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# Investigation of computer-aided engineering of silicone rubber vulcanizing (I)—vulcanization degree calculation based on temperature field analysis

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## Abstract

The equation of vulcanization reaction rate of additive liquid silicone rubber is established by experiment, then the mathematical model of vulcanization ratio is constructed. The new concept of increment of vulcanization ratio is introduced, so the numerical analysis of vulcanization ratio is done. According to statistical theory, the numerical computation expressions of crosslinking structure parameters are derived, while the original molecules are distributed in Flory manner. Handling the reaction heat by the way of internal heat source, the partial differential equation of heat transfer is established in the vulcanization molding area, and necessary approximate treatments are done as well. Adopting weighted margin method, the foundational control equations for calculating the temperature field are derived, and two types of thermal boundary conditions are tackled. On the foundation, the numerical simulation theory of vulcanization molding can be studied, and the computer-aided engineering software of vulcanization molding can be designed.

*Keywords:* Silicone rubber; Vulcanization ratio; Crosslinking structure

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## 1. Introduction

Additive liquid silicone rubber is composed of vinyl silicone rubber, hydrogenated silicone oil, catalyzer, stuffing, and so on. The viscosity of the kind of mixture is lower than that of raw rubber stock, so it is convenient for vulcanization molding. Accordingly, the pugging and preforming and post processing procedures can be omitted, and automation production is easy to be realized. Furthermore, the rubber products have a series of advantages such as excellent copy capability, low percentage of contraction, high tensile strength and tearing strength. Thereby, the additive liquid silicone rubber has developed quickly in recent years, and becomes the emphasis of research and development in organosilicon field in the world. At present, the rubber products have been widely used in tanning industry, plastics industry, automobile industry, mold and die industry, electronic industry, medical apparatus and instruments, duplication of cultural relic [1–4].

In the vulcanization process of additive liquid silicone rubber, the chemical reaction between vinyl silicone rubber and hydrogenated silicone oil is an exothermic reaction. The amount of released reaction heat linearly increases with the increase of vulcanization ratio [5]. In order to design the computer-aided engineering software of the vulcanization process, consequently optimize the process parameters and control the crosslinking structure and predict the quality of silicone rubber products and reduce the production cost, it is important to construct the mathematical model of vulcanization ratio and calculate the crosslinking structure parameters and analyze the thermal coupling between reaction heat and temperature field.

## 2. Establishing equation of hydrosilation rate

### 2.1. Experimental material

The raw rubber is made of linear polysiloxane macromolecule with vinyl, the number-average molecular weight is 30,190. In per gram of raw rubber, the mass of vinyl is $9.8 \times 10^{-3}$ g. Hydrogenated silicone oil is linear

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## Nomenclature

| | |
|---|---|
| $c$ | specific heat at constant pressure, J (Kg K)$^{-1}$ |
| $c_{\text{sivi}}$ | vinyl concentration in reactant, mol m$^{-3}$ |
| $c_{\text{sivi},0}$ | initial vinyl concentration in reactant, mol m$^{-3}$ |
| $c_{\text{sivi}(i)}$ | vinyl concentration in reactant in No. $i$ interval, mol m$^{-3}$ |
| $D$ | vulcanization area, m$^2$ |
| $E_{\text{a}}$ | activity energy, J mol$^{-1}$ |
| $f_{\text{V}}$ | vulcanization ratio |
| $h$ | coefficient of convective heat transfer on boundary between silicone rubber and hot atmosphere, W (m$^2$ K)$^{-1}$ |
| $h_{\text{c}}$ | coefficient of heat transfer on boundary between silicone rubber and LOM prototype, W (m$^2$ K)$^{-1}$ |
| $k$ | coefficient of thermal conductivity of reactant, W (m K)$^{-1}$ |
| $k_0$ | frequency factor, s$^{-1}$ |
| $k_1$ | reaction rate constant, s$^{-1}$ |
| $k_{\text{LOM}}$ | coefficient of thermal conductivity of LOM prototype, W (m K)$^{-1}$ |
| $L$ | reaction heat of raw silicone rubber per unit mass, J Kg$^{-1}$ |
| $L_{\text{g}}$ | surface roughness of LOM prototype, m |
| $N_0$ | number of structure units in every number-average original polysiloxane macromolecule |
| $n$ | outer normal on boundary, m |
| $p_j$ | coefficient of vulcanization intensity, correlated with temperature, expressed by piecewise linearization, K$^{-1}$ |
| $Q$ | quantity of released reaction heat per unit volume from beginning to a certain vulcanization ratio, J m$^{-3}$ |
| $q$ | total crosslinking degree of reactant |
| $q'$ | crosslinking degree of sol |
| $q_2$ | heat-flow density through boundary between silicone rubber and LOM prototype, W m$^{-2}$ |
| $q_j$ | constant coefficient of vulcanization intensity, expressed by piecewise linearization |
| $q_n$ | crosslinking degree of reactant in No. $n$ time step |
| $q_{\text{V}}$ | heat source strength, W m$^{-3}$ |
| $q'_n$ | crosslinking degree of sol in No. $n$ time step |
| $q''_n$ | crosslinking degree of gel in No. $n$ time step |
| $R$ | universal constant of gas, J (mol K)$^{-1}$ |
| $S_n$ | sol fraction of reactant in No. $n$ time step |
| $s$ | length of boundary, m |
| $T$ | temperature of silicone rubber, K |
| $T_{\text{f}}$ | temperature of hot atmosphere, K |
| $T_{(i)}$ | vulcanization temperature in No. $i$ interval, K |
| $T_{\text{LOM}}$ | temperature of LOM prototype, K |
| $T_l$ | temperature of No. $l$ node, K |
| $t$ | vulcanization time, s |
| $W_l$ | weighting function of No. $l$ node |
| $x_{\text{sivi}}$ | conversion ratio of vinyl |
| $Y_0$ | number of crosslinkable units in every number-average original polysiloxane macromolecule |
| $\alpha$ | number-average cracking degree of reactant |
| $\rho$ | density of reactant, Kg m$^{-3}$ |
| $\Gamma$ | boundary of vulcanization area, m |
| $\Delta t$ | step size of finite difference on time, s |

polysiloxane molecule, the number-average molecular weight is 3000. In per gram of silicone oil, the mass of active hydrogen is $5 \times 10^{-3}$ g. The catalyzer is Speier catalyzer. The stuffing is silicon dioxide made through vapor phase process.

When mixing the material, the quantity ratio of active hydrogen to vinyl is 1.15:1, the mass fraction of stuffing is 25%, the mass fraction of catalyzer is 0.002%.

### 2.2. Experimental process and results

The influence of vinyl concentration on reaction rate is studied by mensuration instrument for vulcanization degree, while the vulcanization temperature keeps constant. The results show that the relationship between natural logarithm of vinyl concentration and time is simple equation, which indicates that the vulcanization is a first-order reaction. So the equation of the hydrosilation rate can be described as

$$-\frac{\mathrm{d}c_{\mathrm{sivi}}}{\mathrm{d}t} = k_1 c_{\mathrm{sivi}} \tag{1}$$

Continually using the mensuration instrument for vulcanization degree, the relationship between reaction rate and vulcanization temperature is studied. The results show that the relationship is exponential function. So it can be deduced that the vulcanization is Arrhenius reaction. The Arrhenius equation expressed by exponential form

$$k_1 = k_0\,\mathrm{e}^{-E_{\mathrm{a}}/RT} \tag{2}$$

is fit into Eq. (1), then the following equation of the hydrosilation rate can be obtained

$$-\frac{\mathrm{d}c_{\mathrm{sivi}}}{\mathrm{d}t} = k_0\,\mathrm{e}^{-E_{\mathrm{a}}/RT} c_{\mathrm{sivi}} \tag{3}$$

## 3. Constructing model of vulcanization ratio

The vulcanization ratio $f_{\mathrm{V}}$, namely the conversion ratio of reactant, is defined as

$$f_{\mathrm{V}} = x_{\mathrm{sivi}} = \frac{c_{\mathrm{sivi,0}} - c_{\mathrm{sivi}}}{c_{\mathrm{sivi,0}}} = \frac{\int_{c_{\mathrm{sivi,0}}}^{c_{\mathrm{sivi}}} -\,\mathrm{d}c_{\mathrm{sivi}}}{c_{\mathrm{sivi,0}}} = \frac{\int_0^t -\frac{\mathrm{d}c_{\mathrm{sivi}}}{\mathrm{d}t}\,\mathrm{d}t}{c_{\mathrm{sivi,0}}} \tag{4}$$

Fitting Eq. (3) into the above equation, the mathematical model of vulcanization ratio $f_{\mathrm{V}}$ can be derived

$$f_{\mathrm{V}} = \frac{\int_0^t k_0\,\mathrm{e}^{-E_{\mathrm{a}}/RT} c_{\mathrm{sivi}}\,\mathrm{d}t}{c_{\mathrm{sivi,0}}} = \frac{k_0}{c_{\mathrm{sivi,0}}}\int_0^t \mathrm{e}^{-E_{\mathrm{a}}/RT} c_{\mathrm{sivi}}\,\mathrm{d}t \tag{5}$$

Obviously, the vulcanization ratio $f_{\mathrm{V}}$ is a complex nonlinear function of temperature $T$.

For isothermal process, the vulcanization ratio can be calculated directly by Eq. (5). But in practical process, the reaction temperature is not constant. Usually, the temperature of every spatial point in the reaction field increases with different velocity, and the temperature of the same spatial point increases with different velocity at different time, which causes that the vulcanization ratio cannot be calculated directly by Eq. (5).

Therefore, the new concept of increment of vulcanization ratio is introduced to solve the calculation problem. In order to make the concept clear, the conversion ratio of the reactant at the end of a certain reaction process or a certain phase of the reaction process is defined as fulldose of vulcanization ratio. Namely, if the fulldose of vulcanization ratio at a certain moment in the reaction process is regarded as original state, the infinitesimal vulcanization ratio occurred on this basis is increment of vulcanization ratio. For the convenience of application, the increment of vulcanization ratio is defined as the vulcanization ratio $\Delta f_{\mathrm{V}}$ occurred in transitory time step $\Delta t$. Because $\Delta t$ is far smaller than the whole vulcanization time $t$, the reaction temperature $T$ can be considered as constant in every time step. It can be seen that the higher the computational accuracy is or the more rapidly the temperature increases, the more transitory the time step is.

According to differential calculus, Eq. (5) can be transformed into the following equation,

$$\frac{\partial f_{\mathrm{V}}}{\partial t} = k_0\,\mathrm{e}^{-E_{\mathrm{a}}/RT}\,\mathrm{e}^{-k_0 t\,\mathrm{e}^{-E_{\mathrm{a}}/RT}} = k_0\,\mathrm{e}^{-E_{\mathrm{a}}/RT}(1 - f_{\mathrm{V}}) \tag{6}$$

If $f_{\mathrm{V},n}$ denotes the fulldose of vulcanization ratio in No. $n$ time step, $f_{\mathrm{V},n-1}$ denotes the fulldose of vulcanization ratio in No. $n-1$ time step, $\Delta f_{\mathrm{V},n}$ denotes the increment of vulcanization ratio in the No. $n$ time step, the following equation

$$\left(\frac{\partial f_{\mathrm{V}}}{\partial t}\right)_n = \frac{\Delta f_{\mathrm{V},n}}{\Delta t} + O(\Delta t) = \frac{f_{\mathrm{V},n} - f_{\mathrm{V},n-1}}{\Delta t} + O(\Delta t) \tag{7}$$

can be defined as first-order difference quotient based on backward difference method, where $O(\Delta t)$ denotes the magnitude order of truncation error.

Eq. (6) is fit into Eq. (7). If the truncation error is ignored, the numerical computation expression for calculating the increment of vulcanization ratio can be obtained

$$\Delta f_{\mathrm{V},n} = \frac{k_0\,\mathrm{e}^{-E_{\mathrm{a}}/RT}\Delta t(1 - f_{\mathrm{V},n-1})}{1 + k_0\,\mathrm{e}^{-E_{\mathrm{a}}/RT}\Delta t} \tag{8}$$

According to the definition of backward difference, the numerical computation expression for calculating fulldose of vulcanization ratio can be derived.

$$f_{\mathrm{V},n} = f_{\mathrm{V},n-1} + \Delta f_{\mathrm{V},n} = \frac{f_{\mathrm{V},n-1} + k_0\,\mathrm{e}^{-E_{\mathrm{a}}/RT}\Delta t}{1 + k_0\,\mathrm{e}^{-E_{\mathrm{a}}/RT}\Delta t} \tag{9}$$

Because the initial vulcanization ratio $f_{\mathrm{V},0}$ is equal to zero, the fulldose of vulcanization ratio $f_{\mathrm{V},n-1}$ in No. $n-1$ time step can be calculated, consequently the fulldose of vulcanization ratio $f_{\mathrm{V},n}$ in No. $n$ time step can be obtained.

## 4. Statistical analysis of vulcanization field

### 4.1. Application strategy of statistical theory

Gelation theory can be classified as three kinds of theory, namely statistical theory and kinetics theory and filtration theory [6]. The statistical theory has been developed earliest among them. Compared with other theories, the statistical theory puts emphasis upon thermodynamic equilibrium, consequently, it usually replaces time function by state function. The statistical theory deals with crosslinking system by probabilistic method, so the whole crosslinking process can be tackled, and analysis formula of every physical quantity can be obtained. Therefore, the statistical theory has the characteristics of simplicity and perspicuity [6–8].

In the practical production process of polymer products, the crosslinking reaction parameters such as temperature and functional group concentration in different time or on different spatial point are often different. The phenomenon makes the crosslinking reaction rate in different time or on different spatial point different. Obviously, the statistical theory cannot directly be adopted, to process the reaction system controlled by kinetics.

When the whole crosslinking reaction process is divided into finite phases and the time step of every phase is short enough, the crosslinking reaction in the same phase can be considered to have the same reaction rate on the same spatial point. Consequently, when the whole reaction field is divided into finite elements and the geometrical dimension of every element is small enough, the crosslinking reaction in the same phase can be considered to have the same reaction rate in the same element.

Therefore, if the crosslinking reaction process, controlled by kinetics and under complex condition is reasonably realized discretization, the gelation problem can be studied by the statistical theory in the same phase and in the same element.

### 4.2. Numerical calculation of crosslinking structure parameters

The hydrosilation of liquid silicone rubber is regarded as stochastic reaction. The statistical analysis of crosslinking structure premises the following fundamental assumptions. (1) The gel is infinite macromolecule with three-dimensional network structure. (2) The crosslinking reaction probability of crosslinkable vinyl in sol is equal to the crosslinking reaction probability of crosslinkable vinyl in gel. (3) Cyclization happens in gel, not in sol. (4) Main chain scission cannot happen in vulcanization process. (5) The residuary crosslinking agent is tackled as crosslinking bond.

When the original molecules are distributed in Flory manner, the following equation can be obtained [9]

$$(q' - q)[(1 - q + q\alpha^2)q'^2 + (-q - 3\alpha^2 q + 4\alpha q + q^2 + \alpha^2 q^2 - 2\alpha q^2 - 2\alpha)q' + \alpha^2] = 0 \tag{10}$$

Therefore, $q'$ has three real roots. There must be a real root $q' = q$ among them, expressing that the total crosslinking degree of the reactant is equal to the crosslinking degree of sol before gel point. The other two real roots are shown below

$$q' = \frac{q + 3\alpha^2 q - 4\alpha q - q^2 - \alpha^2 q^2 + 2\alpha q^2 + 2\alpha}{2(1 - q + q\alpha^2)} \pm \frac{\sqrt{(-q - 3\alpha^2 q + 4\alpha q + q^2 + \alpha^2 q^2 - 2\alpha q^2 - 2\alpha)^2 - 4(1 - q + q\alpha^2)\alpha^2}}{2(1 - q + q\alpha^2)} \tag{11}$$

Because the root, which takes positive sign before the radical sign cannot satisfy gelation condition, only the root which takes minus sign before the radical sign is reasonable, which represents the condition after gel point.

In the practical operating condition, $\alpha$ and $q$ take values in the range of $10^{-2}$–$10^{-3}$, so $\alpha^2$ and $q^2$ and $\alpha q$ are far smaller than $\alpha$ and $q$. For simplicity, Eq. (11) can be approximately expressed as

$$q' = \begin{cases} q & q < \dfrac{\alpha}{2} \\ \dfrac{q + 2\alpha - \sqrt{q^2 + 4\alpha q}}{2} & \dfrac{\alpha}{2} \le q \le \dfrac{Y_0}{N_0} \end{cases} \tag{12}$$

According to the functional relationship of crosslinking degree of sol $q'$ and sol fraction $S$, the approximate computation expression of sol fraction $S$ can be obtained

$$S = \begin{cases} 1 & q < \dfrac{\alpha}{2} \\ \dfrac{q + 2\alpha - \sqrt{q^2 + 4\alpha q}}{2q} & \dfrac{\alpha}{2} \le q \le \dfrac{Y_0}{N_0} \end{cases} \tag{13}$$

According to the functional relationship of crosslinking degree of gel $q''$ and sol fraction $S$ and crosslinking degree of sol $q'$, the approximate computation expression of crosslinking degree of gel $q''$ can be obtained

$$q'' = \frac{3q + 2\alpha - \sqrt{q^2 + 4\alpha q}}{2} \quad \frac{\alpha}{2} \le q \le \frac{Y_0}{N_0} \tag{14}$$

According to the definition of fulldose of vulcanization ratio $f_{V,n}$, the relational expression of crosslinking degree $q_n$ and fulldose of vulcanization ratio $f_{V,n}$ can be obtained

$$q_n = Y_0 \alpha f_{V,n} \tag{15}$$

Eq. (15) is fit into Eqs. (12)–(14), the numerical computation expressions of the crosslinking structure parameters can be obtained

$$S_n = \begin{cases} 1 & f_{V,n} < \dfrac{1}{2Y_0} \\ \dfrac{Y_0 f_{V,n} + 2 - \sqrt{Y_0^2 f_{V,n}^2 + 4Y_0 f_{V,n}}}{2Y_0 f_{V,n}} & \dfrac{1}{2Y_0} \le f_{V,n} \le 1 \end{cases} \tag{16}$$

$$q'_n = \begin{cases} Y_0 \alpha f_{V,n} & f_{V,n} < \dfrac{1}{2Y_0} \\ \dfrac{Y_0 \alpha f_{V,n} + 2\alpha - \alpha\sqrt{Y_0^2 f_{V,n}^2 + 4Y_0 f_{V,n}}}{2} & \dfrac{1}{2Y_0} \le f_{V,n} \le 1 \end{cases} \tag{17}$$

$$q''_n = \frac{3Y_0 \alpha f_{V,n} + 2\alpha - \alpha\sqrt{Y_0^2 f_{V,n}^2 + 4Y_0 f_{V,n}}}{2} \quad \frac{1}{2Y_0} \le f_{V,n} \le 1 \tag{18}$$

## 5. Dealing with reaction heat

In the vulcanization process of additive liquid silicone rubber, the chemical reaction between vinyl silicone rubber and hydrogenated silicone oil is an exothermic reaction. The amount of released reaction heat $Q$ linearly increases with the increase of vulcanization ratio $f_V$

$$Q = \rho L f_V \tag{19}$$

In fact, the reaction heat is the internal heat source of temperature field in vulcanization area. The heat source strength $q_V$ is not a constant, which is determined by the rate of $f_V$ to $t$

$$q_V = \frac{\partial Q}{\partial t} = \frac{\partial(\rho L f_V)}{\partial t} = \rho L \frac{\partial f_V}{\partial t} \tag{20}$$

Fitting Eq. (5) into the above equation, the heat source strength $q_V$ can be calculated

$$q_V = \frac{\rho L k_0}{c_{\mathrm{sivi},0}} \frac{\partial \int_0^t e^{-E_a/RT} c_{\mathrm{sivi}}\, dt}{\partial t} \tag{21}$$

## 6. Constructing partial differential equation of temperature field

When the coefficient of thermal conductivity $k$ and specific heat $c$ at constant pressure and density $\rho$ of the reactant are regarded as constants, and the reaction heat is tackled as internal heat source, the partial differential equation of the temperature field in two-dimensional space can be obtained [10]

$$D[T(x,y,t)] = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) + q_V - \rho c \frac{\partial T}{\partial t} = 0 \tag{22}$$

Because the reaction heat couples with the temperature field, Eq. (22) changes into

$$D[T(x,y,t)] = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) + \frac{\rho L k_0}{c_{\mathrm{sivi},0}} \times \frac{\partial \int_0^t e^{-E_a/RT} c_{\mathrm{sivi}}\, dt}{\partial t} - \rho c \frac{\partial T}{\partial t} = 0 \tag{23}$$

The above partial differential equation of temperature field is too complex to achieve its precise solution. On this account, Eq. (23) is approximately tackled as

$$D[T(x,y,t)] = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) + \frac{\rho L k_0}{c_{\mathrm{sivi},0}} \times \frac{\partial \sum_{i=1}^{n} \left[e^{-E_a/RT_{(i)}} c_{\mathrm{sivi}(i)} \Delta t\right]}{\partial t} - \rho c \frac{\partial T}{\partial t} = 0 \tag{24}$$

where

$$\frac{\partial \sum_{i=1}^{n} \left[e^{-E_a/RT_{(i)}} c_{\mathrm{sivi}(i)} \Delta t\right]}{\partial t} = \frac{\sum_{i=1}^{n} \left[e^{-E_a/RT_{(i)}} c_{\mathrm{sivi}(i)} \Delta t\right] - \sum_{i=1}^{n-1} \left[e^{-E_a/RT_{(i)}} c_{\mathrm{sivi}(i)} \Delta t\right]}{\Delta t} + O(\Delta t) \tag{25}$$

is defined as first-order difference quotient. The truncation error $O(\Delta t)$ is ignored, then the following equation can be obtained

$$\frac{\partial \sum_{i=1}^{n} \left[e^{-E_a/RT_{(i)}} c_{\mathrm{sivi}(i)} \Delta t\right]}{\partial t} = e^{-E_a/RT_{(n)}} c_{\mathrm{sivi}(n)} \tag{26}$$

Fitting Eq. (26) into Eq. (24), the following equation can be obtained

$$D[T(x,y,t)] = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) + \frac{\rho L k_0}{c_{\mathrm{sivi},0}} e^{-E_a/RT} c_{\mathrm{sivi}} - \rho c \frac{\partial T}{\partial t} = 0 \tag{27}$$

In the above equation, the internal heat source strength $\rho L k_0 / c_{\mathrm{sivi},0}\, e^{-E_a/RT} c_{\mathrm{sivi}}$ is the linear function of $c_{\mathrm{sivi}}$, which is easy to calculate based an concentration factor by finite element method. However, it is still the complex non-linear function of $T$, and it is hard to calculate based on temperature factor by the numerical method, so an approximate treatment is needed.

The activity energy $E_a$ is 40,000 J/mol, so the curve of $e^{-E_a/RT}$ versus $T$ is shown as fair curve in Fig. 1.

According to the piecewise linearization method, a series

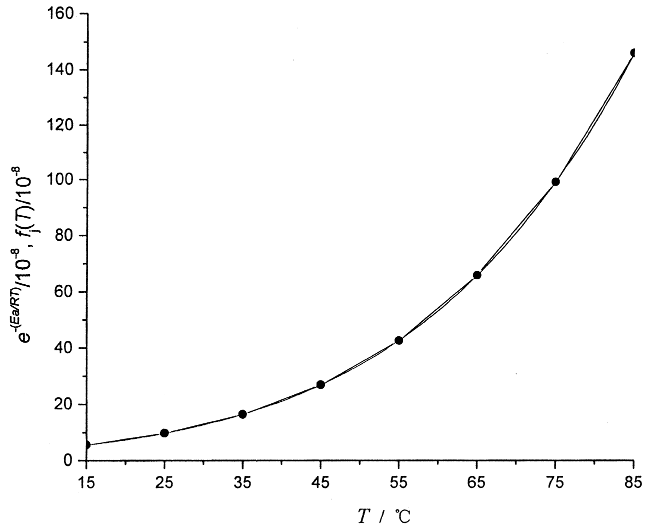

Fig. 1. Comparison of fair curve and piecewise linearization curve.

of points with equal temperature difference can be selected from the curve, and the data are shown in Table 1.

The adjacent two points are linked by a straight segment, which is expressed by a linear function

$$f_j(T) = p_jT + q_j \quad (j = 1,2,\ldots,m) \tag{28}$$

When $T = 15$ °C, $15p_1 + q_1 = 5.5\times10^{-8}$

When $T = 25$ °C, $25p_1 + q_1 = 9.7\times10^{-8}$

The above two equations are solved, the two coefficients $p_1$, $q_1$ can be obtained

$$p_1 = 4.2\times10^{-9}, \qquad q_1 = -0.8\times10^{-8}$$

So the first linear function can be obtained

$$f_1(T) = 4.2\times10^{-9}T - 0.8\times10^{-8} \quad 15 \le T < 25\ ^\circ\text{C}$$

Similarly, the other linear functions can be achieved, as shown below

$$f_2(T) = 6.7\times10^{-9}T - 7.05\times10^{-8} \quad 25 \le T < 35\ ^\circ\text{C}$$

$$f_3(T) = 1.04\times10^{-8}T - 2.0\times10^{-7} \quad 35 \le T < 45\ ^\circ\text{C}$$

$$f_4(T) = 1.58\times10^{-8}T - 4.43\times10^{-7} \quad 45 \le T < 55\ ^\circ\text{C}$$

$$f_5(T) = 2.32\times10^{-8}T - 8.5\times10^{-7} \quad 55 \le T < 65\ ^\circ\text{C}$$

$$f_6(T) = 3.32\times10^{-8}T - 1.5\times10^{-6} \quad 65 \le T < 75\ ^\circ\text{C}$$

$$f_7(T) = 4.67\times10^{-8}T - 2.5\times10^{-6} \quad 75 \le T < 85\ ^\circ\text{C}$$

Therefore, a piecewise linearization curve can be formed based on the above functions, as shown in Fig. 1. Comparing the piecewise linearization curve with the fair one, it can be seen that they are similar. It demonstrates that the following equation is rational

$$\frac{\rho Lk_0}{c_{\text{sivi},0}} e^{-E_a/RT} c_{\text{sivi}} = \frac{\rho Lk_0}{c_{\text{sivi},0}} f_j(T) c_{\text{sivi}}$$

$$= \frac{\rho Lk_0}{c_{\text{sivi},0}} (p_jT + q_j) c_{\text{sivi}} \quad (j = 1,2,\ldots,m) \tag{29}$$

Table 1
A series of points selected from the curve of $e^{-E_a/RT}$ versus $T$

| $T$ (°C) | 15 | 25 | 35 | 45 | 55 | 65 | 75 | 85 |
|---|---|---|---|---|---|---|---|---|
| $T$ (K) | 288 | 298 | 308 | 318 | 328 | 338 | 348 | 358 |
| $e^{-E_a/RT}(10^{-8})$ | 5.5 | 9.7 | 16.4 | 26.8 | 42.6 | 65.8 | 99.0 | 145.7 |

Obviously, the computational accuracy is directly related to $m$. The bigger $m$ is, the more the piecewise linearization curve approximates to the fair curve, and the higher the computational accuracy is.

Fitting Eq. (29) into Eq. (27), the partial differential equation of temperature field, expressed by piecewise linear function, can be obtained

$$D[T(x,y,t)] = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right)$$

$$+ \frac{\rho Lk_0}{c_{\text{sivi},0}} (p_jT + q_j) c_{\text{sivi}} - \rho c \frac{\partial T}{\partial t} = 0 \quad (j = 1,2,\ldots,m) \tag{30}$$

## 7. Derivation of control equation of temperature field

The control equation of temperature field can be derived by functional analysis method or by weighted margin method. In the latter, Galerkin method has been widely applied [11]. Therefore, the following control equation of temperature field is derived by Galerkin method.

$n$ nodal temperatures $T_l(l = 1,2,\ldots,n)$ ($n$ is the number of nodes in the vulcanization area) are taken as $n$ undetermined coefficients, then the trial function can be defined and expressed in tensorial form

$$T(x,y,t) = T(x,y,t,T_1,T_2,\ldots,T_n)$$
$$= T(x,y,t,T_l) \quad (l = 1,2,\ldots,n) \tag{31}$$

Fitting the above formula into Eq. (30), then fitting Eq. (30) into the weighted margin equation

$$\int\int_D W_l D[T(x,y,t,T_l)]\mathrm{d}x\,\mathrm{d}y = 0 \quad (l = 1,2,\ldots,n) \tag{32}$$

the following equation can be obtained.

$$\int\int_D W_l\left[k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) + \frac{\rho Lk_0}{c_{\text{sivi},0}} (p_jT + q_j) c_{\text{sivi}} - \rho c \frac{\partial T}{\partial t}\right]\mathrm{d}x\,\mathrm{d}y$$

$$= 0 \quad (l = 1,2,\ldots,n;\ j = 1,2,\ldots,m) \tag{33}$$

In order to affiliate the surface integral in the vulcanization area with the line integral on the boundary so that the boundary condition of temperature field can be introduced, the Green formula

$$\int\int_D \left( \frac{\partial Y}{\partial x} - \frac{\partial X}{\partial y} \right) dx\, dy = \oint_\Gamma (X\, dx + Y\, dy) \tag{34}$$

must be applied. Therefore, Eq. (33) is rewritten as

$$\begin{aligned} &\int\int_D k\left[ \frac{\partial}{\partial x}\left( W_l \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y}\left( W_l \frac{\partial T}{\partial y} \right) \right] dx\, dy \\ &\quad - \int\int_D \left[ k\left( \frac{\partial W_l}{\partial x}\frac{\partial T}{\partial x} + \frac{\partial W_l}{\partial y}\frac{\partial T}{\partial y} \right) \right. \\ &\quad \left. - \frac{\rho L k_0}{c_{\mathrm{sivi},0}}(p_j T + q_j) c_{\mathrm{sivi}} W_l + \rho c W_l \frac{\partial T}{\partial t} \right] dx\, dy \\ &\quad = 0 \ \ (l = 1, 2, \ldots, n;\ j = 1, 2, \ldots, m) \end{aligned} \tag{35}$$

where $Y$ and $X$ are, respectively,

$$Y = W_l \frac{\partial T}{\partial x}, \qquad X = -W_l \frac{\partial T}{\partial y} \tag{36}$$

Then the first integral in Eq. (35) can be written as

$$\begin{aligned} &\int\int_D k\left[ \frac{\partial}{\partial x}\left( W_l \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y}\left( W_l \frac{\partial T}{\partial y} \right) \right] dx\, dy \\ &\quad = \oint_\Gamma k\left( -W_l \frac{\partial T}{\partial y} dx + W_l \frac{\partial T}{\partial x} dy \right) \end{aligned} \tag{37}$$

There is the following relation on the boundary $\Gamma$ of area $D$ [11]

$$-\frac{\partial T}{\partial y} dx + \frac{\partial T}{\partial x} dy = \frac{\partial T}{\partial n} ds \tag{38}$$

Eqs. (37) and (38) are fit into Eq. (35), then the control equation of temperature field accompanied by reaction heat can be derived

$$\begin{aligned} &\int\int_D \left[ k\left( \frac{\partial W_l}{\partial x}\frac{\partial T}{\partial x} + \frac{\partial W_l}{\partial y}\frac{\partial T}{\partial y} \right) - \frac{\rho L k_0}{c_{\mathrm{sivi},0}}(p_j T + q_j) c_{\mathrm{sivi}} W_l \right. \\ &\qquad \left. + \rho c W_l \frac{\partial T}{\partial t} \right] dx\, dy - \oint_\Gamma k W_l \frac{\partial T}{\partial n} ds \\ &\quad = 0 \ \ (l = 1, 2, \ldots, n;\ j = 1, 2, \ldots, m) \end{aligned} \tag{39}$$

## 8. Dealing with thermal boundary condition

### 8.1. Dealing with boundary condition of silicone rubber and hot atmosphere

The viscosity of liquid silicone rubber is big at the beginning of the reaction, and it rapidly increases with the increase of vulcanization ratio, which results in little extent of convective heat transfer inside itself. Because of the temperature difference inside hot atmosphere, there is natural convective heat transfer on the boundary between silicone rubber and hot atmosphere. Therefore, the thermal boundary condition of silicone rubber and hot atmosphere is the third kind of thermal boundary condition, as shown below

$$-k\frac{\partial T}{\partial n}\Big|_\Gamma = h(T - T_{\mathrm{f}})\Big|_\Gamma \tag{40}$$

Eq. (40) is fit into Eq. (39), then the control equation of temperature field with the boundary condition of silicone rubber and hot atmosphere can be derived

$$\begin{aligned} &\int\int_D \left[ k\left( \frac{\partial W_l}{\partial x}\frac{\partial T}{\partial x} + \frac{\partial W_l}{\partial y}\frac{\partial T}{\partial y} \right) - \frac{\rho L k_0}{c_{\mathrm{sivi},0}}(p_j T + q_j) c_{\mathrm{sivi}} W_l \right. \\ &\qquad \left. + \rho c W_l \frac{\partial T}{\partial t} \right] dx\, dy + \oint_\Gamma h W_l (T - T_{\mathrm{f}}) ds \\ &\quad = 0 \ \ (l = 1, 2, \ldots, n;\ j = 1, 2, \ldots, m) \end{aligned} \tag{41}$$

### 8.2. Dealing with boundary condition of silicone rubber and LOM prototype

Laminated object manufacturing (LOM) prototype is a kind of physical prototype, which is rapidly manufactured with LOM equipment [12]. In the vacuum casting process, liquid silicone rubber easily flows into delicate structure of LOM prototype, which makes the interface between silicone rubber and LOM prototype nearly no pore. Therefore, the thermal boundary condition is the special fourth kind of thermal boundary condition. Namely, the heat-flow density $q_2$ through the interface is only determined by the heat conduction [10]

$$q_2 = -k\frac{\partial T}{\partial n}\Big|_\Gamma = h_{\mathrm{c}}(T - T_{\mathrm{LOM}})\Big|_\Gamma \tag{42}$$

where

$$h_{\mathrm{c}} = \frac{2kk_{\mathrm{LOM}}}{L_{\mathrm{g}}(k + k_{\mathrm{LOM}})} \tag{43}$$

Eqs. (42) and (43) are fit into Eq. (39), the control equation of temperature field with the boundary condition of silicone rubber and LOM prototype can be derived

$$\iint_D \left[ k\left( \frac{\partial W_l}{\partial x}\frac{\partial T}{\partial x} + \frac{\partial W_l}{\partial y}\frac{\partial T}{\partial y}\right) - \frac{\rho L k_0}{c_{\mathrm{sivi},0}}(p_j T + q_j) c_{\mathrm{sivi}} W_l + \rho c W_l \frac{\partial T}{\partial t}\right] \mathrm{d}x\,\mathrm{d}y + \oint_\Gamma \frac{2kk_{\mathrm{LOM}}}{L_{\mathrm{g}}(k+k_{\mathrm{LOM}})} W_l (T - T_{\mathrm{LOM}}) \mathrm{d}s = 0 \quad (l=1,2,\ldots,n;\ j=1,2,\ldots,m) \tag{44}$$

## 9. Conclusions

(1) The new concept of increment of vulcanization ratio is introduced, and the numerical computation expression of vulcanization degree is obtained.

(2) According to statistical theory, the numerical computation expressions of crosslinking structure parameters are derived, while the original molecules are distributed in Flory manner.

(3) The reaction heat is handled by the way of internal heat source, and the heat source strength is calculated and transformed into piecewise linearization function of temperature.

(4) The partial differential equation of heat conduction is established in the vulcanization area, where the reaction heat couples with the temperature field.

(5) Adopting weighted margin method, the control equations for calculating the temperature field are derived. The thermal boundary condition is introduced by Green transformation method.

(6) On the foundation, the numerical simulation theory on vulcanization can be studied, and the computer-aided engineering software of vulcanization process can be designed.

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