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MODELING OF KINETICS OF NONISOTHERMAL VULCANIZATION
OF MASSIVE RUBBER PRODUCTS

The problem of vulcanization (curing) of massive products is considered important for technology of processing of polymers. It is shown, that during structurization compound rubber materials distribution of temperatures on all section is unequal, that results in distinction in structure and properties of such samples. Temperature fields in cuts of a product are designed and dependences of change of structural parameters are established. Kinetic characteristics of process of vulcanization are determined and recommendations on creation and updating of modes of vulcanization massive elastomer products are produced.

Introduction. The modern understanding of a chemical reaction as a dynamic system with nonsteady and nonlinear behavior allows to develop special control methods of vulcanization process, taking into account the non-ideality of the reaction medium. In terms of thermal impact on the object, vulcanization consists in heating a product up to the desired temperature and aging it at this temperature for a predetermined time [1]. One of the most significant factors determining the duration of vulcanization and defining the quality of the product is the cure rate [2–4], which is characterized by the number of formed cross-links between macromolecules per unit time.

When curing the temperature on the surface and in the center of the thick-walled products is unequal. The process takes place in a continuous increase of the temperature in the inner layers, as their heating flows slowly due to low thermal conductivity of the rubber mixture. If the process duration is defined by the conditions necessary to ensure the desired degree of structuring in the center of the product, the surface layers, especially at efficient heat transfer, will be greatly overvulcanized. There appears the danger of scorching, which leads to a loss-of necessary technological and operational properties. The rate of temperature change inside the rubber mixture preform under transient thermal process depends on the thermal physical characteristics of shape and size of curable workpiece, heat transfer conditions and the kind of coolant. The rate of temperature change can be affected by the thermal effect of vulcanization due to the nature and content of the curing agent [4–5].

To reduce the heterogeneity of the properties of the thick-walled articles in the vulcanization they are not recommended to be cured at very high temperatures. In determining the duration of such products curing one should be aware that structuring especially in their center continues for some time after the end of the heating due to the heat absorbed. Therefore, it is not necessary in the heating process to achieve full curing throughout the thickness of the workpiece. To reduce the heterogeneity of warming the heating should be staged or the rubber mixture should be preheated.

The degree of vulcanization of rubbers in the products depends both on their vulcanization characteristics and the temperature of the coolant, its thermal resistance, vulcanization duration, the total thickness of the product, its configuration, the distance of the rubber mixture from the heated surface, thermal physical properties of rubber [6].

For curing thick walled products it is advisable to use heat transfer medium with relatively low parameters in terms of uniformity of temperature fields and the degree of vulcanization. However, such process is time-consuming, that being uneconomical. Rubbers with a sufficiently large induction period, with high speed of subsequent curing and low tendency to reversion are the best decision. In such a process poorly warmed plots of the product will be vulcanized due to the high speed of the process to the optimum, and the surface layers will not be overvulcanized because of the large plateau of vulcanization. Thus, the selection of the vulcanization mode of thick walled products is an important technological problem, it being necessary to recognize that the polysulfide grid, formed during curing i.e. its density determines the properties of the product.

Main part. The temperature of massive elastomeric products throughout the cross section varies during the process of structuring, and hence the degree of curing is different. In this connection there appears necessity of research of the curing process of such samples and to estimate the distribution of temperature field over the entire section. The results of the experiment will allow us to give recommendations on the restablishment and adjustment modes of vulcanization.

The aim of the study is to establish the patterns of change in the speed of structuring tire tread compounds, depending on the change of curing temperature and concentration of the components.

The distribution of the content of free sulfur in the sample is asymmetric and close to the logarithmic-normal random distribution due to poor dispersion of the components.

The experimental samples produced by duplicating and subsequent vulcanization of rubber mixtures of different compositions as well as automotive tires sections in the radial direction were the objects of our research.

The process of formation of the vulcanizates spatial grid was studied by the process of equilibrium swelling in metaxylene. The degree of crosslinking was evaluated by the geometrical dimensions, obtained by means of an optical microscope i.e. initial samples diagonals; diagonals of samples swollen in a solvent for an hour; diagonals of dried for an hour samples were measured.

The equilibrium swelling degree [q_{eq}] was found from the correlation

$$q_{eq} = \frac{2}{\dfrac{L_{dr.s.}^3}{L_{sw.s.}^3} + \dfrac{L_{dr.l.}^3}{L_{sw.l.}^3}},\qquad(1)$$

where $L_{dr.s.}$, $L_{dr.\ l.}$ – diagonal length (smaller and larger) of the dry sample, mm; $L_{sw.s}$, $L_{sw.l}$ – smaller and large length of the diagonals of the swollen sample mm.

To determine the concentration of crosslinking Schwartz technique, based on the weight of the swollen sample was used. Equilibrium degree of swelling ($Q_{eq.}$) which characterizes the marginal increase of the polymer with limited swelling and content of more than 5% of soluble ingredients in a sample was determined by the formula

$$Qeq = \frac{\rho_r}{\rho_s} \cdot \frac{Pd - P_s}{P_s \cdot F},\qquad(2)$$

where p_r, p_s – density of rubber and solvent respectively, g/cm³; P_d, Ps – weight of dry and swollen sample respectively, g; F – relative content of hydrocarbon of rubber in the sample.

The molecular weight of the polymer chain segment (M_g) between the nodes of the spatial grid of the vulcanizate is defined as

$$M_g = \frac{\rho_k \cdot V_s \cdot (V_2^{1/3} - 1/2 \cdot V_2)}{\mu \cdot V_2 + V_2^2 + \ln(1 - V_2)},\qquad(3)$$

where V_s – molecular volume of the solvent; V_2 – polymer volume ratio at equilibrium, i. e.

$$V_2 = \frac{1}{[1 + Q_{pab}]}.\qquad(4)$$

Effective concentration of crosslinks in the vulcanizate n_{ef} was determined from the relation

$$n_{ef} = \frac{\rho_k \cdot N_a}{2 \cdot M_g},\qquad(5)$$

where $N_a = 6{,}023 \cdot 10^{23}$.

Analysis of the experimental curves given in Fig. 1, showed that there observed change in the degree of vulcanization during the transition from the outer layer to the inner: concentration of crosslinking decreases on the distance about 10 mm from the heating surface.

The degree of curing practically does not change near the outer layer and testifies to the isothermal mode of curing on the surface; the remaining sections curing takes place under the conditions of variable temperatures.
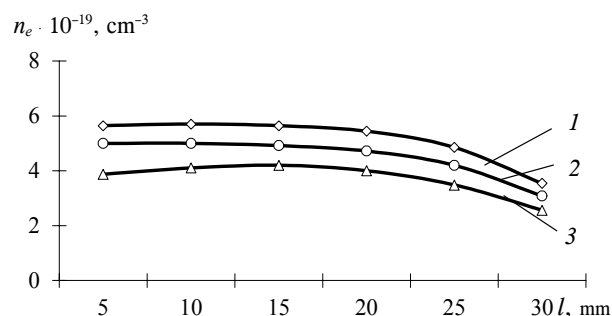

Fig.1. Dependence of the concentration of cross links on the distance from the heating surface:
1 – 145 ° C; *2* – 155 ° C; *3* – 165 °C

It is well known [7–8] that gradients of temperature and time in the rubber vulcanization can be estimated by simultaneous examination of internal heat release during the reaction, heat conduction through the surface of mold rubber, the mass of rubber, heat transfer by convection from the mold (or rubber) in the surrounding space.

Factors impeding the solution of this problem include: determination of the thermal properties dependence of rubber on the temperature; the presence of the internal heat releasing as a result of vulcanization; presence of heat transfer by convection from the mold (or rubber).

Uneven degree of vulcanization on the entire cross section of the tire can lead to some reversion of properties of rubber. Therefore, further studies were carried out in the direction of selection vulcanization conditions ensuring consistency of physical and mechanical properties.

To determine the temperature gradient during curing, and a gradient of curing degree (degree of curing in this case must be regarded as a measure of the thermal effect of the elastomer released till a certain time) is possible by using parameters such as the temperature of the mold, the thickness of the sample and others.

In case of the heat transfer directed through the rubber sample of thickness L general unsteady heat conduction equation, taking into account the internal heat of the curing reaction is as follows:

$$\frac{\partial T}{\partial t} = \frac{1}{\rho \times c} \times \frac{\partial}{\partial x} \left[\lambda \times \frac{\partial T}{\partial x} \right] + \frac{1}{\rho \times c} \times \frac{dQ}{dt}. \qquad (6)$$

The initial conditions: $t = 0$; $0 < x <$ L; $T = T_o$ (rubber array). Boundary conditions: 1) a rubber array: $t > 0$; $x < 0$ and $x > L$; $T = T_m$ (mold surface), $0 < x < L$; $T = T$xt (rubber array); 2) in the case when the cooling takes place after discharging the rubber from the mold: $t > 0$; $x < 0$ and $x > L$; $T = T_{air}$ (air space).

$$\frac{I}{Q_*} \times \frac{dQ_i}{dt} = K_0 \times \left[\frac{Q_* - Q_t}{Q_*} \right]^n \times \exp^{-\frac{E}{RT}}, \qquad (7)$$

where Q_i – heat of vulcanization reaction released during the time t; Q_t – thermal efficiency of the vulcanization reaction per unit of the rubber array; E – activation energy; K_0 – reaction rate constant; n – order of reaction; λ – thermal conductivity; ρ – density; c – thermal capacity of the rubber sample.

The results were obtained using the numerical finite difference method According to the proposed model, the sample is divided into identical finite layers of thickness Δx.

$$T_{i+1,\,n} = \frac{1}{M} \left[T_{i,n-1} + (M-2)T_{i,n} + T_{i,n+1} \right] + \frac{1}{\rho \times c} \times \frac{\Delta Q}{\Delta t} \Delta t. \quad (8)$$

Using the software package Mathcad we calculated temperature fields in the cuts (sections) of product (Fig. 2).
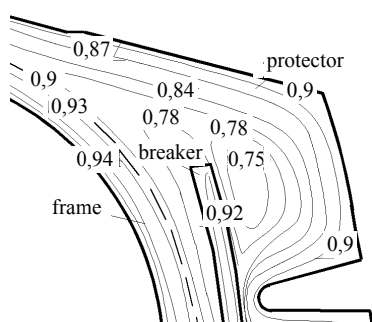
Fig. 2. The estimated degree of vulcanization
of rubber at the least heated zone of the tire 9.00 / 20

It was found that the degree of vulcanization for cuts of product varied. The number of cross-links is higher nearby the heating surface. The concentration of crosslinking decreases with distance from the mold surface. A sharp drop of n_1 near the metallic surface indicates that during vulcanization the outer layer, being vulcanized in a practically isothermal mode undergoes reversion.

Analysis of the data in Fig. 3 shows that the maximum effective concentration of crosslinking n_l corresponds to the minimum content of free sulfur. This confirms the conclusion that with increasing temperature the structuring takes place more rapid.
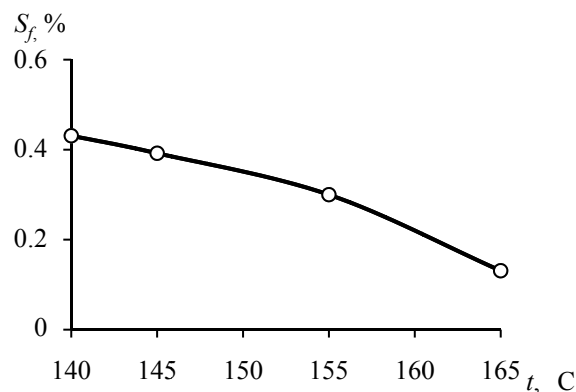
Fig. 3. The content of free sulfur in vulcanizates

The increase of the amount of crosslinking during the curing process occurs up to an optimum, further their reduction is observed: the value n_1 at the end of curing is lower than in the beginning, i.e. the degradation of crosslinks formed occurs.

It should be noted that in the optimum of curing and at subsequent plateau at all studied temperatures the degree of crosslinking is practically unchanged.

To determine the effect of curing conditions (isothermal, non-isothermal mode) on the properties of rubbers the kinetics of the process was investigated by using a "Monsanto" rheometer. According to the reokinetic tests a logarithmic dependence of the dynamic modulus of R on time was built. (Fig. 4). The constant K_2 was determined graphically, the constant K_1, was calculated by the formula

$$K_2 \times \tau_{dis} = - \ln(z / (1 - z)), \qquad (9)$$
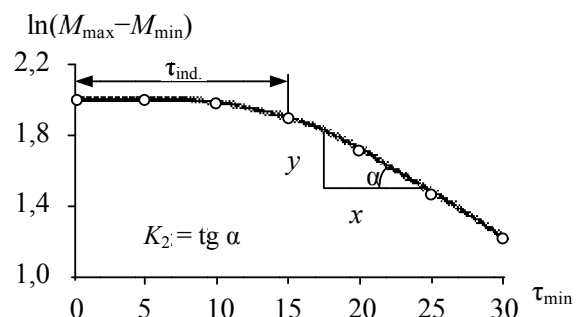
where $z = K_1 / K_2$.

Fig. 4. Logarithmic dependence of the dynamic module
on the duration of vulcanization

The dependences of the change of the vulcanization rate constants of the tread rubber are shown in Fig. 4. It has been established that when

curing at steady state the effect of temperature has less influence on the change of vulcanization properties.
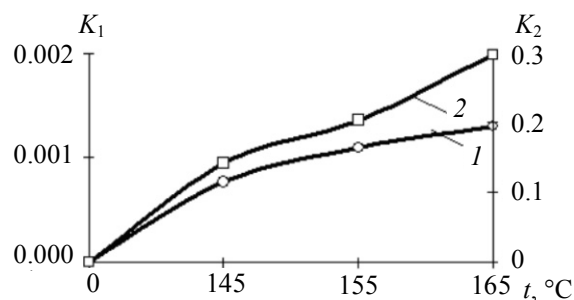

Fig. 5. The dependences of the vulcanization rate constants change on temperature: 1 – the rate constant in the induction period of vulcanization, K_1; 2 – the rate constant in the main period of vulcanization, K_2

The results of the temperature measuring in the central section of the tread during postvulcanization allowed to determine the dependence of the temperature in the center on the time-of the process (Fig. 6).
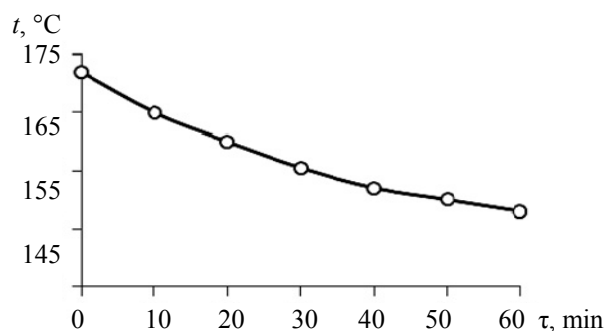

Fig. 6. The time-temperature dependence of post-vulcanization

Modeling of non-isothermal vulcanization was carried out in the package "physical modeling" MV Studium. The model has included a timer that specifies the simulation time; interpolation blocks, changing the value of the temperature at a predetermined timing; block of pulse generator; adder; and a block solving a system of differential-algebraic equations. Satisfactory convergence of results developed by computational methods for the determination of the kinetics of non-isothermal rubber vulcanization and experiment has been established.

Conclusion. Thus, it was found that the degree of crosslinking of massive samples is not the same over the cut of the product, that being confirmed by calculations of temperature fields. When increasing the temperature the differences in the degree of vulcanization are more noticeable, that indicating irregularity of curing at high temperatures. Calibration dependence of the "temperature curing time" allows to calculate required vulcanization time for each mold and temperature. Kinetic cure characteristics and data on the degree of crosslinking allow to determine the temperature and degree of cure at any point of the product. The use of the model of non-isothermal vulcanization for real systems will permit to develop a more optimal vulcanization control algorithm.

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