

Prediction of Cure Level in Thick Rubber Cylinder Using Finite Element Analysis

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Received 20 Feb 2002

Accepted 15 May 2002

ABSTRACT Curing process, or vulcanisation, is essential in the production of rubber components used in most engineering applications. The process inserts chemical bonds between rubber chains to give required mechanical stability as well as improved properties such as elasticity, tensile strength, modulus, and chemical resistance. During the curing process, there is a temperature distribution in thick rubber components as the thermal conductivity of rubber compound is very low. This causes the distribution of cure level from which the performance of such products might be impaired. It is therefore of interest to predict the distribution of cure level in a rubber component using the well-established technique, namely Finite Element Analysis (FEA). Thick cylinder made from natural rubber (NR) was selected for this study. The commercially available FE software (namely NISA II) was employed in association with the specially written software called CURECALC.EXE. To validate FEA prediction, measurement of cure level, determined by crosslink density, at various locations in the cylinder was carried out for comparison purposes. Results indicate that FEA can be used to predict cure level of thick rubber components with acceptable accuracy. The % difference between predicted and experimental values was found to be less than 25%.

KEYWORDS: Cure Simulation, Rubber Component, Finite Element Analysis.

INTRODUCTION

A rubber compound, before it is cured, may possess properties of a very viscous fluid which has no mechanical stability and, given time, will flow and change its shape. Therefore, curing process is vital in the production of rubber components used in many engineering applications. Curing inserts chemical bonds which are often based upon sulphur or peroxide, between rubber chains to give the required mechanical stability. The chemical reaction takes place while the rubber is in the heated mould. Regardless of the compounding recipe, the rate of the reaction is governed mainly by curing condition, particularly the curing temperature. The extent of cure can be determined by measuring degree of crosslinking or crosslink density.

Curing requires both elevated temperature and pressure. Unfortunately, heat does not flow readily through the rubber as its thermal conductivity is approximately 200 times lower than that of steel. This difficulty in heat flow can cause serious problems. In general, curing of thick rubber components takes an enormous time in order to allow rubber at the center to achieve adequate level

of cure whilst in the mould. Insufficient curing time causes the distribution of cure level (ie, rubber adjacent to the heated mould is often overcured whereas that at the center undercured), giving rise to the poor performance of such component. Excessive curing time also has detrimental effect on product quality due to overcure, particularly at the surface area. In the past, estimation of cure level was done by measuring the time/temperature profile of thick component with precisely positioned thermocouples. Lengthy calculations were then employed, using isothermal curing characteristics measured on a curemeter, to estimate equivalent state of cure under the actual time/temperature conditions. The cure simulator was later introduced to convert the time/temperature profile into state of cure.¹ Recently, the newly developed technique named finite element analysis (FEA) has been introduced to compute the distribution of cure level in rubber components and, hence, to predict their performance. Cure simulation involves transient thermal finite element analysis to calculate the nonisothermal temperature histories throughout a product during heating and cooling. It then integrates the thermal results to determine the corresponding cure histories.

Special cure simulation system, namely VACAM-Lab, has been developed and used in many organisations, including Silvertown UK, the Trelleborg Group, Dunlop tyres and the Tun Abdul Razak Research Center.² However, in the present study, commercial finite element software called “NISA II” in association with the software namely “CURECAL.EXE” specially written by PS Oubridge³ was used to predict cure distribution of thick rubber cylinder.

THE CURING PROCESS

Due to low thermal conductivity of rubber compounds, their cure by the application of heat never occurs under steady state thermal conditions. On the contrary, transient conditions prevail throughout the whole of the curing cycle. Moreover, the cure of a product involves two or more stages. For moulded products, the first stage occurs in a heated metal mould. The product is then demoulded and allowed to cool in still air. Alternatively, an intermediate stage may be introduced, whereby the product is placed in an oven for a set time (post-curing) before being allowed to cool.

CURE SIMULATION

With the application of heat, the temperature of the rubber rises and its rate of curing may be described by the Arrhenius function:

$$C_r = z \cdot \exp\left(-\frac{E}{R \cdot T}\right) \quad (1)$$

where C_r is the cure rate, E is the activation energy, R is the gas constant, T is the absolute temperature, and z is an arbitrary constant. It follows that the time to induce 1 unit of cure at temperature T is:

$$t = \frac{1}{C_r} = z' \cdot \exp\left(\frac{E}{R \cdot T}\right) \quad (2)$$

and, relative to some reference temperature T_0 and time t_0 , the time to induce one unit of cure at some other temperature T_1 is:

$$t_1 = t_0 \cdot \exp\left[-\frac{E}{R} \left(\frac{1}{T_0} - \frac{1}{T_1}\right)\right] \quad (3)$$

In the rubber industry, a cure unit (cu) is defined as the cure added in one minute at a temperature of 141.7 °C or 414.9 K. Thus, the number of cure units added in one minute at T degrees absolute is given by:

$$cu = \frac{1}{t_1} = \exp\left[\frac{E}{R} \left(\frac{1}{414.9} - \frac{1}{T}\right)\right] \quad (4)$$

In transient thermal finite element analysis (FEA), the simulation proceeds in small time increments. The temperature at any point may be taken as a linear function of the temperatures at that point before and after the time increment. Consequently, an increment of cure, dc , is added where:

$$dc = cu \cdot dt \quad (5)$$

If, at time $t = 0$, the total cure, C , at a point is zero, then at some time, t , the total cure becomes:

$$C = \int_0^t cu \cdot dt = \int_0^t \exp\left[\frac{E}{R} \left(\frac{1}{414.9} - \frac{1}{T}\right)\right] \cdot dt \quad (6)$$

However, in transient thermal condition, temperature (T) varies simultaneously with time (t) and, hence, the total cure will be a function of both T and t .

Let:

$$C = \int_0^t w(t) \cdot dt \quad \text{where } w(t) = \exp\left[\frac{E}{R} \left(\frac{1}{414.9} - \frac{1}{T}\right)\right]$$

Then:

$$C_{t+dt} = C_t + \int_t^{t+dt} w(t) \cdot dt \quad (7)$$

The software “CURECAL.EXE” has therefore been developed based on the above equations in order to predict the total cure of the rubber subjected to transient thermal condition.

MATERIALS AND METHODS

Rubber Compounds

Two types of carbon black filled NR compounds obtained from the Mould Mate Co, Ltd were used and designated as M039 and M059, respectively.

Determination of Material Properties

Material properties required in the modelling process include compound density (BS903 Part A1), specific heat (using Differential Scanning Colorimeter with specific heat kit), thermal conductivity (using Quick Thermal Conductivity Meter model QTM-500), heat transfer coefficient of rubber to air (based on procedure reported earlier).⁴ The activation energy was obtained from the slope of $\log(\text{cure rate})$ against the reciprocal of absolute temperature. Cure characteristics (cure rate, scorch time and optimum cure time) were obtained from Rheotech MD+ rheometer. Table I summarizes the material properties required for the simulation.

Cure Simulation

Cure simulation of rubber cylinder (3 in. diameter and 3 in. height) was carried out step by step as shown schematically in Figure 1. Curing of the rubber cylinder can be divided into two main steps; heating and cooling. Firstly, the rubber was heated to the required temperature (150 °C) in the heated mould for a certain period of time. NISA transient heat transfer analysis was performed to obtain the thermal results of this step. The final

nodal temperatures were then extracted from the NISA output file. After the heating step, the cylinder was demoulded and allowed to cool down to room temperature. Again, simulation of cooling step was done by NISA transient heat transfer analysis. The final nodal temperatures previously extracted were used as initial nodal temperatures of this step. Finally, the "CURECALC.EXE" software was used to integrate the thermal history of each node into cure unit and, hence, percent cure.

Figure 2 represents FEA model of the cylinder. By taking advantage of symmetry, only a quarter of the cross-section was modelled and the 2-D axisymmetrical elements were used to represent the model. The boundary conditions were applied as shown in Table II. After the transient thermal analyses, the nodal thermal history was integrated and converted into %cure by CURECALC.EXE. The data input required by this program included the activation energy, scorch time and optimum cure time at the reference temperature (141.7 °C).

Validation of FEA Results

Generally, it is necessary to validate the predicted results by comparing them with the experimental

Table 1. The material properties required in the simulation.

Properties	M039	M059
Density (g mm^{-3})	0.00117	0.00116
Specific heat* ($\text{J g}^{-1} \text{K}^{-1}$)	$0.8620 + 0.0093T - 2.0821\text{E-}05T^2$	$0.7878 + 0.0102T - 2.7816\text{E-}05T^2$
Thermal conductivity ($\text{W mm}^{-1} \text{K}^{-1}$)	0.00031	0.00030
Heat transfer coefficient ($\text{W mm}^{-2} \text{K}^{-1}$)	$0.120\text{E-}04$	$0.115\text{E-}04$
Activation energy (kJ mole^{-1})	79.64	83.25
Scorch time at 141.7 °C, t_{s2} (min)	13.8	22.0
Cure time at 141.7 °C, t_{c90} (min)	20.6	33.5

* measured as a function of temperature (T)

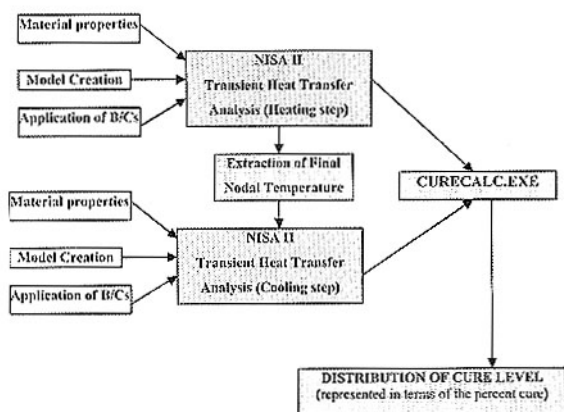


Fig 1. Diagram representing the cure simulation procedure.

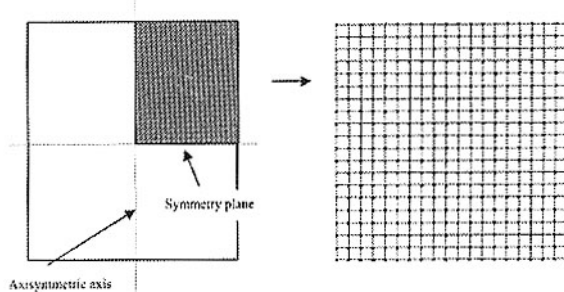


Fig 2. FE model of the rubber cylinder.

Table 2. The boundary conditions applied in the simulation

Simulation step	Boundary conditions
Heating	<ol style="list-style-type: none"> 1. The initial temperatures of all internal nodes were set at ambient temperature (23 °C), except the nodes located at the boundary surface in which their initial temperatures were set at 150 °C. Intimate contact between rubber and hot metal surface was assumed so that the interface thermal resistance could be neglected.⁵ 2. No heat was allowed to transfer across the surfaces of symmetry. 3. Material properties such as density, thermal conductivity and specific heat were then applied to the model.
Cooling	<ol style="list-style-type: none"> 1. The initial temperatures of all nodes were the same as the final nodal temperatures extracted from the heating step. 2. The film temperature along the exposed edges was defined by ambient temperature (23 °C). 3. No heat was allowed to transfer across the surfaces of symmetry. 4. Material properties such as density, thermal conductivity and specific heat were then applied to the model. 5. Finally, the value of heat transfer coefficient of rubber to air was applied to the exposed element faces.

ones. In preparation of rubber cylinders, heating times of 40 and 45 minutes were selected for the curing of M039 and M059, respectively. Such curing times would provide the rubber cylinders with a wide range of cure level (large cure distribution) which is convenient for comparison purpose.

Measurement of cure level at various locations (see also Figure 3) in the rubber cylinder was then carried out. Three specimens for each location were tested. The swelling ratio was selected as the factor indicating the cure level. To convert the swelling ratio into %cure, the standard cure curve (the plot of swelling ratio against %cure) must be established. For each compound, the rubber sheets were prepared by compression moulding technique at 150 °C for various curing times (from 20-100%cure). Rubber specimens were prepared by cutting the sheets into rectangular specimens (3 specimens/sheet) with the dimensions of 1.5x3x0.2 cm. The specimens were weighed and swelling test was performed by soaking the specimens in 100 ml of hexane for 70 hours in the dark place. After taking out the specimens, excessive hexane at the specimen surface was blotted off by filter paper and the specimens were reweighed. The swelling ratio can be calculated by using the following equation;

$$\text{Swelling ratio} = \frac{W_2 - W_1}{W_1} \quad (8)$$

where W_1 and W_2 are specimen weights before and after swelling, respectively.

With reference to the established standard cure curve, the swelling ratio of the specimens taken from various locations of the cylinder could be converted into %cure.

RESULTS AND DISCUSSION

The contour plots of cure distribution, after the cooling step, of the rubber cylinders made of M039 and M059 are given in Figures 4(a) and 4(b), respectively. The cure characteristics of the cylinders show an apparent pattern. The percent cure is lowest at the center of the rubber cylinder and tends to increase with the proximity of the rubber surface. This is attributed to the low thermal conductivity value of the rubber compounds. In the heating step,

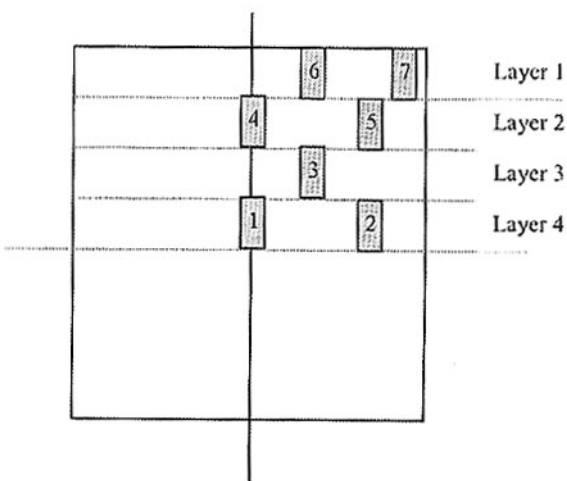


Fig 3. Locations of rubber specimens taken from the four layers of the rubber cylinder.

heat is transferred very slowly from the heated mould into the inner area of the cylinder. If insufficient time is allowed for heat transfer, there exists the temperature distribution. Figures 5(a) and 5(b) represent the contour plot of temperature distribution, after the heating step, of the cylinders made of M039 and M059, respectively. The temperature of the rubber, particularly at the center, still has not reached the mould temperature (150°C), and varies significantly from the center to the surface region (ranging from approx. 125°C to 150°C). After the heating step, the rubber at the center is therefore highly undercured, whereas that at the surface is likely to be overcured as it is subjected to high temperature for a lengthy period of time. Figures 6(a) and 6(b) represent the contour plots of cure distribution, after the heating step, of the cylinders made of M039 and M059, respectively.

Likewise, due to low thermal conductivity, heat in the rubber is also dissipated very slowly to the environment (air) during the cooling step. The rubber is thus cooled down very slowly. Curing of the rubber compounds, particularly in the inner area where the temperature reduction takes place very slowly, could therefore still occur at this step. Comparison of the contour plots of cure distribution obtained before and after the cooling step reveals that the cure level increases significantly during the cooling step.

It should be noted that the degree of curing taking place during the cooling step depends strongly on cure behavior (eg scorch time, optimum cure time and cure rate) of the sample. As can be seen from Figures 6(a) and 6(b), the levels of cure after the heating step in the two samples are quite similar, but after the cooling step (see also Figures 4(a) and 4(b)), the difference in cure levels between the two

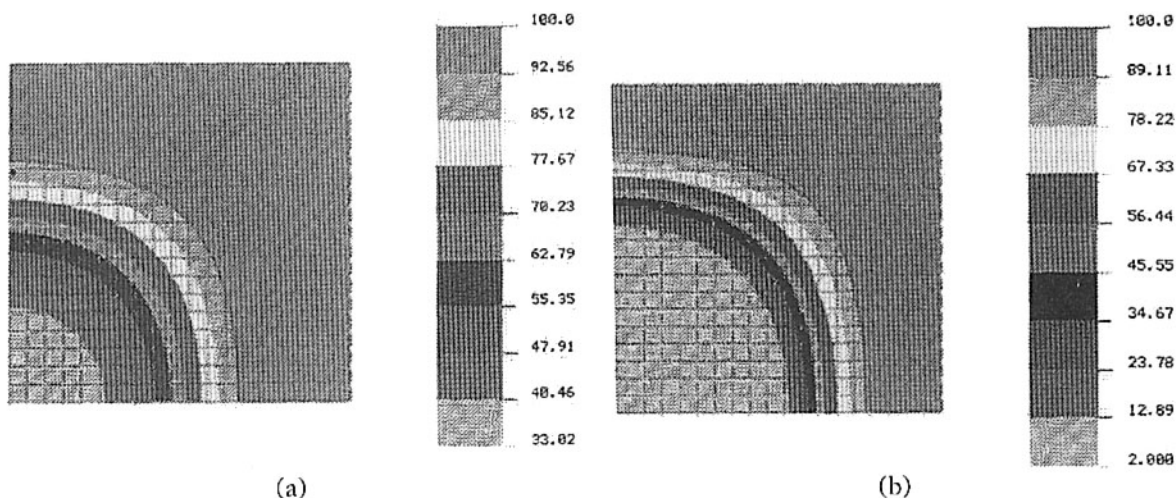


Fig 4. The contour plots of cure distribution (after the cooling step) of the rubber cylinders made of (a) M039 and (b) M059.

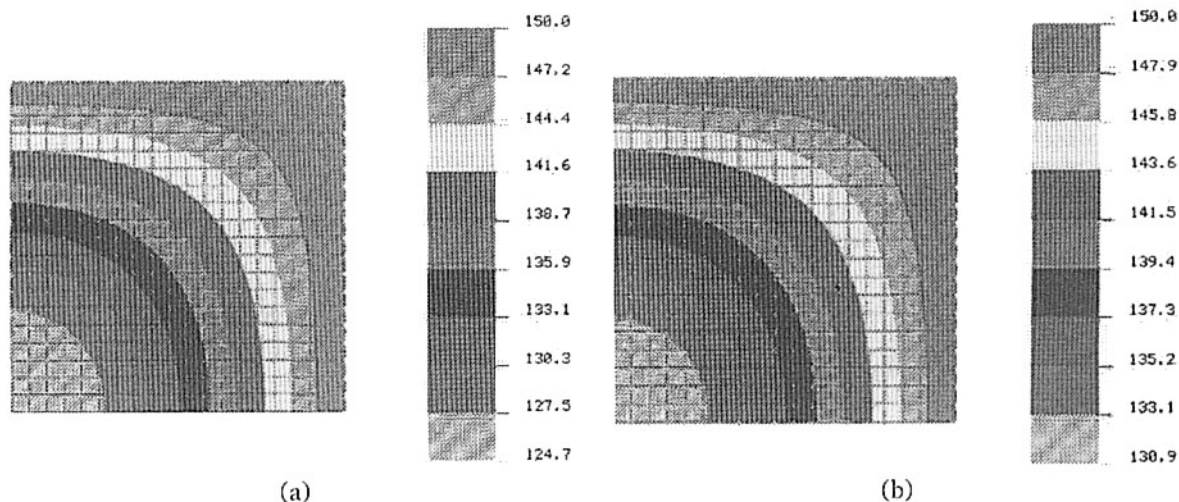


Fig 5. The contour plot of temperature distribution (after the heating step) of the rubber cylinders made of (a) M039 and (b) M059.

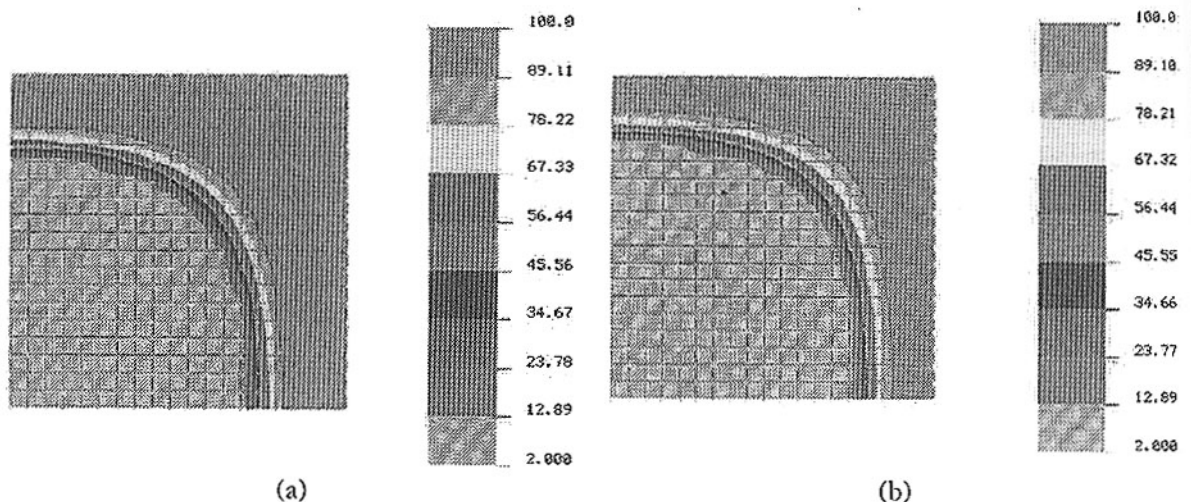


Fig 6. The contour plots of cure distribution (after the heating step) of the cylinders made of (a) M039 and (b) M059.

samples so obvious. During cooling, M039 has a significantly greater degree of curing, compared to M059. The two samples have very similar thermal properties and, hence, thermal history. However, as the two samples were compounded with different types of cure accelerators, their cure behavior is very much different. By comparing the values of scorch time and optimum cure time of the two samples (see Table 1), the results indicate that the accelerators in M039 are more active than those in M059. As a consequence, M039 should possess, under the same thermal history, a greater degree of cure as compared to M059.

In practice, it is recommended that, for large products such as tires, only 25-35% cure at internal regions may be induced whilst in the mould as the cure level will increase during the cooling step or postcure period utilizing the residual heat.⁶ However, it should be remembered that the curing at this point must be sufficient to prevent distortion of product shape and porosity caused by dissolved gases, once the external pressure is removed.⁷

Figure 7 represents the standard plot of swelling ratio against %cure. The swelling ratio is found to be linearly related to %cure as the R-squared values obtained from the regression technique are higher than 0.9. The swelling ratio decreases with increasing %cure. This is due to the fact that, with higher %cure or crosslink density, the average molecular weight between two crosslinks (M_c) decreases. The forces that hold the rubber chains together are increased through crosslinks. The rubber therefore has higher swelling resistance to its good solvent.

The swelling ratios of the specimens taken from various locations of the cylinder as well as their corresponding %cure are given in Table III. The

predicted values of %cure obtained from FEA are also included in the table. The predicted values are not greatly different from the experimental ones as the % difference of all specimens is less than 25%. The results show that FEA can be used to predict cure distribution of rubber components with acceptable accuracy.

Despite the apparent simplicity of the experiment and the simulation, there are sources of potential error, most importantly in the modelling. As far as the simulation is concerned, transient thermal behaviour, in which the temperature at any point within a body varies with both time and position, is controlled by the thermal diffusivity of the material involved. Thus the prediction accuracy depends greatly upon the accuracy of thermal conductivity, specific heat and density of material. During transient thermal analyses, it was assumed that both density and thermal conductivity are independent of temperature over the range 23-150 °C. Small error might arise from this assumption because it was reported earlier that both density and thermal

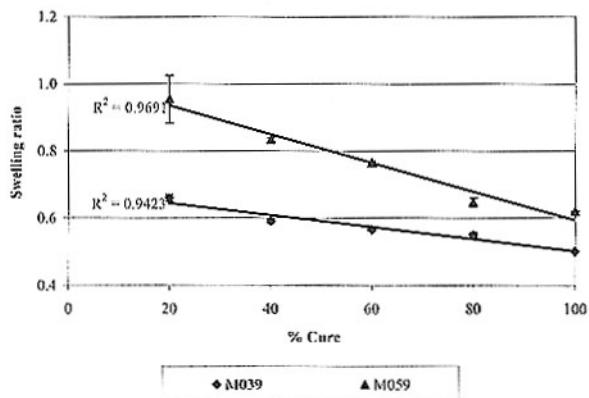


Fig 7. The standard plot of swelling ratio against %cure.

Table 3. Swelling ratio and its corresponding %cure of the specimens taken from various locations (in comparison with FEA results).

Sample	Location	Swelling ratio	Measured % cure	Predicted % cure	% Difference
M039	1	0.603 ± 0.010	43.0 ± 5.7	34.5	19.8
	2	0.546 ± 0.006	75.0 ± 3.3	75.6	0.8
	3	0.575 ± 0.004	58.7 ± 2.4	50.1	14.7
	4	0.554 ± 0.003	70.2 ± 1.8	72.2	2.8
	5	0.516 ± 0.004	91.5 ± 2.0	91.4	0.1
	6	0.505 ± 0.003	97.4 ± 1.4	99.4	2.1
	7	0.507 ± 0.008	96.3 ± 4.5	100.0	3.8
M059	1	3.144 ± 0.060	< 20	2.0	N/A
	2	2.923 ± 0.055	< 20	8.7	N/A
	3	2.979 ± 0.024	< 20	2.0	N/A
	4	2.098 ± 0.046	< 20	12.1	N/A
	5	0.805 ± 0.014	50.0 ± 3.3	62.4	24.8
	6	0.629 ± 0.009	90.9 ± 2.0	97.5	7.3
	7	0.625 ± 0.010	92.0 ± 2.4	99.9	8.6

conductivity of rubber are inversely proportional to temperature.^{8,9} However, it was also reported that, the values of thermal conductivity of carbon black filled compounds changed⁵ slightly in the range of 20-90 °C. In addition, small error might also arise due to the ignorance of the heat produced by the exothermic vulcanisation reaction.

CONCLUSIONS

Taken as a whole, by combining a commercial finite element analysis software with the specially written one, the cure distribution of thick rubber component can be predicted with acceptable accuracy. This technique can be used as a powerful tool for manufacturers to improve the product quality. When the curing time is optimized, the rubber in thick component is cured thoroughly, ie the rubber at the inner area is not undercured whereas that at the surface is not highly overcured. The product performance is thus maximized. In addition, when suitably applied, the technique can be used for productivity improvement. In most factories, curing time of thick rubber components is still based on trial and error or, occasionally, on years of experience. With either of the above methods, the excessive curing time is always employed to ensure that the rubber is properly cured throughout the whole body. When curing time is optimized with state-of-the-art FEA technique, the curing time can be shortened and thus the productivity increased.

ACKNOWLEDGEMENT

The authors wish to thank Department of Chemistry, Faculty of Science, Mahidol University for permitting the use of NISA Software. We are deeply indebted to Mould Mate Co, Ltd for supplying the rubber compounds used throughout the work. Most importantly, we are very grateful to Dr PS Oubridge for supplying the software "CURECAL.EXE" which is the core of this paper.

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