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THE COMBINED STRUCTURE OF NITRILE-BUTADIENE RUBBER BY INFLUENCE OF HEAT AND IONIZING RADIATION IN THE PRESENCE OF TRIAZINE AND MALEIMIDE COMPOUNDS

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Abstract: In this study, the properties of the vulcanizates based on NBR rubber mixtures and in the presence of low molecular weight reactive compounds (SKN-40 + DChDEAST, SKN-40 + DMPhM), vulcanized by the gamma rays and temperature were studied. The degree of crystallinity of the irradiated samples was determined in the presence of tension. An assumption is made about the relationship between the changes and the occurrence of thermoradiation - chemical processes leading to the formation of multifunctional nodes and a change in the number of active network chains in thermoradiation samples of SKN-40 rubber.

Keywords: Elastomer, crosslinking, ionizing radiation, crystallinity, sol-gel analysis

1. Introduction

It is known that radiation vulcanization of elastomers with low molecular weight reactive compounds (LMRC) can also be accompanied by temperature [1,2]. In some cases, for the accelerating of radiation vulcanization process simultaneously with irradiation, it is recommended to heat the sample [3]. However, the process of thermal radiation exposure on elastomeric mixtures still has not been studied much more. There are only fragmentary data that are incomparable for a number of reasons about the effect on the crosslinking rate of an increase in the irradiation temperature for polybutadiene [4] and Styrene Butadiene synthetic rubber (SCS-30 ARKM-15) within 15K to 413K [5], for polysiloxanes up to 573K [6]. Systematic studies of radiation - chemical bonds (crosslinking, destruction, changes in the number of double bonds) and the characteristics of the plasto-elastic properties of rubbers under thermal radiation exposure have not been carried out yet. In this regard, these properties were investigated in this research.

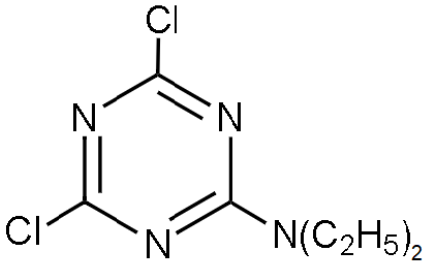
2. Experimental Part

The object of the study is nitrile butadiene rubber SKN-40 and low molecular weight reactive compounds 2,4 dichloro-6-diethylamino simm-triazine (DChDEAST) and 2,4-dimethyl phenyl maleimide (DMPhM).

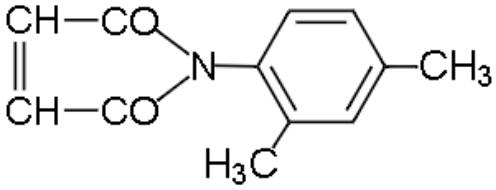
DChDEAST is characterized by non-toxicity, is a yellow powder (T_{pl} = 118), the structure consists of reactive polar groups C-CCl [7].

DMPhM having polar groups NH-N, CH=CH, CH_3, CO has a positive effect on premature crosslinking of NBR and eliminates the restoration of oxidative processes. It is also actively mixed with high molecular weight rubbers during vulcanization.

The studied binary compounds contains 100 phr SKN-40, 3.0 phr DChDEAST (SKN-40 + DChDEAST) and 2.5 phr DMPhM (SKN-40 + DMPhM), respectively. Blends were prepared on a laboratory roller mill at 30-60°C. The plasticization time for each mixture was 7 minutes.



DChDEAST
2,4 dichloro-6-diethylamino
simm-triazine maleimide



DMPhM
2,4-dimethylphenyl
maleimide

Fig.1. The structure of low molecular weight compounds

Radiation - thermal crosslinking of samples by preliminary heating in an electric process at 293, 373, and 423K. The dose rate was 0.13 Gy/sec in order to avoid oxidation processes when irradiated with a Co^{60} gamma-ray apparatus, which had the form of plates with a thickness of 1 mm and was coated with an aluminum foil [8].

Irradiation was carried out at 293 and 423K. The number of crosslinked molecules ($1/M_{nc}$) and network chains was determined by sol-gel analysis. Samples were extracted with hot acetone for 24 hours, dried to constant weight, and then again extracted with cold benzene for 30 hours. The degree of unsaturation of the polymers (the number of double bonds) is determined by the iodine number. [9]

A change in the molecular structure of binary systems during radiation crosslinking was judged by IR Fourier spectroscopy.

3. Results and discussion

The values of the yields of crosslinking (G_c) and degradation (G_d), as well as their relative change with temperature can be determined from the data of the sol-gel analysis. For this study, it is enough to know the change in the yield of the number of crosslinked molecules and the number of active chains of the polymer grid with an increasing the irradiation temperature up to 373K [10].

As can be seen from the results obtained (Fig. 2), the number of crosslinked molecules of polymer systems 1:2 monotonously increases with an increasing radiation dose. In fact, the number of crosslinked molecules at doses of 300 kGy occurs at low speeds. Further, this speed increases with increasing temperature. At a dose of 400 kGy, the number of crosslinked molecules of polymer systems respectively are $1.2 \cdot 10^5$ and $1.7 \cdot 10^5$ mol/cm^3.

It can be seen from the data presented in Fig. 3 that in the case of irradiation of the samples at room temperature (373K) and a dose of 300 kGy, the yield of the number of active chains reaches $7.0 \cdot 10^5$ mol/cm^3 and $8.5 \cdot 10^5$ mol/cm^3. At high doses, especially at temperatures of 373 and 423K, radiation-chemical processes intensify and destructive

phenomena are observed in the irradiated samples. Apparently, this is due to the change in the number and nature of double bonds [11].

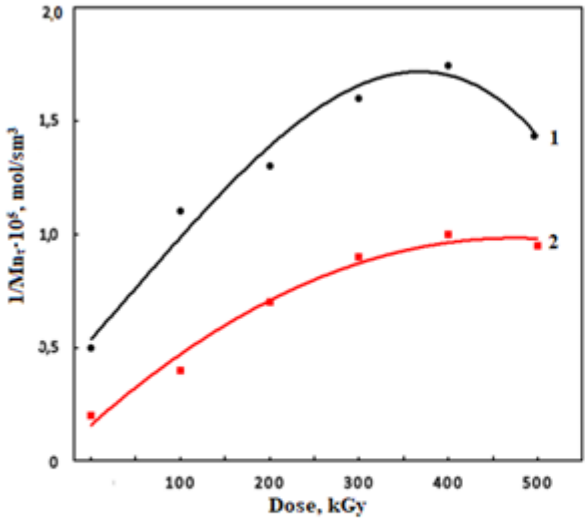


Fig. 2. Dependence of the number of crosslinked SKN-40 molecules on the radiation dose at 293K: 1. System-1; 2. System-2

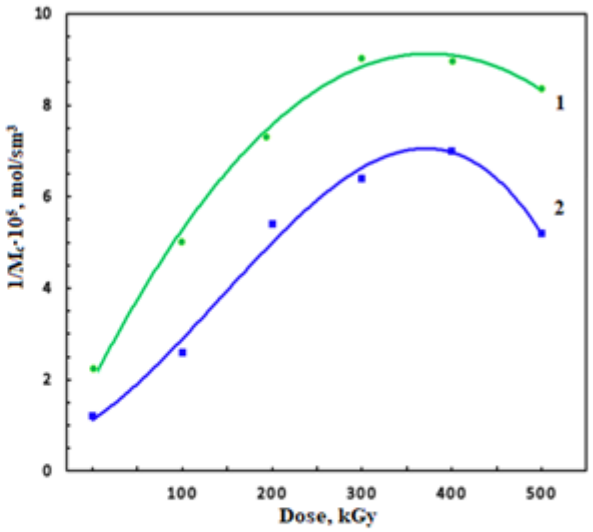


Fig. 3. Dependence of the number of active chains of the SKN-40 rubber network on the radiation dose at 293K: 1. System-1; 2. System-2

At all irradiation temperatures, the degree of crystallinity increases linearly with elongation of the specimen when it is stretched (Fig. 4), which allows one to characterize the intensity of crystallization upon stretching for a given mesh density.

An increase in the radiation dose also affects the strength of vulcanizates: the optimum vulcanization shifts to the area of lower densities of the grid, the strength in the optimum vulcanization significantly decreases (Fig. 5).

The change in the unsaturation of SKN-40 rubber as a result of irradiation was studied by IR spectroscopy. The mechanical properties and crystallinity of vulcanizates was compared in the area of densities of grids. The value of the change in cis - unsaturation is within the accuracy of the method. For the conducting a quantitative comparison of changes in unsaturation the samples were irradiated at 293, 373, and 423K to obtain a grid density of $7.0 \cdot 10^5$ mol / cm^3, which corresponds to a dose of 300 kGy at 433K and 900 kGy at 293K. Doses for comparison is legitimate, since the rate of change in unsaturation remains constant over a wide range of doses [12]. A change in the intensity of the 730 cm^{-1} absorption band corresponding to double bonds in the 1,4-cis configuration and the 1,4-trans configuration was observed. A change in this band can be caused by cis-trans isomerization of rubber, as well as the consumption of double bonds [13].

Calculations showed that irradiation at 293K leads to a 5% change in cis-unsaturation, of which 3% goes to isomerization. An increase in the irradiation temperature to 423K leads to a decrease in cis unsaturation by 9%, of which 5% goes to isomerization, and 4% is consumed [14].

Thus, the increasing irradiation temperature up to 423 K, it reduces the ability to crystallize, worsens the mechanical properties of the vulcanizates, contributes to a significant drop in unsaturation, while the yield of crosslinking increases sharply.

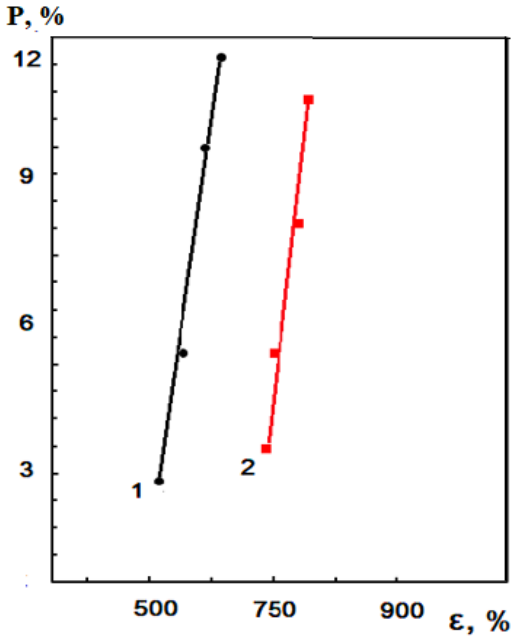


Fig. 4. Dependence of the crystallinity index on the degree of tension for SKN-40 irradiated at temperatures of 293K: 1. System-1; 2. System-2

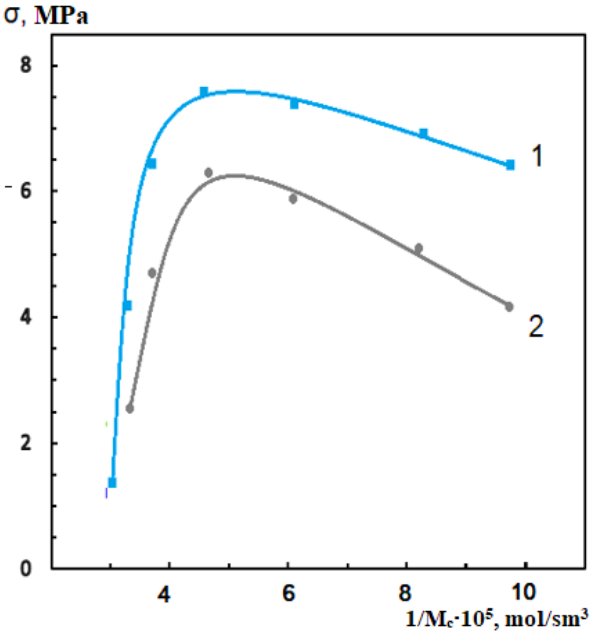


Fig. 5. The dependence of the tensile strength of the irradiated vulcanizate SKN-40 on the number of active chains of the irradiated network at temperatures 293K:1. System-1; 2. System-2

Sol - gel analysis shows that an increase in temperature practically does not lead to additional destruction of rubber, therefore, destruction does not cause the changes in the properties of vulcanizates. An increase in the consumption of unsaturation with increasing temperature is obviously not associated with oxidation, which is confirmed by a comparison of the IR spectra of the irradiated crude rubbers at 423K. An increase in the consumption of unsaturation could be associated with the formation of intramolecular cycles. However, this assumption contradicts the fact that the decrease in unsaturation is accompanied by a significant increase in the number of active chains. In addition, there is a fact that cyclization of rubber does not affect the mechanical properties of vulcanizates [15].

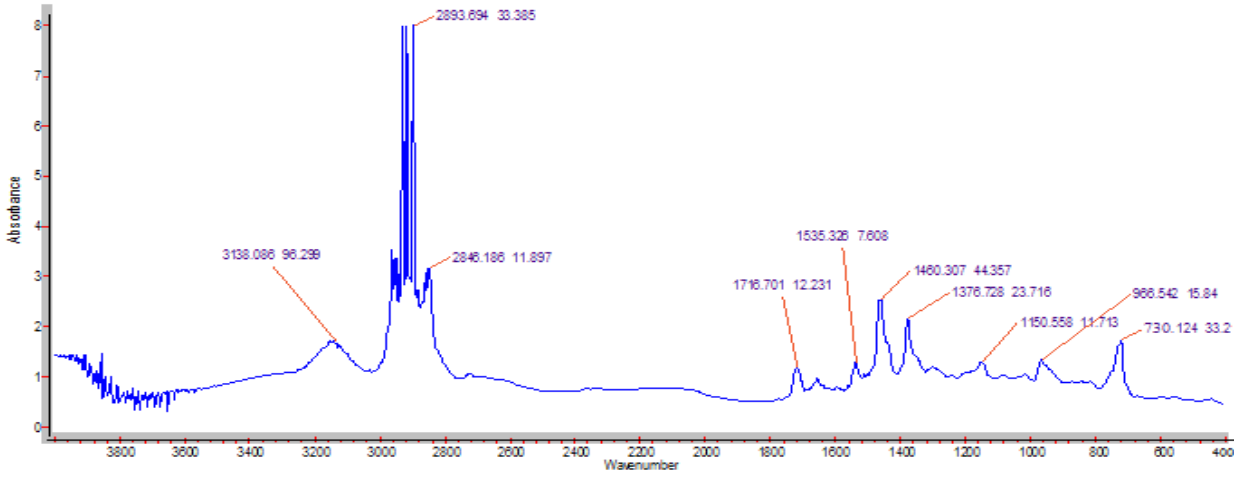


Fig. 5. FTIR spectrum of radiation-thermal crosslinking of elastomeric system 2 (SKN-40 + DMPhM) at 423K and 300 kGy irradiation in air

Obviously, the consumption of unsaturation is associated with the formation of intermolecular crosslinks. If we consider the limiting case when all crosslinks are formed due to double bonds, then a simple calculation shows that the consumption of double bonds in rubber at a dose of 300 kGy (423K) would be 3%. The observed consumption of double bonds is 4%. It can be possible, if only the crosslinking is accompanied by polymerization processes.

Polymerization processes can lead to a deterioration in the properties of vulcanizates. It was found that with an increase in the vulcanization temperature, polymerization processes develop the leading to the formation of multifunctional nodes for the peroxide vulcanization of NBR rubber with a radial nature of initiation. Multifunctional nodes significantly reduce the ability of chains to orient due to the high steric interaction of the parts of molecular chains which is adjacent to the node [16].

It can be assumed that in the case of radiation vulcanization, the formation of multifunctional nodes can occur by the mechanism of the sequential opening of double bonds by analogy with peroxide vulcanization. In addition to the observed significant consumption of unsaturation, the fact that the change in properties with temperature for peroxide and radiation vulcanizates is identical is in favor of this analogy.

4. Conclusion

The features of the degree of structuring of NBR rubber (SKN-40) by the action of heat and The features of the degree of structuring of NBR rubber (SKN-40) and their mixtures in the presence of low molecular weight reactive compounds (DChDEAST, DMPhM) are investigated by the action of heat and ionizing. It was shown that the vulcanization of NBR rubber with low molecular weight reactive compounds under various conditions of crosslinking (vulcanization) and temperature makes it possible to obtain a vulcanizate containing C-C bonds due to the independent vulcanizing effect of DChDEAST, DMPhM. As you know, this set of crosslinks is the way to achieve the optimal properties of the vulcanizates.

At all irradiation temperatures (293, 323K), the output increases the number of crosslinked molecules and the number of network chains. When irradiated with a high dose (700-800 kGy) at a temperature of 293K, cis unsaturation changes by 5%, which 3% goes to isomerization.

By analogy with peroxide vulcanization, it can be assumed that in the case of radiation vulcanization, the formation of multifunctional nodes can occur by the mechanism of the sequential opening of double bonds.

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СОВМЕСТНОЕ СТРУКТУРИРОВАНИЕ БНК ВОЗДЕЙСТВИЕМ ТЕПЛА И ИОНИЗИРУЮЩИХ ИЗЛУЧЕНИЙ С УЧАСТИЕМ ТРИАЗИНОВЫХ И МАЛЕИМИДНЫХ СОЕДИНЕНИЙ

Г.Н. Ахундзада, Ш.М. Мамедов, А.И. Азадалиев, Дж.Ш. Мамедов, Г.А. Мамедова, П.И. Исмайлова

Резюме: В данном исследовании, было изучено свойства вулканизатов смесей БНКс участием низкомолекулярных реакционноспособных соединений, вулканизованными влиянием гамма лучей и температуры. (СКН–40 + ДХДЭАСТ, СКН–40 + ДМФМ). Определена степень кристалличности облученных образцов при растяжении. Высказано предположение о связи происходящих изменений с протеканием терморадиационно – химических процессов, приводящих к образованию полифункциональных узлов и изменению числа активных цепей сетки у терморадиационного образцов каучука СКН-40.

Ключевые слова: эластомер, сшивания, ионизирующее излучение, кристалличности, зол-гель анализ

TRİAZİN VƏ MALEİMİD BİRLƏŞMƏLƏRİNİN İŞTİRAKI İLƏ BUTADEİEN NİTRİL KAUÇUKUNUN TEMPERATUR VƏ İONLAŞDIRICI ŞÜANIN TƏSİRİ İLƏ BİRGƏ STRUKTURLAŞMASI

H.N. Axundzadə, Ş.M. Məmmədov, A.İ. Azadəliyev, C.Ş. Məmmədov, G.A. Məmmədova, P.İ. İsmayılova

Xülasə: Aparılmış tədqiqat işində aşağı molekul kütləli reaksiya qabiliyyətli birləşmələrin (SKN-40 + DXDEAST, SKN-40 + DMFM) iştirakı ilə butadien nitril kauçuku əsasında qarışığının γ şüalanma və temperaturuntəsiri ilə alınmışvulkanizatların xassələri öyrənilmişdir. Şüalanmış nümunələrin dartılma zamanı kristallaşma dərəcəsi təyin edilmişdir. Baş verən dəyişiklikləri, termoradiasion kimyəvi prosesin təsiri ilə-polimer zəncirinin tərkibində polifunksionaldüyünlərin meydana gəlməsi və termoradiasion SKN-40 kauçuku nümunələrində aktiv zəncir torlarının sayının dəyişməsi ilə izah etmək olar.

Açar sözlər:elastomer, tikilmə, ionlaşdırıcı radiasiya, kristallaşma, zol-gel analiz