

Research into Kinetics of Radiation Destruction of Elastomers

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Abstract

The paper analyzes the destruction process of polymers under the impact of mechanical forces, temperature, and ionizing radiation. The theoretical explanation for the destruction of polymers affected by various factors is given. The technological properties and the structure of butyl rubbers obtained by irradiation on a Co⁶⁰ source at various absorbed doses are studied. Vulcanized butyl-based rubber mixtures with different types of vulcanizing group and fillers are the objects of the study. Methods of sol-gel analysis and viscometry showed that the destruction of vulcanizates occurs along the main chain of the polymer. It was found that in the resin vulcanizates there was an intensive destruction of the main chain along with the disintegration of the cross-links, while in the sulfur vulcanizates the radiation destruction to the cross-links was more active.

It is assumed that when the butyl-based rubbers are destroyed, the bond break in the main chain proceeds according to the probability law. A mathematical description of the dynamics of the initial moments of the function of the molecular weight distribution of the polymer as a function of the absorbed dose is obtained. A scheme of reactions describing the destruction processes is proposed. For the degradation process characterization, it is proposed to evaluate it by the Mooney viscosity variations. The parametric identification of the model uses the RMS criterion. The estimation of the model parameters is carried out using the genetic algorithm. The adequacy of the model is confirmed by the Fisher criterion. At the same time, the error of the model did not exceed 5 %. Using the obtained mathematical description, a method for estimating the necessary radiation dose ensuring the required elastic properties of reclaimed rubber and rational consumption of energy resources is proposed.

Keywords

Mathematical model; destruction; rubber; butyl rubber; Mooney viscosity; ionizing radiation.

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Introduction

Chemical transformations of polymers are conditionally divided into the following main types [1]:

– the reaction of crosslinking of macromolecules with each other to form a branched or spatial structure of the three-dimensional polymer;

– reactions of destruction, leading to the rupture of macromolecules under the influence of heating, irradiation, chemical agents, mechanical loads, etc.;

– polymer-analogous reactions that occur in lateral or basic macro-chains and do not affect their length;

– reactions of intramolecular rearrangements followed by the preservation of chain length, and the change in the composition and/or structure of the polymer itself.

Chemical reactions in polymers mainly [2] have a radical mechanism, although ionic reactions are not excluded [3–4].

In general, chemical transformations in polymers are a set of interrelated reactions, the precise nature of many of which has not been established yet.

In the technology of polymers, destruction reactions are of great interest, the course of which is associated with a decrease in the molecular weight

(MM) of the polymer. During treatment, storage and operation, polymers are exposed to the action of heat, light, oxygen of air, mechanical effects and other factors, as a result of which physical and chemical processes develop in them, leading to a change in physical-mechanical properties due to the destruction of macromolecules.

The patterns of destruction of polymers under the influence of various factors are determined mainly by their structure and the nature of the bonds that form the main chain and the side groups of macromolecules. The double bonds contained in the macromolecules of many rubbers determine their high reactivity. However, in all cases, volumetric, polar and other chemically inert side groups change the chemical activity of the polymers.

On the one hand, destruction is an undesirable reaction, as it reduces the MM of the polymer and impairs the physical-mechanical properties of polymers. On the other hand, destruction plays a positive role in obtaining valuable low-molecular substances, in order to partially reduce the MM of polymers in order to facilitate their treatment and for other purposes.

Knowledge of patterns and mechanism of destruction allows for its intensification, when it is desirable, and its suppression or minimization when it is undesirable [7].

The purpose of this research was to study the destruction of rubbers under the influence of ionizing radiations and to create a mathematical description of the process that allows predicting the elastic properties of the destructants obtained.

Theoretical justification of polymer destruction under various factors

Depending on the mechanism, destruction by the probability law and chain destruction are distinguished [7–9]. Chain destruction occurs under the influence of active centers of radical type such as heat, light and radiation.

In the analysis of the destruction processes, it is necessary to take into account that the real polymer material is a complex multicomponent system [10], which is based on a high molecular weight compound. Therefore, in justifying the processes of destruction of polymers, four main stages are distinguished [3]:

- formation of active centers or initiation of processes;
- chain growth (development) as a result of the interaction of active centers with the polymer molecule;
- degenerated branching of the chain or autocatalytic acceleration of the process by the chain mechanism;
- chain interruption.

The final stage is characterized not only by the interaction of the reaction products with each other, but also with other substances. Disproportionation, isomerization reactions, etc. are also possible. These reactions are usually multi-variant and run parallel to each other with the predominance of any of them at a certain stage [4].

The rate of destruction of polymers is usually quite high at the beginning of the process, and then gradually decreases until the conditional limit is reached. In this case, the rate and degree of variation in the molecular weight, and, consequently, the rate of the chemical structure of the rubber depend on the chemical nature and physical state of the polymer, and the reaction conditions (temperature, stress, nature of the environment, equipment type, etc.). A number of parameters (temperature, molecular weight and concentration) significantly affect the destruction processes, changing the properties of the polymer [7].

It was found [11] that the higher the molecular weight of polymers is, the higher is the stress at which the chains are straightened under the same processing conditions, and the longer is the relaxation time. Because of this, the tendency to destruction in high-viscosity systems is higher. The increase in viscosity can be caused both by an increase in the molecular weight and by an increase in the intermolecular interaction. It is necessary to take into account such a peculiarity of the structure of the polymer as the presence in the chain of bonds between the α -methylene groups, which have a lower energy due to conjugation and more subject to destruction [12]. Thus, another factor that plays a decisive role here is the presence of weak bonds in the chains. The influence of weakened bonds is reflected not only in the primary act of destruction, but also on the activity of the macro-radicals formed, the ease of their stabilization, etc. [14].

Currently, the presence and influence of “weak” bonds have been experimentally confirmed and their influence has been studied to a sufficient degree [10, 12–14]; it is shown that weak bonds can also form during the destruction process. An important role is played by the energy of the chemical bond (or internal strength) of the main chain [4].

According to the authors [7], a polymer with a low molecular weight breaks down as a result of the sliding of chains and the overcoming of mainly intermolecular forces. Beginning with a certain degree of polymerization, the smaller, the stronger the interaction of polymer chains, a stable state is achieved: the polymer breaks down as a result of the breakdown of the chemical bonds of the macromolecules. With

further increase in the molecular weight, the strength is practically independent of the chain length [13].

Radiation-chemical transformations of polymers are processes occurring in polymers under the influence of energy radiations and leading to a change in their chemical composition and properties. The main radiation-chemical transformations of polymers include [15] the formation of chemical bonds between macromolecules, such as crosslinking, bond rupture in the main chains, and the formation of molecules of smaller length, i.e. destruction. Contrary to thermal degradation, radiolysis does not cause depolymerization of the polymer and is not a chain process. Radiation destruction always follows the probability law [16, 17].

According to the classification of polymers by type of predominant radiation-chemical transformations, butyl rubber refers to destructible polymers. At the destruction process, the breaking of bonds in the main chain can occur anywhere, therefore, regardless of the initial molecular weight distribution of the polymers upon destruction, it tends to the most probable value. The radiation-chemical yield of destruction is directly proportional to the radiation dose and the molecular weight of destruction products. Due to the destruction processes, treatment of butyl-based rubbers with ionizing radiation makes it possible to obtain materials with given plastic-elastic properties [18–24].

Research into irradiation conditions on the plastic-elastic properties of rubbers

The object of the study is vulcanizates of butyl-based rubber mixtures differing in the type of the vulcanizing group and fillers: BR-D resin-cured vulcanizate and BR-PI and BR-P-II sulfur vulcanizates obtained under different vulcanization modes. The principal composition of the rubber is shown in Table 1.

The rubbers were irradiated at a Co^{60} on the source with doses of 20–100 kGy and received BRR-D, BRR-PI, BRR-P-II cipher regenerates.

The plastic-elastic properties of the obtained regenerates were evaluated according to the viscosity index, which was determined on a Mooney viscometer at 100 °C. The results of the tests are given in Table 2.

The effectiveness of irradiation on the spatial network of the vulcanizate was measured by changing the structural parameters of the samples, which were determined by the method of equilibrium swelling for 72 h in toluene and cyclohexane [25].

The equilibrium degree of swelling, the molecular weight of the rubber chain between the nodes of the spatial mesh and the effective concentration of crosslinks were measured.

Table 1

Principal composition of butyl based rubber composites

Composition	Sample ciphers and component content, % wt.	
	BR-D	BR-PI (BR-P-II)
Butyl rubber	58.1	58.0
Chlorobutyl rubber	–	6.4
SP-1045 Resin	3.5	–
Nairit	2.9	–
Sulfur	–	0.9
Thiuram	–	0.8
Fillers	29.0	29.9

Table 2

The Mooney viscosity of the regenerates obtained at different doses of irradiation

Sample ciphers and irradiation dose, % kGy	Mooney viscosity, eq. units
BRR-D	
20	230
40	132
50	110
70	82
100	65
BRR-PI	
20	225
40	130
50	115
70	84
100	62
BRR-P-II	
20	210
40	115
50	94
70	68
100	55

The equilibrium degree of swelling was calculated by the formula:

$$Q_{eq} = \frac{\rho_r}{\rho_s} \frac{m_{sw} - m_d}{m_d F},$$

where ρ_r , ρ_s are densities of rubber and solvent, respectively, g/cm^3 ; m_{sw} , m_d are the weight of the swollen sample and the weight of the sample after drying, respectively, g; F is the relative content of the hydrocarbon of rubber in the sample determined by the formula:

$$F = M_r / \Sigma M_i,$$

where M_r is weighed rubber in the sample according to the recipe, pts. wt., ΣM_i is total weight of ingredients according to the recipe, pts. wt.

The molecular weight of a portion of the rubber chain between the nodes of the spatial grid of a given vulcanizate was determined by the formula:

$$M_c = \frac{-\rho_r V_s (\sqrt[3]{v_{eq}} - v_{eq}/2)}{\mu v_{eq}^2 + v_{eq} + \ln(1 - v_{eq})},$$

where V_s is molar volume of solvent, cm^3/mol , μ is the polymer-solvent interaction parameter (Huggins constant), equal to 0.56 for toluene, and 0.43 for cyclohexane [26]; v_{eq} is the volume fraction of the polymer in the equilibrium state, is calculated from formula:

$$v_{eq} = \frac{1}{1 + Q_{eq}}$$

Effective concentration of vulcanizate cross-links

$$n_e = \rho_r N_A / 2M_c,$$

where N_A is Avogadro's number, $N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1}$.

The sol-gel analysis was carried out by extracting the samples with acetone for 16 hours in the Soxhlet extractor. When extracted with acetone, the bulk of low molecular weight substances not included in the three-dimensional grid was extracted from the samples [27]. After extraction with acetone, the samples were dried for 24 hours, bringing the mass to a constant value. The mass of the insoluble residue was equated to the weight of the gel fraction. The results were averaged over the three samples. The insoluble gel after drying was swollen in toluene at room temperature for 72 h. The density of the vulcanization grid in the rubber gel fraction was determined by the Flory–Rehner equation [25].

$$n = \frac{-\ln(1 - V_r) + V_r + \chi V_r^2}{V_s \left(V_r^3 V_0^3 - \frac{V_r}{2} \right)},$$

where V_r is volume fraction of rubber in the swollen sample, V_s is molar volume of solvent, V_0 is volume fraction of rubber in the original sample, χ is the Huggins parameter characterizing the interaction of rubber with a solvent (in this experiment χ was taken equal to 0.56). The results of the tests are given in Table 3 and are summarized in Fig. 1, 2.

Table 3

Structural characteristics of the regenerates obtained at different doses of irradiation

Indicators	The sample ciphers and dose of irradiation, kGy														
	BRR-D					BRR-PI					BRR-P11				
	20	40	50	70	100	20	40	50	70	100	20	40	50	70	100
	Equilibrium swelling														
$Q_{eq}, \%$	3.4	3.7	3.8	4	4.6	2.9	3.2	3.2	3.6	4.4	3.1	3.2	3.3	3.8	4.6
M_c	653	679	688	704	753	608	636	636	671	737	626	636	644	688	753
$n_e, \text{cm}^{-3} \times 10^{20}$	4.2	4.1	4.0	3.9	3.7	4.5	4.3	4.3	4.1	3.7	4.4	4.3	4.3	4.0	3.7

Note: Q_{eq} is equilibrium degree of swelling of vulcanizate; M_c is the average molecular weight of the rubber chain segment between the nodes of the spatial grid of vulcanizate; n_e is effective concentration of vulcanizate cross-links.

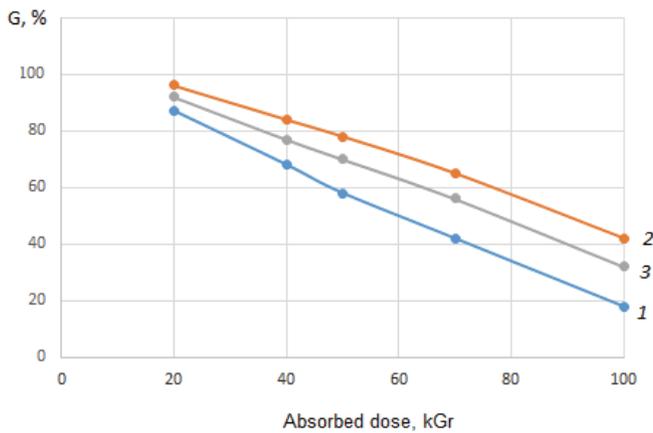


Fig. 1. Variation in the content of the gel fraction as a function of the absorbed dose: 1 – BBR-D; 2 – BRR-PI; 3 – BRR-PH

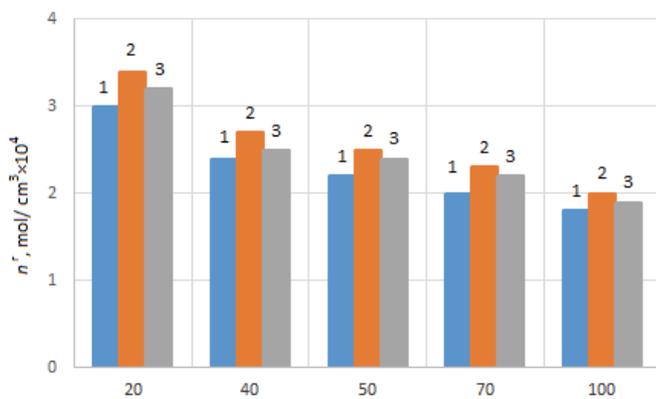


Fig. 2. Variation in the density of chemically cross-linked chains as a function of the absorbed dose: 1 – BBR-D; 2 – BRR-PI; 3 – BRR-PH

Using the sol-gel analysis it was found that with an increase in the irradiation dose, the destruction rate of the gel fraction of the resin vulcanizates is significantly higher than that of sulphur ones (Fig. 1). However, sulphur and resin vulcanizates do not differ significantly by the rate of decrease in active chains (Fig. 2). Obviously, this is due to the fact that in the resin vulcanizates an intensive destruction of the main chain occurs along with cross-link breakage, while in sulphuric vulcanizates the radiation destruction occurs mainly along cross-links.

Mathematical modeling of destruction under the action of ionizing radiation

The basis for constructing a mathematical model for the destruction of rubbers based on butyl rubber under the action of γ -radiation was the approach described by the authors in [28]. This approach allows

evaluating the dynamics of changes in initial moments of the function of the molecular weight distribution of the polymer as a function of the irradiation dose.

Proceeding from the assumption that the act of destruction occurs equiprobably at an arbitrary point x of a macromolecule of length l_{\max} , the distribution function ($F(x)$) along the length of polymer molecules subject to ionizing irradiation will take the form [46]:

$$F(x) = \int_0^x \varphi(l) dl + x \int_x^{l_{\max}} \frac{\varphi(l)}{l} dl, \quad (1)$$

where $\varphi(l)$ is density function of the initial molecular weight distribution.

We consider the initial moments of the function (1). Let M_n^k is k -th initial moment of the distribution function at the n step of irradiation, α_n is mass fraction of polymer chains not involved in the destruction process. Then, if $k \geq 1$

$$M_n^k = \alpha_n M_{n-1}^k + (1 - \alpha_n) \bar{M}_n^k \quad (2)$$

given that

$$\bar{M}_n^k = \int_0^{l_{\max}} x^k dx \int_x^{l_{\max}} \frac{\varphi(l)}{l} dl = \frac{1}{k+1} M_{n-1}^k. \quad (3)$$

From formula (2) with allowance for (3) it follows that:

$$\bar{M}_n^k = \frac{k\alpha_n + 1}{k+1} M_{n-1}^k. \quad (4)$$

Assuming that the increment of the irradiation dose at the n and $n - 1$ steps is equal to $\Delta\theta$:

$$\frac{\Delta M_n^k}{M_n^k} = \frac{k}{k+1} (\alpha_n - 1) \Delta\theta, \quad (5)$$

if $\Delta\theta \rightarrow 0$

$$\begin{cases} \frac{dM^k(\theta)}{M^k(\theta)} = \frac{k}{k+1} (\alpha(\theta) - 1) d\theta; \\ M^k(0) = \text{const}. \end{cases} \quad (6)$$

The solution of equation (6) has the form:

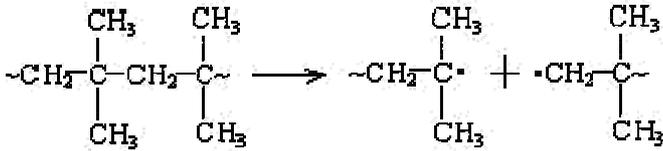
$$M^k(\theta) = M^k(0) e^{\frac{k}{k+1} \int_0^\theta (\alpha(\gamma) - 1) d\gamma}. \quad (7)$$

Expression (7) will allow us to evaluate the dynamics of changes in the initial moments of the distribution function of the polymer composition as a function of the irradiation dose.

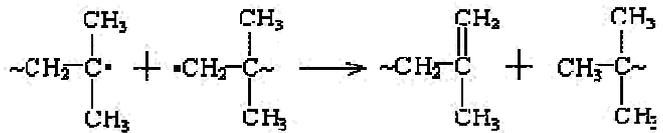
Radiation destruction in polymers and polymeric materials (including in products) [17] is observed

mainly in macromolecules containing a quaternary carbon atom, for example, in polyisobutylene (butyl rubber and materials based on it).

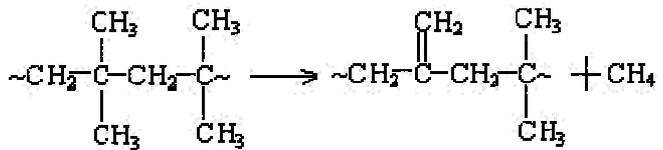
In accordance with the scheme of radiation destruction of polyisobutylene, proposed by the authors [16], initial breaks



are accompanied by disproportionation



This mechanism takes into account the formation of one vinylidene group per break. An additional double link can be formed when methane is split off from the main chain without breaking it.



Final reactions can be represented as

$$P \xrightarrow{k_1} R_1 + R_2, \tag{8}$$

where P is current mass (weight) concentration of the polymer; R_1 and R_2 are concentration of polymer radicals, while

$$P + R = P_0, \tag{9}$$

where P_0 is initial mass (weight) concentration of polymer.

The process of formation of radicals can be described by the equation:

$$\begin{cases} \frac{dR}{d\theta} = k_1(P_0 - R); \\ R(0) = 0, \end{cases} \tag{10}$$

where θ is irradiation dose(kGy); k_1 is constant rate of the polymer matrix destruction $(\text{kGy})^{-1}$.

The solution of equation (10) has the form

$$R(\theta) = P_0(1 - e^{-k_1\theta}). \tag{11}$$

Then, taking into account that

$$\int_0^\theta (1 - \alpha(\gamma)) d\gamma = \int_0^\theta \frac{dR(\gamma)}{P_0} = 1 - e^{-k_1\theta}; \tag{12}$$

$$M^k(\theta) = M^k(0) e^{-\frac{k}{k+1}(1 - e^{-k_1\theta})}. \tag{13}$$

As $M^k(\theta)$ it is not possible to evaluate in real conditions, it is advisable to use an indirect value to describe the process, i.e. the Mooney viscosity ($M_h(\theta)$).

The Mooney viscosity of the polymer composition according to [46] is related to the concentration of radicals by the following expressions:

$$M_v(\theta) = M_v(0) e^{-\frac{1}{\beta+1} \int_0^\theta \frac{dR(\gamma)}{P_0}}; \tag{14}$$

$$M_h(\theta) = M_h(0) e^{-\frac{a}{\beta+1} \int_0^\theta \frac{dR(\gamma)}{P_0}}, \tag{15}$$

where β is Mark-Kuhn-Houwink constant; a is constant; $M_v(\theta)$ is the viscosity-average molecular weight of the polymer at the radiation dose θ .

The resulting relation (15) with (11) represents a mathematical model of the dynamics of variation in the Mooney viscosity during ionization irradiation of the polymeric composition. For using this model, it is necessary to estimate the rate constant k_1 of the polymer matrix destruction.

In the Mathcad environment, the destruction rate constant k_1 was calculated. To evaluate it, experimental data and authors' data [30] describing the change in M_h as a function of the ionizing radiation dose were used. The results of the calculations are given in Table 4.

As a criterion for optimization, the criterion

$$I = \sum_{i=1}^N (M_{h_i}^{\text{cal}} - M_{h_i}^{\text{exp}})^2 \rightarrow \min \tag{16}$$

was used, where N is the number of measurements.

Minimization of the criterion (16) was carried out using the genetic algorithm [31, 32].

Table 4

Model parameters		
a	β	k_1
4.037	0.69	0.0216

The results of calculations using the model (15) for the BRR-D cipher sample are presented in Table 5 and summarized in Fig. 3. The initial values for obtaining the calculated Mooney viscosity values (M_h^{cal}) were the experimental values M_h^{exp} . Data smoothing was performed using the moving average procedure. Computational error Δ_{rel} was in the range from 0.01 to 1.77 %. The model obtained was tested for adequacy using the Fisher criterion and the R^2 -criterion.

The effect of the initial Mooney viscosity M_h and the irradiation dose on the process rate is shown in Fig. 4.

Table 5

Results of calculations and model identification

Irradiation dose kGy	$M_{h_i}^{exp}$, eq. un.	$M_{h_i}^{cal}$, eq. un.	Δ_{rel} , %	R^2	F-criterion
0	–	537.74	–		
20	235	236.55	0.66		
40	135	134.99	0.01	0.99	149.25
50	113	112.99	0.01		
70	85	83.52	1.77		
100	65	64.96	0.06		

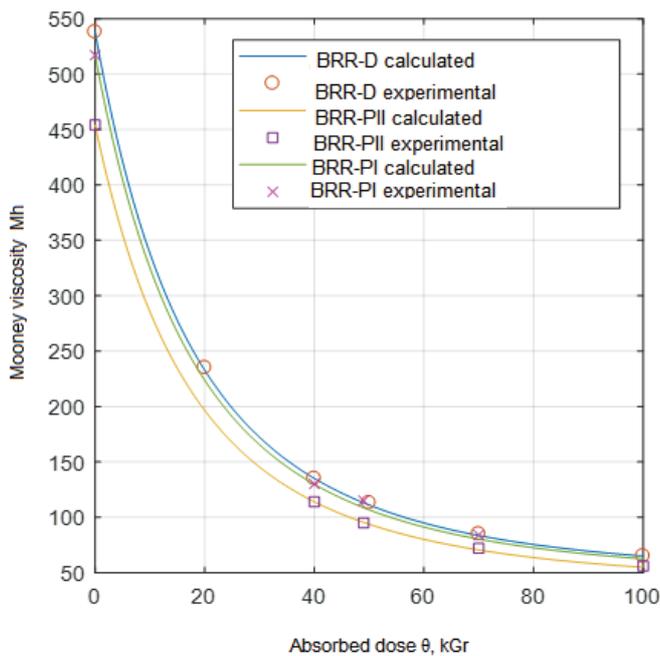


Fig. 3. Dynamics of the Mooney viscosity

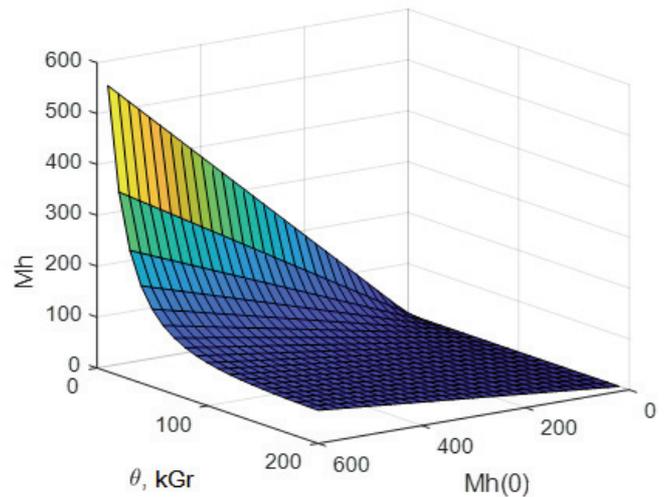


Fig. 4. Dependences of the change in Mooney viscosity on the initial values of this index and the dose of irradiation of butyl rubbers

Let us estimate the limiting value $M_h(\theta)$ for $\theta \rightarrow \infty$. Since

$$\lim_{\theta \rightarrow \infty} [M_h(\theta)] = \lim_{\theta \rightarrow \infty} \left[M_h(0) e^{-\frac{a}{\beta+1}(1-e^{-k_1\theta})} \right] = M_h(0) e^{-\frac{a}{\beta+1}}, \quad (17)$$

if the irradiation dose increases, M_h tends to a constant value, which is due only to the initial Mooney viscosity $M_h(0)$.

The rate of the destruction process by radiation dose is determined by the relation

$$\frac{dM_h(\theta)}{d\theta} = -\frac{M_h(0) a k_1 e^{-k_1\theta} e^{-\frac{a}{\beta+1}(1-e^{-k_1\theta})}}{\beta+1}, \quad (18)$$

and the process speed for $\theta \rightarrow \infty$ tends to zero, which indicates the termination of the destruction process when the radiation dose limit is reached (Fig. 5).

Thus, it is possible to carry out the destruction process at such an irradiation dose, which is necessary to achieve the required plastic-elastic properties, which allows ensuring rational consumption of energy resources and timing for the process of radiation treatment of elastomers.

Setting the measure of achievement of the target value as a deviation from the steady-state value of ϵ and recording the inequality that determines the condition of economic expediency of conducting the process in percentage

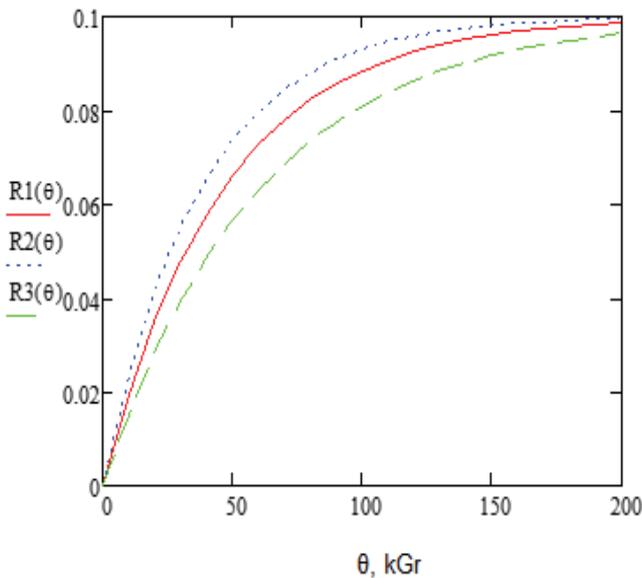


Fig. 5. Correlation between the concentration of radicals and the absorbed dose:
 $R_1(\theta)$ – BRR-D; $R_2(\theta)$ – BRR-PI; $R_3(\theta)$ – BRR-PII

$$\frac{M_h(\theta) - M_h(\infty)}{M_h(\infty)} \cdot 100 \leq \varepsilon [\%] \quad (19)$$

or in fractions of a unit

$$\frac{M_h(\theta) - M_h(\infty)}{M_h(\infty)} \leq \delta \quad (20)$$

Substituting relations (17), we obtain the inequality

$$\frac{M_h(0)e^{-\frac{a}{\beta+1}(1-e^{k_1\theta})} - M_h(0)e^{-\frac{a}{\beta+1}}}{M_h(0)e^{-\frac{a}{\beta+1}}} \leq \delta, \quad (21)$$

a solution, which is relative to θ makes it possible to estimate the radiation dose at M_h , deviating from the steady-state value by not more than δ

$$\theta \geq -\frac{\ln\left[\frac{\ln(1+\varepsilon)(\beta+1)}{a}\right]}{k_1} \quad (23)$$

Note that this dose depends only on the rate constant k_1 , parameters a , β and does not depend on the initial viscosity $M_h(0)$.

For example, to obtain a 5 % deviation of M_h from the steady-state value for the mathematical model obtained above, a dose

$$\theta \geq -\frac{\ln\left[\frac{\ln(1+0.05)(0.69+1)}{4.037}\right]}{0.0216} \geq 180.14 \text{ kGy} \quad (24)$$

is required.

Conclusion

It is established that during the radiation destruction of butyl rubber vulcanizates, the main polymer chain is mainly broken. This leads to a decrease in the MM of the polymer, as evidenced by the viscometric data and sol-gel analysis. With an increase in the absorbed dose, an intensive decrease in the Mooney viscosity is observed with a simultaneous decrease in the content of the gel fraction. At the same time, the density of chemically cross-linked chains varies insignificantly, that is an additional confirmation of the predominant disruption of macromolecules with respect to transverse intermolecular bonds of vulcanizates.

The structural and parametric identification of the model of the investigated process was carried out. Using the model, the dynamics of changes in the concentration of radicals as a function of the absorbed dose was estimated. It is shown that the rate of change in the viscosity of elastomers with an increase in the absorbed dose varies and tends to zero when passing to the limit. Thus, it is possible to determine the necessary dose of radiation necessary to achieve the desired viscosity of the elastomeric compositions.

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