

**THE INFLUENCE OF IRRADIATION TEMPERATURE ON CROSSLINKING BEHAVIOR AND MOLECULAR STRUCTURE OF ISOPRENE NITRILE ELASTOMER**

**Sh.M. Mammadov, A.Kh. Mammadov, R.F. Khankishiyeva, J.Sh. Mammadov, A.Kh. Salehov, G.A. Mammadova, A.S. Azizova**

*Institute of Radiation Problems, MSE AR*  
[shiraz.mamedov@gmail.com](mailto:shiraz.mamedov@gmail.com)

**Abstract:** This study investigates the impact of gamma-ray irradiation temperature (298÷423 K) on the crosslinking rate and mechanical properties of unfilled cures in isoprene nitrile elastomer. By the method of sol-gel analysis, the output dependencies of mesh chains ( $1/M_c$ ), crosslinked molecules ( $1/M_n$ ), and crosslinks ( $n_c$ ) are determined at various temperatures. Additionally, the influence of acrylonitrile content on the curing grid's density change is examined using Fourier spectroscopy. Molecular structure alterations and unsaturation of isoprene nitrile elastomer are studied under irradiation at 423 K and a dose of 500 kGy. The findings provide insights into the rheological aspects and molecular changes in isoprene nitrile rubber during the crosslinking process.

**Keywords:** isoprene nitrile rubber, irradiation, crosslinking, temperature, rheology, crosslinking.

## 1. Introduction

It is well-established that exposing elastomers to high-intensity radiation can lead to a significant increase in sample temperature [1-7]. In certain instances, to expedite the curing process, it is recommended to heat the samples concurrently [8-10]. Elastomers primarily fall into the category of crosslinked polymers; however, the tendency to form crosslinks and the number of cross-linked molecules are varied and are dependent on the chemical structure of the polymer chain, polymer morphology, and irradiation conditions. Moreover, the process efficiency of radiation crosslinking is largely dependent on the method of elastomer preparation [11].

While the radiation-chemical yield of cross-linking and the formation of effective transverse chemical bonds in butadiene nitrification elastomers depend on dose power and absorbed dose, the environment also plays a crucial role in enhancing crosslinking and accelerating radiation-chemical reactions in elastomers [12, 13]. For instance, the presence of oxygen during irradiation has been shown to increase the radiation-chemical yield of crosslinked molecules by 1.5 times, in conjunction with the nature of the elastomer influencing the cross-linking process. The irradiation temperature has been found to enhance crosslinking and effective crosslinks. Therefore, optimizing elastomer properties at lower irradiation doses requires careful consideration and the selection of irradiation technology.

However, the impact of thermal radiation impact on isoprene nitrile elastomer has not been thoroughly investigated to date. Existing data on the effect of increasing irradiation temperature on crosslinking rates for butadiene nitrile elastomers up to 423 K, as well as on saturated and unsaturated elastomers up to 373÷573 K, are fragmented and not systematically mapped for various reasons [14].

A comprehensive study of the systematic relationship between radiation-chemical changes (crosslinking, degradation, changes in the yield of crosslinks, mesh chain numbers, viscosity, sol fraction, and the alteration in double bond content) and the physical and mechanical properties of elastomers under heat and radiation exposure lacks. In this article, the experiments result in the effect of temperature on radiation crosslinking of isoprene nitrile using a sol-gel method of analysis based on the laws of the static theory of net structure.

## 2. Material and Methods

The study used isoprene nitrile elastomer (INE-30) obtained through emulsion polymerization. Radiolysis of evacuated glass ampoules containing 1g of samples was performed using  $\text{Co}^{60}$  gamma-rays at temperatures of 293, 373, and 473 K, with an absorbed energy power of 4.9 Gy/s. Samples were covered with aluminum foil during extrusion to prevent oxidation. Structural parameters and the nature of mesh density were determined through sol-gel analysis and calculated by the Flory-Rehner equation [15]. Additional analyses included Fourier spectroscopy using a Varian 640-IR FT-IR spectrometer and mechanical tests [16-18].

The absorbed dose in the samples was calculated by comparing the electron density in observed dosimetric systems. The inherent viscosity of irradiated elastomer was determined in toluene at 293 K, and calculations were performed using the Mark Houwink equation  $[\eta] = KM^\alpha$ , where the constant value  $K$  was  $4.9 \times 10^4$  and  $\alpha$  was 0.64 (for toluene).

According to the data of the sol-gel analysis, it is evaluated the relative change in crosslinking yield  $G_c$  and  $G_g$  degradation with increasing irradiation temperature from 298K to 423K ( $G_c^{100}/G_c^{25}$ ,  $G_c^{150}/G_c^{25}$ ) and up to 473 K ( $G_c^{200}/G_c^{25}$ ).

## 3. Results and Discussion

Under the influence of irradiation and temperature, the INE-30 structure undergoes significant changes that affect the nature and content of double bonds. As a result of the crosslinking of elastomer macromolecules, a spatial grid is formed. Equations adjusted by high elasticity theory gave the possibility of using them primarily for a qualitative assessment of molecular weight and the average number molecular weight of the sol fraction. Figure 1 shows the data on intrinsic viscosity changes of isoprene nitrile elastomer under the simultaneous action of temperature (298÷473 K) and irradiation ( $D=500$  kGy).

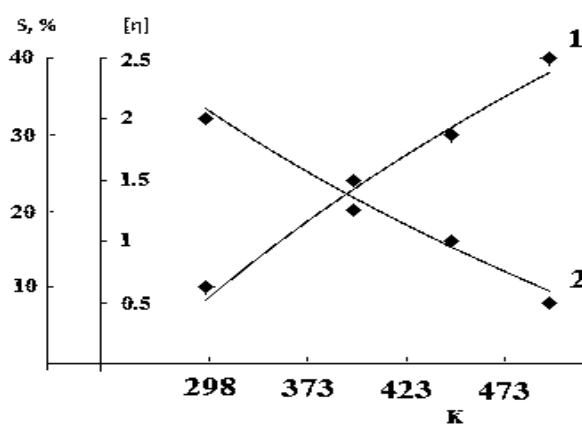


Fig. 1. Dependence of intrinsic viscosity (1) and content of sol-gel fraction (2) with temperature ( $D= 500$  kGy).

Figure 1 illustrates that, for Isoprene Nitrile Elastomer (INE) at 298 K, the intrinsic viscosity is 0.2. As the temperature increases, there is a corresponding increase in the molecular weight of the elastomer. Notably, there is a significant rise in the temperature range of 373÷423 K, accompanied by an improvement in intrinsic viscosity from 0.4 to 2.3. However, with further increases in irradiation temperature (473 K), the intrinsic viscosity decreases (Figure 1, Curve 1). This reduction in INE molecular weight is a consequence of the degradation of the polymer's main chain.

As the temperature increases in the range of 298÷423 K, the elastomer becomes completely insoluble, indicating the crosslinking of polymer chains. The presented data in Figure 1 also demonstrate that the sol fraction decreases at different degrees of grid density (Curve 2). A reduced sol fraction suggests a homogeneous distribution of cross-links in elastomer molecules. This concept of grid homogeneity in elastomers aligns with previous propositions based on certain data. The findings in Figure 1 provide insights into the relationship between temperature, intrinsic viscosity, molecular weight, and sol fraction, shedding light on the crosslinking behavior and structural changes in Isoprene Nitrile Elastomer under varying conditions [19].

As Table 1 shows, the crosslinking outputs ( $G_c$ ) increase with temperature up to 423 K; the value increases by 2-3 times in all samples. Above 423 K, the chain destruction of isoprene nitrile elastomer is observed. At a dose of 500 kGy and 298 K, at temperatures of 373÷423 K, there is a noticeable change in the content of double bonds in all isoprene nitrile isomers. The sharp increase in cross-link yield chains (Table 1) can be explained by the increase in consumption of double bonds.

**Table 1**

The value of crosslinks yields and the act of destruction of irradiated isoprene nitrile elastomers depending on the temperature

Isoprene nitrile with acrylonitrile content, %	Heat temperature, K	$G_{cross}$	$G_{dest}$
10	298	3,5	-
	373	7,8	-
	423	11,3	-
	473	-	1,5
20	298	4,8	-
	373	9,1	-
	423	14,7	-
	473	-	3,2
30	298	5,7	-
	373	11,3	-
	423	16,0	-
	473	-	4,3

Acrylic nitrile links in isoprene chains have a protective effect [20, 21], which manifests itself in a decrease in the yield of cross-links and degradation (Table 1).

The influence of irradiation temperature on crosslinking yield is intricately linked to the

phase state of the elastomer. Specifically, for elastomers in an elastic state, there is an observed increase in the crosslinking rate as the temperature rises. It is noteworthy that greater rigidity in the polymer's structure is associated with a lower yield of cross-links [25]. Additionally, key factors affecting the efficiency of cross-linking experiments include alterations in the spatial grid of the elastic polymer and the surrounding environment.

The effect of irradiation temperature on the parameters of the spatial grid, molecular structure, and unsaturation was investigated by Fourier spectroscopy. This approach allowed for a detailed examination of how variations in temperature affect the intricate aspects of the elastomer's spatial network, molecular composition, and level of unsaturation. The findings from these analyses contribute to a comprehensive understanding of the complex interplay between irradiation temperature, crosslinking efficiency, and the structural characteristics of the elastomer [22].

In dense grids, where the mechanical properties of vulcanizates are compared, the variation in the amount of cis-unsaturation is within the accuracy of the method. For quantitative comparison of unsaturation changes, the samples were irradiated at 298 and 423 K until the density grid was  $1/M_c=12 \cdot 10^{-5} \text{ mol/sm}^3$ , which corresponds to 500 kGy at 298 K. The use of such large doses for comparison is justified since the change rate of unsaturation remains constant in a wide range of doses.

Fourier analysis of the infrared spectrum shows (Figure 2) that temperature exposure causes some significant changes [23-26]. It is also observed that there is a change in the intensity of absorption bands at  $730 \text{ cm}^{-1}$  corresponding to the double bonds in the 1,4 cis-configuration, and  $965 \text{ cm}^{-1}$  corresponding to the configuration of the double bonds. Changing these bands may be due to the cis-trans isomerization of the elastomer and the consumption of the double bonds. Calculations have shown that during irradiation at 298 K, there is a reduction of cis-unsaturation to 4 %, of which 3 % goes to isomerization and only 1 % is spent. Increasing the irradiation temperature up to 423 K leads to a reduction in cis-unsaturation at 9 %, of which 5 % goes to isomerization and 4 % is spent.

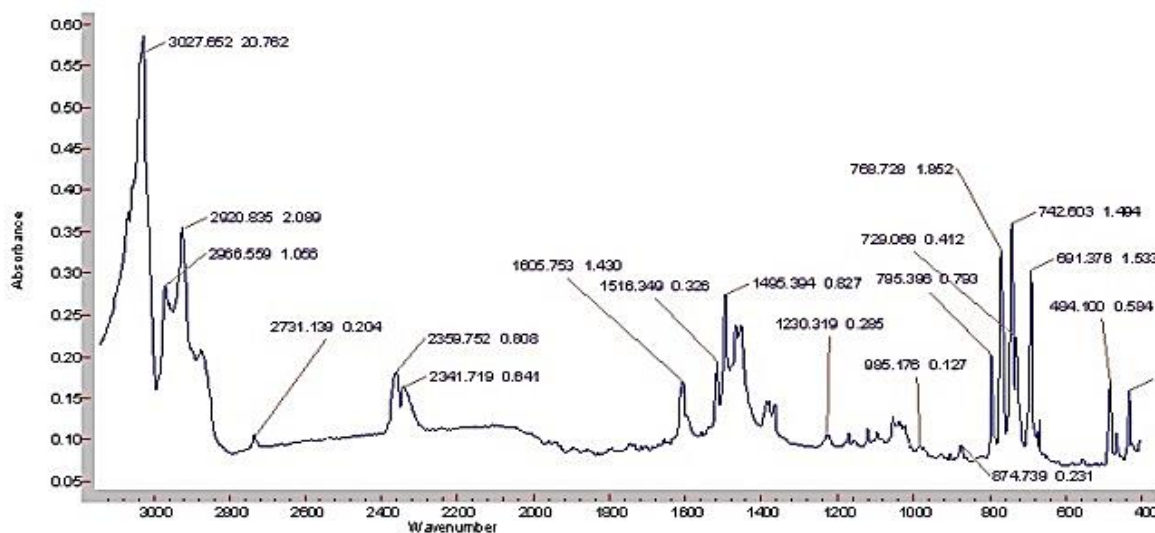


Fig. 2. The IR spectra of irradiated isoprene nitrile elastomers

The change in the content of double bonds was evaluated for elastomers obtained at 500 kGy and when the density of the grid was at temperatures of 298 and 473 K. Upon receipt of the

same mesh density at various temperatures, the doses distinguish between themselves (Table 2).

**Table 2**

Consumption of double bonds in irradiated isoprene nitrile elastomers

Isoprene nitrile with acrylonitrile content, %	Heat temperature, K	Number of chain net, $1/M_c \cdot 10^5$ , mol/cm <sup>3</sup>	Double bonds		
			1,4-trans	1,4-cis	1,2
10	298	3,8	0,54	0,34	0,6
	373	4,6	0,61	0,41	0,9
	423	5,9	0,72	0,54	0,21
	473	17	-	-	-
20	298	4,3	0,63	0,27	0,25
	373	5,0	1,1	0,43	0,57
	423	7,4	1,8	0,66	0,68
	473	-	-	-	-
30	298	5,4	1,4	0,56	0,42
	373	9,7	1,8	0,98	0,74
	423	12,1	2,1	1,1	0,81
	473	-	-	-	-

During the conducted work, some data were obtained regarding the influence of the irradiation temperature on unfilled vulcanizates. It is shown that at lower dense grids of strength at the optimum, the curing is markedly reduced (fig. 3).

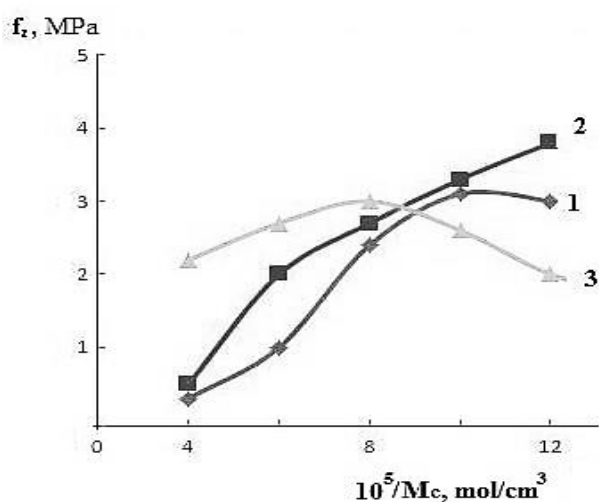


Fig. 3. The dependence of strength-density on vulcanization grid (number of chains in the grid) in isoprene nitrile elastomer by irradiation at 298 (1), 373 (2), 423 (3) K

Thus, increasing irradiation temperature, up to 423 K, decreases the mechanical properties of cures, which contributes to a significant drop in unsaturation, and at the same time, the crosslink output increases rapidly (Figure 4).

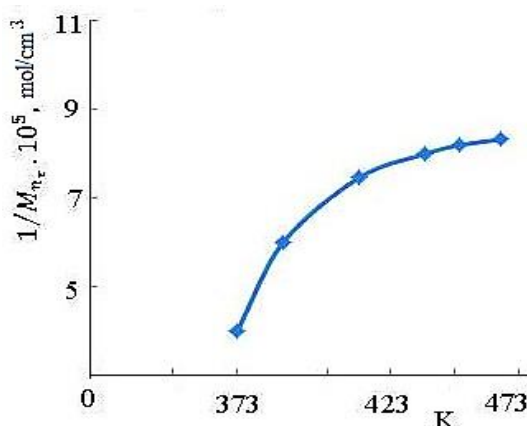


Fig. 4. Dependence on concentration output of links of irradiated IN of temperature

Sol-gel analysis reveals that an increase in temperature leads to the further degradation of isoprene nitrile elastomer. Surprisingly, this degradation is not identified as the cause of the observed changes in the properties of cures. The rise in unsaturation consumption with increasing temperature appears unrelated to oxidation, as evidenced by the absence of changes in IR spectra when comparing irradiated raw elastomers at 473 K. The increased unsaturation consumption could be linked to the formation of intramolecular cycles. However, this assumption is contradicted by the fact that the fall in unsaturation is accompanied by a significant increase in cross-linked molecules to form the cross-links [27].

Figure 5 illustrates that the formation of crosslinks in isoprene nitrile elastomer occurs rapidly, dependent on the irradiation temperature. The effective yield of cross-links at 423 K is 13.0 per 100 eV; further degradation occurs at 443 K. Evidently, the consumption of double bonds (unsaturated) is associated with the formation of intermolecular cross-links.

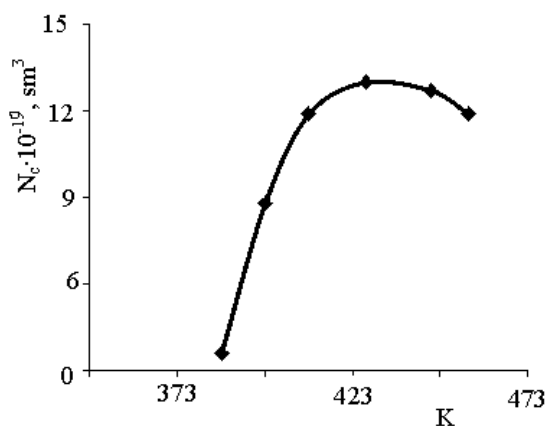


Fig. 5. Dependence of output crosslinks of INE irradiated by 298, 373, 423 K

Examining a scenario where all cross-links are formed as a result of double bond disclosure, a simple calculation indicates that the consumption of double bonds in elastomer at a dose of 500 kGy and 423 K would be in the range of 1.5-2.0%. Analysis of the structural parameters of the cured grid reveals that the number of cross-linked molecules is not very high and stands at 7.4 mol/sm<sup>3</sup> at 423 K. Interestingly, in all experiments, while determining the structural parameters of the grid, the reduction and decay of intermolecular bonds took place at the same temperature (473 K). This provides valuable insights into the intricate relationship between temperature, unsaturation consumption, and the formation of cross-links in isoprene nitrile elastomer.

Thus, data comparison on changes in the nature of the cross-link output, cross-links of chain mesh, consumption of double bonds, and Fourier spectroscopy analysis show that the increase in irradiation temperature by gamma rays in isoprene nitrile elastomer in the range of 298÷423 K is accompanied by a significant increase in the rate of cross-linking and, at the same time, the deterioration of the strength of unfilled cures. It is shown that during the unsaturation decrease in elastomer and sensitivity increase to irradiation, the growth parameter of the grid circuit in the temperature range of 298÷423 K takes place. However, the mechanisms of thermic and radiation processes responsible for the observed changes in properties need to be observed in the future.

#### **4. Conclusion**

As a result of the conducted research on the impact of irradiation temperature on the characteristics of isoprene nitrile elastomer, the following conclusions can be drawn: Crucial factors influencing cross-linking efficiency include temperature, radiation, the spatial grid, and the supramolecular structure of the elastomer. The yield of crosslinks is particularly dependent on the packing of molecules and the presence of double bonds. Otherwise, the study on initiation and the extra temperature effect promotes additional crosslinking that causes the C-C formation of chemical bonds in macromolecules of isoprene nitrile elastomer.

With an increase in temperature at a constant dose, there is an observed rise in the yield of chain grid numbers and cross-links, indicating an intramolecular reaction. This process likely occurs in an elastic medium because isoprene nitrile elastomer is an unsaturated polymer, and the carbon atoms involved in forming double bonds have the lowest ionization potential. During each act of crosslinking, the active site is regenerated, potentially playing a role in the formation of the spatial grid. The obtained results make it possible to conduct directed research in the field of thermic and radiation crosslinking of elastomers in the presence of quasi- and multi-component systems for obtaining elastomeric materials with valuable properties. Exploring thermic and radiation curing instead of thermal curing provides an alternative approach that eliminates the need for peroxides as crosslinking agents in the curing process. This highlights the potential for developing more environmentally friendly and efficient methods for producing crosslinked elastomeric materials.

#### **References**

1. J. Lia, A. Oshima, T. Miura, M. Washio. (2006). Preparation of crosslinked polythersulfone films by high-temperature electron-beam irradiation. *Polymer Degradation and Stability*, 91, 2867-2873. <https://doi.org/10.1016/j.polymdegradstab.2006.09.005>

2. K. Murakami, H. Kudo. (2007). Gamma-rays irradiation effects on polysulfone at high temperature. *Nucl. Inst. and Methods in Physics Research*, B265, 125-129.
3. K. Makuushi. (2003). An introduction to Radiation Vulcanization of Natural Rubber Latex. T. R. I. Global, Bangkok.
4. T. Yasin, S. Ahmed, F. Yoshii, K. Makuuchi. (2002). Radiation vulcanization of acrylonitrile-butadiene rubber with polyfunctional monomers. *Reactive & Functional Polymers*, 53, 173-181.
5. J. Wan, F. Yoshi, K. Makuushi. (2000). Radiation vulcanization of ethylene-propylene rubber with polyfunctional monomer. *Radiation Physics and Chemistry*, 60, 139-142.
6. T. Ware, W. Voit, K. Gall. (2010). Effect of sensitizer length on radiation crosslinked shape-memory polymers. *Radiation Physics and Chemistry*, 79, 446-453.
7. F. Shen, H. A. McKellop, R. Salovey. (1996). Irradiation of chemically crosslinked ultrahigh molecular weight polyethylene. *Journal of Polymer Science, Part B: Polymer Physics*, 24, 1063-1077.
8. F. Su, H. Huang. (2010). Rheology and melt strength of long chain branching polypropylene by reactive extraction with various peroxides. *Polymer Engineering&Science*, 50, 342-351.
9. R. J. Woods, A. K. Pikayev. (1994). Applied radiation chemistry: radiation processing. J. Wiley, Science, 535.
10. Z. Holik, M. Danek, M. Manas, J. Cerny, M. Malachova. (2011). The Influence of Ionizing Radiation on Chemical Resistance of Polymers. *Int. J. Of Mechanics*, 3(5), 210-217.
11. F. Yoshii, K. Makuuchi, S. Kikukiwa, T. Tanaka, J. Saitoh, K. Koyama. (1996). High-melt-strength polypropylene with electron beam irradiation in the presence of polyfunctional monomers. *Journal of applied Polymer Science*, 60, 617-623.
12. A. Lugao, B. Artel, A. Yoshiga, L. Lima, D. Parra, J. Bueno, H. Otaguro. (2007). Production of high melt strength polypropylene by gamma irradiation. *Radiation Physics and Chemistry*, 76, 1691-1695.
13. I. Reinholds, V. Kalkis, R. D. Maksimovs. (2012). The Effect of Ionizing Radiation and Magnetic Field on Deformation Properties of High Density Polyethylene/Acrylonitrile-Butadiene Composites. *J. Chem. Chem. Eng.*, 6(3), 242-249.
14. A. Chmielewski, M. Haji-Saeid. (2004). Radiation Processing technologies. Past, present and future. *Radiation Physics and Chemistry*, 71, 17-21.
15. P. J. Flory, J. Rehner. (1948). Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling. *Chem. Phys.*, 11, 512.
16. D. I. Bower, W. F. Maddams. (1992). The vibrational spectroscopy of Polymers. Cambridge University Press, 337.
17. I. Mustafayev, S. Melikova, E. Hajiyeva, R. Gasimov, M. Bayramov, N. Babayeva. (2023). Spectral Investigations of  $\gamma$ -Irradiated Polyethylene/CdS+ZnS Composite Films. *Acta Phys. Pol. A*, 144(1), 35. [doi: 10.12693/APhysPolA.144.35](https://doi.org/10.12693/APhysPolA.144.35).
18. D. Auhl, J. Stange, H. Munstedt. (2004). Long-chain branched polypropylenes by electron beam irradiation and their rheological properties. *Macromolecules*, 37, 9465-9472.
19. S. Ahmed, A. A. Basfar, M. M. Abdel-Aziz. (2002). Comparison of thermal stability of sulfur, peroxide and radiation cured NBR and CBR vulcanizates. *Polymer Degradation and Stability*, 67, 319-323.
20. S. Mammadov, G. Azizova, R. Khankishiyeva, F. Amirov, G. Mammadova, I. Movlayev, J. Mammadov. (2023). Investigation of the rheological structural parameters of a network of NBR-based vulcanizates with the participation of chlorine-containing. *Journal of New Technology and Materials*, 13(1), 70-74. <https://www.asjp.cerist.dz/en/article/227655>



21. Sh. Mammadov, G. Azizova, G. Mammadova, R. Khankishiyeva, I. Movlayev, J. Mammadov. (2023). The Effect of Composition and Structure of NBR-Based Elastomer Blends in the Vulcanization Process and Study of Their Aging by Exposure to Heat and Radiation. *Journal Chemistry & Chemical Technology*, 17 (4), 829–835. <https://doi.org/10.23939/chcht17.04.829>
22. R. M. Morsy, M. N. Ismaiel, A. A. Yehia. (2013). Conductivity Studies on Acrylonitrile Butadiene Rubber Loaded with different types of Carbon Blacks. *Int. J. of Materials, Methods and Technologies*, 1(4), 22-35.
23. S. Jia, P. Jiang, Z. Zhang, Z. Wang. (2006). Effect of carbon-black treatment by radiation emulsion polymerization on temperature dependence of resistivity of carbon-black filled polymer blends. *Radiation Physics and Chemistry*, 75, 524-531.
24. T. Agayev, N. Gadzhieva, S. Melikova. (2018). Fourier Transform IR spectroscopic study of nano-ZrO<sub>2</sub>+nano-SiO<sub>2</sub>+H<sub>2</sub>O systems upon the action of gamma radiation. *Journal of Applied Spectroscopy*, 85(2), 365-368. <https://doi.org/10.1007/s10812-018-0658-9>
25. S. Baccaro, F. Cataldo, A. Cecilia, F. Padella, A. Santini. (2003). Interaction between reinforce carbon black and polymer matrix for industrial applications. *Nuclear Instrument and Methods in Physics Research, Section B*, 208, 191-194.
26. Y. Liu, G. Wu, D. Long, M. Qi, Z. Zhu. (2005). 60Co  $\gamma$ -irradiation initiated polymerization in ionic liquids – the effect of carbon chain length of monomer. *Nuclear Instrument and Methods in Physics Research, Section B*, 236, 443-448.
27. M. M. Hassan, R. O. Aly, A. El-Ghandour, H. A. Abdelnaby. (2013). Effect of gamma irradiation on some properties of reclaimed rubber/nitrile–butadiene rubber blend and its swelling in motor and brake oils. *J. of Elastomers and Plastics*, 45, 77-94.

## **ВЛИЯНИЕ ОБЛУЧЕНИЯ И ТЕМПЕРАТУРЫ НА ХАРАКТЕР СШИВАНИЯ ИЗОПРЕНА НИТРИЛЬНОГО ЭЛАСТОМЕРА**

**Ш.М. Мамедов, А.Х. Мамедов, Р.Ф. Ханкишиева, Дж.Ш. Мамедов,  
А.Х. Салехов, Г.А. Мамедова, А.С. Азизова**

**Резюме:** Показано, что повышение температуры облучения  $\gamma$ -лучами эмульсионного изопреннитрильного каучука (ИНК) в диапазоне 298÷423К сопровождается значительным увеличением скорости сшивания и в тоже время ухудшением прочности ненаполненных вулканизатов. Методом золь-гель анализом определены зависимости выхода число цепей сетки ( $1/M_c$ ), сшитых молекул ( $1/M_{nc}$ ) и поперечных связей ( $nc'$ ) для ИНК при температуре 298÷423К. Установлены влияния содержания акрилонитрильные (АН) групп каучука в процессе температурном облучении на изменения густоты вулканизационной сетки ( $1/M_c$ ). Изучено молекулярной структуры ИНК и ненасыщенность при температурном облучении (423К, 500кГр) с использованием Фурье спектроскопии.

**Ключевые слова:** изопрен нитрильный каучук, облучение, сшивание, температура, реология, вулканизация.

## İZOPREN NİTRİL KAUCUKUNUN TİKİLMƏSİNƏ RADİASİYANIN VƏ TEMPERATURUN TƏSİRİ

**Ş.M. Məmmədov, A.X. Məmmədov, R.F. Xankişiyyə, C.Ş. Məmmədov,  
A.X. Salehov, G.A. Məmmədova, A.S. Əzizova**

**Xülasə:** Müəyyən edilmişdir ki, emulsion izopren nitril kauçukunun (İNK) qamma şüalarının təsiri ilə vulkanlaşdırılması zamanı temperaturun artması ilə, (298÷423K temperatur diapazonunda) tikilmə sürətinin kəskin artması, həmçinin doymamış vulkanizatların davamlılığının azalması müşahidə olunur. İNK-nun 298÷423K temperatur intervalında zol-gel analiz metodu ilə tikilmə ədədinin zəncir torunun sıxlığı ( $1/M_c$ ), tikilmiş molekulların miqdarı ( $1/M_{n_r}$ ), cərgəli əlaqələrin çıxımının ( $n_c \cdot 10^5$ ) təyin edilmişdir. Kauçukda akril-nitril qrupunun termo-radiasion tikilməsi zamanı zəncir torunun sıxlığına ( $1/M_c$ ) təsiri tədqiq edilmişdir. İNK molekulyar quruluşu və termo-radiasion vulkanlaşma (423K, 500kQr) zamanı doymamışlığı Fure spektroskopiyaya vasitəsilə ilə öyrənilmişdir.

**Açar sözləri:** izopren nitril kauçuku, şüalanma, tikilmə, reologiya, vulkanlaşma.