Research on Application of Simulation Analysis Technology in Vulcanization Time Design of a Rubber Spring

LIU Baibing, WEN Taidou, BU Jiling, XIE Yanfei, and LI Bin

(Zhuzhou Times New Material Technology Co., Ltd, Zhuzhou, Hunan Province, 412007, P.R. China)

Abstract: This paper briefly describes the principles and methods of calculating the vulcanization time of rubber products using a traditional empirical method and a simulation analysis approach. A rubber auxiliary spring was used as an example, and its optimal vulcanization time was calculated via the two aforementioned strategies. The results from calculation were compared with and verified by experimental measurements of the swelling index and vertical stiffness of the products. The results demonstrate that the simulation analysis approach can better predict the curing degree of rubber and reduce the number of production trials and the cost of product development. This study provides a new research direction for subsequent engineering application of vulcanization process parameter design.

Keywords: rubber, vulcanization process, curing degree, positive vulcanization time, simulation.

Vulcanization is the most important step in the manufacturing and processing of rubber products. An appropriate degree of vulcanization is key to realize the best product performance [1]. At present, most of the domestic rubber manufacturers in China use traditional calculation formulae to design the curing process. With the development of science and technology in recent years, researchers have proposed two novel strategies for vulcanization process design. One uses embedded thermocouples to measure the internal temperature elevations in key parts inside the product. The experimental data are then converted into degrees of vulcanization

1

through reasonable vulcanization kinetic models to determine the vulcanization time required. However, such method is time-consuming and high cost. The results also lack sufficient physical insights and fail to provide any basis for evaluating the performance of rubber products. The other approach utilizes computer-based numerical simulation. It can predict the temperature and degree of vulcanization at any locations inside the rubber products, which helps reduce cost of product development and shorten the research and development cycle [2].

To this end, this article takes a rubber auxillary spring as an example and calculates its optimal vulcanization time using a traditional empirical calculation method and a simulation analysis approach based on the Sigmasoft software. The accuracies of these two analytical methods are evaluated by experimentally measuring the swelling index and the vertical stiffness of the product. This study provides a new research direction for subsequent engineering application of vulcanization process parameter design.

1. Research Objects

Figure 1 is a schematic illustration of the structure of a rubber auxiliary spring, which has a circular shape composed of four layers of metal spacers and three layers of rubber. Its maximum outer diameter is 320 mm, and the height is 214 mm. Based on the structural characteristics of the product, the production mold adopts a high-pressure automatic demolding structure. It is equipped with an upper and a lower heating plates, as well as a heating ring in the middle. The dimension of the main body of the mold is Φ550 x 349. Furthermore, layered structures are designed to reduce the formation of defects such as bubbles and to provide space for stock overflow. The rubber matrix is isoprene. The rubber stock is preheated to approximately 60°C, transferred into a barrel, pressurized and extruded to fill into the cavity. The temperatures of the upper, middle, and bottom heating sources are designed to be 170°C, 145°C, and 165°C, respectively.
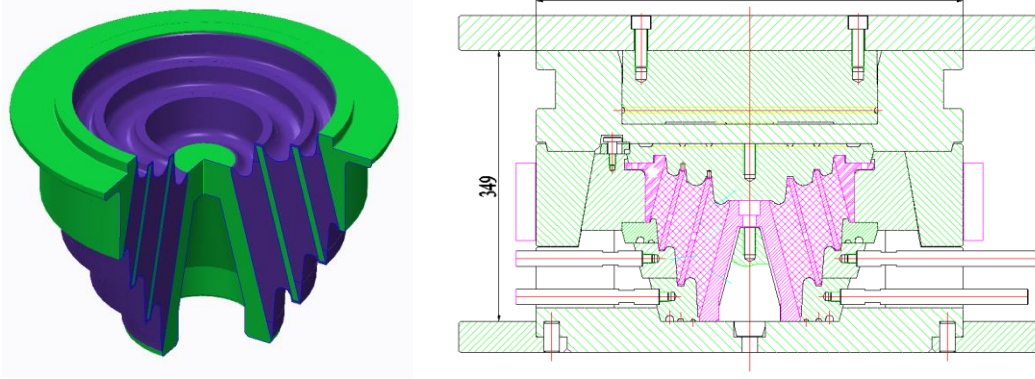
Figure 1. Schematic illustration of the structures of the rubber auxiliary spring and its production mold.

2. Traditional Calculation Method

2.1. Theoretical Basis

The vulcanization temperature and the vulcanization time are negatively correlated. Their relationship can be characterized by the temperature coefficient of vulcanization, which refers to the change of vulcanization time with a temperature difference of 10°C. Based on the definition of the temperature coefficient of vulcanization, van't Hoff equation and Arrhenius equation can be used to calculate the time required to achieve an equivalent degree of vulcanization at different curing temperatures, namely, the equivalent vulcanization time [3].

According to the van't Hoff equation, the relationship between the vulcanization temperature and the vulcanization time is shown as follows:

$$\frac{t_1}{t_2} = K^{\frac{T_2-T_1}{10}} \tag{1}$$

where T_1 and T_2 are the vulcanization temperatures, in Kelvin (K); t_1 and t_2 are the vulcanization times at T_1 and T_2, respectively, in minutes (min); K is the temperature coefficient of vulcanization, unitless.

Since the Arrhenius equation describes the temperature dependence of chemical reaction rate, the relationship between the vulcanization temperature and time is established as:

$$log\frac{t_1}{t_2} = \frac{E}{2.303R}\left(\frac{T_2-T_1}{T_2*T_1}\right) \tag{2}$$

where R is the ideal gas constant, $R = 8.3143$ J/(mol·K); E is the vulcanization activation energy, in kJ/mol.

Both the temperature of vulcanization coefficient, K, in the van't Hoff equation and the vulcanization activation energy, E, in the Arrhenius equations depend on the material properties of the rubber stock and are functions of the vulcanization temperature. However, these two equations fail to consider the effect of product shape on vulcanization time, and the calculation procedures are considerably complicated. Therefore, the two equations have limited success in their engineering applications in the manufacturing of rubber products. Many manufacturers instead use empirical formulae to calculate the vulcanization time of rubber products.

2.2. Brief Introduction of Traditional Empirical Calculation

Rubber is a poor heat conductor. The temperature difference between the surface and the interior increases with the thickness of the section. When the specimen thickness is greater than 6 mm, the influences of heat transfer, heat capacities, mold cavity shape, and the curing characteristics of the rubber stock on vulcanization must be considered. In general, for thick products with a rubber thickness (S) of greater than 6 mm, every 1 mm increase in thickness leads to an increase in the vulcanization time of approximately 47 s. Therefore, an empirical parameter that relates the vulcanization time and the rubber thickness is defined as $H = 47/60 = 0.78$ (s/mm).

Many rubber products are composed of layers of metal spacers and layers of rubber. During vulcanization, the temperatures of the metal spacers and the rubber, prior to their introduction to the mold cavity, are lower than the mold cavity temperature. The actual vulcanization time should thus include the time needed for the rubber stock and metal spacers to be heated inside to reach the cavity temperature, defined herein as the temperature compensation time, t_{comp}. Therefore, the empirical formula for the vulcanization time is:

$$t = T_{c90} + H(S-6) + t_{comp} \tag{3}$$

where, t is the vulcanization time; T_{c90} is the vulcanization time at a predetermined temperature; H is the empirical parameter, $H = 0.78$; S is the maximal thickness of the rubber part in the product; t_{comp} is the temperature compensation time.

The temperature compensation time is affected by the product structure. The temperature compensation time is longer with more internal metal spacers, a more complicated mold structure, and a longer vulcanization time.

The temperature compensation time for this type of product is determined from Table 1.

Table 1. Determination of the temperature compensation time

Number of internal spacers	t_{comp} (min)
1	15
2	25

Note：For products with 0 or 3 internal spacers, their compensation times are determined by other means.

2.3. Calculation of the Vulcanization Time

According to equation (3), the vulcanization time of the spring at 145°C, T_{c90}, is approximately 25 min, the maximum thickness of the rubber parts, S, is 31 mm, t_{comp} is chosen to be 25 min since there are 2 internal metal spacers in the product, and thus the vulcanization time is $t = 25 + 0.78 \times (31 - 6) + 25 = 69.5$ min. For the sake of operation convenience, vulcanization time is taken as an integer multiple of 5, i.e., the calculated vulcanization time is 70 min.

The bubble point method [4] was adopted in the trial production stage. The previously calculated vulcanization time was used as the initial vulcanization time of the first trial, and three vulcanization times of 70 min, 60 min, and 55 min, in descending order, were selected for the entire trial production. Samples were taken from the dissected vulcanized products to determine the degree of crosslinking by various methods such as swelling index measurements. The final vulcanization time of the product was determined by a combination of theoretical calculation and experimental verification.

3. Simulation Analysis

The vulcanization of rubber products at constant pressure under heating is a non-steady heat transfer process, coupled with a large number of crosslinking reactions of rubber materials. Therefore, numerical simulation of rubber vulcanization, in essence, is simultaneously solving the partial differential equation of heat transfer and the kinetic equation of curing reactions. SIGMASOFT is a simulation analysis software developed by MAGMA in Germany that includes a professional rubber vulcanization analysis module. The software builds upon more than 20 years of R&D experience and formulates a unique set of mathematical equations, which can be applied to simulate various rubber curing processes during molding and vulcanization.

3.1. Heat Transfer Equation

Heat transfer during rubber vulcanization is a non-steady process, and the temperature of each part is not only a function of space, but also a function of time. The transient heat transfer equation [5] is:

$$\rho C_p \frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rk\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial r}\left(k\frac{\partial T}{\partial z}\right) + \dot{Q} \tag{4}$$

where T being temperature; t, time; ρ, density; C_p, heat capacity; k, thermal conductivity; $\dot{Q}$, the rate of heat generation during rubber vulcanization.

The thermal conductivity of rubber is a material property affected by the type and the content of carbon black therein. The thermal conductivity, in some cases, increases with temperature, whereas it decreases with increasing temperature in other cases. The density of rubber usually decreases with temperature, and the heat capacity of rubber increases with temperature. In addition, the density and heat capacity also depend on the crosslink density [6]. This study assumes that the rubber density is constant, and the heat capacity varies with temperature and the degree of vulcanization.

3.2. Kinetic Equation of Vulcanization

The vulcanization of rubber is essentially a complex chemical reaction process. The vulcanization kinetic model is a mathematical model that quantitatively describes the relationship between the degree of vulcanization reaction and time and temperature. It is also an important factor for determining the reaction heat of rubber vulcanization. The Sigmasoft software provides three vulcanization kinetic models, i.e., the Nth-order, the Deng–Isayev, and the Kamal models. Herein, the Deng–Isayev model is used to describe the time and temperature dependencies of the degree of vulcanization. The constitutive equation of vulcanization kinetics [7] is given by:

$$\dot{c}(t) = nK_c(T)^{\frac{1}{n}}c^{1-\frac{1}{n}}(1-c)^{1+\frac{1}{n}} \tag{5}$$

where, c refers to the degree of vulcanization; $\dot{c}$ is the time derivative of the degree of vulcanization; $\log_{10}(k_0)$ is the reaction time; n is the reaction order.

Furthermore, the software introduces a scorch index and combines the Arrhenius function to describe the scorch period of rubber vulcanization. As shown in equation (5), when K_c is less than 1, the vulcanization is in the induction phase, otherwise the vulcanization reaction begins.

$$K_c(T) = k_0 e^{-\frac{E_A}{R_G T}} \tag{6}$$

where E_A is the reaction activation energy; R_G is the ideal gas constant; T is the temperature.

3.3. Finite Element Modeling

(1) Geometric Modeling

Based on the structural characteristics of the product and the mold, a finite element analysis model shown in the figure below was built in the Sigmasoft software. It included the product in its entirety and various mold components such as the upper, middle, and bottom heating sources, the injection plug, as well as the upper, middle, and bottom pieces of the mold.
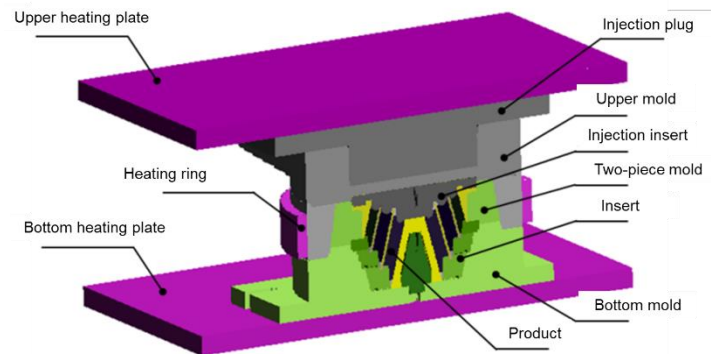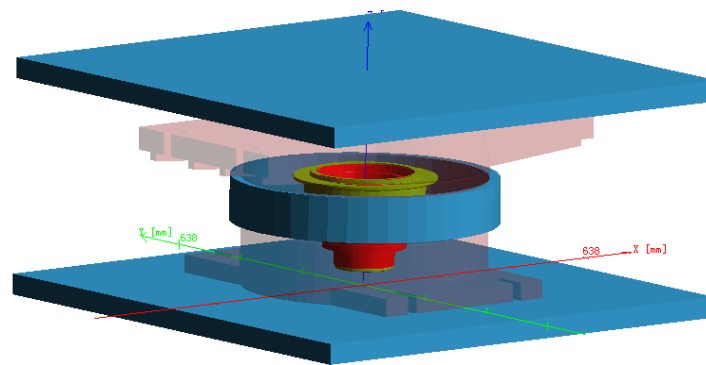
Figure 2. The model for finite element analysis.

(2) Boundary Modeling

This research considers the thermal resistances of interfaces between the product, the heating plates, and the mold, as well as thermal convection and radiation between the mold and its surrounding atmosphere. These considerations collectively bring the simulation analysis closer to the real-world setting. The thermal resistances are characterized by the HTC values, and the HTC values between different components are shown in Table 2 below. The surface heat transfer coefficient for the convective heat transfer between the model surface and air is a function of temperature, as demonstrated in Figure 3. The emissivity coefficient of the mold surface is assumed to be 0.8.

The product vulcanization process parameters were set as follows: the initial temperature of the mold, the metal insert, and the rubber stock were 23°C, 30°C, and 80°C, respectively; in

accordance with the requirements in product vulcanization, the empty vulcanization mold was preheated for 3 hours; the temperatures of the upper, middle and bottom heating plates of the vulcanizer were 170°C, 145°C, and 165°C, respectively; the curing time was 70 min. After the product was released from the mold and placed in a constant-temperature room for 5 hours, the post-vulcanization effect of the product was calculated.

Table 2. The HTC values between different components

| HTC (W/m^2·K)	Rubber	Mold	Heating plates
Mold	C3000	C6000	C6000
Metal insert	C3000	C4000	/
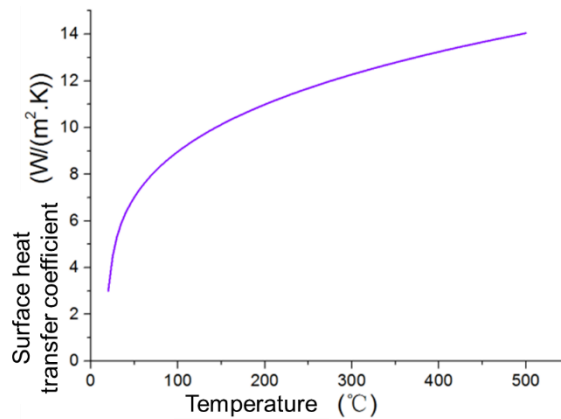
Figure 3. Surface heat transfer coefficient.

3.4. Results from Simulation Analysis

Under the conditions where the heating plate temperatures were at 170°C, 145°C, and 165°C, respectively, the analysis results with a 70-min curing time are described in the following. The temperature of the outer surface of the mold was around 141°C, and the product temperature was between 127.1 and 148.5°C. By arranging three temperature measurement nodes in the product, A, B and C, as shown in Figure 6, the temperature change trajectories of

the rubber during vulcanization and subsequent air cooling were recorded. As can be seen from Figure 7, the temperature rise history of rubber at different positions varied, and the vulcanization of thick rubber products was a non-isothermal process. After the product was released from the mold, due to the poor thermal conductivity of rubber, the rubber parts underwent a long cooling process before they reached room temperature. However, the residual heat offered conditions for continuing crosslinking reactions, a phenomenon known as the post-vulcanization effect. In addition, the rubber in the center area of the product showed a significant temperature lag relative to the parts on the product surface. During the vulcanization phase, the temperature measurement point A near the product surface quickly exchanged heat with the mold surface that were at a higher temperature. The heating rate was faster, and the temperature was higher at point A, compared to the temperature measurement points B and C in the central area. After the product was released from the mold, the temperature measurement point A exchanged heat with the surrounding air before the same events took place for the temperature measurement points B and C. Likewise, the cooling speed at point A was also significantly faster than those at the temperature measurement points B and C.
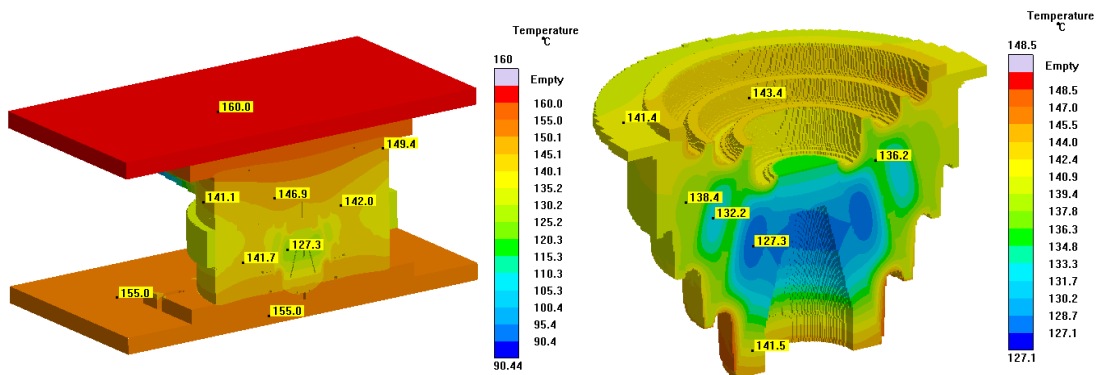
**Figure 4.** The temperature distribution map of the product and the mold.

Figure 5. The temperature distribution map of the product.

10
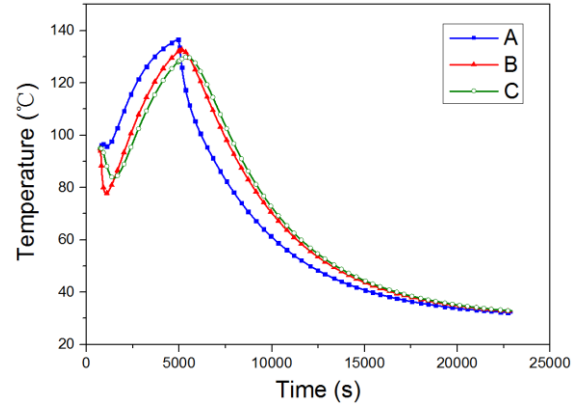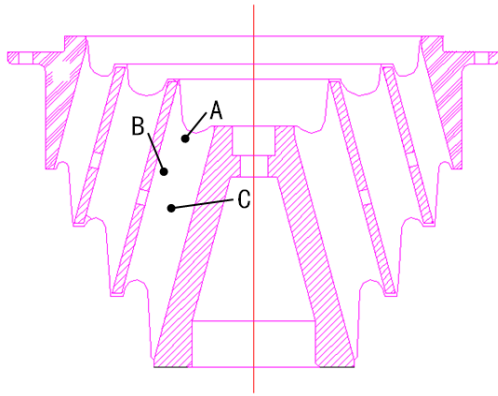
Figure 6. Schematic illustration of the temperature sampling locations.

**Figure 7.** Temperature trajectories over time at different measuring locations.

The calculation result of the vulcanization degree of the product are shown in the following figures. After 70 min of vulcanization, the vulcanization degree of the rubber at the end of vulcanization was 87.4% ~ 100%. After the product was released from the mold, the rubber continued to undergo crosslinking reactions using its own residual heat, and the final vulcanization degree of the rubber reached 99.4% ~ 100%.
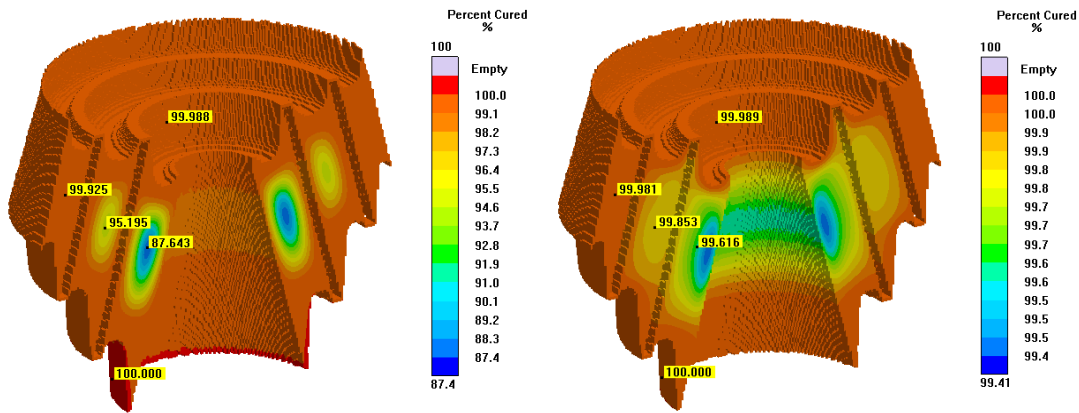
Figure 8. Distributions of the degree of vulcanization post curing.

Figure 9. Distributions of the degree of vulcanization after air-cooling.

The calculations above suggest that, after 70 min of curing and subsequent air-cooling, the rubber parts were completely vulcanized. To explore whether there was room for further optimization of the curing time, under the same process conditions, the curing time was adjusted to 60 min and 55 min, respectively. The calculation results of the degree of vulcanization after air cooling are as follows. The final vulcanization degree with a 60-min curing time reached 98.1% ~ 100%, and the vulcanization degree for the 55-min curing condition reached 96.3% ~ 100%. Informed by practical engineering experience, when the vulcanization degree of the rubber reaches over 98%, its physical and mechanical properties reach a steady state. Therefore, 60 min should be the relative optimal positive vulcanization time of the rubber auxiliary spring. However, in actual engineering applications, due to the influence of factors such as manual operation errors and environmental temperature fluctuations, it is recommended to add a safety time of 5 to 10 min for compensation to ensure the vulcanization quality of products.
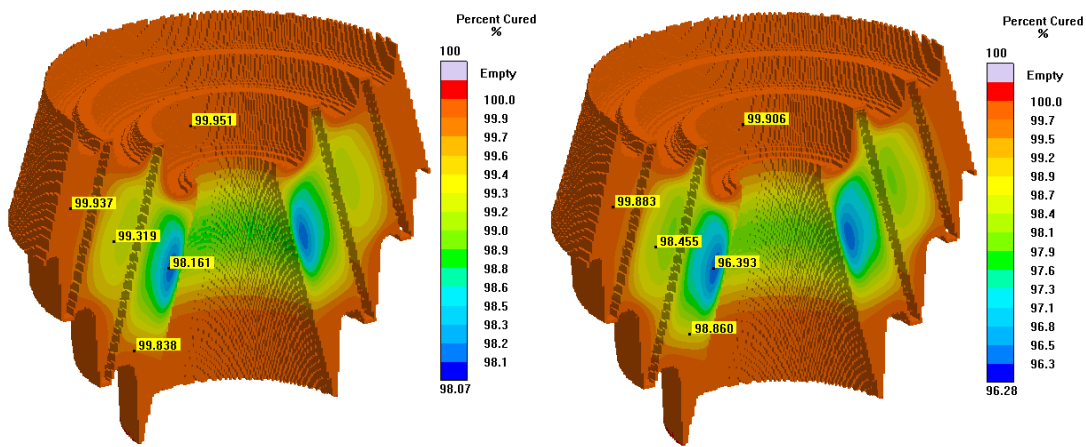
Figure 10. Distributions of the degree of vulcanization with a 60-min curing time.

Figure 11. Distributions of the degree of vulcanization with a 55-min curing time.

4. Experimental Verification

4.1. Swelling Tests

The swelling index refers to the ratio of sample mass at swelling equilibrium to that prior to swelling. Since crosslinked polymers can only swell but not dissolve in organic solvents and the swelling index decreases with an increasing degree of vulcanization before the rubber

reaches over-curing and reversion [8], the value of the swelling index can be used to determine the degree of crosslinking of rubber materials. By comparing the swelling indices of samples with different vulcanization times, the positive vulcanization time can be experimentally determined.

In this study, the temperatures of the upper, middle, and bottom heating plates were at 170°C, 145°C, and 165°C, respectively, three curing time durations 55 min, 66 min, and 70 min were chosen in the production trial, and samples were taken, as depicted in Figure 9, for swelling index measurements. Figure 3 shows the experimental results, where the swelling ratio of sample vulcanized for 60 min was the smallest. This suggests that 60 min was the optimal vulcanization time of the product, confirming the accuracy of the results from simulation analysis.
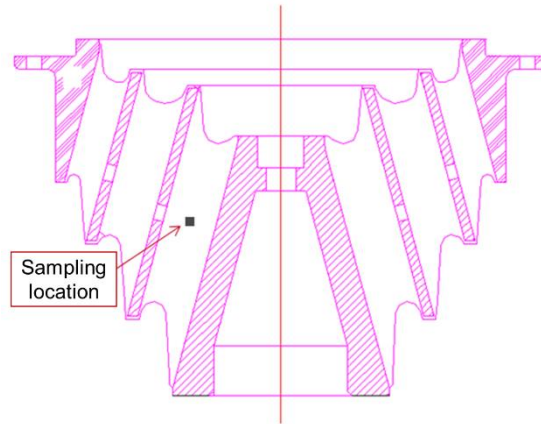

Figure 12. A schematic showing the sampling location for swelling index measurements.

Table 3. Results from swelling index tests

Vulcanization Time	55min	60min	70min
Swelling index	2.89	2.87	2.90

4.2. Vertical Stiffness Tests

During vulcanization, the properties of rubber change with the vulcanization time. The vulcanization curve of the formula FS035A-28B-19 # used in the rubber product is shown in Figure 13.
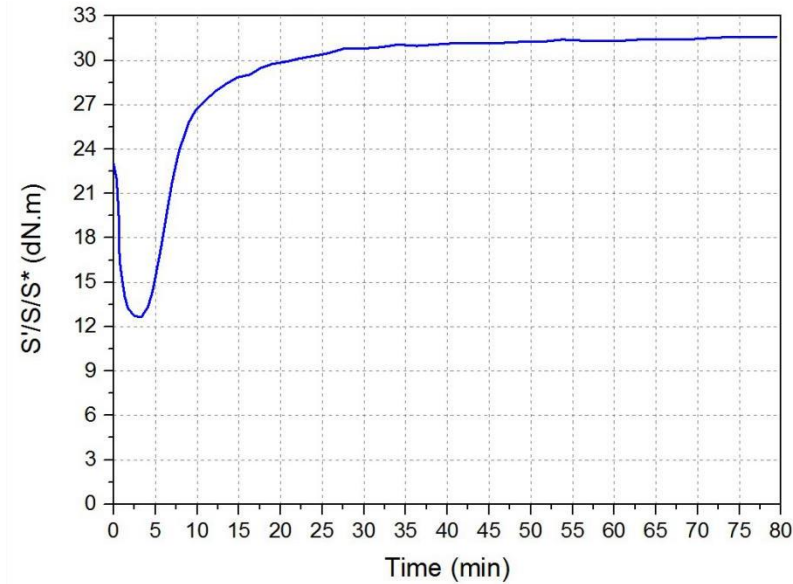
Figure 13. Vulcanization curve.

It can be seen from the vulcanization curve that the product crosslink density gradually increased with vulcanization time and further reached a plateau. The time window of 50–80 min can thus be considered as a vulcanization plateau, where the crosslinking reactions were nearly completed, and the vulcanized rubber product showed the best performance.

The experimental procedures of the vertical stiffness test of this type of auxiliary spring are specified as follows. A vertical load of 0 ~ 184.8 kN ~ 0 was applied, at a speed of 2 mm/s. This cycle was then repeated 3 times. At the 4th cycle, it was unloaded to 90.7 kN. From the unloading curve of the 4th cycle, the tangential stiffness at 90 ± 5 kN was calculated, and the product should meet 2750 N/mm (± 10%).

Two specimens were prepared under the conditions of vulcanization time of 55 min, 60 min and 70 min, respectively. The values of the vertical tangential stiffness are shown in the following table.

Table 4. Results from vertical stiffness measurements.

Curing time (min)	55	60	70
Vertical stiffness （N/mm）	2698/2743	2720/2795	2756/2768
Averaged vertical stiffness （N/mm）	2720	2757	2762

It can be seen from the test results that for products with curing times of 55 min, 60 min, and 70 min, the vertical stiffness of the product increased with the curing time. However, the overall changes were relatively small. This agrees with the large plateau regime in the vulcanization curves. The results are also in good agreement with the Sigmasoft software simulation, where the final vulcanization degrees at 55 min, 60 min and 70 min all reached above 96.3%.

The results of the vertical stiffness test suggest that products with a curing time ranging from 55 to 70 min all reached a positive vulcanization state and the 60 min curing time determined by the Sigmasoft software simulation is accurate and reliable.

5. Conclusions

This study comparatively examines the use of a traditional empirical calculation method and a simulation analysis approach to calculate the vulcanization time of thick rubber products. The traditional calculation method has several inherent disadvantages. Specifically, it does not consider the influence of product shape and the post-vulcanization effect, shows relatively large calculation errors, and requires multiple rounds of trial and error to determine the final vulcanization time. These disadvantages result in high product development costs and prolonged research and development cycles. However, due to the large plateau regime in the vulcanization

curve of rubber materials, this method is still being used as a process design guide by most rubber manufacturers.

This paper proposes the use of a simulation analysis approach based on the Sigmasoft software to calculate vulcanization time. The constitutive equation of vulcanization kinetics can be applied to products of any shape and be solved by integration over space and time regardless of the shape complexity. Furthermore, it can adequately consider the post-vulcanization effect. Compared with the traditional calculation method, the results derived from the simulation analysis approach show much better agreement with experiments with higher accuracies. This simulation approach can not only significantly improve the design efficiency of the vulcanization process, but also reduce the number of production trials, reduce research and development costs, and show great promise for subsequent engineering applications. In the era of Global Industry 4.0, simulation-based design of vulcanization process parameters are expected to become an inevitable trend.

References:

[1] ZHAO Shu-gao, and ZHANG Ping *et al*., Numerical Model of Tire Vulcanization Process, *Tire Industry*, **2001**, 21 (10): 617–622. (In Chinese)

[2] YAN Xiangqiao, A Study on the Finite Element Analysis of Tire Vulcanization Process, Harbin: Harbin Institute of Technology Press, **2001**. (In Chinese)

[3] YANG Qing-zhi, Modern Rubber Technology, Beijing: China Petrochemical Pressure, **1997**: 661–662. (in Chinese)

[4] ZHU Run-ping, A Design Strategy for Vulcanization Time of Thick Rubber Products, *Special Purpose Rubber Products*, **2009** (10), 48–49. (In Chinese)

[5] SHI Bin, WANG Guo-lin, and ZHANG Jian *et al.*, Simulation of Radial Tire Curing Process, *Automotive Technology*, **2008** (10); 56–59. (In Chinese)

[6] WANG Guo-lin, and Fu Nailin *et al.*, Simulation of the Radial Tire Curing Process Based on K-R Kinetic Model, *Journal of Jilin University (Engineering and Technology Edition)*, **2013**, 43 (3): 659–664. (In Chinese)

[7] SIGMA Engineering GmbH. Sigmasoft Manual: Database/Material Models and Boundary Conditions. SIGMA Engineering GmbH, **2013**.

[8] HG/T 3870-2008, A Method of Measuring the Swelling Index of Vulcanized Rubber. Beijing: China Petrochemical Pressure, **2008**. (In Chinese)