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Implementation of an inverse method for identification of reticulation kinetics from temperature measurements on a thick sample

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Abstract—The aim of this article is to identify a reaction function involved in a model of vulcanization by using experimental study on thick pieces of rubber. The methods of determination of the parameters of the model are described, the inverse method is explained, results are given and commented on.

1. INTRODUCTION

RETICULATION kinetics can be determined using various techniques. Data concerning the development of mechanical (rheometry), thermal (differential scanning calorimetry) or dielectric properties can be used. Interpreting the results of these methods can be difficult for two main reasons. The first is linked to non-isothermicity of the samples. The second is that the relation between the properties measured and the degree of transformation is not one-to-one (rheometry, dielectric measurement). Due to diffusion in the sample, transformations are not unsteady. Calorimetric measurements can be taken isothermally or using a programmed rise. To isolate the temperature effect, measurements are taken at different temperature levels. If the reaction starts after a time period long enough for the sample and the calorimeter to have reached a state of equilibrium at the desired temperature, the flow observed is not disturbed by relaxation of the heating transient. For our calorimeter, this phase lasts about one minute. The flow from the unit must be distinguished from the flow released by the reaction. Even if the reaction is slow, the flow is extracted through the sample/measurement head cupel assembly. The regulation response time and the inertia specific to the unit distort the flow measurement signal. This is particularly true at the very beginning of the reaction but subsequently has little effect. During a programming rise, even at a moderate rate, the effects of thermal contact resistances are not negligible and corrections can be made, provided that the contact conditions between the sample and its support do not change. This is difficult to achieve if it is not kept under pressure. The dielectric properties vary according to the degree of reticulation and interpretation of these variations is very difficult. When the desired objective is control over a preparation process, these difficulties emphasize that it is advisable to measure kinetics under conditions which are as close as possible to real implementation conditions. This implies combination of an experiment on a thick sample with a method of parameter identification, by choosing simple geometry. It is then necessary to model the heat transfers linked to a kinetics model.

One of the most common models is the Arrhenius model in which the reaction kinetics are given by:

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{E}{R\theta}\right)(1-\alpha)^n$$

where k_0 is the reaction velocity constant, E is the activation energy and n the reaction order. With this model the reaction velocity is maximum for $\alpha = 0$, therefore at the start of the reaction.

A more general model has been suggested by Kamal and Sourour [1]:

$$\frac{d\alpha}{dt} = [f_1(\theta) + f_2(\theta)\alpha^n](1-\alpha)^m$$

where f_1 and f_2 are functions of the form:

$$f_i = k_i \exp\left(-\frac{E_i}{R\theta}\right).$$

This type of model was adopted by Saad and Scott [2] who have used a method for estimating kinetics

NOMENCLATURE

$C(.)$	product of density and specific heat [J K^{-1} m^{-3}]
E	activation energy [J mol^{-1}]
E_{ind}	induction period activation energy
$f(.), f_1(.), f_2(.)$	Arrhenius functions
$F_g(.)$	product of $w(.)$ transform, $k(.)$ and $g(.)$
$g(.)$	kinetics function
$h(.)$	transformation for integration of induction time
$J(.)$	criterion to be minimized
$k(.)$	Arrhenius function
k_0	reaction velocity constant [s^{-1}]
L	sample width
$L(.)$	Lagrangian
m	number of thermocouples
$p(.)$	adjoint state
$q(.)$	adjoint state
Q	reaction enthalpy [J kg^{-1}]
R	ideal gas constant
t	time [s]
T	time horizon [s]
$t_i(.)$	induction time
T_{ind}	constant specific to the induction period [s]
$u_0(.)$	temperature at $x = 0$
$u_L(.)$	temperature at $x = L$
x	abscissa [m]
$w(.)$	transformation for integration of induction time.
Greek symbols	
$\alpha(.)$	degree of reticulation
$\beta(.)$	enthalpy transform
$\Gamma(.)$	Kirchhoff transform
$\theta(.)$	temperature [°C]
$\theta_0(.)$	initial temperature [°C]
$\theta_j^*(.)$	temperature recorded by thermocouple j [°C]
$\lambda(.)$	conductivity [W K^{-1} m^{-1}]
ρ	density [kg m^{-3}]
$\nabla J(.)$	gradient of criterion.

parameters from differential scanning calorimetry and dielectric measurements.

Isayev and Deng [3] suggest an explicit formulation in time for α, of the form:

$$\alpha(t) = \frac{f(\theta)t^n}{1+f(\theta)t^n}$$

where $f(\theta)$ is an Arrhenius function.

Kong *et al.* [4] suggest division of the curve obtained isothermally into three states in which the velocity is approximated by segments of a straight line.

An approach based on the same idea (division into successive phases) has been suggested by Garnier *et al.* [5]. In this work, reticulation consists of the following periods:

- an acceleration phase up to the maximum reaction velocity, in which flow development with time is modelled by a straight line, which leads to an autocatalytic kinetics law of order 0.5:

$$\frac{d\alpha}{dt} = f_1(\theta)\alpha^{0.5},$$

- a relaxation phase, where kinetics are introduced whose order depends on the extent of the reaction:

$$\frac{d\alpha}{dt} = f_2(\theta)(1-\alpha)^{n(\alpha)},$$

where f_1 and f_2 are Arrhenius laws.

A special feature of some reticulation reactions—notably this one—which is well known by specialists, but often not by heat engineers, is that there exists a period of induction. This phase precedes the reaction phase and the degree of reticulation remains zero. This means that if the material is brought suddenly to a temperature at which it can be transformed, a period of time Δt_i will elapse before time t_i, which corresponds to the start of the reaction. This time can be experimentally linked [6] to the thermal history of the material by a relation of the form:

$$\int_0^{t_i} \exp\left(-\frac{E_{\text{ind}}}{R\theta(M,t)}\right)dt = T_{\text{ind}}.$$

Secondary reactions, with non-zero thermal effects, may occur during this period, but their kinetics are very different from those of curing.

In this model which we have adopted, we have selected this representation of the induction period. The model has been designed to be used in a control algorithm for optimum curing of a thick piece of rubber. It has therefore deliberately been simplified.

2. THERMAL RETICULATION MODEL

The thermal model which we describe considers 1D heat transfers in a range limited by $x = 0$ and $x = L$, with temperature-type boundary conditions imposed. The unknown variables are the temperature $\theta(x, t)$ and degree of reticulation $\alpha(x, t)$ which confirm the system:

$$C(\theta)\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial x}\left(\lambda(\theta)\frac{\partial\theta}{\partial x}\right)+\rho Q\frac{\partial\alpha}{\partial t} \qquad (1)$$

$$\theta(0,t) = u_0(t) \qquad (2)$$

$$\theta(L,t) = u_L(t) \qquad (3)$$

$$\theta(x,0) = \theta_0(x) \qquad (4)$$

$$\frac{\partial \alpha}{\partial t} = k(\theta) g(\alpha) \quad \text{if } t > t_i(x) \tag{5}$$

$$\alpha = 0 \quad \text{if } t < t_i(x) \tag{6}$$

where $k(\theta)$ and $t_i(x)$ are defined by:

$$k(\theta) = k_0 \exp\left(-\frac{E}{R\theta}\right) \tag{7}$$

and

$$\int_0^{t_i(x)} \exp\left(-\frac{E_{\text{ind}}}{R\theta(x,\tau)}\right) \mathrm{d}\tau = T_{\text{ind}} \tag{8}$$

where $\lambda(\theta)$ and $C(\theta)$ represent, respectively, thermal conductivity and specific heat per volume. The other parameters concern the kinetics of the chemical reaction.

Q	is the total enthalpy of the reaction [J kg^{-1}],
E_{ind}	is the activation energy of the induction period [J mol^{-1}],
T_{ind}	is the induction time constant [s],
E	is the activation energy of the reaction [J mol^{-1}],
k_0	is the velocity constant [s^{-1}],
$g(\alpha)$	is a function which represents the variation in reaction velocity as a function of the reticulation degree. The reaction velocity can be factorized into a product of two functions, one of temperature θ, the other of the reticulation degree α.

The kinetics model is described in ref. [6], where the concept of induction period has been used. The kinetics after the start of the reaction are represented by a relation of type:

$$\frac{\partial \alpha}{\partial t} = k(\theta) g(\alpha).$$

We have deliberately chosen to simplify this relation. A single activation energy is considered to represent temperature dependence. The dependence on the reticulation degree is represented by the function $g(\alpha)$. It is not attempted to determine $g(\alpha)$ analytically; it will be seen later that the function will be determined in discrete values of α.

In this study, certain model parameters are already given: thermal parameters $\lambda(\theta)$ and $C(\theta)$, and some kinetic parameter. Q, E_{ind}, T_{ind} and E are assumed to be known, $k_0 g(\alpha)$ is identified.

3. MEASUREMENT OF KNOWN MODEL PARAMETERS

3.1. *Thermophysical properties of the materials used (natural rubber)*

It is assumed that λ and C depend only on the temperature (their variation with α is neglected).

ρ is obtained by weighing and volume measurement. $C(\theta)$ is measured by differential scanning calorimetry (PERKIN ELMER DSC 7 with a programmed rise of 5 K min^{-1}). The thermal conductivity $\lambda(\theta)$ was determined by different techniques in the steady state (protected hot plate) and in the transient state by identifying parameters [5].

We took values:

$$C(\theta) = 1.35464 \times 10^6 + 1.0906 \times 10^4 \theta - 44.198\theta^2 + 0.019528\theta^3 \,\mathrm{J\,m^{-3}\,K^{-1}}$$

(θ is expressed in degrees Celsius and belongs to the interval [40°C, 160°C])

and $\lambda(\theta) = 0.271$ W m^{-1} K^{-1}.

3.2. *Chemical kinetics parameters*

The total reaction enthalpy Q is measured by integration of the heat flow curve obtained by isothermal calorimetry. We found $\rho Q = 2.177 \times 10^7$ J m^{-3}.

The characteristic parameters of the induction period T_{ind} and E_{ind} (formula (8)) are measured by isothermal calorimetry. This yields:

$$\ln(t_i) = \ln(T_{\text{ind}}) + \frac{E_{\text{ind}}}{R\theta}. \tag{9}$$

t_i is defined as the time corresponding to the intersection of the tangent at the point of inflexion on the flow curve and the horizontal corresponding to zero flow (Fig. 1). The graph representation of formula (9) on a logarithmic scale allows T_{ind} and E_{ind} to be calculated.

The accuracy on the induction period is made worse by the high temperature, which is due to the speed of the start of the reaction.

By using weighted least error squares, we found:

$$T_{\text{ind}} = 2.52 \times 10^{-6}\,\mathrm{s}$$

and

$$E_{\text{ind}} = 81.04 \times 10^3\,\mathrm{J\,mol^{-1}}.$$

The activation energy of the reaction is determined by isothermal calorimetry. Relations (5)–(7) allow us to write:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = -\frac{E}{R\theta} + \ln(k_0) + \ln(g(\alpha)) \tag{10}$$

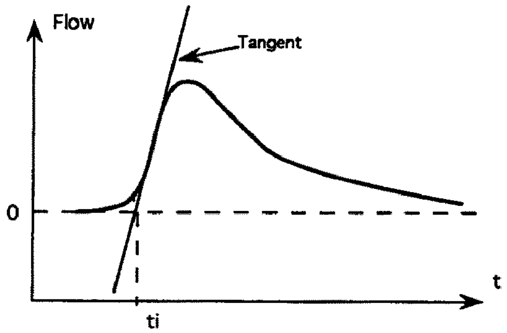

FIG. 1. Definition of induction time t_i.

for a value of α at two different temperature levels θ_1 and θ_2. This gives:

$$\ln\left(\frac{d\alpha}{dt}(\theta_1,\alpha)\right)-\ln\left(\frac{d\alpha}{dt}(\theta_2,\alpha)\right)=\frac{E}{R}\left(\frac{1}{\theta_2}-\frac{1}{\theta_1}\right). \quad (11)$$

Relation (11) allows E to be calculated, with an average being taken over several temperature levels and values of α. As the value obtained does not differ greatly from E_{ind}, we used the same value, i.e. $E = 81.04 \times 10^3\ \text{J mol}^{-1}$.

4. METHOD OF KINETICS IDENTIFICATION

The problem is to identify $k_0 g(\alpha)$ when the only a priori information is $g(1) = 0$ and $g(\alpha) > 0$. The principle behind the method is represented in Fig. 2. We wish to determine the function $g^* = k_0 g(\alpha)$, which minimizes the deviation criterion J between the calculated responses $\theta(x_j, t; g)$ and measurements $\theta_j(t)$. g^* is calculated using a descent method which consists of calculating a sequence of iterated values $1 \ldots n$ such that:

$$J(g^{(1)}) > J(g^{(2)}) > \cdots > J(g^*).$$

The direct model is described by equations (1)–(8), with the unidimensional character of the transfer ensured experimentally. The identification horizon is designated T.

The existence and uniqueness of the solution to equations (1)–(8) with restrictive conditions over g is demonstrated in ref. [7].

Conditions (5) and (6) result in a discontinuity of reaction velocity α at $t = t_i(x)$, since g is not zero.

In addition, induction time $t_i(x)$ depends non-linearly and implicitly on the unknowns θ and α of the problem, making solution of equations (1)–(8) more difficult.

To calculate the gradient of J and allow rigorous digital implementation, the following two functions are introduced:

$$w:\quad \begin{aligned} w(b) &= 0 \quad \text{if } b \leq 0 \\ w(b) &= 1 \quad \text{if } b > 0 \end{aligned} \quad (12)$$

and

$$h:\quad h(t,\theta)=\int_0^t \exp\left(-\frac{E_{\text{ind}}}{R\theta(x,\tau)}\right)d\tau - T_{\text{ind}}. \quad (13)$$

Equations (1)–(8) are written in the form:

$$C(\theta)\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial x}\left(\lambda(\theta)\frac{\partial\theta}{\partial x}\right)+\rho Q\frac{\partial\alpha}{\partial t} \quad (14)$$

$$\theta(0,t) = u_0(t) \quad (15)$$

$$\theta(L,t) = u_L(t) \quad (16)$$

$$\theta(x,0) = \theta_0(x) \quad (17)$$

$$\frac{\partial\alpha}{\partial t} = w(h(t,\theta))k_0\exp\left(-\frac{E}{R\theta}\right)g(\alpha) \quad (18)$$

$$\alpha(x,0) = 0. \quad (19)$$

4.1. *Criterion to be minimized*

The following deviation criterion is introduced:

$$J(g)=\int_0^T \sum_{j=1}^{m}(\theta(x_j,t;g)-\theta_j^*(t))^2\,dt. \quad (20)$$

Let $\theta(x_j, t; g)$ be the solution of equations (14) and (18) at the point x_j at time t for a given function g, and $\theta_j^*(t)$ be the temperature recorded at time t by sensor j; m is the number of sensors.

The criterion gradient is determined by introducing an adjoint state (see ref. [8] where the situation has been studied without an induction time and with coefficients C and λ constant).

4.2. *Calculation of gradient*

The variational formulation corresponding to the problem is first introduced, with the following notation:

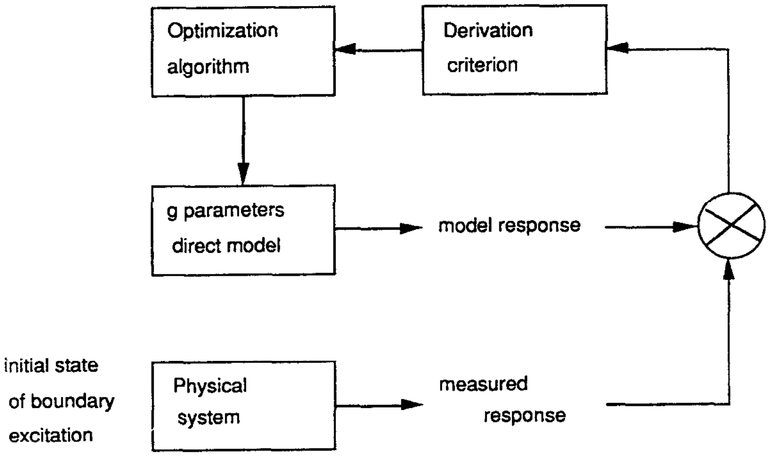

FIG. 2. Principle of parameter estimation.

$$k(\theta) = k_0 \exp\left(-\frac{E}{R\theta}\right)$$

and

$$F_g(\theta, \alpha) = w(h(t, \theta))k(\theta)g(\alpha).$$

The following space is introduced:

$$V = \left\{\varphi \in L^2(0, L), \frac{\partial \varphi}{\partial x} \in L^2(0, L), \varphi(0) = \varphi(L) = 0\right\}.$$

Taking $v \in V$, equation (14) is multiplied by v. After integration by parts and introduction of the Kirchhoff transform:

$$\beta(s) = \int_0^s \lambda(\sigma)\,\mathrm{d}\sigma$$

and the enthalpy transform:

$$\Gamma(s) = \int_0^s C(\sigma)\,\mathrm{d}\sigma,$$

we obtain the following variational formulation:

$$\left(\frac{\partial}{\partial t}\Gamma(\theta), v\right) + \left(\frac{\partial}{\partial x}\beta(\theta), \frac{\partial v}{\partial x}\right) = Q(F_g(\theta, \alpha), v) \quad \text{for all } v \in V \tag{21}$$

$$\theta(0, t) = u_0(t) \tag{22}$$

$$\theta(L, t) = u_L(t) \tag{23}$$

$$\theta(x, 0) = \theta_0(x) \tag{24}$$

where (,) is the inner product in $L^2(0, L)$, $Q = \rho Q_\infty$.

A Lagrangian dependent on the criterion to be minimized (20) and on variational equation (21) is introduced:

$$L(\theta, \alpha, p, q, g) = J(g) + \int_0^T \left\{\left(\frac{\partial}{\partial t}\Gamma(\theta), p\right) + \left(\frac{\partial}{\partial x}\beta(\theta), \frac{\partial p}{\partial x}\right) - Q(F_g(\theta, \alpha), p)\right\}\mathrm{d}t + \int_0^T \left\{\left(\frac{\partial \alpha}{\partial t}, q\right) - (F_g(\theta, \alpha), q)\right\}\mathrm{d}t,$$

where p and q are functions of x and t.

Criterion gradient (20) is calculated as follows multipliers p and q, which form the adjoint state:

(i) consider variables θ, α, p, q and g as independents,

(ii) calculate:

$$\frac{\partial L}{\partial \theta}(\theta(g), \alpha(g), p, q, g) \quad \text{and} \quad \frac{\partial L}{\partial \alpha}(\theta(g), \alpha(g), p, q, g)$$

where $\theta(g)$ and $\alpha(g)$ are solutions of (14)–(18), and solve the system:

$$\frac{\partial L}{\partial \theta}(\theta(g), \alpha(g), p, q, g)\delta\theta = 0 \quad \text{for all permissible } \delta\theta,$$

$$\frac{\partial L}{\partial \alpha}(\theta(g), \alpha(g), p, q, g)\delta\alpha = 0 \quad \text{for all permissible } \delta\alpha, \tag{25}$$

which provides $p(g)$ and $q(g)$,

(iii) write that:

$J'(g) = \frac{\partial L}{\partial g}(\theta(g), \alpha(g), p(g), q(g), g)$ when θ, α, p and q satisfy conditions (i) and (ii).

The effectiveness of this method has been shown in ref. [9] and used in refs. [10–12] for example.

After calculation, multiplier p is therefore the solution of the following equations:

$$C(\theta)\frac{\partial p}{\partial t} + \lambda(\theta)\frac{\partial^2 p}{\partial x^2} + g(\alpha)(w(h(t, \theta))k(\theta) + \frac{\partial h}{\partial \theta}(t, \theta)k(\theta) \otimes \delta_0)(Qp + q) = 2\sum_{j=1}^{m} [\theta(x_j, t) - \theta_j^*(t)] \otimes \delta(x - x_j) \tag{26}$$

$$p(0, t) = 0 \tag{27}$$

$$p(L, t) = 0 \tag{28}$$

$$p(x, T) = 0 \tag{29}$$

where the notation $\otimes\, \delta_0$ represents the generalized derivate of $w(h(t, \theta))$.

Multiplier q is the solution of the system:

$$\frac{\partial q}{\partial t} = -(Qp + q)w(h(t, \theta))k(\theta)g'(\alpha) \tag{30}$$

$$q(x, T) = 0. \tag{31}$$

Finally, the gradient is given by the formula:

$$J'(g) = -(Qp + q)w(h(t, \theta))k(\theta). \tag{32}$$

4.3. *Digital implementation*

Partial derivate equations (13)–(17) were made discrete using a P1 finite elements method in space and a Crank–Nicholson finite difference representation in time. Differential equation (18) was solved digitally by 2nd-order Runge–Kutta method. At this stage, there are two alternatives. Equations (26)–(28) and system (29), (30) can be made discrete to calculate gradient (25). The other method is to start from the discrete formulation of equations (14)–(19) and to introduce a discrete criterion and Lagrangian; all calculations are then made discretely until the gradient is obtained. This method has the advantage of not introducing approximations other than those appearing when the state equations are made discrete, unlike the first method. Details of the discrete calculations appear in refs. [11, 12].

Minimization is carried out using a quasi-Newton gradient method (BFGS's method) from the IMSL library [13].

5. EXPERIMENTAL SYSTEM

The experimental system was designed [5] to ensure unidimensional transfers in the sample in the measurement area.

5.1. *Description of samples, mould and moulding procedure*

The sample is parallelpiped with square cross-section and dimensions $0.150 \times 0.150 \times 0.039$ m. The length of 0.150 m is determined by the size of the press plates, and thickness $l = 0.039$ m fixed so that the measured temperature fields are not disturbed by the heat flows entering through the side faces of the sample and so that they correspond to unidirectional transfers. This was confirmed using a three-dimensional model.

The sample holder was designed to accommodate 9 K-type thermocouples with diameter 0.2 mm. They were carefully produced with butt welding of the wires. Figure 3 shows the sample holder, comprising a steel frame (1) which ensures the assembly is rigid. Teflon parts (2) reduce heat transfer through the side walls of the sample and facilitate mould stripping. A 1 mm-thick metal plate (3) forms the bottom of the cell.

The thermocouples are stretched along the isotherms and separated by approx. 4 mm. They are kept tight by a screw-nut fixing system (4), with a tensioning spring also housed in a teflon part (5).

Figure 4 presents the diagram of the moulding system produced on a press at VIBRACHOC. Vulcanization occurs at a temperature of about 150°C under 150 bar pressure. The upper chamber (transfer pot), in which a piston can move, is connected to the lower chamber, containing the sample holder, by injection orifices. The mould is pre-filled using bands of rubber placed around the thermocouples to minimize the risk of them moving during injection. When pressure is applied, rubber is transferred through injection nozzles placed symmetrically with respect to the sensor plane to balance pressure.

Curing time is approximately two hours due to temperature lag of the press and mould. Flat exchangers supplied by LAUDA K 20 thermostat-controlled baths and insulating plates between the mould and press were added for better control of heating cycles. An initial isothermal state is imposed at approximately 80°C after the sample is put under pressure.

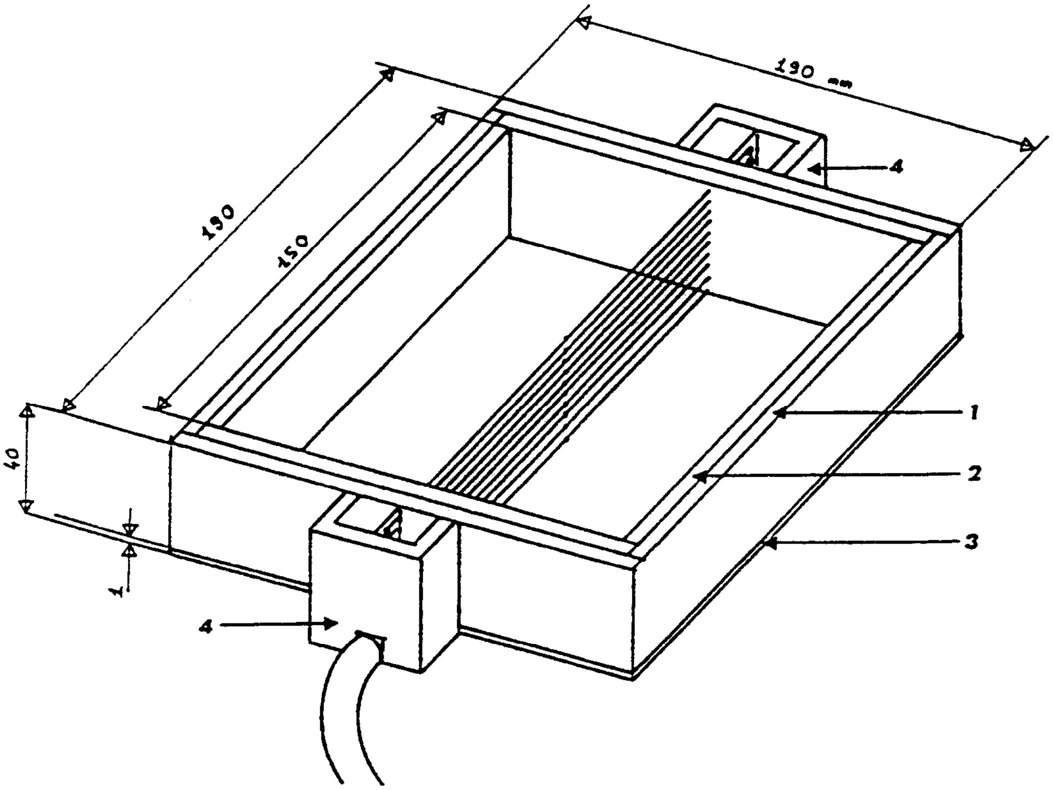

Fig. 3. Sample holder. 1—frame in steel, 2—frame in teflon, 3—metallic sheet (1 mm), 4—two devices of thermocouples fixation.

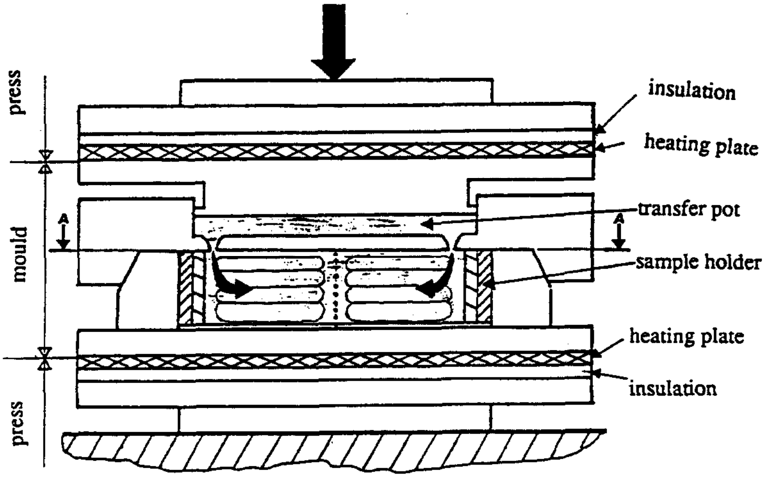

FIG. 4. Moulding apparatus.

5.2. *Experimental temperature fields during vulcanization*

Temperatures were acquired during the whole curing cycle on several samples fitted with instruments. The data acquisition system controlled by an HP 85 microcomputer comprises a Keithley 705 channel scanner and a Keithley 295 A voltmeter with 100 nV resolution. The data acquisition frequency is about 30 s.

Figure 5 shows the development of the temperature represented by the thermocouples. It is noted that for times of less than 5000 s, these profiles do not differ from conventional conduction profiles. However, for times of 5000–7000 s, the effects of the reaction are noticed, with accelerated core heating even as far as gradient inversion.

6. IDENTIFICATION RESULTS

The experimental fields were used as data for the identification algorithm. The two end thermocouples were taken as boundary conditions and the criterion calculated from the measurements of the seven inside thermocouples. Cubic spline interpolation was used to calculate the temperatures of the different sensors at the same times (they are slightly time-shifted due to the scanning). The calculation time step was fixed at 30 s. The product $k_0 g(\alpha)$ was identified at six points. The initial value chosen is $k_0 g(\alpha) = 1 \times 10^7\,\mathrm{s}^{-1}$. The value $g(1) = 0$ is imposed. Forty-four iterations show a convergence towards the values of Fig. 6.

This result was obtained with a mean square deviation of 0.21 K. A remarkable result is convergence towards a $g(\alpha)$ function such that $g(0) \simeq 0$. This implies that a kinetics model where the reaction velocity is non-zero at the start of the process is inappropriate.

Figures 7(a)–(g) show the excellent agreement obtained throughout the process. However, a slight deviation is noticed at the end of curing; it may be due to the fact that variation of C with the degree of reticulation α is not considered. As for the conduc-

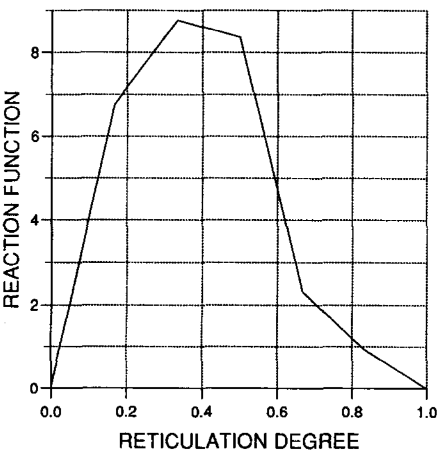

FIG. 5. Temperature as a function of time, given by nine thermocouples.

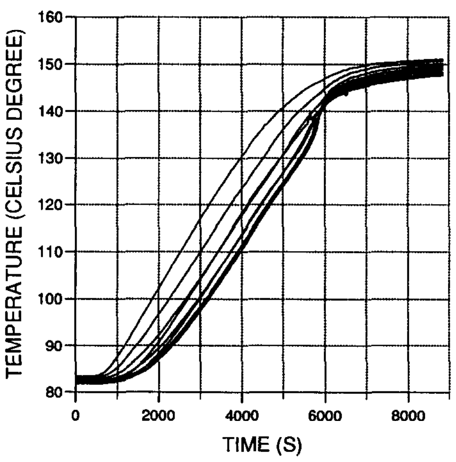

FIG. 6. Kinetic function $g(a)$ obtained by parameter estimation.

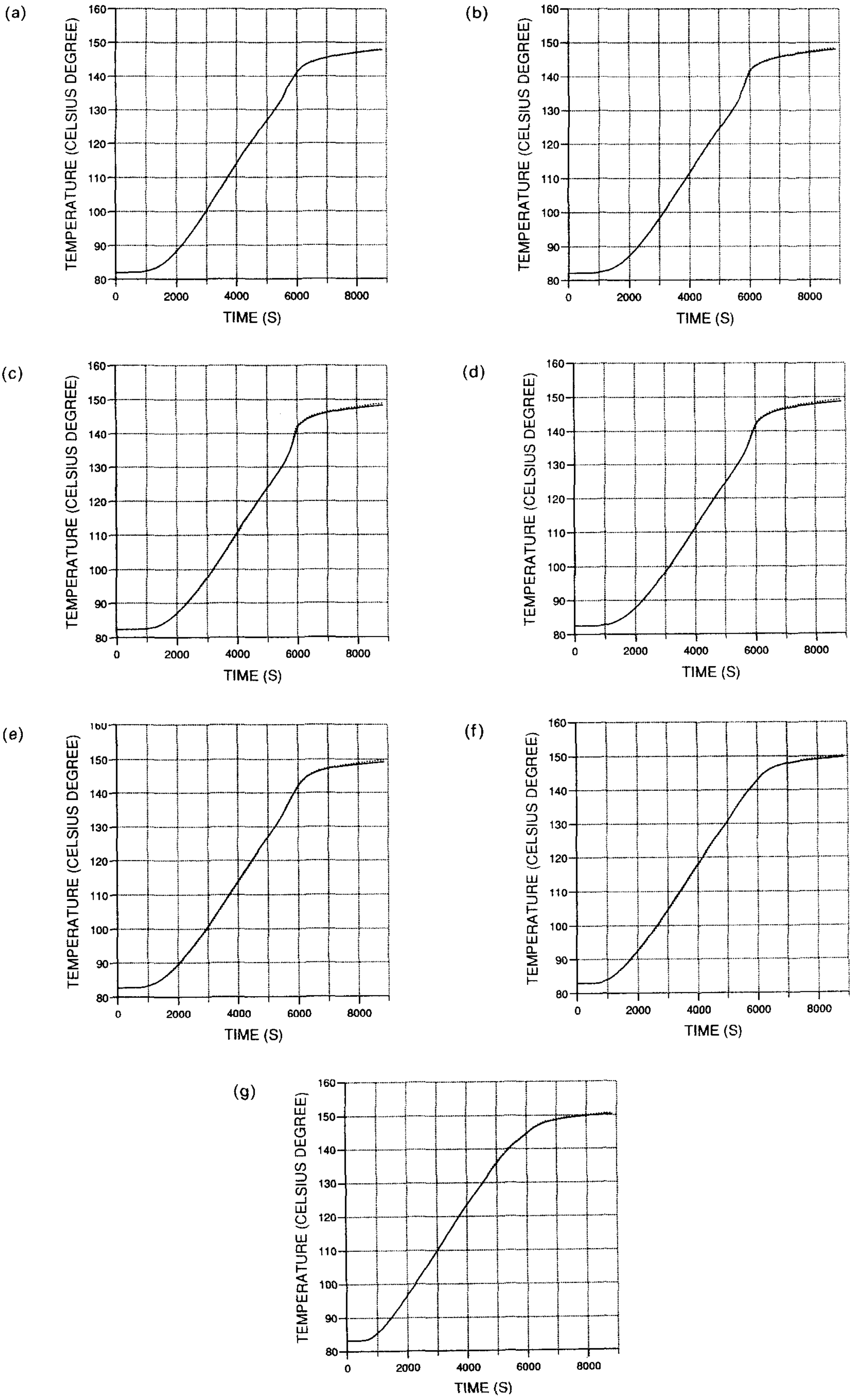

Fig. 7. (a)–(g) Comparison of calculated and measured temperatures for thermocouples 2–8: solid line = calculated temperature; dotted line = experimental temperature.

tivity, it depends very little on the latter, which may be explained considering the small number of molecules concerned by curing (a few percent in natural rubber).

7. CONCLUSION

In this study, the feasibility of an inverse method for identifying the reticulation kinetics of an elastomer from temperature readings has been demonstrated. We deliberately chose a kinetics expression which did not particularize the influence of α in the $g(\alpha)$ function. This function was defined by points. The only a priori assumption on the form of the kinetics was factorization of temperature dependence. The form of kinetics obtained is, however, comparable to that obtained by other methods [6]. An interesting result is the value obtained for $\alpha = 0$. It is noted that the value $g(0)$ identified is very close to zero. This indicates that at the start of the reaction $\mathrm{d}\alpha/\mathrm{d}t \simeq 0$. The $g(\alpha)$ curve shows a maximum.

Another important value is the reactivity k_0, also identified ($5 \times 10^6\ \mathrm{s}^{-1}$) and consistent with the calorimetric measurements. The use of this type of method therefore appears a promising approach to construction of new kinetics characterization equipment, when methods are available to allow it to be used without sensors in the core of the material.

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