MODEL FOR PREDICTING MECHANICAL PROPERTIES OF SILICONE SHEET DURING PYROLYSIS WITH CONSTANT HEATING RATE

A. HADJOUDJ, J.C. DAVID and J.M. VERGNAUD

Laboratory of Materials and Chemical Engineering, U.E.R. of Sciences, 23 Dr. P. Michelon, University of St-Etienne, Saint-Etienne 42100 (France)

(Received 2 July 1985)

ABSTRACT

Experiments for measuring the variation of mechanical properties of materials as a function of temperature and time during pyrolysis are highly time-consuming. Moreover, these measurements are destructive, and cannot be made for materials pyrolysed in real conditions. In order to predict the values of mechanical properties in tension (modulus, ultimate tensile strength and elongation at break) during pyrolysis, a model has been described. The model takes into account not only heat transferred through the heated phase–material interface by convection and through the material by conduction, but also the laws describing the variation of material properties as they have been obtained under isothermal conditions. Calculated results have been found to be in good agreement with experiments, in the case of silicone rubber sheets. The use of the model can be extended to other applications, as far as pyrolysis is concerned.

INTRODUCTION

The uses for silicone rubber are numerous and, in a number of cases, unique because of a particular property of silicone rubber. The published literature may not cover all of the uses to which these special rubbers have been put [1].

A variety of aerospace uses have been found for silicone rubbers [2]. Uses in aerospace depend upon the stability of silicone rubber under extreme environmental conditions. A major and developing field has been that of automotive uses [3]. A review of the increasing use of silicone rubber in automotive applications has shown a doubling of use in six years [4].

Silicone rubber has been used as coatings for protection against weathering, solvents, chemicals and aerospace environments [5]. The sound-damping effect of these coatings was studied and shown to be dependent on filler content, temperature and film thickness [6]. Silicone elastomers find applications as flame-resistant materials because of their better resistance to ignition [7], lower combustibility and low-toxicity smoke compared with other materials [8].

A great many studies have concentrated on understanding and improving the heat-aging characteristics of silicone rubber [1,9]. The assessment of irreversible changes was studied by aging samples at a specified temperature and evaluating mechanical properties at intermittent intervals at room temperature. These studies are of interest for industrial applications, because in everyday life some silicone rubber sheets may be used several times in succession as a fire-retardant coating if the fire is put out in a short time. Some knowledge is needed in this case, not specifically on the pyrolysis of the material with subsequent loss in weight and chemical degradation, but on the variation in mechanical properties of this material, reversible or not.

Our objective in this paper is essentially concerned with the determination of the kinetics of the decrease in mechanical properties of silicone rubber sheets while submitted to heat either under isothermal conditions or with a programmed temperature. In order to enhance these studies in reducing time-consuming experiments, a model has been set up allowing pyrolysis simulations in various applications. This model has been verified in the case of a rather high rate of heating ($35°C$ min^{-1}) while heat is transferred from air to the face of the rubber sheet by convection. Based on a numerical method with finite differences, the model [10–12] takes into account not only heat transferred through the air–sheet interface by convection and through the rubber sheet by conduction, but also the kinetics of the variation in mechanical properties obtained as a function of time and temperature. These kinetics for the variation in mechanical properties have been determined beforehand by pyrolysing several samples under isothermal conditions at various times.

THEORY

The silicone rubber sheet has been subjected to heat treatment through air at a constant heating rate. The following assumptions are considered.

(i) Heat flow is conducted as convection heat from the air to the coating face. The convection is free, because there is no air flow.

(ii) Heat is transferred by conduction through the coating. Thermal properties are assumed to be constant for the silicone sheet while heating and pyrolysis (or rather the beginning of pyrolysis, since there is only a slight weight loss due to plasticizer) are taking place.

(iii) Mechanical properties are following the laws obtained previously under isothermal conditions for short times.

Heat transfer by free convection

Heat transfer by free convection can be studied by using dimensionless numbers, Prandtl and Grashof moduli, giving therefore the value of Nusselt's

number and the coefficient of heat transfer through the air–sheet interface [11].

In this work, we preferred to obtain the coefficient of heat transfer from measurements of temperature in two parts of the sheet: on the face and at the midplane.

Heat transfer through the sheet by convection

As the heat flow is unidirectional along the sheet thickness, the temperature increase, in any place taken in the sheet follows the well-known equation

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

where α is the thermal diffusivity of silicone rubber.

Numerical analysis

It the sheet of thickness L is divided into a number of equal finite slices of thickness Δx by temperature-reference planes, a heat balance calculated inside the sheet gives

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

where $T_{i+1,n}$ is the temperature at time $(i+1)\,\Delta t$ and at the slice n.

The dimensionless number M is equal to

$$M = \frac{(\Delta x)^2}{\Delta t} \frac{I}{\alpha} \tag{3}$$

as a function of increments of space Δx and time Δt.

For both faces of the rubber sheet, the following equation

$$T_{i+1,0} = \frac{1}{M} \left[N T_{i,\text{air}} + (M-1-N) T_{i,0} + T_{i,1} \right] \tag{4}$$

takes into account heat transfer by convection with Nusselt's number N and heat transfer by conduction through the slices next to the faces. $T_{i+1,0}$ is the temperature on the face at time $(i+1)\,\Delta t$, and N is obtained by

$$N = \frac{h \Delta x}{\lambda} \tag{5}$$

where h is the coefficient of heat transfer through the air–rubber interface by convection and λ is the thermal conductivity of the rubber.

Calculation of mechanical properties

The following mechanical properties of the rubber sheet have been determined by considering the elongation: the modulus E, ultimate tensile

strength τ_r and elongation at break ϵ. Some equations have been obtained as a function of time and temperature from experiments conducted under isothermal conditions.

Modulus

$$E = E_0 + A\,t + B\,\exp\,-(Ht) \qquad (6)$$

Ultimate tensile strength

$$\tau_r = \tau_{r\infty} + C\,\exp(-k_c t) - D\,\exp(-k_D t) \qquad (7)$$

Elongation at break

$$\epsilon_r = (\tau_r/E + R)/S \qquad (8)$$

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

EXPERIMENTAL

Material

Silicone sheets of 1 mm thickness have been used. The overall composition (in weight) is: 51% methylsilicone rubber; 45% glassy silica; and 4% non-volatile additives.

Heat treatment

Experiments for heat treatment of rubber samples (H3) have been made by using a cylindrical oven of diameter 4 cm and length 50 cm (Thermolyne Furnace, Sybron Thermolyne).

Thermal treatments are conducted either under isothermal conditions or in a scanning mode.

Temperatures on the face of a rubber sheet and at the midplane have been registered during heating in transient conditions ($37.5°C\ s^{-1}$) in order to obtain experimentally the coefficient of heat transfer for convection through the air–rubber interface.

The samples are extracted from the oven at various times and cooled down in water.

Measurement of properties

Standard tests in elongation have been performed on the samples: ultimate tensile strength (ASTM 412); elongation stress–strain properties (BS 903 A4) with the modulus and elongation at break, by using a dynamometer (Adamel Lhomargy DY 14).

Calculation

Calculations of temperature and mechanical properties have been obtained as a function of time by using a microcomputer (Micral-R2E) and the following values for parameters: $M = 4$, $N = 0.083$, $\Delta x = 0.02$ cm, number of slices $= 5$, $\alpha = 1.47 \times 10^{-3}$ cm^2 s^{-1}, $h = 2.77 \times 10^{-3}$ cal s^{-1} cm^{-2} deg^{-1}, $\lambda = 7 \times 10^{-4}$ cal s^{-1} cm^{-1} deg^{-1}.

RESULTS

Determination of mechanical properties of silicone sheets as a function of temperature and time

Standard dumb-bell samples have been used for determining the variation of their mechanical properties as a function of temperature and time of pyrolysis. Test pieces have been heated and taken out of the oven at definite times for evaluation. For the purpose of this work, we have evaluated some strain and stress properties in tension. Three samples have been tested in each case and the results averaged.

The variation of static modulus as a function of temperature and time of pyrolysis is illustrated in Fig. 1. Two results are of interest.
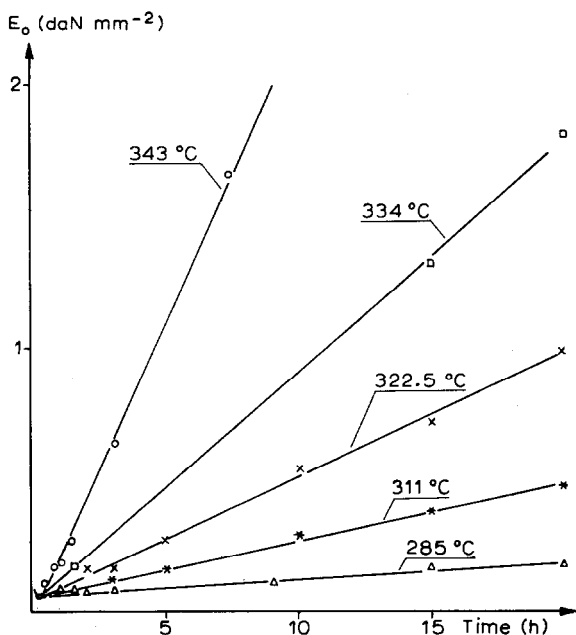

Fig. 1. Variation of static modulus in tension (dN mm^{-2}) as a function of temperature and time, as obtained under isothermal conditions.
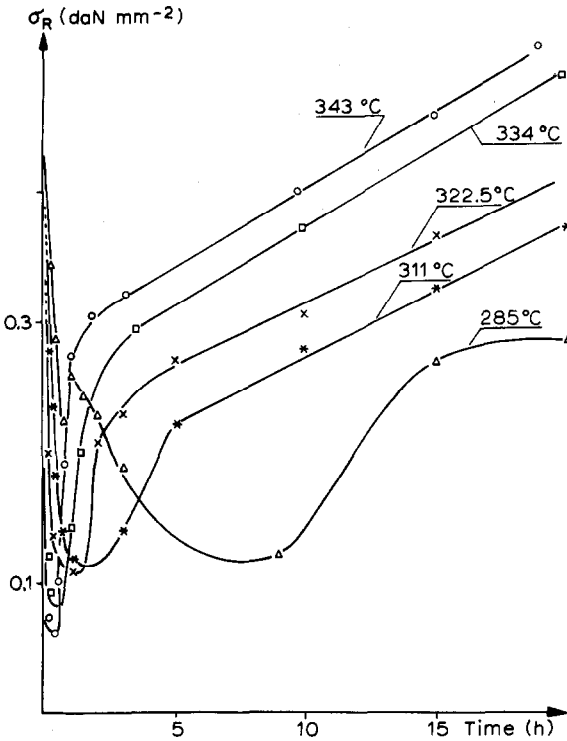
Fig. 2. Variation of ultimate tensile strength (dN mm^{-2}) as a function of temperature and time, obtained under isothermal conditions.

(i) No appreciable variation can be seen for the modulus in tension when the temperature is lower than 322°C.

(ii) For temperatures higher than 334°C, a decrease in the modulus can be seen at the beginning of pyrolysis (times < 15 min) followed by an increase proportional to the time.

This surprising decrease in the value of the modulus may be due to a chain-shortening making shorter chains more plastic.

Figure 2 illustrates the variation of ultimate tensile strength (UTS) of silicone rubber sheets during the pyrolysis. In the same way as for the modulus, a decrease in the UTS is shown at the beginning of pyrolysis, followed by an increase in UTS. This increase in UTS may result from a reticulation of silicone chains.

As shown in Fig. 3, pyrolysis under isothermal conditions is responsible for a decrease in elongation at break for the samples. The higher the temperature, the lower the value of elongation at break. However, the result is slightly complicated for short times, especially < 5 h.

Coefficients of eqns. (6)–(8) have been calculated from these experimental data, as shown in Table 1.
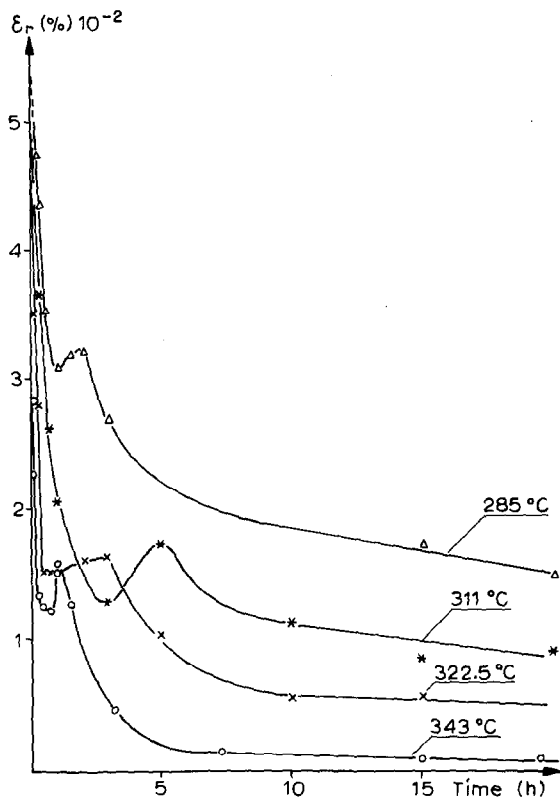
Fig. 3. Variation of elongation (%) at break as a function of temperature and time, obtained under isothermal conditions.

TABLE 1

Coefficients for variation of mechanical properties

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	$\tau_{r\infty} = 0.4531 - \dfrac{0.3912}{0.4531}[(0.3912 - X - D \times t)]$

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

Elongation

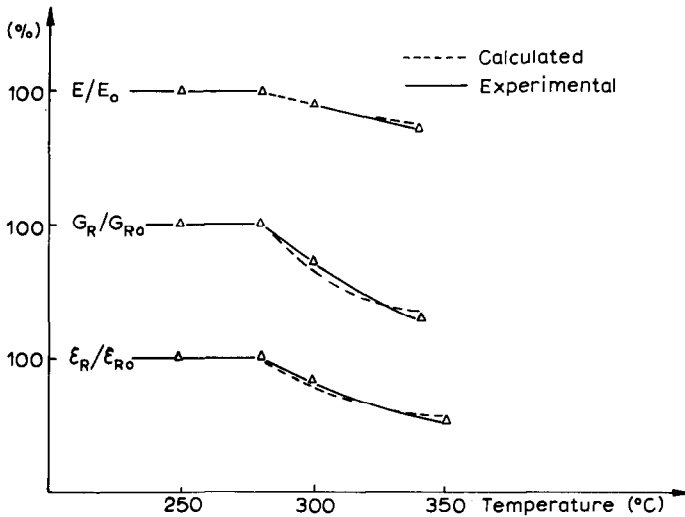$$\epsilon_r = \left(\frac{\tau_r/E + 0.9831}{0.9215} - 1 \right) 100$$

Fig. 4. Variation of mechanical properties during a pyrolysis cycle with a constant heating rate of 37.5°C min^{-1}: ------, calculated; ———, experimental.

Prediction by calculation of the variation of mechanical properties during pyrolysis

The model described above has been used for calculating the mechanical properties in tension for the material during pyrolysis at a constant rate of heating (37.4°C min^{-1}). As Fig. 4 bears out, calculated and experimental curves are very well superposed during the pyrolysis cycle, proving the validity of the model.

Of course, this model is available for different pyrolysis cycles with various rates of heating. It can be used with great interest for repetitive cycles, because these kinds of tests are highly time-consuming.

For pyrolysis cycles of higher severity (higher temperature and longer times), the model can be of help for predicting the conditions (time and temperature) at which the material must be considered as destroyed. Of course, in this case, other equations obtained from experimental data under isothermal conditions must be used for determining the mechanical properties of the material as a function of temperature and time.

CONCLUSIONS

Because of the lack of methods able to predict variation of mechanical properties of materials during the pyrolysis, experiments are highly time-consuming for heat-aging studies. The model elaborated in this paper takes into account not only heat transferred by conduction through the material and

through a heated air–material interface, but also the laws describing the variation of mechanical properties as a function of temperature and time. The calculated results obtained in the case of a constant heating rate are in good agreement with experiments, proving the validity of this model.

The model could be used in other various cases of heating and test conditions, e.g., with various thicknesses of the material. The variation of properties must have been previously determined under isothermal conditions as a function of temperature and time. The model is surely of interest for simulating pyrolysis in real conditions when extractions of samples for measurements are distinctive for the material.

REFERENCES

1 E.L. Warrick, O.R. Pierce, K.E. Polmanteer and J.C. Saam, Rubber Chem. Technol., 52(3) (1979) 473.
2 R.W. Phillips, L.V. Tolentino and S. Feuerstein, J. Spacecr. Rockets, 11 (1977) 501.
3 J.V. Del Gatto, Rubber World, 164 (1971) 43.
4 T.J Gair and W.W. Wadsworth, S.A.E. Tech. Pap., 720 (1972) 129.
5 E.T. Novikova, V.F. Leonova and L.B. Egorov, Stroit. Mater., 8 (1976) 35.
6 A.A. Rashchenho, V.Y. Kruglitskaya and Z.E. Zavadskaya, Ukr. Khim. Zh., 37 (1971) 1071.
7 L.T. Lauer and L.B. Guy, Rubber Age, 102 (1970) 63.
8 P. Falconnet, Off. Plast. Caoutch., 21 (1974) 573.
9 V.M. Bhatnagar and J.M. Vergnaud, J. Therm. Anal., 27 (1983) 159.
10 M. Abdul and J.M. Vergnaud, Thermochim. Acta, 76 (1984) 161.
11 M. Abdul, V.M. Bhatnagar, J.C. David and J.M. Vergnaud, Thermochim. Acta, 74 (1984) 175.
12 M. Abdul, V.M. Bhatnagar and J.M. Vergnaud, Fire Safety J., 8 (1985) 135.