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ELABORATION OF THE ELASTOMER MATERIAL RESISTANT TO AGGRESSIVE ENVIRONMENT BASED ON BUTADIENE-NITRILE RUBBER BY THE RADIATION-CHEMICAL METHOD AND STUDY OF ITS PROPERTIES

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Plaintiff: **Haji Vahid Natig Akhundzada**

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ABSTRACT

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The dissertation work was carried out in the "Radiation chemistry and technology of polymers" laboratory of the Institute of Radiation Problems of the Azerbaijan National Academy of Sciences.

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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and degree of elaboration. Currently, the development of high-quality, oxidizing and aggressive environment-resistant rubber products based on synthetic rubbers is an important problem for many industries. This problem is more relevant for the oil, petrochemical, shipbuilding and machine-building industries, which work in difficult conditions, as a thickening material in various aggregates. In recent years, a lot of research work has focused on obtaining new elastomeric materials (EM) and improving their properties according to specific application areas[1].

Butadiene-nitrile rubber (NBR) is a rubber with great industrial potential. The reason for this is that it is easy to process, and the price is cheaper than other synthetic rubbers, it has high resistance to oils and fuels, and low gas permeability. About 80% of the produced NBR is used for machine building and the automobile industry. However, the unsaturation of the main chain of butadiene leads to poor resistance to thermal wear and limits the field of application. To overcome this, various compositions and vulcanization technologies based on NBR have been tested over the years.

The vulcanization process is an important step in rubber production, increasing the elasticity of rubber and reducing its plasticity. As can be seen from the well-known numerology, along with the correct selection of ingredients, it is possible to significantly change a number of complex valuable properties of rubber by choosing the right technological process and vulcanization mode.

Research has shown that cross-links during traditional sulfur vulcanization consist of polysulfide or disulfide bonds, which, although they ensure high properties such as tensile and fracture toughness of the rubber, reduce the resistance of the rubber to reversion and fatigue. The radiation vulcanization method , which is considered an alternative, has become one of the promising tools in recent years. Compared to

[1] *Sh.M.Mammadov, Fundamentals of technology of synthesis, processing and vulcanization of NBR., Lap Lambert. Academic Publishing,351 p. (2016)*

traditional methods, the advantages of this method are that the density of crosslinks can be controlled, construction can proceed in a solid state, there is no need for additional catalysts, accelerators or other fillers, and it is cheaper and environmentally friendly.

By this method, the predominance of C-C bonds between molecules allows obtaining EM resistance to high temperatures and aggressive environment. It is known that the formation of radiation-chemical yield (RCY) and effective cross-linking depends on the dose strength, absorbed dose, irradiation conditions, and the selection of multifunctional chemical modifiers, building agents, and sensitizers used in the EM processing stage[2].

A number of studies have been conducted on the use of various types of small molecule compounds and sensitizers to increase radiochemical yield and accelerate radiochemical reactions in elastomers.[3] Based on the literature review, it was determined that chlorine-containing compounds are more active in this process, and with the increase in the number of chlorine atoms, the building process in rubber is strengthened. Although few scientific works can be found on the use of various triazine and halogenated compounds in radiation vulcanization. However, almost all of the works are related to sulfur vulcanization.

It should be noted that research in this direction is almost non-existent in our country. Hexachloro p-xylene (HCPX) and 2,4 dichloro-6-diethylaminosymtriazine (DCDEAST), bis-4-trichloromethyl-phenyl-dichloromethane (TCMPhDCM) and 2,4 dimethylphenyl maleimide (DMPhM) by radiochemical method the vulcanization process with its presence has not been studied before. In connection with the above, testing the use of known and new

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[2] *R. J. Woods, A. K. Pikayev. Applied radiation chemistry: radiation processing. J. Wiley, Science, 535 p. (1994)*

[3] *Makuuchi K., Cheng S. Radiation processing of polymer materials and its industrial applications. New Jersey: John Wiley & Sons, Inc, 321 p. (2012)*

effective agents based on butadiene-nitrile rubber (NBR), studying the characteristics of construction processes under the influence of temperature and radiation, and researching the processes of obtaining new EM resistant to aggressive environments are of both theoretical and practical importance. is relevant.

Research goals and objectives. The main goal of the dissertation work is to study the laws of construction kinetics of composite materials obtained by radiation-chemical method (thermoradiolysis) based on SKN-40 rubber, depending on the radiation dose, temperature and the nature of the polyfunctional compounds (PFC) used, by improving the technological and physical-mechanical properties of the compositions. was the purchase of an elastomeric material resistant to an aggressive environment.

In order to achieve the goal stated in the thesis, the following issues were resolved:

1. Determination of ingredients (recipe) based on SKN-40 rubber by thermoradiolysis method with the presence of halogen-containing, triazine and maleimide compounds and obtaining vulcanizates based on it;
2. Studying the essence of the construction process in SKN-40 rubber as a result of the effect of polyfunctional compounds (PFC) by radiation-chemical method;
3. Studying the effectiveness of maleimide and triazine compounds with various polyfunctional groups as building agents and sensitizers in the vulcanization of SKN-40 rubber;
4. Studying the technical and operational indicators of materials purchased on the basis of SKN-40 rubber;
5. Suggesting the recommended composition and method of vulcanization for the purchase of elastomeric materials that are resistant to high temperature, aggressive environment and can work in multiple deformation conditions used in oil, cable, electrical engineering and machine building industries;

Objects and methods of research. Butadiene-nitrile co-polymer SKN-40 with up to 40% acrylonitrile as a research object when preparing the rubber mixture. Obtaining elastomeric material resistant to aggressive environment with the help of various small molecule polyfunctional compounds by radiation-chemical method is the main subject of research.

Various physico-chemical experimental methods, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM), Fourier Infrared (IR) (FT-IR) and Electron Paramagnetic Resonance (EPR) spectroscopy were used in the research work. Composition of samples of hydrocarbon content was also investigated in Gas Chromatograph by Flame Ionization Detector (FID). The structural parameters of the spatial network, vulcanizates parameters, radiation-chemical yield (RCY), the number of built molecules ($1/M_{n\tau}$), the number of effective row connections ($1/M_s$) were determined by the method of sol-gel and rheological analysis. Standard analysis was also performed to determine the physical and mechanical properties of EM (GOST and ASTM). Also, the chemical explanation of the bonds formed in the obtained samples, the structures of the newly obtained compounds (the mechanism of formation of crystalline or amorphous phases) were studied by X-ray Phase Diffraction spectroscopy.

The main provisions defended:

- The possibility of simultaneous use of halogen-containing, maleimide and triazine compounds as vulcanizing agent, accelerator and sensitizer for radiation-chemical vulcanization of SKN-40 rubber was studied.
- polyfunctional compounds on the rheological properties of vulcanizate, the structural parameters of the spatial network, the molecular structure of rubber and the formation of effective cross-links was studied.
- Studies were conducted on determining and justifying the reaction mechanism that ensures the formation of a labile microstructure in the composite under the influence of hexachloro-p-xylene (HCPX), a chlorine-containing aromatic compound.
- The effect of chemical additives included in the formulation of rubber compounds (accelerators, fillers, sensitizers, plasticizers,

etc.) on their technological, physical-mechanical and thermo-aggressive durability properties has been studied, and a new product based on SKN-40 has been developed for the production of rubber products with a long service life under heavy working conditions. an optimized rubber mixture composition was proposed.

Scientific novelty of the research.

- For the first time, various metal oxides as activators, 2,4-dichloro-6-diethylaminosymtriazine (DCDEAST) and bis-4-trichloromethyl-phenyl-dichloromethane (TCMPhDCM) compounds as sensitizers were used for the radiation-chemical vulcanization process of SKN-40 rubber. the effect of hexachloro p-xylene (HCPX) and 2,4 dimethylphenyl maleimide (DMPhM) was studied.
- The use of Agidol-2 (2,2-methylene-bis-4-methyl-6-tert-butylphenol) as a thermal stabilizer and antioxidant in the SKN-40 based mixture was studied .
- For the first time, the joint effect of ZnO and MgO oxides on the radiation-chemical vulcanization process carried out with the participation of HCPX, DMPhM and DCDEAST substances was studied.
- The influence of irradiation conditions in air or vacuum on the structural properties of SKN-40-HCPX binary mixture was studied for the first time.

Theoretical and practical significance of research. A method of vulcanization of elastomeric materials designed for long-term operation under aggressive environment and high temperature, complex dynamic loading conditions is recommended. This method provides radiation-chemical vulcanization with the presence of studied small-molecule compounds (HCPX, DCDEAST, DMPhM), allows obtaining an elastomer resistant to thermal wear in air and aggressive environment and dynamic endurance during multiple stretching. The vulcanizates obtained as a result of the research can be used as curing materials in the oil industry.

Approval and application of the research work: 7 articles required to be published in periodical scientific publications included in the international summarizing and indexing systems of Higher Attestation Comission related to the PhD thesis. was published. In total, the dissertation was reflected in 11 scientific works (7 articles and 4 theses).

The results of the dissertation were discussed at the following international and national scientific conferences: I International scientific conference of young researchers (Baku - 2017) , XXI international youth scientific school "Actual problems of magnetic resonance and their application" (Kazan, 2019), XII International Conference "Nuclear and Radiation Physics" (Almaty, 2019), V Interdisciplinary scientific forum "New materials and promising technologies" (Moscow, 2019),

The name of the institution where the dissertation work was performed. The thesis work was carried out at the Institute of Radiation Problems of the Azerbaijan National Academy of Sciences, at the Laboratory of Radiation Chemistry and Technology of Polymers and Experimental Industrial Plant. The morphological characteristics of the obtained composites were performed at the Nanotechnology Center of Baku State University.

The total volume of the dissertation with a sign indicating the volume of the structural sections of the dissertation separately. Dissertation work covers whole 145 posted on the page. It consists of an introduction, 5 (four) chapters, a conclusion, a bibliography with 152 titles, a list of abbreviations and conventional signs, including 40 pictures and 21 tablea. The volume of the dissertation (excluding spaces in the text, pictures, tables, graphs, appendices and the bibliography) is 190300 marks (introduction - 13405 , chapter I - 60200, chapter II - 30100, chapter III - 32905, chapter IV - 22590, chapter V - 27900 conclusion - 3200 marks).

CONTENTS OF THE WORK

Introduction, the relevance of the topic is justified, the goals and tasks of the work, the object and subject of the research, research methods, scientific innovation, practical importance and other important characteristics of the work are given.

The first chapter is an overview and describes the structure, physical-chemical properties of samples obtained by various vulcanization methods based on synthetic rubbers, and their fields of application. The main focus here focused on the influence of the composition of elastomer mixtures on the construction process and the properties of the obtained material. The changes in the properties of the obtained materials as a result of the influence of various parameters. At the same time, the possibilities of variation of their properties depending on these parameters were investigated, and the parameters optimized from the point of view of potential application were determined.

The second chapter is devoted to methods of obtaining elastomeric materials resistant to an aggressive environment by a radiation-chemical method based on butadiene-nitrile co-polymer. Here, the physico-chemical and technical indicators of the primary materials, building agents, fillers and plasticizers, antiradical substances, accelerators, stabilizers and activators used in the research work, as well as the technological basis of the radiation-chemical vulcanization method used in obtaining samples are explained in detail. The scheme of the process is given in figure 1. The required amount of ingredients determined for the production of SKN-40-based mixtures is mechanically mixed on a roller at the initial stage, and then pressed in a hydraulic press at a temperature of 180º C for 5 minutes. Heated and vulcanized with the help of Co^{60} , a source of ionizing radiation .

Basic physico-chemical and mechanical research methods of studying the composition, structure and properties of the studied samples have been described and their theoretical bases have been explained .

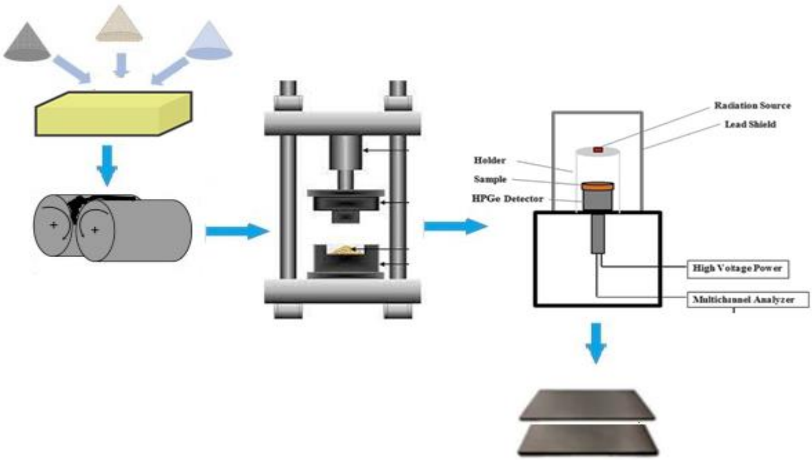

Figure 1. Schematic description of the technological process. 1 - ingredients; 2 - to mix the components; 3 - hydraulic press; 4 – gamma-ray device; 5 – vulcanizates

The third chapter is dedicated to the study of structural, plasto-elastic and rheological properties of vulcanizates used in the production of elastomeric material **.** Here, the change of plasto-elastic properties and spatial network parameters of binary and quasi-systems during mechanical dissolution, depending on the dose of γ-irradiation and the used PFC, was studied. First, the role of hexachloro-p-xylene (HCPX), a small molecular chlorine-organic compound, as a curing agent was investigated in the radiation vulcanization process of SKN-40 elastomer. In order to determine the optimal amount of HCPX to be used, the influence of its thickness on the density of the polymer network and the strength of the vulcanizate (tensile strength limit) was studied (Fig. 1).

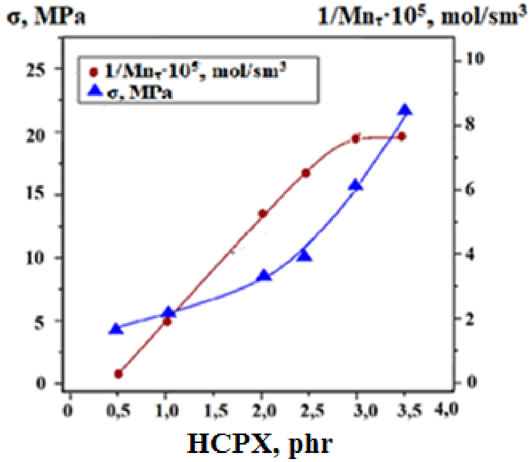

Figure 2. For SKN-40 elastomer, depending on the hardness of the HCPX compound, the number of molecules built and the breaking point during tension (σ, MPa)

It can be seen from Figure 2 that as the density of the binding agent in the system increases, the number of bound molecules increases, but the tensile strength limit is 3.0 kv.h of HCPX. although it increased up to the concentration, it decreased with increasing the concentration. Taking into account the obtained result, this consistency was used in the next researches.

Figure 3 shows the variation of the characteristic viscosity of the binary system SKN-40-HCPX (100 wt/h of rubber - 3 cubic meters of HCPX) depending on the radiation dose (in air). As can be seen from the given graph, the characteristic viscosity for the SKN-40-HCPX system at a dose of 100 kGy is 0.7. An increase in viscosity is observed with the increase of the absorbed dose, which is associated with the process of intramolecular construction in the polymer. As the absorbed dose increased above 400 kGy, the characteristic viscosity decreased. The decrease in the molecular weight of the vulcanizate is due to the increase in the destruction process in the polymer chain.

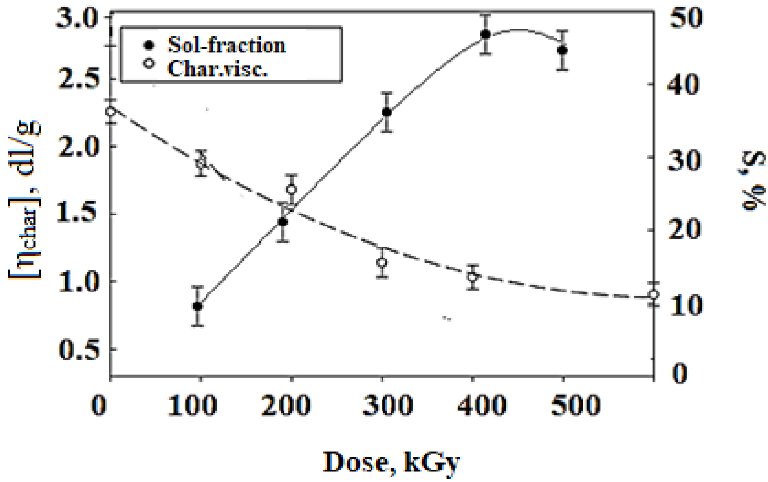

Figure 3. Characteristic viscosity for SKN-40-HCPX binary system and the dependence of the amount of the sol fraction on the radiation dose

It is known that one of the important factors affecting the efficiency of the process during radiation vulcanization is the radiation conditions (air or vacuum). For this purpose, the studied binary system was irradiated at the same doses in both vacuum and air conditions. Figure 4 shows the effect of radiation dose in air and vacuum on the construction speed, as a function of the number of constructed connections. Based on Charlisby's theories, the calculated radiation chemical yield (G_{rkch}) for 100 eV absorbed energy is $21 \cdot 10^{-19}$, contact/cm^3 at a dose of 400 kGy and decreases gradually at doses higher than 500 kGy. This indicator is greater than in previous studies for SKN-40 mixtures. Note that for high molecular weight SKN-40, ~ G_{rcy} = 9 for 100 eV.

In vacuum, this output was determined to be relatively low, and in the sample irradiated with a dose of 400 kGy, it is equal to $14 \cdot 10^{-19}$, connections / cm^3. This is explained by the positive effect of oxidation processes in the air on construction.

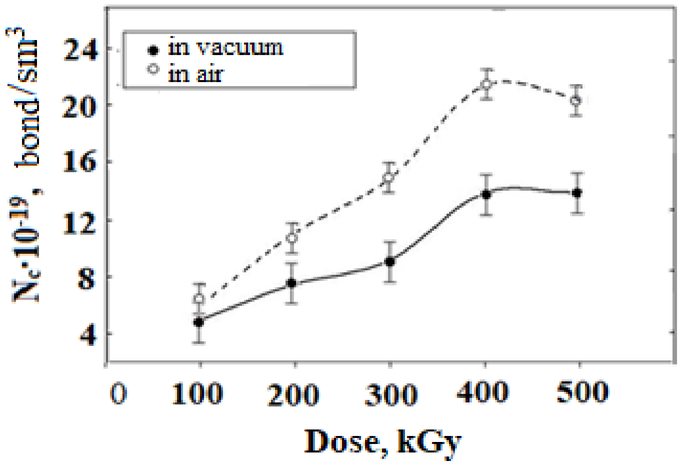

Figure 4. Radiation-Chemical Yield on the radiation dose for the SKN-40-HCPX binary system

In radiation vulcanization processes, polyfunctional compounds are used to reduce the absorbed dose required for cross-linking. This sensitizer allows to increase the density of the polymer network built with the help of special compounds, as well as the optimal properties of the cross-linked polymer using small doses. These compounds can reduce and even eliminate the possibility of destructive processes occurring under the influence of ionizing radiation.

Considering the above, polyfunctional monomers 2,4 dichloro-6-diethylaminosymtriazine (DCDEAST) and bis-4-trichloromethyl-phenyl-dichloromethane (TCMPhDCM) were first tested as sensitizers for the SKN-40 mixture and compared. For the experiment, composites with the given composition shown in Table 1. were prepared on the basis of SKN-40 and irradiated in doses of 100-500 kGy.

Table 1. Composition of the studied systems

Components	Compound recipes in part per hundred of rubber (phr)		
	System 1	System 2	System 3
SKN-40	100	100	100
TXMFDXM	2.5	-	2.5
DXEAST	-	2.5	2.5

Figure 5, according to the change in the number of molecules built for all three systems, the number of built molecules $1/M_{n_c}$ at almost all doses is maximum for the SNK-40-DCDEAST-TCMPhDCM system.

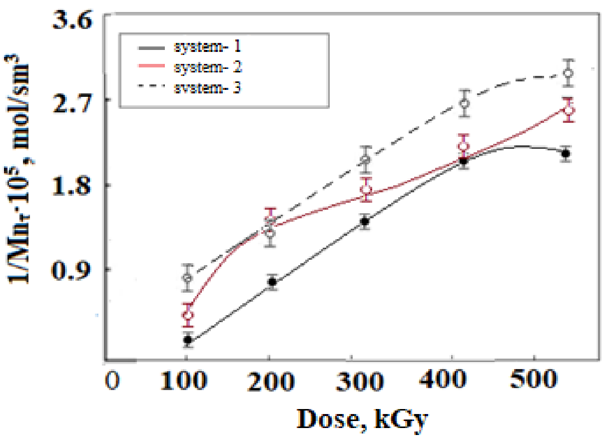

Figure 5. Variation of the number of assembled molecules for all three systems as a function of radiation dose

Based on the obtained results, it was determined that both chlorine-containing organic compounds can be used as sensitizers for SKN-40 elastomer in the radiation vulcanization process.

By increasing the number of radicals (ions) generated in the system during radiation-chemical vulcanization, sensitizers create the basis for the rapid progress of the building reaction and the creation of new C-C connections. However, the vulcanizates built at the expense of this type of communications have a number of advantages as well as disadvantages.

In order to obtain elastomeric materials with the required performance properties, it is important to have other labile connections. In order to investigate the possibility of the sensitizers themselves participating in the reaction and creating new labile connections at the expense of their own fragments, 300 and 500 kGy doses of irradiated mixtures were extracted in toluene. Based on the monomer remaining in the extract, it was possible to determine the amount of monomer incorporated into the elastomer. The results are given in table 2 .

Table 2. Elastomer-related polyfunctionality in SKN-40-based systems after exposure to radiation amount of monomers

Dose, kGy	Elastomer related polyfunctional amount of monomers, %	
	DCDEAST	TCMPhDCM
300	74.2	69.4
500	82.3	78.6

Table 2, it is concluded from the data that the studied polyfunctional monomers bind to n elastomer molecules under the influence of radiation. The main goal of the conducted research is to determine the optimal concentration amount of polyfunctional monomers, the dose range depending on vulcanization parameters. For this purpose, the influence of polyfunctional monomer - 2,4 dimethylphenyl maleimide (DMPhM) on the radiation construction process of SKN-40 brand elastomer with the presence of HXPK was studied. Analyzes showed that the characteristic viscosity $_{[char]}$ of SKN-40 elastomer irradiated at different doses with the presence of HCPX changes depending on the density of the DMPhM compound η.

In the SKN-40-HCPX-DMPhM system, it was determined that the construction practically did not occur at doses less than 100 kGy, and the amount of gel fraction in the vulcanized composite with a dose of 100 kGy was 6%. As the amount of radiation dose increases, the amount of gel fraction increases monotonically and reaches 58% at 400 kGy.

It is known that metal oxides are used as an activating agent in the vulcanization process involving compounds with polyfunctional groups. The nature of the metal oxide used at this time affects both the speed of the vulcanization process and the structural parameters of the vulcanizate. Investigating the role of various types of metal oxides in SKN-40-based elastomer mixtures under the influence of radiation was one of the issues raised in the research. For this purpose, ZnO, CuO, CaO and MgO oxides, which react with HCl molecule at different speeds, were separately added to the SKN-40-HCPX system and the effect on the construction process was compared for each sample.

Table 3. The effect of various metal oxides on the vulcanization process determined in a Muni viscometer (423 K)

Chlorine is an organic compound 3 wt/h	Metal oxide 5 wt/h	Beginning of the construction process τ_5, min.	Building speed factor $\tau_{35} - \tau_5$, min.
1	2	3	4
HCPX	ZnO	3.8	4.2
	MgO	4.0	6.0
	CdO	4.4	6.6
	Al_2O_3	5,6	6,7

The process of construction is directly affected by the chemical composition of the elastomer, as well as the mode of vulcanization. For this purpose, the component systems shown in table 4. were vulcanized by three different methods: temperature, radiation and thermoradiation, and the amount of rows and built connections is presented in table 5.

Table 4. Chemical composition of the studied samples

Components	100 wt/h. according to the rubber		
	Systems		
	1	2	3
SKN-40	100	100	100
DCDEAST	3, 0	-	-
TCMPhDCM	-	3.0	-
DMPhM	-	-	3, 0
ZnO	5, 0	5, 0	5, 0
Rubrax	1, 5	1, 5	1, 5
Agidol	2, 0	2, 0	2, 0

Agidol-2 (2,2-methylene-bis-4-methyl-6-tert-butylphenol) is a well-known stabilizer in the thermal literature and effectively protects EM based on unsaturated diene rubbers from aging due to the effects of oxidants and provides high performance of the rubber during operation in an aggressive liquid environment. provides stability.

At this stage of the research, it was of interest to use the highly reactive compound Agidol-2 as an antioxidant. As can be seen, the effect of vulcanizate on the construction process of the used PFBs is different depending on the construction conditions.

Table 5. Dependence of the amount of row and built connections for different 3 systems based on SKN-40 on construction conditions

Elastomer system	Mode of vulcanization					
	Thermal (143˚Cx40')		Radiation D=400 kGy		Thermoradiation 180˚C x 5'+D=300 kGy	
	Number of row connections, $1/M_{n\tau}$	The number of connections made, cm^3	Number of row connections, $1/M_{n\tau}$	The number of connections made, cm^3	Number of row connections, $1/M_{n\tau}$	The number of connections made, cm^3
System-1	1.4	6.4	0.8	2.9	2.1	7.5
System-2	1.1	5.9	1.0	2.4	1.7	6.3
System-3	0.8	4.7	0.8	2.2	1.1	3.8

Taking into account parameters such as specific surface area (75-85 m^2/g), oil number (90-110 ml/100 g), the brand P324 obtained by the furnace method was selected as a filler. SKN-40-based vulcanizate, whose physical and mechanical properties were studied, was irradiated to a dose of 500 kGr and its content was 2.0 wt/h. DMFM, 3.0 wt/h. DCDEAST, 5.0 wt/h. ZnO and 50 wt/h. contains P324 filler. Physicomechanical properties of the received vulcanizates are presented in table 6.

The application of technical carbon with a dispersed structure causes a change in the space drying parameter of irradiated vulcanizates, and the strength limit increases significantly, as well as the resistance to thermal wear increases. It was found that the strength limit increases monotonically with the increase of the radiation dose (up to 500 kGy). At higher (600 kGy) doses, the elastomer loses elasticity and elongation is found to decrease by 5%.

Table 6. Effect of temperature and radiation dose on the physical and mechanical properties of filled vulcanizates based on SKN-40

Indicators	Thermal vulcanization (150°C), min.		Radiation vulcanization , kGy		
	20	40	200	400	600
Conventional stress during stretching , MPa	11.4	20.0	6.2	13.4	10.3
Conventional tensile strength , MPa	10.7	13.7	8.1	8,9	9.3
Relative elongation , %	680	620	710	710	690
Thermal wear coefficient (150°C, 150 hours):					
For durability	0.62	0.85	0.54	0.59	0.62
According to relative elongation , ε, %	0.44	0.57	0.48	0.55	0.58
According to the dynamic tolerance , N , MPa	0.58	0.65	0.57	0.61	0.63
Mass change during swelling in gasoline-benzene mixture (3:1, 80°C, %)	47	41	53	42	38

Chapter Four, It is dedicated to the study of structural changes in NBR – HCPX – ZnO and NBR – HCPX – DMPhM – ZnO polymer systems. Analysis of the Fourier IR spectrum of the systems showed that a number of spectral changes occur. (Fig. 6.). Changes occur here at 1440 cm^{-1} and 1340 cm^{-1} , which in turn correspond to the CH_2 bonds of the -C≡N group. Based on the changes occurring in those intervals, the presence of -C-CH- bond can be shown, which in turn is somewhat difficult to prove by IR spectroscopy alone. Also, the presence of the C-Cl bond in the interval of 750 cm^{-1} is clearly visible here. It is important to note that although the DCDEAST molecule contains a chlorine atom, the appearance of the signal at 1230 cm^{-1} can be explained by the viscosity of the substance .

A change in the range of 2230-2320 cm^{-1} is visible in all spectra. In the NBR spectrum, this change is seen in the interval of 2230 cm^{-1} , which in turn indicates the existence of a triple bond -C≡N (carbon-nitrogen). In the shifts in the range of 2320 cm^{-1} , we can see spectra describing the complex structure of the -C≡N group and metal oxides. Changes in the IR spectra of NBR-based mixtures after exposure to radiation can be explained by the reactions occurring in CH groups attached to nitrile in the polymer molecule, as well as in double-bonded CH_2 groups.

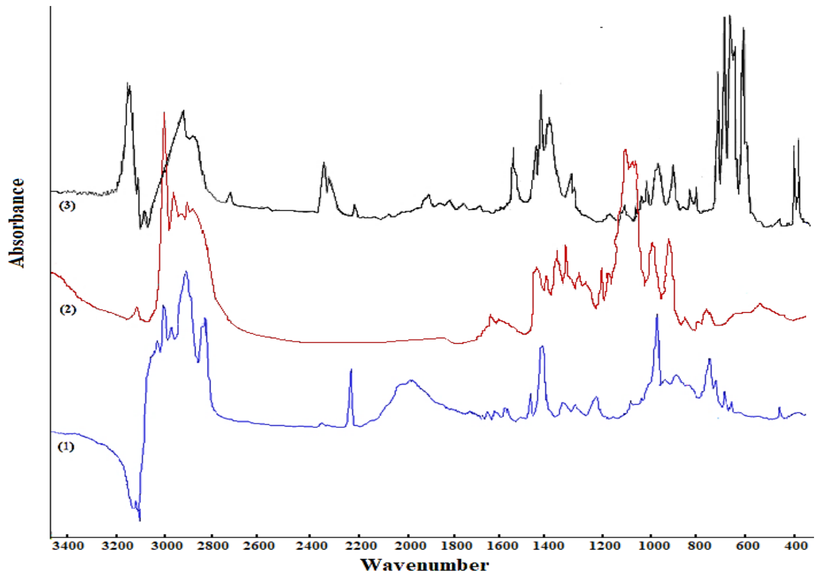

Figure 6. FTIR spectra of the studied composites: NBR (1), BNK + DCDEAST (2), NBR + DMPhM (3)

Since the research object is a polymer, whether or not radicals are formed in these samples, and the mechanism of formation of the formed radicals were considered important aspects in this research work. For this purpose, EPR analyzes of the samples were conducted. Although EPR studies were performed on several samples under irradiation, comparisons were made on only one sample (NBR – DCDEAST). Corresponding results were obtained in other samples and the presence of regularity was proved during EPR studies.

Figure 7 shows the EPR spectrum of the NBR - DCDEAST composite irradiated with a dose of 100 kGy, where two radicals appear as a result of irradiation. Also, g factor g=3.314 and g=3.908 of the peaks in the EPR spectra of the non-irradiated sample and the significant increase of g factors during irradiation suggest that chemical transformations have taken place, in other words, construction has taken place.

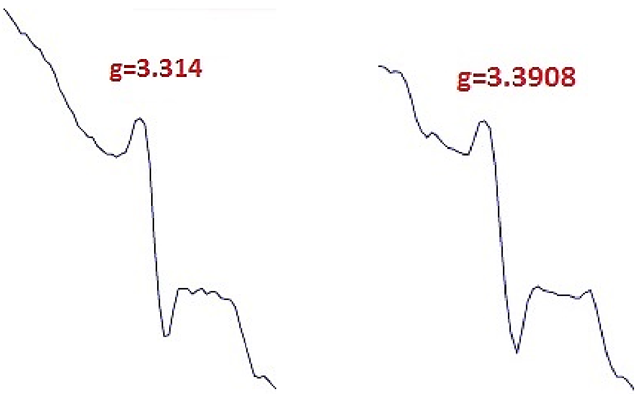

Figure 7. Radicals formed in irradiated samples EPR spectrum

In the dissertation work, the processes taking place on technical carbon and non-carbon surfaces were studied by means of SEM (fig. 8 and 9). Samples were photographed on a SEM JEOL JSM-7610F Schottky Field Emission Scanning Electron Microscope. From each sample, 5 (five) different parts were analyzed by magnifying 30,000 (thirty thousand) times. 100 nm bars are shown in the figures for comparison.

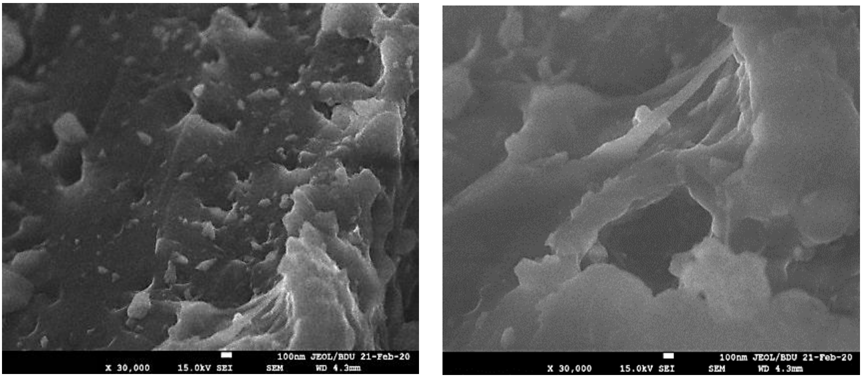

Figure 8. Specimens made without technical carbon

As can be seen from the pictures, as a result of the vulcanization process without the participation of technical carbon, quite rough surfaces were created. It is also obvious that the processes taking place on the surface are chaotic in the samples taken without the presence of technical carbon.

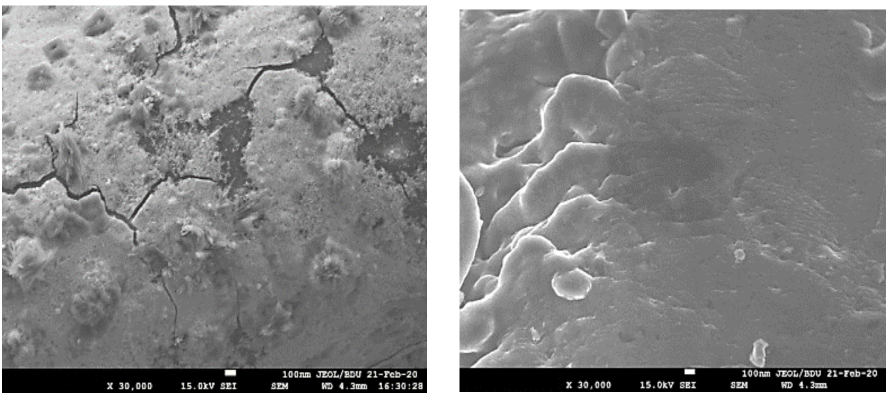

Figure 9. Samples made with technical carbon

However, on the contrary, chaotic deviations on the surfaces are not visible in vulcanization products with the presence of technical carbon .

Also, there are no irregularities on the surfaces in the samples obtained with technical carbon, structuring and regularity are noticeable on the surfaces. This can be explained by the fact that the used filler itself participates in the construction due to the effect of radiation.

The samples were studied by EDXS (Energy-dispersive X-ray spectroscopy) Energy Dispersive Gamma Spectroscopy in the SEM device. In this method, samples with technical carbon and without carbon were examined (Fig. 10).

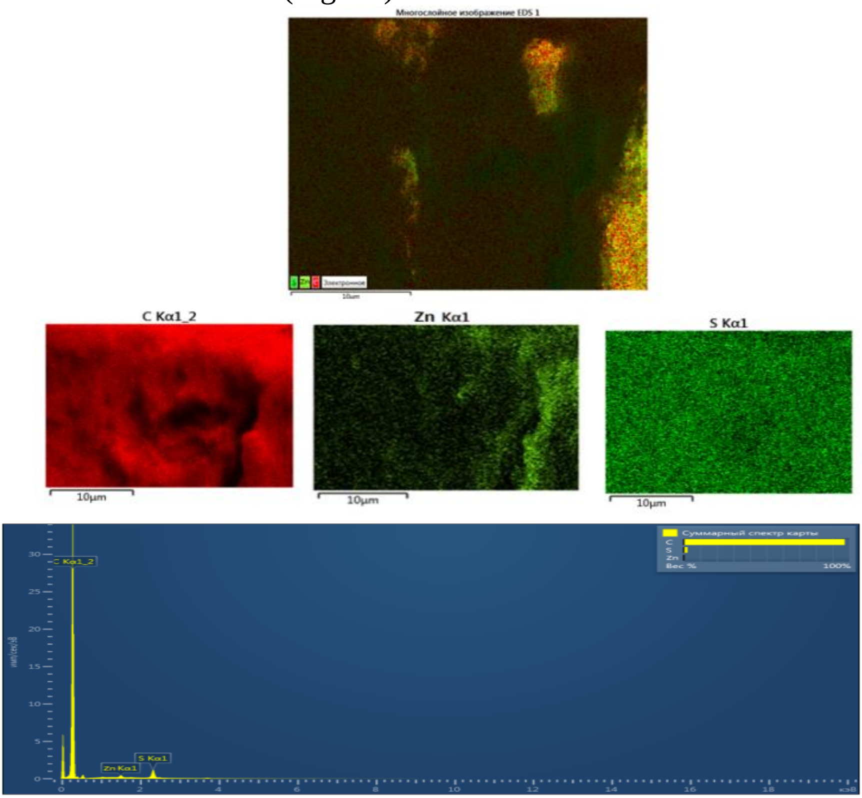

Figure 10. EDXS indicators of technical carbon-free samples

The results of the analysis show that the samples mainly contain C (carbon), Al (aluminum) and elements. The fact that the general background does not turn red is proof that the samples were taken without technical carbon. Also, Zn indicates zinc oxide (ZnO) .

In order to more accurately investigate the distribution of structural changes and metal oxide particles, the Transmission Electron Microscope device was used within the framework of dissertation ii. Samples were drawn in a JEOL JEM-2100F device with a power of 100 kV, by spraying the dissolved substances on the microscope grids through a medical syringe (Fig. 11).

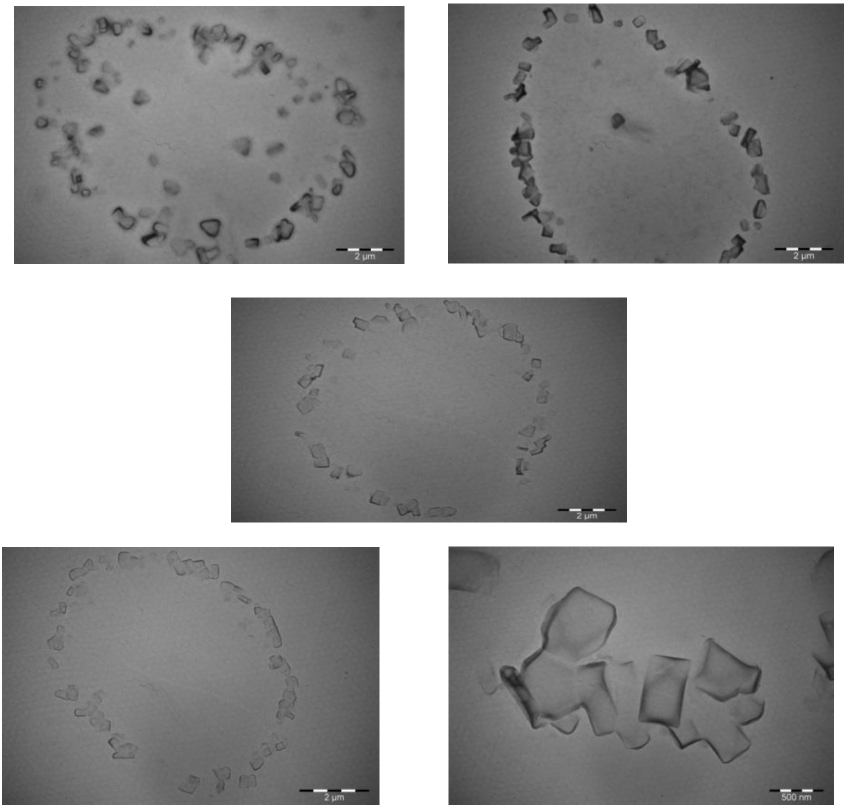

Figure 11. TEM analyzes of the obtained samples

Four samples were taken for analysis, respectively, irradiated, non-irradiated, with technical carbon and without technical carbon. It can be seen from the results of TEM analysis that metal oxides in all samples were distributed with certain regularity and formed oval structures. After the samples were magnified approximately 70,000 (seventy thousand) times, it was found that metal nanoparticles with sizes up to 200 nm agglomerate and join together and become more stable. This shows that the mechanical mixing is well done and the metal oxides are not chaotically but harmoniously distributed inside the samples.

X-ray analysis of samples is one of the important methods for their identification. So, in addition to determining the structure of these samples, it is possible to determine the sizes of the particles formed here. First, the X-ray analysis of SKN-40 elastomer taken as matrix is given in figure 12 .

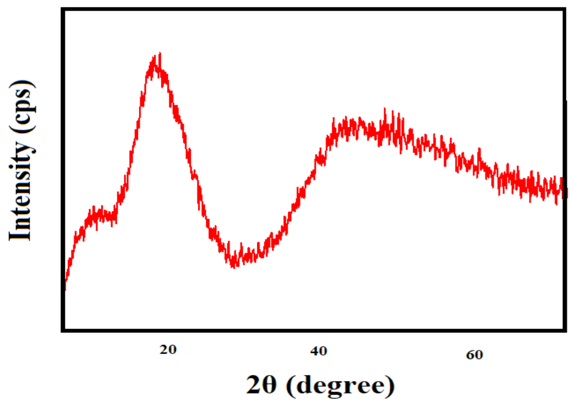

Figure 12. X- ray diffractograms of SKN-40 elastomer

From the diffraction pattern shown in Figure 12 , a broad peak with a characteristic amorphous structure is observed in the NBR $2\theta = 20°$ range. No crystalline structure is present here.

SKN-40 – HCPX – DMPhM – ZnO composite samples before and after irradiation are given in figure 13. In the diffractogram of the non- irradiated SKN-40 – HCPX – DMPhM –

ZnO composite , the peak observed at 2 θ =36.7° refers to the ZnO nanoparticles formed in the hexagonal phase. This peak corresponds to the Miller index of (101) and is identified in the crystallographic database with card number PDF code no: 00-036-1451. The other two peaks are identified by card number No.01-075-0576 when compared to the Joint Committee on Diffraction Standards (JCPDS). Here, it can be observed that ZnO nanoparticles are formed in the hexagonal phase. These peaks also correspond to Miller indices (200) and (203), respectively.

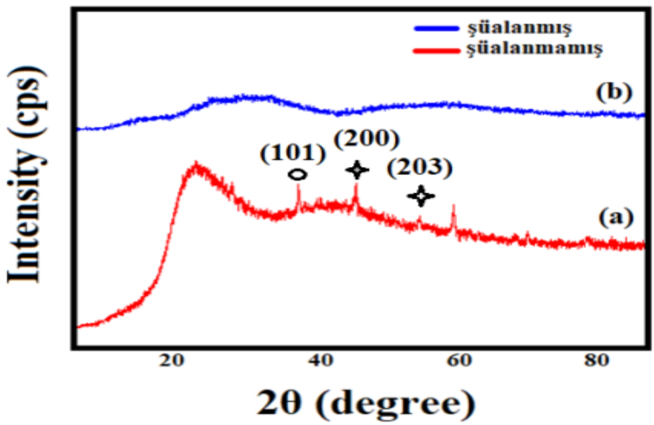

Figure 13. SKN-40 – HCPX – DMPhM – ZnO X-ray diffractometers of the composite. a) non-irradiated, b) irradiated

The X-ray diffractograms of the samples obtained from the irradiation of these samples are given in figure 13 (b). As a result of the effect of radiation, the crystallographic structure formed here was relatively dispersed and an amorphous structure was formed.

HCPX – DMPhM – ZnO – the average size of the nanoparticles formed inside the technical carbon composite was calculated as 78.06 nm.Thus, it can be said that crystalline structures were formed in the matrix during the construction of polymers as a result of thermal treatment . This can be explained by the excitation of the carbon chains included in the composition of the polymer and the formation of new connections between them and the crystallization process. In constructions caused by radiation, the resulting structure is a relatively weak crystalline structure or generally an amorphous structure .

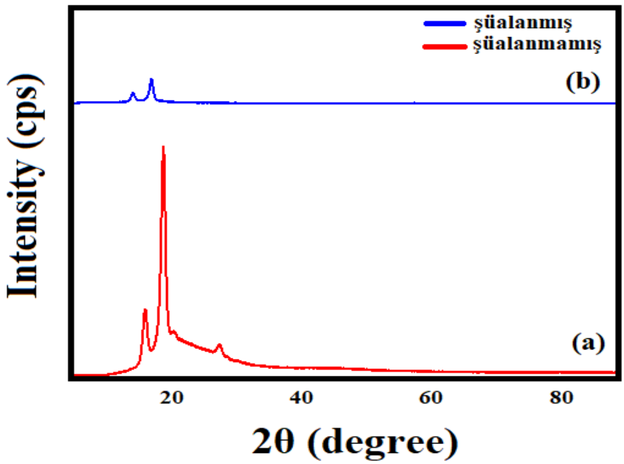

Figure 14. SKN-40 – HCPX – DMPhM – ZnO – technical carbon X-ray diffractometers of the composite. a) non-irradiated, b) irradiated

The fifth chapter the technological aspects of radiation-chemical vulcanization of SKN-40 with the participation of various components , the effect of an aggressive environment on the strength properties of elastomers, the effect of temperature on the mechanical properties of vulcanizates, the effect of chemically aggressive environments on the aging of vulcanizates were investigated.

The composition of the composition is shown in table 3. When choosing low molecular weight compounds for building SKN-40 rubber, the chemical interaction between the two phases was taken into account. It should be noted that SKN-40 elastomer has a high hardness according to Defoe (1700-2500 gs), it mixes very poorly with low-molecular products.

ED-5 epoxy resin was used as a modifier to facilitate the plasticization process and give flexibility in Vardana. ZnO added to the initial composition was used as an activator. TXMFDXM, 2,4-dichloro-diethylaminosym-triazine-stabilizer (DCDEAST) and 2,4-dimethylphenylmaleimide (DMPhM) were used to evaluate the effectiveness of chlorinated aromatic compounds as building agents . The composition of the proposed mixture is given in table 7.

Table 7. Composition and amount of components in thermo-radiation vulcanizates based on SKN-40

Component	Quantity (phr, 100 phr of elastomer)
SKN- 40	100
DAEMK	3.0
HCPX	3.0
DCDEAST	2.0
TCMPhDCM	2.0
Agidol -2	5.0
ZnO	3.0
MgO	2.0
ED-5	3.0
Fuel oil	0.5
Technical carbon (P324)	60
T=180°C×5' D =300 kGr	

It is known that the operational property of EMs depends significantly on the temperature of the environment they are in contact with. In order to study the influence of these factors, the properties of PFB-containing EM were tested before and after contact with the aggressive environment of drilling rigs and other equipment used in petroleum engineering that require the operation of solid aggregates. The results of the analyzes are given in table 8. The properties of all three types of technological processes were investigated using heat and ionizing radiation (table 8.). Rubber data obtained by radiation-chemical method showed that SKN-40-based vulcanizates containing PFC (HCPX, DCDEAST, DMPhM) swell less in an aggressive environment than known compositions obtained with the presence of sulfur; At 80-

100˚C, it has a high wear coefficient in water and oil-containing solutions. The value of residual deformation during compression after contact with liquid medium of these vulcanizates was found to be lower than thermal and radiation-chemical vulcanizates. This is explained by the formation of CC bonds with higher strength compared to polysulfur bonds (bond energy C-C = 66.2 kcal / mol, C-S-C = 52 kcal / mol) giving high thermal and physical-mechanical stability to radiation vulcanizates.

Table 8. Operational indicators of filled vulcanizates based on SKN-40 after aging in aggressive environments

Indicators	Vulcanization type		
	Thermal (143˚Cx40')	Radiation D = 500 kGy	Radiation-chemical 160˚C x 5'+D=300 kGy
Tensile strength (MPa) (80-100 ˚C) in the environment			
Sea water	11	9	13
Oil solution	10	10	14
Pyro condenser	12	11	12
Residual deformation accumulation of compression , ε, (100 ˚C)			
Sea water	70	55	58
Oil solution	63	47	51
Pyro condenser	60	42	45
Thermal wear coefficient , K (100 ˚C)			
Sea water	0.77	0.79	0.75
Oil solution	0.87	0.81	0.89
Pyro condenser	0.69	0.72	0.82
Swelling rate , wt. %			
Sea water	114	85	88
Oil solution	68	71	57
Pyro condenser	71	56	48

The strength of radiation vulcanizates is lower than thermal and radiation vulcanizates, but the resistance to thermal wear and solvents is superior to them.

Analyzing the deformation properties of elastomers requires long-term loading, high temperatures and an active environment. One of these conditions is sufficient to change the deformation properties of elastomers. Moreover, by studying the workability, residual strain accumulation, equilibrium modulus and relaxation stress of elastomeric materials, the rubber material can be characterized with sufficient accuracy. As can be seen from Table 9, a different change in the properties of the elastomer is observed during aging of the TS-1 fuel in the stressed state. Thus, as in air, the accumulation of residual deformation increased continuously with increasing temperature in fuel. The obtained regularities confirm the conclusions about the increase in the contribution of the destruction process during aging in fuel and air.

In the presence of static tension, the increase in destruction processes is one of the signs of mechanical activation of the chemical process.

Table 9. Effect of temperature on the properties of the proposed radiation-chemical vulcanizates based on SKN-40 in air and fuel

T, aging, ^{0}C	Construction rate, γ (24 pp.)		Permanent deformation during compression (E, residue, 20%, 24s)		Balance module , E %		Relaxation stress $\sigma_{t/}$ $\sigma_{0,}$ M Pa (24 s)	
	In the air	in fuel TS -1	in the air	In fuel TS -1	in the air	In fuel TS-1	in the air	In fuel TS-1
100	9.7	3.6	60	40	20	40	0.9	0.8
125	12.8	5.9	70	50	40	60	0.8	0.7
150	16.0	8.3	80	65	60	80	0.7	0.6
200	21.0	12.4	90	75	80	100	0.7	0.5

Table 9. also shows that the change in stress relaxation after aging of elastomers is different. The difference in stress relaxation in elastomers can be explained by high adsorption capacity . The difference in relaxation processes in air and fuel is explained by two elementary relaxation processes in elastomers; 1-regrouping of the supramolecular structure; 2-regrouping of chemical bonds.

KEY SCIENTIFIC RESULTS

1. Based on SKN-40 brand butadiene-nitrile co-polymer and various polyfunctional monomers, the regime for radiation-chemical vulcanization method was determined and elastomeric mixtures were obtained. It was determined that vulcanizates irradiated in an oxygen environment are superior to vulcanized samples in vacuum due to their plasto-elastic properties.
2. It was determined that 100 cubic meters 2-3 cubic meters per polymer mixture. addition of small molecular monomers with reactive polyfunctional groups (DMPhM, TCMPhDCM, DCDEAST, HCPX) allows to improve spatial structure parameters and rheological properties of SKN-40 elastomer vulcanized by γ-rays. Also, it was determined that the use of zinc oxide as an activator and P324 (oven TC) as a filler allows to achieve higher results. 3 kut. h. diallyl ester of maleic acid (DAEMK) was also found to increase the rate of the vulcanization process.
3. It was determined that 2,4-dichloro-6-diethylaminosymtriazine (DCDEAST) and bis-4-trichloromethyl-phenyl-dichloromethane (TCMPhDCM) compounds, whose effect as a sensitizer was studied for the first time , are both effective in the construction reaction. However, in the system obtained with the presence of DCDEAST the number of buildings is more than the other system. So, as a result of the effect of temperature and radiation It is assumed that the degradation products of these compounds create new labile bonds with the elastomer . This is confirmed by comparing the amount of elastomer-related polyfunctional monomers (82.3% for DCDEAST, 78.6% for TCMPhDCM) by extraction method in toluene.
4. It was determined that in mixtures and vucanisates obtained on the basis of SKN-40 brand butadiene-nitrile co-polymer and various polyfunctional monomers, the radiation chemical yield and the number of effective molecules built, the amount of the gel fraction, as the radiation dose increases increases

monotonically . Thus, while the amount of gel fraction in the SKN-40-HCPX-DMPhM composite vulcanized with a dose of 100 kGy is 6%, it increases to 58% when the dose reaches 400 kGy. At doses higher than 500 kGy, on the contrary, a decrease in these parameters is observed.

5. Based on SKN-40 by radiation-chemical vulcanization and selected building agent, sensitizer, accelerator, filler, antioxidant, plasticizer, elastomeric materials (rubber) resistant to aggressive liquid muit and numerous deformations and wear in the temperature range of 100-200º C due to their physical and mechanical properties. was possible to obtain. Based on the general complex properties, the obtained materials can be recommended for the preparation of binder material for various aggregates in the oil and gas extraction, machine building and shipbuilding industries.

Published science on the topic of the dissertation list of works:

1. Sh.M.Mammadov, **H.N.Akundzada**, R.FKhankishiyeva, J.S.Mammadov, G.A.Mammadova, P.I.Ismayilova, A.K.Mammadov, A.I.Azadaliyev, M.N.Mirzayev, Effect of gamma irradiation on the crosslinking process of nitrile-butadiene rubber with triazine and maleic compounds, Journal of Optoelectronic and Biomedical Materials, 2020, 12(3), p. 81-87.
2. R.F.Khankishiyeva, **H.N.Akundzada**, O.H.Akberov, E.O.Akberov, S.M.Mammadov, Z.A.Aslanli, Effect of nano-dimensional powders of metal oxides on the physico mechanical properties of vulcanized nitrile rubber / New Materials, Compounds and Applications, 2018, 2(1) , p. 90-102
3. **H.N.Akundzada**, R.F.Khankishiyeva, S.B.Aliyeva, Mammadov J.S.Mammadov, Ahmedova S.V.Ahmedova, S.M.Mammadov, Character of crosslinking isoprene nitrile elastomer with influence of irradiation and temperature / Journal of Baku Engineering University - Chemistry And Biology, 2017, 1(1), p. 87-95
4. **H.N.Akhundzada**, Influence of technical carbon on the structure and properties of elastomers / News of the Pedagogical University, 2019, 67(4), p.124-131.
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7. **H.N.Akundzada**, The effect of hexochlorocyclopentadiene and chlorine-containing cyclic organic derivatives of dicarboxylic acid on the structure of the butadiene-nitrile rubber SKN-40 under the influence heat and γ-irradiation / Journal of Radiation Researches, V. 6, №1, 2019, p. 65-69
8. Sh.M.Mammadov, **H.N.Akundzada**, R.FKhankishiyeva, J.S.Mammadov, XXI international youth scientific school "Actual problems of magnetic resonance and their application" Kazan, September 23-27, 2019
9. Sh.M.Mammadov, **H.N.Akundzada**, R.FKhankishiyeva, J.S.Mammadov, Development of a radiation-chemical technology for the elaboration of the aggressive-resistant elastomer materials / 12th International Conference "Nuclear and Radiation Physics", Almaty, June 24-27, 2019
10. Sh.M.Mammadov, **H.N.Akundzada**, R.FKhankishiyeva, J.S.Mammadov, Study of the structural and mechanical properties of elastomeric nanocomposites based on butadiene - nitrile rubber / V Interdisciplinary scientific forum «New materials и п ерспективные technology", Moscow, 2019, 30 October-1 November
11. Sh.M.Mammadov, **H.N.Akundzada**, R.FKhankishiyeva, J.S.Mammadov, Thermal and radiation vulcanization of butadiene-nitrile rubber in the presence of maleimide and chlortriazine compounds / Dedicated to the 96th anniversary of the birth of national leader Heydar Aliyev Republican Scientific Conferences, 10 May, 2019

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