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Rheometers with square root of time–temperature programming for the cure of rubbers

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Abstract

Because of the drawbacks resulting from using a constant temperature, calorimetry has been developed with scanning mode and temperature programming with a constant heating rate. Following this way, a theoretical approach was made with moving die rheometers, showing some advantages over the method done under isothermal conditions. However, if it usual to vary the temperature linearly with time, it is shown that a better way consists in increasing the temperature of the dies with the square root of time. The theoretical study of this new method is made enabling the evaluation of the torque–temperature curves. Some advantages are obtained with respect to the linear programming, coming from the principle of this new method. Thus, the rate of heating is faster at the beginning of the process when the rubber sample is heated up to a temperature where the reaction starts, and becomes lower within the temperature range where the reaction develops. A method has been elaborated for evaluating the kinetic parameters from these torque–temperature curves. The effect of the parameters of interest, with the value of the rate of heating and the thickness of the rubber sample, is determined. Thus the value of the heating rate should be between 10 and 50 $K/min^{0.5}$. A slight change in the thickness of the sample over the average value of 0.2 cm is of little effect. The profiles of temperature developed through the thickness of the sample are flatter than those obtained with the isothermal rheometer, leading subsequently to more uniform profiles of the state of cure, as they are obtained by calculation. Moreover, shorter times of experiment are obtained over the method based on the linear programming temperature system. The kinetic parameters such as the activation energy and the pre-exponential factor, as well as the overall order of the reaction, are thus obtained from only one experiment.

Keywords: Moving die rheometer; Rubber; Temperature programming

1. Introduction

In curing rubbers, the samples should be heated up to a temperature at which the irreversible reaction starts, the fresh plastic uncured material leading to an elastic three-dimensional molecular network. Thus, consisting of the stages of heat transfer through the sample thickness, followed by the cure reaction slightly exothermic, the process of curing rubbers is rather complex. Moreover, kinetically speaking, the cure reaction itself is complex, even if it often expressed in terms of temperature and of the activating agent concentration by an Arrhenius' equation [1,2]. From the economical point of view, the cure of rubbers is of great importance, resulting from the time necessary to get good products and also from the fact that a final material badly cured should be rejected without possible recycling.

The process of cure has often been analysed by considering heat transfer by conduction through the rubber and heat generated by the reaction. The state of cure was evaluated by using the swelling in toluene of the rubber samples cured at various times and temperatures, but as said by the authors, the method was tedious and highly time-consuming [3]. Other methods were developed by measuring and calculating the temperature profiles developed through the thickness of the sample at various times: one, by introducing a temperature reference at 149 °C and a rate coefficient of cure increased by a factor of 1.85 per 10 °C [4]; the other with a reference of temperature of 150 °C and assuming that the rate of cure doubles for each 10 °C increase in temperature [5]; a constant time conversion of

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Nomenclature

b	heating rate °C/min$^{0.5}$
C	heat capacity of the rubber in Eq. (6)
Δt	increment of time for calculation
Δx	increments of space for calculation
E	activation energy of the cure reaction
n	order of the overall cure reaction
λ	thermal conductivity of the rubber
k_0	pre-exponential factor for the rate of the cure reaction in Eq. (3)
M	dimensionless number expressed by Eq. (8)
Q	heat generated by the cure reaction
ρ	density of the rubber
S	function defined by Eq. (10) used for calculating the state of cure of the rubber
T	temperature (K)
T_0	temperature at which the programming of temperature starts:25 °C
TN_n	new temperature after elapse of time Δt at position n
x	longitudinal abscissa through the thickness of the rubber
Z	value of the torque as a fraction of its maximum value in Eq. (1)

1.3 per 10 °C was also found for the sulphur vulcanisation of EPDM blends around the reference temperature of 150 °C [6]. Numerical models taking into account all the known facts, especially heat conduction through the sample and the heat generated by the cure reaction have been built and tested, either for the cure of NR with sulphur [2,7,8] or EPDM with peroxide [9]. These models are capable of evaluating not only the profiles of temperature developed through the sample but also the profiles of state of cure, provided the kinetics of the cure reaction is known. The main difference between rubbers and thermosetting resins stays in the enthalpy of cure, which is much larger for thermosets. This fact should have been of importance for the selection of the methods used in determining the parameters of the kinetics of cure.

Calorimetry is widely used for studying the cure of thermosetting resins, either under isothermal conditions or in scanning mode. Thus, the heat flux emitted by the exothermic reaction is recorded as a function of time when the apparatus is kept at constant temperature or of temperature in scanning mode. In the seventies and the early eighties, the workers preferred using the method with constant temperature [10–12]. However, in-depth studies [13,14] showed that in this case, the process is far from being simple. In fact, the fresh uncured resin initially at room temperature, when dropped into the calorimeter kept at the selected temperature, leads to a very large endothermic heat flux associated with the conduction heating stage, which hides the first part of the reaction; and only when the temperature of the sample is high enough, the exothermic heat flux resulting from the exothermic cure reaction is observed. Moreover, there is a narrow temperature window width over which meaningful data can be obtained. Thus, from these drawbacks, calorimetry in scanning mode proved to be the best method [2,13]. A few attempts have been made for using the calorimetry techniques for the cure of rubbers. Thus, the differential scanning calorimetry (DSC) technique has been employed for determining the temperature at which the reaction starts [11,12], or for measuring the cure enthalpy [1,2,11–14]. Isothermal calorimetry (DC) has also been used for evaluating the kinetics parameters of the cure reaction of normal rubbers with sulphur [10], of ethylene/propylene/diene monomer (EPDM) cured with peroxide [9, 11] by assuming that the rate of cure varies with temperature according to an Arrhenius equation.

Due to their low enthalpy of cure, rubbers have been studied by using other methods consisting of monitoring the viscosity or torque change of the sample during the cure, while this sample is kept at a constant temperature. Thus, the Mooney viscometer, the Wallace–Shawbury curometer, the oscillating disc rheometer (ODR) and the moving die rheometer (MDR) have been developed and marketed, the MDR being introduced more recently in 1985 [15]. In the MDR, a thin sheet of rubber (around 2 mm) at room temperature is introduced between the two dies kept at the desired temperature, the lower die oscillates and a reaction torque transducer is positioned above the upper die. Because of a better heat transfer, thinner samples, and another die design, it has been found that the MDR gives shorter times of cure than the ODR [15]. The MDR should be used successively at three different temperatures to allow evaluation of the kinetics of the cure reaction, which are selected through a temperature window of around 30 K. From the fractional modulus–time values obtained, the activation energy and the pre-exponential factor have been calculated with the MDR for EPDM compounds [6, 16]. Very often the modulus change with time follows first order kinetics and the rate constant varies with temperature according to an Arrhenius equation [16]. Of course, the heat generated by the cure reaction is not considered, which is not a great drawback when the cure enthalpy is low.

Various drawbacks appear with the MDR run under isothermal conditions. (i) The one with the narrow temperature range over which meaningful data can be obtained [1,2,12]; a low temperature for cure studies leads to very long times, while too high a temperature is limited by the induction period for the cure to initiate. (ii) The other with the temperature through the sample; in isothermal MDR, the applied temperature is the set apparatus temperature and not the true sample temperature: at the beginning, the sample initially at room temperature is introduced into the dies of the MDR kept at the selected temperature and it takes some time for thermal equilibrium to establish [17]. When the cure enthalpy is not negligible, some other gradients of temperature develop through the sample, resulting from the internal heat generated by the reaction..

Thus, instead of using the MDR under isothermal conditions, the theory of the process has been developed when the MDR is run in scanning mode, by programming the temperature with a constant rate of heating [18]. The advantages of this new method were shown, based essentially on its principle, as only one experiment is necessary for evaluating the kinetic parameters of the cure, and also that the profiles of temperature and of the state of cure are rather flat in the sample, proving its good homogeneity.

It should be said that, if the constant heating rate has been selected for programming the temperature in various techniques, as the gas phase chromatography and calorimetry, and proposed as well for the MDR [18], it is perhaps not the best way to increase the temperature. The drawback of the linear heating rate results also from its principle, as the rate of increase in temperature remains the same irrespective of the phenomenon that takes place in the sample. On the contrary, it seems better to increase the rate of heating during the stage of heating and to decrease it when the reaction occurs. Thus, a reduction in time during the heating stage also reduces the time of experiment, and the stage of reaction is considered upon a longer time.

The first purpose in this paper is to describe a new method for the MDR where the temperature is increased with the square root of time. The theory of the process of heating and of the resulting cure is established, enabling the evaluation of the kinetic parameters of the cure reaction, such as, not only the energy of activation and the pre-exponential factor, but also the order of the overall reaction which is not assumed to be one.

On the other hand, the process is studied during the stages of heating and of the cure, allowing the determination of the profiles of temperature developed through the thickness of the rubber sample, as well as the profiles of the sate of cure, in order to obtain perfect knowledge on this method.

2. Theoretical

The following two parts are considered:

(i) The treatment of the data obtained via the MDR technique in scanning mode with the square root - temperature programming.
(ii) The calculation of the profiles of temperature and of state of cure developed through the thickness of the sample with this new technique.

2.1. Mathematical treatment of the MDR in scanning mode

The following assumptions are made:

(i) perfect contact is attained between the rubber sample and the dies; thus the temperature is constantly the same on each face of the die-rubber interface.
(ii) the temperature is increased with the square root of time
(iii) the kinetics of torque change follows a nth-order kinetics
(iv) The increase with temperature of the rate of torque can be expressed by an Arrhenius equation.

By putting

$$Z = \frac{\mathrm{Torque}_t}{\mathrm{Torque}_\infty} = \frac{\mathrm{SOC}_t}{\mathrm{SOC}_\infty} \tag{1}$$

and the rate of heating b defined by:

$$T = T_0 + bt^{0.5} \tag{2}$$

the differential equation under isothermal condition expressing the ratio of the torque value in term of temperature:

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = k_0(1-Z)^n \exp\left(-\frac{E}{RT}\right) \tag{3}$$

becomes in scanning mode with the square root of time–temperature dependence:

$$\frac{\mathrm{d}Z}{\mathrm{d}T} = \frac{2k_0}{b^2}(1-Z)^n(T-T_0)\exp\left(-\frac{E}{RT}\right) \tag{4}$$

By integrating between T_0 and T, it becomes:

$$Z = 1 - \left[1 + (n-1)\frac{2k_0}{b^2}\int_{T_0}^{T}(T-T_0)\exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]^{\frac{1}{1-n}} \tag{5}$$

By plotting $\ln(\mathrm{d}Z/\mathrm{d}T)$ versus $\ln(1-Z)$, the order n of the overall reaction of cure can be obtained, being equal to the slope.

In the same way, by plotting $\ln[(\mathrm{d}Z/\mathrm{d}T)(1-T)^n]$ versus the reciprocal temperature $1/T$, the slope gives the value of the energy of activation.

2.2. Process of heating and cure with the MDR

The following assumptions are made:

(i) the rubber sheet is heated by unidirectional conduction through its thickness
(ii) good contact is made at the rubber/die interface
(iii) internal heat is generated by the overall cure reaction which is a *n*th-order reaction with respect to the vulcanising agent; the rate being expressed in terms of temperature by an Arrhenius equation.

2.2.1. Mathematical treatment

The equation of unidirectional heat conduction is:

$$\rho C \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \rho \frac{\partial Q}{\partial t} \tag{6}$$

where the contribution of the exothermic cure reaction is in the right hand side.

The rate at which heat is evolved from the cure reaction is expressed by Eq. (3).

2.2.2. Numerical treatment

As no analytical solution exists for the problem, it is resolved by a numerical treatment [2]. The thickness of the sample in the dies of the MDR is divided into slices of constant thickness Δx, each slice being defined by an integer n, while the time is divided into increments of time Δt.

The principle is as follows: the new temperature TN_n at position n after elapse of time Δt is expressed in terms of the previous temperatures at the same and adjacent places:

$$TN_n = \frac{1}{M}[T_{n-1} + (M-2)T_n + T_{n+1}] + \frac{\Delta Q}{C} \tag{7}$$

with the dimensionless number M

$$M = \frac{(\Delta x)^2}{\Delta t} \frac{\rho C}{\lambda} \tag{8}$$

The state of cure is expressed by:

$$\mathrm{SOC} = 100Z \tag{9}$$

while Z is obtained by integrating Eq. (3):

$$Z = 1 - \exp(-S) \tag{10}$$

where the function S is defined by:

$$S_t = k_0 \int_0^t \exp\left(-\frac{E}{RT_t}\right) \mathrm{d}t \tag{11}$$

with the recurrent relationship:

$$S_{t+\Delta t} = S_t + k_0 \Delta t \exp\left(-\frac{E}{RT_t}\right) \tag{12}$$

and:

$$S_0 = 0 \tag{13}$$

Thus the profiles of temperature and state of cure can be calculated at any time through the thickness of the sample.

3. Experimental

3.1. Materials used for the cure

EPDM compounds containing 2% sulphur are used (Hutchinson). Their main composition is given as follows (w/w %): elastomer: 33; C black: 50; plasticizer: 13; vulcanising agent: 2; other chemical: 3.

3.2. Apparatus

A Monsanto 2000 E Moving Die Rheometer (MDR Alpha Technologie) is used under isothermal conditions within the range of 140–160 °C, for determining the kinetic parameters of the cure, except for the enthalpy of cure.

A calorimeter C80 (SETARAM) is run in scanning mode with a heating rate of 0.2 K/min for determining the enthalpy of cure.

The heat flux is recorded as a function of temperature (or time). Samples around 6 g are placed into a cylindrical holder with an internal diameter of 1.7 cm.

3.3. Characteristics of the cure and of heat transfer

The values of the kinetic parameters of the cure, as well as the thermal parameters are shown in Table 1.

4. Results

The following three parts are considered:

(i) Calculation of the torque with the new method, using the square root of time–temperature dependence.
(ii) Method of determination of the kinetic parameters from the torque–temperature histories by using a simple method.
(iii) Evaluation of the profiles of temperature and of state of cure during the process with this method.

Table 1
Kinetic and thermal parameters

$\ln k_0 = 17.117$ $K_0(\mathrm{s}^{-1})$
$E/R = 9{,}537$ kJ/mol
$\rho = 1170$ kg/m^{-3}
$C = 2.34$ kJ/kg K
$\lambda = 0.25$ W/m K
$n = 0.654$
Enthalpy of cure $= 13$ kJ/k

4.1. Calculation of the change in torque with the method

The torque has been calculated as a function of temperature when the temperature of the dies of the MDR is varied with the square root of time (Fig. 1), by using Eq. (5), and the kinetic parameters shown in Table 1, as they were obtained from the MDR experiments run under isothermal conditions. The evolution of the torque with temperature (Fig. 1) and with time (Fig. 2) is drawn in these Figures for various heating rates ranging from 10 to 50 K/min$^{0.5}$.

This calculation is based on the assumption that the temperature of the die is constantly the same as that of the rubber sample, meaning that a high coefficient of heat conduction exists either at the die–rubber interface or through the rubber thickness. This is the reason why the profiles of temperature developed through the rubber thickness are evaluated in Section 4.4, in order to make sure that this assumption is possibly right. It must be said that this assumption is also made in the MDR run under isothermal conditions when the sample at room temperature is introduced in the dies kept at the selected temperature, which is far from being true [2,17,18].

Three different values for the heating rate are selected between the rather large 10–50 K/min$^{0.5}$ range.

The following conclusions from Figs. 1 and 2 are worth noting:

(i) The change in torque with temperature, as shown in Fig. 1, follows S-curves, starting at about the same temperature of the die.

(ii) The effect of the heating rate is of great importance, the curves being shifted to higher temperature values when the heating rate is increased, as shown in Fig. 1. The curves are not exactly shifted through a translation way as for the linear programming of temperature [18].

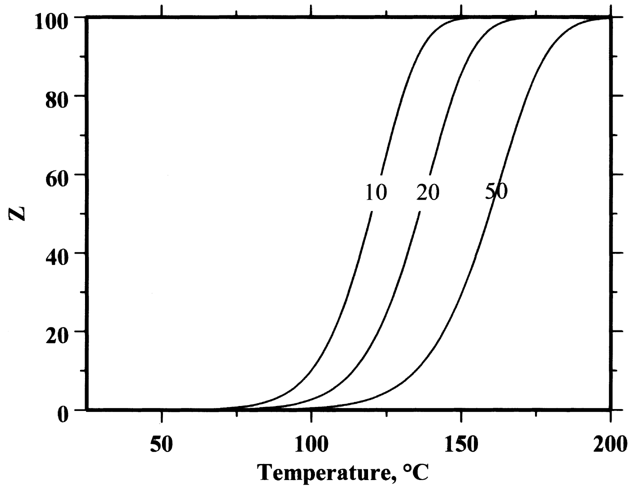

Fig. 1. Torque–temperature histories as a function of temperature obtained with the MDR apparatus run in scanning mode with the square root of time–temperature programming for various heating rates (shown in K/min$^{0.5}$).

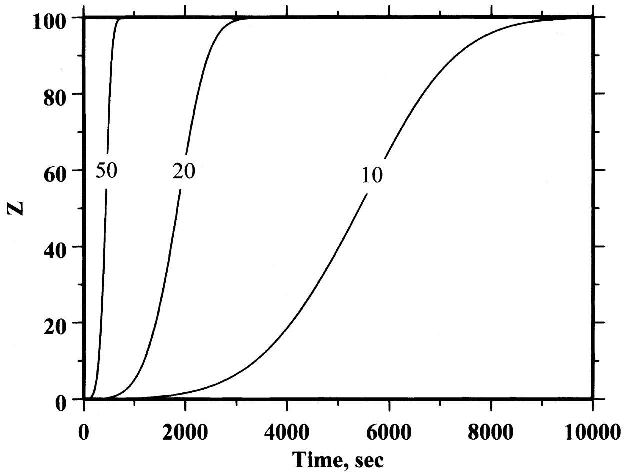

Fig. 2. Torque–temperature histories as a function of time obtained with the MDR apparatus run in scanning mode with the square root of time–temperature programming for various heating rates (shown in K/min$^{0.5}$).

(iii) The temperature of the die for which the torque is maximum, highly depends on the value of the heating rate, with the following statement: the higher the heating rate is, the higher the value of the temperature necessary for the torque to reach the maximum value.

(iv) The change in torque with this method, expressed as a function of time, in Fig. 2, is of interest. Thus, other S-curves are also obtained. However, the effect of the value of the heating rate appears to be of great importance. Because of the square root of time temperature dependence, the curves are obtained at a much lower time when the heating rate is larger.

(v) As shown in Fig. 3, the time of the scanning can be reduced by using a two-step process of heating, with a high heating rate up to the temperature at which a torque change is observed, followed by the heating rate selected for the purpose. For instance, in Fig. 3, the dies of the MDR are heated up to 75 °C at the heating rate of 200 K/min$^{0.5}$. Thus it takes 3 s for the sample surface

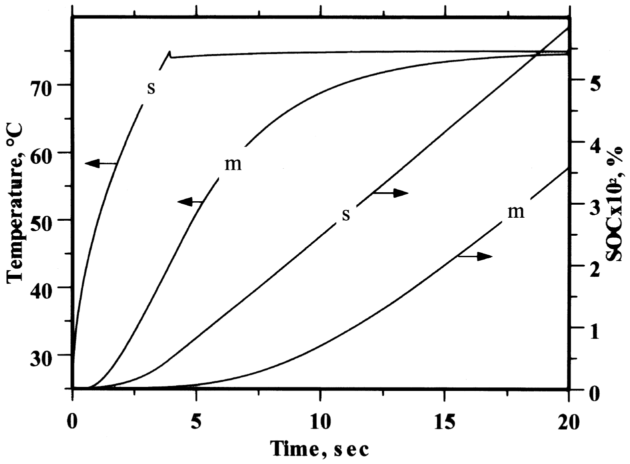

Fig. 3. Effect of a fast heating stage up to 75 °C, with a heating rate of 200 °C/min$^{0.5}$, on the profiles of temperature (left) and of state of cure (right) through the sample. Surface—s; mid-plane—m.

Table 2
Time (s) necessary for the torque to reach 50 and 95% of its maximum

		10	20	50	2	5	10	140	150	160
New method[a]	95	5860	2040	500						
	50	4260	1640	385						
Linear programming[b]	95				4900	2060	1060			
	50				4400	1860	980			
Isothermal conditions[c]	95							1530	770	380
	50							890	435	210

[a] With heating expressed in K/min$^{0.5}$.
[b] With heating rate expressed in K/min.
[c] With temperature expressed in °C.

and 15 s for the mid-plane of this sample, to reach the temperature of the die at 75 °C, while a negligible increase in the state of cure has been obtained, at 0.06% at the surface and 0.04% at the mid-plane, during this stage of high heating rate.

(vi) Of course, this first stage of high heating rate is especially of interest when a rather low heating rate is selected for curing the rubber sample.

4.2. Comparison of the time of experiment with other methods using the MDR

The data shown in Table 2, with the times necessary for the torque to get typical values, are of interest. They are able to make comparison between the three ways of using the MDR: under isothermal conditions at three selected temperatures, with a linear programming of temperature, when the temperature is increased with the square root of time. Two series of time are considered, for the torque reaching 50 and 95% of the maximum value, leading to a few comments:

(i) Under isothermal conditions, it clearly appears that the time strongly varies with the temperature selected for the experiment, very short at 160 °C, and rather long at 140 °C.

(ii) For the linear programming, reasonable values are obtained at 10 °C/min, which are of the same order of magnitude as those obtained under isothermal conditions.

(iii) With the new method, a heating rate of 50 °C/min$^{0.5}$, or even a value between 50 and 20 °C/min$^{0.5}$, gives similar times.

(iv) The change in torque with time is of interest. The ratio of the times necessary for the torque to reach 50 and 95% of its maximum is chosen. A high value for this ratio means that the time of cure is long, when the state of cure is progressing from 50 to 95%. A value of this ratio of 1.75 is obtained for the isothermal MDR, of 1.1 for the linear temperature programming, and of 1.3 when the temperature is varied with the square root of time. Thus, if the linear temperature programming brings some advantage over the isothermal MDR as proved in earlier studies [18], the new method allows the cure phenomenon to take place over a longer time, being more separated that in the case of the linear temperature programming, which is an advantage.

4.3. Determination of the kinetic parameters of the cure by using this new method of scanning mode

Of course, it is of great interest to determine precisely the kinetic parameters of the cure from the torque–temperature curves obtained with the MDR run in scanning mode when the temperature is increased with the square root of time. As mentioned previously, in assumption (iv), the change in the torque is expressed by the Arrhenius' equation (3), in which the three parameters should be determined.

By plotting $\ln(dZ/dT)$ versus $\ln(1 - Z)$, as shown in Fig. 4, a rather straight line is obtained, the slope of which is the order of the overall reaction of cure.

By plotting $\ln[(dZ/dT)(1 - Z)^n]$ versus the reciprocal temperature expressed in K, a straight line is obtained, whose slope is equal to the value of E/R (Fig. 5). The value

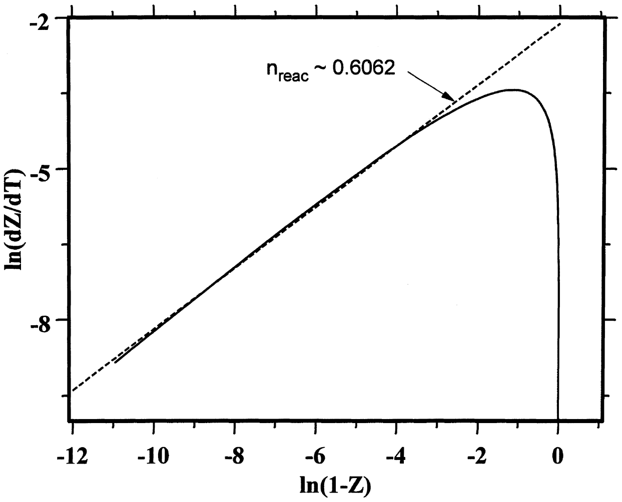

Fig. 4. MDR in scanning mode with the square root of time–temperature programming. Evaluation of the order of the overall reaction by using our method.

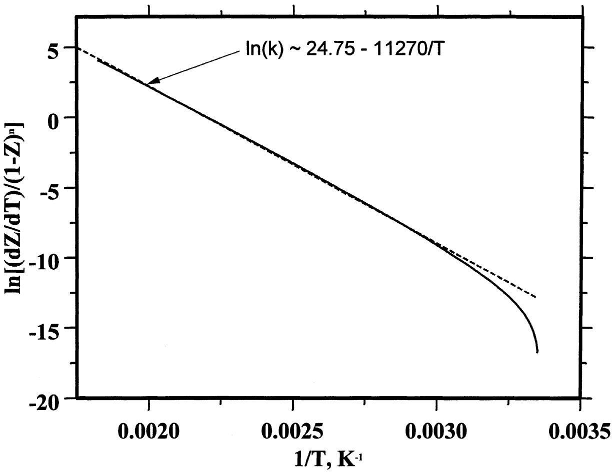

Fig. 5. MDR in scanning mode with the square root of time–temperature programming. Evaluation of the parameters of the overall reaction expressing the temperature dependence.

of the pre-exponential factor k_0 is obtained by using two ways, the one by extrapolating the curve in Fig. 5, and the other by using Eq. (3).

Some conclusions can be drawn from these results:

(i) The Freeman–Carroll's method has not been used, being very complex either in using or also for interpreting the data [19].
(ii) The more single method based on using Eq. (3), expressing the rate of change of the modulus as a function of temperature, is far more easier to use.
(iii) A straight line is obtained over a wide range, either for determining the order of the overall reaction, or the two parameters expressing the temperature dependence of the rate of the reaction.
(iv) Finally, the results obtained for these three parameters (n, E, k_0) are identical to those introduced for calculating the change in torque when the temperature is varied with the square root of time.

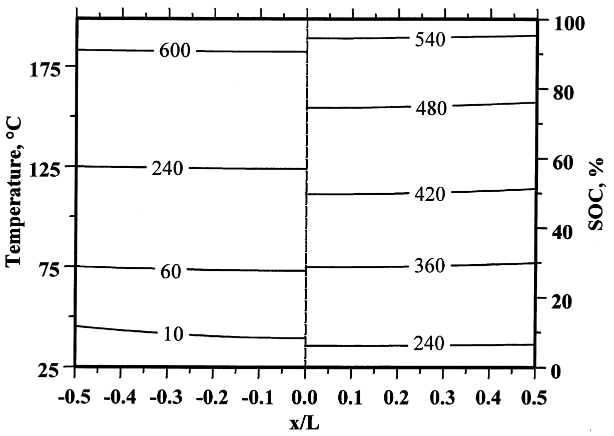

Fig. 6. Profiles of temperature (left) and of SOC (right) obtained through the 0.2 cm thick rubber sample in the MDR in scanning mode with the heating rate of 50 °C/min$^{0.5}$, time in seconds.

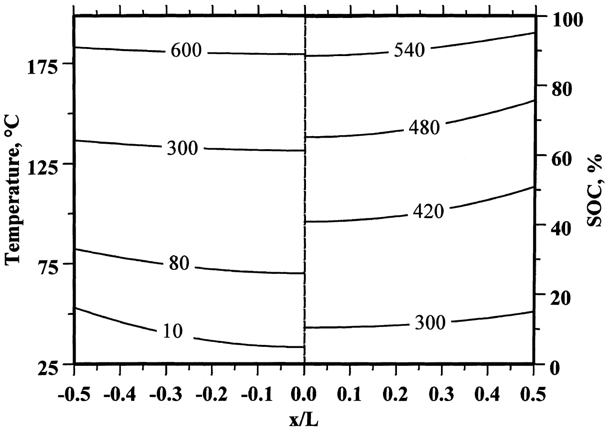

Fig. 8. Profiles of temperature (left) and of SOC (right) obtained through the 0.5 cm thick rubber sample in the MDR in scanning mode with the heating rate of 50 °C/min$^{0.5}$, time in seconds.

4.4. Evaluation of the profiles of temperature and of state of cure in the sample, when temperature varies with the square root of time

The profiles of temperature, as well as the corresponding profiles of state of cure, are calculated by using the numerical model and the data shown in Table 1.

The values of these profiles are drawn in Fig. 6 for half the thickness of the sample, as the system is symmetric, when the thickness of the sample is 0.2 cm, and in Fig. 8 when it is 0.5 cm. Moreover, the evolution of the temperature and state of cure in typical places in the sample, such as the surface in contact with the die and the mid-plane, is drawn in Fig. 7 when the thickness of the sample is 0.2 cm, and in Fig. 9 when it is 0.5 cm.

From the curves in these figures, some observations are worth noting:

(i) For the usual thickness of the sample, e.g. 0.2 cm, the profiles of temperature are nearly flat during the whole

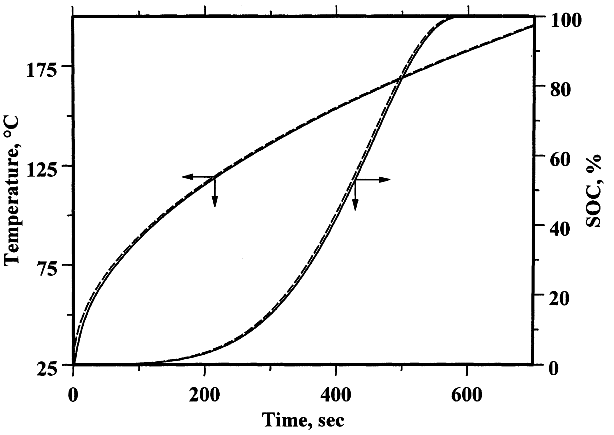

Fig. 7. Temperature–time (left) and SOC–time (right) histories obtained in the 0.2 cm thick rubber sample with the MDR apparatus run in scanning mode with the heating rate of 50 °C/min$^{0.5}$. Full line—mid-plane; dotted line—surface of the sample in contact with the die.

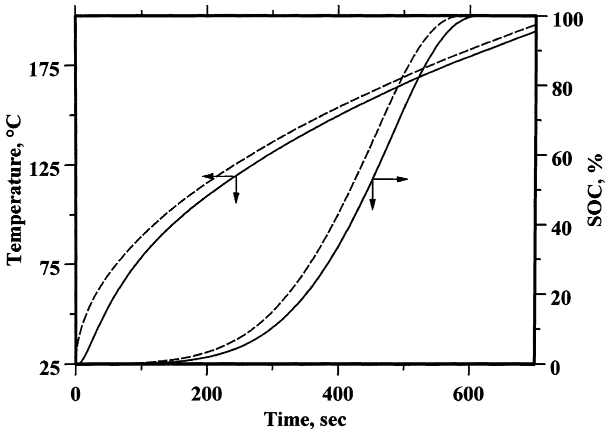

Fig. 9. Temperature–time (left) and SOC–time (right) histories obtained in the 0.5 cm thick rubber sample with the MDR apparatus run in scanning mode with the heating rate of 50 °C/min$^{0.5}$. Full line—mid-plane; dotted line—surface of the sample in contact with the die.

process of heating. In the same manner, the profiles of state of cure are flat, meaning that the rubber is homogeneously cured. Similar results are shown in Fig. 7.

(ii) Moreover, in Fig. 7, the evolution of the temperature clearly appears, either for the heating die or at the mid-plane of the sample. The S-shaped curve is also obtained for the state of cure expressed as a function of time.

(iii) As shown in Fig. 8, using a larger thickness of 0.5 cm is responsible for appreciable gradients of temperature up to 100 s and following gradients of state of cure, where the higher values for temperature and state of cure is attained on the surface of the sample in contact with the heating die. This fact, of course, results from the finite rate of heating by conduction through the rubber [2,18].

(iv) The results given in (iii) also appear in Fig. 9 where a significant difference in temperature and state of cure is observed between the surface and the mid-plane of the sample.

5. Conclusions

In the same way as for the other two techniques, such as the gas phase chromatography or the calorimetry, using the moving die rheometer with a programming of temperature offers advantages over the method run under isothermal conditions. With the isothermal MDR, at least three experiments, selected within a narrow width temperature window, are needed for determining the kinetic parameters, while only one experiment is necessary when the temperature is programmed. Generally, a linear temperature programming has been chosen for the first two techniques, and this way of increasing the temperature has been used in a recent study [18].

Nevertheless, a linear temperature programming is not the best way of increasing the temperature. When the temperature is varied with the square root of time, the rate of heating is faster at the beginning of the process when the sample is simply heated up to the temperature at which the cure reaction starts, this rate of heating becoming lower within the temperature range when the cure reaction takes place. Two advantages of this new technique over the linear temperature programming appears, in reducing the profiles of temperature and state of cure through the sample, leading to a more homogeneous system, and in reducing the time of experiments.

A simple method for determining the kinetic parameters, e.g. the order of the overall cure reaction, the energy of activation and the pre-exponential factor, from the S-shaped curve expressing the change in modulus with temperature has been presented. The evaluation of this method of calculation is perfect, as it enables to obtain the same values of the kinetic parameters as those introduced for determining the curve expressing the change in modulus with temperature.

An additional way of reducing the time of experiment has been suggested by increasing the rate of heating during the first stage of heating when no reaction takes place.

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