

УДК 678.4.028

O. V. Karmanova, PhD (Engineering), assistant professor (VSUET);
V. I. Molchanov, PhD (Chemistry), assistant professor (VSUET);
Zh. S. Shashok, PhD (Engineering), assistant professor (BSTU)

ON SOLVING THE PROBLEM OF KINETICS OF VULCANIZATION WITH THE USE OF NUMERICAL METHODS

A new approach of describing kinetics of curing was proposed. This allowed for formal adjustment of the previously proposed scheme of vulcanization, application of a mathematical model to kinetic curves of any shape and analytical evaluation of isothermal cure kinetics on the basis of economical laboratory experiments. The method of studying kinetics of vulcanization is based on the assumption that individual stages of the vulcanization process significantly differ in speed. To determine rate constants for individual stages the rheometric curve was divided into some areas. It allowed to use only a specific set of ordinary coupled reactions of the first and second order for describing vulcanization of rubbers under analysis. Software for solving direct and inverse problems of the kinetics of isothermal cure was developed.

Introduction. Vulcanization of raw rubber (which is a complex chemical process with a great number of reactants) is characterized by specific regularities of duration or kinetics and leads to formation of a uniform three-dimensional network from raw rubber macromolecules. Rubber properties are formed during the process of vulcanization, but in the course of the process their changes are not uniform, i. e. the kinetic curves don't coincide: they pass through the maximum in conformity with some properties and through the minimum – with others; in the majority of cases kinetic curves “property – duration of the process” are characterized by the initial period, subsequent period of prevailing structurization, plateau of vulcanization (where levels of properties are preserved under such temperature conditions) and final period of prevailing reversion of units, rupture of the cross linking network. The existing calculation analytical and engineering methods of describing kinetics of vulcanization are mainly applicable to individual types of kinetic curves.

Main part. The process of vulcanization starts with formation of a supramolecular complex of the vulcanization accelerator and activator. This complex interacts with the molecule of sulfur S_8 to form a sulfuring agent of vulcanization. This agent is polysulfide with a chain of sulfur atoms from 2 to 20. The activated sulfurization agent is subjected to dissociation and in the course of the reaction with a carbon allyl atom it forms polysulfide bounded by the raw rubber molecule on one side and by the vulcanization accelerator molecule on the other. Pertyl radical is formed, it interacts with the carbon allyl atom of another molecule of raw rubber and forms a cross-linking chemical bond. The polysulfide bonds /linkages/ may further undergo reactions of dissociation resulting in decrease of their sulfiding or complete destruction.

Production formulations contain a combination of activators and accelerators of sulfur vulcanization. In the majority of cases reciprocal activation of the components increases the number of conju-

gated chemical reactions, resulting in cross-linking of macromolecules which effects the speed of vulcanization, tendency to scorch and reversion of rubber properties.

In traditional mathematical simulation of physico-chemical processes of vulcanization there may occur some difficulties in coordinating the postulated kinetic mechanism with the experimental data. Firstly, the mechanism of the reaction involves many stages. Secondly, equations for describing the kinetics of the individual stages aren't linear due to binary reactions and the exponential dependence of speed on temperature. Traditional methods used to define coefficients in case of rigid systems of ordinary differential equations will be unstable, which will require making supplementary algorithms for their stabilization or application of Bayesian procedures. Due to the given causes it is important to create simpler mathematical models to adequately describe complex physico-chemical reactions of vulcanization.

In the phenomenological analysis of kinetics of mix curing we vividly observe the course of the process on a complex mechanism. At temperature of 443 K the kinetic curve of vulcanization, based on the results of the rheometric tests has the maximum, but the assymetric character of the curve cannot be interpreted with the help of equations of reactions of the first and second order which occur successively. The fractional order of the reversion determined by the methods of formal kinetics presupposes a parallel course of several reactions engaging various active centers of macromolecules. The proposed kinetic model suggests that in the final stage of polysulfide crosslinking, bonds dissociation resulting in formation of products of raw rubber modification by sulfur are accompanied by parallel reactions of cross-linking of elastomer macromolecules by labile polysulfide and stable monosulfide crosslinks. Sulfuric vulcanization of diene raw rubbers, including the stage of reversion, were previously formally described by a system of kinetic equations [1].

The data obtained in the rheometric tests can be used for calculating several alternative variants of the model, but traditional methods of analysis of processes in time don't permit to clearly separate the processes and synergetic interaction.

Solution of the problem required an independent method to determine the number of formal mechanisms of reactions responsible for structurization of the elastomeric composition. There were developed the method and software for providing separation and analysis of parallel processes of cross-linking based on presentation of the process in the frequency area where the kinetic curves are easily linearized and can be interpreted. For further analysis it is desirable to formulate a conjecture on the set of components of the reaction, the type of kinetic law for each of the processes. The given approach permits to use only a specific set of ordinary coupled reactions of the first and second order for describing vulcanization of rubbers under analysis.

Development of the method of analyzing the kinetics of the vulcanization reaction of multicomponent elastomer compositions is based on the fact that individual stages of the vulcanization process significantly differ in speed. Alongside with slow stages of formation of the vulcanization active agent there appear extremely fast stages occurring on the radical mechanism. In similar cases conditions of fast stage quasi-equilibrium are used for solving equations of chemical kinetics.

For determination of the constants of individual stage speed the rheometric curve was divided into several areas: in the first area reactions between the accelerator, activator and sulfur result in formation of an active sulfuring complex which is an active agent of vulcanization (AAV), in the second area AAV leads to formation of cross-links between the raw rubber molecules, and in the third one there prevail reactions of degradation of the vulcanization network.

Constants of individual stages and speed of formation of vulcanization network in each area were determined with the help of methods of formal kinetics. In the first and area the constants k_1 , k_2 and ratio k_4/k_3 were determined by Korans method [1]. The effective value of the constant k_3' was obtained by numerical solution of the equation in the second area within the interval from $t = \tau_{dis}$, corresponding to the complete consumption of AAV, till the time of reaching the vulcanization degree, equal to 95% (τ_{95}):

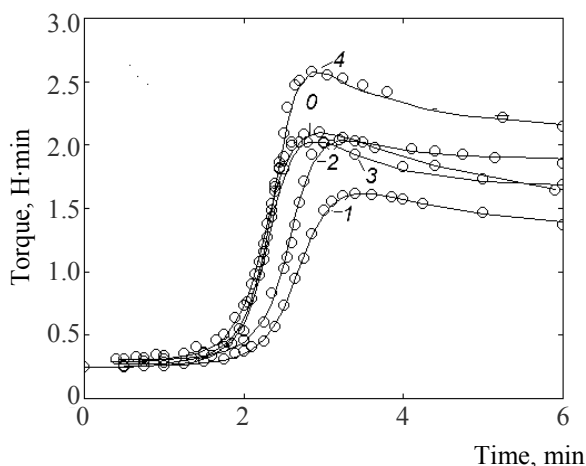
$$C_{Vu} = \frac{C_B}{C_B + 1} \cdot \frac{k_3^1 \cdot e^{k_2(t - \tau_{dis})} - k_2 \cdot e^{k_3^1(t - \tau_{dis})}}{k_2 - k_3^1} - \left(1 - \frac{C_B}{C_B + 1}\right) \cdot e^{k_3^1(t - \tau_{dis})},$$

where C_{Vu} – concentration of vulcanization network units related to maximal density of cross-linking; C_B – relative concentration of pertylny radical; k_3' – effective assessment of the constants k_3 and k_5 . On the basis of this method the constant of units k_6 consumption was determined on the stage of reversion.

The problem-oriented programmed product in language C++ was developed on the basis of exceptional algorithms tested on the experimental and simulated data obtained on the basis of the given model with addition of casual error for solution of direct and inverse problems of isothermic vulcanization kinetics. Solution of the inverse kinetic problem was realized in the form of an algorithm of gradientless search with account of a priori information obtained by solution of the above-mentioned equations. Variants of this program permit to calculate the activation energy of individual stages of the process.

The figure presents the data on investigation of kinetics of synthetic polyisoprene vulcanization by sulfur in the presence of accelerator CBS, stearin and zinc white pigment. The dosage of accelerators, sulfur and stearin acid varied in accordance with the design of the experiment-simplex in three-dimension space which is a part of a compositional three-level plane of the second order. The content of the accelerator, sulfur and stearin in the center of the plane is 1.26, 2.10, 1.41 phr or 6.9, 3.4, 3.5 mmole per 1 mole of double bonds, respectively.

Comparison of the experimental and calculated data (Figure) revealed sufficient similarity of the results. Since decrease of temperature leads to the change of the rheometric curve shape towards increase of the vulcanization plateau there may appear temperature when reversion isn't observed. By excluding from consideration some constants which are in this case equated to zero and simplifying the model by dismissing stoichiometric coefficients it is possible to obtain boundary stationary states. In three cases: $k_5 = 0$ (lack of polysulfide cross-links in the vulcanizate); $k_6 = 0$ (irreversibility of formation of polysulphide cross-links in a vulcanizate) and $k_7 = 0$, $\alpha = \gamma = 1$ (lack of internal formation of molecular bound sulfur) – the solution of the system of kinetic equations describes a vulcametric curve with a very wide vulcanization plateau without reversion. Consideration $k_7 = 0$, $\alpha > \gamma = 1$ describes a vulcametric curve without the maximum with a continually increasing module. In general at $k_i > 0$ all three main forms of vulcametric curves are possible. The shape of the curve depends on the ratio of values of individual stage speed constants k_i and stoichiometric coefficients α , β , γ .



Kinetics of vulcanization at 190°C of rubber mixes based on SKI-3 with various content of vulcanization group phr, respectively sulfur + accelerator CBS:

0 – 2.1 + 1.26; 1 – 1.5 + 0.89; 2 – 3.0 + 0.89;

3 – 1.5 + 1.78; 4 – 3.0 + 1.78;

○ experimental data, — calculated data

This approach to determining the contribution of each reaction to formation of cross-links of the vulcanization network finds it difficult to solve the problem of occurrence of parallel processes of

structurization – destruction and their interrelations. The solution can be found after making some tests of the experimental design made in accordance with the proposed kinetic models. Several alternative variants are calculated on the basis of the obtained data and by the casual method we select a formal mechanism of the reaction which is responsible for elastomer composition structurization.

Conclusion. The proposed approach to describing the kinetics of vulcanization as simultaneous processes of structurization and destruction allows to adjust the previously proposed formal kinetic scheme of vulcanization, to apply the mathematical model to kinetic curves of any shape and to perform analytical assessment of the kinetics of isothermal vulcanization on the basis of economical laboratory experiments.

References

1. Карманова, О. В. Исследование кинетики вулканизации непредельных каучуков с учетом образования металлоорганических комплексов / О. В. Карманова, В. И. Молчанов, Ж. С. Шашок // Труды БГТУ. – 2011. – № 4: Химия, технология орган. в-в и биотехнология. – С. 64–66.

Received 20.03.2012