# Experimental Determination of Rubber Curing Reaction Heat Using the Transient Heat Conduction Equation\*

M. JUMA and M. BAFRNEC

Department of Chemical and Biochemical Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, SK-812 37 Bratislava e-mail: juma@chtf.stuba.sk

#### Received 1 April 2003

This paper presents a method for the experimental determination of reaction heat of rubber curing, which is based on solution of the transient heat conduction equation with an internal heat source. The experimental technique of the LIST method, which was originally developed for measuring thermal diffusivity of rubber compounds, was used to estimate the reaction heat of rubber curing. Value of  $43 \times 10^3$  J kg<sup>-1</sup> was obtained for curing reaction heat of a commercial rubber sample with the following composition: 47.54 mass % of natural rubber (SMR 20), 9.00 mass % of synthetic rubber (SKD 2), 3.00 mass % of synthetic rubber (Vestenamer 8012), 2.69 mass % of sulfur, 0.97 mass % of accelerator (Vulcacid DZ), 0.07 mass % of inhibitor (Duslin G-80), and 36.73 mass % of carbon black and other components. The overall error in predicting the reaction heat by this method is less than 15 %.

Simulation of a rubber curing process can considerably influence the cost of process development and optimization of process conditions. However, the simulation results obtained by mathematical modelling are applicable only in the case when parameters of the model are authentic. The most important result of rubber curing simulation is the determination of the optimal curing time.

During the curing process, rubber compounds are heated to a temperature of about 200 °C and then cooled. The curing time is divided into two periods. During the first period, the product is heated from its initial temperature to the vulcanization temperature. The second period is the time needed for chemical reaction (creation of sulfidic cross-links). In this case the mathematical model of rubber curing is a combination of the transient heat conduction equation in solid elastomer composites and the rate equation of the chemical reaction. For calculation of both the temperature distribution and the distribution of crosslinks one needs to know all heat conduction, thermodynamic, and reaction kinetic properties.

Vulcanization of rubber is generally an exothermic reaction. For this reason, the heat of reaction could affect the curing time of rubber products. The amount of reaction heat evolved depends upon several factors. The most important of them are: polymer type, number and type of cross-links (monosulfidic, bisulfidic or polysulfidic), and vulcanizing agent [1].

Estimation of rubber curing reaction heat via the bond energy method is difficult and inaccurate because many different reactions take place during the curing process. With an acceptable accuracy this property can be estimated only experimentally. For experimental determination of the curing reaction heats various methods and experimental techniques such as DC (Differential Calorimetry), DSC (Differential Scanning Calorimetry), DMA (Dynamic Mechanical Analysis), dielectric spectroscopy, etc. have been used [2-6]. The most often used method is Differential Scanning Calorimetry. However, the availability of this method for rubber vulcanizates is disputable, because of the small size of samples, which are used in the commercial DSC experiments. The representative sample of rubber compounds is a sample with relatively big dimensions because of their heterogeneity and anisotropy in microscopic level. Rubber vulcanizates are consisting of more components, which are mixed to a limited degree of homogeneity. In this case the samples with a weight of some milligrams, which are used in major commercial calorimeters, cannot be representative.

In this work an alternative method for experimental determination of the reaction heat of vulcanization is presented, which is based on solution of the transient heat conduction equation with an internal heat source. However, the LIST method can only be used if the heat conduction properties of the composite mate-

<sup>\*</sup>Presented at the 30th International Conference of the Slovak Society of Chemical Engineering, Tatranské Matliare, 26—30 May 2003.

rial (thermal diffusivity and thermal conductivity) are known. This simple experimental technique enables measurement of both the overall thermal diffusivity and the reaction heat, while there is no need of expensive and sophisticated instruments. Moreover, it is possible to use large representative macrocomposite samples of rubber products. A detailed description of the LIST technique is given in [7, 8].

# THEORETICAL

Mathematical model of the rubber curing process consists of the transient heat conduction equation and the rate equation of sulfidic cross-links creation

$$\frac{\partial t}{\partial \tau} = a_x \frac{\partial^2 t}{\partial x^2} + a_y \frac{\partial^2 t}{\partial y^2} + a_z \frac{\partial^2 t}{\partial z^2} + \frac{q'}{\rho c_p} \qquad (1)$$

$$q' = \Delta H_{\rm r} \frac{\mathrm{d}C}{\mathrm{d}\tau} \tag{2}$$

$$\frac{\mathrm{d}C}{\mathrm{d}t} = K_{\mathrm{C}}^{(n)} (1-C)^n \text{ for } \tau > \tau_{\mathrm{inc}}$$
(3)

where  $a_x$ ,  $a_y$ , and  $a_z$  are the thermal diffusivities in directions x, y, z, C the molar concentration of sulfidic cross-links, t temperature,  $\tau$  time,  $\tau_{\rm inc}$  incubation time,  $\Delta H_{\rm r}$  molar reaction enthalpy,  $\rho$  density,  $c_p$  specific heat, n reaction order, and  $K_{\rm C}^{(n)}$  is the *n*th-order conversion rate constant.

Both the conversion rate constant and incubation time depend on temperature

$$K_{\rm C}^{(n)} = K_{\rm 0C}^{(n)} \exp\left(\frac{-E_1}{RT}\right) \tag{4}$$

$$\tau_{\rm inc} = \tau_{0\,\rm inc} \exp\left(\frac{E_2}{RT}\right) \tag{5}$$

R being the universal gas constant, T the local temperature,  $K_{0C}^{(n)}$ ,  $\tau_{0 \text{ inc}}$ ,  $E_1$ , and  $E_2$  the kinetic constants of vulcanization.

The degree of cross-linking is often expressed by the degree of vulcanization (X), which is defined as  $X = C/C_{\infty}$ .  $C_{\infty}$  is the molar concentration of cross-links at the end of the curing process.

Time-dependent distributed energy source q' (eqns (1) and (2)) represents the amount of heat generated by chemical reaction in the differential volume element dx dy dz during the time period  $d\tau$  (see Fig. 1). For  $\tau < \tau_{\rm inc}$ , no reaction occurs and therefore the value of q' is equal to zero. A detailed analysis of transient heat conduction in rubber elastomer composites is given by Juma et al. [9].

In the case of heat conduction in only one direction eqn (1) is transformed to

$$\frac{\partial t}{\partial \tau} = a \left( \frac{\partial^2 t}{\partial x^2} + \frac{q'}{\lambda} \right) \tag{6}$$



Fig. 1. Differential volume element dx dy dz for analysis of the curing reaction heat.

where  $\lambda = a\rho c_p$  is the thermal conductivity of material.

For initial and boundary conditions

$$\begin{aligned} \tau &= 0 \quad 0 \le x < l \qquad t = f(x,0) \\ \tau &> 0 \qquad x = 0 \qquad t = t_{\rm w}(0,\tau) = b_0 + b_1 \tau \\ \tau &> 0 \qquad x = 0 \qquad \left. \frac{\partial t}{\partial x} \right|_{x=l} = 0 \end{aligned} \tag{7}$$

the finite difference solution of eqn (6) has the following form

$$\begin{split} t_{i}^{j+1} &= \\ &= \frac{a\Delta\tau}{(\Delta x)^{2}} \left[ t_{i-1}^{j} - 2t_{i}^{j} + t_{i+1}^{j} + \frac{t_{w}^{j+1} - t_{w}^{j}}{i^{2}} + \frac{q'(\Delta x)^{2}}{\lambda} \right] + \\ &+ t_{i}^{j} = \\ &= \frac{a\Delta\tau}{(\Delta x)^{2}} \left[ t_{i-1}^{j} + t_{i+1}^{j} + \frac{t_{w}^{j+1} - t_{w}^{j}}{i^{2}} + \frac{q'(\Delta x)^{2}}{\lambda} \right] + \\ &+ \left( 1 - \frac{2a\Delta\tau}{(\Delta x)^{2}} \right) t_{i}^{j} \end{split}$$
(8)

where l means half of the sample plate thickness,  $t_w$  is the boundary temperature,  $i = 1, 2, 3, \ldots$  represents spatial and  $j = 0, 1, 2, \ldots$  temporal coordinate. If the thermal diffusivity a and the thermal conductivity  $\lambda$  related to vulcanization temperature are known, q' can be calculated by eqn (8) using the experimentally measured data of a temperature field.

#### EXPERIMENTAL

The experimental technique LIST for determination of the rubber curing reaction heat was originally developed for measurement of thermal diffusivity of



Fig. 2. Scheme of the apparatus for measurement of the rubber curing reaction heat. HP1, HP2 – heating plates, PID – controller, DL – data logger.

rubber compounds and reinforced rubber composites [7, 8]. Fig. 2 shows the scheme of an apparatus using the LIST technique for measurement of the reaction heat of rubber curing.

The sample of measured material consists of two identical discs with a diameter of 100 mm and a thickness of 5 mm. Each part of the sample is formed from unvulcanized rubber at a temperature of around 110 °C. For measurement of the reaction heat the unvulcanized samples must be placed in the moulds, between a pair of heating plates (HP1, HP2) and clamped under pressure. First after clamping the sample between the heating plates both the sample and the heating plates are heated to a given initial temperature. Then, an appropriate rate of temperature increase of the heating plates is chosen. Finally, after initializing the preprogrammed temperature control of the heating plates the measurement of transient temperature field can begin. The temperature of both



Fig. 3. Effect of the reaction heat upon the temperature difference between the centre and the surface of fresh (solid line) and vulcanized (dotted line) sample. Rate of the surface temperature increase 1 °C min<sup>-1</sup>, initial temperature 110 °C.

The sample used in this study was a commercial rubber, which contained 47.54 mass % of natural rubber (SMR 20), 9.00 mass % of synthetic rubber (SKD 2), 3.00 mass % of synthetic rubber (Vestenamer 8012), 2.69 mass % of sulfur, 0.97 mass % of accelerator (Vulcacid DZ), 0.07 mass % of inhibitor (Duslin G-80), and 36.73 mass % of carbon black and other components, which do not take part in the chemical reaction.

## **RESULTS AND DISCUSSION**

The value of the curing reaction heat  $\Delta H_{\rm r}^{\rm v}/({\rm J}\,{\rm m}^{-3})$  can be predicted by the following equation

$$\Delta H_{\rm r}^{\rm v} = \int_{\tau_{\rm inc}}^{\tau} q' \mathrm{d}\tau \tag{9}$$

The immediate values of q' were calculated using eqn (8) and the measured temperature data. The originally developed evaluation software computes the values of q' for chosen temperature steps (in this study 1°C) by the minimization criterion  $f_i = \sum (t_c - t_{ex})^2 = \min, t_c$  being the temperature between the two parts of sample calculated by eqn (8) and  $t_{ex}$  the temperature measured experimentally at the same position. An average value of the measured temperatures between the two parts of sample was calculated. The temperature dependence of the thermal diffusivity data was estimated by the LIST method [1]. The temperature dependence on the thermal conductivity was neglected. Constant value of 0.240 W m<sup>-1</sup> K<sup>-1</sup>, measured by a commercial device (ISOMET, Applied Precision, Slovakia), was used.

The effect of reaction heat upon temperature measured in the sample centre is shown in Fig. 3. These results reveal that vulcanization of the sample begins at a temperature near  $130 \,^{\circ}$ C. With a rate of temperature increase of  $1 \,^{\circ}$ C min<sup>-1</sup> vulcanization continues up to a temperature near  $195 \,^{\circ}$ C.

Fig. 4 shows variation of q' with temperature, which enables also determination of the starting point of vulcanization. As the vulcanization temperature increases linearly with the curing time, the value of reaction heat  $\Delta H_r^{\rm v} = 50.26 \times 10^6$  J m<sup>-3</sup> was calculated by numerical integration of the data presented in Fig. 4. In order to test the LIST method reproducibility, experiments were repeated several times for the same material giving the standard deviation value of  $\pm 5 \times 10^3$  J m<sup>-3</sup>. Taking into account the average value of



Fig. 4. Variation of the reaction heat with temperature. Rate of the surface temperature increase  $1 \,^{\circ}\text{C} \, \text{min}^{-1}$ , initial temperature  $110 \,^{\circ}\text{C}$ .

the rubber density at given temperature range (1170 kg m<sup>-3</sup>), the specific reaction heat of rubber curing of  $43 \times 10^3$  J kg<sup>-1</sup> was obtained, which is in good agreement with the values found in the literature (8  $\times 10^3$ —90  $\times 10^3$  J kg<sup>-1</sup>) for rubber samples of different compositions.

The released reaction heat affects the temperature in each point of the sample, thus influencing the heat flux from the heated surfaces of the sample to its centre. Large amount of reaction heat can cause the situation that temperature in the centre of sample is higher than the temperature in its neighbourhood. In such case the heat flux direction will be changed, an undesirable event from the point of view of reaction heat estimation by the LIST method. Moreover, the temperature difference between the surface and the centre of sample can be influenced by the rate of surface temperature increase.

The accuracy of the value of reaction heat determined by this method depends upon several factors. The most important of them is the accuracy of temperature measurement, accuracy of thermal diffusivity and thermal conductivity measurements, sample thickness measurement, and temperature control of heating plates.

By analyzing individual sources of errors  $(\Delta H_{\rm r}^{\rm v} = f(t, \Delta x, a, \lambda))$  it was estimated that the overall error in predicting the reaction heat by the LIST method is less than 15 %.

### REFERENCES

- Bhowmick, A. K., Hall, M. M., and Bernary, H. A., Rubber Products Manufacturing Technology. Decker, New York, 1994.
- Armand, J. Y. and Vergnaud, J. M., *Thermochim. Acta* 116, 111 (1987).
- Immelman, E. and Sanderson, R. D., Thermochim. Acta 207, 177 (1992).
- Tsang, C. F. and Hui, H. K., Thermochim. Acta 367– 368, 169 (2001).
- Alig, I., Jenninger, W., and Schawe, J. E. K., *Ther*mochim. Acta 330, 167 (1999).
- Lu, M. G., Shim, M. J., and Kim, S. W., *Thermochim.* Acta 323, 37 (1998).
- Juma, M. and Bafrnec, M., J. Reinf. Plast. Compos. 19, 1024 (2000).
- Bafrnec, M., Juma, M., Toman, J., Jurčiová, J., and Kučma, A., *Plast. Rubber Compos.* 28, 482 (1999).
- Juma, M., Bafrnec, M., and Toman, J., Transient Heat Conduction in the Reinforced Rubber Materials, 12th Slovak Rubber Conference, Púchov, 2000.