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EFFECT OF GAMMA IRRADIATION ON THE CROSSLINKING PROCESS OF NITRILE- BUTADIENE RUBBER WITH TRIAZINE AND MALEIC COMPOUNDS

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The effect of γ-irradiation on the crosslinking process of nitrile butadiene rubber (NBR) with the participation of 4-dichloro 6-diethylamino-simmtriazine (DChDEAST) and 2,4-dimethylphenyl maleimide (DMPhM) was investigated. The molecular structure of the binary systems NBR + DChDEAST and NBR + DMPhM was determined by Fourier spectroscopy. Fourier transform infrared spectroscopy (FTIR) was used to determine the molecular structure of binary composite systems NBR + DChDEAST and NBR + DMPhM. The relative concentration of double bonds was predicted by determining its absorption by the optical density at the maximum absorption (967, 912 and 750 cm^{-1}). It was found that at radiation doses above 250 kGy, the the number of crosslinks in irradiated blends were 1.05×10^4 and 0.66×10^4 mol /cm^3, respectively. The sensitizing effects of triasine and maleic compounds in radiation-chemical processes was investigated as well. Comprehensive studies of the structure and spatial network parameter of crosslinked NBR showed that the introduction of low molecular weight triazine and maleimide compounds increase the radiation-chemical yield (G_c) and this process also affect to increase the number of crosslinked molecules ($1/M_{n\tau}$) and molecular weight of elastomers in turn.

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1. Introduction

It is known that the radiation-chemical crosslinking yield (G_c) and the formation of effective transverse chemical bonds in the NBR depend both on the dose rate and the absorbed dose [1,2] and on the irradiation condition. To increase the crosslinking yield and accelerate the radiation-chemical reactions occurring in elastomers, various low-molecular additives and sensitizers have been proposed [3,4]. So, there is evidence of the use of hexachloro-paraxylene and chlorine-containing dicarboxylic derivatives for NBR as a curing agent [5,6]. It was established [7] that in the presence of chlorine-containing dicarboxylic acids, the radiation-chemical yield (RCY) of the crosslinkes increases by 2–3 times and crosslinking depends on the nature of the elastomer. It should be noted that the yield of crosslinking and effective crosslinking increases with increasing acrylonitrile content in the elastomer [2].

Earlier, the kinetics of thermoradiation structuring of NBR in the presence of maleimide compounds was studied [8, 9]. The elastomers formed in this process may contain a set of cross-links of various energies. In addition, chlorine-containing substances are often introduced into the composition of the elastomer as a sensitizers, which makes it possible to achieve optimal properties of elastic materials at lower radiation doses [10]. However, at present, the role of chlorine-containing low molecular weight compounds, 4-dichlor 6-diethylamino-simmtriazine

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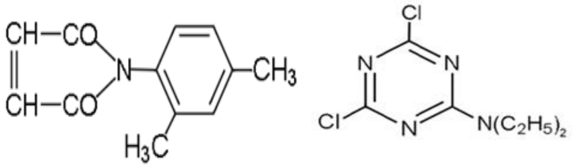
(DChDEAST) and 2,4-dimethylphenyl maleimide (DMPhM) as crosslinking agents and sensitizers in radiation-chemical processes has not been studied. Known data are incomplete and fragmentary. In this regard, it is significant to study the effect of γ-radiation on the crosslinking of NBR (SKN-40) with the participation of DChDEAST and DMPhM and to establish the sensitizing and crosslinking ability of these compounds.

2. Experimental

2.1. Materials

The object of the study is nitrile butadiene rubber (NBR) NBR Russian brand production (GOST № 54556-2011). As a crosslinking agent, 2,4-dichloro 6-diethylamino simmtriazine (DChDEAST) was used. For the reducing absorbed dose, 2, 4-dimethylphenyl maleimide (DMPhM) was added into the system.

The molecular structure of both low molecular weight reactive compounds are shown in the Fig. 1, respectively.



a) *b)*

Fig. 1. The molecular structure of low molecular crosslinking agent:
a) 2, 4-dimethylphenyl maleimide; b) 4-dichloro 6-diethylamino simmtriazine.

Recommended as a crosslinking and sensitizing agent for NBR, it contains active polar groups C-Cl, NH, C_2H_5, CH_3, CO, which activates the crosslinking process in the NBR macromolecule [11]. To activate the process, radiation-chemical crosslinking was introduced into the composition of zinc oxide.

2.2. Preparation of irradiation crosslinked composites

Elastomeric composite were prepared on laboratory rollers (outer diameter 470 mm, working distance 300 mm, speed of rotation of the rollers 24 rpm). After thoroughly mixing, the NBR for 3-5 min with a friction of 1: 2, elastomeric mixtures were prepared (weight parts per 100 weight parts of rubber) containing 3.0 phr. DChDEAST and 5.0 phr of zinc oxide and without it. Then the samples were molded in the press in the form of plates with a 3 mm film only at 80 ° C. Under the same conditions, elastomeric mixtures were made in the presence of 4.0 phr. DMPhM and 5.0 phr zinc oxide. The structure and identity of the used low molecular weight compounds were confirmed by Fourier and UV spectroscopy, NMR, elemental analysis and melting points.

Irradiation of the elastomer was performed with Co^{60} gamma rays at a power of 0.13 Gy/sec. The absorbed dose was 0-500 kGy. Samples in grams were placed in glass ampoules and a container (plastic). The absorbed dose was estimated using a ferrosulfate dosimeter [12]. Calculation of the dose, absorption, and the studied objects is performed according to the procedure [13], based on the obtained readings of the dosimetric system. Changes in the molecular structure of the irradiated crosslinked quasi-binary mixture were observed by Fourier spectroscopy. The spectra of the samples were recorded before and after irradiation. The spectra were interpreted in accordance with the correlation tables [14]. The calculation was carried out according to the Flory-Rener formula. Molecular mass (intrinsic viscosity) was determined by capillary viscometry on a Ubbelohde Viscometer [15]. The change in intrinsic viscosity was evaluated using the Mark-Hauwink formula.

3. Results and discussion

The analysis of the IR-spectrum system NBR + DChDEAST shows that it does not occur in the light of the alternating current (Fig. 2). Accurate light intensity poles 1440 cm^{-1}, switching to deformed welding knit -C≡N group -CH_2 and polish at 1340 cm^{-1}, insulated trolley -C-CH- transceiver. Increase the intensity of the pole with a thickness of 750 cm^{-1}, with a C-Cl [18]. It is important to note that even when the molecule DChDEAST is absorbed by the atom of chlorine, the boundary, the viscosity, the intensity of the pole at 1230 cm^{-1}. In addition, the alternating variations in the spectral region 2230-2320 cm^{-1}. Intensity strip 2230 cm^{-1}, transmitted in the spectrum of NBR, with a voltage-gated welding pulse -C≡N [15], retaining doses of 250 kGy. In a light weighing new weights 2320 cm^{-1}, so that we can see the authors [20], describing the complex structure of the band-C≡N and metal chlorides.

Changes in the IR spectra of NBR-based mixtures after radiation exposure can be explained due to the reactions that occur in the nitrile-linked -CH-groups, as well as in the double-bonded -CH_2-groups in the polymer molecule.

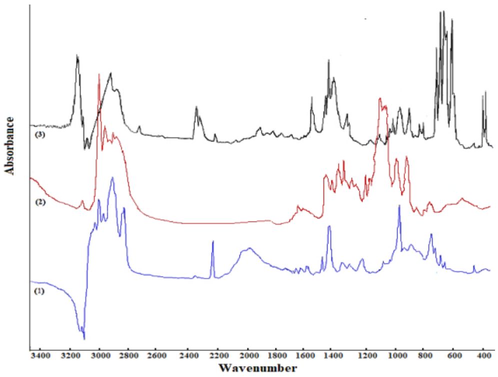


Fig. 2. FTIR spectra of investigated composite samples: NBR (1), NBR + DChDEAST (2), NBR + DMPhM (3).

The most affordable method for determining the molecular weight of a polymer is a viscometric method, based on a straightforward dependence of viscosity on concentration, which occurs for dilute polymer solutions. Only the molecular chain length is determined by the viscometric method and branching is not taken into account [21].

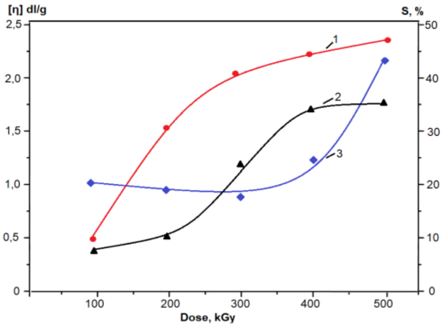


Fig. 3. Dependence of the characteristic viscosity of elastomeric systems (1. SKN-40 2. SKN-40 + DMPhM) and the sol fraction in the sample (3. SKN-40 + DChDEAST) on the radiation dose.

In Fig. 3. The data on the change in the characteristic viscosity of polymer systems with the participation of DChDEAST and DMPhM depending on the dose of radiation are presented. It follows from Fig. 2 that, at low doses of 100 kGy, the intrinsic viscosity for these polymer systems is 0.7 and 0.4. The molecular weight of the elastomer increases and a viscosity of 0.4 to 2.5 is achieved with an increase in the absorbed dose above 400 kGy and the characteristic viscosity decreases by an increase in the absorbed dose (Fig. 3).

A decrease in the molecular weight of the elastomer is the result of degradation of the polymer backbone. An increase in viscosity in the range of the absorbed dose of 100-400 kGy may be due to the formation of spatial structures due to the intramolecular crosslinking reaction.

The amount of soluble sol fraction even at irradiation doses of 100 kGy reaches 15% and after irradiation with 400-500 kGy the polymer completely becomes insoluble, which indicates the structuring of polymer chain molecules. Consequently, the increase in the molecular weight of the elastomer observed upon irradiation is carried out with the participation of vinyl bonds located at positions 1.2 [22].

Naturally, the formation of effective cross-links at doses up to 50 kGy occurs at low rates, and the rate increases with increasing dose for both SKN-40 + DChDEAST and SKN-40 + DMPhM. At a dose of 200 kGy, the number of effective cross-links formed in the SKN-40 + DChDEAST system is 2.1×10^{-19} bonds/cm^3 and in SKN-40 + DMPhM is 1.6×10^{-19} bonds/cm^3 (Fig. 4.).

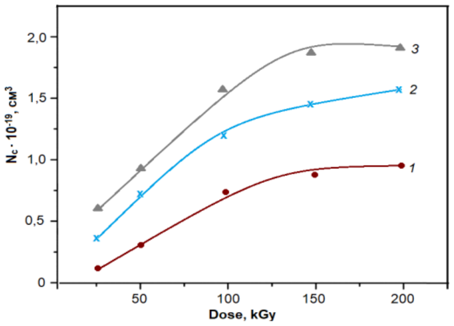


Fig. 4. Dependence on the absorbed dose, the yield of effective crosslinks in binary systems (1-NBR + DChDEAST (3); NBR + DMPhM (2); NBR (1). Irradiation was carried out in air.

From the data presented in Fig. 4, it can be seen that, when it is irradiated in air at 20° C, the crosslinking of SKN-40 are increased slightly in the presence of DChDEAST and DMPhM and the rate of crosslinking yield of the the irradiated system SKN-40 + DChDEAST is higher than in SKN-40 + DMPhM. It is identified that DChDEAST is more reactive; moreover, the resulting number of crosslinks diverges to form crosslinks in the NBR macromolecule.

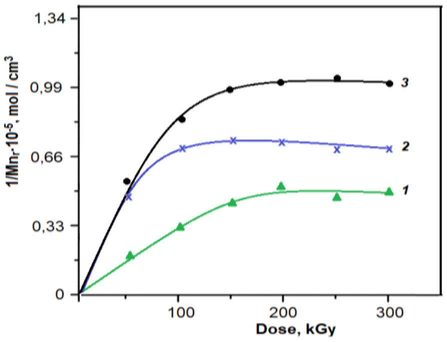


Fig. 5. Dependence on the absorbed dose, the yield of the number of molecular molecules in the systems: 1.NBR; 2. NBR + DMPhM; 3. NBR + DChDEAST;

It should be noted that the polar groups activate the yield of crosslinking during irradiation. The number of crosslinks in both systems decreases at the doses greater than 250 kGy in the room temperature.

When irradiating elastomeric binary systems involving zinc oxide at absorbed doses of 50-300 kGy, the opposite picture is observed. At the same dose of 300 kGy, the number of crosslinks (G_c) in the SKN-40+DChDEAST system is 1.5×10^{-5} mol/cm^3 and for SKN-40 + DMPhM system is 1.1×10^{-5}, mol/cm^3.

It is known that radiation crosslinking of NBR with low molecular weight organic reactive compounds is activated by metal oxides [23]. To confirm the assumption of the reaction of SKN-40 + DChDEAST and DMPhM upon irradiation, we carried out a number of experiments. At a different dose, the sol-gel analysis was used to determine and calculate the number of DChDEAST molecules per one crosslinking formation. The data given in the table show that DChDEAST with a dose increase, the amount of chlorine decreases slightly and the amount of bound chlorine increases. The amount of chlorine that interacts with zinc oxide to form $ZnCl_2$ also increases. This is evidenced by the fact that the processes of chlorine cleavage from the DChDEAST molecule occur simultaneously, its interaction with zinc oxide with the formation of chlorides, and finally the addition of DChDEAST to the elastomer.

Table 1. The effect of DChDEAST and DMPhM in the chemical composition of NBR elastomer containing 5.0 phr ZnO, with radiation exposure

Crosslinking agents	Irradiation dose, kGy	Chlorine content in the sample, %			The contents of DChDEAST and DMPhM in the extract, %	The number of crosslinked molecules $(1 / M_{n\tau})$ of DChDEAST and DMPhM on the formation of crosslinking
		General	Crosslinked	The introduced amount in complex with ZnCl2		
DChDEAST	150	80	13,8	3,6	7,4	2,6
	300	71.3	47,1	11,8	traces	1,8
DMPhM	150	-	-	-	traces	1,32
	300	-	-	-	traces	0,54

In this case, the concentration of crosslinks in the sample increases, and the number of DChDEAST and DMPhM molecules per one crosslink decreases with increasing dose.

Changes showed that with a dragging dose, the gel fraction noticeably increases in both systems. The formation of insoluble gel fractions at low doses (50 kGy) is higher in the SKN-40 + DChDEAST + ZnO system; the maximum gel content (70-60%) in SKN-40 in the presence of DChDEAST and DMPhM indicates that these agents are involved in the process stitching. Based on the above facts, we can assume the following: crosslinking of SKN-40 with DChDEAST at a dose of 300 kGy in the absence of activators (ZnO) probably occurs through the decomposition of DChDEAST with the chlorine being shed from molecules of DChDEAST. The biradicals formed in this case accept hydrogen from the macroradicals of the elastomer. The resulting macroradicals of the elastomer further interact with each other or with the chlorine atom.

4. Conclusions

Comprehensive studies of the structure and spatial network parameter of crosslinkedNBR showed that the introduction of low molecular weight triazine and maleimide compounds leads to an increase in the radiation-chemical yield (G_c), the number of crosslinked molecules ($1/M_{n\tau}$) and effective crosslinks (nc’). The observed effect depends on the absorbed dose on the composition of the structure, unsaturation, polar groups, as well as the isomeric groups (1,4 trans isomers) of the rubber and increase the effects in radiation-chemical processes.

The introduction of triazine compounds 3.0 phr in the composition of the elastomer increases the dispersion of the phase of both systems, which allows you to change the 15% unsaturation at above 100 kGy dose.

Maleimide is highly soluble in rubber; moreover, the effective structuring (sensitization of the process) action of maleimide rises in the presence of zinc oxide activator. It is likely that triazinemaleimide by exposure to ionizing radiation in the presence of zinc oxide, as a result of the interaction of double bonds of triazine and maleimide rings with elastomer macromolecules formed by the action of radicals (ion-molecular), crosslinking occurs, which increases the molecular mass by lowering the soluble sol fraction. In conclusion, we note that DChDEAST and DMPhM can be used in radiation-chemical technology as a crosslinking and sensitizing agent for the vulcanization of NBR with a low absorbed radiation dose.

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