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Numerical Investigation of Curing Process in Reaction Injection Molding of Rubber for Quality Improvements

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Abstract. A large number of rubber products are formed into their final shape by vulcanization. In particular, curing process of rubber is the final step in manufacturing many rubber products and determines both the quality of the resulting product as well as production costs. This paper is devoted to the simulation of rubber curing process in a three-dimensional model. The effects of final temperature of mold are investigated on curing process and quality of final product. The results were compared with the experimentally measured data, which confirmed the accuracy and applicability of the method.

Introduction

Curing process of rubber compounds has a crucial influence on the quality and service performance of the final product. For example, tensile and tear strength of rubber compounds will highly improve after the appropriate curing process [1]. The progress of the curing reactions is defined quantitatively in terms of the fractional degree of conversion of rubber compound, usually designated α. To model the kinetics it is necessary to derive an equation expressing $d\alpha/dt$, the rate of change of α by time, as a function of α and temperature. Numerical simulations applied to injection molding have basically started in the early 1970's [2, 3]. These first developments were applied to the filling stage in 2D simple geometries [4, 5]. Most recently reported simulations are dedicated to the static analysis of heat transfer and curing kinetics, and on the assumption that the curing stage could be decoupled from the filling stage. In the present study a mathematical model for the simulation of the vulcanization process of rubber compounds has been developed. The model is based on the finite element solution of the 3D transient conduction heat transfer equation that has been solved with Fluent. For this purpose, a UDF code is devoted for solving heat transfer equation in conjunction with an empirical cure kinetic model for the evaluation of the degree of cure (state of cure) in rubber. In the following sections, the governing equations and mathematical model are described and then the finite element working equations associated with this problem are introduced. The computational results are presented by investigating effects of parameters, and finally the conclusions are drawn.

Theoretical Heat Transfer Equation

The differential equation governing transient three-dimensional heat conduction with application to rubber technology is [6]:

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(k\frac{\partial T}{\partial y}\right) + \frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right) + \dot{Q} \tag{1}$$

where T is temperature, t is time, ρ is density, c_p is the specific heat, k is the thermal conductivity and Q is the heat generation rate per unit volume. Density of rubber compounds normally decreases when temperature increases. However, due to high pressure used in press machine the volume of the mold cavity can be considered to be nearly constant and therefore the density can be well assumed constant [7]. Heat capacity of rubber increases with increasing of temperature and state-of-cure. Since the temperature dependency of heat capacity cannot be described by a simple mathematical equation, a table of heat capacity-temperature that is directly measured by the DSC experiment has been used [8]. Thermal conductivity of the rubber is a function of temperature and is assumed to be described by a linear equation [9] as:

$$k = a - bT \ . \tag{2}$$

As mentioned Q is the heat generation rate due to vulcanization reaction and is related to the rate of cure. If the degree of cure is defined as:

$$\alpha = \frac{\Delta H_t}{\Delta H_\infty} = \frac{Q_t}{Q_\infty} \ . \tag{3}$$

then the rate of heat generation is given by:

$$\dot{Q} = Q_\infty \left(\frac{d\alpha}{dt}\right) \ . \tag{4}$$

∞) is a material property and can be determined by an isothermal or non-isothermal DSC experiment [10].

Cure Reaction Kinetic

The vulcanization of elastomers is a process whereby chemical crosslinks are introduced between the elastomer chains, resulting in the formation of a three-dimensional network. For curing of rubbery materials, the state of cure or degree of cure, α, which represents the extent of reaction, has been described by many empirical models [11]. In this work, following kinetic model is described by a Kamal-type equation [12]:

$$\alpha = \frac{k.(t-t_i)^n}{1+k.(t-t_i)^n} \ , \tag{5}$$

i are rate constant and induction time respectively, which have an Arrhenius dependence on temperature, as follows:

$$k = k_0.\exp\left(-\frac{E}{RT}\right) \tag{6}$$

$$t_i = t_0.\exp\left(\frac{T_0}{T}\right) \tag{7}$$

0 are model properties. In order to determine these parameters various techniques have been developed in turn: the Mooney viscometer, the Wallace–Shawbury curometer, the oscillating disc rheometer (ODR), and the moving disc rheometer (MDR), in addition to the calorimetry techniques. The isothermal calorimetry and its counterpart in scanning mode, the isothermal moving disc rheometer (MDR), and the improvement of this last technique with the rubber process analyzer run in scanning mode, are considered [10].

Table 1. Physical and thermal properties of the model components

Part name	Density [kg/m^3]	Thermal conductivity [W/m.°C]	Heat capacity [J/kg.°C]
Rubber	1120	0.5	1180
Mold	7700	50	460

Table 2. Cure model parameters

Part name	k_0	n	E [J/gmol]	t_0 [s]	T_0 [K]	Q_1 [J/m^3]
Rubber	1.4×10^{25}	2.91	260622	4.104×10^{-10}	11713	4.54×10^{6}

i in equation (7) is the induction time. During this time the degree of cure is zero, because no chemical reaction takes place inside the rubber. In other words, only physical changes occur in the rubber. The curing stage of elastomeric materials is a highly nonisothermal process and thus a nonisothermal cure kinetic model should be selected. So the induction time is replaced by the “characteristic time” concept, as proposed by Isayev and Deng [11].

$$\bar{t} = \int_0^t \frac{dt}{t_i(T)} \tag{8}$$

$i(T)$ is the dependence of induction time to temperature described by Equation (7). When the value of characteristic time t becomes equal to one, the upper limit of t is considered as induction time dt) is described by a Kamal-type equation [13].

$$\frac{d\alpha}{dt} = S_\alpha = nk^{1/n}\alpha^{(n-1)/n}(1-\alpha)^{(n+1)/n} \tag{9}$$

Boundary Conditions

The boundary conditions used in the present study are first specified nodal temperature in upper and lower surface of mold and then convection type conditions in lateral walls.

Results and Discussion

Based on the above described mathematical model and simulation of rubber part and mold, this assembly was placed in a platen press (see Fig. 1 for CAD drawing of top view of the model).
Selected elements A and B are the nearest and farthest elements to surface of mold, respectively.
Temperature profiles of selected elements are represented in Fig. 4. These elements have been chosen to investigate the variations of the temperature and state of cure at different regions of the rubber compound.
In order to validate the accuracy of the developed model, the state of cure profiles for one of these points is compared with experimentally measured temperature, which is shown in Fig. 5. Very good agreement can be observed between the model predictions and the actual data. The variations of state of cure by time for the two elements inside the rubber are shown in Fig.s 6. Due to the different temperature histories because of the heat conduction and high thickness of rubber, various profiles for state of cure at each element were obtained.

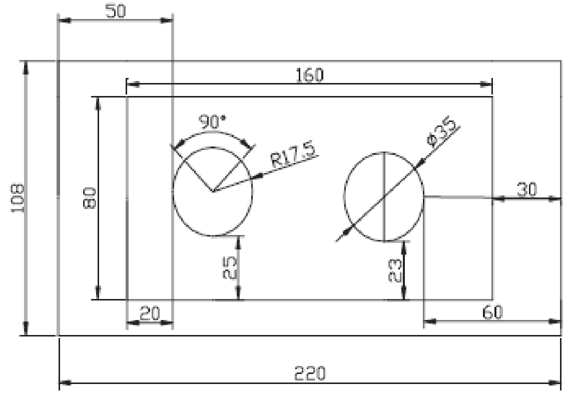

Fig. 1. Drawing of rubber and mold (thickness = 33mm, All units are in mm)

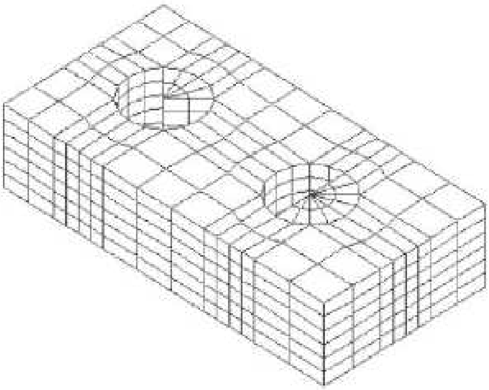

Fig. 2. Finite element mesh of the rubber part

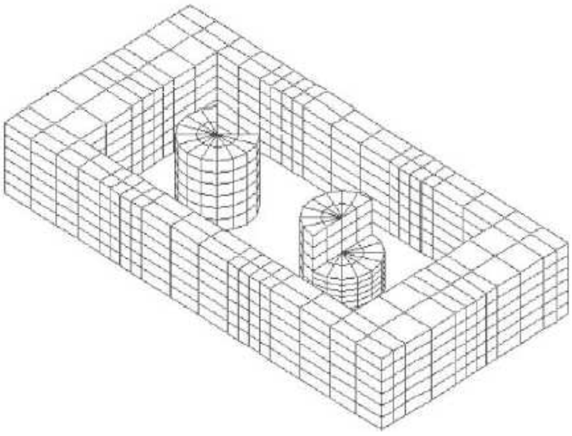

Fig. 3. Finite element mesh of the mold

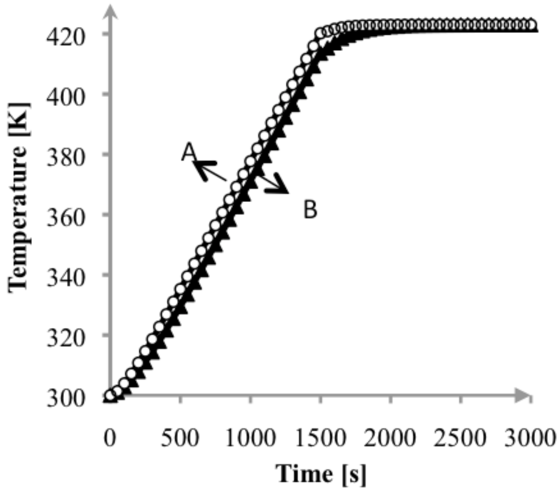

Fig. 4. Variation of temperature with time for elements A and B.

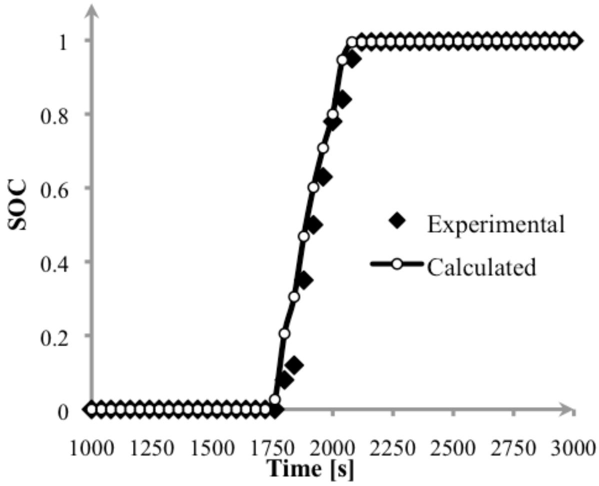

Fig. 5. Comparison between experimentally measured and predicted values of state of cure

For having a uniform curing process, all the rubber part must simultaneously reach the end of curing (soc $\approx$ 1). As it can be seen in Fig.6, every selected element has a unique curing profile that means the rubber does not have a uniform curing stage. In order to overcome this problem, an applicable method is developed. In this approach the final temperature of mold is decreased.

Maximum difference between end times of curing happens for elements A and B. This issue is presented in Fig. 7.

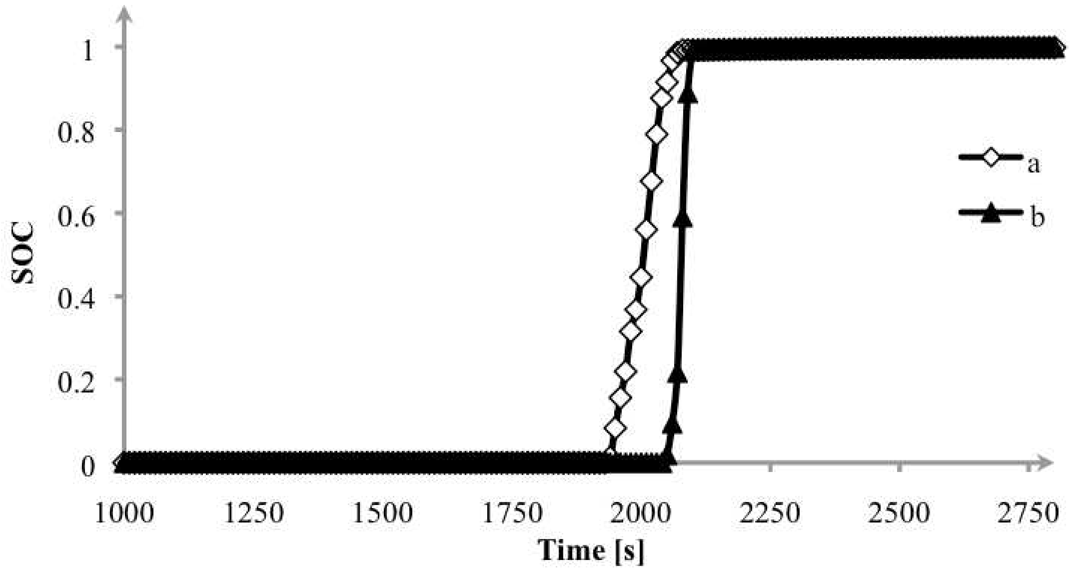

Fig. 6. Variation of state of cure with time for elements a and b

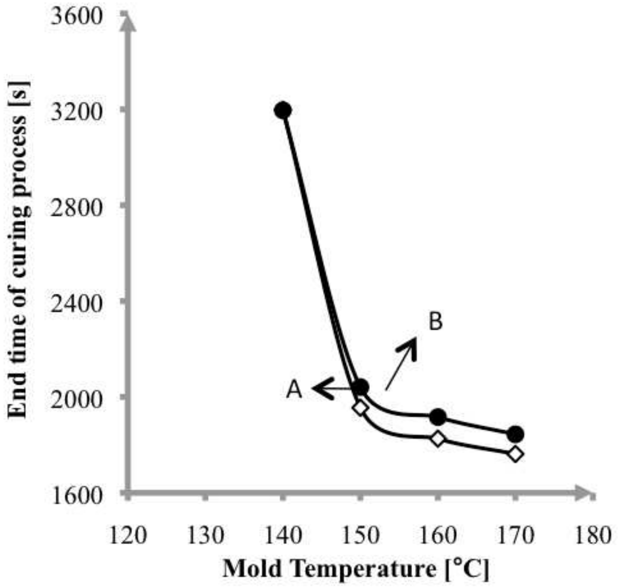

Fig. 7. Variation of end time of curing process vs. mold temperature for elements A and B.

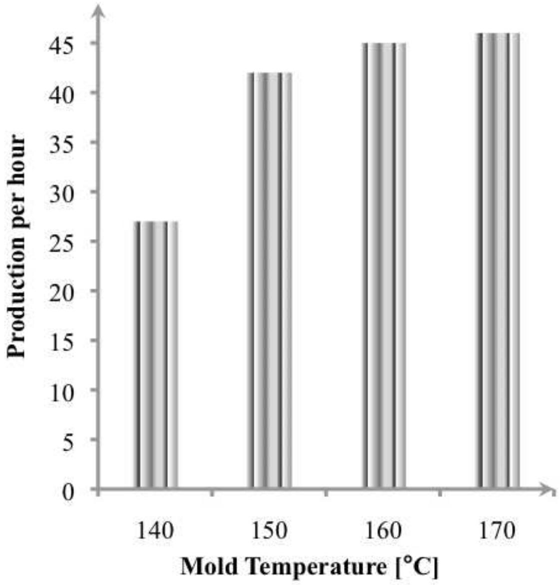

Fig. 6. Production per hour for different mold temperature

It is also shown that by reducing mold temperature this difference is reduced as well. The reason is that the reduction of mold temperature leads to a more significant reduction of parameter *k* in elements closer to walls, i.e. element A, which with respect to equation 5, will finally result in a higher increase of end time of curing for element A compared with element B. This trend continues until 140°C where end time of curing for both elements is the same. At this temperature however, end time of curing is increased significantly, which means better quality but much less production rate. This might not be economically efficient.

Fig. 8 indicates the production rates for different temperatures. It can be observed that the production rate at 140°C is nearly half of the rate at 170°C. The difference between end times of curing of elements A and B at 170°C is 80 seconds, which will not yield a fine quality rubber.

Mold temperature of 150°C has been selected to optimize both rubber quality and production rate, where the difference between end times of curing of A and B elements is 20 seconds, which yields good quality, and the production rate is as high as in 170°C.

Conclusions

A 3D finite element model was produced for the simulation of the vulcanization process of rubber parts in molds. A computer code was employed in Fluent to model non-isothermal curing kinetic. This computer model can be used to simulate the curing process of a complex rubber part. The applicability of the developed model has also been verified by the comparison of the calculated state of cure profile with experimentally measured data. At end in order to improve the quality of the rubber part, the optimized temperature of mold was found.

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