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MODELLING OF VARIATION IN PROPERTIES OF SILICONE SHEET DURING PYROLYSIS WITH HEATING–COOLING CYCLES

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ABSTRACT

A model is described which takes into account heat transfer by convection through an air–rubber sheet interface and conduction through the rubber, as well as the variation of mechanical properties as a function of time and temperature. It is able to predict the decrease in mechanical properties during successive heating–cooling cycles for a silicone rubber sheet. Mechanical properties in elongation (modulus, ultimate tensile strength, elongation at break) have been previously determined as a function of time under isothermal conditions at various temperatures. This model is effective for pyrolysis of silicone rubber conducted at temperatures lower than 350°C.

INTRODUCTION

There are so many uses of interest for silicone rubber that the published literature may not cover them all [1]. Silicone rubber has been used as coatings for protection against weathering, solvents, chemicals and aerospace environments [2]. Silicone elastomers find applications as flame-resistant materials because of their better resistance to ignition [3], low-toxicity smoke and combustibility compared with other materials [4].

Silicone rubbers are very often used in electrical applications, especially for insulating electric heating wires. The ideal insulating material should have sufficient mechanical strength and flexibility, the ability to resist moisture and high temperatures, and good heat conductivity. The high flexibility of silicone rubbers makes them ideal for insulating electric wires used for heating, especially when these are used as sheathed cables wound around the material to be heated [5]. In this last case it is of interest to study the behavior of the rubber silicone used for insulation, when heated under various conditions and especially when heating–cooling cycles are used. Experiments may be time-consuming and modeling of the process to allow mathematical simulations is required.

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Our objective in this paper has been to determine the decrease in mechanical properties of silicone rubber sheets when submitted to heating–cooling cycles. The heating rate of rubber was rather high (35°C min^{-1}), heat being transferred from air to the face of the rubber by forced convection. The cooling period of the rubber was obtained by exposing the rubber for a definite time to air at room temperature, heat being transferred from the rubber face to air by free convection. The model set up for heating–cooling cycles is able to improve these studies by reducing time-consuming experiments. The model [6–8] takes into account heat transferred through the air–sheet interface by convection and through the rubber sheet by conduction, and the kinetics are followed by the variation in mechanical properties. An explicit method with finite differences has been used for the numerical analysis. Kinetics for the variation in mechanical properties have been established previously by pyrolysing several samples under isothermal conditions.

THEORETICAL

Silicone rubber sheets were subjected to successive cycles of heating and cooling. Heating of the rubber was obtained through air at a constant heating rate (35°C min^{-1}) by forced convection inside an oven; the cooling period was obtained by extracting the rubber sheets from the oven and placing them in air at room temperature for a definite time.

Several assumptions are made: (i) heat flow is conducted by convection through the air–rubber interface; (ii) heat is transferred through the rubber by conduction. The thermal properties of silicone rubber are considered as constant during the heat treatment; (iii) the variation of mechanical properties as a function of temperature and time was obtained previously by studying under isothermal conditions.

Heating period

Heat transfer by convection on rubber faces

Since heat was transferred by convection, we can use either the dimensionless Prandtl, Grasshof and Nusselt module to obtain the coefficient of heat transfer through the air–sheet interface, or the value of the coefficient of heat transfer calculated from experiment [6]. We have used the value of the coefficient of heat transfer obtained from experiment, by measuring the temperature on the face and at the midplane of rubber sheets.

Heat transfer by conduction through the sheet

The heat flow can be considered as unidirectional along the thickness of

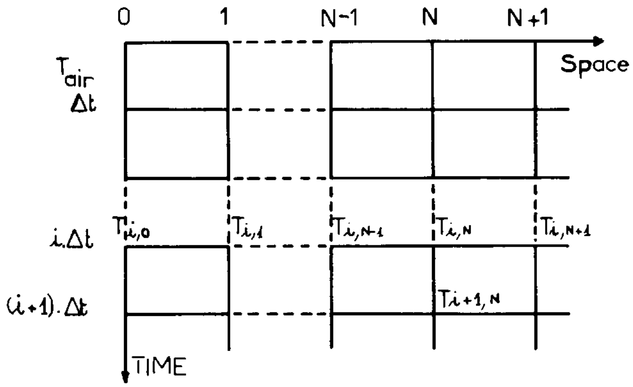

Fig. 1. Space–time diagram for temperatures in rubber sheets in contact with air.

the sheet since this dimension is much smaller than the other dimensions. Thus the increase in temperature follows the classical equation

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \tag{1}$$

where α, the thermal diffusivity of silicone rubber, is assumed to be temperature independent. Equation 1 cannot be solved by a mathematical treatment only, because of the boundary conditions with the heating on rubber faces by convection.

Consider the sheet of thickness L as divided into a number of equal slices of thickness Δx by temperature-reference planes [9,10] (Fig. 1). Then the heat balance inside the sheet is calculated as

$$T_{i+1,n} = \frac{1}{M}\left[T_{i,n-1} + (M-2)T_{i,n} + T_{i,n+1}\right] \tag{2}$$

where $T_{i+1,n}$ is the temperature obtained at the slice n and at the time $(i+1)\Delta t$. The dimensionless number M is given as a function of increments of space Δx and time Δt. As the diffusivity is assumed to be constant for the silicone rubber during heat treatment, the coefficient M is also constant. The best value for this coefficient is between 3 and 7.

For both faces of the rubber sheet, it is necessary to take into account heat transfer by convection through the air–rubber interface and heat transfer by conduction through the slices next to the faces. The dimensionless Nusselt number corresponds to the heat transfer by convection on both rubber faces. The following equation was used

$$T_{i+1,0} = \frac{1}{M}\left[NT_{i,\mathrm{air}} + (M-1-N)T_{i,0} + T_{i,1}\right] \tag{3}$$

where $T_{i+1,0}$ is the temperature on the rubber faces at time $(i+1)\Delta t$. The

Nusselt number N is a function of the coefficient of heat transfer on the rubber faces and rubber conductivity λ

$$N = \frac{h\Delta x}{\lambda} \tag{4}$$

Cooling period

As air was kept motionless during the cooling period, heat transfer from rubber to air was obtained by natural convection. It is simple to calculate the value of the coefficient of heat transfer in this case as a function of dimensionless numbers such as the Prandtl–Grasshof–Nusselt module.

The free convection is conducted in a laminar range, because of the low value of the Grasshof number

$$G_R P_R = 9.52 \times 10^5 \tag{5}$$

and the Nusselt number is given as follows

$$N_u = a(G_R P_R)^{0.25} \tag{6}$$

where the value of the coefficient a depends on the position of the rubber sheet. In the case of a vertical plane $a = 0.56$.

Equation (2) may also be used for the cooling period in the same way as for the heating period, when the inside of the rubber sheet is considered. The following equation is used for the rubber face

$$T_{i+1,0} = \frac{1}{M}\left[T_{i,1} + (M - 1 - N')T_{i,0} + N'T_{\text{air}}\right] \tag{7}$$

where $T_{i,0}$ is the temperature on the rubber at time $i\Delta t$; T_{air} is the temperature of air; $T_{i,1}$ is the temperature at the first slice of the rubber. Although the modulus N' resembles the modulus N shown for the heating period, it has a different value

$$N' = \frac{h'\Delta x}{\lambda} \tag{8}$$

where h' is the coefficient of heat transfer during the cooling period, obtained from the Nusselt number. λ is the thermal conductivity of rubber.

EXPERIMENTAL

Material

Samples (H3) cut in silicone sheets of 1 mm thickness were used. The composition (weight per cent) was: 51% methylsilicone rubber; 45% glassy silica; 4% non-volatile additives.

Heat treatment

Thermal treatment was conducted under isothermal conditions for determining the variation in mechanical properties of rubber with temperature, and with heating–cooling cycles. During the heating period of every cycle, rubber sheets were placed at the inside of a cylindrical oven. The cooling period was obtained by extracting rubber sheets from the oven and placing them vertically in motionless air at room temperature.

Temperatures on the face and at the midplane of a rubber sheet were registered during a heating–cooling cycle, to obtain the coefficient of heat transfer through the air–rubber interface for the heating and cooling period.

The rubber samples were extracted from the oven at various times, cooled in water, and tested to determine their mechanical properties.

Measurement of mechanical properties

Rubber samples were tested using standard tests in elongation with a dynamometer (Adamel Lhogmargy DY14). Ultimate tensile strength (ASTM 412), modulus and elongation at break was determined.

Calculation by using the model

Temperature and mechanical properties were calculated as a function of time by using the model described above. Parameters used are listed in Table 1.

RESULTS

Variation in mechanical properties of silicone as a function of isothermal heating treatment

Experiments were carried out under isothermal conditions, at various temperatures. Three samples were tested in each case and the results averaged. The increase in static modulus in elongation (E) as a function of

TABLE 1

Parameters for simulation

Heating: $M = 4$, $\Delta x = 0.02$ cm, $N = 0.083$, $h = 2.8 \times 10^{-3}$ cal cm^{-2} deg^{-1}
Cooling: $M = 4$, $\Delta x = 0.02$ cm, $N' = 0.02$, $h' = 6.9 \times 10^{-4}$ cal cm^{-2} deg^{-1}
$\lambda = 7 \times 10^{-4}$ cal cm^{-1} deg^{-1} s^{-1}, $\alpha = 1.47 \times 10^{-3}$ cm^2 s^{-1}
Number of slices = 5

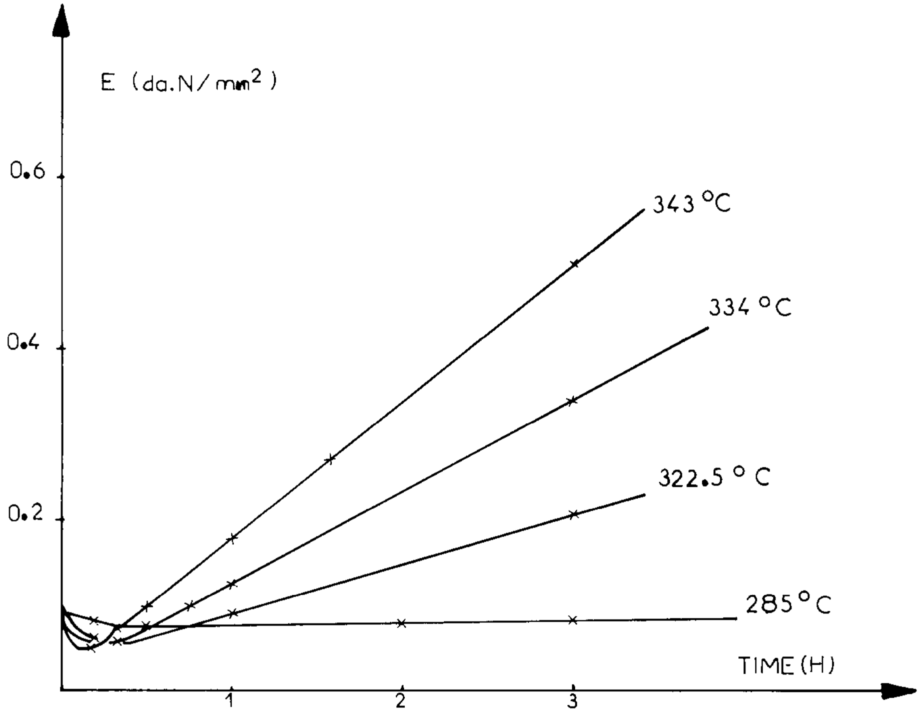

Fig. 2. Modulus in tension (dN mm^{-2}) as a function of temperature and time, obtained under isothermal conditions.

temperature and time is shown in Fig. 2. As previously explained, the decrease in the value of the modulus is due to chain-shortening making the rubber more plastic. The variation of the ultimate tensile strength (UTS) of silicone rubber with heating treatment is illustrated in Fig. 3. Pyrolysis under isothermal conditions produced a decrease in elongation at break for silicone rubber samples (Fig. 4).

The variation in mechanical properties of silicone rubber samples as a function of temperature and time has been evaluated from experimental values and expressed by the following equations (Table 2).

Modeling of the pyrolysis

The model described was used for calculating the profiles of temperature developed through the sheet of silicone rubber during heating and cooling periods. Measurement of temperature was performed at the midplane of the rubber sheets. Experimental and calculated temperature at midplane–time curves agree very well over the whole cycle (Fig. 5), providing the accuracy of the model.

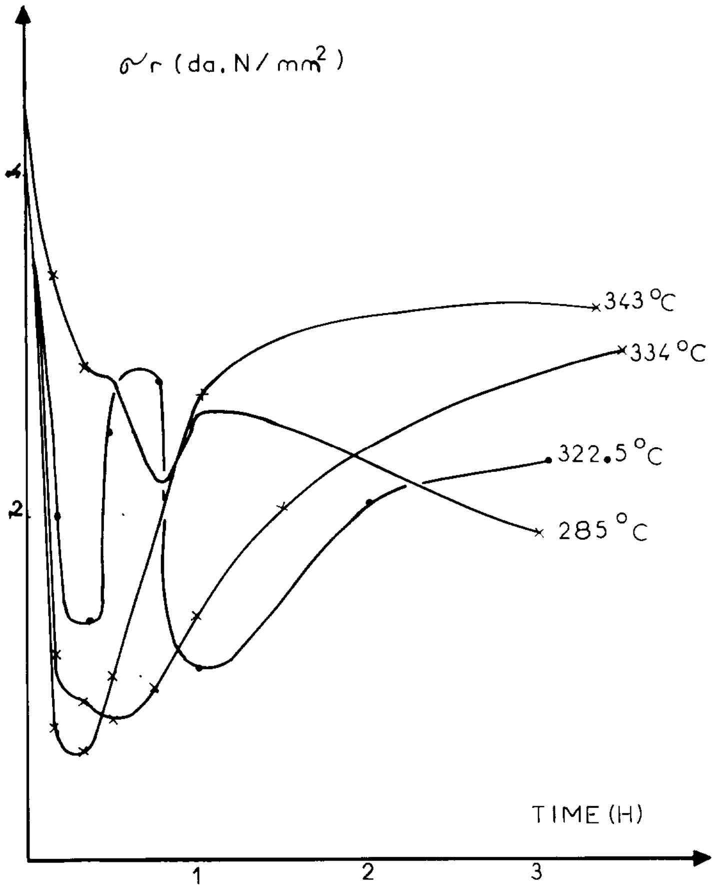

Fig. 3. Ultimate tensile strength (dN mm^{-2}) as a function of temperature and time, obtained under isothermal conditions.

This model may also be used for various successive heating–cooling cycles. This is an advantage since these tests are highly time-consuming. However, great care must be taken in calculating the variation in mechanical properties of silicone rubber. Conditions used in pyrolysis cycles (temperature and time) must not be more severe than those used in isothermal experiments.

Calculation of mechanical properties

Some of the mechanical properties of silicone rubber sheets were calculated during the heating–cooling cycle, and measured at the end of the cycle. Results are shown in Fig. 6 (for one cycle) for mechanical properties in tension: the modulus, ultimate tensile strength and elongation at break. As previously reported [5] a decrease in these mechanical properties can be

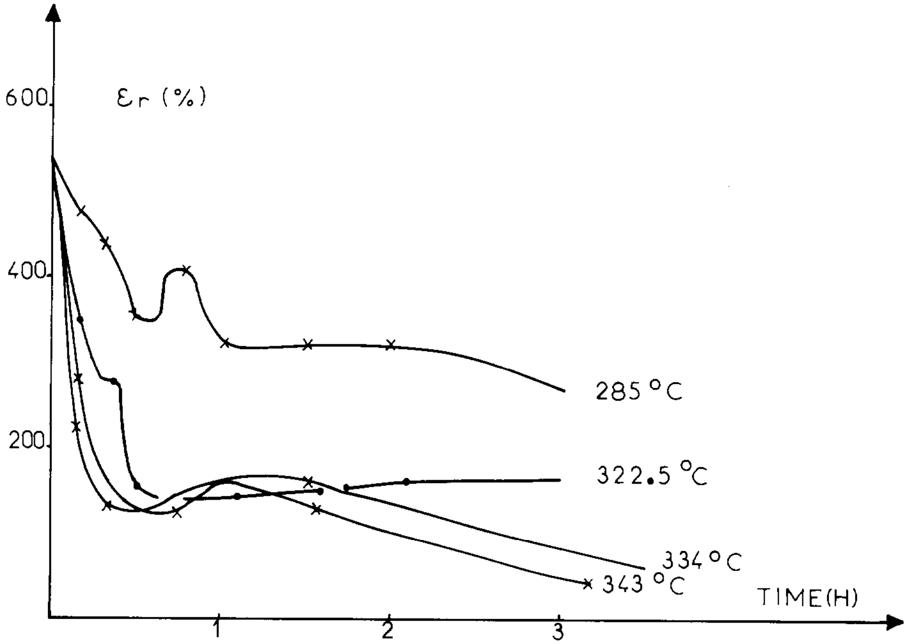

Fig. 4. Elongation at break (%) as a function of temperature and time, obtained under isothermal conditions.

TABLE 2

Mechanical properties vs. temperature and time under isothermal conditions

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Modulus

$E = E_0 + At + B \exp - (Ht)$

Ultimate tensile strength

$\sigma_r = \sigma_{r\infty} + C \exp(-k_c t) - D \exp(-k_D t)$

Elongation at break

$\epsilon_r = (\sigma_r / E + R)/S$

where A, B, C, D, H, R, S, k_c and k_D are coefficients determined from experiment.
Modulus

$E_0 = 8.16 \times 10^{-6} \times \exp(4986.5/T)$

$A = 9.7 \times 10^{11} \times \exp(-18240/T)$

$B = 0.0903 - E_0$

$H = 338(T-273)^{0.2} - 1044$

UTS $\sigma_{r\infty} = 0.4531 - 0.3912/0.4531[(0.3912 - X - D \times t)]$

For $T < 322.5°\text{C}$	For $T > 322.5°\text{C}$
$C = 71851 \times \exp(-6945.3/T)$	$C = 1.22 \times \exp(-402/T)$
$k_c = 0.1109 \times \exp(1607/T)$	$k_c = 353.9 \times \exp(-2027/T)$
$k_D = 1.74 \times 10^{10} \times \exp(-14765/T)$	$k_D = 1.81 \times 10^{10} \times \exp(-14148/T)$
$X = 3035/T - 4.85$	$X = 292.6/T - 0.297$
$D = 0.4535 - 262.7/T$	$D = 1.73 \times 10^{-3} - 1.54/T$

Elongation

$\epsilon_r = ((\sigma_r / E + 0.9831)/0.9215 - 1)100$

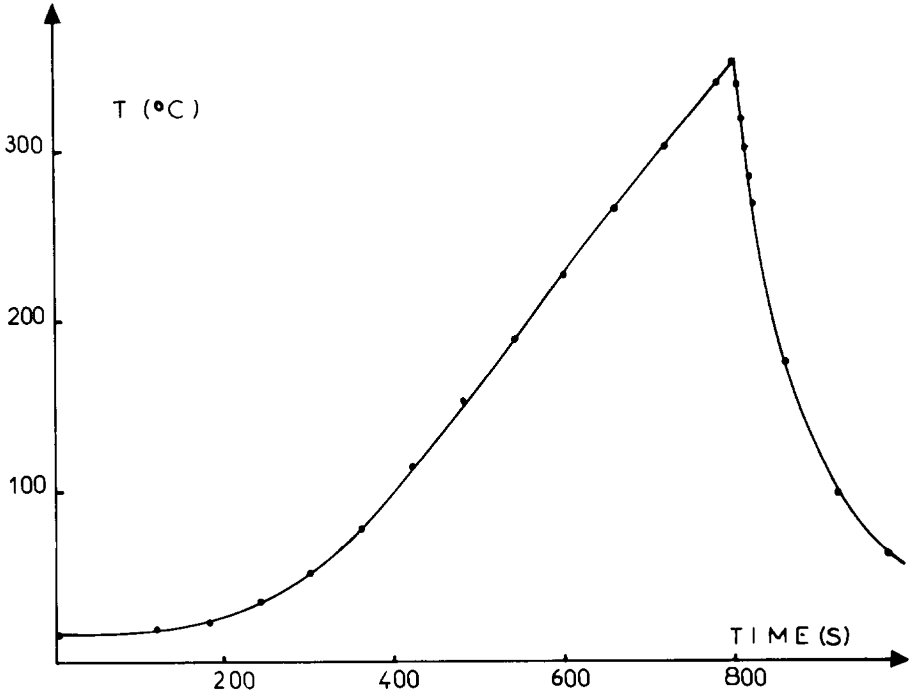

Fig. 5. Temperature at the midplane of a rubber sheet as a function of time. (———) Calculated, (●) experiment.

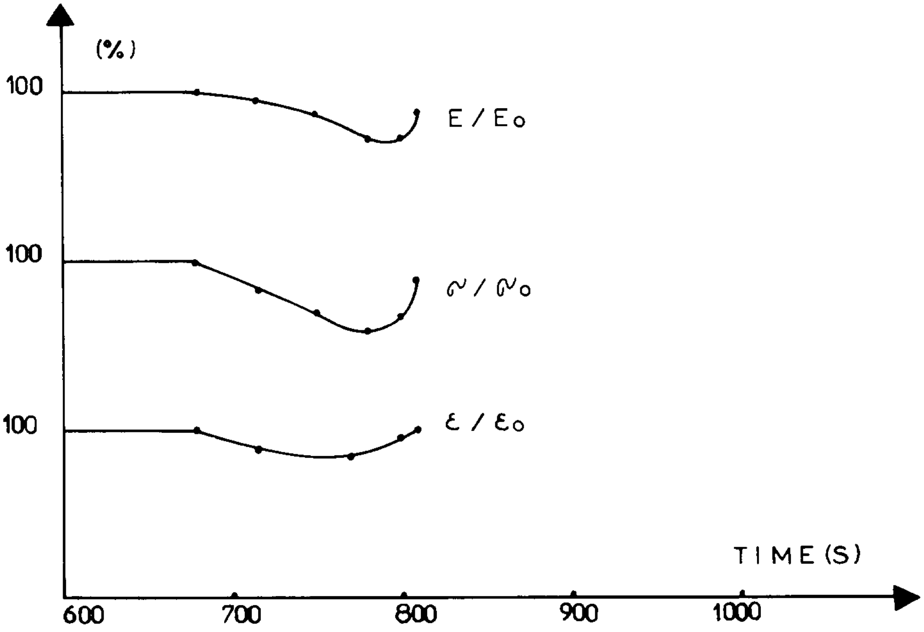

Fig. 6. Variation of mechanical properties of rubber sheets as a function of time during one heating–cooling cycle.

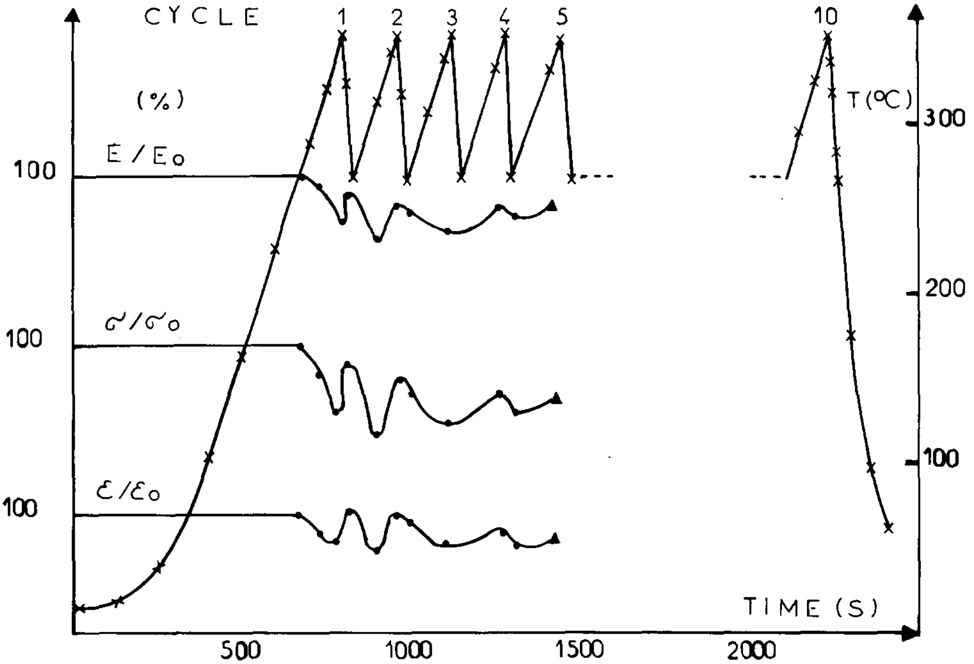

Fig. 7. Variation of mechanical properties for a rubber sheet as a function of time during five heating–cooling cycles in succession.

observed during the heating period. During the cooling period, an increase in these properties can be demonstrated.

Variations in these mechanical properties are clearly shown as a function of time in Fig. 7. The mechanical properties of the final material were measured at the end of five heating–cooling cycles in succession. Calculated and experimental results are in good agreement, proving the validity of the model.

CONCLUSIONS

Experiments for determining the variation of mechanical properties of a material during heating are highly time-consuming, especially if heat treatment when not severe corresponds to heat-aging treatment. Simulation is of interest for this problem, modeling and computerization is helpful. A model described in this paper simultaneously takes into account heat transfer and variation in mechanical properties. Heat is transferred by convection through the air–silicone sheet interface and by conduction through the rubber silicone sheet. Successive heating–cooling cycles were used, allowing the model to give mechanical properties of the material under heating conditions.

These results and the model are of interest in determining the capability of materials at work under heating and stress conditions. Unlike mechanical tests, this method does not destroy material samples.

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