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A variable reaction order model for prediction of curing kinetics of thermosetting polymers

Lei Zhao, Xiao Hu*

School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

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Abstract

Based on the study of the curing reaction of an fluorinated aliphatic cyanate ester resin using an isothermal Differential Scanning Calorimetric (DSC) method, a new kinetics model with variable reaction order was proposed to describe the curing of thermosetting resins in both the chemical controlled and diffusion controlled regions. α–T_g relationship was used to calculate the diffusion controlled reaction rate constant during cure. Then the chemical and diffusion rate constants were combined in the Simon–Gillham equation to model the overall rate constant for the entire reaction. By using the overall rate constant combined with the variable reaction order, a simple model can be built up for prediction of curing kinetics of thermosetting polymer in both the chemical and the diffusion controlled regions. The new model is simple, easy to use and has very good agreement with the experimental results.

Keywords: Curing of polymers; Kinetics; Variable "*n*" model

1. Introduction

Thermosetting polymers play an important role in industry because of their flexibility in tailoring the desired ultimate properties. In order to understand and control the curing process and to achieve optimum properties, it is imperative to study the kinetics aspects of its cure reaction, as they drive the complex changes in morphology and structure of the polymer during its processing operations.

Many studies have been conducted on the curing reaction kinetics of thermosetting resins such as epoxy, bismaleimides and polycyanurate employing various techniques, experimental procedures and data analysis methods [1–10]. Among them, isothermal Differential Scanning Calorimetric technique is the most frequently used. A variety of kinetics models have been developed to relate the chemical reaction rate to time, temperature, and curing conversion. In general, the kinetics models of thermosetting resins fall into two main types: *n*th order model and autocatalytic model. For an *n*th order kinetics model, the following equation stands [11]:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

where α is the curing conversion, n is the reaction order which is a constant independent of temperature and conversion, $d\alpha/dt$ is the reaction rate, and k is the apparent rate constant. The reaction rate constant k is temperature dependent and given by Arrhenius relationship:

$$k = Ae^{-E/RT} \tag{2}$$

where E is the activation energy, R is the gas constant (8.314 J/K), T is absolute temperature, and A is the pre-exponential or frequency factor. From Eq. (1), two characteristics can be derived for the curing reaction with nth order. One is that the reaction rate is maximum at the beginning of the curing reaction ($\alpha = 0$), and the other is that the relationship between $\ln(d\alpha/dt)$

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* Corresponding author.
E-mail address: asxhu@ntu.edu.sg (X. Hu).

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and $\ln(1-\alpha)$ must be linear, the slope of the linear curve is equal to the reaction order n and the intercept is equal to $\ln k$.

The effectiveness of the nth order kinetics model has been postulated by some researchers [12–14]. However, this model can only be applied to the earlier stage of the curing reaction of thermosetting resins, because in general, thermosetting materials exhibit the vitrification phenomenon, which greatly reduces the reaction rate before complete conversion is achieved. After vitrification, the cure process exhibits a diffusion controlled mechanism and as a consequence, the experimental conversion and conversion rate are much lower than those predicted by the above kinetics equation [15–17]. Therefore, the above nth order model does not satisfy the observed reduced reaction rate condition at the later reaction stage of the cure where the reaction becomes very slow before a complete conversion is achieved. Understanding the diffusion phenomenon of thermosetting reaction is important for achieving optimum properties of the cured resin. For curing high performance resins such as cyanate ester and bismaleimide, it is important to have a working equation to describe the entire curing process in order to obtain the optimum properties of the cured resin.

To characterize the entire curing of thermosetting reaction system, a two-step plateau kinetics model was proposed [18], which treats the kinetics model as composed of two simply nth order models:

$$\frac{d\alpha}{dt} = k_1(1-\alpha)^{n_1} \quad (\alpha < \alpha_{\text{onset}})$$

$$\frac{d\alpha}{dt} = k_2(\alpha_{\max}-\alpha)^{n_2} \quad (\alpha \geq \alpha_{\text{onset}}) \tag{3}$$

where k_1 and k_2 are the rate constants in chemical controlled and diffusion controlled regions, respectively, n_1 and n_2 are reaction orders. $\alpha_{\max}$ is the maximum or plateau conversion and α_{onset} is the onset conversion where the reaction shifts from chemical controlled to diffusion controlled. An advantage of this model is its simplicity in presentation. However, there may be some inconsistency in the region where the reaction changes from a chemical controlled to diffusion controlled processing. In addition, the chemical or physical meanings of certain parameters such as k_2 and n_2 are not clearly defined.

Another model was proposed using more fundamental approach, by considering the overall reaction rate constant to be composed of two components, one associated with the diffusion controlled reaction step and another with the chemical controlled reaction step [6,19]. This model is in the same form as Eq. (1). However, the overall reaction rate constant was defined as:

$$\frac{1}{k} = \frac{1}{k_T} + \frac{1}{k_D} \tag{4}$$

where k is the overall rate constant, k_T is the rate constant of chemical controlled region described by Arrhenius relationship, and k_D is the diffusion rate constant. k_T is a function of curing temperature (T), while k and k_D are functions of conversion (α) and curing temperature (T). The preceding equation shows that the overall rate constant is governed at one extreme by the Arrhenius rate constant when $k_T \ll k_D$ (prior to vitrification), and at the other extreme by the diffusion rate constant when $k_D \ll k_T$ (after vitrification) [18]. k_D can be described as a function of glass transition temperature by a WLF-type equation [7,8]:

$$\log\frac{k_D}{k_{D-\text{onset}}} = \frac{C_1\left[T_{g_{\text{onset}}} - T_g(\alpha)\right]}{C_2 + \left|T_{g_{\text{onset}}} - T_g(\alpha)\right|} \tag{5}$$

where C_1 and C_2 are fitting constants, $k_{D-\text{onset}}$ is an adjustable parameter, $T_{g_{\text{onset}}}$ is the glass transition temperature at the onset conversion of diffusion control. $T_g(\alpha)$ is the glass transition temperature at the conversion α.

After combining Eqs. (1) and (4), the simple nth order model can be applied in the entire curing range of thermosetting polymer. It should be pointed out that even in the chemical controlled region, the nth order kinetics model with a fixed reaction order is only accurate within a narrow range of conversion. Large error may result when this model is used to predict the cure kinetics in wider range of conversion although this has often been overlooked in literatures so far [13–15].

This is understood because the fixed reaction order model is based on the assumption that the functional groups have equal reactivity and maintain the same reaction mechanism during the entire curing process. This assumption can be accepted for reaction systems with low molecular weight, but for curing of thermosetting resins, this assumption may not be accurate because the reactivity of the functional groups decreases with the increase of curing conversion due to increasing viscosity. The increase in the viscosity reduces the mobility and accessibility of the reactive functional group and results in decreasing reactivity and possibly varying reaction mechanism. In this work, we take into account of this effect and a kinetics model with variable reaction order n was proposed.

The cure kinetics of cyanate ester has attracted much research attention. Cyanate ester resins are known to cure via a cyclotrimerization to form a polycyanurate network as shown in Fig. 1. To understand and control the curing processing of this new generation thermosetting resin to design suitable processing parameters and achieve optimum properties, it is imperative to study the kinetics aspects of its cure reaction, as they drive the complex changes in morphology and structure of the polymer during its processing operations.

Fluoromethylene cyanate ester $NCOCH_2(CF_2)_6CH_2OCN$ (DFCy) was developed recently for optic–electrical applications. Unlike most aromatic cyanate esters, it is not meant to be used as the matrix for high performance fiber reinforced composites, due to its significantly low T_g (about 92 °C). However, DFCy possesses the lowest dielectric constant (2.3–2.6) among the known cyanate ester resins. And it also has low refractive indices in the range 1.382–1.447 as well as low optical loss, which makes it attractive in optic–electrical

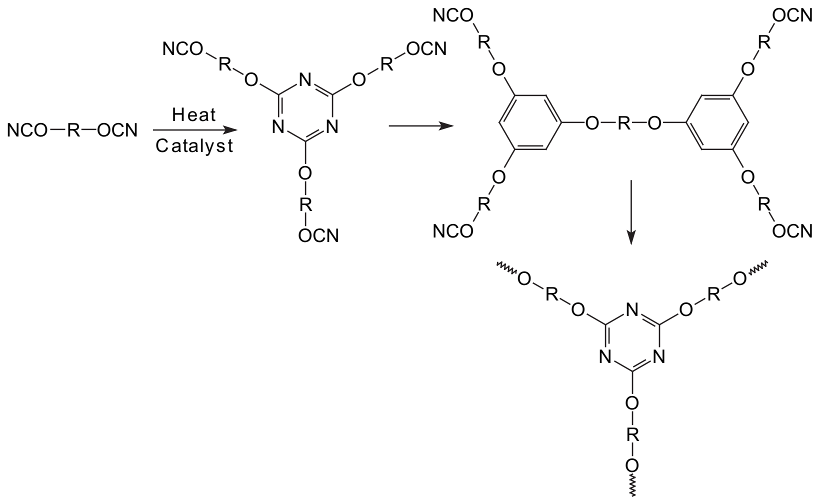

Fig. 1. Polycyclotrimerization reaction of cyanate ester to form triazine network.

applications. Snow et al. attempted to use a second order autocatalytic kinetics model to describe the curing reaction of DFCy but the assumption was found to be incorrect, because they obtained a negative value of the reaction rate constant, which is inconsistent with the mechanism associated with the rate law [20].

In this study, the kinetics of DFCy cyanate ester was investigated in detail. DSC was used to obtain the reaction kinetics data. New models were developed to accurately describe the curing reactions in both the chemical and the diffusion controlled regions for the isothermal measurement.

2. Experimental

2.1. Material

The $NCOCH_2(CF_2)_6CH_2OCN$ (2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorooctanediol dicyanate ester, DFCy) was from Oakwood products Inc. It is a white solid powder.

2.2. Conversion and T_g measurement of partially cured resin

DSC measurements were performed using a TA instrument DSC 2010. Before the measurement, the temperature, baseline and heat flow calibrations were carried out by the recommended procedures using pure indium with a melting point 156.4 °C and heat of fusion, $\Delta H_f = 6.80$ cal/g.

The percentage conversions of partially cured polymers were determined by the following procedures. Sample, around 5 mg, was hermetically sealed in an aluminum pan. The sample was then cured in the DSC cell at an isothermal temperature for different periods of time. The cured sample was quenched in ice-water and scanned again from room temperature to 400 °C at 5 °C/min. The DSC scans yielded the T_g and residual heat of reaction, ΔH_{res}. The temperature corresponding to the midpoint of the endothermic deflection of the baseline was taken as the T_g. ΔH_{res} was calculated from the exotherm area, as shown in Fig. 2(a). The conversion α of each sample was calculated from the equation below:

$$\alpha = \frac{\Delta H_{tot} - \Delta H_{res}}{\Delta H_{tot}} \tag{6}$$

where ΔH_{tot} is the total heat of reaction, which was calculated from the exotherm area of an uncured sample divided by the mass of the sample.

2.3. Isothermal DSC measurement

Curing kinetics study was performed using an isothermal method. To select suitable temperatures for the required isothermal experiments, a dynamic DSC scan at a heating rate of 5 °C/min was first obtained (Fig. 2(b)). Temperatures above but near the onset of reaction were chosen. This method could avoid the improper choice of temperature. Isothermal experiments were carried out at 140, 150, 160, 170, 180 and 190 °C in this work.

In an isothermal experiment, the sample pan was placed in the DSC cell at 50 °C, and nitrogen gas was used for purging at a flow rate of 60 cc/min. After the system becomes stabilized, the temperature was raised to the isothermal curing temperature at a heating rate of 200 °C/min. This is to minimize the unrecorded reaction heat during the initial heating before data collection was initiated. After holding at this isothermal temperature till there is no change in the heat flow, the experiment is stopped. The conversion at time t, $\alpha(t)$, can be determined from Eq. (7):

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{tot}} \tag{7}$$

where $\Delta H(t)$ is the enthalpy of the reaction at time t. For a given isothermal temperature, $\Delta H(t)$ is the accumulative

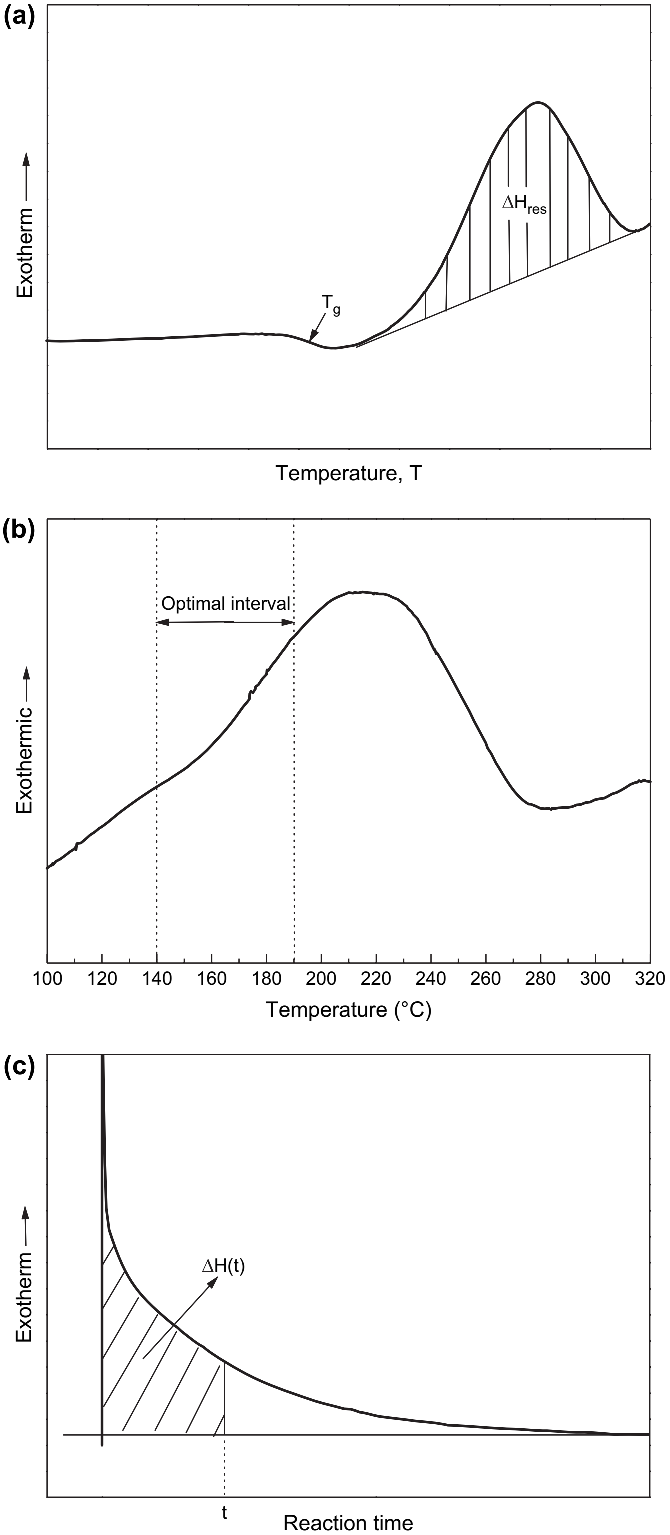

Fig. 2. (a) Schematic diagram of the measurement of ΔH_{res} and T_g; (b) selection guide of the isothermal curing temperatures; (c) calculation of $\Delta H(t)$ by partial integration.

heat of reaction up to curing time t and given by the area above the baseline and below the curve, as shown in Fig. 2(c). The baseline is a straight tangential line to the horizontal part of the isothermal DSC curing curve.

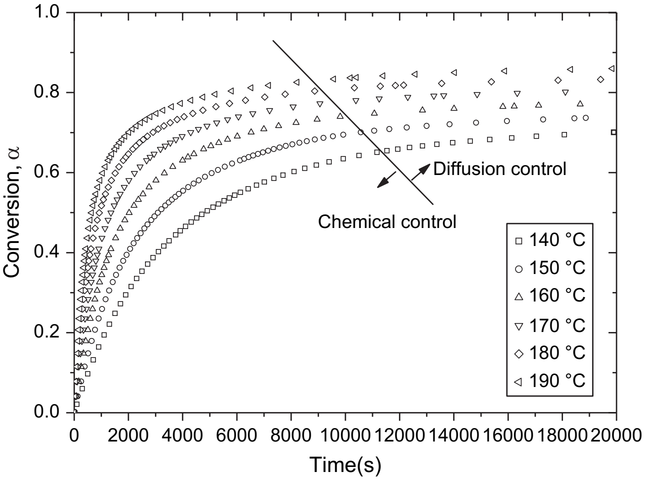

Fig. 3. Experimental data of conversion versus curing time for DFCy. The solid line is an arbitrary division of chemical controlled and diffusion controlled regions.

3. Results and discussion

3.1. Second order autocatalytic model

Fig. 3 shows the experimental curves of conversion (α) versus curing time (t) of DFCy at isothermal curing temperatures from 140 to 190 °C at intervals of 10 °C.

The reaction rate, $d\alpha/dt$, can be obtained by differentiating the α–t curve. $(d\alpha/dt)$–t curve of DFCy at different isothermal curing temperatures 140–190 °C is plotted and is shown in Fig. 4.

The kinetics of the aromatic cyanate cyclotrimerization polymerization has been characterized by several models and the following has been reported to have particularly good agreement with conversion in the early stages of the polymerization.

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1-\alpha)^2 \tag{8}$$

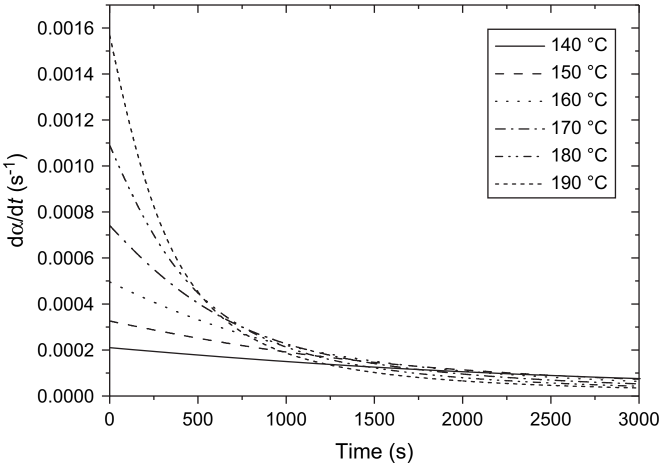

Fig. 4. Reaction rate versus curing time at different isothermal temperatures for DFCy.

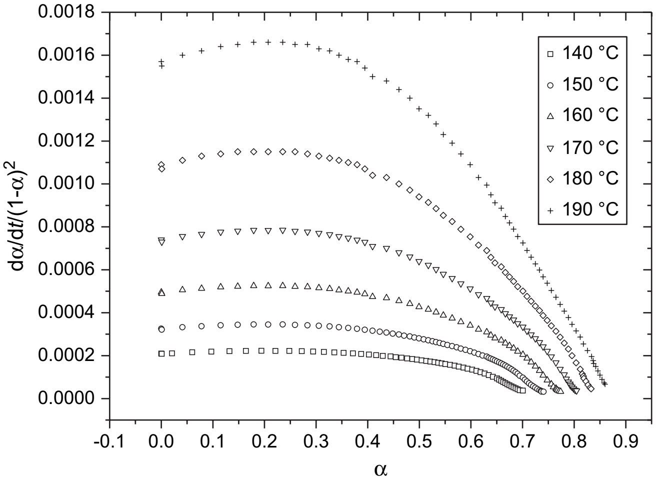

Fig. 5. $(d\alpha/dt)/(1-\alpha)^2$ versus conversion α at different isothermal temperatures for DFCy.

where α is the conversion of the cyanate groups, and k_1 and k_2 are empirical rate constants. Reaction time and conversion data at temperatures 140–190 °C are plotted according to this model in Fig. 5.

It can be seen from Fig. 5 that at early polymerization stage, the relationship between $(d\alpha/dt)/(1-\alpha)^2$ and α can be considered as linear and they are approximately parallel to the X axis, the slope is near to zero, which means $k_2 \approx 0$. Therefore, the autocatalytic effect is very weak and can be neglected. The reaction resembles the *n*th order reaction kinetics. Also it can be seen from Fig. 5 that there is an increasing deviation from linearity with increasing conversion, indicating that the reaction kinetics cannot be simply considered as second order.

3.2. Variable ‘n’ kinetics model for chemical controlled region

Since kinetics cannot be accurately described the second order autocatalytic model, in this study, we build up a variable reaction order model, which is simple, easy to use and has very good agreement with the experimental results.

It can be observed from Fig. 3 that the reaction rate ($d\alpha/dt$) of the cyanate ester reaction is initially rapid and then slows down after the transition from a chemical controlled to a diffusion controlled mechanism. Finally the conversion reaches a plateau towards maximum conversion (α_{max}). The plateau conversion can be empirically expressed as [21]:

$$\alpha_{max} = p_1\left(\frac{1}{T_1} - \frac{1}{T}\right) \tag{9}$$

where p_1 is a fitting parameter, T is the curing temperature, and T_1 is the theoretical critical temperature below which no cure reaction could occur ($\alpha_{max} = 0$). An approximate transition from the chemical control to diffusion control was marked by an indicative line in Fig. 3. It can also be seen that the onset conversion, α_{onset}, at which the reaction becomes dominated by diffusion, increases with increasing curing temperature, as does the maximum or plateau conversion.

Using a similar approach reported earlier [6], in this present study, the relationship between the onset conversion and the curing temperature is established:

$$\alpha_{onset} = p_2\left(\frac{1}{T_2} - \frac{1}{T}\right) \tag{10}$$

where p_2 is a fitting parameter, T is the curing temperature, and T_2 is the hypothetical critical temperature below which no chemical controlled reaction could occur ($\alpha_{onset} = 0$) when $T = T_2$. In Eqs. (9) and (10), the upper bound of α_{max} and α_{onset} is unity. The parameters p_1, p_2, T_1, and T_2 can be obtained from curve fitting of α_{max} and α_{onset} versus curing temperature T, as shown in Fig. 6 ($p_1 = 601.5$ K, $p_2 = 664.8$ K, $T_1 = 278.6$ K, and $T_2 = 293.0$ K). In this study, the conversions at 20,000 s were taken approximately as the α_{max}. The values of α_{onset} are obtained by comparing the experimental data and our variable ‘*n*’ kinetics model shown in Fig. 11, which are estimated as the points where the experimental data deviate significantly from the proposed model due to the onset of the diffusion controlled mechanism. This will be discussed in detail later.

Fig. 4 shows that the reaction rate ($d\alpha/dt$) is maximum at the beginning of the reaction ($t = 0$). The kinetics resembles the *n*th order reaction kinetics. Hence the plot of $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ should be linear with the slope equal to the reaction order n.

Fig. 7 shows the plots of $\ln(d\alpha/dt)$ against $\ln(1-\alpha)$ for DFCy. However, it can be seen that the relationship between $\ln(d\alpha/dt)$ and $\ln(1-\alpha)$ is approximately linear at the initial reaction stage ($\alpha \le 0.35$) at the isothermal curing temperatures studied in this work, then it deviates considerably from linear relationship at higher conversions. The abrupt change in slope seen in Fig. 6 indicates that the reaction mechanism shifts from chemical controlled to diffusion controlled. The shift is marked at an onset conversion, α_{onset}, which increases with increasing temperature. Their relationship can be described

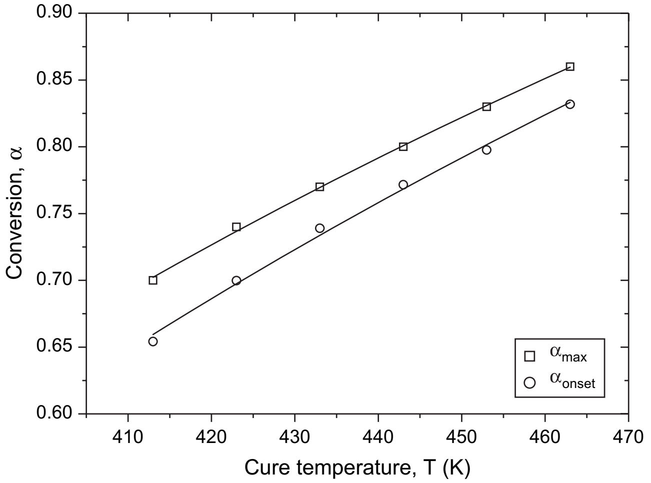

Fig. 6. Maximum conversion and onset conversion versus curing temperatures for DFCy.

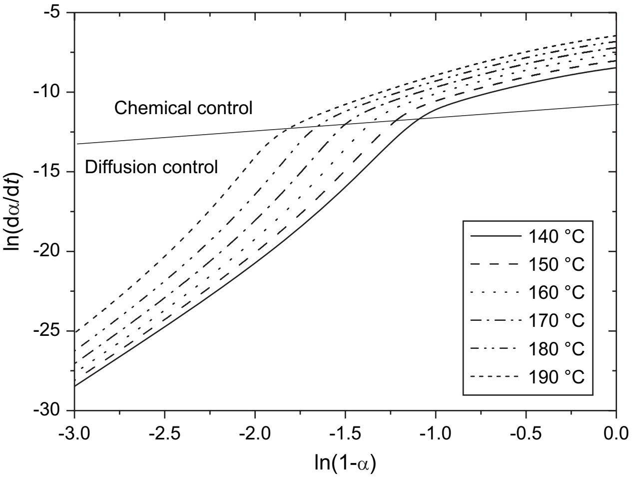

Fig. 7. Plots of $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ at different isothermal temperatures for DFCy.

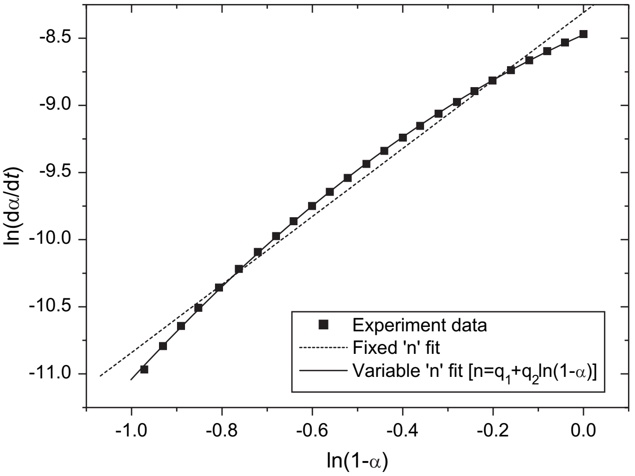

Fig. 8. Plots of $\ln(d\alpha/dt)$ as a function of $\ln(1-\alpha)$ at the isothermal temperature of 140 °C.

by Eq. (10). In a normal nth order kinetics model, the 'n' values are obtained from the linear fitting of $\ln(d\alpha/dt)$ against $\ln(1-\alpha)$ at different reaction temperatures. However, the linear relationship assumption is only valid at initial stage of reaction ($\alpha \leq 0.35$). Therefore, large errors are expected in this fixed 'n' kinetics model at moderate and high conversion regions. Fixed 'n' kinetics model may be useful as a simplistic approximation for processing control of thermosetting polymers, but it is inaccurate and cannot provide insight into the understanding of the fundamentals in curing reactions. In fact, in the chemical controlled region, it can be seen from Fig. 7 that the relationship between $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ deviates significantly from linear relationship. Based on this observation, a variable 'n' kinetics model is proposed in this study.

In this study, we assume a conversion dependent reaction order n and the kinetics model for the chemical controlled region is modified as:

$$\frac{d\alpha}{dt} = k(1-\alpha)^{n(\alpha)}, \quad [n(\alpha) = q_1 + q_2 \ln(1-\alpha)] \tag{11}$$

where the reaction order is not a constant, but a function of conversion $n = n(\alpha)$. q_1 and q_2 are the fitting parameters.

To further illustrate this variable 'n' model, an enlarged plot of $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ in the chemical controlled region at 140 °C is shown in Fig. 8 as an example.

It can be seen that using the variable 'n' kinetics model resulted in much better fitting to the experimental data than the fixed 'n' model. The reaction order, n, actually did not keep constant during the curing process at the isothermal temperatures studied. At the initial stage of the reaction, the reaction order is the lowest. With the increase of the curing conversion or reaction time, the reaction order also increases.

The rate constant k is temperature dependent and given by Arrhenius relationship. According to Arrhenius equation (Eq. (2)), the activate energy E and frequency factor A can be obtained by plotting $\ln(k)$ against $1/T$ as shown in Fig. 9. The obtained E and frequency factor A for DFCy were 67,248 J/mol and 63,704 s^{-1}, respectively.

Eq. (11) was used to fit the experimental data of $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ for each isothermal temperature studied (the fit for data obtained at 140 °C was shown in Fig. 8 as an example). It can be observed that the conversion predicted by the variable 'n' kinetics model is closer to the experimental data in comparison to fixed 'n' model. It can be clearly seen from Fig. 10(a)–(c) shows that the variable 'n' model is notably better in the chemical controlled region and has almost perfect fitting to the experimental data at early stage of the curing reaction.

Fig. 11 shows the comparison of experiment α–t data versus that predicted by the variable 'n' reaction kinetics model for DFCy.

In Fig. 11, all the experimental data obtained at different isothermal temperatures agree well with the variable 'n' kinetics model prediction throughout the chemical controlled region ($\alpha < \alpha_{onset}$). The experimental data then deviate from the model at certain conversion as expected. For different isothermal temperatures, the values of α_{max} are also different. It can be seen that the higher the isothermal temperature, the

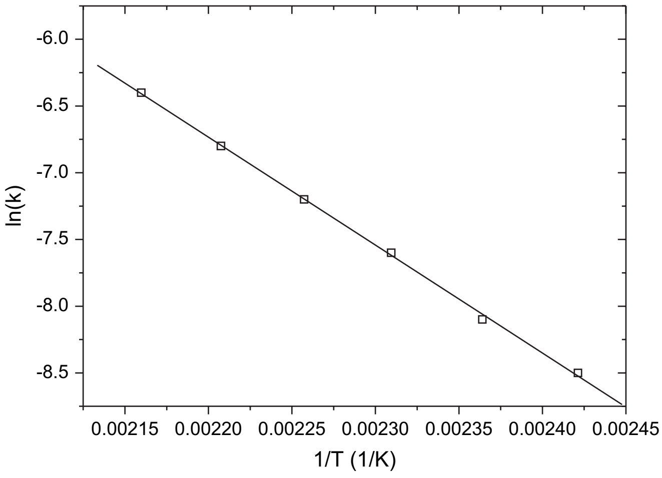

Fig. 9. Arrhenius plots of the rate constants in chemical controlled and diffusion controlled regions as a function of $1/T$.

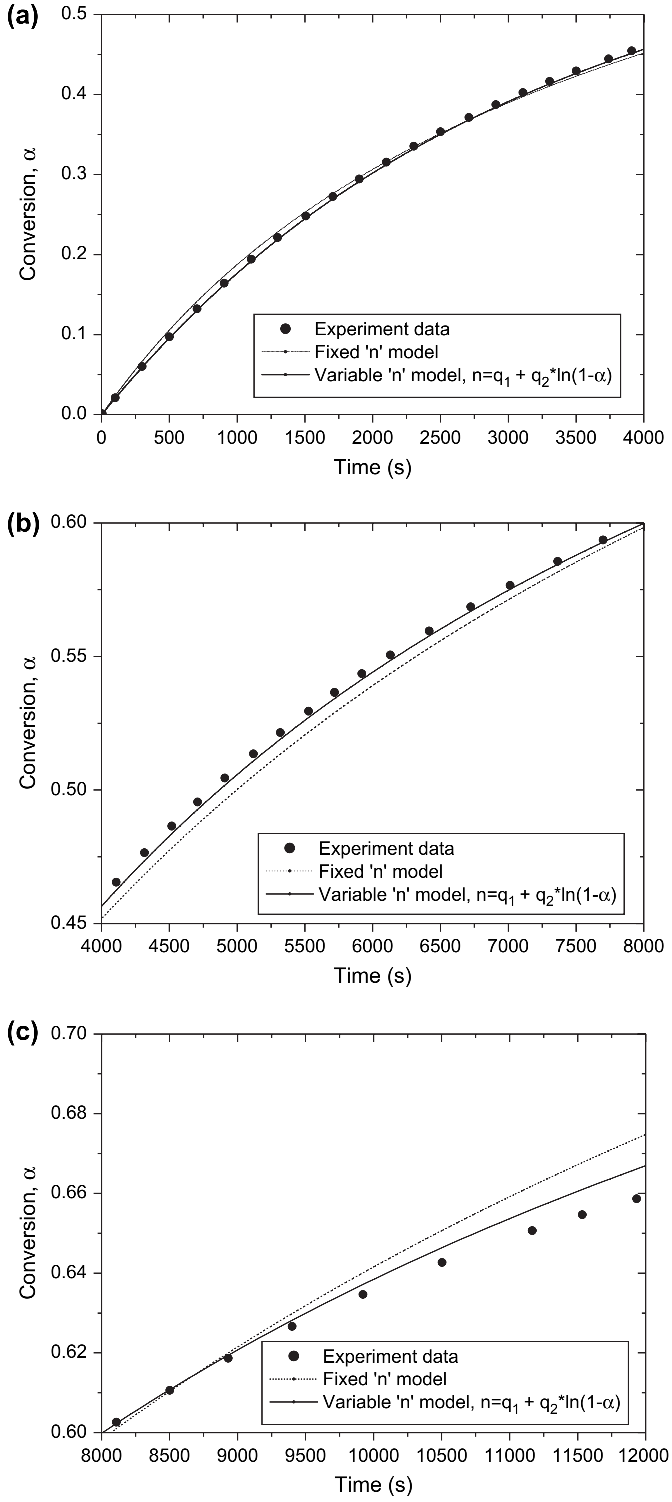

Fig. 10. Comparison of fixed '*n*' model and variable '*n*' model at isothermal temperature 140 °C.

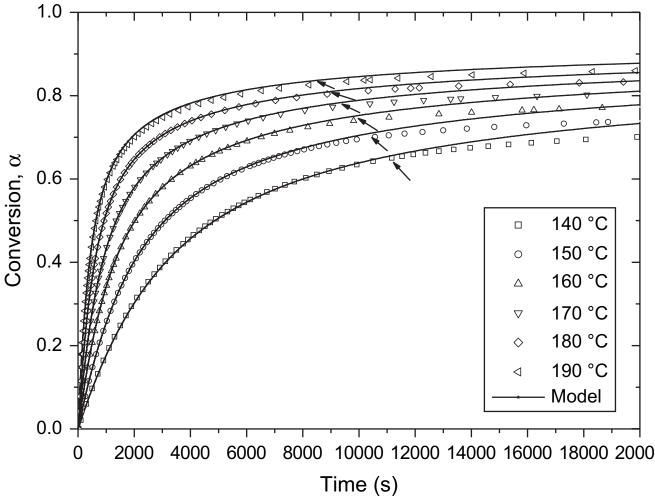

Fig. 11. Comparison of experimental data versus variable '*n*' kinetics model in chemical controlled region.

higher the onset conversion. This agrees well with Eq. (10) and Fig. 6 as discussed earlier.

When $\alpha > \alpha_{\text{onset}}$, the reaction mechanism shifts from chemical controlled to diffusion controlled. Thus the model based on Eq. (11) is not applicable. The reaction system shows viscoelastic behavior and the reaction rate becomes much slower than that in the chemical controlled region. The rate constant in the diffusion controlled region can be described in terms of the well-known WLF equation.

3.3. Variable '*n*'–WLF kinetics model

In this study, a new kinetics model, which combines the variable '*n*' kinetics model and the WLF equation, is proposed for the entire conversion range of the curing reaction. A similar approach adapted by Simon and Gillham [7] is used (Eq. (4)).

In practice, k_T can be obtained by fitting the experimental data at the early curing stage ($\alpha < \alpha_{\text{onset}}$). The overall rate constant k can be determined from the following equation:

$$k = \frac{\mathrm{d}\alpha/\mathrm{d}t}{(1-\alpha)^n} \tag{12}$$

Then the diffusion rate constant k_D can be obtained from Eq. (4). However, a kinetics model is proposed using the variable '*n*' approach in this study, where $n = n(\alpha) = q_1 + q_2 \ln(1-\alpha)$ as described in Eq. (11). In this case:

$$k = \frac{\mathrm{d}\alpha/\mathrm{d}t}{(1-\alpha)^{q_1+q_2\ \ln(1-\alpha)}} \tag{13}$$

The experimental overall rate constant as a function of conversion at an isothermal curing temperature of 140 °C is shown in Fig. 12 as an example. It can be seen that in the chemical controlled region, $k \approx k_T$. Then there is a region where both chemical control and diffusion control are effective, i.e., k_T is comparable to k_D. At the later curing stage, the reaction is dominated by diffusion controlled mechanism, $k \approx k_D$. Eq. (13) is in fact a new versatile and universal equation and we name it as Hu–Zhao equation.

The diffusion rate constant is expected to be inversely proportional to the relaxation time of the polymer segments. It was suggested that the temperature dependence of k_D can be described by WLF equation [7,8] (Eq. (5)).

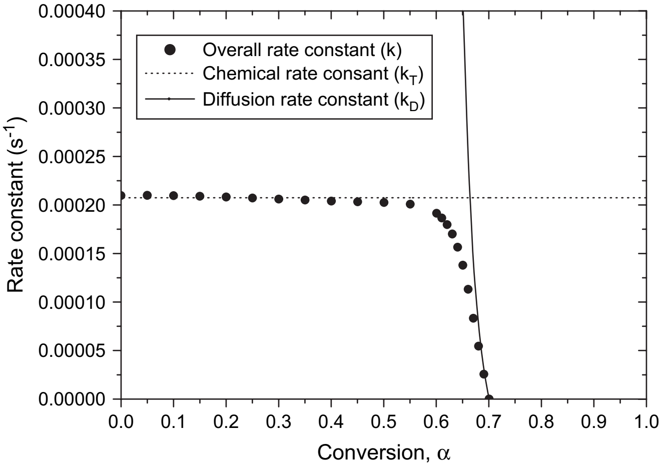

Fig. 12. Relationship between overall rate constant and α at 220 °C for DFCy. Where k and k_T are obtained experimentally. k_D is then calculated using Eq. (4).

Since the relationship between k_D and conversion has been established, once the correlation between glass transition temperature, T_g, and conversion is established, the diffusion rate constant k_D can be expressed explicitly as a function of temperature and conversion. Then the unknown parameters in Eq. (5) can be obtained accordingly. The measured T_g of DFCy as a function of conversion is given in Fig. 13. The experimental curve was fitted using Dibenedetto equation [21,22]:

$$T_g(\alpha) = \frac{(1-\alpha)T_{g_0} + \lambda\alpha T_{g_\infty}}{1-\alpha+\lambda\alpha} \tag{14}$$

where α is the conversion. T_{g_0} is the theoretical glass transition temperature of the polymer at very low conversion. T_{g_∞} is the glass transition temperature of the fully cured polymer and λ is a fitting parameter. Both T_{g_0} and T_{g_∞} are obtained by curve fitting the experimental data using the Dibenedetto equation.

Once the relationship between conversion and glass transition temperature is established, the parameters in Eq. (5) can be obtained by plotting the logarithm of diffusion rate constant k_D versus $(T_{g_{onset}} - T_g)/(C_2 + |T_{g_{onset}} - T_g|)$. The fitting constant C_2 is accepted as the WLF universal constant, 51.6. The obtained parameters for the variable 'n'–WLF kinetics model are listed in Table 1. The comparison of experimental data versus those calculated from the model is shown in Fig. 14. It can be seen that the variable 'n'–WLF type kinetics model describes the curing behavior very well. Excellent agreement between experimental data and model is observed for the entire conversion range at different isothermal temperatures, including both chemical controlled and diffusion controlled regions.

In summary, the equations used in the variable 'n'–WLF kinetics model are listed below. Table 1 lists the kinetics parameters for DFCy.

$$\frac{d\alpha}{dt} = k(1-\alpha)^{q_1+q_2\ \ln(1-\alpha)}$$

$$\frac{1}{k} = \frac{1}{k_T} + \frac{1}{k_D}$$

$$k_T = Ae^{-E/RT}$$

$$\log\frac{k_D}{k_{D-onset}} = \frac{C_1\left[T_{g_{onset}} - T_g(\alpha)\right]}{C_2 + \left|T_{g_{onset}} - T_g(\alpha)\right|}$$

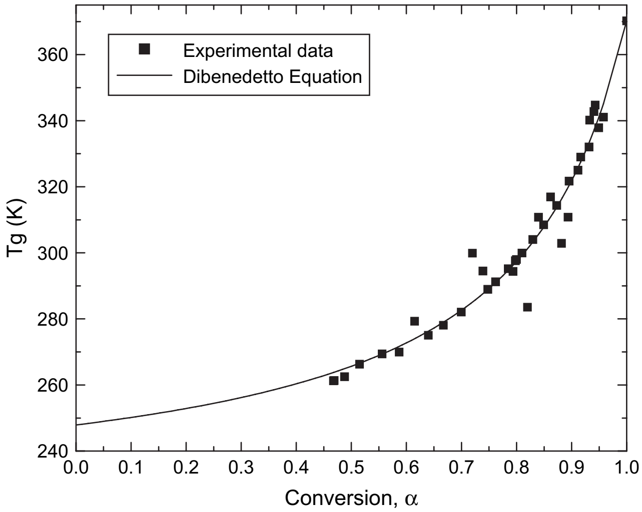

Fig. 13. Plots of T_g versus conversion for DFCy.

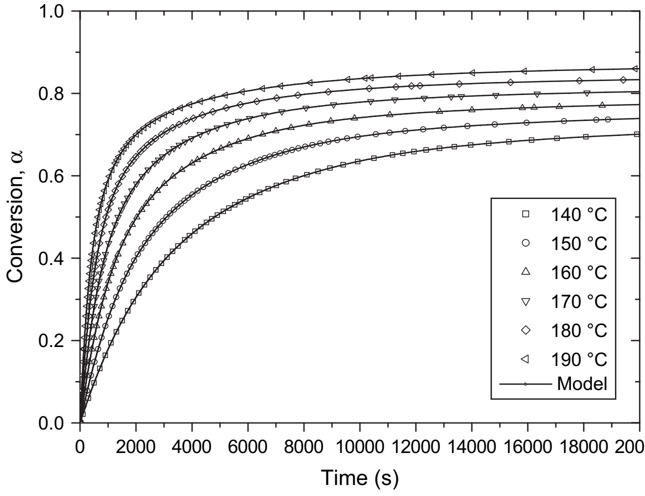

Fig. 14. Comparison of experimental data versus variable 'n'–WLF type kinetics model.

Table 1
Parameters of variable 'n' kinetics model for DFCy

$A = 63{,}704$ (s^{-1})	$E = 67{,}248$ (J/mol)	$q_1 = 1.5$	$q_2 = -1.0$
$T_{g_0} = 247.9$ (K)	$T_{g_\infty} = 370.2$ (K)	$\lambda = 0.17$	$p_2 = 664.8$ (K)
$C_1 = 8.16$ (K)	$C_2 = 51.6$ (K)	$k_{D-onset} = 2.24 \times 10^{-3}$ (s^{-1})	$T_2 = 278.6$ (K)

$$\alpha_{\text{onset}} = p_2\left(\frac{1}{T_2} - \frac{1}{T}\right)$$

$$T_g(\alpha) = \frac{(1-\alpha)T_{g_0} + \lambda\alpha T_{g_\infty}}{1-\alpha+\lambda\alpha}$$

4. Conclusions

The kinetics study of the aliphatic cyanate ester DFCy indicates that the reaction follows *n*th order kinetics model in the chemical controlled region and approaches a plateau conversion at certain curing temperature, which is less than complete conversion. The diffusion limitation occurs at certain onset conversion, and this onset conversion increases with the increase of isothermal curing temperature. Results indicate that the reaction order '*n*' may not a constant throughout the whole reaction time. A conversion dependent reaction order was proposed, based on which a new kinetics model, which combines the variable '*n*' kinetics model and WLF equation, was established to describe both the chemical and the diffusion controlled regions. For the temperature range studied (140–190 °C), the new variable '*n*' kinetics model predicts the experimental data with excellent accuracy. This variable '*n*' kinetics model or Hu–Zhao equation should be applicable for other thermosetting systems which follow the *n*th order kinetics in general.

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