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Determination of thermophysical characteristics of vulcanizable rubber products by the mathematical modeling method

S G Tikhomirov[1], Y V Pyatakov[1], O V Karmanova[2] and A A Maslov[1]

[1] Information and control systems department, Voronezh state university of engineering technologies, Revolution Av., 19 Voronezh, Russia
[2] Chemistry and chemical technology of organic compounds and polymers processing department, Voronezh state university of engineering technologies, Leninsky Av., 14 Voronezh, Russia

E-mail: tikhomirov_57@mail.ru, pyatakovjv@mail.ru, karolga@mail.ru, imasslove@mail.ru

Abstract. The studies of the vulcanization kinetics of elastomers were carried out using a Truck tyre tread rubber compound. The formal kinetic scheme of vulcanization of rubbers sulfur-accelerator curing system was used which generalizes the set of reactions occurring in the curing process. A mathematical model is developed for determining the thermal parameters vulcanizable mixture comprising algorithms for solving direct and inverse problems for system of equations of heat conduction and kinetics of the curing process. The performance of the model is confirmed by the results of numerical experiments on model examples.

1. Introduction

The intensification of the process of vulcanization is one of the main ways to reduce the cost of production of rubber products. Calculated methods for developing vulcanization regimes are the most effective and economically viable. They are based on modern theoretical concepts of heat transfer and kinetics of vulcanization. Also they allow to analyze and search the optimal mode of curing as existing in real production and design. This makes it possible at the design stage to evaluate the technological possibilities for implementing new designs and to plan the choice of materials and equipment.

The change in properties of vulcanization of rubber typically passes through the following four stages:

Stage I An induction period. There is no significant change in properties compared with raw rubber;

Stage II The vulcanization process. The rubber properties change monotonically, reaching the optimum properties of the vulcanized rubber;

Stage III The vulcanization plateau. The properties are maintained at the optimum level;

Stage IV Reversion or re-vulcanization. The properties of rubber deteriorate compared with the optimal.

In the presence of a vulcanization plateau, expensive thermal energy will be consumed in case of overheating. And in the case of underheating of a particular site the required set of properties will not be achieved and the product will be of poor quality. In connection with foregoing, it is very important

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to choose a vulcanization mode, which provides high quality products with the least energy costs, that is very important in the context of a continuous increase of energy prices.

For quantify the kinetics of vulcanization of rubbers under variable temperature conditions various methods have been proposed [1-3]. The most widely used method is reduced to calculating the effect of E and the equivalent time τ of vulcanization. To calculate the effect of vulcanization, the concept of intensity of vulcanization I is introduced as a quantity characterizing the rate of change of the acquired vulcanization properties of rubber depending only on changes in vulcanization temperature t. Taking the vulcanization intensity at temperature t_o as a unit, the intensity at temperature t in dimensionless units is expressed as follows [4]:

$$I = \frac{K \cdot (t - t_0)}{10}.$$

The effect of vulcanization E in the time interval from τ_1 to τ_2 for variable temperature and constant temperature coefficient of vulcanization K is represented in the following form:

$$E = \int_{\tau_1}^{\tau_2} K^{\frac{t(\tau)-t_0}{10}} d\tau.$$

To evaluate the effect of variable temperatures $t(\tau)$ it is necessary to know how the temperature t is changing in time τ and which values have temperature coefficient of vulcanization. Therefore, physical and mathematical modeling of temperature fields and degrees of vulcanization of rubbers in the product are used to optimize the vulcanization process of rubber products in the modern technology.

Equivalent time must be calculated and associated with vulcanization characteristics of rubbers for all layers of the product, especially for the internal, poorly heated and outer, highly heated layers where there is a danger of correspondingly under-vulcanization or re-vulcanization. The reaction rate of vulcanization and the degree of its perfection depend on the temperature of vulcanization, and therefore depend on the amount of heat supplied to the system [5] and released as a result of the reactions [3]. The amount of heat released during the reaction increases as the vulcanization temperature rises. The kinetics of heat release is correlated with the kinetics of addition of sulfur reaction.

It is established [7] that an increase in the vulcanization temperature practically does not affect the value of the coefficient of thermal conductivity, but reduces the value of thermal diffusivity of rubber compounds. Thus, thermophysical characteristics of rubbers significantly affect the process of heat transfer, however, they are not well studied for rubber compounds based on rubber regular structure.

2. Materials and methods

The kinetics of vulcanization was investigated using samples of the model rubber compounds based on butadiene-sterile rubber and industrial rubber compound based on a combination of stereoregular isoprene, butadiene, and styrene-butadiene rubbers intended for the production of tread of truck tires. Cylindrical samples of height 25 mm and diameter of 50 mm were vulcanized at various temperatures between the plates of the experimental setup equipped with sensors for temperature control in the sample at the surface of the plates and in the center.

The intensification of the process of vulcanization is one of the main ways to reduce the cost of production of rubber products. The calculated methods for developing vulcanization modes are the most effective and economically viable. They are based on modern theoretical concepts of heat transfer and kinetics of vulcanization. Also they allow to analyse and search the optimal mode of curing as existing in real production and design. This makes it possible at the design stage to evaluate the technological possibilities for implementing new designs and to plan the choice of materials and equipment.

Based on the analysis of literature data on the mechanism and kinetics of vulcanization of rubbers sulfur-accelerator vulcanizing systems formal kinetic scheme is proposed. This scheme, shown in Figure 1, generalizes a set of reactions occurring in the process of vulcanization.

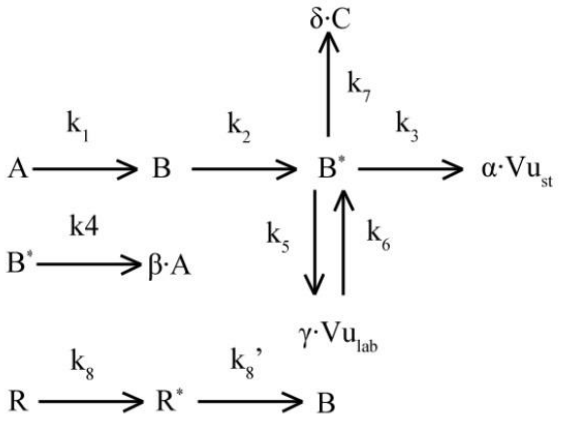


Figure 1. A kinetic scheme of vulcanization process.

A is the actual vulcanizing agent, *B* is the crosslinking precursor, *B** is its active form, *C* is the intramolecular bound sulfur, Vu_{St}, Vu_{Lab} are the stable and labile sites of the vulcanization grid, *R* is the rubber, *R** is the macroradical of the rubber, formed as a result of thermofluctuation decay; α, β, γ and δ are stoichiometric coefficients, k_1, k_2, k_3, ..., k_8, k_9 (k_8') are reaction rate constants related to the corresponding stages of the process.

3. Materials and methods

3.1. Formulation and solution of the direct problem for the system of equations of the kinetics of the process of vulcanization

The set of reactions occurring in the vulcanization process is described by a system of differential equations (DE):

$$\begin{cases} \dfrac{dC_A}{dt} = -k_1 \cdot C_A - k_4 \cdot C_A \cdot C_{B^*}, \\ \dfrac{dC_B}{dt} = k_1 \cdot C_A - k_2 \cdot C_B + \beta \cdot k_4 \cdot C_A \cdot C_{B^*} + k_9 \cdot C_{R^*}, \\ \dfrac{dC_{B^*}}{dt} = k_2 \cdot C_B - (k_3 + k_5 + k_7) \cdot C_{B^*} + k_6 \cdot C_{VuLab} - k_4 \cdot C_A \cdot C_{B^*}, \\ \dfrac{dC_{VuSt}}{dt} = \alpha \cdot k_3 \cdot C_{B^*}, \\ \dfrac{dC_{VuLab}}{dt} = \gamma \cdot k_5 \cdot C_B - k_6 \cdot C_{VuLab}, \\ \dfrac{dC_C}{dt} = \delta \cdot k_7 \cdot C_{B^*}, \\ \dfrac{dC_{R^*}}{dt} = k_8 \cdot C_R - k_9 \cdot C_{R^*}, \\ \dfrac{dC_R}{dt} = -k_8 \cdot C_R. \end{cases} \quad (1)$$

Initial concentration:

$$\begin{cases} C_A(0) = \varsigma \cdot [S_8] \cdot [A_C] \cdot [Akt]^{\theta} \cdot [C_R(0)]^{\eta}, \\ C_B(0) = 0, \\ C_{B^*}(0) = 0, \\ C_{VuSt}(0) = 0, \\ C_{VuLab}(0) = 0, \\ C_C(0) = 0, \\ C_{R^*}(0) = 0, \\ C_R(0) = C_R(0)^{\eta}. \end{cases} \quad (2)$$

The temperature dependence of the rate constants of the process is determined on the basis of generalized equation of Arrhenius [5]:

$$k_i(T) = k_{i0} \cdot e^{-\frac{E_i}{R \cdot T}}, \qquad i = 1,2,\dots,9 \quad (3)$$

Further, the direct problem of kinetics (DPK) is the problem of finding the concentration of vulcanization nodes as a function of time.

When solving the DPK, the process is considered proceeding according to the proposed scheme (Figure 1). The purpose of the solution is to find the concentration of vulcanization nodes relative to the maximum cross-link density as a function of time.

$$X(t) = \frac{\left(C_{VuSt}(t) + C_{VuLab}(t)\right)}{C_{max}}, \qquad C_{max} = \max_{t \in [0,t_k]} [C_{VuSt}(t) + C_{VuLab}(t)]. \quad (4)$$

The problem reduces to the solution of the DE system (1-3), which is carried out by the Runge-Kutta method.

The expression for reaction rate constants (3) contains the temperature T, which is due to the need to determine the temperature fields in the products to be vulcanized.

At the present time, more and more widespread methods are found for calculating the temperature fields in the development of thermal vulcanization regimes, along with the experimental determination of temperatures. [1, 2]. The necessity for preliminary determination of thermophysical characteristics (TC) - heat capacity coefficients, thermal conductivity, etc., which depend on the temperature and composition of the cured mixture - is one of the complexities of using computational methods [1,2].

3.2. The formulation of the direct problem for the system of heat conduction equations

The methodology of calculation of thermophysical parameters of the mixture in the present work is based on the mathematical model represented by the heat equation:

$$C(T) \cdot \frac{\partial T(l,t)}{\partial t} = \lambda \cdot \frac{\partial^2 T(l,t)}{\partial l^2} + q(l,t), \qquad l \in (0,L), \qquad t \in (0,t_k). \quad (5)$$

$$T(l,0) = T_0(l), \qquad l \in [0,L]. \quad (6)$$

$$T(0,t) = T_{top}(t), \qquad T(L,t) = T_{bottom}(t), \qquad t \in [0,t_k].$$

(7)

In equations (5)-(7) *T(l,t)* are temperature; *q(l,t)* is heat release density at a point at $l \in [0, L]$ at time *t*:

$$q(l,t) = q_0 \cdot m_s \cdot \frac{\partial X(l,t)}{\partial t}. \quad (8)$$

X(l,t) is degree of completeness of the process of vulcanization; q_0 is the coefficient of heat release; m_s is mass fraction of sulfur in the mixture and composition of the rubber compound; *L* is the thickness of the test sample; t_k is the final time moment; *C(T)* is the coefficient of the volume heat capacity and its dependence on temperature are approximated by a linear function of the form:

$$C(T) = C_0 + C_1 \cdot T, \quad (9)$$

λ is coefficient of thermal conductivity.

In the future, direct task (DPK) for the system of heat conduction equations will be called the task of determining the function *T(l, t)* satisfying the equation (5), primary (6) and boundary (7) conditions for given values of thermophysical parameters C_0, C_1, λ.

4. Results and discussion

4.1. The solution of the direct problem for the system of heat conduction equations

We introduce a function *S(T)* defined as follows:

$$S(T) = \int_0^T C(T')dT' = \int_0^T (C_0 + C_1 \cdot T') \cdot dT' = C_0 \cdot T + \frac{C_1}{2 \cdot T^2}, \quad (10)$$

In this case, equation (5) can be written in the form

$$\frac{\partial S\big(T(x,t)\big)}{\partial t} = \lambda \cdot \frac{\partial^2 T(l,t)}{\partial l^2} + q(l,t), \qquad l \in (0, L), \qquad t \in (0, t_k). \quad (11)$$

The initial condition (6) will be:

$$\begin{cases} S(l,0) = S_0(l); \\ \Lambda(l,0) = \Lambda_0(l). \end{cases} \quad l \in [0, L] \quad (12)$$

Accordingly, the boundary conditions (7) will have the form

$$\begin{cases} S(0,t) = S_{top}(t); \\ S(L,t) = S_{bot.}(t); \\ \Lambda(0,t) = \Lambda_{top}(t); \\ \Lambda(L,t) = \Lambda_{bot.}(t). \end{cases} \quad t \in [0, t_k] \quad (13)$$

In (12), (13):

$$\begin{cases} S(l,0) = S\big(T(l,0)\big); \\ S_{top}(t) = S\left(T_{top}(t)\right); \\ \Lambda(l,0) = \Lambda\big(T(l,0)\big); \\ \Lambda_0(l) = \Lambda\big(T_0(l)\big); \\ S(0,t) = S\big(T(0,t)\big); \\ S(L,t) = S\big(T(L,t)\big); \\ \Lambda(0,t) = \Lambda\big(T(0,t)\big); \\ \Lambda_{top}(t) = \Lambda\left(T_{top}(t)\right). \end{cases} \quad (14)$$

We use explicit difference scheme to solve the differential equation (11) under conditions (12)-(14):

$$S_k^{n+1} = S_k^n + \frac{\Delta t \cdot \lambda \cdot (T_{k+1}^n - 2T_k^n + T_{k-1}^n)}{\Delta l^2} + q_0 \cdot \Delta t \cdot \frac{\partial X(l_k, t_n)}{\partial t}; \quad (15)$$

$$T_k^{n+1} = \frac{2 \cdot S_k^{n+1}}{\sqrt{C_0 \cdot C_1 + 2C_1 \cdot S_k^{n+1}} + C_0}; \; k = 1,2,\dots,K-1; n = 1,2,\dots,N-1. \quad (16)$$

$$S_k^n = S(T_k^n);\; L_k^n = L(T_k^n);\; T_k^n = T(l_k, t_n);\; l_k = \Delta l \cdot k;\; t_n = \Delta t \cdot n;\; \Delta l = \frac{L}{K}; \Delta t = \frac{t_k}{N}.$$

K is number of intervals over the spatial variable, *N* is number of sampling intervals by time. To ensure the stability of the solution (15), (16) the sampling intervals selected from the condition:

$$\Delta t \le \frac{C_0 \cdot \Delta l^2}{2\lambda}. \quad (17)$$

The right side of equation (11) contains the value *q(l,t)* that is determined by the relation (8) in terms of the quantity *X(l,t)*, which according to (4) is determined by solving the system of equations (1), (2). In turn, rate constants included in (1) on the basis of Arrhenius equation (3) are functions of the temperature.

Thus the solution of the direct problem of heat conduction and the direct problem of the kinetics is the simultaneous solution of equations (1), (2) and (5)-(7), which we carry out iteratively in the following sequence:

- to suppose as the initial approximation in (8) $X(l,t) = X^0(l,t) = 0$, calculate temperature $T(l,t)$ with $X(l,t) = X^{(0)}(l,t) = 0$ using the algorithm (16) and suppose $T^{(0)}(l,t) = T(l,t)$;
- to substitute the value $T^{(0)}(l,t)$ into the expression for the rate constants (3) and determine the value $X^{(1)}(l,t)$ by solving the system of equations of the kinetics (1)-(4);
- to calculate temperature $T^{(1)}(l,t)$ with $X(l,t) = X^{(1)}(l,t)$ using the algorithm (16).

As a condition of completion of the iterative process it is supposed the condition

$|T^{(m+1)}(l,t) - T^{(m)}| < \xi$ where ξ is a given accuracy of calculations.

4.2. Determination of thermophysical parameters

The inverse problem of heat conduction means the problem of determining the thermophysical parameters *C0, C1, λ, q0* using measured values of temperature of test specimens based on the reference data on thermophysical characteristics of the ingredients of the mixture.

T(l,t) is supposed function satisfying the system of equations (5)-(7). Then, the same function satisfies the system of equations of the form:

$$(1 + x_1 \cdot T) \cdot \frac{\partial T(l,t)}{\partial t} = x_2 \cdot \frac{\partial^2 T(l,t)}{\partial l^2} + x_3 \cdot m_s \cdot \frac{\partial X(l,t)}{\partial t}, \qquad l \in (0, L), \qquad t \in (0, t_k), \tag{18}$$

$$T(l,0) = T_0(l), \qquad l \in [0, L] \tag{19}$$

$$T(0,t) = T_{top}(t), \qquad T(L,t) = T_{bottom}(t), \qquad t \in [0, t_k] \tag{20}$$

$$x_1 = \frac{C_1}{C_0}, \qquad x_2 = \frac{\lambda_1}{C_0}, \qquad x_3 = \frac{q_0}{C_0}.$$

On the other hand, if the function *T(l, t)* satisfies the system of equations (18)-(20), then it will satisfy the system of heat conduction equations (5)-(7) when the values of thermophysical parameters: *S0=C0, C1=C0• x1, λ = C0• x2, q0= C0• x3*.

The values of the parameters x1, x2, x3 are determined by minimizing the function

$$F(x) = \sum_{m=1}^{K^{samp.}} \sum_{i=1}^{N_m} [T_{i,m}^{meas.} - T_m^{calc.}(\boldsymbol{x}; l_0, t_i)]^2 \tag{21}$$

where $\boldsymbol{x}=(x_1, x_2, x_3)^T$, $T_{i,m}^{meas.}$ are values of the temperature of *m-th* testing sample in the middle part ($l_0=L/2$), measured in time t_i, the; $T_m^{calc.}(\boldsymbol{x}; l_0, t_i)$ are values of temperature for given values of the $\boldsymbol{x}$ calculated by solving the system of equations (18)-(20); $K^{samp.}$ - the number of samples.

The value of the parameter C_0 is determined depending on the composition according to the reference data. Indeed, the $m_1, m_2, \ldots, m_M$ are supposed as mass fraction of the ingredients of the mixture; *M* is the number of ingredients; $c_1, c_2, \ldots, c_M$ - specific heat capacity, $\rho_1, \rho_2, \ldots, \rho_M$ - density of the ingredients of the mixture defined according to the reference data at a certain temperature t_0 (in the future, we assume $t_0 = 20°C$).

Then at the temperature t_0 the thermal conductivity of the mixture can be calculated by the formula [2]:

$$C(T_0) = \frac{\sum_{n=1}^{K} c_n \cdot m_n}{\sum_{n=1}^{K} \frac{m_n}{\rho_n}} \tag{22}$$

Substitute the value obtained in (9), and determine the value of C_0:

$$C_0 = \sum_{n=1}^{K} \frac{c_n \cdot m_n}{[(1 + x_1 \cdot T_0) \cdot \sum_{n=1}^{K} \frac{m_n}{\rho_n}]} \tag{23}$$

The minimization function $F(\boldsymbol{x})$ in (21) will implement Newton's method. For this decompose function $T_m^{calc.}(\boldsymbol{x};l_0, l_i)$, included in the right hand side of (21) in a Taylor series in a neighbourhood of a point of the k approximation and limited to the linear part of the decomposition, we get:

$$T_m^{calc.}\left(x^{(k+1)}; l_0, t_i\right) = T_m^{calc.}\left(x^{(k)} + \Delta x^{(k)}; l_0, t_i\right) \approx$$
$$\approx T_m^{calc.}\left(x^{(k)}; l_0, t_i\right) + \nabla T_m^{calc.}\left(x^{(k)}; l_0, t_i\right) \cdot \Delta x^{(k)}$$

Substituting the resulting expression in (21), we obtain

$$F\left(x^{(k+1)}\right) = F\left(x^{(k)} + \Delta x^{(k)}\right) \approx$$
$$\approx \sum_{m=1}^{K^{samp.}} \sum_{i=1}^{N_m} \left[T_{i,m}^{meas.} - T_m^{calc.}\left(x^{(k)}; l_0, t_i\right) - \nabla T_m^{calc.}\left(x^{(k)}; l_0, t_i\right) \cdot \Delta x^{(k)}\right]^2 = \quad (24)$$
$$= \sum_{m=1}^{K^{samp.}} \sum_{i=1}^{N_m} \left[\Delta T_{i,m} - \nabla T_m^{calc.}\left(x^{(k)}; l_0, t_i\right) \cdot \Delta x^{(k)}\right]^2,$$

$$\Delta T_{i,m} = T_{i,m}^{meas.} - T_{i,m}^{calc.}\left(x^{(k)}\right),\ \Delta \boldsymbol{x}^{(k)} = \boldsymbol{x}^{(k+1)} - \boldsymbol{x}^{(k)}$$

$K+1$ approximation we find from the condition of minimum (24):

$$\frac{\partial F(\boldsymbol{x}^{(k)} + \Delta \boldsymbol{x}^{(k)})}{\partial \Delta x_j^{(k)}} = 0, j = 1,2,3; \quad (25)$$

where

$$\Delta \boldsymbol{x}^{(k)} = \boldsymbol{A}^{-1} \cdot \boldsymbol{b}, \quad (26)$$

where is $\boldsymbol{A} = \left\|a_{n,l}\right\|_{3\times 3}$ the matrix with elements

$$a_{n,l} = \sum_{m=1}^{K^{samp.}} \sum_{i=1}^{N_m} \frac{\partial T_m^{calc.}\left(x^{(k)}; l_0, t_i\right)}{\partial x_n^{(k)}} \cdot \frac{\partial T_m^{calc.}\left(x^{(k)}; l_0, t_i\right)}{\partial x_l^{(k)}}, n, l = 1,2,3; \quad (27)$$

$$b = \sum_{m=1}^{K^{samp.}} \sum_{i=1}^{N_m} \Delta T_{i,m} \cdot \nabla T_m^{calc.}\left(x^{(k)}; l_0, t_i\right); \quad (28)$$

Thus, the value of point $k+1$ approximation is determined by the formula

$$\boldsymbol{x}^{(k+1)} = \boldsymbol{x}^{(k)} + \Delta \boldsymbol{x}^{(k)}. \quad (29)$$

The conclusion of the iterative algorithm (29) is implemented with one of the conditions:
- $|\nabla F(\boldsymbol{x}^{(k+1)}| \le \varepsilon_1$, (the magnitude of the gradient $F(\boldsymbol{x}^{(k+1)})$);
- $|\Delta \boldsymbol{x}^{(k)}| \le \varepsilon_2$, (the absolute difference between values in adjacent iterations)
- $F(\boldsymbol{x}^{(k+1)}) > F(\boldsymbol{x}^{(k)})$ (in ascending order of the objective function)
- $k + 1 > K_{max}$ (the number of iterations)

where $\varepsilon_1, \varepsilon_2$ values.

4.3. Calculation of model examples of solution of direct problems of heat conduction equations

Example 1. To verify the performance of the algorithm for solving the direct problem in the example the calculation of the temperature field of the sample with thickness $L=2.5\times10^{-2}$ m was carried out. The thermophysical parameters of the sample correspond to parameters of rubber compounds used for the production of automobile tires:

$$C(T)=8000000 + 4900\cdot T\ ,\ \text{J}\cdot\text{kg}^{-1}\cdot\text{deg}^{-1},\ \lambda=0.35,\ \text{W}\cdot\text{m}^{-1}\cdot\ \text{deg}^{-1}.$$

The boundary values of the temperature represented by the dependencies:

$$T_{top}(t) = T_{bot.}(t) = \begin{cases} 0{,}2t + 30.0 & t \le 600; \\ 150.0 & 600 \le t \le 2700; \\ 276.0 - 7/150t & t \ge 2700. \end{cases}$$

the initial value of the temperature $T_0(x) = 30℃$

The sampling time dt = 1.0 sec; ς=1.65; η = 0; θ = 1.5; S_8=0.057456 mole/kg;
Ac = 0.065664 mole/kg; Act = 0.453974 mole/kg; R_1=0.003453; α=1.0; β=2.0; γ=1.0; δ=1.0.
The activation energies of the stages of the process:
$E_1=E_2=E_3=E_4=E_5=E_6=E_7=E_8=E_9=1.081\times10^5$, J×mole^{-1};

Preexponential coefficients of reaction rates in stages:
$k_1=6.448\times10^{10}$, s^{-1}; $k_2=1.29\times10^{11}$, s^{-1}; $k_3=1.934\times10^{-8}$, s^{-1}; $k_4=1.29\times10^{11}$, s^{-1}×kg×mole^{-1};
$k_5=6.448\times10^{-9}$, s^{-1}; $k_6=2.579\times10^{-9}$, s^{-1}; $k_7=9.027\times10^{10}$, s^{-1}; $k_8=3.224\times10^{11}$, s^{-1};
$k_9=6.448\times10^{10}$, s^{-1}.

The coefficient q_0 is supposed to be equal to 4.0×10^8, J•kg^{-1}.

The calculation was performed for the time interval from 0 to 3600 sec. The results of calculations is shown in Figure 2.

The values of temperature field, which performed with different number of discretization points in the spatial coordinate, is shown in Table. 1. As can be seen from Table 1, the difference between the solutions obtained when K=12 and K=24 does not exceed 0.1 °C.

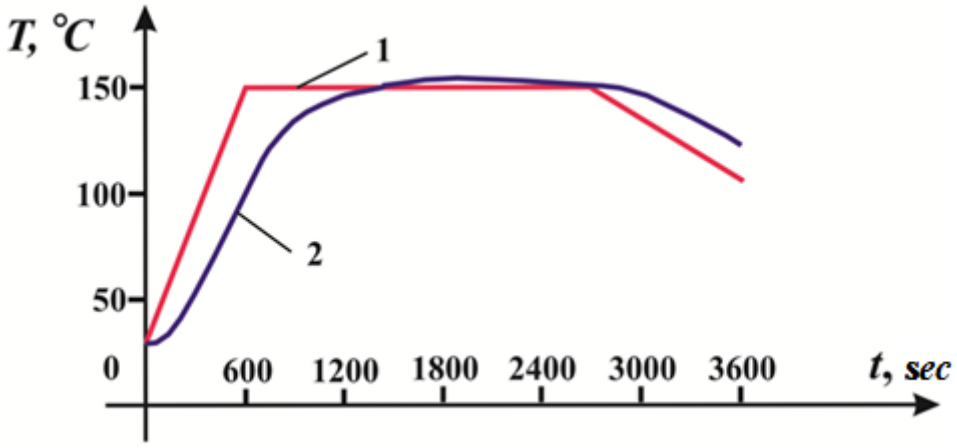


Figure 2. For example 1. 1 is a graph of the temperature on the upper and lower boundaries, 2 is a graph of the temperature in the center of the rod.

Table 1. Comparison of the results of calculations performed with different number points discretizing spatial coordinates.

	The temperature in the center of the rod , °C		
	The number of points of discretization the length of the rod		
A time value, sec	6	12	24
100	32.28	32.05	31.99
250	47.14	46.84	46.76
500	84.08	83.81	83.74
750	121.47	121.58	121.62
1000	139.15	139.43	139.50
2000	153.84	153.80	153.79
3000	146.69	146.76	146.78
3600	122.49	122.51	122.51

Example 2. In this example, we performed a computational experiment, whose goal was to test the performance of the algorithm for solving the inverse problem (IP) for the system of equations of heat conduction.

The testing was performed in the following sequence: at first, for given values of thermophysical parameters

(C_0= 8000000, j•kg^{-1}•deg^{-1}; C_1= 4900, j•kg^{-1}•deg^{-2}; λ=0.35, W·m^{-1}·deg^{-1}; q_0= 4.0×10^8, J·kg^{-1})

the calculation of the temperature $T(t)$ in the center of the rod was carried out using the algorithm for solving the direct problem (DP). Then, for the known temperature field $T(t)$ (calculated by algorithm of DP) the thermophysical parameters C_1, λ, of the sample q_0 were determined using the algorithm of IP. The other initial data are the same as in the previous example.

The values C_1=2450, J•kg^{-1}•deg^{-2}; λ = 0.175 W•m^{-1}•deg^{-2}; q_0 =0.0, J•kg^{-1} have been given as a priori (initial) values of determined parameters in the algorithm of solving the inverse problem.

The results of solving the inverse problem are presented in Table. 2.

Table 2. The results of solving the inverse problem.

Defined parameters	The results of solving the inverse problem by iteration of the optimization cycle				The exact solution
	1st iteration	2nd iteration	3rd iteration	4th iteration	
C_1	5057.76	4517.10	4890.53	4900.32	4900.00
L_0	0.297819	0.342972	0.354871	0.355009	0.35
q_0	874.89×10^5	3359.18×10^5	3990.81×10^5	4000.06×10^5	4000.00×10^5

5. Conclusion

As a result of the performed researches, a technique for determining the thermophysical parameters of the vulcanizable mixture was developed, including algorithms for solving direct and inverse problems for the system of heat conduction equations and the kinetics of the vulcanization process. The proposed solution of the direct problem is finding the concentration of vulcanization of nodes relative to the maximum density of cross-linkage, as a function of time. The solution of the direct problem for the system of equations of thermal conductivity was carried out using an explicit difference scheme. To solve the system of equations describing the kinetics of the process, the Runge-Kutta method was used. The proposed method for solving the inverse problem of the kinetics of vulcanization - the determination of the thermophysical parameters on the measured values of temperature of test specimens based on the reference data thermal characteristics of blend components. Minimization of

functions of the residuals was carried out using the Newton method. The performance of the method is confirmed by the results of numerical experiments on model examples.

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