Thermochimica Acta, 149 (1989) 93–100
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PREDICTION OF THE 'STATE OF CURE' OF AN UNSATURATED POLYESTER BY DIFFERENTIAL SCANNING CALORIMETRY, AND INVESTIGATION OF ITS VARIATION WITH TEMPERATURE AND KINETIC PARAMETERS

J.P. AGRAWAL *, J.Y. ARMAND and J.M. VERGNAUD

Laboratory of Materials and Industrial Chemistry, Faculty of Science and Techniques, University of Saint-Etienne, Saint-Etienne (France)

(Received 28 October 1988)

ABSTRACT

Kinetic parameters of an unsaturated polyester have been determined by DSC. A simple method for predicting 'state of cure' (SOC) using kinetic parameters is proposed. The effect of variation of temperature and of kinetic parameters on SOC has also been investigated.

INTRODUCTION

Unsaturated polyesters and epoxy resins used for the inhibition of rocket propellants are generally in the liquid state and are transformed to the solid state, consisting of a three-dimensional network, on the addition of curing agents. Curing does not occur fully at this initial stage but continues to advance subsequently, leading to changes in mechanical properties [1–4]. This phenomenon is known as 'post-curing' and its extent should be as limited as possible in commercial as well as military applications. In the case of inhibitors for rocket propellants, if post-curing is of a high order it can lead to bond separation between inhibitor and propellant, so that the very purpose of inhibition is defeated [5,6].

The occurrence of post-curing can be considerably reduced by increasing the amount of curing agents added, the temperature of the curing process, etc., but these methods have their own limitations. For instance, increasing the temperature of curing will also enhance the migration of explosive or non-explosive plasticizers from rocket propellants to inhibitors [5]. Similarly, increasing the amount of curing agents added will shorten gel time G_t and thereby increase the exothermic peak temperature E_{PT}, which is likely to

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* On study leave from the Explosives Research and Development Laboratory, Pashan, Pune, India.

0040-6031/89/$03.50

cause cracks in the inhibitor and is therefore not desirable. Further, if E_{PT} increases excessively, the autoignition temperature of the propellant may be reached during gelling or curing, resulting in an explosion [7].

The object of the present investigation is to predict 'state of cure' (SOC) using kinetic parameters determined by DSC. Another object is to study the effect of variation of temperature and kinetic parameters on the SOC of unsaturated polyester. This study will be of significant interest to polyester manufacturers, processors and users, as the SOC data obtained will enable them to select appropriate processing and curing temperatures, bearing in mind the overall limitations of the system.

EXPERIMENTAL

Apparatus

The experiments were performed using a DSC 111 (Setaram, France) working under scanning mode at a heating rate of 1 K min^{-1} (horizontal mode). The sample ($\approx$ 120 mg) was hermetically sealed in a stainless steel cylinder or holder (external diameter $\approx$ 5.5 mm) which was placed in the vessel close to the heat-flux detector. The heat-flux detector continuously emits signals which are proportional to the heat transferred per unit time through the cylinder or holder. When the run was over, the calorimeter and sample were cooled to room temperature and the sample was again scanned under the same conditions in order to obtain the base line for the heat-flux–time curve.

Materials

The unsaturated polyester Norsodyne 574 (Trade name, by C.d.F. Chimie, France) used for this study has the following properties: density (at 20 °C), 1.11 g cm^{-3}; viscosity (at 25 °C), 2.5 ± 0.3 P; acid value, 24 ± 3 mg KOH per gram of resin, styrene content, 38.0%; gel time, 5–6 min; exothermic peak temperature, 160–175 °C.

Methyl ethyl ketone (MEK) peroxide in dimethyl phthalate (DMP) and cobalt naphthanate also in DMP were used as catalyst and accelerator for the curing of the polyester, in the proportion 1.6% each by volume.

ASSUMPTIONS AND CALCULATIONS

A heat-flux–temperature curve was obtained by calculation using a Hewlett–Packard 86 after storing the data and determining the kinetic parameters using the Freeman–Carroll method [8].

Models of this process generally take into consideration not only the kinetics of heat evolved from the reaction but also heat transfer by conduction through the material [9–12] leading to the development of temperature and SOC profiles within the material. Heat transfer is a particular problem if the experiments are conducted at high temperatures. In this case, the temperature of study was low, resulting in a rate of reaction so low that the reaction required a long time for completion. Consequently, there was enough time for heat transfer to occur throughout the material, so this did not become a limitation. It is assumed that the reaction proceeded under isothermal conditions. It is also assumed that the temperature and the SOC remained the same throughout the material.

The mathematical model used to describe the kinetics of the reaction is [13,14]

$$\frac{1}{Q_\infty}\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_0(1-\alpha)^n \exp(-E/RT) \tag{1}$$

where $\alpha = Q_t/Q_\infty$ represents the extent of the reaction, Q_t is the heat evolved up to time t, Q_∞ is the total enthalpy, K_0 is the pre-exponential factor (s^{-1}), n is the order of the overall reaction, E is the activation energy (cal mol^{-1}), R is the gas constant (i.e. 1.987 cal K^{-1} mol^{-1}), and T is the absolute temperature.

On integrating, we obtain

$$\ln\left[1-\frac{(\mathrm{SOC})_t}{(\mathrm{SOC})_\infty}\right] = -K_0 \exp(-E/RT)t \tag{2}$$

if $n = 1$, and

$$\frac{1}{1-n}\left[1-\left\{1-\frac{(\mathrm{SOC})_t}{(\mathrm{SOC})_\infty}\right\}^{1-n}\right] = K_0 \exp(-E/RT)t \tag{3}$$

if $n \neq 1$, where $(\mathrm{SOC})_t$ is the SOC at time t (i.e. $Q_t/Q_\infty \times 100$), which is determined by taking $(\mathrm{SOC})_\infty = 100$.

RESULTS AND DISCUSSION

Heat-flux–temperature histories are of interest as these are directly recorded by the calorimeter running in scanning mode. The experimental curve is shown in Fig. 1. The kinetic parameters calculated on the basis of this curve, are as follows: enthalpy, 40.05 cal g^{-1}; activation energy E, 21.68 kcal mol^{-1}; order of reaction n, 1.0; pre-exponential factor K_0, 1.8×10^{11} s^{-1}; reaction rate constant K (at 303 K), 4.16×10^{-5} s^{-1}.

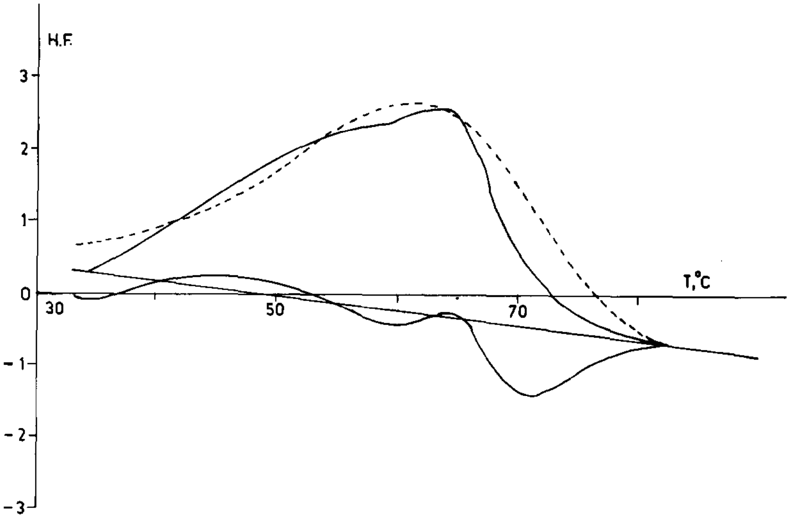

Fig. 1. Heat-flux–temperature profiles of unsaturated polyester in scanning mode: —— experimental; — — — theoretical.

The heat-flux–temperature curve obtained using eqn. (1) and these kinetic parameters (Fig. 1) is in agreement with the experimental curve. This indirectly supports the correctness of the kinetic parameters as given above.

Effect of variation of temperature on SOC

From the graphical presentation of variation of SOC with temperature shown in Fig. 2, it can be seen that the effect of variation of temperature on SOC is pronounced. At 293 K, the time required for 50% SOC is 15.81 h, and this increases to 105.06 h for 99% SOC. Similarly, the time required for 99% SOC at 293 K is 105.06 h. At 313 K it is reduced to 9.73 h for the same SOC. In short, the generalization may be made that the higher the temperature of processing/curing, the shorter the time necessary to reach a given value of SOC, which is similar to a general finding reported in the literature [15,16]. One more point of interest which comes to light from Fig. 2 is that variation of SOC with temperature starts right from the beginning.

This information is of vital importance to users and processors of polyesters, enabling them to select processing and curing temperatures with the overall requirements of the system in question in mind.

Effect of variation of temperature on reaction rate constant

The variation of the reaction rate constant *K* with temperature is shown in Table 1. It is clear that the value of *K* increases steadily as the temperature increases from 283 to 313 K.

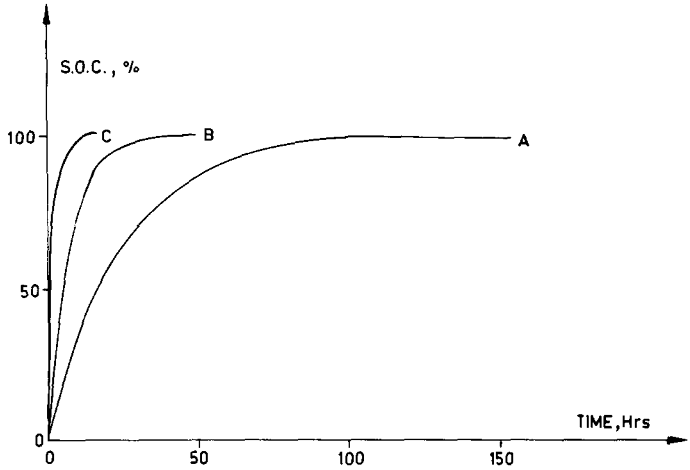

Fig. 2. Effect of variation of temperature on SOC: (A) $T = 293$ K; (B) $T = 303$ K; (C) $T = 313$ K.

TABLE 1

Variation of rate constant (K) with temperature

Temperature (K)	K (10^{-5} s^{-1})
293	1.22
298	2.27
303	4.16
308	7.47
313	13.14

Effect of variation of kinetic parameters on SOC

Activation energy

From the graphical presentation of variation of SOC with variation in activation energy E shown in Fig. 3, it can be seen that the time required to achieve a given value of SOC increases with increasing E. This is as expected, because if the activation energy is higher, more energy will be required to attain the same degree of SOC and the time required will thereby be increased. Similarly, of course, the lower the value of E, the lower the time necessary for the SOC to reach a given value. This is in agreement with data already reported in the literature [17] for a mixture of rubber (NR and SBR in the ratio of about 2/3).

In the same way as for variation of temperature, the significance of the effect of variation of E on SOC is also apparent right from the initial stages.

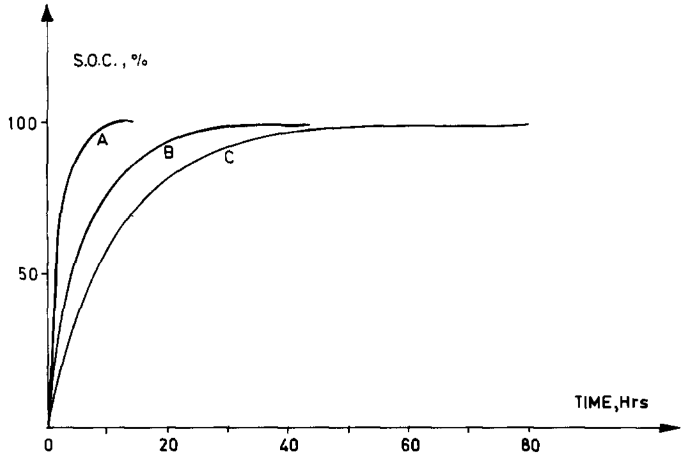

Fig. 3. Effect of variation of activation energy E on SOC: (A) $E = 21.0$ kcal mol^{-1}; (B) $E = 21.68$ kcal mol^{-1}; (C) $E = 22.0$ kcal mol^{-1}.

Pre-exponential factor

The importance of variation of the pre-exponential factor K_0 on SOC is presented graphically in Fig. 4. It is evident that the time required to achieve a given value of SOC and K_0 are inversely related. Thus, as the value of K_0 increases from 1.5×10^{11} to 2.1×10^{11}, the time required for achieving 99% SOC decreases from 36.9 to 26.4 h. This is in agreement with data already reported by Ferradou and Vergnaud [18]. Figure 4 also indicates that the effect of K_0 is more pronounced in the region of 40–90% SOC.

Reaction rate constant

The effect of variation of the reaction rate constant K on SOC is shown graphically in Fig. 5, which indicates that the time required to achieve 99%

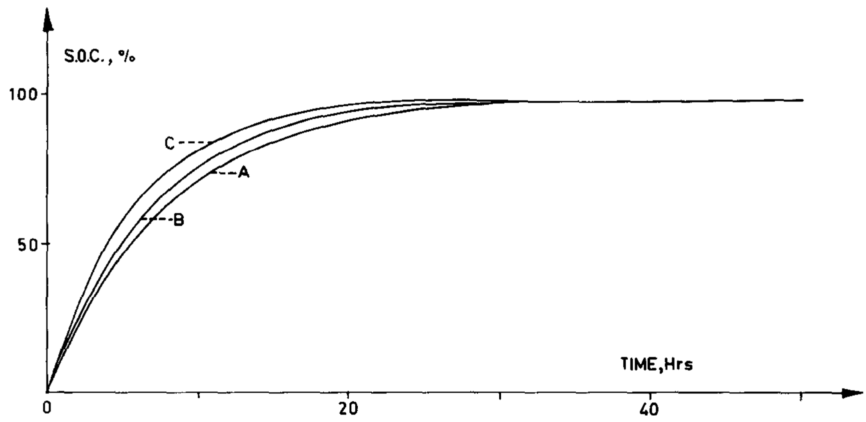

Fig. 4. Effect of variation of pre-exponential factor K_0 on SOC: (A) $K_0 = 1.5 \times 10^{11}$; (B) $K_0 = 1.8 \times 10^{11}$; (C) $K_0 = 2.1 \times 10^{11}$.

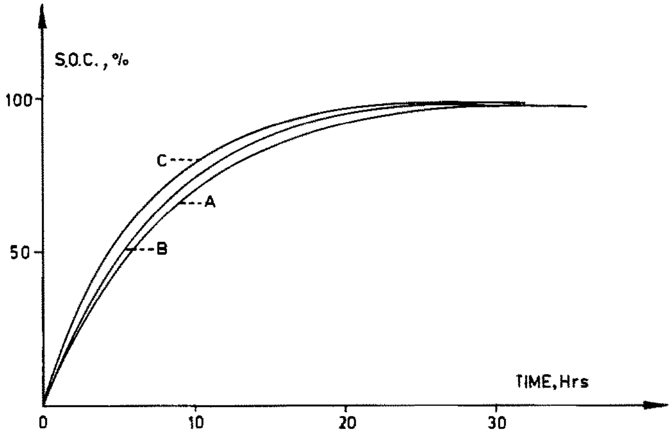

Fig. 5. Effect of variation of reaction rate constant K on SOC: (A) $K = 3.5 \times 10^{-5}$; (B) $K = 4.0 \times 10^{-5}$; (C) $K = 4.5 \times 10^{-5}$.

SOC decreases as the value of K increases. If K increases, the speed of reaction increases and the time required to achieve 99% SOC is thereby decreased. This is a general finding and is well known.

Order of reaction

The overall order of reaction n has been determined as 1.0 and unsaturated polyester requires only 30.74 h to achieve 99% SOC at 303 K. However, if n is 0.6, the time required to reach the same SOC at the same temperature is 14.05 h, and this becomes 88.63 h, if n is 1.4 (time calculated using eqn. (3). Thus, if n decreases, the time required to achieve a given value of $(\mathrm{SOC})_t$ also decreases; on the other hand, if n increases, the time required to achieve a given value of $(\mathrm{SOC})_t$ also increases. Figure 6 shows

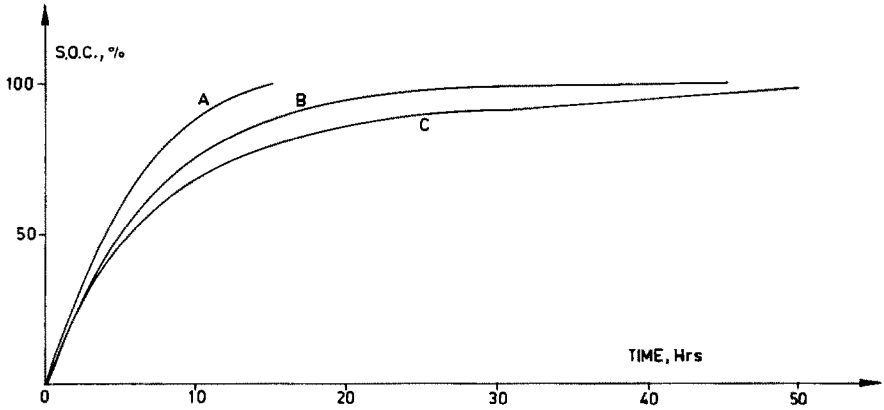

Fig. 6. Effect of variation of order of reaction n on SOC: (A) $n = 0.6$; (B) $n = 1.0$; (C) $n = 1.4$.

that the effect of variation of n starts becoming significant from 40% SOC onwards, corroborating earlier findings for the case of rubber [19].

A comparison of the effects of various kinetic parameters on SOC shows that among all kinetic parameters, variation in E has a predominant effect on the time required to achieve a given value of SOC, and the effect of this variation starts right from the initial stages. A similar effect is also observed with variation in the temperature of curing/processing.

ACKNOWLEDGEMENTS

The authors are grateful to C.d.F. Chimie, France for supplying samples of unsaturated polyester.

J.P.A. is grateful to the French Government (C.I.E.S., Paris) for their invitation to come to France as a Visiting Scientist, and a fellowship.

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