the rolling direction into slabs of about 0,2 mm thickness, and the sheets were pressed in clean molds of a hydraulic press. The molds were brought to 423K and held at this temperature for 10 min at a pressure of 100 atm.

For the irradiation of the samples were placed in a 1 g vial of glass evacuated for hours 1,3 h 10^{-1} Pa residual pressure. The exposure to radiochemical processing was performed in air at room temperature inside of the source $\text{Co}^{60} \gamma$ -radiation was used for irradiation giving a dose rate of about 4.9 kGy/h. Irradiation of samples was carried out at the Institute of Radiation Problems, Azerbaijan. The absorption currents of samples calculated by comparing the electron densities of the investigated dosimetry systems (Drobny, 2012). (Scheme 3.)



Scheme 3. Mixing and irradiation crosslinking scheme of nanocomposites based on NBR

For the morphological observation of nanocomposites was used JEOL-JSM-5400 (Japan) scanning electron microscope (SEM).

The crosslink density (v_T) of the vulcanisates was determined by their equilibrium swelling in toluene based on the Flory-Rehner equation (Flory & Rehner, 1943). The Huggins parameter of the elastomer-solvent interaction (χ) was calculated from the Equation (1):

$$\chi = 0.3809 + 0.6707 V_{\rm r} \tag{1}$$

where V_r is the volume fraction of the elastomer in the swollen gel.

The intrinsic viscosity of the crosslinked polymer was determined in toluene at 293 K in a manner known per se on an Ubbollode viscometer. The calculation was carried out by the equation. Mark Hauwink $[\eta_x] = KM\alpha$ for the constant k = 4.9 104 and $\alpha = 0.64$ (for toluene).

The molecular structure and isomeric composition of nanocomposites NBR were recorded on Fourier-transform IR Spectrophotometer (FTIR) in the 3000 to 700 cm⁻¹. Rubber films were prepared by applying the solution (toluene) to a substrate and evaporation of the solvent constant (Bellamy, 1980).

The nanocomposite samples for mechanical tests carried out on dumbbell shaped specimens of 4 mm width and 50 mm length. Tensile strength (TS), elongation at break % (E_b), and modulus at 100% elongation were determined measured in accordance with ASTM D-412 using a tensile testing machine P-5.

3. Results and discussion

Binding of NBR using accelerator DSCB in the presence of nanopowders of metal oxide, consists, as a rule, of two components of different structure: sol and gel fraction. In principle, any technological characteristic of cross-linked rubbers will obviously be a function of the relative content and structural features of each of the components.

As shown by the results of the study, at high temperatures (423 K), the interaction of DSCB with NBR molecules leads to the formation of a three-dimensional network, as evidenced by the increase in Mooney viscosity (Table 1), the polymers themselves in the absence of a cross-linking agent under the same conditions are structured to an insignificant degree. The dependence of plasticity on the degree of cross-linking of polymer systems is presented in Table 2. With different degrees of cross-linking (423 K, 500 kGy), the samples obtained with ZnO exhibit increased ductility as compared to samples containing Al_2O_3 and, at the same time, their viscosity decreases with respect to the mesh of the samples was achieved by varying the rigidity of the polymer systems.

A similar picture is observed in irradiated samples containing ZnO and Al_2O_3 in nanopowders. The nature of the change in the rheological properties of nanocomposites at a nanopowder content of 4.1 and 5.7 weight/parts.

It is known that the reactions of rubbers with cross-linking agents can proceed along radical, ionic or ion-radical mechanisms. To determine the type of reaction when rubber was crosslinked with disulfochloride aromatic compounds (DSCB), the effect of free radical scavengers (nanopowders) on the density of the spatial grid arising from the interaction of the elastomer with DSCB was investigated.

The introduction of the acceptor (ZnO, Al₂O₃) into the elastomeric mixture with DSBB affects the number of chain chains and the number of cross-linked molecules formed during crosslinking in different ways. Thus, when structuring with butadienenitrile rubber with DSCB, nano-sized zinc oxide increases, and alumina reduces the number of bonds, which is characteristic of the reaction proceeding along the radical mechanism. In all likelihood, the role of a nanosized oxide in this system is even more diverse: first, it can cause activation of a double bond, an elastomer that acts as an acceptor of hydrogen chloride, which is liberated during the interaction of the NBR and the cross-linking agent to form strong cross-links; And in the systems described above, it is possible to participate in the formation of bonds, adsorption character.

nin.	System	Realogical indicators				Structural parameters of the spatial grid				
Stitching mode, K, n		Mooney viscosity Mo	Plasticity, con.un.	Rigidity, Gs	Characteristic Viscosity[n], dl/g	Number of mesh chains, 1/M _c ·10mol/sm ³	Number of cross- linked molecules 1/M _m ·10 ⁴ , ol/sm ³	Extent of cross- linkin, γ	Content of sol fraction S,%	The equilibriumdegree of swelling, M _s ,%
423 K x 40'	NBR- DSCB- ZnO	58,0	0,31	1350	1,1	8,0	1,56	21,6	0,52	47,0
	NBR- DSCB- Al ₂ O ₃	51,0	0,27	1410	0,5	2,0	1,0	13,4	0,31	52,3
D=500 kGy	NBR- DSCB- ZnO	42,9	0,48	1400	0,6	3,0	0,72	12,0	0,36	39,6
	NBR- DSCB - Al ₂ O ₃	38,4	0,24	1400	0,4	1,5	0,45	9,0	0,32	42,3
	None oxides	35,0	0,12	1600	0,3	1,1	0,28	12,3	-	28,0

Table 2	Indicators	of NBR	cross-linking	under the	action c	of tem	perature and	v-irradiation
	mulcators	UINDI	cross-miking	under the	action	л ют	Jerature and	y-maulation

To assess the crosslinking processes of swelling samples in toluene solutions, the sol-gel analysis (Litvinov & De, 2002) determined structural parameters, the number of crosslinked molecules extracted within 48 hours. Cold acetone in an argon atmosphere of thermal and irradiated samples. In the presence of a ZnO nanopowder, the crosslinking reaction proceeds intensively (Table 1), the number of crosslinked molecules (1/Mnc) in this case is 2 times greater in comparison with mixtures involving nanopowders of alumina.

The results of the study showed that the NBR crosslinking process in the absence of nanopowders proceeds slowly and the degree of cross-linking is low (Table 2). Accelerations of the process of NBR crosslinking are observed in the presence of a zinc oxide nanopowder, characterized by the greatest reactivity. The number of chains of the grid (1/ Mc) in the elastomer increases almost 2 times. The introduction of nanopowders of alumina less affects the speed of cross-linking and the density of the mesh.

It is known that the radiation-chemical yield of cross-linking (Gc) and the formation of effective cross-links in the NBR depends both on the absorbed dose and on the metal oxides (Luther & Bachmann, 2008). Analysis shows that irradiation in air at 293 K cross-linking of polymer systems increases insignificantly. In the irradiated system (NBR-DSCB-ZnO), the rate of crosslinking is higher than in NBR-DSCB-Al2O3. This is explained by the fact that the selected banded dose (500 kGy) has a significant effect on both the process speed and the radiation-chemical yield (G) the

number of grid chains (1/Mc) and the number of crosslinked molecules (1/Mnc). At the same time, it should be noted that the activating ability of metal oxides is influenced by the particle size and the specific surface area. Thus, ZnO provides a high rate of cross-linking of the mixtures in comparison with Al2O3.

The amount of soluble sol fraction of (S) polymer systems after heat treatment (423 K x 40') is 0.59 and in irradiated samples at 500 kGy is 0.34 that the polymer is completely insoluble, which indicates the cross-linking of polymer chain molecules (see table 2).

As can be seen from the results obtained, the introduction of nanopowders of metal oxides exerts a noticeable effect on the intrinsic viscosity (η char), the absence of nanopowders in the polymer system proceeds slowly both in thermal and irradiated samples (Fig. 1,2)



Figure 1. The kinetics of change of the intrinsic viscosity polymer composite systems at heating 423 K : 1.NBR; 2. NBR/DSCB/n-Al₂O₃ 3. NBR/DSCB/n-ZnO



Figure 2. The kinetics of change of the intrinsic viscosity polymer composite systems of irradiation dose (100-500 kGy):
1. NBR; 2. NBR/DSCB/n-Al₂O₃: 3.NBR/DSCB/n-ZnO

Thus, the analysis of the results of the above studies allows us to conclude that we use the frequency of the grid to show the polymer systems based on NBR, when they are crosslinked by the action of heating (423 K) and irradiation (500 kGy) with participation of DSCB are provided in the presence of nanopowders of zinc oxide. This is explained by the greatest degree of crosslinking and the formation of adsorption bonds in the polymer network.

It is known (Chalmers, 2000) that chlorine ionically or radically reacts vigorously in the presence of metal oxides. The resulting metal chlorides, in turn, can both activate the cross-linking process and cause an independent cross-linking effect. Consequently, the role of nanopowders of metal oxides when NBR is crosslinked by disulfochloride aromatic compounds will be determined on the one hand by the rate of chlorine binding, and on the other hand by the effect of the resulting metal chlorides on the rate and degree of cross-linking of the polymers.

Since the role of metal chlorides as crosslinking agents in NBR is significantly higher than other unsaturated rubbers, it is clear that the accelerating action of high activity nanooxides, especially zinc oxide in mixtures, is understandable. This is due to the fact that the zinc chloride formed during the reaction readily reacts with the nitrogen-containing side groups of the polymer, leading to the formation of weakly strong coordination bonds. The fact of the formation of such bonds in the NBR system in the presence of nanopowders of zinc oxide is confirmed by the data of IR spectroscopy (Fig.3).



Figure 3. FTIR spectrum of nanocomposite systems: 1. NBR/DSCB/n-ZnO 2. NBR/DSCB/n-Al₂O₃ 3. NBR/DSCB

When the NBR-DSCB-ZnO (Fig 3(2)) systems and NBR zinc chloride are heated (Fig. 3 (1)), the intensity of the 2230 cm⁻¹ (-C \equiv N) absorption band is similar and the appearance of a new band 2242 cm⁻¹, characteristic of Complex compounds of zinc chloride with nitrile rubber groups (Macosko, 1994). When the NBR-DSCB system is heated up (Fig. 3(3)), the latter was not detected.

Thus, the degree of action of nanopowders of metal oxides on the rate of crosslinking of polymer systems is related to their ability to bind chlorine in ionic or radical form, as well as the effect of their processes on the cross-linking of metal chlorides formed as a result of the reaction.

Obviously, when the NBR is crosslinked, the nanoscale metal oxides serve as the hydrogen chloride acceptor, which is released upon interaction of the NBR with DSCB. Confirmation of this is the formation of zinc chloride in the system in the process after irradiation (800 kGy) and heating 423 K x 40' (Table 3).

Investigations in the field of labile cross-links in butadiene-nitrile rubbers with metal oxides aimed at studying the nature of the forces acting on the interface between NBR molecules and metal oxides and clarifying the nature of the diffusion (sorption) penetration in the polymer and the formation of labile bonds are mainly at the level of molecular Structure of polymers and the sizes of structural, elements, resolved by an optical microscope.

There is information on the effect of polymer properties and also the nature and state of the surface of metal oxides on the sorption of oxide particles in polymer dispersions (Mou *et al.*, 2012). Immediate observations of the phenomena occurring at the interface between NBR phases of nanoparticles, metal oxides at the level of the size of structural elements resolved by an electron microscope have been little studied; Meanwhile, they could significantly deepen the idea of the mechanism of the process of the formation of cross-links in NBR in the presence of nanopowders metal oxides.

	Systems		Crosslinking	Irradiated Systems		Doze,	Without
Physico-mechanical properties	NBR- DSCB-n ZnO	NBR-DSCB- nAl ₂ O ₃	time, min	NBR- DSCB-n ZnO	NBR- DSCB- nAl ₂ O ₃	kGy	nano oxide powders
	1	2		1	2		
Tensile strength, MPa	11,3	8,0		6,2	5,1		4,9
Relative elongation,%	690	730	40	770	795	500	800
Shore hardness, A	38	31		32	30		27
Rebound elasticity,%	41	45		48	50		50
The accumulation of residual deformation at compression, (20%, 423 K, 72 h)	42	56	40	62	50	500	35
Changing the mass in a mixture of benzene-petrol (3: 1) 353 K, 24 hours.	38	45	40	31	44	500	26

 Table 3. Physico-mechanical properties of nanocomposites

The morphological structure of nanocomposites was determined with scanning electron microscopy (JEOL JSM 6360LA, JEOL, Tokyo, Japan). Prior to the observation, small portion of sample was cut and mounted on an aluminum stub and sputter coated with a thin layer of Au/Pd to avoid electrostatic charging during SEM examination.

According to the results of electron microscopy, nanocomposites consist of isolated electron-contrast nanostructured ZnO, Al_2O_3 nanoparticles of predominantly spherical shape (Fig.4). The nature of the distribution of nanoparticles in the polymer matrix is uniform. (Figure 3 (1), (3)). The broadest poly dispersion is observed for the ZnO nanocomposite and varies from 2-12 nm with a maximum nanoparticle content of 20-25 nm.

This effect of nanoparticle metal oxides on the polymer composition, resulting in the formation of carbon-carbon bonds in the presence of DSCB, during the crosslinking, zinc chloride is formed, which is capable of activating the crosslinking process in NBR (Shoushtari Zadeh Naseri & Jalali-Arani, 2016; Aoshuang et al., 2002). Consequently, the zinc chloride formed in the nano system will participate in the formation of cross-links, such as



The change in the mechanical characteristics of nano vulcanizates in any physical field is ultimately due to the occurrence of competing processes of crosslinking and breaking of chemical bonds, as well as to changes in the potential of intermolecular interaction.



Figure 4. SEM images of vulcanisate surfaces

At the same time, the nature and depth of these changes are determined by the specific type of external impact on nanoscale polymer systems. Sequential or simultaneous exposure to temperature and radiation can lead to the cross-linking of nanocomposites (quasi systems) in a given direction.

When determining the physico-mechanical properties of unfilled nanovulcanizates based on NBR, it was established that nano-zinc together with DSBB reactivity for all types of vulcanization. Radiation vulcanizates are inferior to thermal strength properties (Table 3).

To determine the influence of temperature ($423K \times 40^{\circ}$) and γ -radiation on nanocomposites, it was established that in the case of thermal vulcanizates containing in the polymer system ZnO and DSCHB, the accumulation of residual compression deformation and the degree of swelling are lower, the decrease in the change in the mass of radiation and thermal nanovalents Growth of the yield of transverse C-C bonds. At a dose of 800kGy, the elastomer loses its elasticity and elongation.

Increasing the dose to 1000 kGy leads to the destruction of the spatial grid of radiation vulcanizates. Thus, the conducted studies allowed to reveal the influence of the nano-oxide (ZnO, Al_2O_3) initiator on the thermal and radiation crosslinking of the NBR and to establish the efficiency of the cross-linking (DSCB) and incipient action of nano metal oxides up to the temperature and the irradiation dose of 423K and 500-800kGy doses. Nano powders of ZnO and Al_2O_3 in radiation chemical processes. The obtained data on the parameters of the spatial grid and the mechanical properties of

thermal and radiation vulcanizates are subject to the possibility of expanding the field of application of the materials.

However, the mechanism of the effect of nano-sized powders of metal oxide on the thermal and radiation chemical processes that cause the observed change in properties is subject to further study.

4. Conclusion

This research work has revealed the rol of naooxides metals and crosslinking agent as filler in composites based on butadiene nitrile rubber. Thus, the presence of dencity crosslinks in nanocomposites can be view by a notable the fall the degree of crosslinking when they are swelling in a solvent. In nanocomposites without nanooxides and with aluminum oxide, this phenomenon is practically not observed.

The zinc chloride formed in the system will participate in the formation of coordination cross-links interaction with macromolecules of NBR, which is results to the formation of metal-containing polymeric nanocomposites, characterized by uniform the distribution of nano zinc oxide particles measuring 20-25 nm in the polymer matrix. Nano particles of oxide alumina which has a small reactivity has a very low effect on this process.

The obtained results indicate that removal of hydrogen chloride from the reaction sphere promotes the effective stabilization of ZnO nanoparticles in the early stages and forms carbon-carbon strong chemical bonds. In addition, it was to be expected that the zinc chloride formed in the system would participate in the formation of coordination cross-links.

Thus, analysis of the results of the conducted studies allows us to conclude that elastomeric materials based on NBR and metal nanooxide obtained by radiationchemical method in the presence of a cross-linking agent (DSCB) gives the better overall properties: ageing-heat resistance, dynamic endurance and exposed to aggressive environments than sulfur-vulcanized, while by strength properties inferior compared thermoradiation vulcanizates.

Acknowledgement. This work supported by the Science Development Foundation under the President of the Republic of Azerbaijan- *Grant № EIF-KETPL-* 2-2015-1(25)-56/10/1

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