Research on Vulcanization Process Simulation of Butyl Rubber Based on A New Characterization Model of Curing Degree

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SUMMARY

Butyl rubber is an isobutylene/isoprene copolymer and is provided with good properties including low permeability to gases, good thermal stability and high resistance to oxygen and ozone action, among others. It is well known that the end-use rubber properties depend on the state of cure distribution in the rubber products. This work aimed to predict the state of cure in vulcanization process of butyl rubber by the finite element simulation based on a new characterization model. For describing the cure state, the new characterization model of curing degree was developed, which was implemented in finite element simulation model by the secondary development of ABAQUS software subroutine UVARM. To improve the accuracy, the vulcanization reaction heat was also considered, which was implemented by the subroutine HETVAL. Results indicated that the predicated results of curing degree based on the simulation model are according to the experiments. The model can be well distinguished the curing stages and its degree, such as under curing, positive curing, over curing. It would give a valuable guide for optimizing the vulcanization processing of butyl rubber or other vulcanized rubbers.

Keywords: Butyl rubber; Vulcanization process; Finite element simulation; Characterization model

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INTRODUCTION

Butyl rubber has been used in a great variety of applications, such as inner tubes, tubeless tire liners, rings, construction sealants, hoses, etc. [1], due to their unique properties, exceptionally low gas and moisture permeability and outstanding resistance to heat aging, weather, ozone, chemical attack, flexing, abrasion and tearing [2]. However, it must be vulcanized to yield useful, durable end use products for most applications. Vulcanization process triggers a cascade of chemical reactions, which result in the formation of chemical crosslinks, a three-dimensionally networked polymer with suitable material properties. A prediction method for rubber vulcanization process has historically received considerable attention in manufacturing process for rubber products.

In recent years, there exists increasing demand for simulation driven design which will cut down the cost and time required for its development, especially for thick parts [3]. In order to model the vulcanization process, it is important to develop a characterization model of curing degree and analyze the thermal coupling between reaction heat and temperature field. Owing to this fact, many researchers have attempted to develop predicted models for the temperature and state-of-cure during the vulcanizing process. Coran [4] proposed a simplified model for curing kinetics which includes the acceleration, crosslinking and scorch-delay. After that, improved chemical kinetics model was developed by Ding et al. [5]. Abhilash et al. [6] assumed one-dimensional heat conduction model for curing process simulation of a 20 mm thick rubber slab. Curing process of a 50 mm thick rubber sheet was studied by Likazor and Krajnc [7, 8], it was indicated that good agreements between the predicted and measured results of temperature and curing degree have been obtained. Recent studies on kinetic models reviewed by Ghoreishy [9]. In the study, ABAQUS finite element software has been used in conjunction with a subroutine UMATHT to solve the heat conduction equation and the rubber cure kinetics, simultaneously [10]. Then, finite element method was extended for optimization of the curing time of a thick rubber article [11]. It was shown that the finite element method in conjunction with appropriate kinetic model can be successfully used to simulate the rubber curing process. Yau et al. [12] studied the temperature in curing process of large rubber product by finite element method, and good agreement was observed. Marina Fernando et al. [13] and Zhang et al. [14] also predicted the curing process by finite element method. In summary, the finite element method was useful to simulate the curing process of rubber. Most of the studies were focused on the fitting of the curing curves for determining the state of cure. However, curing stages (such as under curing, positive curing and over curing) were not easy to distinguish in the current studies, which was important for the optimization rubber curing process in industrial scale.
This work aims to develop a novelty characterization model for curing process simulation of butyl rubber. Based on the model, the curing stages and its degrees can be distinguished easily, which has important guiding significance for vulcanization process optimization of rubber products.

MODELS FOR CHARACTERIZING THE CURING PROCESS

Various kinetic models have been developed to predict cure behavior of rubber products. The minimal requirement of the model is to at least describe the rheometry data for isothermal conditions. Depending on the origin, the developed models can be classified in two categories, which are called as mechanistic kinetic models [5, 15-18] and empirical models [19-22]. The former models need to acknowledge the underlying chemistry of vulcanization, which is usually difficult in mathematical modeling due to its rigorous equations [10]. Therefore, empirical models are adopted, which are regression models that fit the experimentally measured data based on the assuming a particular functional form. The empirical model of curing degree $\varepsilon$ is usually expressed by the Eq. (1) [16], then improved by many researchers [20-22]. The power law type models were used for non-isothermal, three dimensional design problems by Ghoreishy, etc. [22]:

$$\frac{d\varepsilon}{dt} = f(\varepsilon, T)$$ (1)

where $t$ is the elapsed time, $T$ is the temperature.

**Figure 1** shows the typical curing curve of rubber, which is obtained from a cure meter. It can be seen that there are four stages in the curing process. The above models show the change trend of cure behavior, however, the degree of the three curing stages (under-curing, positive curing, over-curing) are difficult to characterize.

According to the definition of M10 and M90, which are shown at **Figure 1**. $M_n$ was defined as:

$$M_n = ML + (MH - ML) \times n\%$$ (2)

In this study, a new characterizing model for state of cure named Departure of Torque (DOT) is presented, which is given as:

$$S = \begin{cases} 
  n - 100 & t_n < t_{100} \\
  100 - n & t_n > t_{100}
\end{cases}$$ (3)
where $S$ is the DOT, $n$ is a number between 0 and 100, which is the function of curing time.

Then, the degree of the three curing stages can be given:

\[
\begin{align*}
S < -10 & \quad \text{Under curing stage} \\
-10 \leq S \leq 3 & \quad \text{Positive curing stage} \\
S > 3 & \quad \text{Over curing stage}
\end{align*}
\]  

(4)

**Figure 1.** Typical curing curve of rubber. $M_L$–minimum torque; $M_H$–maximum torque; $t_H$–optimum cure time; $t_{10}$–scorch time; $t_{90}$–cure time; $t_{REV97}$–reversion time. $M_{10} = M_L + (M_H - M_L) \times 10\%$; $M_{90} = M_L + (M_H - M_L) \times 90\%$; $M_{REV97} = M_L + (M_H - M_L) \times 97\%$

**FINITE ELEMENT MODELS**

**Thermal Boundary**

In the curing process, heat flux on surfaces due to convection is governed by:

\[q_c = h(T_s - T_\infty)\]  

(5)

where $q_c$ is the heat flux across the surface, $h$ is a reference film coefficient, $T_s$ is the temperature at this point on the surface, and $T_\infty$ is the ambient temperature value.
Heat flux on a surface due to radiation to the ambient is governed by:

\[ q_r = \varepsilon \sigma (T_s - T_z)^4 - (T_\infty - T_z)^4 \]  

(6)

where \( q_r \) is the heat flux across the surface due to the radiation, \( \varepsilon \) is the emissivity of the surface and \( \sigma \) is the Stefan–Boltzmann constant and \( T_z \) is the value of absolute zero on the temperature scale being used.

The equation of the transient heat conduction in the finite element simulation is given as:

\[ \rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) + Q \]  

(7)

where \( T \) is the temperature, \( t \) is the time, \( \rho \) is the density, \( C_p \) is the specific heat, \( k \) is the thermal conductivity and \( Q \) is the heat generation rate per unit volume, respectively. Normally density of rubber decreases with increasing of temperature [7], however, it can be considered to be constant due to the high pressure used in press machine [9].

**User Subroutine Development**

There are some basic features associated with the modeling of rubber curing process that the ABAQUS cannot take them into consideration, such as reaction heat and curing degree. Therefore, a subroutine is necessary to be added to the core of the finite element software. HETVAL and UVARM are two user subroutines which can be tailored based on the selected kinetics, and implemented into the finite element model [9]. In order to calculate the curing degree, the user subroutine UVARM was selected in this work. A FORTRAN code is developed to carry out the DOT part of our modeling and implemented it into UVARM. The solution technique in this subroutine is based on the update of the \( S \) at each increment. **Figure 2** shows the flowchart of the UVARM code.

**Meshing and Modeling**

The commercial finite element software ABAQUS was used for the solution of the heat transfer equation. The user subroutine UVARM was linked to the finite element code to perform the \( S \) calculations. The developed algorithm was used for the simulation of the curing process of a rubber article with hot
plate. The finite element model was developed to simulate the curing process of butyl rubber in plate vulcanizing machine. Figure 3 and Figure 4 show the 3D model and the meshing in 2D cross section, respectively. The upper and lower plates were given the constant temperature boundary conditions of 150°C.
RESULTS AND DISCUSSION

Figure 5 shows the steady-state temperature field in rubber plate vulcanizing process. It can be seen that, the maximum temperature in the steady state is 150°C and the minimum value is 146°C, the temperature error is acceptable.
Figure 6a shows the DOT field in the curing time of 3000 s. It can be seen that the range of S is from -9.9 to -9.0, the rubber has just entered its positive curing stage based on the definition of S; the range of S in the curing time of 5400 s is from -0.06 to 0.06, which is in the best curing stage (seen in Figure 6b); Figure 6c shows the DOT field in the curing time of 9000 s. Results indicate that the range of S is 3 to 3.2, the rubber has just reached the boundary of the over curing stage; the range of S in the curing time of 12000 s is from 9.29 to 9.76, which is over curing obviously (seen in Figure 6d).

![Figure 6a](image1)
![Figure 6b](image2)
![Figure 6c](image3)
![Figure 6d](image4)

**Figure 6. DOT fields under different curing time.** (a) 3000 s, (b) 5400 s, (c) 9000 s, (d) 15000 s

It can be seen that the rubber curing boundary conditions and the heat transfer conditions are not exactly the same, but the results are credible due to its error is very small comparing the curing time by using the rheometer.

Table 1 shows the results of predicted and measured curing degree. It can be seen that the predicted curing degree is according to the measured results, the difference is less than 1%. Based on the DOT method, it can be also used to optimize the curing process of other thick rubber products, such as tire.
Table 1. Predicted and measured curing degree

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curing time/min</td>
<td>50</td>
<td>90</td>
<td>150</td>
<td>250</td>
</tr>
<tr>
<td>Average DOT $S$</td>
<td>-9.45</td>
<td>0</td>
<td>3.1</td>
<td>9.5</td>
</tr>
<tr>
<td>Predicted curing degree</td>
<td>0.905</td>
<td>1</td>
<td>0.969</td>
<td>0.905</td>
</tr>
<tr>
<td>Measured curing degree</td>
<td>0.912</td>
<td>0.998</td>
<td>0.961</td>
<td>0.91</td>
</tr>
</tbody>
</table>

CONCLUSIONS

In spite of various numerical researches were carried out in the field of rubber vulcanization process, there are still some very precise points that have not been addressed for this topic in the literature. In this study, a new characterization model of curing degree is developed for describing the cure state, which is the DOT characterization method.

In this model, we have tried to accurately calculate the degree of the three curing stages of the butyl rubber, which can be also used for other rubber products, especially for optimization thick rubber products. Moreover, the comparison between the predicted and experimentally measured curing degree has been performed in this work. Results indicate that the curing degree has very good agreement with the actual data.

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