

## ISOTHERMAL TRANSFORMATION OF DYNAMIC DSC CURVES FOR THERMOSETTING POLYMERS IN CURING KINETICS ANALYSIS

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To predict the isothermal course of a reaction from the dynamic DSC curves, the application of isothermal DSC curve transformation has been proposed. To perform such a transformation, it is sufficient only to determine the effective activation energy. To transform integral dynamic curves,  $\alpha(T)$ , into isothermal ones,  $\alpha(t)$ , a better equation has been derived and its validity has been demonstrated on the example of two typical thermosetting systems. In addition, it has been shown that the transformation of differential curves,  $\frac{d\alpha}{dT}(T)$ , into isothermal ones  $\frac{d\alpha}{dt}(\alpha)$ , readily allows determination of the kinetic function and rate constants. The procedure used to obtain information on the curing kinetics for thermosetting resins is characterized by simplicity and reliability and can work at  $E = E(\alpha)$ .

To describe reactions occurring in an isothermal DSC process, the equation to be used is as follows:

$$\frac{d\alpha}{dt} = A \exp(-E/RT) \cdot f(\alpha) \quad (1)$$

while in a dynamic DSC process it is as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E/RT) \cdot f(\alpha) \quad (2)$$

where  $\alpha$  is the fractional conversion,  $\alpha = \frac{\Delta H}{\Delta H_0}$  where  $\Delta H$  and  $\Delta H_0$  are the partial and total heat values, respectively,  $t$  is the time,  $A$  is the pre-exponen-

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tional factor,  $E$  is the apparent activation energy,  $R$  is the universal gas constant,  $T$  is the absolute temperature, and  $f(\alpha)$  is some function of the fractional conversion. It is often assumed that  $f(\alpha) = (1-\alpha)^n$ , where  $n$  is the reaction order.

A great number of methods are available to determine the kinetic parameters of a reaction from dynamic DTA-DSC and TG curves, but it still remains a problem to obtain reliable values of these parameters. Certain authors are of the opinion that it is impossible in principle to determine reliable kinetic parameters from dynamic TG and DTA-DSC data [1].

It is not surprising that an increasing number of papers are being published where kinetic parameters are obtained from the results of an isothermal experiment [2-5], and all the leading firms (Perkin-Elmer, Du Pont, MOM) therefore provide their instruments with the facilities to perform such an experiment. However, it is not always possible to carry out the experiment.

The main hindrance is the loss of information on the process outset during the introduction of the isothermal mode. Higher heating rates will not solve the problem either. On rapid heating, thermosetting resins may swell; consequently, DSC curves can not be reproduced and, moreover, instrument failure may result. In many cases, therefore, the dynamic experiment remains preferable.

Equivalent conversion methods have been introduced by Ozawa, Flynn *et al.*, Reich *et al.* and Friedman [6-9] for the calculation of  $E$  values as reliable as those obtained from the results of the isothermal experiment [10].

Generally, it is a more difficult task to determine other kinetic parameters, as one must often find not only the reaction order, but also the function  $f(\alpha) \neq (1-\alpha)^n$ . Without  $f(\alpha)$ , the pre-exponential factor can not be determined. The well-known equations proposed by Horowitz and Metzger, and Kissinger *et al.* [11] often yield very approximate and even inappropriate data. It is probably due to this fact that most papers concerned with DSC data-based reaction kinetics often determine only  $E$ , less often  $n$  and seldom  $f(\alpha)$ .

Recently, some interesting studies have been published, for example [12], in which all kinetic parameters are determined from one curve, even for a multi-stage process. On the other hand, there are no papers where the kinetic parameters derived from the dynamic DSC data for the curing of thermosetting polymers are then used to predict the course of the reaction in the isothermal mode.

The present paper suggest that, to predict the isothermal course of a reaction from the dynamic DSC data and to find  $n$ ,  $A$  and  $f(\alpha)$  more accurately, we should use the method of isothermal transformation of dynamic curves (ITDC). The idea of this method in the most general (differential) form was introduced by Merzhanov *et al.* [13, 14]. We propose that transformation of the dynamic DSC curves be performed not only in the differential form, but primarily in the integral form, as the latter represents a simpler procedure to establish  $\alpha(t)$  at  $T = \text{const}$ . This helps significantly in optimization of the curing process of a particular thermosetting systems.

The ITDC method consists in determining the activation energy from the dynamic DTA-DSC and TG curves by an equal conversion method (e.g. the Reich method), and then transforming  $\alpha(T)$  or  $\frac{d\alpha}{dT}(T)$  at  $\beta = \text{const}$ . into  $\alpha(t)$  or  $\frac{d\alpha}{dt}(\alpha)$  at  $T = \text{const}$ . Thus, the obtained isothermal curves allow prediction of the reaction course in the isothermal mode at a given  $T$ , and also allow derivation of the missing kinetic parameters  $n$ ,  $A$  and  $f(\alpha)$  from these curves by means of the conventional procedures used in isothermal kinetic analysis. The simplest way to transform the  $\alpha(T)$  curves into the isothermal  $\alpha(t)$  ones (there are other more complicated procedures, not discussed in this paper) is through the application of the expression proposed by Doyle [15] to estimate the time of isothermal aging from the TG data:

$$\log t_i = \log \frac{E}{\beta R} + \frac{E \log e}{RT_i} + \log p(x_\alpha) \quad (3)$$

where  $t_i$  is the time of reaction in the isothermal mode at  $T_i$  until the fractional conversion  $\alpha$  is achieved,  $p(x)$  is the temperature integral tabulated by Doyle, and  $x_\alpha = \frac{E}{RT_\alpha}$ , where  $T_\alpha$  is the temperature at which  $\alpha$  is achieved in the TG or DTA-DSC processes at a heating rate  $\beta$ . Equation (3) was derived by integrating and comparing Eqs (1) and (2) with regard to the assumption that  $E$ ,  $A$ ,  $f(\alpha)$  and  $\alpha$  are equal under isothermal and dynamic heating. Thus, the transformation using Eq. (3) will be valid provided this assumption is fulfilled, which is not always the case.

If  $x > 20$ , then  $\log p(x) = -2.315 - 0.4567x$ , and the approximation introduced by Doyle may be applied:

$$\log t_i = \log \frac{E}{\beta R} + \frac{0.4343E}{RT_i} - \frac{0.4567E}{RT_\alpha} - 2.315 \quad (4)$$

which at  $x = 20$ , however, gives a significant error (15%) in comparison with Eq. (3). With this in mind, we assume that

$p(x) = e^{-x} \left( \frac{1}{x^2} - \frac{2!}{x^3} \right)$  and propose a more precise and convenient approximation:

$$\ln t_i = \ln \frac{RT_\alpha^2}{E\beta} + \frac{E}{R} \left( \frac{1}{T_i} - \frac{1}{T_\alpha} \right) - \frac{2RT_\alpha}{E} \quad (5)$$

the error of which is 4% or less at  $10 < x < 60$ .

The transformation of  $\frac{d\alpha}{dT}(T)$  curves at  $\beta = \text{const.}$  into  $\frac{d\alpha}{dt}(\alpha)$  curves at  $T = \text{const.}$  can be performed by means of an equation similar to that proposed in [13]:

$$\ln \frac{d\alpha}{dt} = \ln \left( \beta \frac{d\alpha}{dT} \right) + \frac{E}{R} \left( \frac{1}{T_\alpha} - \frac{1}{T_i} \right) \quad (6)$$

This equation is readily derived by subtracting Eq. (2) from Eq. (1) in the logarithmic form and assuming that  $E$ ,  $A$ ,  $f(\alpha)$  and  $\alpha$  are equal under isothermal and dynamic heating. It should be taken into consideration that  $\beta \frac{d\alpha}{dT} = \frac{d\alpha}{dt} \Big|_{T_\alpha}$  i.e. it is proportional to  $\frac{dH}{dt}(t)$  at  $T_\alpha$ .

The integral curves having been divided on the  $\alpha$  coordinate with a small step (0.05-0.1),  $t_i$  is found by means of Eqs (3) - (5) for each  $\alpha$ ; thus,  $\alpha(t)$  is attained for a given  $T_i$ . Likewise, the differential curves can be transformed by using Eq. (6).

If  $f(\alpha) = (1 - \alpha)^n$ , then  $n$  and  $A$  can readily be determined from the  $\alpha(t)$  curve. The transformation helps significantly in finding  $f(\alpha) = (1 - \alpha)^n$ . The function  $f(\alpha)$  can be determined more accurately by applying the transformation  $\frac{d\alpha}{dT}(T) \rightarrow \frac{d\alpha}{dt}(\alpha)$ , because Eq. (6) is precise, in contrast with Eqs (3)-(5).

The efficiency of ITDC can be demonstrated for two thermosetting compositions. The first (EDA) comprises epoxy resin ED-22, iso-methyl-tetrahydrophthalic anhydride (iso-MTPHA) as a curing agent and naphthylene benzimidazole (NBI) as a catalyst, in the mass ratio 100 : 80 : 0.5. The second is N,N'-hexamethylenebismaleimide (HMBMI), the homopolymerization of which has been well studied by IR spectroscopy [16].

### Experimental

The DSC curves for EDA curing were obtained with a DSC-2 (Perkin-Elmer) scanning calorimeter, and the data for HMBMI with a DSC-990 (Du

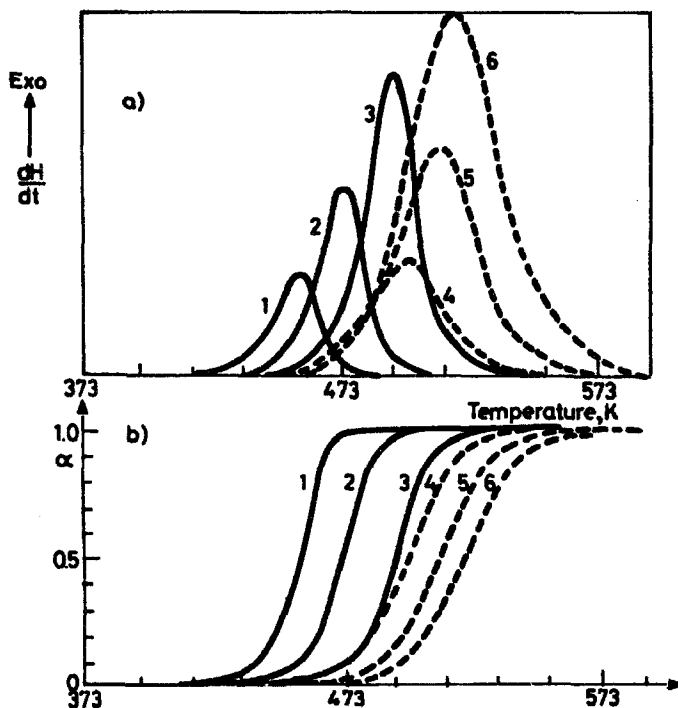


Fig. 1 a,b Isothermal transformation of dynamic DSC curves for thermosetting polymers: the first composition (EDA) contains ED-22, iso-MTPHA and NBI (100:80:0.5), while the second is N,N'-hexamethylenebismaleimide (HMBMI). (a) initial DSC curves; (b) integrated DSC curves 1, 2 and 3 for EDA at 5, 10 and 20 deg/min, respectively, and curves 4, 5 and 6 for HMBMI at 1.6, 3.4 and 6.4 deg/min, respectively

Pont) scanning calorimeter. Sample masses were 10-12 mg and 20-25 mg, respectively. The heating rates were 5, 10 or 20 and 1.6, 3.4 or 6.3 deg/min. The atmosphere was air.

## Results and discussion

The activation energy was found by Reich's method [8], all calculations being performed with the aid of specially-developed computer programs. The effective activation energy values are listed in Table 1. The initially ob-

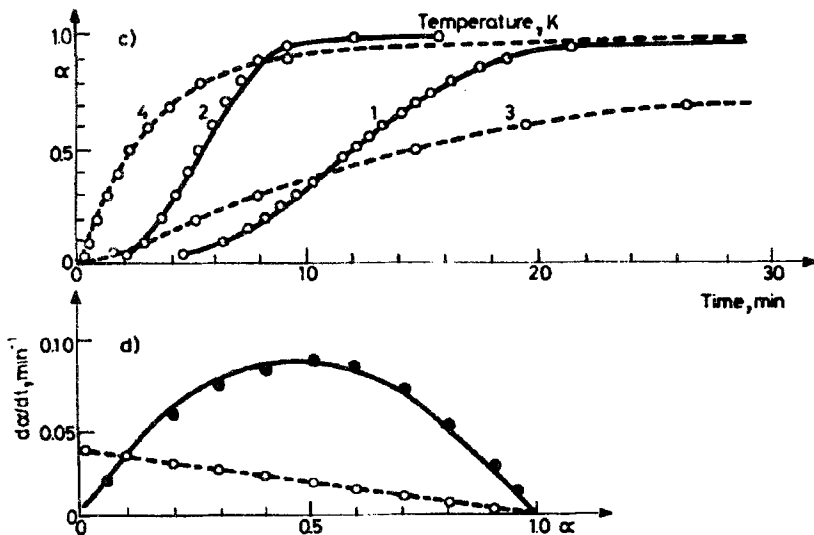


Fig. 1 c,d Isothermal transformation of dynamic DSC curves for thermosetting polymers: the first decomposition (EDA) contains ED-22, iso-MTPHA and NBI (100 : 80 : 0.5 ), while the second is  $N,N'$ -hexamethylenebismaleimide (HMBMI). (c) the transformation  $\alpha(T) \rightarrow \alpha(t)$  1 - for EDA,  $T_i = 433$  K; 2 - for EDA,  $T_i = 453$  K; 3 - for HMBMI,  $T_i = 493$  K; 4 - for HMBMI,  $T_i = 523$  K; o - calculated curves, ----- experimental curves; (d) the transformation  $\frac{d\alpha}{dT}(T) \rightarrow \frac{d\alpha}{dt}(\alpha)$ , 1 - for EDA,  $T_i = 433$  K; 2 - for HMBMI,  $T_i = 523$  K; 3 - points according to the derived equation  $\frac{d\alpha}{dt} = (k_o + k\alpha)(1 - \alpha)$

tained DSC curves are shown in Fig. 1a, and the integrated ones in Fig. 1b. The transformation  $\alpha(T) \rightarrow \alpha(t)$  was performed by means of Eq. (5) for

EDA at 433 and 453 K, and for HMBMI at 493 and 523 K (Fig. 1c, curves 1-4, shown by dotted lines).

An isothermal experiment was carried out at 433 and 453 K to verify the transformation of the dynamic DSC curves for EDA.

The isothermal DSC curves after integration are also given solid lines in Fig. 1c. Figure 1c reveals that the calculated data are in good agreement with the experimental results. This confirms the fact that the activation energy of curing for the system involved was calculated correctly and that Eq. (5) is well appropriate in this case. It was not possible to carry out such verification for HMBMI, due to the high rate of reaction at the starting moment, which did not allow the obtaining of reproducible curves and their correct integration. Selective testing, however, by means of curing in a precise thermostat for the calculated period of time up to fractional conversions of 0.3, 0.5, 0.8 and 1.0 at  $T_i = 493$  and 523 K showed that the conversion values obtained in this way agree fairly well with the predicted values (the relative error is  $\pm 10\%$ ). Figure 1 also reveals that once ITDC has been performed we can make a definite assumption concerning the function  $f(\alpha)$ . For example, Fig. 1c shows that for EDA  $f(\alpha) \neq (1 - \alpha)^n$ , but has a more complicated form, e.g.  $f(\alpha) = (\alpha_0 + \alpha^m)(1 - \alpha)^n$  (autocatalyst), since the reaction rate is close to zero at the starting moment. It can also be seen that for HMBMI  $f(\alpha) = (1 - \alpha)^n$ , as the reaction rate at the starting moment is maximum. To make such assumptions from the analysis of the profiles of the original integral of differential dynamic curves is not possible. Moreover, the well-known methods, particularly that of Borchard and Daniel [17], used to analyse such curves yielded  $E = 120$  kJ/mol and  $n = 1$ , i.e. the activation energy was higher by a factor of two than that desired and the function was not found to be different from  $(1 - \alpha)^n$ .

The transformation  $\frac{d\alpha}{dT}(T) \rightarrow \frac{d\alpha}{dt}(\alpha)$  allows us to specify the function  $f(\alpha)$  for EDA and HMBMI. Straight line 2 in Fig. 1d shows that the reaction order for HMBMI homopolymerization is close to 1. This agrees fully with the results reported in [16], where  $E$  is found to be 140.5 kJ/mol (compare with the values listed in the Table). Once ITDC has been performed, it is possible to calculate the pre-exponential factor:  $A = 2.15 \cdot 10^{13} \text{ min}^{-1}$  for HMBMI.

From Fig. 1d, it can be seen that the maximum in curve 1 is in the vicinity of the point 0.5 and the curve is nearly symmetrical, i.e.  $m = n = 1$  is most likely. If  $\alpha = 0$  is excluded, the starting reacting rate may not be found to be equal to zero, yet it is low. Figure 2, presenting the initial parts of the curves

at 433 and 453 K at higher magnitude, clearly shows that these curves tend to a definite value of starting rate. We fit them to zero by substituting  $\frac{d\alpha}{dT} = 0$ ; this is obtained if we draw the baseline (Fig. 1a): at the point where it touches the DSC curve; the peak height is zero. Therefore, when the single "main" activation energy has been determined and the DSC curve transformation has been performed, we can obtain  $\frac{d\alpha}{dt}(\alpha)$  and find another rate constant, which enables us to write the equation for the reaction as follows:

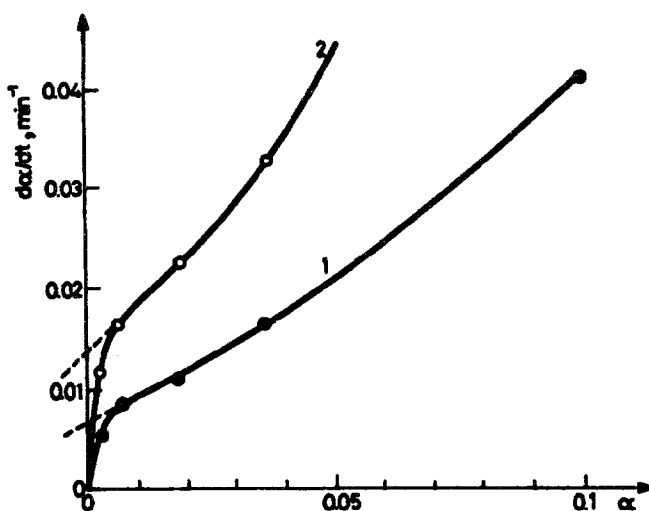


Fig. 2 Initial parts of the curves  $\frac{d\alpha}{dt}(\alpha)$  for EDA; 1 - at  $T_i = 433$  K; 2 - at  $T_i = 453$  K

$$\frac{d\alpha}{dt} = (k_o + k\alpha)(1 - \alpha) \quad (7)$$

where  $k_o = A_o \exp\left(\frac{-E_o}{RT}\right) = 4.57 \cdot 10^4 \exp\left(\frac{-56500}{RT}\right);$

$$k = A \cdot \exp\left(\frac{-E}{RT}\right) = 4.87 \cdot 10^6 \exp\left(\frac{-60300}{RT}\right).$$



**Table 1** Effective activation energy values obtained by Reich's method for the polymerization of thermosetting systems

$\alpha$	EDA		HMBMI	
	$T\alpha$ , K ( $\beta = 10$ deg/min)	E, kJ/mol	$T\alpha$ , K ( $\beta = 3.4$ deg/min)	E, kJ/mol
0.1	456	58.0±1.3	486	130±14
0.2	463	59.5±1.2	496	135±16
0.3	467	60.0±1.2	502	138±17
0.4	470	60.3±1.3	507	139±17
0.5	473	60.3±1.3	511	139±16
0.6	475	60.3±1.2	516	139±13
0.7	478	60.0±1.1	520	133±14
0.8	481	59.3±1.7	525	132±5.2
0.9	485	56.5±2.0	534	122±1.6
1.0*	518	56.5±2.0	573	122±1.6

\*Due to the large scattering of E at  $\alpha = 1.0$ ,  $E_{1.0} = E_{0.9}$  at this point

In conclusion, we would like to note the following advantages of the use of ITDC to investigate the curing kinetics of thermosetting resins:

- It provides a simple procedure to obtain  $\alpha(t)$  at  $T = \text{const}$ . This  $t$  dependence of  $\alpha$  is necessary to optimize the curing process.
- It allows the obtaining of reliable values of the kinetic parameters through the application of the equal conversion method for  $E$  and by means of simple procedures used in isothermal kinetic analysis for the other kinetic parameters.
- It allows the prediction of the isothermal reaction course at  $E = E(\alpha)$ , as reported in reference [13] and confirmed by experimental results [18]. This last advantage is more important for thermosetting resins, because  $E$  often changes significantly during the curing process.

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**Zusammenfassung** - Zur Prognose eines isothermen Reaktionsverlaufes anhand der DSC-Kurven wird die Anwendung einer Transformation der isothermen DSC-Kurven vorgeschlagen. Zur Durchführung einer solchen Transformation ist es ausreichend, die effektive Aktivierungsenergie zu bestimmen. Zur Transformation ganzer dynamischer Kurven  $\alpha(t)$  in isotherme Kurven  $\alpha(T)$  wurde eine bessere Gleichung erhalten und ihre Gültigkeit anhand von zwei charakteristischen Duroplast-Systemen demonstriert. Es wurde außerdem gezeigt, daß eine Transformation von Differentialkurven  $\frac{d\alpha}{dT}(T)$  in isotherme Kurven  $\frac{d\alpha}{dt}(\alpha)$  leicht die Bestimmung der kinetischen Funktion und der Geschwindigkeit konstanten ermöglicht. Das Verfahren, was zur Ermittlung von Informationen über die Vernetzungskinetik von duroplastischen Harzen angewendet wurde, ist durch Einfachheit und Verlässlichkeit gekennzeichnet und gilt für  $E = E(\alpha)$ .