Polymer 51 (2010) 3814–3820

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Autocatalytic curing kinetics of thermosetting polymers: A new model based on temperature dependent reaction orders

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A R T I C L E I N F O

Article history:
Received 25 March 2010
Received in revised form
26 May 2010
Accepted 27 May 2010
Available online 17 June 2010

Keywords:
Autocatalytic reactions
Curing kinetics model
Thermosetting polymers

A B S T R A C T

Herewith we discuss a new model for thermoset polymers that follow the autocatalytic curing kinetics. This model is proposed upon investigation of the crosslinking reaction of 2,2′-Bis(4-cyanatophenyl)isopropylidene (BACy), under isothermal conditions over a range of temperatures between 180 °C and 260 °C without catalyst. BACy undergoes crossslinking via a trimerization mechanism of the nitrile groups following an autocatalytic kinetics rather than an *n*th order kinetics. Comparing with other autocatalytic kinetics models, the new model takes into account that the reaction orders of the curing reactions in the polymers are temperature dependent variables rather than constants. The new model provides excellent agreement with the experimental data in a wide range of conversions and reaction temperatures.

1. Introduction

Thermosetting resins including cyanate esters or polycyanurates continue to play an important role in several key industries including aerospace, energy, automotive, coatings, microelectronics and optoelectronics because of their versatility in tailoring desired properties. Their applications span structural, such as those in composites, and functional, such as those in lithography, waveguides, and other photonic devices. Understanding and accurate controlling of the curing process is a pre-condition to select suitable processing parameters and to achieve optimum properties. It is, therefore, imperative to study the kinetics of the cure reactions, as it is a governing factor of morphology and structure development of the polymers. Many studies have been conducted on the curing kinetics of thermosetting polymers, and a variety of kinetic models have been proposed to relate the reaction rate to time, temperature, and conversion [1–18]. In general, the kinetics models of thermosetting resins fall into two main types, (1) *n*th order model and (2) autocatalytic model because there are two categories of crosslink reactions differentiated by whether the maximum rate of reaction occurs at zero conversion or at a finite conversion value. The *n*th order model is often simple expressed by the reaction rate equation [1]:

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

where α is the conversion, n is the reaction order, $d\alpha/dt$ is the reaction rate, and k is the apparent rate constant. Equation (1) automatically assumes that n is a constant independent of temperature and conversion and predicts a linear relationship between $\ln(d\alpha/dt)$ and $\ln(1-\alpha)$. In most studies so far, these assumptions were accepted although there are often large discrepancies from the reality. In our earlier study, we attempted to address such discrepancies by recognizing that the assumed linear relationship is often only valid at very low conversion and substantial deviation was seen at moderate and high conversion. An alternative model was proposed which was able to provide excellent description of reactions that follows *n*th order kinetics [6].

However, the *n*th order model cannot describe the progress of complex reactions of some thermosetting resin systems in which autocatalysis presents [8–11,18–25]. For example, Equation (1) predicts the maximum of reaction rate at zero conversion which is not the case for the category of thermosetting resins including epoxy/amine systems and some bismaleimides [11] and the polycyanurate reported in this study. Instead there is a different model proposed first by Kamal et al. [18,19] based on studies of epoxy resins which represents autocatalytic curing kinetics as shown in Equation (2).

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

where k_1 and k_2 are two individual rate constants following Arrhenius temperature dependency. Two reaction orders m and n are introduced that are constants. The autocatalytic kinetics model

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doi:10.1016/j.polymer.2010.05.056

derived from Equation (2) predicts maximum reaction rate ($d\alpha/dt$) at an intermediate conversion ($\alpha > 0$). Mathematically, at the point of maximum reaction rate, $d(d\alpha/dt)/d\alpha = 0$, hence the following equation can be derived from Equation (2):

$$\left(\alpha^m - \frac{m}{m+n}\alpha^{m-1}\right)\Big|_{\frac{d\alpha}{dt}=\left(\frac{d\alpha}{dt}\right)_{\max}} = -\frac{n}{m+n}\frac{k_1}{k_2} \tag{3}$$

Usually $k_1 << k_2$, then we have:

$$\alpha_{\max} = \alpha|_{\frac{d\alpha}{dt}=\left(\frac{d\alpha}{dt}\right)_{\max}} \approx \frac{m}{m+n} \tag{4}$$

For a typical autocatalytic reaction, $\alpha_{\max}$, the conversion at which the reaction rate reaches its maximum is around 0.3–0.4 [26]. This model has been found useful and received much attention [8–11,18–25] because it is able to address the inability of the Equation (1) in describing reactions of many thermosetting polymers when maximum rate of reaction is not at zero conversion ($t = 0$ or $\alpha = 0$) due to autocatalysis. However, controversy remains in literatures because of the limitations of this model. One of the limitations arose from the fact that both m and n are not necessarily constants, although this model is still widely used even though serious inconsistency exists between the theory and experimental data because of lack of alternative models. This work is therefore devoted to derive a new kinetics model for autocatalytic curing reactions. Curing kinetics of catalyzed cyanate ester systems has been reported and different techniques, such as DSC [27,28], FTIR [29], and DEA (Dielectric analysis) [30] have been employed to monitor the curing reaction. Polycyanurate is selected in this study not only because of its proven significance in aerospace and electronics [31–35] and its potentials in optical telecommunications, [36–42] but also because it serves as a good model compound for reaction kinetics studies. Its reaction may follow either nth order or autocatalytic kinetics depending on whether a catalyst is used. However, very few studies were reported on the curing kinetics of uncatalyzed aromatic polycyanurates [43,44]. Although the catalyzed polycyanurate systems are often used in composites applications, uncatalyzed systems are important for dielectric or photonic applications, because the use of catalysts may be detrimental to their dielectric or optical properties. In the present study, we selected 2,2′-Bis(4-cyanatophenyl)iso-propylidene (BACy) with no added catalyst, which provides an ideal platform to derive new autocatalytic kinetics models. By introducing a temperature dependency of reaction orders, an alternative model is derived which provides accurate prediction of autocatalytic reaction kinetics in thermosets.

2. Experimental

2.1. Materials and characterization techniques

2,2′-Bis(4-cyanatophenyl)iso-propylidene (BACy) is from Ciba (under the trade name is AroCy® B-10, purity > 99%). Its chemical structure is shown in Fig. 1. It is thoroughly dried before experiment. DSC measurements were performed using a TA instrument DSC 2010. Sample (around 5 mg) was hermetically sealed in aluminum pans for the analysis. Before the measurement, the temperature, baseline and heat flow calibrations were carried out by the recommended procedures using pure indium of melting point 156.4 °C and heat of fusion, $\Delta H_f = 6.80$ cal/g.

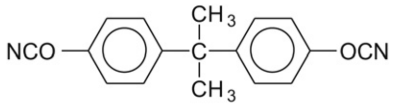

Fig. 1. Chemical structure of 2,2′-Bis(4-cyanatophenyl)iso-propylidene.

2.2. Determination of relationship between T_g and conversion

The percentage conversions of partially reacted polymers were determined by the following procedures. The samples were cured in the DSC cell at an isothermal temperature for different periods of time. The reaction was quenched after different levels of the partial curing and the samples were then scanned again from room temperature to 400 °C at 5 °C/min. The latter scans give information on both the T_g and the residual heat of reaction, $\Delta H_{\text{residue}}$ of the polymer at different conversions. The temperature corresponding to the midpoint of the endothermic deflection of the baseline was taken as the T_g. $\Delta H_{\text{residue}}$ was calculated from the exothermic peak area. The conversion α of each sample was calculated from Equation (5):

$$\alpha = \frac{\Delta H_{\text{total}} - \Delta H_{\text{residue}}}{\Delta H_{\text{total}}} \tag{5}$$

where ΔH_{total} is the total heat of reaction of the monomer which was determined using DSC.

2.3. Isothermal DSC measurement

Reaction kinetics was followed using an isothermal mode using DSC. To select suitable temperatures for the required isothermal experiments, a dynamic DSC scan at a heating rate of 5 °C/min was first obtained (shown in Fig. 2). Temperatures above but near the onset of reaction were chosen. This method could avoid the improper choice of temperature, which may be too high or too low. Isothermal experiments were carried out at 180 °C, 200 °C, 220 °C, 240 °C, and 260 °C. In the isothermal experiment, the sample pan was placed in the DSC cell at a temperature of 50 °C, and nitrogen gas was used for purging at a flow rate of 60 cc/min. After the system reached equilibrium, the temperature was quickly raised to the isothermal curing temperature at a heating rate of 200 °C/min. This is to minimize unrecorded reaction heat during the initial heating before data collection was initiated. After holding at the isothermal temperature till there is no change in heat flow, the experiment is stopped. The conversion at time t, $\alpha(t)$, can be determined from the equation:

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{\text{total}}} \tag{6}$$

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

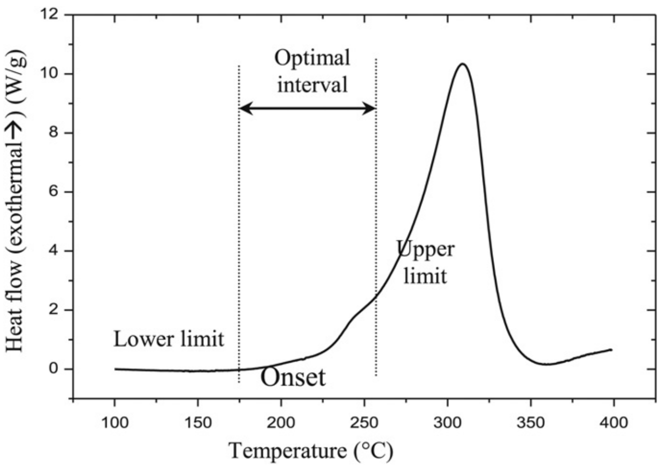

Fig. 2. Selection of isothermal curing temperature.

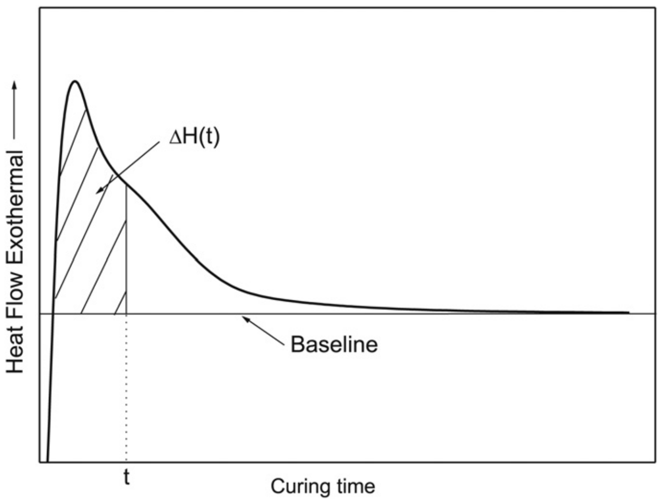

Fig. 3. A typical isothermal DSC curing curve.

up to curing time t and given by the area above the baseline and below the curve, as shown in Fig. 3. The baseline is a straight tangential line to the horizontal part of the isothermal DSC curve.

3. Results and discussion

The isothermal curing kinetics of BACy was systematically investigated at five different curing temperatures between 180 °C and 260 °C at a 20 °C interval. Fig. 4 shows the plots of the experimentally determined conversion (α) versus curing time (t) of BACy at different isothermal temperatures. It can be seen that the increase of conversion with time is initially slow, then becomes more rapid, and then slows down again before the conversion finally reaches a plateau towards the maximum. The plot of $\alpha-t$ shows an 'S' shape which is the characteristic feature of autocatalytic kinetics and different from those of the reactions following the *n*th order kinetics model. This is particularly notable in $\alpha-t$ curves of lower curing temperatures. Usually, there is a trace amount of phenol impurities in the monomers of aromatic polycyanurate which resulted from the synthesis process. These phenol impurities have some catalytic effect for the initiation of the cyclotrimerization of cyanate esters. Because the phenol concentration is very low, the reaction rate is also very low, until sufficient amount of reaction intermediates are generated, which autocatalyze of the reaction leading to reaction rate acceleration. Another important phenomenon is the diffusion at the later curing stage [28,29]. At low conversion, the concentration of the functional groups is high and the mobility of the molecules is not constrained. At higher conversion, however, the viscosity of the reaction system increases with time due to the increase of molecular weight. The mobility of the reactive groups is constrained and the reaction eventually becomes diffusion controlled. Finally a plateau conversion is reached since the molecular weight and the viscosity become infinitely high. Virtually no further reaction can be observed at this point, unless the temperature is raised to increase the mobility of the molecular chains.

As mentioned earlier, the reaction behavior of thermosetting polymers may follow two different types of kinetics models, namely *n*th order model and autocatalytic model. To predict the curing kinetics of BACy, the relationship between the reaction rate versus time or conversion was obtained by differentiate the $\alpha-t$ experimental curves which lead to the $(\mathrm{d}\alpha/\mathrm{d}t)-t$ plots $(\mathrm{d}\alpha/\mathrm{d}t)-\alpha$ plots in Figs. 5 and 6 respectively. If the reaction can be described by an *n*th order kinetics model, the reaction rate should be the highest

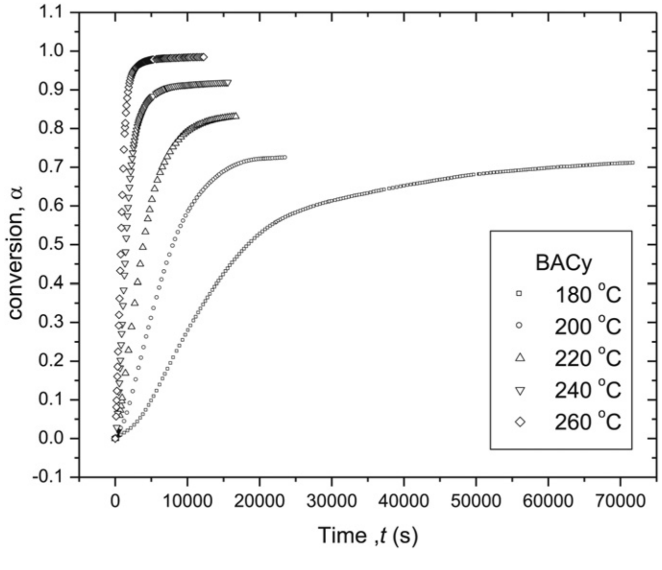

Fig. 4. Experimentally measured conversion,α versus reaction time, t of BACy at different isothermal temperatures between 180 and 260 °C.

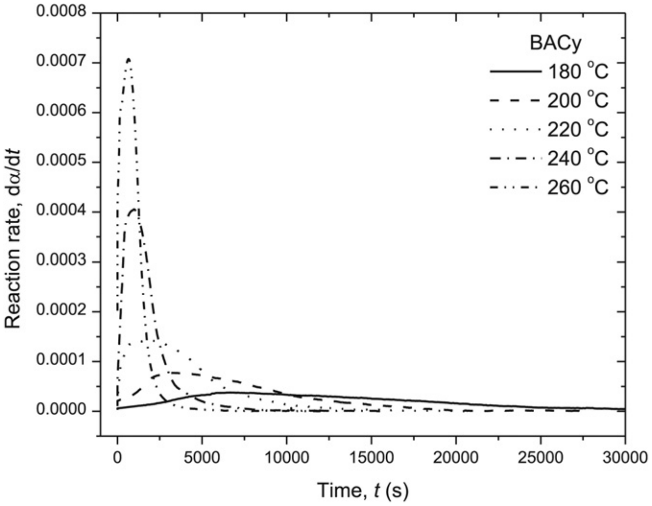

Fig. 5. Reaction rate as a function of reaction time of BACy at different isothermal temperatures.

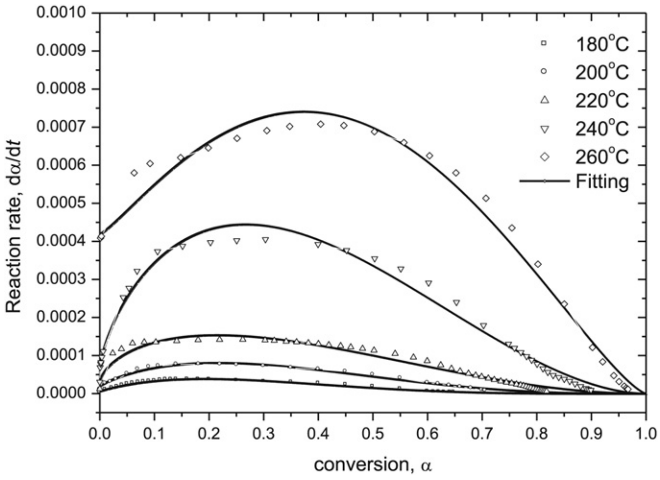

Fig. 6. Reaction rate as a function of conversion of BACy at different isothermal temperatures.

Table 1
Curing kinetics parameters for BACy.

T (K)	k_1 (s^{-1})	k_2 (s^{-1})	k_2/k_1	m	n	$\alpha_{max} = m/m + n$	α_{max}[a]
453	6.6×10^{-6}	3.3×10^{-4}	50	0.93	3.63	0.20	0.16
473	2.0×10^{-5}	5.4×10^{-4}	27	0.88	2.80	0.24	0.18
493	4.0×10^{-5}	9.1×10^{-4}	23	0.84	2.30	0.26	0.23
513	1.0×10^{-4}	1.9×10^{-3}	19	0.86	1.86	0.31	0.29
533	2.9×10^{-4}	2.7×10^{-3}	9	0.91	1.21	0.43	0.42

[a] α_{max}: experimentally determined conversion of maximum reaction rate.

at the beginning of the curing reaction ($\alpha = 0$ or $t = 0$). If the reaction follows an autocatalytic model, however, the reaction rate reaches its maximum value at a certain intermediate conversion. It can be observed in Figs. 5 and 6 that the maximum reaction rate does occur at an intermediate conversion, α_{max}. Therefore the reaction of BACy follows an autocatalytic kinetics model. Attempts were made to curve fit the experimental $(d\alpha/dt) - \alpha$ plots, as shown in Fig. 6, using Equation (2). The kinetics parameters k_1, k_2, m and n from this curve fitting are given in Table 1.

It can be seen from Fig. 6 and Table 1 that k_2 is always higher than k_1 although the k_2/k_1 ratio decreases from 50 to 9 when the temperature increases from 453 to 533 K. This indicates that the autocatalytic effect becomes less notable at higher temperatures, which is consistent with the fact that the shape of conversion versus time curve is more '*S*-like' at lower temperatures (see data in Fig. 4). In addition, α_{max}, at which the reaction rate reaches maximum, increases with temperature, and there is a very good agreement between the experimentally obtained α_{max} values and those calculated from Equation (4). This is different from some other previous reported thermosetting curing systems [3–5], in which the maximum reaction rates were found at similar conversion in different temperatures. The reason for this difference is probably originated from the competition between the autocatalytic and non-autocatalytic reaction which may be material dependent.

The plots of reaction orders m and n versus curing temperature of BACy are shown in Fig. 7. It is interesting that a linear relationship between the reaction order n and temperature was observed in Fig. 7. Although the reaction order m can be approximately regarded as a constant in this particular case, both m and n can be expressed in general by

$$n(T) = n_0 + p_0 T \tag{7a}$$

$$m(T) = m_0 + q_0 T \tag{7b}$$

where T is the curing temperature, m_0, q_0, n_0 and p_0 are fitting parameters, in this particular case, $m_0 = 0.88$, $q_0 \approx 0$, $n_0 = 16.86$ and $p_0 = -0.0294\ K^{-1}$.

Previous reports on autocatalytic curing kinetics of thermosetting polymers also showed large temperature dependency of m and n in various polymer systems [8–11,23–25], constants m and n, are usually used in theoretical treatment of data. In many studies, average m and n values over a temperature range were used to fit the data. Although further studies are necessary in order to have more clear understanding on the temperature dependency of reaction orders m and n [17], the fact that the reaction orders may vary with temperature is certain. Both increasing and decreasing trends of m and n were reported with increasing temperature in different filled or non-filled polymers. Furthermore, the assumption of an overall 2nd order reaction, i.e., $m + n$=2 [23], is only true to some polymers [10,11,17]. Therefore, the autocatalytic reaction kinetics of polymers, e.g., the uncatalyzed BACy, should not be simply described by Equation (2). In the present discussion on curing kinetics, a different and more general treatment is taken. By considering the effect of temperature on m and n, a more accurate equation is obtained,

$$\frac{d\alpha}{dt} = \left(k_1 + k_2 \alpha^{m_0 + q_0 T}\right)(1-\alpha)^{n_0 + p_0 T} \tag{8}$$

where reaction orders m and n are temperature dependent and expressed in Equation (8), Although for BACy $q_0 \approx 0$, the equation is applicable for other systems with different p_0 and q_0 values.

The activation energies (E_1 and E_2) can be obtained by Arrhenius plots of $\ln(k_1)$ and $\ln(k_2)$ versus $1/T$ as shown in Fig. 8, which give $E_1 = 94{,}957$(J/mol), $E_2 = 52{,}120$(J/mol), $A_1 = 510{,}936\ s^{-1}$ and $A_2 = 327\ s^{-1}$. If the parameters, k_1, $k_2 m_0$, q_0, n_0 and p_0 in Equation (8) are known, the theoretical prediction of α versus t can be obtained by integration:

$$t = \int_0^{\alpha} \frac{d\alpha}{\left(k_1 + k_2 \alpha^{m_0 + q_0 T}\right)(1-\alpha)^{n_0 + p_0 T}} \tag{9}$$

A comparison of theoretical prediction and experimental curves of α versus t is shown in Fig. 9. It can be seen that the model which took into account of the temperature dependency of reaction orders (Equation (8)) gives much more accurate prediction of experimental data than does Equation (2) using the average reaction orders. Prediction using Equation (8) has very good agreement with the

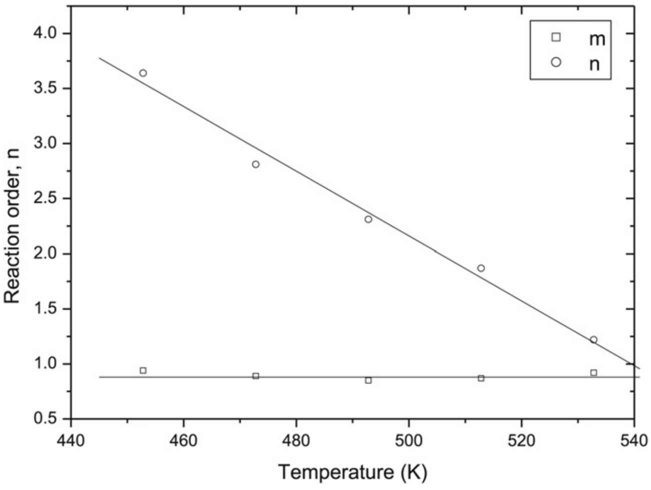

Fig. 7. Plots of reaction order as a function of reaction temperature for BACy.

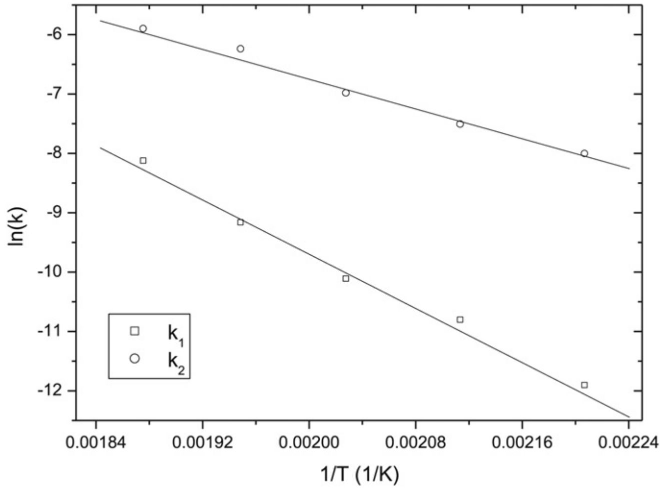

Fig. 8. Plots of $\ln(k)$ as a function of $1/T$ for BACy.

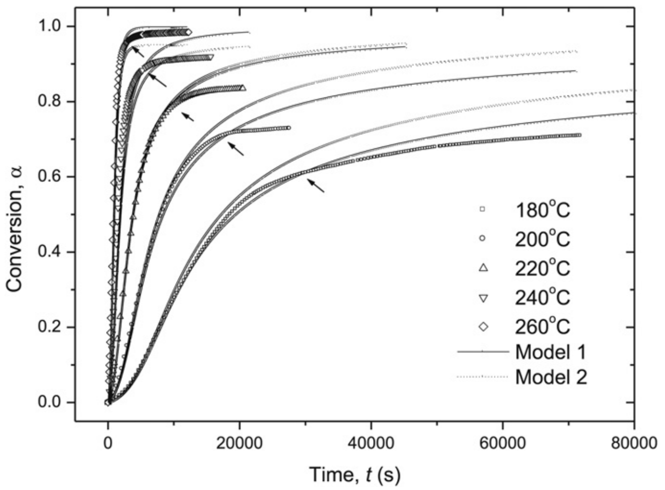

Fig. 9. Comparison of model prediction and experimental α–t curves. Model 1 is based on the new model by considering temperature dependent reaction orders. Model 2 refers to Equation (2) where m and n are assumed constants. (Arrows mark the onset deviation from chemical controlled to diffusion controlled reaction).

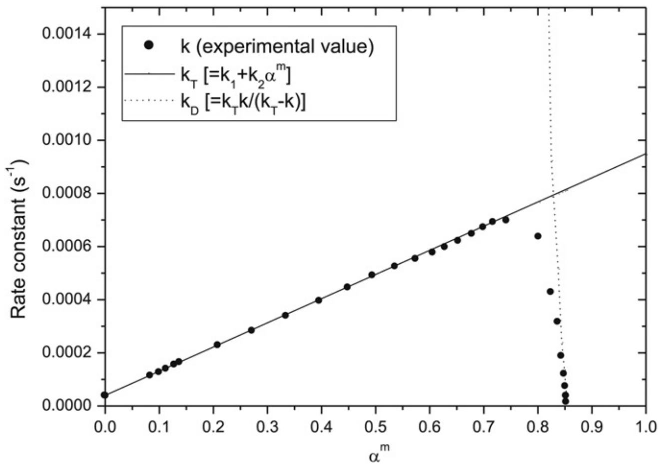

Fig. 11. Relationship between the overall rate constant k and α^m at 220 °C.

experimental data in the chemical controlled region. The prediction only begins to deviate from experimental data at higher conversions due to the onset of diffusion controlled kinetics. Therefore, as expected in this case, the model over estimates the reaction rate in Equation (8) at conversions above α_{onset} when diffusion controlled can no longer be ignored. However, this over estimation can be readily rectified by adopting a similar approach as previously discussed concerning an nth order kinetics model [45]. Fig. 9 also indicates that α_{onset}, at which the reaction kinetics begins to shift from chemical controlled to diffusion controlled is temperature dependent. α_{onset} decreases with increasing temperature, and can be empirically expressed as:

$$\alpha_{\text{onset}} = p_1\left(\frac{1}{T_1} - \frac{1}{T}\right) \tag{10}$$

where p_1 is a constant, T is the reaction temperature, and T_1 is a hypothetical critical temperature below which no chemical controlled reaction could occur (i.e., $\alpha_{\text{onset}} = 0$ when $T = T_1$). p_1 and T_1 can be obtained from curve fitting, as shown in Fig. 10. Equation (10) is a semi-empirical equation reflecting an increasing α_{onset} with temperature, and satisfies the condition of, when $T = T_1$, $\alpha_{\text{onset}} = 0$.

Although most reported studies on thermosets which undergo autocatalytic reaction focused on the chemical controlled region using Equation (2) initially proposed by Kamal, it is important to have a model that is also able to predict the diffusion controlled reaction. In order to derive a kinetics model to describe the entire curing conversion range including the chemical controlled and diffusion controlled regions, a unified generic expression is used:

$$\frac{d\alpha}{dt} = k(1-\alpha)^{n_0+p_0T} \tag{11}$$

Note Equation (11) has a similar form as Equation. However, k in Equation (11) is not a simple constant but an overall rate constant given by Equation (12) [4,6],

$$\frac{1}{k} = \frac{1}{k_T} + \frac{1}{k_D} \tag{12}$$

where k_T is the rate constant in the chemical controlled region and is temperature dependent as described by Arrhenius relationship, k_D is the diffusion rate constant, which is a function of both conversion (α) and temperature (T). Equation (12) shows that the overall rate constant is governed at one extreme by the Arrhenius rate constant when $k_T << k_D$ (prior to vitrification), and at the

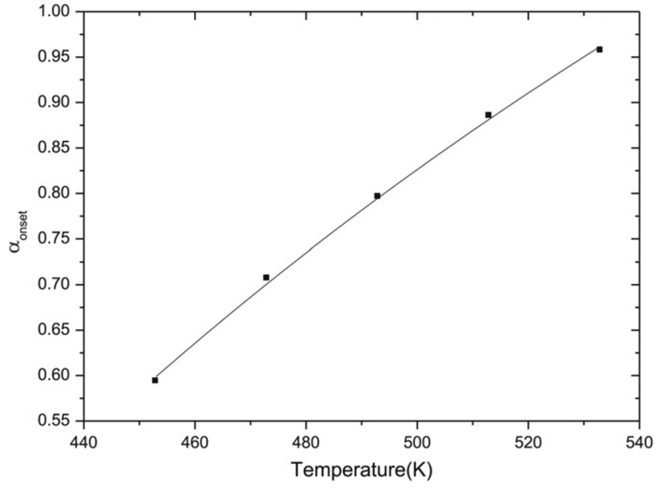

Fig. 10. Onset conversion at which the system becomes diffusion controlled as a function of reaction temperature.

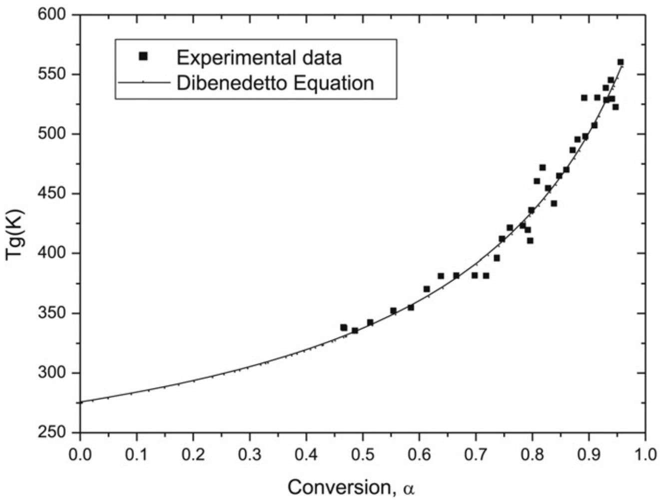

Fig. 12. Tg versus conversion α for BACy.

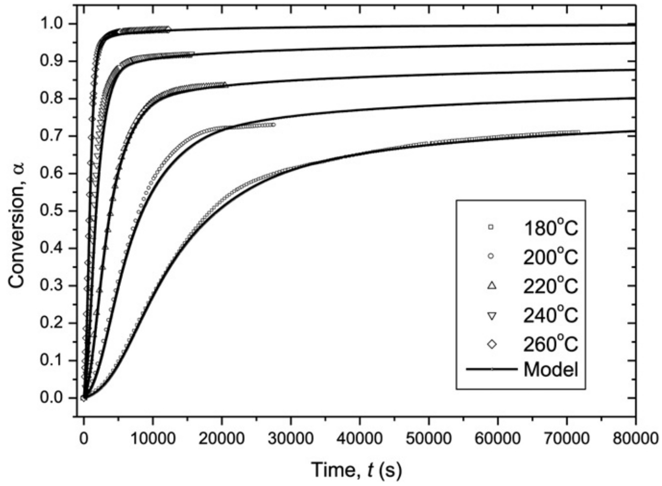

Fig. 13. Comparison of experimental data and prediction using the new model based on temperature dependent reaction orders and after unified combining with WLF treatment.

other extreme by the diffusion rate constant when $k_D << k_T$ (after vitrification) [29].

The overall rate constant k can be determined from experimental data after rearranging Equation (11),

$$k = \frac{d\alpha/dt}{(1-\alpha)^{n_0+p_0T}} \tag{13}$$

On the other hand, the rate constant in the chemical controlled region, i.e., $\alpha < \alpha_{onset}$, k_T is given by:

$$k_T = k_1 + k_2\alpha^m = k_1 + k_2\alpha^{m_0+q_0T} \tag{14}$$

Then the diffusion rate constant k_D can be calculated using Equation (12). The relationship between k (determined experimentally) and α^m at different isothermal temperatures can be established. The relationship at 220 °C is shown in Fig. 11 as an example. It can be seen that in the chemical controlled region, $k \approx k_T = k_1 + k_2\alpha^m$, which follows the solid line. Then there is a region in which both chemical control and diffusion control take effect, i.e., the value of k_T is comparable to k_D. As the conversion increases, the reaction is eventually dominated by diffusion controlled kinetics, and then $k \approx k_D$.

The diffusion rate constant k_D is known to be inversely proportional to the relaxation time of the polymer chain segments, and can be described by a WLF expression [7]:

$$\log\frac{k_D}{k_{D-onset}} = \frac{C_1[\mathrm{Tg}_{onset} - \mathrm{Tg}(\alpha)]}{C_2 + |\mathrm{Tg}_{onset} - \mathrm{Tg}(\alpha)|} \tag{15}$$

or

$$\log k_D = \log k_{D-onset} + \frac{C_1[\mathrm{Tg}_{onset} - \mathrm{Tg}(\alpha)]}{C_2 + |\mathrm{Tg}_{onset} - \mathrm{Tg}(\alpha)|} \tag{16}$$

where$C_1$and C_2 are constants, $k_{D-onset}$ and Tg_{onset} are the diffusion rate constant and the glass transition temperature at α_{onset} respectively. $\mathrm{Tg}(\alpha)$ is the glass transition temperature at conversion α.

By taking the constant C_2 as 51.6, the universal WLF constant [45], $k_{D-onset}$ and C_1 can be obtained by plotting $\log k_D$ versus $[\mathrm{Tg}_{onset} - \mathrm{Tg}(\alpha)]/C_2 + |\mathrm{Tg}_{onset} - \mathrm{Tg}(\alpha)|$. Equation (16) defines k_D as a function of α because $\mathrm{Tg}(\alpha)$ is established experimentally in Fig. 12, which shows the measured Tg of BACy as a function of conversion. The data can be fitted using the Dibenedetto equation [46]

$$\mathrm{Tg}(\alpha) = \frac{(1-\alpha)\mathrm{Tg}_0 + \lambda\alpha\mathrm{Tg}_\infty}{1-\alpha+\lambda\alpha} \tag{17}$$

where Tg_0 and Tg_∞ are the theoretical glass transition temperatures of the polymer at very low conversion and after complete reaction, λ is a polymer dependent parameter related to the lattice energy and segmental mobility.

Therefore, the relationship between k_D and α can be established, and then a new unified kinetics model for thermosets which undergoes autocatalytic curing reaction is established by (1) taking into consideration the temperature dependency of the reaction orders in the chemical controlled region and (2) by combining with the diffusion controlled region using the WLF equation. A comparison between the unified model and experimental data is given in Fig. 13, which clearly shows that there is an excellent agreement between the experimental data and the kinetics model in both chemical and diffusion controlled regions.

The equations used in this new kinetics model are summarized below and the obtained values of the parameters in this study are given in Table 2.

$$d\alpha/dt = k(1-\alpha)^{n(T)}$$

$$n(T) = n_0 + p_0T$$

$$1/k = 1/k_T + 1/k_D$$

$$k_T = k_1 + k_2\alpha^{m(T)}$$

$$m(T) = m_0 + q_0T$$

$$k_{1,2} = A_{1,2}\mathrm{EXP}(-E_{1,2}/RT)$$

$$\log\frac{k_D}{k_{D-onset}} = \frac{C_1[\mathrm{Tg}(\alpha_{onset}) - \mathrm{Tg}(\alpha)]}{C_2 + |\mathrm{Tg}(\alpha_{onset}) - \mathrm{Tg}(\alpha)|}$$

$$\alpha_{onset} = p_1(1/T_1 - 1/T)$$

Table 2
Summary of parameters obtained from the new kinetics model in this study.[a]

A_1=508,897 (s^{-1})	E_1 = 94,957 (J/mol)	A_2 = 326 (s^{-1})	E_2 = 52,120 (J/mol)
m_0 = 0.88	q_0 = 0	n_0 = 16.86	p_0 = −0.0294 (K^{-1})
$k_{D-onset}$ = 9.33 × 10^{-4} (s^{-1})	C_1 = 2.54 (K)	C_2 = 51.6 (K)	
p_1 = 1096 (K)	T_1 = 363 (K)		
Tg_0 = 295.8 (K)	Tg_∞ = 632.3 (K)	λ = 0.225	

A_1, A_2, E_1, and E_2 are the pre-exponent constants and activation energies from Arrhenius equations corresponding to k_1 and k_2 in Equation (2).
m_0, n_0, q_0, and p_0 are defined in Equation (7). q_0 and p_0 quantify the gradients of change of m and n respectively with temperature.
$k_{D-onset}$ is the diffusion rate constant at α_{onset}.
C_1 and C_2 are constants in WLF equation.
p_1 is a constant in Equation (10) which should be materials dependent, while T_1 is the hypothetical critical temperature below which no chemical controlled reaction could occur. Tg_0 is the glass transition temperatures at conversion 0. Tg_∞ is the glass transition temperatures after complete curing of polymer. λ is a polymer dependent fitting parameter in DiBenedetto equation.

[a] Notes.

$$\mathrm{Tg}(\alpha) = \frac{(1-\alpha)\mathrm{Tg}_0 + \lambda\alpha\mathrm{Tg}_\infty}{1-\alpha+\lambda\alpha}$$

4. Conclusions

Based on the study of uncatalyzed BACy, which undergoes an autocatalytic reaction in the chemical controlled region, a new kinetics model is established. An advantage of this new model is that it incorporates mathematically the temperature dependency of the reaction orders *m* and *n*. Although the reaction orders can have substantial variation with reaction temperature in thermosetting polymers, constant reaction orders, usually the average values, were used for curve fitting in the literature. The new kinetics model predicts the experimental data of BACy more accurately in the chemical controlled reaction region than does the existing models assuming constants *m* and *n*. This new model is further unified by combining with a WLF treatment and the overall model is able to accurately describe reaction kinetics in the entire conversion range of the curing reaction. Although developed based on study of BACy, this model or at least the treatment towards developing it is not restricted to this particular polymer and may be successfully applied to other thermosetting polymers following autocatalytic reaction kinetics.

Acknowledgements

The authors wish to thank for funding from DSTA, Singapore and one of the authors (LZ) would like to express gratitude to Nanyang Technological University, Singapore for provision of PhD scholarship.

References

[1] Harsch M, Kocsis JK, Holst M. European Polymer Journal 2007;43:1168–78.
[2] Maazouz A, Texier C, Taha M, Alglave H. Composites Science and Technology 1998;58:627–32.
[3] Christopher WW, Wayne DC, Andy AG. Polymer 1997;38:3251–61.
[4] Goodwin AA. Polymer International 1993;32:87–92.
[5] Boey FYC, Qiang W. Polymer 2000;41:2081–94.
[6] Zhao L, Hu X. Polymer 2007;48:6125–33.
[7] Lars A. SAMPE Journal 1991;27:27–36.
[8] Zhou TL, Wang X, Liu XH, Xiong DS. Carbon 2009;47:1112–8.
[9] Erdogan BC, Seyhan AT, Ocak Y, Tanoglu M, Balkose D, Ulku S. Journal of Thermal Analysis and Calorimetry 2008;94:743–7.
[10] Coasta ML. Materials Research 2005;8:65–70.
[11] Macan J. Thermochimica Acta 2004;414:219–25.
[12] Fernandez R, Darlas BF, Oyanguren PA, Mondragon I. Thermochimica Acta 2009;493:6–13.
[13] He Y. Thermochimica Acta 2001;367–368:101–6.
[14] Kim DH, Kim SC. Polymer Engineering and Science 1989;29:456–62.
[15] Senen PA, Arturo LQ, Mercedes PP, Montserrat V, Pilar P. Journal of Polymer Science: Part A: Polymer Chemistry 1998;36:1001–16.
[16] Han S, Yoon HG, Suh KS, Kim WG, Moon TJ. Journal of Polymer Science: Part A: Polymer Chemistry 1999;37:713–20.
[17] Michelle LC, Luiz CP, Mirabel CR. Materials Research 2005;8:65–70.
[18] Kamal MR, Sourour S. Polymer Engineering and Science 1973;13:59–64.
[19] Kamal MR. Polymer Engineering and Science 1974;14:231–9.
[20] Rosso P, Ye L. Macromolecular Rapid Communications 2007;28:121–6.
[21] Darlas BF, Rueda L, Stefani PM, Caba KDL, Mondragon I, Eceiza A. Thermochimica Acta 2007;459:94–103.
[22] Nakanishi H, Satoh M, Norisuye T, Qui TCM. Macromolecules 2006;39:9456–66.
[23] Ryan ME, Dutta A. Polymer 1979;20:203–6.
[24] Dutta A, Ryan ME. Journal of Applied Polymer Science 1979;24:635–49.
[25] Sidi S, Kamal MR. Polymer Engineering and Science 1982;22:349–53.
[26] Thomas R, Durix S, Sinturel C, Omonov T, Goossens S, Groeninckx G, et al. Polymer 2007;48:1695–710.
[27] Mathew D, Nair CPR, Krishnan K. Journal of Polymer Science: Part A: Polymer Chemistry 1999;37:1103–14.
[28] Isabel H, Clara MG, Marcos DR, Mondragon I. Polymer International 2000;49:735–42.
[29] Bartolomeo P, Chailan JF, Vernet JL. European Polymer Journal 2001;37:659–70.
[30] Bartolomeo P, Chailan JF, Vernet JL. Polymer 2001;42:4385–92.
[31] Hamerton I, editor. Chemistry and technology of cyanate ester resins. Glassgow: Chapman and Hall; 1994.
[32] Nair CPR, Dona M, Ninan KN. Advances in Polymer Science 2001;155:1–99.
[33] Hamerton I, Hay JN. Polymer International 1998;47:465–73.
[34] Graver RB. Cyanate esters – high performance resins. In: Seymour RB, Kirshenbaum GS, editors. High performance polymers: their origin and development. Elsevier Science Publishing Co., Inc; 1986.
[35] Galy J, Gerard JF, Pascault JP. Reactivity of cyanate-ester resins and characterization polycyanurate networks. In: Abadie MJM, Sillion B, editors. Polyimides and other high-temperature polymers. Netherlands: Elsevier Science Publishers; 1991.
[36] Dreyer C, Bauer M, Bauer J, Keil N, Yao H, Zawadzki C. Microsystem Technologies 2002;7:229–38.
[37] Dreyer C, Schneider J. Macromolecular Symposia 2003;199:307–19.
[38] Sharma SK, Misra SCK, Tripathi KN. Journal of Nonlinear Optical Physics & Materials 2003;12:1–5.
[39] Bauer M. Plastic optical components. United States Patent 5780159. 1998.
[40] Bauer M. Waveguide systems or structures or parts thereof, containing polycyanate copolymers prepared from polyfunctional cyanates and fluorinated monocyanates. United States Patent 6716958. 2004.
[41] Bauer M. Temperature insensitive optical waveguide device. United States Patent 6757469. 2004.
[42] Bauer M. Optical waveguides derived from a combination of poly(perfluorocyclobutanes) and polymeric cyanates. United States Patent 6853790. 2005.
[43] Chen CC, Don TM, Lin TH, Cheng LP. Journal of Applied Polymer Science 2004;92:3067–79.
[44] Georjon O, Galy J, Pascault JP. Journal of Applied Polymer Science 1993;49:1441–52.
[45] Chen YT, Macosko CW. Journal of Applied Polymer Science 1996;62:567–76.
[46] Dibenedetto AT. Journal of Polymer Science: Part B: Polymer Physics 1987;25:1949–69.