THE RELATIONSHIP BETWEEN ISOTHERMAL AND NON-ISOTHERMAL KINETICS FOR THERMOSET CHARACTERIZATION

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ABSTRACT

General relationships are developed for obtaining a non-isothermal (dynamic) rate equation from a knowledge of the isothermal kinetics of the system. Applications to several important specific forms of the isothermal rate expressions are given.

INTRODUCTION

Kinetic characterization is of fundamental importance for the processing of reactive polymeric systems. The determination of the kinetic parameters governing the curing reactions of thermosets is usually conducted by means of a series of isothermal experiments using conventional methods and techniques. Non-isothermal experiments have the attraction of being simpler and more rapid for providing comparable useful information relating to thermoset cure. Although several papers have appeared in the literature pertaining to the relationship between isothermal and non-isothermal cure kinetics [1—5], no general correlation or procedure is available for obtaining the non-isothermal (dynamic) rate expression from the isothermal rate equation, particularly for cases where the isothermal rate equation may be of very general form.

Following the publication of an article by MacCallum and Tanner [6], an extensive discussion appeared in the literature pertaining to the relationship between isothermal and non-isothermal kinetics. MacCallum and Tanner [6] suggested that the procedure for the development of a non-isothermal rate expression involving the inherent assumption that the isothermal rate is equivalent to the dynamic or temperature varying rate, was incorrect. They maintained that under non-isothermal conditions the dynamic rate of fractional conversion, $\alpha(t, T)$, is given as

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T + \beta \left(\frac{\partial \alpha}{\partial T}\right)_t \tag{1}$$

where $(\partial \alpha/\partial t)_T$ is the isothermal rate and $\beta = dT/dt$ is the heating rate. Similar arguments have been made by Prime [4,5] in his studies of the dynamic

cure of thermosetting polymers. Although several studies [4—7] have claimed that the isothermal reaction rate must be expressed as $(\partial \alpha / \partial t)_T$, a number of investigators [8—10] have questioned the validity of eqn. (1), particularly the physical meaning of the partial derivative $(\partial \alpha / \partial T)_t$.

Hill [8] maintained that the partial derivative $(\partial \alpha / \partial T)_t$ is effectively zero based on an argument that when time is fixed the number and position of particles or reactive species is also fixed. MacCallum [11] refuted this notion by considering the analogy where the reaction volume is changed by the addition of an inert diluent at some constant rate. He argued that the temperature, T, and the partial derivative $(\partial \alpha / \partial T)_t$ are analogous to the reactant volume, V, and the partial derivative $(\partial \alpha / \partial V)_t$. MacCallum concluded that the term $(\partial \alpha / \partial T)_t$ must therefore exist. Sestak and Kratochvil [12,13] have reviewed this problem in terms of rational thermodynamics and constitutive equations. They argued that eqn. (1) is a direct consequence of a constitutive equation of the form

$$\alpha = \alpha(t, T) \tag{2}$$

They stated that both of the partial derivatives in eqn. (1) are non-zero and gave a physical interpretation for the differences between the isothermal and non-isothermal kinetic expressions.

Non-isothermal characterization techniques are generally less time consuming as compared to isothermal experimental studies, thereby making them more attractive for routine industrial, quality control, or research applications. However, it is evident from eqn. (1) that the non-isothermal kinetic expression ($\beta \neq 0$) is not equivalent to the isothermal rate expression ($\beta = 0$). The following sections describe the general relationships that can be used to develop the non-isothermal rate equation from a knowledge of the isothermal kinetics. Some important specific forms of the isothermal rate expression are also discussed.

NON-ISOTHERMAL RATE EQUATIONS

Equation (2) expresses the fact that the fractional degree of conversion, α is a function of both time and temperature. Therefore, the total differential $d\alpha$ is expressed as follows

$$d\alpha = \left(\frac{\partial \alpha}{\partial t}\right)_T dt + \left(\frac{\partial \alpha}{\partial T}\right)_t dT \tag{3}$$

Alternatively eqn. (3) may be expressed in the following form

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T + \left(\frac{\partial \alpha}{\partial T}\right)_t \frac{dT}{dt} \tag{4}$$

Denoting the heating rate, dT/dt, as β and rearranging eqn. (4) yields

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T \left[1 + \beta \frac{(\partial \alpha / \partial T)_t}{(\partial \alpha / \partial t)_T}\right] \tag{5}$$

General form of isothermal rate equation

The isothermal rate equation is given in general form as follows

$$\left(\frac{\partial \alpha}{\partial t}\right)_T = f(\alpha, T) \tag{6}$$

Integration of eqn. (6) gives

$$\int \frac{d\alpha}{f(\alpha, T)} = h(\alpha, T) = t + \phi(T) \tag{7}$$

However, initially at $t = 0$, $\alpha = 0$ and thus from eqn. (7)

$$h(0, T) = \phi(T) \tag{8}$$

$$\left(\frac{\partial h}{\partial T}\right)_t = \frac{d\phi}{dT} \tag{9}$$

The partial derivative on the left-hand side of eqn. (9) may also be expressed as

$$\left(\frac{\partial h}{\partial T}\right)_t = \left(\frac{\partial h}{\partial \alpha}\right)_T \left(\frac{\partial \alpha}{\partial T}\right)_t + \left(\frac{\partial h}{\partial T}\right)_\alpha \tag{10}$$

Combining eqns. (7), (9) and (10) yields

$$\frac{(\partial \alpha/\partial T)_t}{(\partial \alpha/\partial t)_T} = \frac{d\phi}{dT} - \left(\frac{\partial h}{\partial T}\right)_\alpha \tag{11}$$

Substituting eqn. (11) into eqn. (5) results in the following expression for the dynamic rate equation

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T \left[1 + \beta\left(\frac{d\phi}{dT} - \left(\frac{dh}{\partial T}\right)_\alpha\right)\right] \tag{12}$$

All of the terms on the right-hand side of eqn. (12) may be determined from the isothermal rate equation. The difficulty in deriving these quantities is dependent upon the complexity of the integral appearing in eqn. (7). A rather general form of isothermal rate equation is expressed by the following form

$$\left(\frac{\partial \alpha}{\partial t}\right)_T = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{13}$$

where k_1 and k_2 are kinetic rate constants having an Arrhenius dependence on temperature, and m, n are kinetic exponents. Equation (13) has been found to give a realistic description of the isothermal kinetic behavior of several thermosetting systems [14,15]. For the usual case where m and n have non-integer values, the function $h(\alpha, T)$ may be evaluated by approximating the term $(1 - \alpha)^{-n}$ by means of an infinite series expansion [16]. Thus

$$h(\alpha, T) = \sum_{j=0}^{j=\infty} \frac{\Gamma(n + j)}{j! \, \Gamma(n)} \sum_{i=0}^{i=\infty} \frac{(-k_1)^i}{(k_2)^{i+1}} \frac{\alpha^{j+1-(i+1)m}}{j + 1 - (i + 1)m} \tag{14}$$

Equation (14) satisfies both the ratio test and the root test for convergence. In this case, $h(0, T) = \phi(T) = 0$. Evaluating the derivative $(\partial h/\partial T)_\alpha$ from eqn. (14) and substituting into the dynamic rate expression given by eqn. (12) yields

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T \left[1 - \beta\left(\sum_{j=0}^{j=\infty} \frac{\Gamma(n+j)}{j!\,\Gamma(n)} \sum_{i=0}^{i=\infty} \frac{(-k_1)^i}{(k_2)^{i+1}}\left(\frac{i(E_1 - E_2) - E_2}{RT^2}\right) \frac{\alpha^{j+1-(i+1)m}}{j+1-(i+1)m}\right)\right]$$

(15)

where E_1 and E_2 are the activation energies associated with the kinetic rate constants k_1 and k_2, respectively. In certain special cases m and n have integer values and simple closed form analytical expressions may be derived for the function $h(\alpha, T)$ and the dynamic rate equation.

(i) $m = 1, n = 1$

$$h(\alpha, T) = \frac{1}{k_1 + k_2}\left[\ln\left(\frac{k_1 + k_2\alpha}{1 - \alpha}\right)\right]$$

(16)

$$\phi(T) = \frac{\ln k_1}{k_1 + k_2}$$

(17)

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T \left[1 + \frac{\beta}{(k_1 + k_2)RT^2}\left\{\left(\frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}\right)\ln\left(\frac{k_1 + k_2\alpha}{k_1(1 - \alpha)}\right) + \left(\frac{\alpha k_2(E_1 - E_2)}{k_1 + k_2\alpha}\right)\right\}\right]$$

(18)

(ii) $m = 1, n = 2$

$$h(\alpha, T) = \frac{1}{(k_1 + k_2)^2}\left[k_2 \ln\left(\frac{k_1 + k_2\alpha}{1 - \alpha}\right) + \frac{k_1 + k_2}{1 - \alpha}\right]$$

(19)

$$\phi(T) = \frac{k_2 \ln k_1 + k_1 + k_2}{(k_1 + k_2)^2}$$

(20)

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T \left[1 + \frac{\beta}{(k_1 + k_2)^2 RT^2}\left(\frac{\alpha(k_1 E_1 + k_2 E_2)}{1 - \alpha} + \frac{\alpha k_2^2(E_1 - E_2)}{k_1 + k_2\alpha}\right.\right.$$
$$\left.\left. + \frac{k_1 k_2(E_2 - 2E_1) - k_2^2 E_2}{k_1 + k_2}\ln\left(\frac{k_1(1 - \alpha)}{k_1 + k_2\alpha}\right)\right)\right]$$

(21)

Isothermal rate equation expressed as the product of two separable functions

In many kinetic studies the isothermal reaction rate is expressed as the product of two separable functions, namely, a function dependent on temperature, $g(T)$, and a function dependent on the fractional degree of conversion, $f_1(\alpha)$. Thus

$$\left(\frac{\partial \alpha}{\partial t}\right)_T = f(\alpha, T) = f_1(\alpha)g(T)$$

(22)

Substituting eqn. (22) into eqn. (7) yields

$$h(\alpha, T) = \frac{1}{g(T)} \int \frac{d\alpha}{f_1(\alpha)} = \frac{h_1(\alpha)}{g(T)} = t + \phi(T) \tag{23}$$

Rearranging eqn. (23) gives

$$h_1(\alpha) = g(T)t + \phi_1(T) \tag{24}$$

where $\phi_1(T) = g(T)\phi(T)$. Initially at $t = 0$, $\alpha = 0$ and thus from eqn. (24)

$$h_1(0) = \phi_1(T) \tag{25}$$

However, $h_1(0)$ is a constant and therefore

$$\frac{d\phi_1}{dT} = \frac{d(g\phi)}{dT} = 0 \tag{26}$$

Differentiating eqn. (23) with respect to temperature yields

$$\left(\frac{\partial h}{\partial T}\right)_\alpha = -\frac{h_1(\alpha)g'(T)}{[g(T)]^2} = -(t + \phi(T))\frac{g'(T)}{g(T)} \tag{27}$$

where $g'(T)$ denotes the derivative $dg(T)/dT$. Therefore eqn. (12) becomes

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T \left[1 + \frac{\beta}{g(T)}\left(tg'(T) + \frac{d\phi_1(T)}{dT}\right)\right] \tag{28}$$

However, since $d\phi_1/dT = 0$, the non-isothermal kinetic rate equation simplifies to

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T \left[1 + \beta t \frac{d}{dT}(\ln g(T))\right] \tag{29}$$

If the reaction is governed by a single Arrhenius kinetic rate constant such that

$$g(T) = k = Ae^{-E/RT} \tag{30}$$

then

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T \left[1 + \frac{\beta t E}{RT^2}\right] \tag{31}$$

For the case of a linear heating rate eqn. (31) reduces to the following form

$$\frac{d\alpha}{dt} = \left(\frac{\partial \alpha}{\partial t}\right)_T \left[1 + \frac{E(T - T_0)}{RT^2}\right] \tag{32}$$

where T_0 is the initial temperature. For the case where $g(T)$ has the form given by eqn. (30), eqn. (31) indicates that the ratio of the dynamic to the isothermal rate is independent of the functional dependence on the degree of conversion, $f_1(\alpha)$. Equation (32) has also been derived and discussed by Prime [4].

CONCLUSIONS

For any reactive system, the non-isothermal (dynamic) rate equation may be derived from a knowledge of the isothermal kinetic expression. The derivation and form of the dynamic rate equation is simplified considerably for the case where the isothermal kinetics are expressed as the product of two separable functions. Under these circumstances, the ratio of the dynamic to the isothermal rate is a function of temperature, whereas in the more general case this ratio is dependent on both the temperature and the degree of conversion.

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