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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

STUDY OF PHYSICOCHEMICAL PROPERTIES OF COMPOSITES BASED ON BUTADIENE NITRILE COPOLYMER AND METAL OXIDE NANOPARTICLES OBTAINED BY RADIATION-CHEMICAL METHOD

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Applicant: **Rana Faig Khankishiyeva**

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The work was perfomed at the Institute of Radiation Problems of Azerbaijan National Academy of Sciences (ANAS)

Scientific Sleever: – Doctor of Chemistry Science
Shiraz Majnun Mammadov

Official opponents:

– Doctor of Chemistry Sciences, Correspondent member of ANAS, Academician
Adil Abdulkhalig Garibov

– Doctor of Chemistry Sciences, Professor
Minavar Jafar Ibrahimova

– Candidate of Chemical Sciences
Hikmat Mammadrza Hajiyev

The Dissertation Council **BFD 1.22** of Higher Attestation Commission under the President of Republic of Azerbaijan operates at the Institute of Radiation Problems of the Azerbaijan National Academy of Sciences

Chairman of the Dissertation Council:
Corresponding member of ANAS,
Doctor of Chemical Sciences, Professor
Islam Israfil Mustafayev

Scientific Secretary of the Dissertation Council:
Doctor of philosophy in Chemistry
Ulviyya Aydin Guliyeva

Chairman of the scientific seminar:
Doctor of Chemical Sciences,
Associate Professor
Arzu Islam Najafov

GENERAL CHARACTERISTICS OF THE WORK

The actuality of the subject. The relevance of the topic of scientific research is determined by the fact that at present, elastomers based on nitrile rubbers are finding more and more applications due to their properties that are resistant to gasoline and oils, a wide temperature range of operation, low gas permeability, as well as resistance to radiation and thermal air aging. Due to the above properties, nitrile elastomers work mainly in harsh conditions and are used in the manufacture of products and parts that come into direct contact with aggressive media, in the electrical, mechanical and petrochemical industries, such as oil-fuel hoses, gaskets, oil seals, seals, etc.

NBR-based elastomers are also used to provide insulating protection and cable passages that operate briefly under dynamic load conditions. In recent years, in connection with the emergence of new areas of application of nitrile elastomers, the constant tightening of requirements for them, namely, the improvement of the technological properties of mixtures and the increase in dynamic endurance, resistance to aggressive media, the question of creating new elastomer materials has arisen, which is in the focus of research attention.

Numerous studies have shown that one of the main problems in the rubber industry is environmental pollution, as various chemicals are used in the production processes.

In addition, according to data provided by the European Union (EU), the rubber industry annually consumes about 100 thousand tons of ZnO and other zinc-containing chemical additives as activators[1].

To reduce the use of zinc in products, the EU has developed the Eco Zinc concept. Due to the small specific surface, only a small part of the finely dispersed ZnO reacts with the accelerator. As a result, most of this compound remains in the vulcanizate and is considered toxic to the body when released into the environment.

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[1] *Charles, W.M.B., Marja E.J.P., Dick T.H.M.S // The european union risk assessment on zinc and zinc compounds: The process and the facts. , –2005. Vol. 1(4), –p. 301–319.*

In this regard, in recent years, rubber product manufacturers have been looking for new technological methods and low-component formulations that can minimize the concentration of chemicals, while at the same time producing rubber materials with improved properties, which determines the relevance of the research topic. In recent years, in connection with the emergence of new areas of application of nitrile elastomers, the constant tightening of requirements for them, namely, the improvement of the technological properties of mixtures and the increase in dynamic endurance, resistance to aggressive media, the question of creating new elastomer materials has arisen, which is in the focus of research attention.

Note that the acrylonitrile-butadiene copolymer undergoes crosslinking when exposed to high energy radiation [2]. Numerous studies have shown that one of the main advantages of this technology is that the vulcanization is carried out without sulfur and dithiocarbamates, which are commonly used in traditional vulcanization and cause environmental pollution. Due to the formation of cross-links between macromolecules and a three-dimensional structure, an increase in molecular weight and a change in the chemical, structural, and physico-mechanical properties of the polymer occur.

The use of radiation methods in nanotechnology is ideal for creating new functional polymeric materials with improved properties. Also, it is possible to control the size and distribution of nanoparticles in the matrix. In filled polymer nanosystems, under the action of ionizing radiation, a spatial network is formed not only in the matrix, but also between elastomer macromolecules and filler particles. As the authors point out, nanoparticles in this system act as energy absorption centers and allow activation of the polymer crosslinking process. It should be noted that many studies have been devoted to the study of the structure and thermomechanical properties, the nature of the transformation of the structure of polymers at the molecular and supramolecular levels under ionization effects. However, from the

[2] *Mammadov S. M. Fundamentals of synthesis, processing and vulcanization of nitrile-butadiene rubbers. Germany: Lap Lambert, 2015, p. 650.*

analysis of scientific data, it was revealed that the same composition of the composite can give directly opposite results. There is little data on the effect of pre-heat treatment on the properties of composites obtained by the radiation method.

The issues of the influence of nanosized oxide fillers on the process of structure formation during radiation vulcanization and on the physicomechanical and operational properties of compositions based on nitrile butadiene rubbers have received little attention, both theoretically and practically. The mechanism of the process of NBR radiation crosslinking in the presence of nanoparticles was studied. Thus, the relevance of the problem from a scientific and applied point of view, the insufficient level of its development determined the choice of topic, the purpose and objectives of this study.

Purpose and objectives of the study.

In view of the foregoing, the purpose of this work is to obtain NBR-based elastomeric materials with an improved set of physical, mechanical, technological, electrical and heat-resistant properties, in the presence of active nanosized metal oxides using radiation-chemical technology. Realization of the set goal determined the need to solve the following tasks:

- to develop promising technological methods for vulcanization of nanocomposites synthesized on the basis of NBR;
- comparative analysis of the influence of the nature of nanosized metal oxides (ZnO, Al_2O_3 and ZrO_2) as activators in the process of vulcanization of elastomer mixtures by the radiation-chemical method in the presence of a cross-linking agent 1,3-disulfochloride benzene;
- to investigate the structural features of the samples and explain the main elements of the mechanism of NBR crosslinking, with the participation of a chloraromatic compound and metal nanooxides;
- to conduct a comparative study of the effect of ZnO, Al_2O_3 and ZrO_2 nanoparticles on the physical, mechanical and operational properties of elastomeric materials obtained by the radiation-chemical method based on NBR, a cross-linking agent, a sensitizer, a filler and a plasticizer;

- to study the effect of ionizing γ-radiation on the structural morphology of composite systems synthesized on the basis of NBR and metal oxide fillers;
- to develop a highly efficient technological process of vulcanization, to optimize the formulation and parameters of new materials, taking into account the conducted research, based on nitrile butadiene elastomer in the presence of nano-metal oxides with high rheological, physical-mechanical, electrical and operational properties.

Object of study and methods. Nitrile butadiene rubber (NBR), a copolymerization product of butadiene and acrylonitrile, was chosen as the object of the dissertation work. Three types of metal oxides ZnO (20–25 nm), Al_2O_3 (20–30 nm), and ZrO_2 (20–30 nm) were used as an activator. As an accelerator, crosslinking agent, sensitizer and filler in radiation-chemical processes, low-molecular chlorine-containing, triazine compounds and carbon black. Modes and methods for obtaining nanocomposites from metal oxide powders are described in the second chapter of the dissertation. To activate the process of radiation-chemical vulcanization under the action of γ - radiation (Co^{60}) used the installation MRX-γ-25M.

The work uses complex physical and chemical experimental methods. Structural parameters of the spatial grid of the composite were judged according to sol-gel analysis, kinetic parameters of the vulcanization process according to Mooney viscosity (rheometer Monsanto 1500S), rheological properties according to the Flory-Rener theory and Mark-Hovingk formulas (Ubellode VPZh-2,). Using spectrological methods (SEM, XRF, UV-VIS, Fourier IR and EPR), changes were studied as a result of exposure to radiation, temperature and thermal radiation on the composite material, the construction mechanism, and the morphological analysis of the vulcanizate. The mechanical properties of vulcanizates, as well as aging in various aggressive media, were studied on a universal tester, in accordance with the standards (ASTM and GOST). The electrical properties of the obtained nanocomposites were determined using an E7-20 immittance meter (RLC). To determine the thermophysical properties of the elastomer, TGA/DSC methods were used.

The following tasks have been fulfilled to achieve the set goal:

1. Research results to elucidate the role of metal nanooxides (ZnO, Al_2O_3 and ZrO_2) chlorine-containing, epoxy, triazine compounds in the process of radiation-chemical crosslinking of butadiene-nitrile rubber.
2. Research results to determine the order of effectiveness of metal oxides (ZnO, Al_2O_3, ZrO_2) as an activator in the process of vulcanization of binary and quasi-systems based on NBR.
3. Results of a study on the effect of temperature and ionizing γ-radiation on the efficiency of structure formation and surface morphology of polymer nanocomposite based on NBR.
4. Explanation of the main elements of the probable mechanism of the reaction that occurs during the interaction of the studied metal nanooxides and chlorine-containing aromatic compounds with NBR during radiation-chemical vulcanization.
5. Elucidation of the effectiveness of the action of the spatial structure (C-C, C-S_x -C) on the rheological, physical-mechanical, electrophysical properties of elastomeric materials.
6. New formulations of elastomeric materials for sealing purposes, operating in aggressive conditions, with an increased level of performance properties.

Scientific innovation:

- The scientific novelty of the research lies in the development of a new science-based technological solution for the modification of nitrile rubber with the participation of nanosized particles (ZnO, Al_2O_3 and ZrO_2) and polyfunctional additives, using radiation - chemical technology.
- For the first time, the sequence of three different nanooxides, ZnO, Al_2O_3 and ZrO_2, differing in their band gap, as an activator in the process of thermal, radiation and thermoradiation vulcanization, as well as the relationship between their structure and activity, was determined. The effect of metal nanooxides on the vulcanization process was also studied in the presence of a crosslinking agent (DSCB), a sensitizer (DAPST), a filler (CB) and a plasticizer (fuel oil: bitumen). The effect of ZnO, Al_2O_3 and ZrO_2 nanopowders on the structural, mechanical, electrical, and thermophysical properties of binary and quasi-systems

based on NBR was studied for the first time using radiation-chemical technology.

- The probable mechanism of the course of the radiation-chemical structuring of NBR with the participation of nanosized particles (ZnO, Al_2O_3 and ZrO_2) and DSHB was first explained. The particle size, polymorphic composition, structure and morphology of nanocomposites have been studied.
- It was found that the activating ability of metal nanooxides depends on the band gap and their activity towards chlorine in ionic or radical form.
- The effect of the sensitizer 2,4-diamino-6-phenyl s-triazine (DAPST) on the structural parameters of the network of NBR radiation vulcanizates in the presence of metal nanooxides was studied for the first time.
- For the first time, the physical-mechanical and performance characteristics of elastomeric materials were studied during radiation-chemical vulcanization of NBR, with the participation of nanosized metal oxides.

Theoretical and practical values of the work. The research materials and the obtained generalized results can be used in the framework of scientific research and theoretical knowledge. The established regularities of the influence of metal nanooxides on the physicochemical properties of NBR and the properties of vulcanizates make it possible to make a targeted choice of metal oxide nanopowders and reactive low molecular weight compounds, taking into account the requirements for the final product. The possibility of improving the technical properties of mixtures and elastomer materials based on NBR, intended for operation at elevated temperatures and under conditions of complex dynamic loading, is shown. The results of the study of radiation-chemical vulcanization in the presence of a nanoparticle activator, a cross-linking agent, a sensitizer, a plasticizer and a filler make it possible to obtain elastomeric materials that are superior to sulfur materials in terms of physical and mechanical properties. Based on the results obtained, the composition of the elastomeric sealing material was determined to be resistant to wear in sea water

and oil solutions at a temperature range of 80-120ºC, as well as to the effects of numerous deformations and dynamic loads.

Scientific novelty and technical solution of the work are protected by the patent of the Republic of Azerbaijan **(No. İ 2018 0063).**

Approbation of work. The dissertation was published in 5 scientific articles, 4 of which are included in the international EAC indexing systems (Web of Science and Chemical Abstract System) and secured by 1 patent. In total, the dissertation is reflected in 20 scientific papers (5 articles, 1 patent and 14 theses).

The main results of the dissertation were presented and reported at the following scientific conferences and seminars: IX International Scientific and Practical Conference " Actual Problems of Chemistry" (Baku - 2015) , Republican Conference dedicated to the 90th anniversary of Academician T. N. Shakhtakhtinsky (Baku - 2015), X International Conference "Nuclear and Radiation Physics" (Almaty-2015), Materials of the Republican Scientific Conference "Chemistry of Macromolecular Compounds, Organic Synthesis and Composite Materials", dedicated to the 50th anniversary of the Institute of Polymer Materials (Sumgayit-2016) , IV International scientific conference of Young Researchers (Baku - 2016), X International Scientific and Practical Conference " Actual Problems of Chemistry" (Baku-2016) , XX Republican Scientific Conference of Doctoral Students and Young Researchers (Baku - 2016), IX Baku International Mammadaliyev Conference on Petrochemistry (Baku - 2016), XI International Conference " Nuclear and Radiation Physics " International Conference "Nucleus - 2017" (Almaty-2017), I International scientific conference of young researchers (Baku - 2017) , XIV International scientific conference of young scientists "Youth in Science - 2017" (Minsk-2017), XVI Kurchatov Interdisciplinary Youth Scientific School, dedicated to 7 5th anniversary of the National Research Center "Kurchatov Institute" (Moscow-2018), V Interdisciplinary Scientific Forum "New Materials and Advanced Technologies" (Moscow- 2019), III International Scientific Forum "Nuclear Science and Technology" (Almaty-2021).

The research was carried out in the Laboratory of Radiation Chemistry and Polymer Technology of the Institute of Radiation

Problems of the National Academy of Sciences of Azerbaijan (2015-2021). The morphological features of the obtained composites were studied at the Nanotechnology Center of Baku State University, and thermal properties at the Institute of Joint Nuclear Research (Dubna).

Structure and scope of the dissertation: The dissertation consists of an introduction five chapters, a conclusion and a list of 199 cited sources. The total volume of the work consists of 192 pages, including 108 pages of text only (222720 characters), 65 figures and 23 tables.

In the introduction the relevance of the topic, the purpose of the work, the issues that need to be resolved to achieve the goal, the objects of research, scientific novelty, the main scientific provisions submitted for defense are substantiated. Also, the practical and scientific significance of the research carried out, approbation and publication of the dissertation work is substantiated.

Chapter I is devoted mainly to the analysis of scientific literature. Here, methods for vulcanizing elastomers are considered, which are characterized by a number of advantages, the main of which are the provision of production of elastomer products using a more environmentally friendly technology and the creation of products with new properties and improved performance. The effectiveness of the use of new methods is due to the possibility of creating high-performance technologies, where γ-sources and electron accelerators are used as vulcanization equipment. The replacement of micron-sized powders in rubber compositions by nano-sized powders has become a general trend in the development of new materials over the past few decades, giving an advantage over traditional methods. Attention is paid to formulating rubber compounds based on NBR with chlorine-containing compounds and to the development of technological modes of vulcanization of elastomeric materials designed to operate in complex dynamic loading modes under the influence of various factors.

Chapter II describes the properties and characteristics of the used objects of study, the composition and formulation of rubber compounds (Table 1) and the technology of their manufacture (Fig. 1).

Table 1. Composition of the studied systems

Polymer systems №	Compounding recipe of rubber (parts per 100 parts of rubber by weight).														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
NBR	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Sulpur	-	-	-	-	-	-	-	-	-	-	-	-	0.2	0.2	0.2
DSChB	-	4.0	4.0	4.0	-	4.0	4.0	4.0	-	4.0	4.0	4.0	4.0	4.0	4.0
ZnO	4.0	4.0	4.0	4.0	-	-	-	-	-	-	-	-	4.0	-	-
Al_2O_3	-	-	-	-	4.0	4.0	4.0	4.0	-	-	-	-	-	4.0	-
ZrO_2	-	-	-	-	-	-	-	-	4.0	4.0	4.0	4.0	-	-	4.0
П-324	-	-	-	50.0	-	-	-	50.0	-	-	-	50.0	50.0	50.0	50.0
Fuel oil	-	-	-	3.0	-	-	-	3.0	-	-	-	3.0	3.0	3.0	3.0
DAPhST	-	-	3.0	3.0	-	-	3.0	3.0	-	-	-	3.0	3.0	3.0	3.0
Bitumen	-	-	-	5.0	-	-	-	5.0	-	-	-	5.0	5.0	5.0	5.0

Vulcanization methods: Thermal vulcanization - 423Kx40'; Radiation vulcanization – D=0–500 kGy; Thermal-radiation vulcanization - 423K x 5 min, 250 kGy;

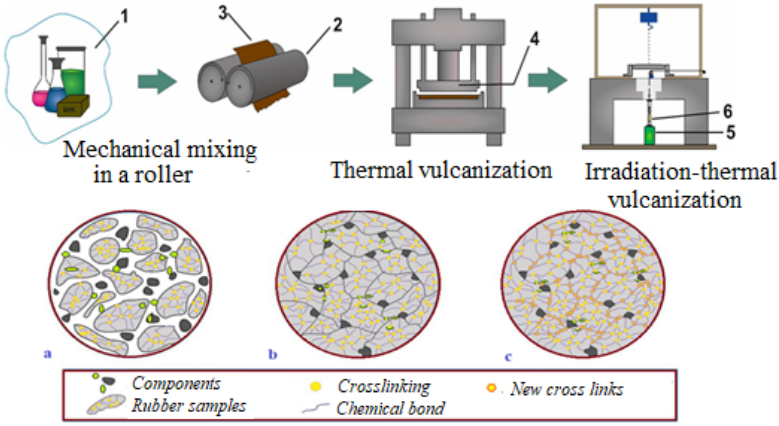

Figure 1. Scheme of the process of thermo- and thermo-radiation vulcanization: 1 - ingredients; 2- rollers for mixing components; 3 - rubber compound; 4 - hydraulic press; 5 - Co ^{60} source ; 6 - vial for samples

Chapter III, Investigated the effect of three nanooxides, ZnO (20-25 nm), Al_2O_3 (20-30 nm) and ZrO_2 (20-30 nm), differing in the band gap (3.37, 8.58 and 5.15 eV, respectively), on the rheological, structural parameters and plasticization properties (vulcanization parameters) of binary and quasi-systems based on NBR. The choice of nanosized oxides under study is justified by varying the value of electronegativity, which determines the polarizing ability of the oxide. The adsorption capacity of oxides, which is related to the specific surface area, is also taken into account. The presence of intermediate particles ensures efficient absorption of γ rays by these materials and makes it possible to activate the process of polymer crosslinking. To interpret the studied factors, we analyze the results obtained.

As can be seen from Table 2, the introduction of metal oxide nanopowders has little effect on the plasticization rate of the systems. The plasticization process was carried out on rollers at low temperature (323K). The nature of their action is largely determined by the content of the gel. Since, if the molecular weight of the sol fraction slows down in the presence of ZrO_2 and Al_2O_3 , then when ZnO is introduced into the NBR mixture, a noticeable acceleration of the process is observed, by about 40%. In the process of initial plasticization in the NBR− Al_2O_3 and NBR− ZrO_2 systems, microdestruction occurs to a greater extent than in the ZnO− NBR system. However, it should be noted that the use of nanosized particles of fillers and the high polarity of BNR can be technologically difficult. First, nanoparticles are prone to agglomeration, and as a result, the particle size increases rapidly during machining, and the specific surface area decreases. Secondly, it is very difficult to distribute nanoparticles over the entire volume of the matrix, which leads to poor dispersion and the formation of coagulation-flocculation structures in unvulcanized mixtures. To solve this problem, 1,3-disulfochloride benzene (DSCB), a chloraromatic compound containing active groups $–SO_2Cl$, was added to the system, and plasticization was carried out.

From the data presented in table. 2. it can be seen that the introduction of DSCB into the system has a noticeable effect on the rate of structuring of mixtures, effective plasticizing effects on the composite are manifested, and also greatly increases the Mooney viscosity and gel content.

The tests carried out showed that NBR structuring is affected by the types of nanopowder. Since, in all samples, ZnO provides a higher rate of structuring, compared with Al_2O_3 and ZrO_2, despite their almost identical polarizing ability. This can be explained by the fact that, in an oxide containing a more electronegative cation (Zn^{2+}), due to a decrease in the binding energy with oxygen, catalytic, chemical activity and reactivity when interacting with a chlorine-containing compound. It has been established that the activation energy of chemisorption with the breaking of molecules into radicals also decreases with a decrease in the specific surface area of nanoparticles, which coincides with the range of activity of the oxides used: $\mathbf{A_{ZnO} > A_{Al2O3} > A_{ZrO2}}$.

Table 2. Characteristics of the studied samples

Composites systems	Plasticization Time, min.	Content, gel in rubber, %	Degree of swelling in toluene,%	Molecular weight of sol fraction×10^4	Mooney Viscosity u.d.	Plasticity, %	Hardness, Hs
NBR+ZnO	3	57,1	48,4	19	50	0,29	1310
BNK+DSChB+ZnO	5	65,8	44,1	17	50	0,25	1100
BNK+ DSChB +ZnO +S	7	72,7	40,0	16	65	0,21	1000
BNK+ DSChB +ZnO+S+ CB	10	81,3	31,3	12	68	0,20	800
BNK+Al_2O_3	5	45,2	61,6	9	40	0,32	1400
BNK+ DSChB +Al_2O_3	8	54,0	58,4	10	49	0,30	1250
BNK+ DSChB +Al_2O_3 +S	12	58,6	50,2	12	61	0,27	1100
BNK+DSHB+Al_2O_3 +S+CB	14	62,3	45,3	13	63	0,23	1000
BNK+ZrO_2	7	42,3	65	7	35	0,30	1350
BNK+DSHB+ZrO_2	10	49,7	62	6	42	0,27	1120
BNK+DSHB+ZrO_2 +S	12	54,3	59	6	50	0,25	1050
BNK+DSHB+ZrO_2 +S+ CB	15	59,9	57	5	55	0,22	900

Thus, when going from binary systems to multicomponent mixtures based on BNR, the increase in the gel fraction can be explained by the formation of oxidized fragments in the macromolecule, as well as the interaction of the components with each other. The molar mass of the sol fraction in NBR composites decreases, so the Mooney viscosity, especially in mixtures with CB, increases.

In the DSHB molecule, there are two functional groups - acid chloride and sulfochloride, which differ significantly in chemical properties from each other and are characterized by high reactivity. At the same time, the NBR macromolecule contains reactive hydrogens (active centers) at the tertiary carbon atoms in the units of butadiene and acrylic acid nitrile. It is also known that oxides are characterized by increased reactivity with respect to hydrogen chloride, which accelerates the process of rubber crosslinking. In addition, if we take into account the fact that the role of metal chlorides as structuring agents for nitrile butadiene rubbers is higher than for other elastomers, then the accelerating effect of high activity metal oxides, especially ZnO, in mixtures based on NBR becomes clear.

The use of the viscometric method for evaluating the effectiveness of the effect of DSCB and metal oxide powders on the change in the molecular weight of the polymer makes it possible to obtain more detailed information about the processes occurring in rubber during vulcanization under the action of heat and ionizing radiation. (fig. 2.) The dependences of the intrinsic viscosity of thermal unfilled NBR vulcanizates with DSCB with nanosized metal oxides on the duration of heating are shown. Changing the viscosity from the required level does not lead to a significant change in the molecular weight of the rubber. As the duration of heating increases, the viscosity of the solutions increases monotonically. The inherent viscosity of the NBR+DSCB+ZnO system increases from 0.4 to 2.2 dl/g. With an increase in the absorbed dose above 400 kGy, the intrinsic viscosity of the studied samples decreases.

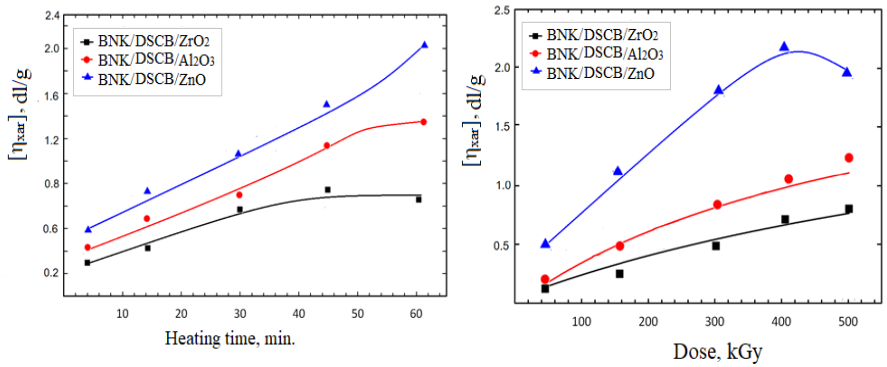

Figure 2. Kinetics of intrinsic viscosities of thermal and radiation vulcanizates

The decrease in the molecular weight of rubber is the result of degradation of the polymer backbone. The increase in viscosity in the range of values of the absorbed dose of 400-500 kGy in the systems NBR + DSCB +Al_2O_3 and NBR + DSCB + ZrO_2 is possibly associated with the formation of spatial structures as a result of reactions within the molecular cross-linking.

The amount of insoluble gel-fraction already at irradiation doses of 100 kGy increases by 15%, and after irradiation at 400-500 kGy, the polymer becomes completely insoluble. The maximum gel content (87%) in the NBR+DSCB+ZnO system indicates cross-linking of the molecules of the polymer chains with the DSCB. The calculation of the radiation-chemical yield of the concentration of cross-links (G_{n_c}') showed that the number of cross-links for the system NBR + DSCB + Al_2O_3 is $3.0 \cdot 10^{-19}$ cm^3 , and for a system with ZnO this figure is $6.0 \cdot 10^{-19}$ cm^3 . Also investigated are the change in mechanical properties, tensile strength and relative elongation at break of mixtures NBR + DSCB + ZnO and NBR + DSCB + Al_2O_3 , depending on the irradiation dose and the resulting data are presented in fig. 3. It can be seen that the non-irradiated mixtures achieved relatively low tensile strength values. On the other hand, the values of tensile strength achieved both for the NBR + DSCB + Al_2O_3 system and for the NBR + DSCB + ZnO system increased with the irradiation dose reaching its

maximum value at 400 kGy, and then decreased with further dose increase. As expected, the elongation values for both mixtures decrease with increasing irradiation dose. This systematic decrease in values may be due to induced crosslinking under the action of γ - irradiation.

The decrease in the elasticity of mixtures with an increasing dose of irradiation can also be explained by additional binding between nanoparticles and rubber due to a large amount of free radicals formed under the action of irradiation. Therefore, increased radical recombination is likely to result in a strong chemical bond with increasing radiation dose.

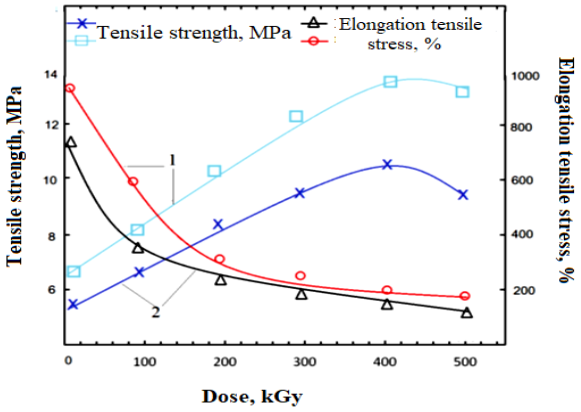

Figure 3. Effect of irradiation dose on tensile strength and relative elongation at break of nanocomposites based on NBR :1- NBR + DSCB + ZnO; 2- NBR + DSCB + Al_2O_3

In Chapter IV, the radiation-chemical transformations of NBR are studied in the presence of a cross-linking agent and nano-metal oxide. Study of the irradiation-chemical interaction of NBR with DSCB-ZnO, DSCB-Al_2O_3 , DSCB-ZrO_2 by IR-Fourier spectroscopy (Fig. 4.). Based on the IR spectra, it can be concluded that during the heating of the NBR + DSCB + ZnO systems due to the elimination of active chlorine from aromatic rings, the chemical interaction of the sulfur curing agent with the double bonds of the polymer occurs. The resulting cross-links contain sulfone groups. Based on this, the main

attention in the study was paid to the study of the intensity of the stretching vibration band of the free nitrile group, located in the region of 2237 cm $^{-1}$ and characterized by exceptional stability, both in frequency and in form for all composites. As can be argued, the ionic interaction between the Zn^{2+} group present in ZnO and the -C≡N and -C-Cl groups were a key factor in obtaining the cross-linked NBR-based material.

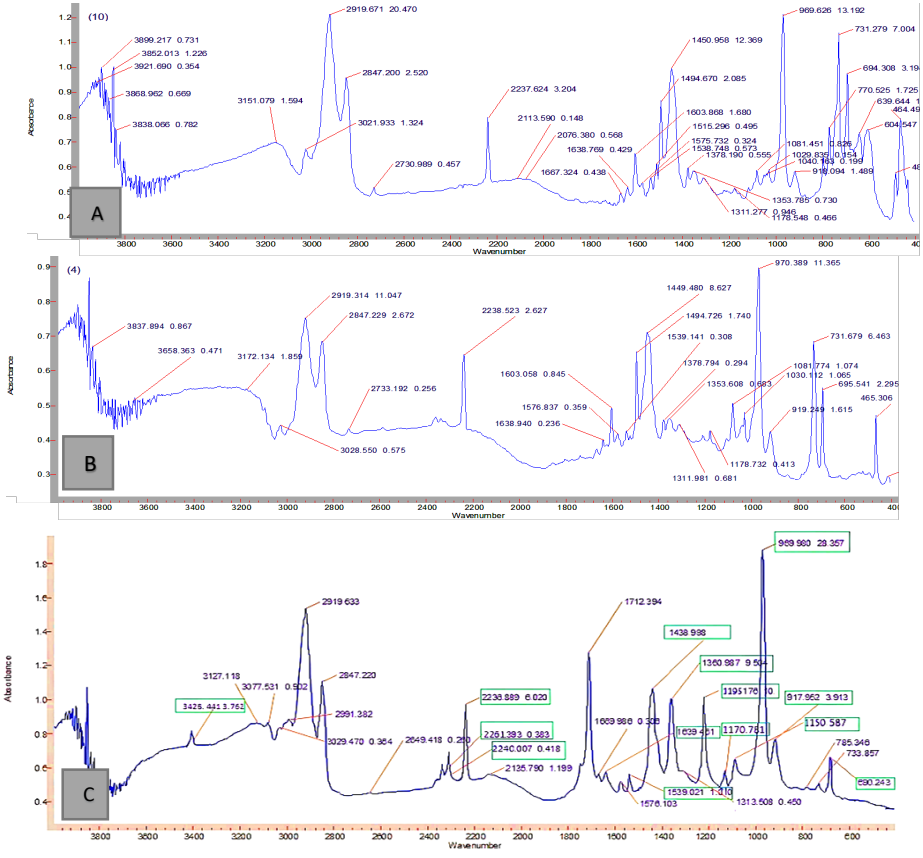

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Figure 4. IR spectra of nanocomposites NBR-Al_2O_3-DSCB (a) and NBR-ZrO_2 -DSCB (b) and NBR+DSCB+ZnO (c) obtained by irradiation (D = 500 kGy)

In addition, it was to be expected that the zinc chloride formed in the system would participate in the formation of labile coordination cross-links. Indeed, in the IR spectra of the NBR-ZnO - DSCB system, a band at 2240 cm^{-1} appears, which can be associated with the formation of a complex between zinc chloride and the lone pair of nitrogen electrons.

Based on the above experimental and literature data for the process of crosslinking systems NBR-ZnO-DSCB, we can assume the following possible mechanism, presented in Fig.5.

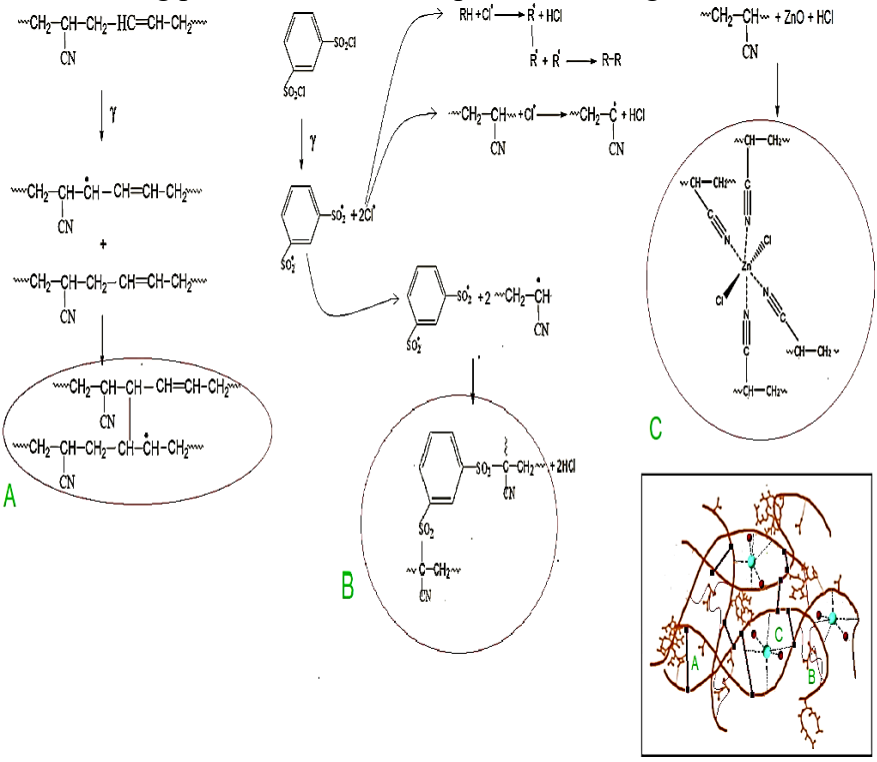


Figure 5. Probable scheme of radiation vulcanization of NBR-ZnO-DSCB: A - radical crosslinking of NBR, B - Decomposition of DSCB and formation of a spatial structure, C - Formation of a coordination complex

To confirm the radical mechanism of the reaction, the EPR signals of NBR -based elastomeric composites contained in DSCB and ZnO were studied. The studied samples were stored from the moment of irradiation with γ -rays until measurement for 2 months in the dark at room temperature. On fig 6 shows the EPR absorption spectra of samples based on NBR irradiated at different doses (100 and 500 kGy). As it turned out, the EPR waveforms depend on the radiation dose. At low doses, the signal has an asymmetric complex shape and is a superposition of signals from several types of different radicals. This behavior can be associated, on the one hand, with a large number of ingredients inside the elastomeric matrix capable of generating radicals, and, on the other hand, with numerous reactions between them. In these vulcanizates , the concentration of free radicals increases, and many different types of radicals (g = 2.0024 and 2.0048, ΔH = 2.8 and 2.3 mTl) can be identified, which can be formed as a result of the reaction of DSCB and ZnO.

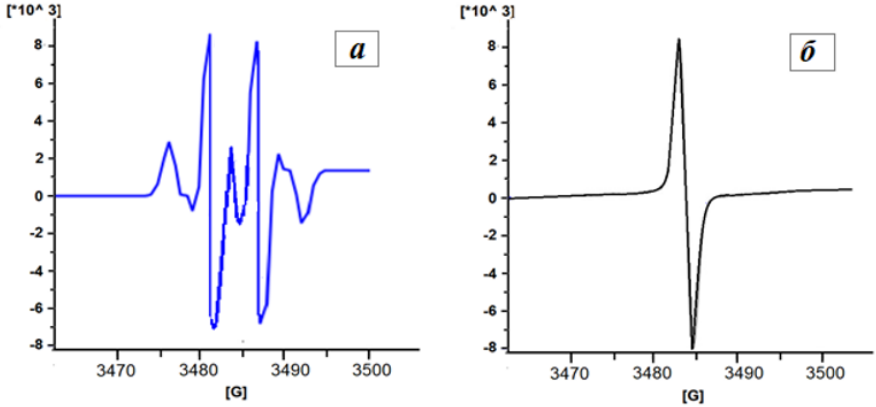


Figure 6. EPR spectra in the NBR + DSCB + ZnO system at radiation doses of 100 kGy (a) and 500 kGy (b)

As the radiation dose increases from 100 to 500 kGy, the intensity and shape of the EPR spectrum change (Fig. 5a) . and traces of hyperfine structure (HFS) are not observed. With an increase in the

irradiation dose to 500 kGy, the EPR spectrum acquires a narrow symmetrical singlet line with a width of ΔH=4.13 mTl and g=2.0041. According to the ratio of intensities and values and g - factor , they can be attributed to allyl radicals. These radicals are highly reactive and readily react via allylic hydrogen abstraction in the diene monomer and some of them react with other polymer and radicals to form C-C crosslinks.

Change in the shape of the EPR signal with increasing dose (Fig. 5. (b)) irradiation is also explained by the fact that the concentration of radicals inside the elastomeric medium increases, which leads to a decrease in the distance between them, as a result of which the orbits of unpaired electrons in neighboring radicals overlap and recombination of radicals occurs with the formation of a crosslink.

Based on the above experimental and literature data for the process of crosslinking systems NBR-ZnO-DSCB, we can assume the following possible mechanism, presented in Fig.6.

Scanning Electron Microscopy (SEM) was used to study the state of the surface of the polymer film, in order to evaluate the dispersion of filler particles in the elastomer before and after irradiation. According to the SEM results (Fig. 7), it can be argued that the nanocomposites consist of isolated electron-contrast nanoparticles (ZnO, Al_2O_3, and ZrO_2) and are characterized by a set of fine-grained particles with characteristic sizes ranging from 20 to 300 nm. Agglomerates up to 800 nm were also noted. As can be seen from fig. 7. (b, c, d) over the entire volume of the polymer matrix, a continuous, as well as inhomogeneous distribution of ZnO, Al_2O_3 and ZrO_2 nanoparticles is observed.

Heterogeneity and uneven distribution of inorganic components in the volume of the sample can substantiate the high surface energy of the nanoparticles. Since they create micro-sized accumulations of particles (agglomerates) with a complex structure, therefore, they lead to a decrease in their surface area. This leads to a decrease in the interface between MeO and other components. Such agglomerates are visible in all samples. These particles can cause an increase in

cross-link density in vulcanizates, which can degrade the performance of the elastomer.

On the other hand, it turned out that under radiation (250 kGy) with the participation of DSCB, the distribution pattern of nanoparticles in the polymer matrix changed and became more uniform. Figure 8 (a, b, c) shows the surfaces of nanosamples exposed to γ-radiation (250 kGy).

The figure shows both agglomerates and individual nanoparticles. Radiation treatment of the corresponding samples contributes to the destruction of large agglomerates and the formation of nanosized particles (less than 100 nm), and also significantly increases their packing density due to the effect of interfacial interaction of rubber and nanofillers.

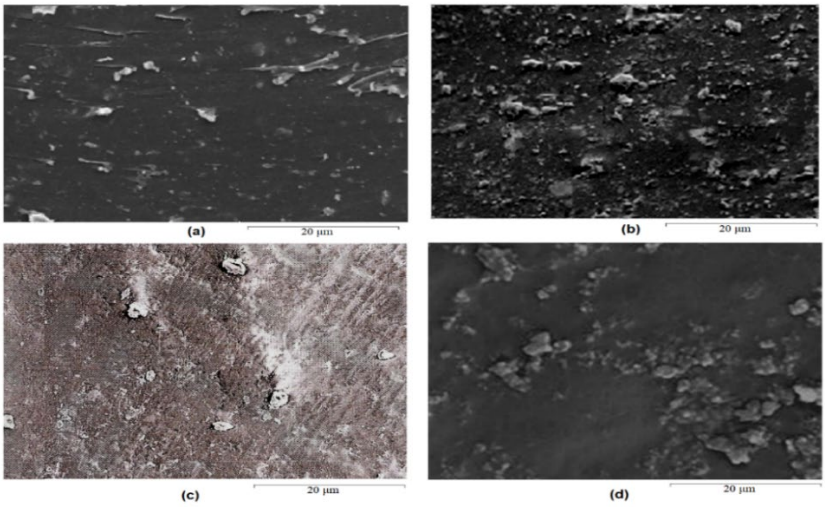


Figure 7. SEM image of non-irradiated NBR-based composites with metal nanooxide: a - pure NBR, b - ZnO, c - Al_2O_3, d- ZrO_2

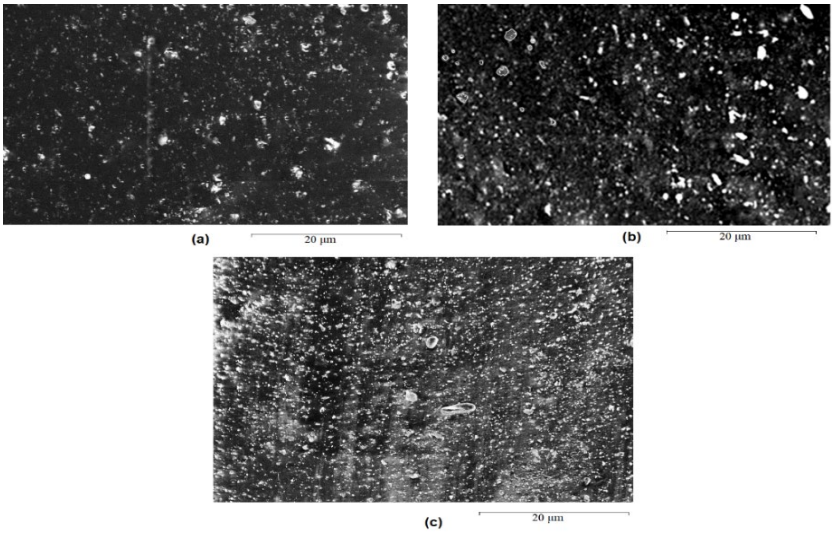
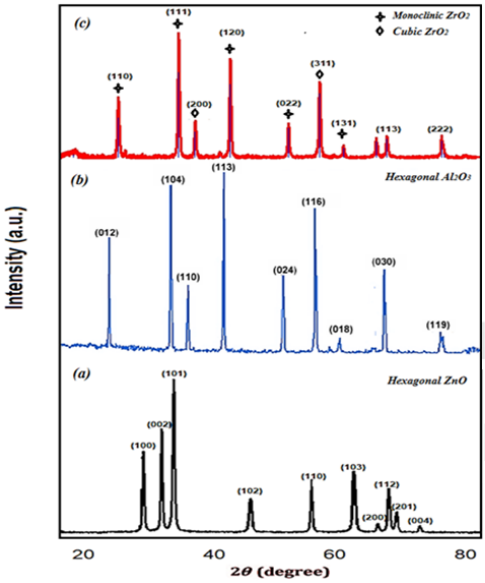


Figure 8. SEM image of irradiated NBR-based nanocomposites with the participation of metal nanooxides: a - ZnO, b - Al_2O_3, c - ZrO_2

Subsequently, X- ray diffraction analysis of unvulcanized rubber compounds filled with oxides of Zn , Al , Zr and other additives was carried out in order to understand the structure of these samples and determine the size of the particles formed here. Apparently, the strongest peaks belong to nanoparticles of the hexagonal ZnO phase and are observed in the range 2θ=31-69°, corresponding to (100), (002), (101), (102), (110), (103) , (112) (JCPDS PDF #36-1451). In samples with Al2O3 addition, diffraction peaks 2θ = 26.9°, 35.1°, 37.0°, 43.4°, 57.5°, 68.1°, 69.2° and 77.9°, gratings (012), (104), (110), The values (113), (024), (116), (030), (119) correspond to the value of the α-Al2O3 hexachannel (JCPDS No. 87-0245). In samples filled with ZrO2, 67.5% monoclinic (JCPDS no. 81-1314) and 32.5% cubic (JCPDS no. 49-1642) phases were observed. The size of crystalline particles in the composite was calculated by the Debye-Scherrer method, and the results are presented in Figure 9.



ZrO_2	Al_2O_3	ZnO
28.12	25.59	29.80
34.16	35.14	41.04
46.35	37.78	44.17
59.56	43.36	50.81
64.12	52.55	61.87
69.78	57.52	67.93
78.19	66.55	79.15
92.06	68.20	81.24
116.90	101.21	128.43
65.4	54.21	64.93

Figure 9. XRD analysis of binary nanocomposites based on NBR and metal nanooxide: a- ZnO, b- Al_2O_3 , c- ZrO_2

In addition, the spectra in all mixtures show clear changes at low Bragg angles with the appearance of a broad peak between 2θ =10° and 30°, which is characteristic of amorphous structures and is attributed to the presence of rubber.

On fig. 10. UV-VIS spectra of pure NBR and NBR composite modified with nano-ZrO_2 are shown at room temperature after irradiation at various doses. The UV spectra of NBR observed at 294 nm are due to the transition of the polymer from π to π *. Samples containing ZrO_2 absorb radiation over a larger range than pure polymers. In other words, the intensity and width of the peaks for all composites is significantly higher than for the pure polymer. This is due to the interfacial interaction between the polymer and nanoparticles as a result of radiation.

It should be noted that, depending on the irradiation dose, some of the observed signals in the UV-VIS spectrum remained unchanged, and

some of them, showing a slight shift in the absorption peak towards a longer wavelength, changed, and new signals also appeared. It has been found that the electronic transitions associated with the $n \rightarrow \pi^*$ transition of C=N bonds in NBR are shifted to higher wavelengths for all composites. The studies performed have shown that nanocomposites with the participation of ZrO_2 absorb light at a wavelength of more than 280 nm, and the intensity of optical absorption increases with an increase in the irradiation dose. With an increase in the radiation dose from 100 to 250 kGy, the intensity of absorption increases with increasing dose. The intensity and width of UV peaks are maximum for nanocomposites irradiated at a dose of 250 kGy.

As is known, the width and intensity of the UV peak is associated with the agglomeration of nanoparticles, which prevents the passage of light energy through the matrix. The band gap of the films was estimated using the Tauc relation. By calculating the optical band gap, one can also study the distribution and dispersion of filler particles over the volume of the composite. On fig. 10. shows the dependence of $(\alpha h\upsilon)^2$ on the photon energy for irradiated NBR-based composites.

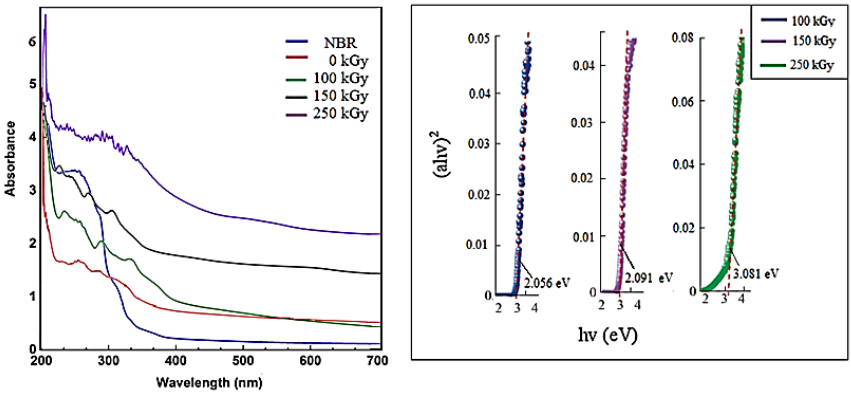


Figure 10. UV-VIS analysis of binary nanocomposites based on NBR and metal nanooxide: a- ZnO, b- Al_2O_3 , c- Zr_2

The optical band gap (E_g) is derived from the intersection of the extrapolated lines from the linear part of the curve with the hυ axis.

An increase in the absorption energy of conduction electrons from 2.056 to 3.081 eV indicates a decrease in particle size with increasing dose.

In order to obtain elastomeric materials with improved physical and mechanical properties, the rubber compounds proposed by us, obtained by thermal and thermoradiation methods, were compared with a model mixture obtained as a result of sulfur vulcanization.

Table 3. Mechanical properties of vulcanizates based on nitrile-butadiene rubber obtained by different methods

Mechanical parameters	Type of vulcanization		
	Sulphur	Irradiation	Thermo-radiation
Stress at 300%, MPa	10	8	12
Tensile Strength (σ), MPa	25	18	26
Elongation at break (ε_b), %	480	600	460
Hardness (Shore A)	65	60	65
Compression set resistance *(20%, 150˚C, 72 h.)*	62	57	52
Dynamic endurance during cyclic stretching (N) (150%, 500 cyc/min)	20	20	23
Aging coefficient, K, % (150˚C, 150 h.)			
by tensile strength (σ)	0,70	0,82	0,85
by elongation at break (ε)	0,52	0,62	0,64
by dynamic endurance (N)	0,75	0,77	0,77
Change of mass after swelling in mix of benzyl-benzene (3:1) (353K, 24h), %	38	30	27

The composition of the mixture - 100 wt.h. NBR: ZnO - 4.0; DSHB - 4.0; DAFST - 3.0, fuel oil: bitumen - 3.0, carbon black P324 - 50.0.

Note: During thermal vulcanization, in addition to mixture 2.0, with thermal radiation 0.2 kb.h. sulfur is included.

The results of the study show that vulcanizates obtained with cross-links (C-C) are superior in resistance to aromatic hydrocarbons polysulfide bonds (C - S_x - C), as was observed, for example, when gasoline-benzene (3:1) acts on radiation vulcanizates from NBR elastomer (Table 3). And the strength and elastic properties of

thermoradiation vulcanizates are higher than those of radiation and sulfur. To determine the effect of temperature and operating conditions on the performance of elastomeric materials (seals), which are used as a sealant on drilling rigs, comparative tests were carried out in aggressive environments.

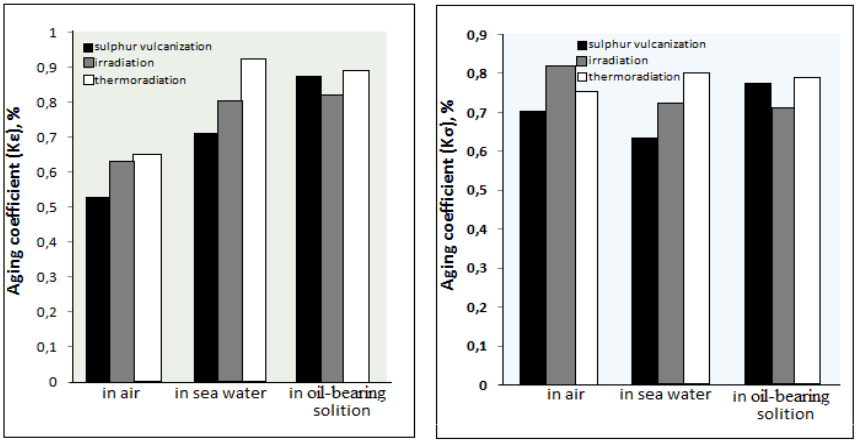


Figure 11. Dependence of ageing coefficients on tensile strength and elongation at break in air and corrosive media

The data obtained indicate that the degree of swelling and accumulation of residual compressive strain in sulfur seals is less, and the coefficient of thermal aging in sea water and oil-bearing solutions is greater than that of sulfur elastomers. The tensile strength after contact with the medium for radiation vulcanizates was lower than that of sulfur and thermoradiation (Table 5.). It is believed that the distribution of cross-link lengths between neighboring nodes in the vulcanization network makes it possible to easily rearrange molecular chains under the action of mechanical stresses. But in the case of energetically weak bonds (such as –C-S_x-C-), molecular chains break when stretched. The presence of a large number of such bonds in the structure of the vulcanizate leads to a deterioration in thermal stability and a decrease in reversion resistance. Heat-resistant C-C bonds irreversibly fix these stresses, and easily rearranged polysulfide bonds promote relaxation processes. The result is a grid without strong internal stresses.

NBR is a highly polar rubber due to the highly polar C≡N group, which introduces significant orientational polarization into the dielectric properties and compared to most non-polar polymers, it has a higher dielectric constant.

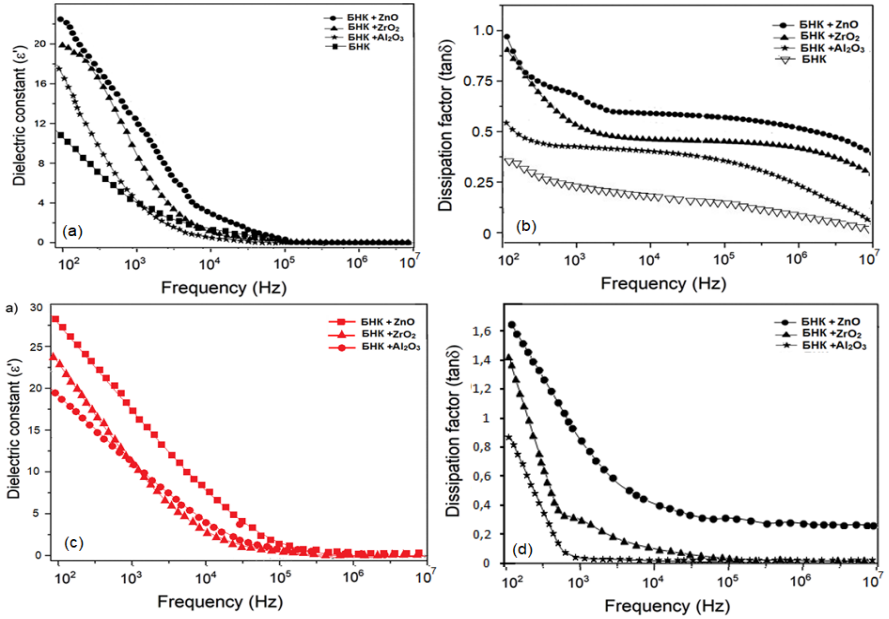


Figure 12. Frequency dependence of ε' and tgδ nanocomposites before (a, b) and after irradiation (c, d)

An effective method for increasing the dielectric constant of rubber is to fill it with inorganic powders with a high dielectric constant (ε). From Fig.12. it can be seen that both non-irradiated and irradiated MeO/NBR composites show the same trend. Therefore, the increase in the value of ε' after irradiation is associated with the formation of defects in the band gap of the polymer as a result of chain breaks. These defects may indicate the presence of carrier traps in the band gap of the polymer. Moreover, the increase in the dielectric parameters (ε and tgδ) of the irradiated composites is due to the enhancement of the Maxwell-Wagner polarization of space charges at the polymer-filler interface.

It was observed that the composite films with ZnO had the highest dielectric losses, which were 23.3 and 28.6 at 100 Hz, respectively, for non-irradiated and irradiated samples. The results showed that all fillers tend to improve dielectric properties and can be used as a built-in capacitor.

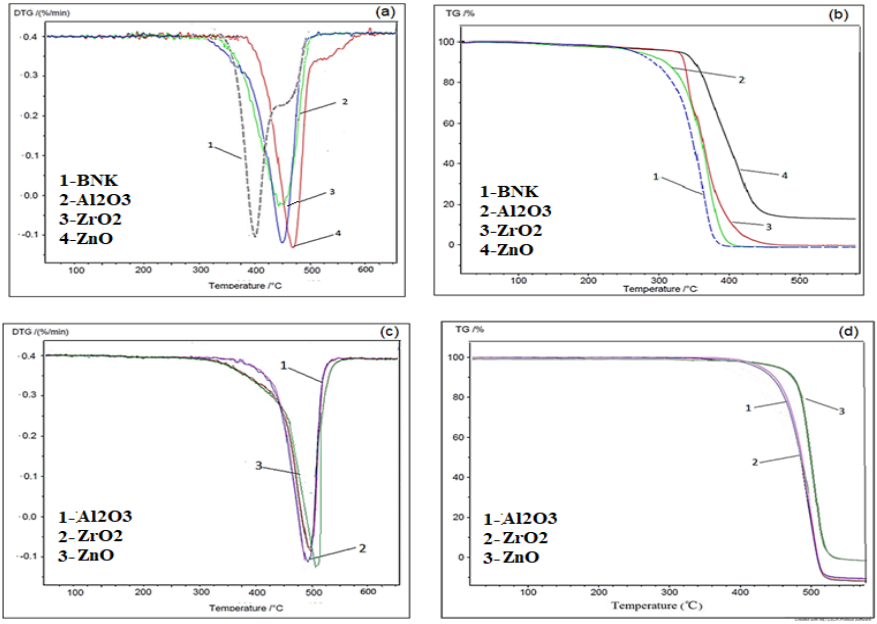


Figure13. Change of thermal properties of NBR-based composites: a, b before irradiation; c, d after irradiation (D=500kGy)

The thermal properties of the vulcanisates were measured in scanning TGA/DSC. The thermograms in Fig. 13 shown that the curves differ little from each other in all NBR-based samples. However, if the initial decomposition temperatures (T10%) are compared, this is between 436 and 445°C in the unirradiated samples and higher in the irradiated composites (454-467°C). The active degradation temperature (T90%) in the irradiated ZnO-based composite is 502°C, while in the Al_2O_3- and ZrO_2-based samples it is 492°C and 489°C, respectively. This may be attributed to an increase in cross-link density during radiation curing and the formation of heat-resistant -C-C- bonds.

MAIN SCIENTIFIC RESULTS

1. The scientific basis of the technology for obtaining composite materials based on a copolymer of butadiene-nitrile and nano-oxides of metals (ZnO, Al_2O_3 , ZrO_2) by the method of radiation-chemical vulcanization have been developed.

2. On the example of NBR-based model mixtures, a series of activities of nanometal oxides $A_{ZnO} > A_{Al2O3} \geq A_{ZrO2}$, differing in the band gap, in the process of sample structuring under the influence of temperature and radiation was established for the first time. It has been shown that the use of metal nanooxides as an activator in the process of radiation-chemical vulcanization increases the radiation-chemical yield (RCY) and the concentration of effective cross-links in vulcanizates .

3. By IR-Fourier spectroscopy and chemical-analytical method, the mechanism of radiation-chemical reactions was proposed. It has been established that -CH, $-CH_2$, -C≡N and double carbon bonds are involved in the transformation reactions occurring in the NBR system, where a higher reactivity of ZnO with respect to DSCB and rubber than Al_2O_3 and ZrO_2. During radiation dissociation, the active fragments of DSCB interact with the elastomer, and the cleaved chlorine interacts with Zn^{2+} ions to form zinc chloride. The 2240 cm^{-1} band identified in the spectra is possibly associated with the formation of a complex between $ZnCl_2$ and the lone pair of nitrogen electrons, which is involved in the formation of labile coordination bonds with the nitrile group of rubber (-C≡N-Zn).

4. Analysis of the experimental data obtained in the study of mixtures with the participation of compounds containing polyfunctional groups showed that in the presence of a chlorine-containing cross-linking agent - DSCB, a sensitizer - DAFST, a filler (CB) and a plasticizer - fuel oil: bitumen, there is a decrease in the formation of coagulation-flocculation structures and increase in physical and mechanical properties of vulcanizates. It has been established that thermoradiation vulcanizates with C-C and $C-S_x-C$ cross-links have the best set of physical and mechanical properties.

5. It has been established that in the samples obtained under the influence of radiation, the dispersion increases, the number of agglomerates decreases, and the particle sizes range from 40-65 nm. It was found that nanofillers significantly improve the dielectric and thermal properties of the polymer matrix by changing the structural morphology. It has been determined that the increase in the dielectric parameters (ε and tgδ) of irradiated composites at a dose of 500 kGy is due to an increase in the Maxwell-Wagner polarization of space charges at the polymer-filler interface.

6. On the basis of the conducted studies, the optimal formulation (composition) for the preparation of a sealant intended for use as a rubber material for industrial use was determined. It was found that the vulcanizate, including, per 100 wt. h. NBR: 4.0 wt.h. n-ZnO; 4.0 parts by weight – DSCB; 3.0 parts by weight - DAFST, 0.2 wt.h. sulfur, 3.0 wt.h. - bitumen: fuel oil, 50.0 wt.h. – CB (P324), obtained by thermoradiation method (423K x 5', 250 kGy) , has excellent performance properties due to its mechanical and physical properties. Based on this composition, elastomeric materials are obtained that are resistant to aggressive liquids (sea water and oil solution) and wear properties under the influence of temperature.

THE MAIN RESULTS OF THE DISSERTATION WERE PUBLISHED IN THE FOLLOWING PUBLICATIONS:

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