

Crosslinking of Unsaturated Elastomers in Presence of Aromatic Chlorine-Containing Compounds

Shiraz M. Mammadov, Elvin M. Aliyev, Adil A. Garibov

Abstract—The role of the disulfochloride benzene in unsaturated rubbers (SKIN, SKN-26) which is in the systems of SKIN+disulfochloride benzene and SKN-26+disulfochloride benzene was studied by the radiation exposure. By the usage of physical, chemical and spectral methods the changes in the molecular structure of the rubber were shown after irradiation by γ -rays at 300 kGy. The outputs and the emergence of the crosslinking in the elastomers for each system depending on absorbed dose were defined. It is suggested that the mechanism of radiation occurs by the heterogeneous transformation of elastomers in the presence of disulfochloride benzene.

Keywords—Acrylonitrile-butadiene rubber; cross-linking; poly-functional monomers; radiation; sensitizer; vulcanization

I. INTRODUCTION

THE cross-linking of the unsaturated elastomers is one of the advanced methods. It has a predetermined set of properties. For the usage of this method firstly it demands to know the basic patterns of change in physical and chemical properties of chemical linking the different polymer macromolecules during cross-linking. The emergence of cross-linking in the copolymers by the new properties can be associated not only with the act of linking, but also can be caused by the structural changes which occur as a result of this reaction [1]-[6].

For the characterization of the structure of polymers, the density value of the spatial grid is an important concept. It is known that to achieve the optimal properties of elastomers, it requires the fairly large doses, which increases the cost of the material. The introduction of some low molecular weight compounds can decrease absorbed dose without compromising the basic properties of the rubber [5], [7]-[10].

The greatest practical application has the solid fine powder low molecular weight organic sensitizers [11]-[19].

In this regard, very topical issues are the sensitization and radiation cross-linking for the unsaturated elastomers. However, further parameters of cross-links of the unsaturated elastomers which obtained by the radiation-chemical method in the presence of disulfochloride aromatic compounds remained almost unexplored.

II. MATERIALS AND METHODS

A. Materials

The object of the investigation was unsaturated

acrylonitrile-butadiene rubber (SKN-40) which obtained by the emulsion polymerization [4]. The disulfochloride benzene (DSCB) [20]-[22], which is obtained by the interaction of the chlorosulfonic acid [23] through benzene, was used as a sensitizing crosslinking agent.

B. Methods

Dissolution of DSCB in the elastomer was performed by mechanical plastification on the rolls. After through mixing for 3-5 min polymer binary heterogeneous mixture which contains 100 mass part of rubber and 8 mass part of DSCB was prepared.

The radiolysis of the binary mixtures was carried out by the γ -rays of Co^{60} by the usage 6.9 Gy/s irradiation dose. The calculation of the absorbed dose of investigated object was fulfilled by the method [2]. The samples by the weight 1 g were placed in the glass vials ("Ray") and were evacuated to a residual pressure of $1,33 \cdot 10^2$ Pa. The characteristic viscosity of the irradiated binary mixtures (1, 2) were determined in toluene at 293K by a known procedure for the type of viscometer Ubbedolleh at constant $K=4.9 \cdot 10^4$ and $X=0.64$ (for toluene) [24]. For the quantitative characteristics of the spatial grid of the irradiated samples were used these parameters: $1/M_c$, $1/M_{nt}$ the number of chain grid and the number of cross-linked molecules in the rubber (mol/sm^3) respectively. They can be determinate by the sol-gel analysis [24], which is based on sequential extraction of samples, firstly acetone and then toluene. The magnitude of radiation-chemical yield (RCE), $1/M_c$ and $1/M_{nt}$ were calculated by the equation Flory-Rehner [25]. Changes in the molecular structure of the irradiated cross-linked rubber were determined by IR spectroscopy. The irradiated rubber system (1,2) was dissolved in toluene within 48h. The rubber films were prepared by coating solution to substrate and a constant evaporation of the solvent. As a substrate the KBr spacer were used. For the measurements of the spectrums at $700\text{-}2200\text{ cm}^{-1}$ and at $2000\text{-}4000\text{ cm}^{-1}$ the LiF spacer and NaCl spacer were used, respectively, and for the avoiding oxidation process the films were dried to their constant weight in vacuum desiccator. The substrate was mounted in a holder with film and was placed to the sample compartment of the spectrophotometer. The spectra of cross-linked samples were recorded before and after irradiation.

Determination of free radicals in the irradiated samples was carried out by study of mixtures of the spectrometer RE-1306 at low temperature 77K in vacuum. The samples were prepared urgently submerged vials in liquid nitrogen, where they will in further experiments and measurements. As

Prof. Dr. Sh. M. Mammadov, PhD student E. M. Aliyev and Prof. Dr. A. A. Garibov are with the Institute of Radiation Problems of ANAS, Baku, AZ 1107 (phone: (+994 12) 539 33 91; e-mail: nukl@box.az).

reference changing of EPR spectra for the determination g-factors and line widths the Mn^{+2} of MnO ions were used. Identification of IR and EPR spectra were carried out in accordance with the correlation tables. [26]-[29].

III. RESULTS AND DISCUSSION

As shown the results of the research at 100 kGy dose occurs interaction of DSCB with molecules of isoprene nitrile and acrylonitrile-butadiene rubbers, leading to the formation of three-dimensional grid as evidenced by growth of the number of cross-links (N_c) and the number of crosslinked molecules $1/M_{s,T}$ (Fig. 1) with increasing doses of irradiation. The elastomers do not staple or sew in a little extent without cross linking agents under the same conditions.

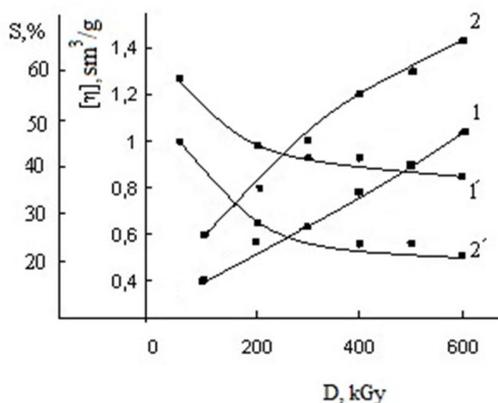


Fig. 1: The dependence of characteristic viscosity of rubber (1-SKIN+DSCB; 2-SKN-26+DSCB) and the content of the sol fraction (1'-SKIN+DSCB; 2'-SKN-26+DSCB) versus to the irradiation dose in the samples.

Fig. 1 shows data on changes in characteristic viscosity in the systems of SKIN+DSCB, SKN-40+DSCB depending on irradiation dose. From Fig. 1 it follows that in both systems viscosity increases monotonically at low doses (100kGy). With the increasing of the absorbed dose the molecular weight of rubber is going up. The characteristic viscosity increases from 0.3 to 0.9 for system SKIN+DSCB and for a system SKN-26+DSCB from 0.5 to 1.2. With the increasing of the absorbed dose higher than 500kGy the intrinsic viscosity falls down (Fig. 1).

The decreasing of molecular weight of the rubbers is the cause for the destruction of macromolecules of polymers. The increased viscosity in the range of values for sensitizing dose between 400-500kGy may be relate to the formation of spatial structures which cause intramolecular cross-linking reactions.

The number of soluble sol fraction was irradiated at 200kGy dose, achieved for both rubbers in range between 50-30% and polymer was irradiated between 400-500kGy which becomes completely insoluble and indicates the structuring of molecules in the polymer chains. Consequently, the increase of the molecular weight of rubber was observed during irradiation which was carried out by vinyl links which is

located at the position 1 and 2 [12], [30]-[34]. Certainly, that the formation of the effective cross-linking occurs at 20kGy dose with low rates. Furthermore, these rates increase with the irradiation dose in the systems of SKIN+DSCB (1) and SKN+DSCB (2). The obtained number of effective cross-linking at 300 kGy, in first system is equal to $4,1 \cdot 10^5$ mol/sm³, and in second system $9,2 \cdot 10^5$ mol/sm³ (Fig. 2).

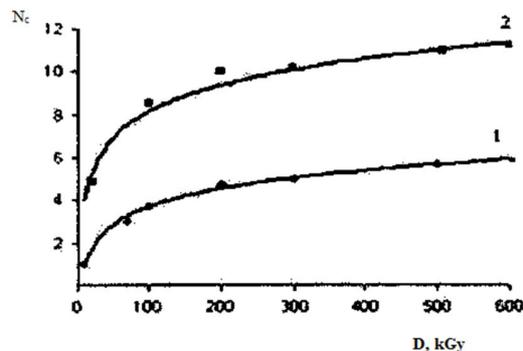


Fig. 2: The dependence of cross-links (N_c) versus to the irradiation dose for isoprene nitrile (1) and acrylonitrile butadiene (2) rubbers with DSCB (3 mass part per 100 mass part of rubber).

Fig. 2 shows that during the irradiation of (SKIN+DSCB; SKN+DSCB) systems the crosslinking increases slightly.

In the irradiated SKN-26+DSCB system the rate of cross-linking is higher than in the SKIN+DSCB. It is explained that the SKN-26 contains 1.4 trans-isomers more than others. About nature of the interaction of the rubbers with DSCB is judged by the changing on the IR-spectra (Fig. 3).

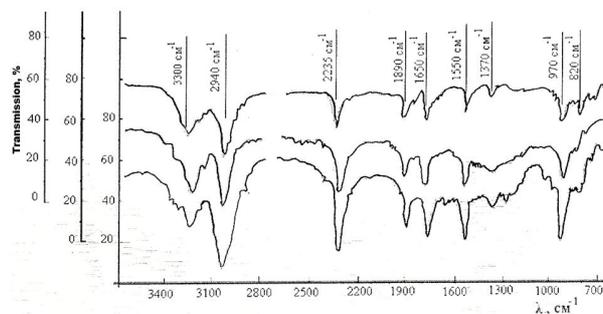


Fig. 3: IR spectrums of unsaturated elastomers (SKIN, SKN-26) with sensitizer 8 mass, part of disulfochloride benzene after 500kGy. a) initial SKN-26; b) irradiated SKN-26+DSCB; c) irradiated SKIN+DSCB.

After irradiation, the films in the case of both rubbers the intensity decreases after absorption at 1360, 1195 and 1170 cm^{-1} which is characteristic for the $-SO_2Cl$ group, as well as the emergence of a new band at $1150cm^{-1}$ related to the sulfonic group $-SO_2$ [19]-[22]. And in either case there is a reduction of the maximum intensity at $1650cm^{-1}$, which is characteristic for the vibrations of the $-C=C-$ groups. In cis-isoprene rubber by the influence of DSCB was observed cis-trans isomerization of the polymer molecules. It is the

evidence for the increase in absorbance band at 967cm^{-1} which is characteristic for CH=CH trans configuration and a decrease in absorbance band at 730cm^{-1} , which is associated with the fluctuations of the CH groups in the cis position.

The chemical reaction between sensitizing agent and the double bonds of the polymers undergo by the elimination active chlorine from the sulphochloride groups for the acrylonitrile-butadiene rubber + DSCB system. As a result, the obtained cross-linked chains contain $-\text{SO}_2-$ group.

It is known that radiation cross-linking of the unsaturated elastomers with aromatic chlorinated compounds is activated by metal oxides. For confirmation of the assumptions about the direction of the reactions of SKN-26 with DSCB, irradiation was conducted several studies. By the usage of different doses the contents of total and combined chlorine in the samples which contains DSCB were determined and were counted the number of molecules DSCB due to the formation for one crosslink.

Nevertheless, the amount of chlorine increases, which came into reaction with zinc oxide for the formation chlorides, and, finally, for the conjunction DSCB to the elastomer molecules. Aforesaid, it is confirmed with the fall in the content of DSCB in toluene extract almost complete binding to the cross linking agent with the elastomer. The concentration of the cross-links in the sample increases and the number of molecules for per one DSCB crosslink is reduced with the increasing dose.

The measurements showed that with increasing of the doses the content of the gel fraction increases significantly in both systems. The formation of the insoluble fraction at low doses (sensitization) is higher in SKN-26+DSCB+ZnO. The maximum gel content (80-90) in SKIN and SKN-40 in the presence of DSCB suggests that DSCB participates in the process of sensitization and crosslinking.

By the usage of these facts, it can be explain that the stitching of SKN-26 by DSCB at 300kGy can probably occur without zinc oxide, but within stitching the tertiary carbon atoms which is located at 1,2 position of the polymer can participate in stitching. However, it is known that the number of units of 1.2 for rubber SKN- 40 is almost 10%. Therefore, it is recognized that determining effect on the crosslinking has tertiary carbon atoms bound to the nitrile group.

Confirmation of radiation mechanism of the reactions, the growth of the number of crosslinks (N_0) and cross-linked molecules ($1/M_{nt}$) for sensitization unsaturated elastomers (SKIN, SKN-26) was found in studies of this system of detection of the free radical which is equal to EPR signal (Fig. 4).

The electrons in all investigated samples on the EPR spectrum was characterized by a narrow singlet line without a trace over the fine structure in the cold mode 77K. At the highest dose (500kGy) in sensitized elastomer the intensity signal changes, there is a weak broadening in the appearance of a well-resolved spectrum for the radical in the form of two narrow singlet with width $\Delta H=1.3\text{mT}$, ($q=2.0031$) and $\Delta H=1.1\text{mT}$ ($q=2.0031$).



Fig. 4. EPR spectra of unsaturated elastomers with sensitizer DSCB, irradiated by dose 500kGy in cold conditions at 77K: 1. The spectrum of irradiated elastomer SKIN in the presence of 8 parts DSCB. 2. The spectrum of irradiated elastomer SKN-26 in the presence of 8 parts DSCB.

The observed phenomenon is probably related to the uneven allocation of radicals in the bulk samples. During radiolysis of polymeric systems which contains electro acceptor polar groups involved in the course of the processes of electron capture by these groups. Positive and negative ions must react with the varied reactions of free radicals [26]. By the studying one or another method on the recommendation of macro radicals the adding low molecular sensitizers (DSCB) to the elastic media can conclude about the microstructures of the molecular chains of the elastomers.

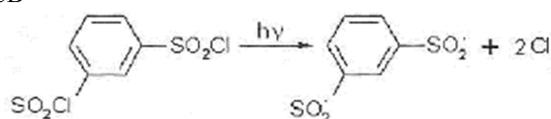
The appearance of the irradiated elastomer systems at the molecular level can be expected to explain the following manner. In these systems (SKIN+DSCB, SKN-40+DSCB) the dispersed particles has been strongly adsorbed, and then has been shown to the high molecular weight fraction. With the highest level of the influence dose the concentration of radicals in the polymer environment, which leads to an increase in distance between them increased. Therefore an over lapping of the orbits of the unpaired electrons on adjacent radicals [26].

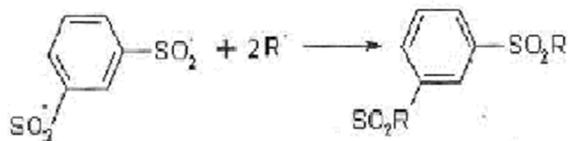
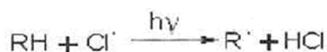
On the basis of these studies the following scheme is suggested for the radiation-chemical reactions of unsaturated rubbers structuring with DSCB.

Thus, these data suggest that DSCB is effective in the radiolysis as crosslinking agents (sensitizers) for unsaturated elastomers.

In conclusion, disulfochlorid aromatic compounds can be used as a sensitizer for radiation vulcanization of unsaturated elastomers (SKIN, SKN-26).

Scheme: The reaction scheme of acrylonitrile rubber with DSCB





IV. CONCLUSION

In the present work the radiation-chemical cross-linking of unsaturated elastomers in the presence of sensitizer agent disulfochloride benzene was reported.

The chemical structure of macromolecules and presence of the disulfochloride benzene affected to the crosslinking process. The radiation crosslinking of unsaturated elastomers can be characterized quantitatively by the value of radiation-chemical yield of cross-linked molecules, effective cross-links.

The useful cross-linking sensitizers containing active halogen vigorously react with carbon molecules of unsaturated elastomer part (SKIN and SKN-26).

The number of soluble sol fraction was achieved for both elastomers within 30-50% at 200kGy and after irradiation at 500kGy polymers become completely insoluble. Increasing the molecular weight of the elastomers during irradiation occurs by the participating of the vinyl bonds which is located at 1,2 position of microstructure.

The yield of number of cross-linked molecules (G_{Mnx}) and effective cross-links (G_{Nc}) of the system SKIN+DSCB at 300kGy is $4,2 \cdot 10^5$ and $4,1 \cdot 10^5$ mol/cm³. Interaction of DSCB with elastomers found that there is a decrease of intensity of the bands after absorption at 1360, 1195 and 1170cm⁻¹ which are characteristic to -SO₂Cl groups. In the study of this system free radicals corresponding on EPR signal was detected. The electrons in all samples were studied on the EPR spectrum which is characterized by a narrow singlet line without trace of the hyperfine structure of the cold mode 77K. There is a slight extension of the appearance of fine lines which allowed spectrum of the radical in the form of a narrow singlet width $\Delta H = 1,3mTl$ and $\Delta H = 1,1mTl$.

V. REFERENCES

- [1] Charlesby A. (1960) Atomic radiation and polymers. Pergamon press. New York, p. 520.
- [2] R.J. Woods, A.K. Pikayev (1994) Applied radiation chemistry: radiation processing. J. Wiley, Science, p 535.
- [3] 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): 210-17.
- [4] Mammadov S. M., Yadreyev F.I., Rivin E.M. (1991) Butadien-nitrilniye kauchuki I rezini na ix osnove. Baku: Elm, p. 280.
- [5] N. A. Shaltout, M. M. AbouZeid, M. A. Mohamed, A. A. El Miligy, E. M. A. Bary (2008) Radiation Vulcanization of Nitrite Butadiene Rubber/Butadiene Rubber Blends. J. of Macromol. Sci.; Part A: Pure and Applied Chemistry, vo.I:

225-31. DOI: 10.1080/10601320701842043.

[6] G. Markovic, M. Marinovic-Cincovic, V. Jovanovic, S. Samarzija-Jovanovic, J. Budinski-Simendic (2009) The Effect Of Gamma Radiation On The Ageing Of Sulfur Cured NR/CSM and NBR/CSM Rubber Blends Reinforced By Carbon Black. Chemical Industry & Chemical Engineering Quarterly, 15 (4): 291-98. DOI: 10.2298/CICEQ0904291 M.

[7] 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(1): 77-94. DOI: 10.1177/0095244312445523.

[8] T. Yasin, Ahmed, F. Yoshii, K. Makuuchi (2002) R adiation vulcanization of acrylonitrile-butadiene rubber with polyfunctional monomers. Reactive&Functional Polymers, vo. 53: 173-81. DOI: 10.1016/S1381-5148(01)00112-2.

[9] Ping Xiang, Xiu-Ying Zhao, Da-Ling Xiao, Yong-Lai Lu, Li-Qun Zhang (2008) The Structure and Dynamic Properties of Nitrile-Butadiene Rubber/Poly(vinyl chloride)/Hindered Phenol Crosslinked Composites. J. 10.1002/app.27337.

[10] Mammadov Sh. M., V.Y. Hasanov, A.M. Alaskarov, A.K. Salekhov, G.M. Farajov (2006) Radiacionnaya vulkanizatsiya elastomernikh smesey na osnove nasishennogo etilepropilenovogo kauchuka. Chem. probl., №4: 646-50.

[11] Kuzminsky A.S., Fedoseeva T.S., Makhlis F.A. (1973) Radiacionnaya khimiya polimerov. M.: Nauka, p. 292

[12] Mammadov S. M. (1990) Aktualniye problemi radiatsionnix issledovaniy. Baku: Elm, p. 260

[13] M. Rojek, J. Stabik, (2006) Butadiene-acrylonitrile elastomers as PVC modifiers. J. of Achievements in Materials and Manufacturing Engineering, 17(1-2): 41-48.

[14] Mammadov S. M. (2007) The Fourth Eurasian Conference on Nuclear Science and its Application. Ankara, p. 165.

[15] Mammadov S.M., Garibov A.A., Gasanov V.Y., Velibekova G.Z. (2010) Radiolysis of a mixture of butadiene-nitrile rubber with polyvinyl chloride, 44(4): 298-301. DOI: 10.1134/S0018143910040028.

[16] Japaneze patent 205404/81 (1981) Elastomer mixture. In.C: C 08 F 8/04.

[17] Patent AZE N I 20090198 (2009) Radiasiya usulu ila vulkanizatsiya edilmis rezin qarishigi. In.C: C 08L 9/00, C 08L 9/02.

[18] Mammadov S.M. (2005) Bessernoye strukturirovaniye BNK s celyu polucheniya agressivoustoychivikh elastomernikh materialov. J. Prikladnoy Khimiyi. №1: 72-6.

[19] Mammadov S.M. (2005) Vliyaniye y-oblucheniya na prosess sshivaniya v prisutstvii sensibilizatorov i GKHPK. Azerb. Khim. Jur., №1: 78-82.

[20] Mammadov S. M. (2004) Issledovaniya prosessa strukturirovaniya butadiene-nitrilnogo kauchuka v prisutstvii poligalogenmetilsoderjashikh soedineniy. Processes of Petrochem. and oil Refining, 2(17): 48-57.

[21] Mammadov S.M., Evstigneeva R.P., Saricheva I.K., Zakharova E.P. (1991) Radiacionnoye sshivaniye elastomerov v prisutstvii chloresoderzhashikh i khromanovikh soedineniy.

Khimiya Visokikh Energiy, 25(5): 438-42.

[22] Mammadov S.M. (2004) Radiasionno-khimicheskoye sshivanye elastomerov na osnove SKN-40

proizvodnimi difenilkhloropropana. J Kauchuk i rezina, № 1:9-11.

[23] Degtyarev E.V., Zakharov N.D. (1985) vliyaniye oksidov metallov na strukturu i svoystva rezin na osnove BNK. Visokomol. Soedineniya, 17 (2): 1223.

[24] Kuznetsov E.V., Divgun S.M., Budarina S.M., Avvakumova N.I., Ekrenkov V.F. (1977), Praktikum po khimii i fizike polimerov, M.: Khimiya, p. 380.

[25] Flory P.J., Rehner J.I. (1943) Statistical Mechanics of Cross-Linked Polymer Networks I. Rubberlike Elasticity. J. Chem. Phys., Is. 11: 512-20.

[26] Bellamy L.J. (1980) The Infrared Spectra of Complex Molecules. Chapman and Hall, v.1,4, p.33.

[27] O'Keefe, Jerome F. (2004) Identification of polymers by IR spectroscopy. Rubber World, 230(3): p. 27.

[28] Roy Crompton (2007) Determination of additives in polymers and Rubbers. Rapra Technology, p.68

[29] D.I. Bower, W.F. Maddams (1992) The vibrational spectroscopy of Polymers. Cambridge University Press, p. 337.

[30] S.M. Mammadov, A.A. Garibov, O.H. Akperov, S.A. Rzayeva, A.K. Salehov, S.S. Ahmadova (2012) The Influence of γ -Irradiation on Structuration in Solutions of BNR and Properties of Films. Open J. of Phys. Chem.2: 182-84. DOI: 10.4236/ojpc.2012.23024.

[31] S.M. Mammadov, S.A. Rzayeva, A.A. Garibov, O.H. Akperov, T.F. Gojayeva, J.S. Mammadov (2012) Study of Influence of Copolymer Vinyl Chloride and Vinyl Acetate on the Properties of Butadiene Nitrile Rubber. J. of Composite Mat. 2(6): 137-4. DOI: 10.5923/j.comaterials.20120206.04

[32] Mammadov S. M. (2005) Plastikasiya i strukturirovaniye smesey butadiene-nitrilnogo kauchuka i polivinilkhlorida v prisutstvii khlorosoderzhashikh soedineniy. J. Kauchuk i rezina, № 6: 14-6.

[33] Mammadov S.M. Garibov A.A., Salehov A.H. (2009) Vliyaniye Gamma izlucheniya na sopolimerizasiyu butadien-nitrilnogo kauchuka diefirom maleinovoy kisloty. Khimiya i Khimicheskaya Tekhnologiya, 52(12): 93-9

[34] 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): 242-49

Shiraz M. Mammadov was born in 1944 in Aghdash city (Azerbaijan). He finished Sumgait chemico-technological college on direction of technology of synthetic polymer (1962) and chemical faculty at Azerbaijan State University (in present Baku State University) (1968). Between 1962 and 1972 he worked at Sumgait synthetic rubber factory, orgsynthesis and also at Mingechaur RTI factory as an assistant, operator, shift supervisor, chief of lab, technician and foreman.

In 1972, he entered the Radiation Investigations of AS of Azerbaijan for PhD degree. In 1982, he presented his "The features of radiation-chemical vulcanization of BNR in presence of chlorine containing compounds" thesis at Yaroslavl Polytechnic Institute.

In 2002, presented "The features of a structure formation in BNR and an influence of them on physical-chemical and exploitation rubber" doctoral thesis. Since 1987 until recent days he is the chief of nuclear chemistry and technology of polymers at Institute of Radiation Problems of NAS of Azerbaijan and a teacher in Macromolecular chemistry departments at Baku State University.

Main research directions: radiation-chemical synthesis of polymers, processing of polymers and composite materials, nanochemistry, preparation of an aggressive durable elastomeric materials for oil and mechanical engineering industry. He is an author of 2 monographs, more than 200 papers and patents