

Mathematical Modelling and Numerical Simulation of the Non-isothermal In-mold Vulcanization of Natural Rubber^{*}

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Abstract According to the vulcanization kinetic equation of natural rubber (NR) established in the isothermal situation, the numerical computation expression of the degree of cure under non-isothermal condition is constructed by means of incremental method. The description of non-isothermal in-mold vulcanization process is carried out by the finite element method. The mold-opening time, the rubber and mold temperatures, the degree of rubber cure and its distribution characteristics are numerically analyzed, by changing the key formulas and parameters in the process including the temperature of curing medium, the concentration of 2-mercaptobenzothiazole, the heat transfer manner of mold side, and the convective heat transfer coefficient of heating boundary. The quantitative results will help engineers to design proper formulas and optimize processing conditions.

Keywords: Natural rubber; Non-isothermal vulcanization; Degree of cure; Processing conditions; Finite element simulation.

INTRODUCTION

Natural rubber (NR) exhibits such outstanding properties as high tensile strength, high abrasion resistance and high resilience, so it is one of the most widely used elastomers^[1, 2]. Vulcanization is an important procedure in rubber goods manufacturing process^[3]. In the course of vulcanization, three-dimensional molecular networks are formed by crosslinking reaction, and the degree and type of crosslinks determine the end-use properties of vulcanizates^[4]. The crosslink density and network structure depend on both formulas and processing conditions^[3, 5].

Mold-opening time, temperature distribution and degree of cure are the three essential parameters of rubber vulcanization. The degree of cure represents the conversion ratio of vulcanization reaction, which depends on time and temperature. The heterogeneous distribution of the degree of cure will give rise to the heterogeneous distribution of properties, which is adverse to vulcanizates. In order to increase the distribution homogeneousness of the degree of cure, it is important to investigate the profile of temperature and degree of cure during vulcanization and the relationship among time, temperature and degree of cure. A few researchers have performed numerical simulations on these topics^[6–16]. However, there are few systematic studies on the simulation of non-isothermal in-mold vulcanization of NR.

Hence this work is to simulate the non-isothermal in-mold vulcanization of NR and analyze the effect of key formulas and processing parameters on the mold-opening time, the temperature field and the degree of cure.

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ESTABLISHING MATHEMATICAL EXPRESSIONS OF THE DEGREE OF CURE

Vulcanization is a chemical process and therefore its simulation necessarily involves the characterization of kinetic parameters^[12]. The phenomenological kinetic model, proposed by Wang *et al.*^[17–19], is used in this paper. Wang *et al.*^[18] investigated the accelerated sulfur vulcanization of NR by vulcameter under isothermal conditions. They considered that the vulcanization before the maximum torque consisted of three stages: (1) the first stage, not a first-order reaction, corresponds to the period before t_{dis} at which accelerators and/or their intermediates react to depletion; (2) the second stage follows first-order kinetics, in which crosslinking takes place rapidly; (3) the third stage is the one when torque approaches the maximum value.

According to Refs. [17–19], the third stage takes place when the degree of cure generally exceeds 0.95. In practice the optimal cure is often defined as the state when the degree of cure reaches 0.9 on the curve of torque versus time. Therefore, the simulated processes mostly stay at the first two stages. Moreover, the kinetic equation and data obtained at the second stage are used continuously at the third stage.

Usually, the relationship between curing reaction rate constant and temperature can be expressed by Arrhenius equation^[18], hence the mathematical expression of the degree of cure under isothermal conditions at the first two stages can be obtained as:

$$f_v = \begin{cases} 1 - \exp[-(B_1 t)^\alpha] & (0 \leq t < t_{\text{dis}}) \\ 1 - A \exp(-B_2 t) & (t \geq t_{\text{dis}}) \end{cases} \quad (1)$$

where f_v denotes the degree of cure, t the cure time, α the modified coefficient of the kinetic equation, A the constant at a given temperature in the kinetic equation. B_1 and B_2 represent $k_{10}\exp(-E_1/RT)$ and $k_{20}\exp(-E_2/RT)$ respectively, where k_{10} and k_{20} denote the frequency factors, E_1 and E_2 the activation energies of vulcanization, R the universal constant of gas, T the vulcanization temperature.

In the practical fabrication of rubber products, the vulcanization is a non-isothermal process. Usually, the temperature of every spatial point in the reaction field increases with different rates, and the temperature of the same spatial point increases with different rates at different time points, which cause that the degree of cure cannot be calculated directly by Eq. (1).

In order to solve the above-mentioned problem, the incremental method is introduced. On the basis of discretization strategy, $f_{v,n}$ is defined as the degree of cure at time $n \cdot \Delta t$, and then $f_{v,n-1}$ is defined as the degree of cure at time $(n-1) \cdot \Delta t$, where Δt denotes the time step. Because the time step Δt is far smaller than the whole vulcanization time t , the reaction temperature T can be considered as a constant in every time step, and then the increment of the degree of cure happening in every time step can be calculated by means of the isothermal vulcanization kinetic equation. Hence the numerical computation expression for calculating the degree of cure can be derived as:

$$f_{v,n} = \begin{cases} \frac{f_{v,n-1} + \alpha B_1^\alpha (n\Delta t)^{\alpha-1} \Delta t}{1 + \alpha B_1^\alpha (n\Delta t)^{\alpha-1} \Delta t} & (0 \leq f_{v,n} < f_{v,\text{dis}}) \\ \frac{f_{v,n-1} + B_2 \Delta t}{1 + B_2 \Delta t} & (f_{v,n} \geq f_{v,\text{dis}}) \end{cases} \quad (2)$$

where $f_{v,\text{dis}}$ denotes the degree of cure at the time t_{dis} .

The initial degree of cure $f_{v,0}$ is zero, and Δt can be set according to practical conditions. Other parameters in Eq. (2) are given in Ref. [18] or can be calculated by use of the data given in Ref. [18]. Therefore $f_{v,n-1}$ can be calculated, and $f_{v,n}$ can be derived consequently.

ESTABLISHING GEOMETRIC MODEL

Considering the symmetry of the geometric model, only the left part of the geometric model is presented and described, including the outer mold area and the inner rubber area, as shown in Fig. 1.

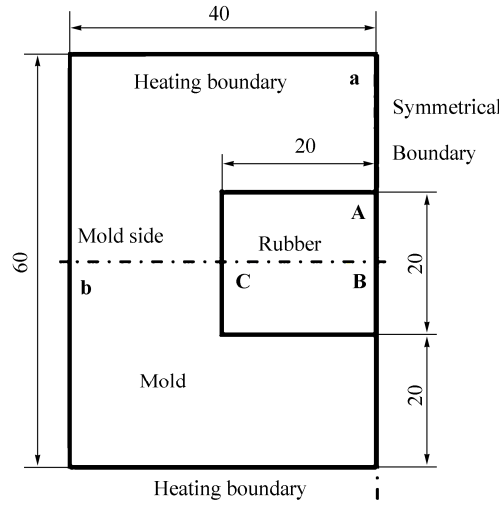


Fig. 1 Geometric model for vulcanization modeling (unit: mm)

The top and bottom of the mold are heating boundaries which are in contact with curing media, namely saturated vapor. The left side of the mold can be exposed to air or insulated from air. Two representative points **a** and **b** in mold, three representative points **A**, **B** and **C** in rubber are chosen to show the results.

ESTABLISHING PARTIAL DIFFERENTIAL EQUATION OF TEMPERATURE FIELD

Under the above precondition, supposing that the thermal conductivity, specific heat capacity and density of materials are constants, the two-dimensional partial differential equation of rubber temperature field can be described as^[20]:

$$D_R [T_R(x, y, t)] = \lambda_R \left(\frac{\partial^2 T_R}{\partial x^2} + \frac{\partial^2 T_R}{\partial y^2} \right) - \rho_R c_R \frac{\partial T_R}{\partial t} = 0 \quad (3)$$

where D_R denotes the rubber area, T_R the rubber temperature, λ_R the thermal conductivity of rubber compound, ρ_R the density of rubber compound, c_R the specific heat capacity of rubber compound at constant pressure.

The two-dimensional partial differential equation of mold temperature field can be obtained with the same form:

$$D_M [T_M(x, y, t)] = \lambda_M \left(\frac{\partial^2 T_M}{\partial x^2} + \frac{\partial^2 T_M}{\partial y^2} \right) - \rho_M c_M \frac{\partial T_M}{\partial t} = 0 \quad (4)$$

where D_M denotes the mold area, T_M the mold temperature, λ_M the thermal conductivity of mold material, ρ_M the density of mold material, c_M the specific heat capacity of mold material at constant pressure.

In order to calculate the temperature field by finite element method, the area is discretized into E elements and n nodes. Accordingly, the temperature of the whole area is dispersed to n nodal temperatures T_l ($l = 1, 2, \dots, n$).

The governing equation of the temperature field can be derived by Galerkin method^[15]:

$$\iint_D \left[\lambda \left(\frac{\partial W_l}{\partial x} \frac{\partial T}{\partial x} + \frac{\partial W_l}{\partial y} \frac{\partial T}{\partial y} \right) + \rho c W_l \frac{\partial T}{\partial t} \right] dx dy - \oint_{\Gamma} \lambda W_l \frac{\partial T}{\partial n} ds = 0 \quad (l = 1, 2, \dots, n) \quad (5)$$

where D denotes the rubber or mold area, W_l the weighting function of l -th node of rubber or mold area, Γ the boundary of rubber or mold area, n outer normal on boundary, s the length of boundary. T , λ , ρ and c represent temperature, thermal conductivity, density and specific heat capacity of rubber or mold, respectively.

DEALING WITH THERMAL BOUNDARY CONDITIONS

Boundary between Mold and Curing Medium

On the boundary between mold and saturated vapor which is used as curing medium, there is convective heat transfer. Therefore, the thermal boundary condition of mold and curing medium is the third kind of thermal boundary condition^[20]:

$$-\lambda_M \frac{\partial T_M}{\partial n} \Big|_{\Gamma_M} = h(T_M - T_f) \Big|_{\Gamma_M} \quad (6)$$

where T_f denotes the temperature of curing medium, h the convective heat transfer coefficient on the heating boundary, Γ_M the boundary of mold area.

Eq. (6) is substituted into Eq. (5), then the governing equation of the temperature field with the boundary condition of mold and curing medium can be obtained:

$$\iint_{D_M} \left[\lambda_M \left(\frac{\partial W_{l,M}}{\partial x} \frac{\partial T_M}{\partial x} + \frac{\partial W_{l,M}}{\partial y} \frac{\partial T_M}{\partial y} \right) + \rho_M c_M W_{l,M} \frac{\partial T_M}{\partial t} \right] dx dy + \oint_{\Gamma} h W_{l,M} (T_M - T_f) ds = 0 \quad (l = 1, 2, \dots, n) \quad (7)$$

where $W_{l,M}$ denotes the weighting function of l -th node in the mold area.

Boundary between Mold and Air

When the mold is exposed to air, there is natural convective heat transfer between mold and air. Besides, there is also radiative heat transfer between mold and surroundings. The thermal boundary condition of mold and air can also be considered as the third kind of thermal boundary condition^[21]:

$$-\lambda_M \frac{\partial T_M}{\partial n} \Big|_{\Gamma_M} = (\alpha_{C,M} + \alpha_{R,M})(T_M - T_a) \Big|_{\Gamma_M} \quad (8)$$

where $\alpha_{C,M}$ denotes the natural convective heat transfer coefficient on the boundary between mold and air, $\alpha_{R,M}$ the radiative heat transfer coefficient on the boundary between mold and air, T_a the temperature of air and surroundings.

On the assumption that all surfaces are gray surfaces, $\alpha_{R,M}$ can be expressed by Eq. (9) under simulation conditions^[20]:

$$\alpha_{R,M} = \frac{\varepsilon_1 C_0 \left[\left(\frac{T_M}{100} \right)^4 - \left(\frac{T_a}{100} \right)^4 \right]}{T_M - T_a} \quad (9)$$

where ε_1 denotes the emissivity of mold, C_0 the black body radiation coefficient.

Eqs. (8)–(9) are fit into Eq. (5), then the governing equation of the temperature field with the boundary condition of mold and air can be obtained as:

$$\begin{aligned} & \iint_{D_M} \left[\lambda_M \left(\frac{\partial W_{l,M}}{\partial x} \frac{\partial T_M}{\partial x} + \frac{\partial W_{l,M}}{\partial y} \frac{\partial T_M}{\partial y} \right) + \rho_M c_M W_{l,M} \frac{\partial T_M}{\partial t} \right] dx dy \\ & + \oint_{\Gamma_M} W_{l,M} \left(\alpha_{C,M} + \frac{\varepsilon_1 C_0 \left[\left(\frac{T_M}{100} \right)^4 - \left(\frac{T_a}{100} \right)^4 \right]}{T_M - T_a} \right) (T_M - T_a) ds = 0 \quad (l = 1, 2, \dots, n) \end{aligned} \quad (10)$$

Boundary between Mold and Rubber

Because nearly no pore exists on the interface between rubber and mold, the thermal boundary condition of rubber and mold is assumed to be the special fourth kind of thermal boundary condition, namely on the boundary between mold and rubber, the temperature and heat flux of the two areas should be equal, respectively. The heat flux (q) through the interface is only determined by heat conduction^[15]:

$$q = -\lambda_M \frac{\partial T_M}{\partial n} \Big|_{\Gamma_M} = h_c (T_M - T_R) \Big|_{\Gamma_M} \quad (11)$$

In Eq. (11), h_c denotes the heat transfer coefficient on the interface between mold and rubber, which can be expressed as:

$$h_c = \frac{2\lambda_M \cdot \lambda_R}{L_g (\lambda_M + \lambda_R)} \quad (12)$$

where L_g denotes the surface roughness of mold cavity.

Eqs. (11)–(12) are fit into Eq. (5), then the governing equation of the temperature field with the boundary condition of mold and rubber can be obtained:

$$\begin{aligned} & \iint_{D_M} \left[\lambda_M \left(\frac{\partial W_{l,M}}{\partial x} \frac{\partial T_M}{\partial x} + \frac{\partial W_{l,M}}{\partial y} \frac{\partial T_M}{\partial y} \right) + \rho_M c_M W_{l,M} \frac{\partial T_M}{\partial t} \right] dx dy \\ & + \oint_{\Gamma_M} \frac{2\lambda_M \cdot \lambda_R}{L_g (\lambda_M + \lambda_R)} W_{l,M} (T_M - T_R) ds = 0 \quad (l = 1, 2, \dots, n) \end{aligned} \quad (13)$$

RESULTS AND DISCUSSION

The formula of rubber compound, used in Ref. [18], is as follows (in parts per hundred of rubber, phr): natural rubber, 100.0; sulfur, 3.0; zinc oxide, 5.0; stearic acid, 0.5; and 2-mercaptobenzothiazole (MBT), variable.

On the basis of the above-mentioned numerical computation expressions, the temperature fields of the mold and rubber compound are simulated by the finite element method. The detailed calculation steps of the temperature fields are listed in Ref. [16]. Then the degree of cure f_v on every spatial point is calculated.

Calculated Example and Verification

A simulation sample (sample 1) is designed to analyze the vulcanization of NR under the above-mentioned preconditions. The main simulation conditions are listed in Table 1. As shown in Fig. 1, the simulated results on points **a** and **b** in the mold area and points **A**, **B**, and **C** in the rubber area are outputted.

It can be seen from Fig. 2 that the temperature of point **a** is higher than the temperature of point **b**, because point **a** is directly in contact with the hot curing medium, whereas point **b** is exposed to cool air. Because point **A** directly contacts the mold, the temperature of point **A** gets to a relatively higher level than the one of point **B**. By comparing T_M with T_R , it can be discovered that the homogeneousness of the temperature distribution in the mold is better than that in the rubber, resulting from the much greater thermal conductivity of the mold material. Obviously, the temporal evolution and spatial distribution characteristics of the rubber temperature field are similar to those of Illustration 4 in Ref. [16] and Illustration 3 in Ref. [14].

The changes of the degree and rate of rubber cure with time for different points are shown in Fig. 3. The distribution of the degree of cure is similar to that of rubber temperature, which can be explained by means of the Arrhenius equation that describes the relationship between reaction rate constant and temperature.

The partial derivative of the degree of cure versus time, *i.e.* $\partial f_v / \partial t$, can be considered as the conversion rate of reaction system. It can be seen from Fig. 3 that the value of $\partial f_v / \partial t$ reaches a maximum and then declines. The maximum reaction rate does not occur at the initial moment of the vulcanization, which supports the autocatalytic characteristic of the accelerated sulfur vulcanization. It can also be seen that higher temperature

leads to higher reaction rate at the initial stage of vulcanization; at the end stage of vulcanization, the reaction rate in the inner area exceeds that in the outer area, due to the lower concentration of reactants in the outer area. The simulated results are consistent with the results given in Refs. [12, 22].

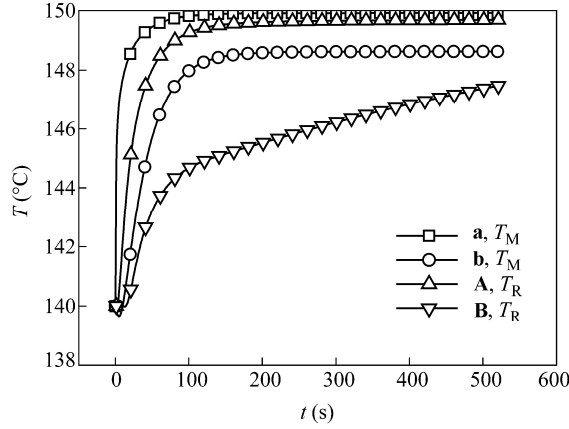


Fig. 2 Curve of the temperature of mold and rubber versus time (sample 1)

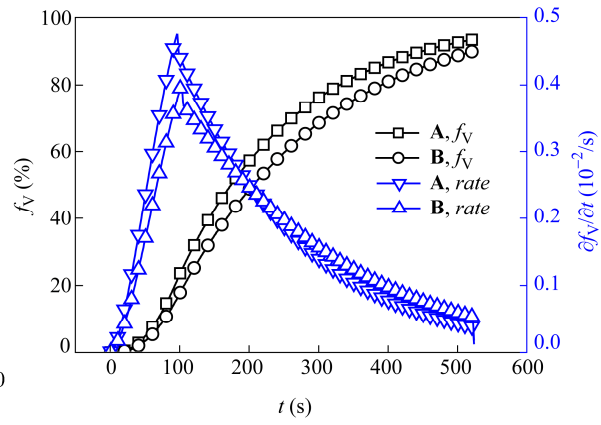


Fig. 3 Curve of the degree and rate of rubber cure versus time (sample 1)

Effect of the Temperature of Curing Medium on Vulcanization

In order to analyze the effect of the temperature of curing medium on the rubber vulcanization, several other simulation samples are made besides sample 1. The temperatures of curing medium in samples 2–6 are 145, 155, 160, 165 and 170 °C, respectively. Other conditions are the same as those of sample 1 listed in Table 1.

Table 1. Main simulation conditions of sample 1

No.	$T_{R,0}$ (°C)	$T_{M,0}$ (°C)	T_f (°C)	c_{MBT} (phr)	h (W/(m ² ·K))	Heat transfer manner of mold side	T_a (°C)
1	140	140	150	1.0	10000	Being exposed to air	25

Because the reaction rate differs from point to point, the whole vulcanization area cannot get to the optimal cure state at the same time. Therefore, the mold-opening time in this paper is defined as the time when the minimum degree of cure in vulcanization area ($f_{V,min}$) reaches the optimal degree of cure ($f_{V,o}$).

It can be seen from Fig. 4 that the increase of the curing medium temperature will lead to the remarkable decrease of the mold-opening time because of the higher reaction rate under higher temperatures. The difference between $T_{R,A}$ and $T_{R,B}$, *i.e.* ($T_{R,A}-T_{R,B}$), could characterize the homogeneousness of the temperature field of the rubber compound. The value of ($T_{R,A}-T_{R,B}$) is determined by thermal conductivity, temperature gradient and cure time. When the temperature of curing medium increases, the temperature gradient between the outer and the inner of rubber is enlarged. In the meanwhile, the mold-opening time decreases, which causes the increase of ($T_{R,A}-T_{R,B}$) at the end of vulcanization. Hence, the increase of the temperature of curing medium will enlarge the heterogeneousness of rubber properties. Furthermore, elevated temperature will cause the increase of the overcuring tendency in the surface layer and the consequent reduction of crosslinking density^[23]. As a result, the temperature of curing medium should be designed with all round considerations.

Effect of MBT Concentration on Vulcanization

In order to analyze the vulcanization characteristics of NR with different concentrations of MBT (c_{MBT}), four simulation samples (samples 7–10) are designed, in which c_{MBT} is 0.7, 1.0, 1.3 and 1.6 phr, respectively. The values of $T_{R,0}$, $T_{M,0}$ and T_f in samples 7–10 are 150 °C, 150 °C and 160 °C, respectively ($T_{R,0}$ and $T_{M,0}$ represent the initial temperature of rubber and mold, respectively). Other conditions are the same as those of sample 1 listed in Table 1.

The curves of mold-opening time and rubber temperature uniformity versus MBT concentration are shown in Fig. 5. The result indicates that the rate of curing reaction increases with c_{MBT} changing from 0.7 phr to 1.6 phr, which is because the activation energy of reaction decreases with the increase of MBT level, as shown in Ref. [18]. In addition, when c_{MBT} increases, the concentration of active accelerator complex increases, and then more sulfur molecules (S_8) are activated, more active sulfurating agents are produced consequently^[24].

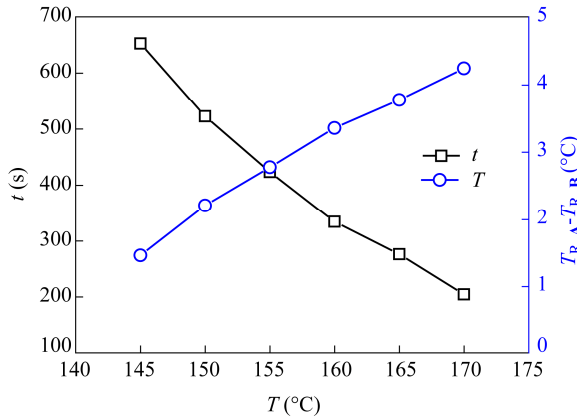


Fig. 4 Curve of mold-opening time and rubber temperature uniformity versus curing medium temperature

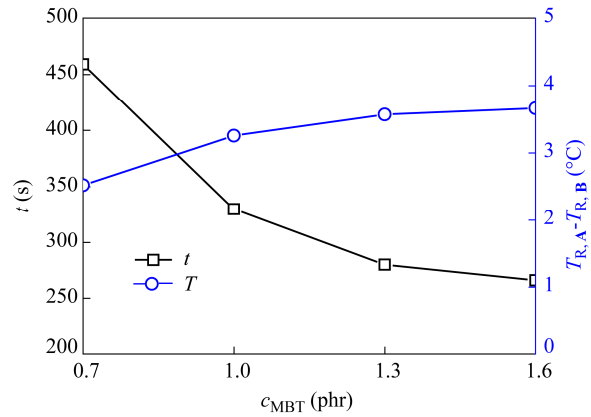


Fig. 5 Curve of mold-opening time and rubber temperature uniformity versus 2-mercaptobenzothiazole concentration

It is shown that the heterogeneousness of the rubber temperature field becomes slightly larger as c_{MBT} increases, mainly caused by the reduction of the mold-opening time. The difference in the degree of cure between points A and B at the end of vulcanization under different c_{MBT} conditions is from 3.7% to 4.0%, indicating that the heterogeneousness of the degree of cure is not sensitive to c_{MBT} . This is because that the reaction rates in both the outer and the inner of rubber compound increase simultaneously with the increase of c_{MBT} .

Effect of the Heat Transfer Manner of Mold Side on Vulcanization

In order to reveal the effect of the heat transfer manner of mold side on the vulcanization, two samples (samples 1 and 11) are established. The side of mold in sample 11 is insulated from cool air, so the boundary is regarded as an adiabatic boundary. Other conditions in sample 11 are the same as those of sample 1 listed in Table 1.

It can be seen from Fig. 6 that the rubber temperature in sample 1 is always less than that in sample 11. This phenomenon can be explained as follows. In the case of sample 1, the mold side is directly exposed to cool air, so there exists a notable temperature gradient in the mold. But in the case of sample 11, the mold side is an adiabatic boundary, so the uniformity of mold temperature in sample 11 is better than the one in sample 1.

In addition, the difference in the distribution uniformity of the degree of cure between the two samples is quite small, which can be explained as follows. The degree of cure is determined by both temperature and time. Compared with sample 1, the rubber temperature in sample 11 is higher, whereas the mold-opening time is shorter.

Even if the distribution homogeneousness of the degree of cure is not obviously improved in the simulation, the mold side should be insulated from cool air in terms of efficient and energy-saving production.

Effect of the Heat Transfer Coefficient of Heating Boundary on Vulcanization

The convective heat transfer coefficient (h) is determined by such variables as the viscosity and density of condensate, the velocity and ingredient of vapor, the surface geometry and flow conditions^[20, 25]. Therefore, the value of h depends on practical processing conditions, and it is difficult to be estimated accurately. Since the main objective of the numerical analysis in this section is to demonstrate the changing tendency of mold-opening

time and rubber cure uniformity affected by the convective heat transfer coefficient, the value of h is selected in the general range as given in literatures.

In addition to sample 1, samples 12–18 are designed to analyze the effect of h on the rubber vulcanization. The general range of h for condensation is 5000–100000 W/(m²·K)^[21]. Furthermore, the average coefficient obtainable in pure dropwise condensation may be as high as 115000 W/(m²·K)^[25]. Under the above conditions, the values of h in samples 12–18 are designated to be 5000, 8000, 12000, 15000, 18000, 20000, 23000 W/(m²·K), respectively. Other simulation conditions are the same as those of sample 1 listed in Table 1.

The curves of mold-opening time and rubber cure uniformity versus the convective heat transfer coefficient of heating boundary are shown in Fig. 7. The increase of h , namely the increase of the efficiency of heat transfer between curing medium and mold, results in the decrease of the mold-opening time. However, the extent of reduction becomes smaller and smaller, which can be explained by that the value of h becomes large enough whereas the temperatures of curing medium are arranged to be the same in samples 12–18.

By the same token, the distribution heterogeneousness of the degree of cure at the end of vulcanization under different h conditions keeps nearly constant.

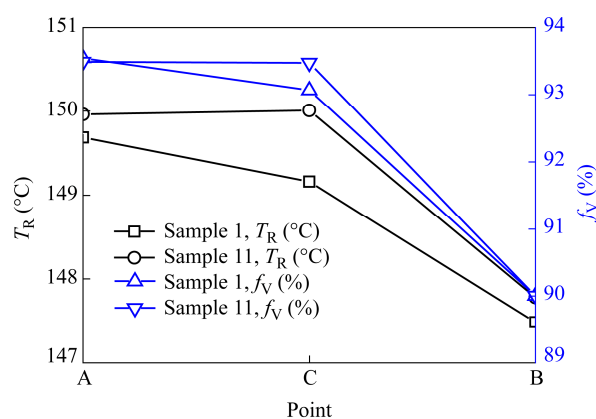


Fig. 6 Distribution of the temperature and degree of rubber cure under different thermal boundary conditions of mold

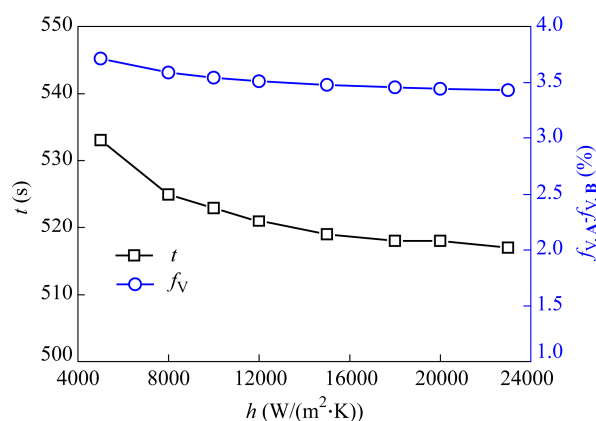


Fig. 7 Curve of mold-opening time and rubber cure uniformity versus the convective heat transfer coefficient of heating boundary

In the light of engineering practice, both the difference in the mold-opening time and the distribution heterogeneousness of the degree of cure in different h situations can be neglected. Hence, considering energy saving, the convective heat transfer coefficient of heating boundary is not necessarily improved to an exorbitant level.

CONCLUSIONS

The autocatalytic characteristic of natural rubber accelerated sulfur vulcanization is supported by the simulated results. The distribution uniformity of the degree of cure remains on almost the same level regardless of the high or low ratio of accelerator (MBT) concentration to the sulfur dosage.

The temperature of curing medium should be designed in terms of the cure cycle and the distribution uniformity of the degree of cure. In view of the temperature controlling accuracy and energy-saving production, the mold side should be insulated from air. At a given temperature of curing medium, the convective heat transfer coefficient of heating boundary is not necessarily improved to an exorbitant level.

REFERENCES

- 1 Ding, W.B., Wang, L., Yang, Q., Xiang, W.D., Gao, J.M. and Amer, W.A., *Int. Polym. Proc.*, 2013, 28(2): 132
- 2 Rahimi, A. and Mashak, A., *Plast., Rubber Compos.*, 2013, 42(6): 223
- 3 Aprem, A.S., Joseph, K. and Thomas, S., *Rubber Chem. Technol.*, 2005, 78(3): 458
- 4 Jia, Y.X., Wang, X.X., Feng, L.G. and An, L.J., *Eur. Polym. J.*, 2009, 45(6): 1759
- 5 Akiba, M. and Hashim, A.S., *Prog. Polym. Sci. (Oxford)*, 1997, 22(3): 4751
- 6 Wang, X.X., Jia, Y.X., Feng, L.G. and An, L.J., *Macromol. Theory Simul.*, 2009, 18: 268
- 7 Isayev, A.I. and Wan, M., *Rubber Chem. Technol.*, 1998, 71(5): 1059
- 8 Han, I.S., Chung, C.B., Jeong, H.G., Kang, S.J., Kim, S.J. and Jung, H.C., *J. Appl. Polym. Sci.*, 1999, 74(8): 2063
- 9 Ghoreishy, M.H.R. and Naderi, G., *J. Elastomers Plast.*, 2005, 37(1): 37
- 10 Shojaei, A., *Int. Polym. Proc.*, 2006, 21(4): 421
- 11 Bruger, T. and Broock, U.Von., *Kautsch. Gummi Kunstst.*, 2007, 60(7/8): 368
- 12 Arrillaga, A., Zaldua, A.M., Atxurra, R.M. and Farid, A.S., *Eur. Polym. J.*, 2007, 43(11): 4783
- 13 Yan, X.Q., *Polym. J.*, 2007, 39(10): 1001
- 14 Nozu, S., Tsuji, H., Itadani, M., Fujiwara, W. and Ohnishi, K., *J. Mater. Process. Technol.*, 2008, 201(1/3): 720
- 15 Jia, Y.X., Sun, S., Liu, L.L., Xue, S.X. and Zhao, G.Q., *Polymer*, 2003, 44(1): 319
- 16 Jia, Y.X., Sun, S., Xue, S.X., Liu, L.L. and Zhao, G.Q., *Polymer*, 2002, 43(26): 7515
- 17 Wang, P.Y., Qian, H.L., Yu, H.P. and Chen, J., *J. Appl. Polym. Sci.*, 2003, 88(3): 680
- 18 Wang, P.Y., Qian, H.L. and Yu, H.P., *J. Appl. Polym. Sci.*, 2004, 92(5): 3260
- 19 Wang, P.Y., Qian, H.L. and Yu, H.P., *J. Appl. Polym. Sci.*, 2006, 101(1): 580
- 20 Incropera, F.P., Dewitt, D.P., Bergman, T.L. and Lavine, A.S., *Fundamentals of Heat and Mass Transfer*, Wiley, New York, 2007
- 21 Welty, J.R., Wicks, C.E., Wilson, R.E. and Rorrer, G., *Fundamentals of Momentum, Heat and Mass Transfer*, Wiley, New York, 2001
- 22 Choi, D., Kader, M.A., Cho, B.H., Huh, Y.I. and Nah, C., *J. Appl. Polym. Sci.*, 2005, 98(4): 1688
- 23 Fan, R.L., Zhang, Y., Li, F., Zhang, Y.X., Sun, K. and Fan, Y.Z., *Polym. Test.*, 2001, 20(8): 925
- 24 Ding, R. and Leonov, A.I., *J. Appl. Polym. Sci.*, 1996, 61(3): 455
- 25 McCabe, W.L., Smith, J.C. and Harriott, P., *Unit Operations of Chemical Engineering*, McGraw-Hill, New York, 2001