

УДК 678.028.2:51.001.57(045)

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## DEVELOPMENT OF MATHEMATICAL MODEL OF CURING TWO-PHASE POLYMERIC SYSTEMS

During research of kinetics of curing of two-phase elastomeric composites the new kinetic model, allowed to explain heterogeneity of the grid which was formed in this process of curing crosslink was developed. In numerical experiments it is shown that average extent of sewing together of all system increases more slowly, than when curing in lack of diffusion of vulcanizing substances, and the speed of curing and the general extent of sewing together of a composite as a whole decreases.

**Introduction.** The vulcanized rubber powder is obtained by grinding out-of-products operation rubber. It comprises rubber polymer which undergoes no significant structural changes and can be used for partial replacement of rubber in the rubber compound. These rubber blends are two phase systems in which most particles are pulverized vulcanizate (*PV*) are the dispersed phase and the properties of the manufactured rubber articles are largely determined by the degree of crosslinking during curing phase. Analysis of the patterns of the vulcanization of rubber mixtures filled *PV* shows [1] that, due to the different content curatives in each phase, the process of vulcanization of the dispersed phase and the dispersion medium flows with different velocities.

**Main part.** In industrial environments often use a phenomenological approach to study the kinetics of vulcanization. To this end, a vulcanization reaction conditionally divided into three periods, in each of which the kinetic equation different from that used in the adjacent areas. The number of parameters in these equations is not more than 4, and the order of the reaction is usually fractional. Dependence of reaction rate on temperature is satisfactorily described by the Arrhenius equation.

A more detailed kinetic approach to the description of the curing process requires knowledge of the sequence of chemical reactions leading to the formation of cross-links between the molecules of rubber, so the model should be chosen most accurate diagram of the main reactions. Complex reaction system leads to a system of nonlinear partial differential equations which are typically difficult to solve. Appropriate assumptions and simplifications are made to facilitate the achievement of numerical solutions in most practical cases. Initial assessment of the kinetic parameters can often be obtained through non-linear approximation subroutines rheometric curve.

Important advantages of the kinetic approach, compared with the phenomenological, are as follows: a kinetic approach based on an understanding of the reaction mechanism and embodies a definite

physical meaning, this approach allows you to create a simulation model of the process as a whole, not dividing it into separate time periods, makes it possible to create a generalized isothermal curing model being developed for production environments.

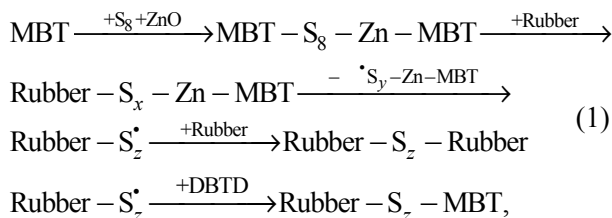
During the vulcanization of mixtures of polymers, due to varying concentrations of the individual phases, interfacial mass transfer occurs molecular compounds. Diffusion of components vulcanizing group leads to the formation of heterogeneous grid crosslinks in different phases. Crosslinking kinetics of each phase can be calculated by the simultaneous solution of systems of equations for several samples with different ratios of the polymer phases and curatives. Solution of the inverse kinetic problem is largely based on the methods of authenticated during the computational experiment.

Preliminary study of the kinetics of vulcanization of various models using computers efficiently plan laboratory experiment to create an adequate description of the curing process, to take into account the possibility of formation of interpenetrating network structures filled above the percolation threshold and to provide assurance allocation class models corresponding to the processes occurring in nonlinear dynamical system of the chemical nature.

Existing methods for measuring the kinetics of vulcanization of rubber based on preposition of proportionality concentration of cross-linking of the shear modulus. Therefore, when analyzing the kinetics of vulcanization single sample can provide information only about the average cross-link density. Crosslinking kinetics of each phase can be calculated only at the joint solving systems of equations for the samples with different ratios of phases. In order to simplify the model used in the *PV* and the original rubber compound made one recipe. Reactivity of each rubber in the same phase can explain difference in the rate of crosslinking during curing phase in the initial concentration of curatives.

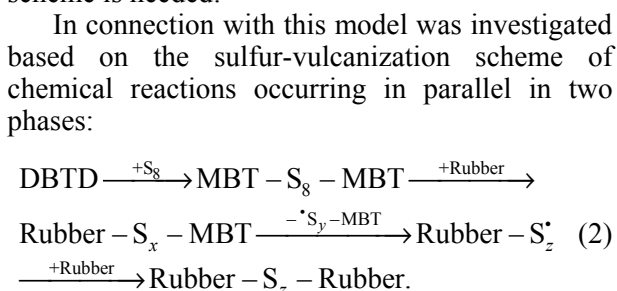
The complex shape changes depending concentration of cross-linking time suggests an inhibitory effect of intermediates. The most probable

reaction mechanisms were determined by the method of systematic kinetic analysis based on the general scheme of possible chemical reactions occurring during curing [2, 3], taking into account the concentration of elastic filler and curing agents. For the rubber composition phase the following reaction scheme is needed [4]:

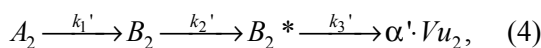
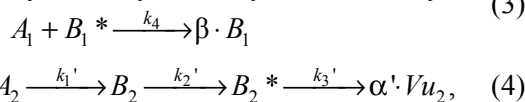
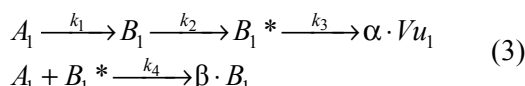


where MBT – mercaptobenzothiazole (product recovery DBTD); S<sub>8</sub> – sulfur molecule; ZnO – zinc oxide; MBT – S<sub>8</sub> – Zn – MBT – sulphurating active agent; Rubber – S<sub>x</sub> – MBT – a product of interaction sulfurizing agent with rubber, rubber – S<sub>z</sub> – pertiilny radical; DBTD – dibenzthiazoldisulfid; Rubber – S<sub>z</sub> – Rubber – tetra-functional unit vulcanite network.

For phase elastic filler the following reaction scheme is needed:



where A<sub>i</sub> – curing agent (MBT – S<sub>8</sub> – MBT or MBT – S<sub>8</sub> – Zn – MBT); B<sub>i</sub> – product of its interaction with rubber (Rubber – S<sub>x</sub> – MBT); B<sub>i</sub>\* – pertiilny radical (Rubber – S<sub>z</sub>\*); V<sub>ui</sub> – tetra – functional unit vulcanizate network (Rubber – S<sub>z</sub> – Rubber); α, β – stoichiometric coefficients. Indices 1 and 2 correspond to the components of the dispersion medium and the dispersed phase. The diffusion of molecules in the two-component curing agent system with the chemical transformations depends on the concentration difference and the rate of chemical reactions:



$$\begin{cases} \frac{d[A_1]}{d\tau} = -D \cdot F \cdot ([A_1] - [A_2]) - \sum_{i=1,4} k_i [A_1], \\ \frac{d[A_2]}{d\tau} = D \cdot F \cdot ([A_1] - [A_2]) - \sum_{i=1,4} k_i' [A_2], \end{cases} \quad (5)$$

where D – mass transfer coefficient; F – area of the interface is proportional to the weight fractional PV; [A<sub>1</sub>] and [A<sub>2</sub>] – concentration of the curing agent in the rubber composition and vulcanized rubber particles, respectively; k<sub>i</sub> and k<sub>i</sub>' – reaction rate constant with participation vulcanizate agent in the phases of the rubber composition and vulcanized rubber.

The model takes the assumption that the concentrations of low molecular weight substances that do not exceed a few percent power spring concentration of components in phases do not depend on the degree of crosslinking of phases, and the rate of diffusion of macromolecules elastomer negligibly small.

In the study of vulcanization are most commonly used: differential scanning calorimetry, chemical analysis and rheometry. Differential scanning calorimetry allows you to explore individual components vulcanizing groups and their interaction in the binary and ternary systems themes, but the interpretation of the data obtained in the study of more complex systems is difficult because of the increasing dimension of the system of equations. Using the oscillating disc rheometer (kyurometra) is based on the fact that the concentration of vulcanizing ties is proportional to the shear modulus vulkanizate sample. Degree of cure can be defined in the following way:

$$X = (G'_t - G'_0) / (G'_\infty - G'_0), \quad (6)$$

wherein X – degree of curing; G'<sub>t</sub> – shear modulus at time t; G'<sub>0</sub> – shear modulus at time 0; G'<sub>∞</sub> – shear modulus after vulcanization reaction.

It was assumed that the mechanical behavior system is described by simple models consisting of two components with different elastic modules, for example: the shear modulus G, which determines the amount of torque when tested on reometer, obeys Takayanagi [5]:

$$G = \left( \frac{\varphi}{(1-\lambda) \cdot G_1 + \lambda \cdot G_2} + \frac{(1-\varphi)}{G_2} \right)^{-1}, \quad (7)$$

where G<sub>1</sub> and G<sub>2</sub> – elastic modules components – phase and the dispersion medium, respectively; λ и φ – empirical parameters, reflecting the nature of mixing the composition product is equal to the volume fraction of the dispersed phase.

Original research and filled with carbon black P-234 compositions based on rubber SKS-30ARK filled 0 – 50 pts. wt. pulverized vulcanizate with particle size 0.25 – 0.50 mm, was performed on a rheometer Monsanto-100S. The kinetic curve for the original rubber composition is adequately described by the equations of the Quran [3, 4], but the description of the kinetics of vulcanization

filled crumb composition equations only the Koran does not result in agreement with experimental data.

In the computational experiment has been investigated a number of models. Fig. 1 shows the simulation results for the two models with different values of the coefficient of mass transfer between phases.

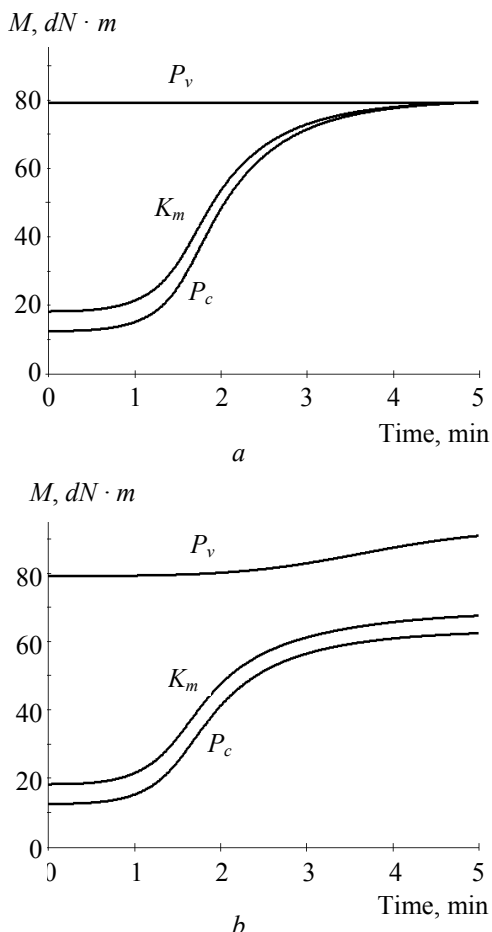


Fig. 1. Structuring kinetics for models of the composite filled 20 pts. wt. crushed rubber: *a* – for lack of a mass transfer, ( $D=0$ ); *b* – in the conditions of a mass transfer ( $D=1$ );  $P_v$ ,  $P_c$  extent of structuring crushed rubber and rubber mix;  $K_m$  – average extent of sewing together of a composite, in relative units given to a reometric curve for rubber mix

Analyzing the kinetic curves for the composition  $K_m$  model (*b*), taking into account the diffusion of curatives, allows us to describe the increase in torque after achieve optimum technical vulcanization.

To determine the rate constants for the individual stages of vulcanization rheometric curve was divided into three areas: an induction period, the grid forming crosslinks between the molecules of the rubber, vulcanization reversion region grid. In each of the selected areas by the Qur'an [6] deter-

mined the constants of the first and second stages of  $k_1$ ,  $k_2$  and the ratio of the rate constants of the fourth and third stages  $k_4/k_3$  (table).

Table  
Effective values of speed constants  
of filled rubber mixes at 463 K

Content PV, pts. wt.	$k_1/k_1'$	$k_2/k_2'$	$k_3/k_3'$	$k_4/k_4'$
0,0	0,21/-	2,49/-	20,9/-	249/-
5,0	0,12/0,12	2,6/1,9	20,3/17,3	350/358
10,0	0,12/0,16	2,7/2,3	20,8/15,3	379/392
20,0	0,12/0,08	2,7/2,4	20,0/17,8	320/350
50,0	0,07/0,10	3,1/3,0	20,3/19,6	369/477

The obtained values of constants used as an initial approximation for the subsequent determination of kinetic parameters of reactions. Integration of the system of ordinary differential equations was carried out by the Runge-Kutta method of order 5. Solution of the inverse kinetic problem was conducted by Powell for minimized functional  $F(k)$ :

$$F(k) = \sum_{i=1}^N w_i \sum_j \left[ y_{ij}(k, t_j) - x_{ij}(t_j) \right]^2, \quad (8)$$

where  $k$  – constants of individual reaction steps,  $N$  – number of experiments carried out at different concentrations of crushed vulcanizate;  $w_i$  – weights;  $y_{ij}(k, t_j)$  – calculated values of the shear modulus;  $x_{ij}(t_j)$  – experimental values.

Average relative deviations between the model and the experimental values do not exceed 2%. Shown in Fig. 2 The system of equations (1) - (4) for a mixture containing 20 pts. wt. crushed vulcanized adequately describes the experimental data (Fisher's exact test,  $F = 235,3$ ).

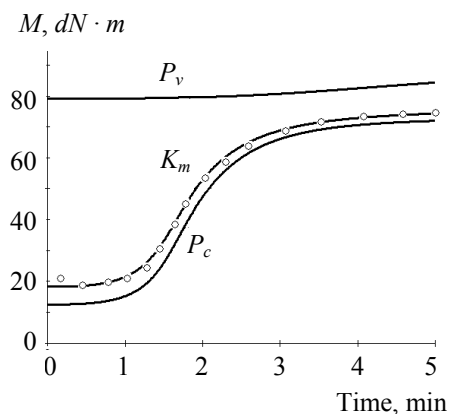


Fig. 2. Kinetics of sulfuric curing at 463 K compositions from SKS-30ARKP filled 20 pts. wt. crushed rubber:  $\circ$  – experimental values,  $P_v$ ,  $P_c$  – extent of structuring crushed rubber and rubber mix;  $K_m$  – average extent of sewing together of a composite

**Conclusion.** Model studies show that the initial concentration gradient between the phases of the vulcanizing agents and similar rate constants degree phase vulcanization of the rubber composition, vulcanized fast to the end of the process is lower than in the absence of diffusion. The qualitative analysis of the model revealed a mechanism for accelerating the process of vulcanization of rubber compounds in the presence of *PV*. The average value of the shear modulus of the entire system increases slower than in the absence of mass transfer vulcanization, and vulcanization rate and total crosslinking degree of the composite generally is reduced.

During vulcanization the formation of chemically inhomogeneous structure of chemical spatial grid near the particles takes place. It affects the strength of compositions containing vulcanized rubber powder. The rate of crosslinking is less than *PV*, but the degree of crosslinking after curing process is higher. The average degree of crosslinking of the entire system ( $K_m$ ) increases slower than in absence of diffusion vulcanization curatives.

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*Received 01.01.2013*