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New way of using rheometers in scanning mode for the cure of rubbers☆

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Abstract

Rheometers, especially the moving die rheometer (MDR), is used under isothermal conditions for the cure of rubbers. Thus, at least three experiments are necessary at different temperatures selected within a rather narrow temperature window, for determining the kinetic parameters of the cure. Moreover, it takes some time for the sample to attain the selected temperature, and for a high temperature of the dies, the reaction takes place before thermal equilibrium has reached. With this new way of using the rheometer, the dies with the rubber samples in them are heated from the room temperature up to the selected final temperature, with a constant heating rate. Calculations have been done for evaluating the performances of this method. The kinetic parameters such as the activation energy and the pre-exponential factor, as well as the order of the overall reaction, are obtained from only one experiment. The temperature in the sample is constant and nearly the same as that of the heating dies. The profiles of temperature and of the state of cure developed through the sample thickness are rather flat during all the processes. The parameter of interest, with the value of the heating rate, should be between 2 and 10°C/min, and perhaps much better between 2 and 5°C/min. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Moving die rheometer; Rubber; Enthalpy

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1. Introduction

In the same way as for thermosetting resins, the process of curing rubbers is rather complex, since it consists of the stages of heat transfer through the rubber and internal heat generated by the overall cure reaction. The cure reaction is highly complex and the reaction starts at a given temperature depending on the nature of the vulcanizing agent. Thus, the rubber is heated in the mould at a temperature for which the reaction takes place. The cure of rubbers is of great importance from the economic point of view, since a product badly cured with poor mechanical properties cannot be recycled and hence should be rejected.

The determination of the kinetics of cure is of great interest, as this kinetics is the basis for evaluating the operational conditions of the cure: temperature and time for a given dimension of the sample. Rheometers are widely used, and especially the moving die rheometer (MDR) introduced in 1985 [1]. The sample, about 0.2 cm thick, is placed between the heated dies, with the lower die oscillating and a reaction torque transducer positioned above the upper die. It was found that the MDR gives shorter times of cure than the oscillating die rheometer (ODR), owing to faster heat transfer resulting from the smaller thickness, and different torque values owing to the die design. For the rheometer run under isothermal condition, the conversion at time t is obtained from the change in torque from the minimum up to time t, as a fraction of the total torque change [2]. The MDR is used at various temperatures, and thus the temperature-dependence of the process can be obtained. Two experimental limitations can be considered:

(i) The one with the temperature range over which meaningful data can be obtained [2]. The lower temperature for cure studies lead to very long times. The higher temperature is determined by the induction period for the cure reaction to initiate. Thus it can be said that a temperature window of around 20–30°C width is found, over which meaningful data can be obtained [2].
(ii) Another problem appears with the temperature of the sample. In isothermal MDR, the applied temperature is the set apparatus temperature and not the true sample temperature, especially in the following cases: at the beginning, the sample at room temperature is introduced

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Nomenclature

b	rate of heating in scanning mode
C	heat capacity of the rubber
Δx, Δt	increment of space along the rubber thickness, increment of time
E	activation energy
h	coefficient of heat transfer at the die–rubber interface
λ	thermal conductivity
k_0	pre-exponential factor
M	dimensionless number (Eq. (15))
p	order of the overall cure reaction
Q_t, Q_∞	heat evolved from the cure reaction up to time t, and completion, respectively
ρ	density of the rubber
SOC	state of cure defined in Eq. (21)
S	function defined in Eq. (17)
T	temperature
TN_n	new temperature after elapse of time Δt at position n
T_0, T_f	initial and final temperatures in scanning mode
T_die, $T_{t,\mathrm{s}}$	temperature of the die and that of the rubber surface in contact with the die at time t, respectively
t	time
x	abscissa taken along the rubber thickness
Y	ratio of the torque values (Eq. (1))
Z	ratio of the heat generated by the cure reaction (Eq. (12))

into the slabs of the MDR kept at the selected temperature and it takes some time for the equilibrium in the sample to establish; because of local heating arising from the exothermic reactions, some gradients of temperature are developed through the sample, especially when the cure enthalpy is not very low. Nevertheless, the kinetic parameters of the overall cure reaction can be determined from the MDR experiments [3], such as the energy of activation and the pre-exponential factor, the order of the reaction often taken as one, but the cure enthalpy is not obtained.

Other methods have also been used for determining the kinetic parameters of the overall reaction of cure. They consist of taking into account the heat generated by this overall cure reaction. The state of cure is thus defined by the enthalpy evolved up to time t as a fraction of the total enthalpy evolved [2,4]. The calorimetry techniques have been widely used not only for measuring the cure enthalpy [2,4–7], but also for determining the kinetic parameters [4,8] by assuming that the heat evolved from the overall reaction can be expressed in terms of temperature by an Arrhenius equation. Isothermal calorimetry was used preferably in the early eighties, in spite of its drawbacks [4], but finally the calorimetry in scanning mode was found to be the best method [9].

The process of cure has been analysed by considering heat transfer by conduction through the rubber and heat generated by the reaction. The state of cure was evaluated from the temperature–time history at any place in the rubber by introducing a temperature of reference at 149°C and a rate coefficient of cure assuming that the reaction rate increases by a factor of 1.85 per 10°C [10]. The profiles of temperature developed through the rubber were calculated by assuming that the rate of cure doubles for each 10°C increase in temperature around a reference temperature of 150°C [11]. A constant time conversion of 1.3 per 10°C was found for the sulphur vulcanization of EPDM blends with a reference temperature corresponding to 150°C [3]. The state of cure has been evaluated by using the swelling in toluene of thin rubber samples cured at various times and temperatures [12].

Numerical model have been built and tested for the cure of rubbers with sulphur [4,13] and of EPDM with peroxide [14]. The heat transfer by conduction through the rubber and heat generated by the cure reaction are taken into account, leading to the profiles of temperature and of state of cure developed through the samples at any time.

The first objective in this paper is to show that the MDR could be used in scanning mode with a constant heating rate, in order to eliminate the drawbacks of the MDR run under isothermal conditions, and to show that the kinetic parameters of the cure reaction can be obtained from this torque–temperature curve.

The other purpose is to evaluate mathematically the torque change as a function of temperature, as well as the kinetic parameters from this curve. Moreover, a numerical model is built in order to determine the profiles of temperature and state of cure developed through the sample cured in the MDR run either in scanning mode or under isothermal conditions.

2. Theoretical

2.1. Establishment of the equations in the MDR in scanning mode

2.1.1. Assumptions

(i) Perfect contact is obtained between the rubber and heating dies; thus the temperature is constantly the same on each face of the die–rubber interface.

(ii) The rate of heating of the MDR is constant between the initial and final temperatures T_0 and T_f.

(iii) The kinetics of torque change follows a first-order equation (in fact, this assumption is not obligatory).

(iv) The increase with temperature of the rate of torque is expressed by an Arrhenius equation.

2.1.2. Mathematical treatment for the MDR in scanning mode

By putting

$$Y = \frac{\mathrm{Torque}_t}{\mathrm{Torque}_\infty}, \tag{1}$$

the differential equation under isothermal condition

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = k_0(1 - Y)\exp\left(-\frac{E}{RT}\right) \tag{2}$$

becomes with the constant heating rate b

$$b = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{3}$$

$$\frac{\mathrm{d}Y}{\mathrm{d}T} = \frac{k_0}{b}\,(1 - Y)\exp\left(-\frac{E}{RT}\right) \tag{4}$$

expressing the ratio of the torque values as a function of temperature.

By integration between T_0 and T_f, it becomes

$$Y_T = 1 - \exp\left(-\frac{k_0}{b}\int_{T_0}^{T_\mathrm{f}} \exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right) \tag{5}$$

2.1.3. Mathematical treatment for evaluating the kinetic parameters from the curve obtained in scanning mode

Eq. (4) in logarithmic form is, when the order is p

$$\ln\frac{\mathrm{d}Y}{\mathrm{d}T} = \ln\frac{k_0}{b} + p\ln(1 - Y) - \frac{E}{RT} \tag{6}$$

which becomes with finite differences [15]

$$\Delta\ln\frac{\mathrm{d}Y}{\mathrm{d}T} = p\,\Delta\ln(1 - Y) - \frac{E}{R}\Delta\left(\frac{1}{T}\right) \tag{7}$$

or

$$\frac{\Delta\ln\dfrac{\mathrm{d}Y}{\mathrm{d}T}}{\Delta\ln(1 - Y)} = p - \frac{\dfrac{E}{R}\Delta\left(\dfrac{1}{T}\right)}{\Delta\ln(1 - Y)} \tag{8}$$

which can be written in the simple form

$$A_T = p - \frac{E}{R}B_T \tag{9}$$

By plotting A_T as a function of B_T, the slope gives the activation energy E and the intercept p (which is taken as 1 in this paper).

The pre-exponential factor k_0 can be calculated finally in Eq. (6).

2.2. Calculation of the profiles of temperature and state of cure through the sample in the MDR

2.2.1. Assumptions

(i) With the MDR under isothermal conditions, the temperature of the dies is constant. There is a high but finite coefficient of heat transfer between the die and the rubber, resulting from a good contact.

(ii) With the MDR in scanning mode, the temperature is the same on both sides of the die–rubber interface.

(iii) In the MDR in scanning mode or under isothermal conditions, heat is transferred by conduction through the rubber.

(iv) Internal heat generated by the cure reaction can be expressed in terms of temperature by an Arrhenius equation.

2.2.2. Mathematical expressions

The equation of uni-directional heat transfer by conduction through the rubber is

$$\rho C\frac{\partial T}{\partial t} = \lambda\frac{\partial^2 T}{\partial x^2} + \rho\frac{\partial Q}{\partial t} \tag{10}$$

The boundary expressions under isothermal condition of the MDR are

$$-\lambda\frac{\partial T}{\partial x} = h(T_\mathrm{die} - T_{t,\mathrm{s}}) \tag{11}$$

The rate of heat generated by the cure reaction is

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = k_0(1 - Z)\exp\left(-\frac{E}{RT}\right) \tag{12}$$

with

$$Z = \frac{Q_t}{Q_\infty} \tag{13}$$

2.2.3. Numerical treatment

As the problem is not mathematically feasible, it is resolved by a numerical treatment.

The thickness of the rubber is divided into slices of thickness Δx, each slice being characterized by an integer n. From the heat balance evaluated in each slice, the new temperature TN_n in a slice is obtained in terms of the previous temperatures at the same and adjacent positions [4]

$$\mathrm{TN}_n = \frac{1}{M}[T_{n-1} + (M - 2)T_n + T_{n+1}] + \frac{\Delta Q_n}{C} \tag{14}$$

with the dimensionless number

$$M = \frac{(\Delta x)^2}{\Delta t}\frac{\rho C}{\lambda} \tag{15}$$

The state of cure is obtained as follows:

The conversion Z is expressed by:

$$Z = 1 - \exp(-S) \tag{16}$$

where the function S is

$$S_t = k_0\int_0^t \exp\left(-\frac{E}{RT_t}\right)\mathrm{d}t \tag{17}$$

The relationship required to obtain S after elapse of time

Δt is

$$S_{t+\Delta t} = S_t + k_0 \Delta t \exp\left(-\frac{E}{RT_t}\right) \tag{18}$$

with

$$S_0 = 0 \tag{19}$$

Heat evolved during the increment of time Δt is given by

$$\Delta Q = Q_\infty (Z_{t+\Delta t} - Z_t) \tag{20}$$

and the state of cure at time t (or temperature T) is

$$\mathrm{SOC}_n = 100 Z_n \tag{21}$$

3. Experimental

3.1. Material

The rubber used was an EPDM compound containing 2% peroxide. The main composition was (in w/w%): elastomer 33; C black 50; plasticizer 13; vulcanizing agent 2; other chemicals 3.

The peroxide was (Perkadox 14–40) bis (*tert*-butyl 1-peroxyisopropyl) benzene.

3.2. Apparatus

A Monsanto 2000 E MDR (Alpha Technologies) was used under isothermal conditions, at various temperatures within the 160–190°C range. The thickness of the sample was 0.2 cm.

The calorimeter C 80 (SETARAM) was used in scanning mode with a heating rate of 0.2 K min^{-1} and a sample of around 6 g.

3.3. Characteristics of the cure and of heat transfer

Enthalpy: 13 kJ kg^{-1} $\rho = 1180\ \mathrm{kg\ m^{-3}}$
C: 2 kJ $\mathrm{kg^{-1}\ K^{-1}}$ $\lambda = 0.25\ \mathrm{W\ m^{-1}\ K^{-1}}$

4. Results

Two kinds of results are considered: the ones obtained or calculated with the MDR run under isothermal conditions, and the others calculated with the MDR in scanning mode.

4.1. Results with the MDR under isothermal conditions

4.1.1. Determination of the kinetic parameters

The time necessary for the torque to attain given ratios of its maximum value (5, 50 and 95%) is shown at various temperatures in Table 1, as well as the values of the rate constant k_T.

Table 1
Torque versus time (min:s)

T (°C)	Torque (dNm)		t (05)	t (50)	t (95)	$k_T \times 10^3$ (s^{-1})
	Min	Max				
160	2.7	10.6	1:13	9:17	26:00	
170	2.5	11.8	0:34	4:33	18:12	2.79
180	2.5	11.1	0:25	1:58	7:37	6.81
190	2.4	11.1	0:17	0:50	2:59	18.08

From the values in Table 1, it appears that the times necessary for the torque to reach 50 or 95% of the maximum value are rather long at 160°C and very short at 190°C. Thus it can be said that the temperature window width over which meaningful data are obtained is around 20–30°C as already found for rubbers vulcanized with sulphur [2]. Moreover, the higher value of the torque obtained at 160°C is lower than the corresponding values at the higher temperature ranging from 170 to 190°C. The values of k_T were determined from the torque values obtained at each temperature by using Eq. (2). As shown in Fig. 1 where $\ln(1 - Y)$ is plotted versus time, nearly straight lines are obtained, being a proof for the 1st order reaction of cure. The values of k_T are collected in Table 1 for the various temperatures.

By plotting the logarithm of these k_T values as a function of the reciprocal absolute temperature (Fig. 2), the values of the activation energy are obtained from the slope of these straight lines. The values of the pre-exponential factor k_0 are evaluated by fitting the two members of Eq. (2).

The value of the kinetic parameters obtained through the MDR experiments done under isothermal conditions are collected in Table 2.

Some remarks are made from these results:

(i) As shown by various authors for the cure of rubbers [8,10–12], the temperature dependence of the rate of cure can be expressed by an Arrhenius equation. This is also true in the present case as within the 170–190°C range, a straight line is obtained by plotting $\ln k_T$ as a function of

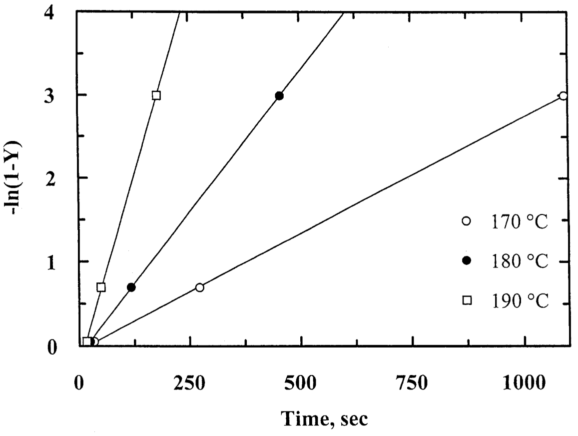

Fig. 1. MDR under isothermal conditions within the 170–190°C range. $\ln(1 - Y)$ versus time, for various temperatures.

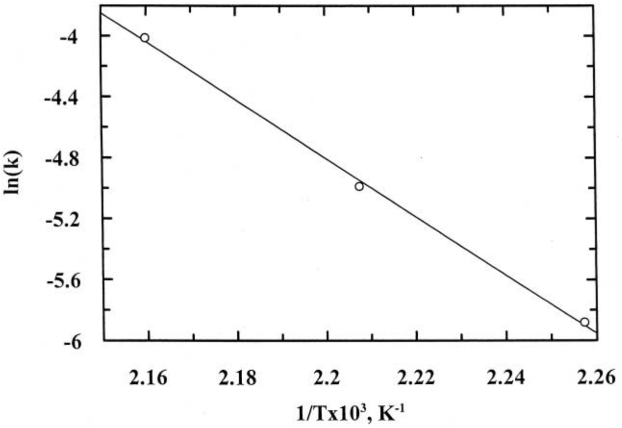

Fig. 2. MDR under isothermal conditions within the 170–190°C range. Evaluation of the activation energy. ln k vs. the reciprocal absolute temperature.

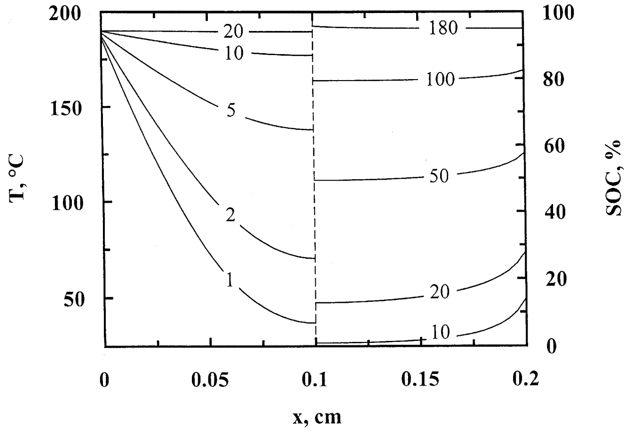

Fig. 3. MDR under isothermal conditions at 190°C. Profiles of temperature developed through the rubber sample at various times (left). Profiles of state of cure developed through the rubber sample at various times (right).

the reciprocal temperature. This range is rather narrow as previously said for the cure of rubbers [5–7].

(ii) The value of the activation energy is around 160 kJ mol^{-1}. This value for the activation energy is of the same order of magnitude as that obtained by several authors: 126 kJ mol^{-1} [16] or 140 kJ mol^{-1} [17].

4.1.2. Profiles of temperature and state of cure through the rubber in the MDR

The profiles of temperature (left) and state of cure (right) developed through the sample calculated by using the numerical model are shown in Fig. 3 when the temperature of the dies is constant at 190°C. The value considered for the coefficient of heat transfer at the rubber–die interface is very high, with a value of 100 for the dimensionless number hL/λ [4]. This means that the contact is almost perfect. The temperature–time and state of cure-time histories are drawn at various places through the rubber sample (Fig. 4), as they are obtained by calculation with the numerical model.

The following observations can be made:

(i) The temperature of the rubber surface nearly reaches the value of that of the die, because of the high value taken for the dimensionless number hL/λ and thus for the coefficient of heat transfer at the rubber–die interface.

Table 2
Kinetic parameters for the cure reaction

	For 170°C < T < 190°C	$n = 1$
Values obtained with MDR isothermal		
	$E/R = 19156.3$ K	$\ln k_0 = 37.34$
Values used for the MDR in scanning mode		
	$E/R = 19156$ K	$\ln k_0 = 37.3$
Values calculated from the MDR in scanning mode		
	$E/R = 19156$ K	$\ln k_0 = 37.3$

(ii) In spite of the small thickness (0.2 cm) of the sample, and the high coefficient of heat transfer at the die–rubber interface, it takes some time for the sample to reach thermal equilibrium (nearly 10–20 s) because of the low heat conductivity in the rubber.

(iii) The cure reaction starts before the thermal equilibrium is reached, in various places through the rubber. This fact is especially true for the rubber in contact with the die, but it also appears clearly at the mid-plane of the rubber sheet, either in Fig. 3 (right) or in Fig. 4.

(iv) Gradients of state of cure are thus developed through the thickness of the rubber. Obviously, the value is higher on the surface in contact with the die, as also shown in Fig. 3. Thus after 20 s, a state of cure between 20 and 30% is obtained in the rubber.

(v) Thus an heterogeneity is observed in the sample, especially at the beginning of the process, resulting

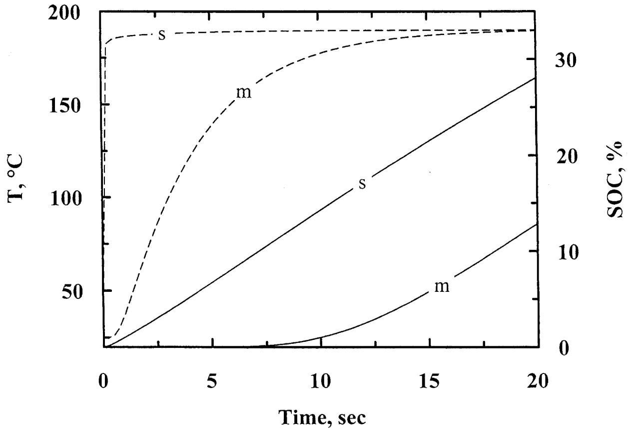

Fig. 4. MDR under isothermal conditions at 190°C. Variation of the temperature and state of cure as a function of time, in various places; (s) on the surface; (m) at the midplane. Temperature, (- - -); state of cure (—).

from the gradients of temperature and above all from the gradients of state of cure developed through the rubber.

4.2. Results with the MDR run in scanning mode

4.2.1. Calculation of the torque–temperature curves

In scanning mode of the MDR, the temperature of the dies and the rubber starts at room temperature (25°C), and increases constantly with time. The value of the torque at time t as a ratio of the maximum value of the torque Y is drawn as a function of the die temperature. The curves are drawn in Fig. 5 for various values of the heating rate ranging from 2 to 10°C/min. The values necessary for drawing curves are calculated by using Eq. (5). Some comments are worth noting:

(i) Calculation is made by using Eq. (5), based on the assumption that thermal equilibrium through the rubber is obtained at any time. In fact, as shown precisely in Fig. 6, a gradient of temperature is developed through the thickness during the scan, this gradient being proportional to the heating rate [4]. Nevertheless, the larger difference through the rubber thickness is rather low (0.3 and 0.6°C for the heating rate of 5 and 10°C/min, respectively). This fact appears in Fig. 7 where the profiles of temperature and state of cure are shown using a larger scale.

(ii) Typical *S*-curves are obtained, starting at around the same temperature of the dies. These curves have the same shape.

(iii) The value selected for the heating rate is of great interest. A very wide range is used from 2 to 10°C/min in Fig. 5. An increase in the heating rate shifts the *S*-curve toward a higher temperature through a translational way [4].

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

(v) A comparison between the torque values and the state of cure is of interest. For the longer times, the ratio of the torque values is about the same as that of the state of cure. For instance at 190°C, it is around 95% at 180 s, and 50% after 50 s.

(vi) At 190°C, and for a short time of 17 s, the ratio of torques is 5% and the profile of state of cure varies from 5 to 10.

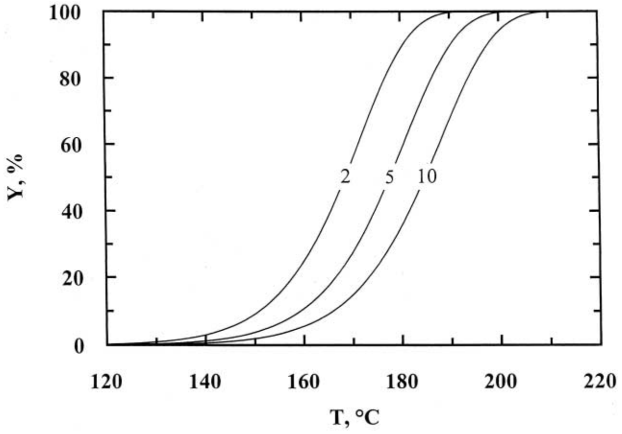

Fig. 5. MDR in scanning mode. Variation of the torque value as a function of the temperature of the MDR, with various heating rates (2–5–10°C/min).

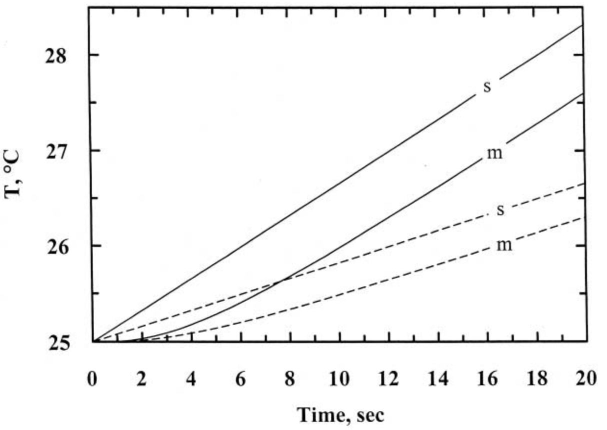

Fig. 6. MDR in scanning mode. Increase in temperature in the rubber with the die temperature, for different values of the heating rate. On the rubber surface (s). At the midplane (m). Heating rate: 10°C/min (—); 5°C/min (- - -).

4.2.2. Calculation of the profiles of temperature and state of cure in the rubber

It is of interest to determine the temperature profiles developed in the rubber sample when the MDR is driven in scanning mode. This calculation is made by considering the heat transfer by conduction through the rubber sample, using the numerical model. The results are shown in Fig. 6 with the temperatures on the surface in contact with the die and at the midplane of the rubber, plotted as a function of the time. The profiles of temperature (left) and of state of cure (right) developed through the thickness of the rubber sample are drawn at various times in Fig. 7 when the heating rate is 5°C/min.

The following facts deserve mention:

(i) The temperature on the surface of the rubber is constantly the same as that of the die whatever the value of the heating rate is. This fact results from the good contact at the rubber–die interface, and also because that the rubber and dies are at the same temperature at the beginning of the process.

(ii) The temperature at the midplane, initially at 25°C (room temperature) does not follow exactly the temperature of the die at the beginning of the process. It takes some time for the temperature at the midplane to vary,

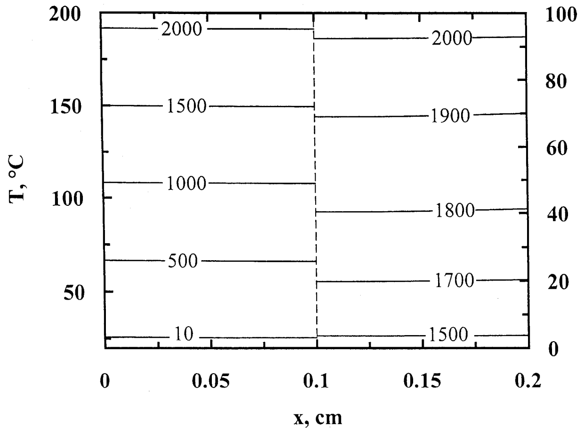

Fig. 7. MDR in scanning mode. Profiles of temperature (left) and state of cure (right) developed through the rubber sample at various times. Heating rate = 5°C/min.

because of the slow rate of heat transfer through the rubber, as shown in Fig. 6.

(iii) The temperature at the midplane of the rubber is thus shifted to a lower value, during the process of scanning of the MDR. The difference between the temperature at the midplane and on the surface of the rubber increases with the value of the heating rate, as already shown in calorimetry run in scanning mode [16]. After a rather short time of 20 s, this difference becomes constant to around 0.7 and 0.35°C when the heating rate is 10 and 5°C/min, respectively. This difference is in fact proportional to the heating rate [4].

(iv) These results for the temperature profiles are also shown in Fig. 7 (left) when the heating rate is 5°C/min. The profiles of temperature are nearly flat during the whole process with a difference of temperature of 0.35°C between the surface and the midplane of the rubber.

(v) The gradients of state of cure shown in Fig. 7 (right) are nearly flat during the whole process. This fact results from the flat profiles of temperature through the rubber.

4.2.3. *Evaluation of the kinetic parameters from the results obtained in scanning mode*

Of course, it is of great interest to determine the kinetic parameters from the torque–temperature curves obtained with the MDR used in scanning mode. These parameters can be determined from the curves shown in Fig. 5 by using either the method based on Eq. (8) called the Freeman–Carroll method or the simple method based on fitting the parameters in Eq. (4).

Another method is of interest, based on Eq. (6), by plotting $\ln(dY/dT)$ as a function of the reciprocal temperature. As shown in Fig. 8, a straight line is obtained with a slope proportional to the activation energy (E/R), when the value of $\ln(1 - Y)$ is negligible. This fact occurs when Y is less than 60%.

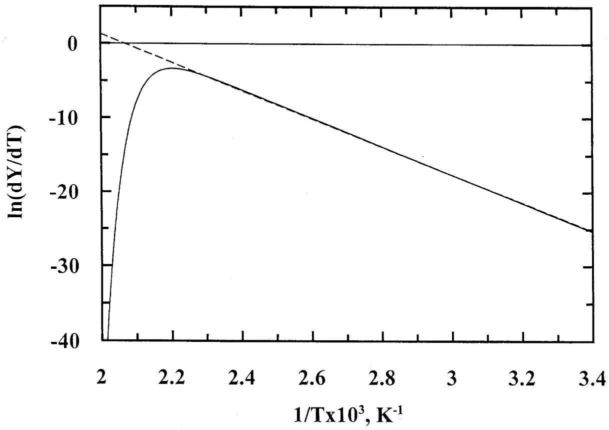

Fig. 8. MDR in scanning mode. Evaluation of the kinetic parameters.

The interest of these methods is worth discussing.

(i) The Freeman–Carroll method [15] is very well-known, but of tedious use.

(ii) The method based on fitting the parameters in Eq. (4) is a method of least squares linear or non-linear. It is very simple when the order of the overall reaction of cure can be considered as one.

(iii) The method is shown in Fig. 8, using the plots of $\ln(dY/dT)$ as a function of the reciprocal temperature is easy to use, especially for a first-order reaction of cure. The value of the activation energy is obtained from the slope of the straight line. The value of the pre-exponential factor k_0 is determined by using Eq. (4), or from the value of the intercept of this straight line on the $\ln(dY/dT)$ axis when $1/T$ tends to zero.

(iv) The effect of a change in the order of the overall reaction around one, within the 0.7–1.3 range, was found to be rather small on the rate of the reaction or rubbers, and on the profiles of temperature and of state of cure developed through the thickness of the sheets [18,19].

5. Conclusions

The two methods based on the way of using the MDR apparatus, either under isothermal conditions or in scanning mode, have been analysed. The advantages and the drawbacks of these methods have been examined in detail. A mathematical treatment has been established for the MDR in scanning mode. Thus comparisons can be made between these two techniques.

The MDR under isothermal conditions necessitates three experiments at least at various temperatures. These temperatures should be carefully selected, because a narrow temperature window width exists over which meaningful data are obtained. On the other hand, the MDR can be driven in scanning mode with only one experiment with the same sample. The main parameter of interest for this new way of using the MDR is the heating rate. As a conclusion, a value ranging from 2 to 10°C/min, or much better from 2 to 5°C/min should be selected. Of course, a low value for the heating rate is responsible for a long time of experiment. But this time can be reduced by starting the process of scanning at a temperature higher than room temperature, for instance 100–120°C in the present case.

The profiles of temperature and state of cure developed through the rubber are interesting pieces of information. Thus, it has been shown that the rate of heat transfer through the rubber is rather low, and from this fact it takes some time for thermal equilibrium in the rubber to establish. For the MDR in scanning mode, a slight gradient of temperature is developed at the beginning of the experiment, but after a short time it becomes constant. With the isothermal MDR, the process is more complex: the rubber initially at room temperature is placed between the heated dies, creating strong gradients of temperature over a time of around 20 s. During this time, the cure takes place especially near the die surface. Thus it can be said that over this time, there is an heterogeneity through the rubber.

Finally, the process is similar in the MDR and calorimetry techniques, with heat transfer and cure reaction. After being utilized under isothermal conditions a few decades ago, the calorimetry is now widely used in scanning mode, and perhaps the MDR method could also follows the same history.

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