

Study on phenomenological curing model of epoxy resin for prediction of degree of cure

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Abstract Curing course of Huntsman 1564/3486 epoxy resin system was studied under dynamic and isothermal curing conditions by differential scanning calorimetry technique. The autocatalytic cure kinetic model was established to describe the curing behaviour. A new modified phenomenological curing model based on the Olivier's model was proposed to predict the relationship between the degree of cure and the couple of time and temperature. Then, the degree of cure was calculated by both the kinetic model and the modified Olivier's model. A comparison of the results calculated with the experimental data show that the modified Olivier's model is more accurate in the later stage of the curing course, especially at high temperatures. The modified Olivier's model is simple and easy to use, could be applied to predict the degree of cure at isothermal temperatures well in engineering.

Keywords Degree of cure · Phenomenological model · Curing kinetic

Introduction

Epoxy resin is one of the most used thermosetting polymer matrix for its good mechanical strength and corrosion resistance. It plays an important role in industry. As a matrix of composites, the curing course of the resin is a

crucial procedure of the composites manufacture process. The degree of matrix cure, which is also called the conversion ratio of the matrix, has great impact on the properties of the composites directly. Due to the limitation of engineering application, inhomogeneous distribution of temperature maybe exist in the manufacture procedures of composites, which leads the inhomogeneous curing degree of the matrix.

In order to understand and control the curing process to achieve optimum properties of the resin matrix, it is imperative to study the relationship between the degree of cure and the couple of time and temperature, as it drives the complex changes in morphology and structure of the polymer during its processing operations. Many studies have been conducted on the curing reaction of thermosetting resins employing various techniques, experimental procedures and data analysis methods [1–12]. Among them, isothermal differential scanning calorimetric (DSC) technique is the most common usage. The principle of the DSC technique is that the degree of cure α at any time during the curing course could be expressed as the quotient of the integration of the isothermal heat flow curves at any time. The experimental data which is related to the degree of cure, time and temperature can be acquired through isothermal DSC at different temperatures. Based on the experimental data fitting, the phenomenological model could be established and used for the curing course prediction.

A variety of kinetics phenomenological models have been developed to relate the chemical reaction rate to time, temperature and the degree of cure. 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:

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$$\frac{d\alpha}{dt} = K_0(1 - \alpha)^n \quad (1)$$

where $d\alpha/dt$ is the cure rate, α is the degree of cure, K_0 is the rate constant, which is related to the temperature and n is the reaction order. For an autocatalytic kinetics model, the rate equation is [13, 14]:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha)^m(1 - \alpha)^n \quad (2)$$

where K_1 , K_2 are rate constants which are related to the temperature, and m , n are reaction orders. By assuming the zero-initial cure rate, K_1 can be eliminated from the equation, and it is rewritten as follows:

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (3)$$

It has been demonstrated that the epoxy-amine systems follow autocatalytic kinetics by many studies [15].

The effectiveness of the kinetics model has been postulated by some researchers [16–18]. 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 changes the reaction rate before complete conversion is achieved. After vitrification, the cure process exhibits a diffusion-controlled mechanism and as a consequence, the experimental degree of cure and curing rate are different than those predicted by the kinetics equation [19–21]. Therefore, the kinetics model does not satisfy the observed reduced reaction rate condition at the later reaction stage of the cure.

Besides the kinetics models, Olivier proposed a phenomenological model when studying the curing course and the curing residual stress levels, as assuming α is the function of the couple of time and temperature for any value of α greater than 0.4 [22]. The equation of the Olivier's phenomenological model stands:

$$\alpha = 1 - \frac{1}{\exp[F \exp(-\frac{E_a'}{RT})(t - t_0)]} \quad (4)$$

where F is pre-exponential factor, E_a' is apparent activation energy, T is curing temperature, t is curing duration time, t_0 is integration time constant ($t_0 =$ time for which $\alpha = 0.4$) and R is universal gas constant. Based on Olivier's model, α could be determined immediately from time and temperature values [23].

In the present study, the isothermal DSC measurement was used to obtain the experimental data of a low viscosity epoxy resin system. A new model based on Olivier's phenomenological model was proposed to accurately predict α in the later stage of the epoxy resin curing reaction. The kinetics model and the new modified model based on

Olivier's model were investigated in detail; a comment on both of them was given as well.

Experiment

Material

The low viscosity Huntsman 1564/3486 epoxy resin system was used for experiment. The Huntsman 1564 is a modified bisphenol-A type epoxy, and the Huntsman 3486 is a polyamine curing agent, both of them were manufactured by the Huntsman products Inc, USA. The epoxy resin is a clear liquid, and the curing agent is a clear colourless to a slightly yellow liquid at room temperature.

Measurements

Curing study was performed using an isothermal DSC method. DSC measurements were performed using a NETZSCH instrument STA 449C. Before the measurement, the temperature, baseline and heat flow calibrations were carried out by the recommended procedures using pure indium.

To acquire the total reaction heat of the cure, dynamic DSC scan was first obtained at different heating rates of 2, 3, 5, 8 and 10 °C/min. Isothermal curing experiments were carried out at 50, 60, 70, 80, 90, 100 and 110 °C, respectively. Nitrogen gas was used for purging at a flow rate of 40 mL/min. The experiment was stopped when there is no change in the heat flow at this isothermal temperature.

Results and discussion

Dynamic DSC

Figure 1 shows the dynamic DSC curves of epoxy resin system at different heating rates. The onset temperature T_i , the terminal temperature T_f were marked in the figure, and the peak temperature T_p at different heating rates can be obtained directly from the curve. The line between the T_i and the T_f is the baseline. The whole area of the exothermal peak is directly proportional to the total quantity of reaction heat released during the cure reaction. These peaks have been used to estimate the total heat release of cure reaction H , because in the dynamic DSC measurement at different heating rate, the cure reaction is considered to be completed [14]. The calculated H which is referred to a gram of epoxy was listed in Table 1. The highest value would be the total reaction heat of cure, H_u , which is also referred to a gram of epoxy as shown in Table 1.

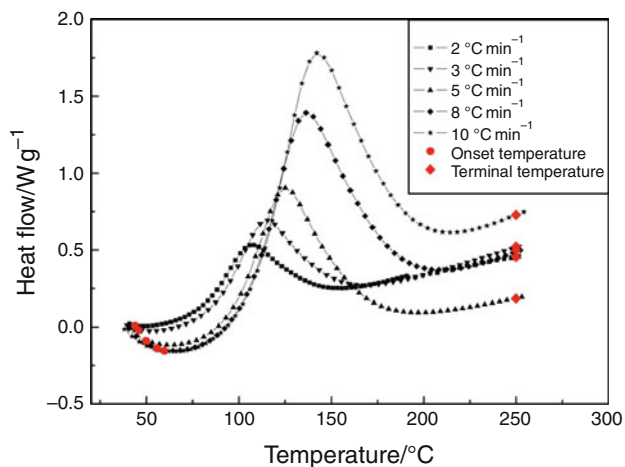


Fig. 1 The dynamic DSC curves

Table 1 Dynamic reaction heat of cure at different heating rates

Heating rate/°C min ⁻¹	H/J g ⁻¹	H _u /J g ⁻¹
2	585	
3	601	
5	637	637
8	634	
10	629	

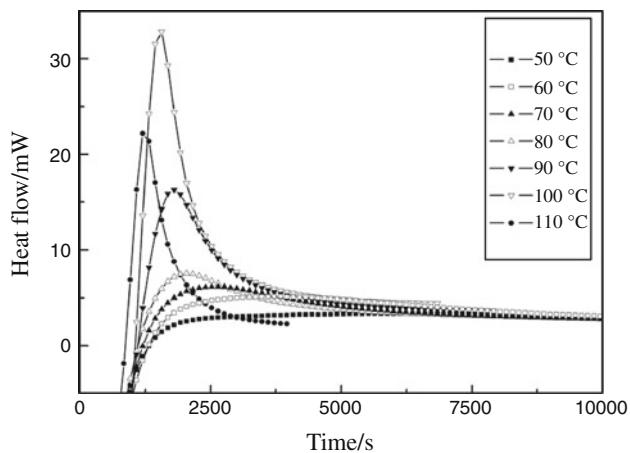


Fig. 2 Isothermal DSC exothermic curves

Isothermal DSC

Figure 2 shows the isothermal DSC exothermic curves of the epoxy resin system at different temperatures. These curves were used to evaluate the kinetic parameter of the cure reaction. H_u could be considered as a constant over the whole cure reaction. The heat of cure is directly proportional to the area under the DSC curve. The fractional conversion calculated from the fractional areas under the DSC curve is the degree of cure α . The fractional extent of conversion at a given temperature could be expressed as:

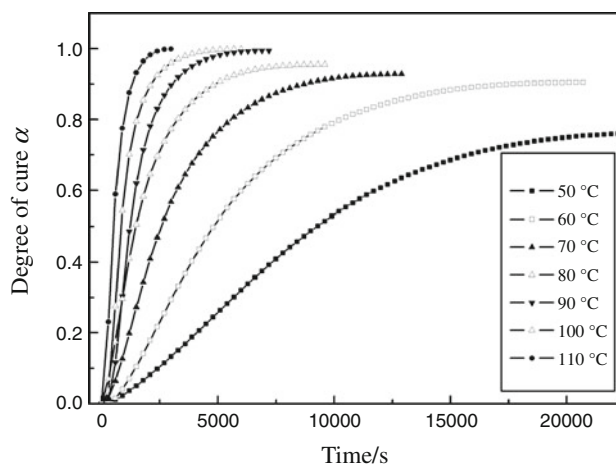


Fig. 3 Curves of α versus time at different isothermal temperatures

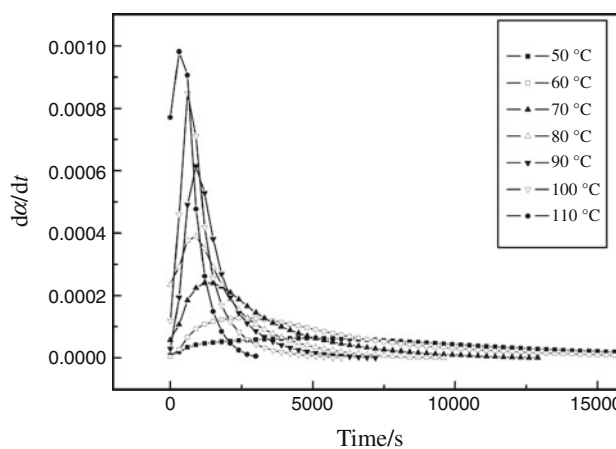


Fig. 4 Curves of $d\alpha/dt$ versus time at different isothermal temperatures

$$\alpha = \frac{H(t)}{H_u} \tag{5}$$

where $H(t)$ is the heat of reaction of partially cured at the time t [13, 14]. Thus, curves of degree of cure α versus curing time at different isothermal temperatures were obtained as shown in Fig. 3.

Kinetics model

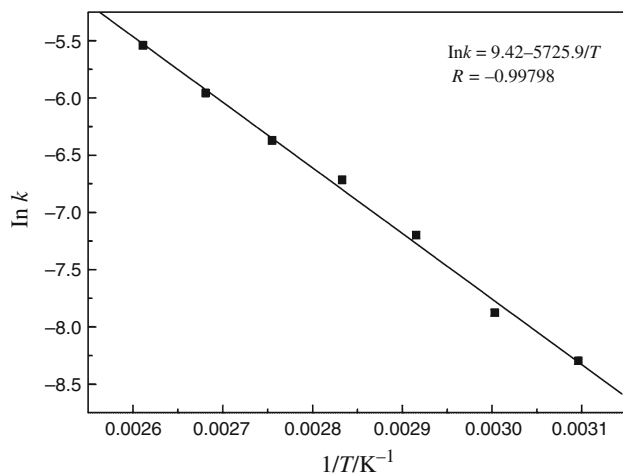
The rate of the cure reaction is defined as $d\alpha/dt$, which is calculated as Eq. 6:

$$\frac{d\alpha}{dt} = \frac{dH(t)/H_u}{dt} \tag{6}$$

The relationship between calculated $d\alpha/dt$ and curing time was plotted in Fig. 4. It is shown that the rate of the cure reaction was increasing with the increment of curing time at the beginning of the reaction, after reaching the peak, the rate was decreasing. The reaction was autocatalytic as the peak of

Table 2 Kinetic parameters at different temperatures

$T/^\circ\text{C}$	k	m	n	R^2
50	0.0002492	0.5212	2.075	0.9378
60	0.0003799	0.4350	1.592	0.9915
70	0.0007480	0.4748	1.619	0.9839
80	0.001211	0.4931	1.549	0.8838
90	0.001710	0.4798	1.307	0.9955
100	0.002583	0.5087	1.333	0.9847
110	0.003916	0.7193	1.242	0.5883

**Fig. 5** Relationship between $\ln k$ and $1/T$

the rate was not appearing at the beginning of the reaction. The rate equation of the autocatalytic kinetics model was shown in Eq. 3. The cure reaction orders (m, n) and the reaction constant (K) could be calculated through curves fitting of the data plotted in Figs. 3 and 4. These values were listed in Table 2.

The values of m and n varied within the temperature range studied, which indicated that the reaction mechanism varied with reaction temperatures. The reason is that the epoxy resin system underwent a complex series of curing reactions [24]. The mean value was calculated to be the reaction order parameter [25].

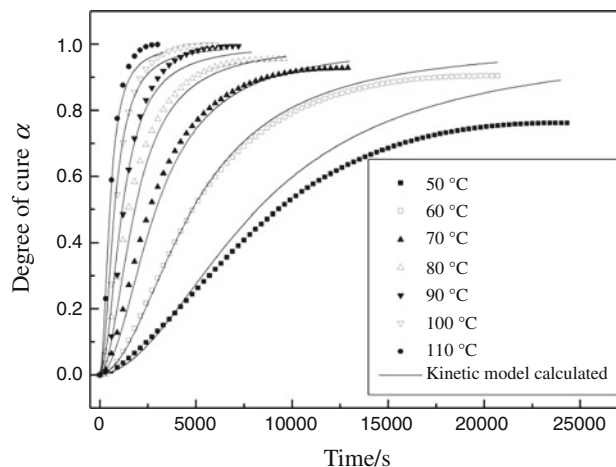
The rate constants k exhibited Arrhenius behaviour. Eq. 7 was used to describe the relationship between the rate constants and the temperatures.

$$k = Ae^{-E_a/RT} \quad (7)$$

where A is the pre-exponential factor and E_a is the apparent activation energy. To determine A and E_a , Eq. 7 could also be described as:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (8)$$

The relationship between $\ln k$ and $1/T$ was plotted in Fig. 5. The slope of the fitting straight line was 5725.9 and the intersection was 9.42. It is found that A was $12.33 \times 10^3 \text{ s}^{-1}$.

**Fig. 6** Curves of kinetic model calculated and experimental α versus time at different temperature

Thus, the curing kinetic model equation of the Huntsman 1564/3486 epoxy resin system can be expressed as:

$$\frac{d\alpha}{dt} = 12.33 \times 10^3 \exp\left(\frac{-5725.9}{T}\right) \alpha^{0.5188} (1 - \alpha)^{1.531} \quad (9)$$

To get the relationship between α and time at invariable temperatures, the differential equation Eq. 9 has to be solved. Thus, the classic Runge–Kutta method was used to get numerical solutions of Eq. 9. The classic Runge–Kutta method is a Fourth-order numerical method, the function value of local truncation error could reach Fifth-order. The overall set of equations is as follows [26]:

$$\begin{aligned} \alpha_{n+1} &= \alpha_n + \frac{1}{6}(K_1 + 2K_2 + 2K_3 + K_4) \\ K_1 &= hf(t_n, \alpha_n) \\ K_2 &= hf\left(t_n + \frac{h}{2}, \alpha_n + \frac{K_1}{2}\right) \\ K_3 &= hf\left(t_n + \frac{h}{2}, \alpha_n + \frac{K_2}{2}\right) \\ K_4 &= hf(t_n + h, \alpha_n + K_3) \end{aligned} \quad (10)$$

where h is the time step, $f(\alpha, t) = d\alpha/dt$. In the present work, $h = 100 \text{ s}$, the temperature was invariable and the boundary condition was that when $t = 0$, $\alpha = 0$. The solutions gave the relationship between α and time at invariable temperatures.

A comparison of the experimental data and α calculated by kinetic model at different isothermal temperatures was shown in Fig. 6. It can be seen that in the earlier stage of the curing course, α calculated by kinetic model had good agreement with the experimental data, but in the later stage, there is some deviation between calculated α and the experimental data, especially the final degree of cure. The reason is that the vitrification phenomenon of the epoxy resin greatly changed the reaction rate before achieving the complete conversion [24].

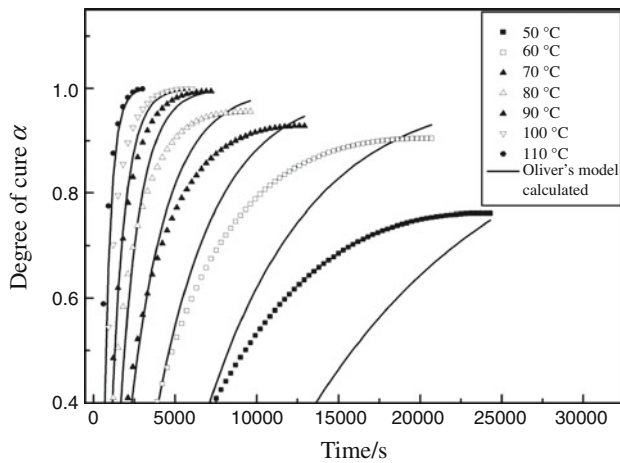


Fig. 7 Curves of Olivier’s model calculated and experimental α versus time at different temperature

Modified Olivier model

Olivier’s phenomenological model was shown in Eq. 4. In this model, α could be determined immediately from time and temperature values for any value of α greater than 0.4 [22, 23]. To find the model parameters in Eq. 4, it is defined as:

$$P = F \exp\left(-\frac{E'_a}{RT}\right) \tag{11}$$

Thus, Eq. 11 could be expressed as follows:

$$-\ln(1 - \alpha) = P(t - t_0) \tag{12}$$

$-\ln(1 - \alpha)$ could be calculated versus t according to Fig. 4. Then, the parameters P could be obtained by linear fitting the data. t_0 could be found immediately in Fig. 3. After P and t_0 were fixed, α could be calculated by Olivier’s model. Results obtained by Olivier’ model and the experimental data were shown in Fig. 7.

It can be seen that there was great deviation between α calculated by Olivier’s model and the experimental data. So, the Olivier’s model cannot be applied immediately to the Huntsman 1564/3486 epoxy resin system. In order to make the model more accurate and extend the model capacity to calculate α for any value in the whole curing course, Olivier’s model was rewritten as follows:

$$\alpha = 1 - \frac{1}{\exp\left[F \exp\left(-\frac{E'_a}{RT}\right) \left(t - A' \exp\left(\frac{T_i}{T}\right) - t_i\right)\right]}$$

$$\Leftrightarrow \text{if} \left\{ \left(t \geq A' \exp\left(\frac{T_i}{T}\right) - t_i\right) \right\}$$

$$\alpha = 0 \Leftrightarrow \text{if} \left\{ t < A' \exp\left(\frac{T_i}{T}\right) - t_i \right\} \tag{13}$$

where T_i is defined as the initial curing temperature constant, t_i is defined as the initial curing time constant, A' is

the pre-exponential factor. This model refined the t_0 contained in the Olivier’s model, which stands for the time when α equals to 0.4. It is defined as the function of the curing temperature. Eq. 13 is called the modified Olivier model.

To find the model parameters, it is defined as:

$$Q = A' \exp\left(\frac{T_i}{T}\right) - t_i \tag{14}$$

Using Eqs. 11 and 14 to replace the formula in Eq. 13, thus Eq. 13 could be expressed as follows:

$$\alpha = 1 - \frac{1}{\exp[P(t - Q)]} \tag{15}$$

$$-\ln(1 - \alpha) = P(t - Q) \tag{16}$$

The relationship between $-\ln(1 - \alpha)$ and t was shown in Fig. 4, linear fitting the data, the parameters P and Q were obtained and listed in Table 3. The variance showed that the relationship between $-\ln(1 - \alpha)$ and t was well linearity.

Then, the values of P , Q were employed in Eqs. 11 and 14 to obtain the parameters of modified Olivier’s model, F , E'_a , A' , T_i and t_i , through the no-linear fitting which is shown in Figs. 8 and 9.

Table 3 The parameters of the equation

$T/^\circ\text{C}$	$P/10^{-5} \text{ s}^{-1}$	Q/s	R^2
50	8.156	931	0.9977
60	15.83	503	0.9969
70	27.04	361	0.9944
80	44.43	298	0.9947
90	82.98	268	0.9989
100	122.1	249	0.9968
110	232.2	217	0.9909

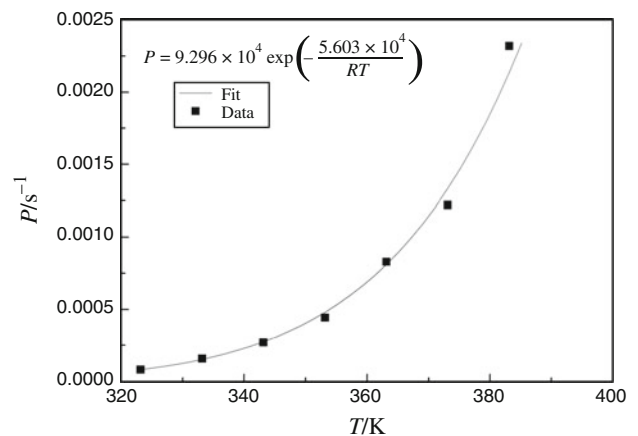


Fig. 8 No-linear curve fitting of P versus T

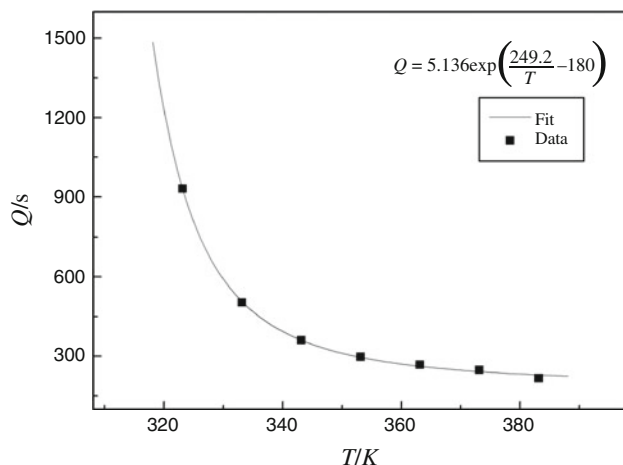


Fig. 9 Non-linear curve fitting of Q versus T

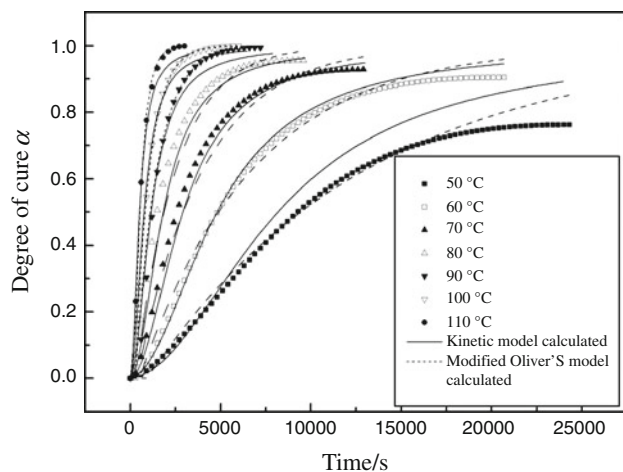


Fig. 10 Curves of calculated and experimental α versus time at different temperature

After all the parameters were obtained, the modified Olivier's model for the Huntsman 1564/3486 epoxy resin system can be expressed as:

$$\alpha = \begin{cases} 1 - \frac{1}{\exp\{9.297 \times 10^4 \exp(-\frac{6739}{T})[t - 5.136 \exp(\frac{249.2}{T}) - 180]\}} & \text{if } \left\{ t \geq 5.136 \exp\left(\frac{249.2}{T}\right) - 180 \right\} \\ \alpha = 0 & \text{if } \left\{ t < 5.136 \exp\left(\frac{249.2}{T}\right) - 180 \right\} \end{cases} \quad (17)$$

The curves of α versus time at different isothermal temperatures were calculated as Eq. 17. The comparison of experimental data versus α calculated by the modified Olivier's model and the cure kinetic model at different

isothermal temperatures was shown in Fig. 10. It can be seen that during the later stage of the curing course, especially at the high temperatures (when $T \geq 90$ °C), α calculated by the modified Olivier's model was well accordant to the experimental data, where there was obvious deviation between α calculated by the kinetic model and the experimental data.

Conclusions

In the present work, the relationship between the degree of cure and the couple of time and temperature was studied under isothermal and dynamic curing conditions by DSC technique. The autocatalytic cure kinetic model and the new modified Olivier's phenomenological model based on the Olivier's model of degree of cure were established. The curves of α versus time at different isothermal temperatures were calculated by the equation of the kinetic model and the modified Olivier's model, respectively, and compared with the experimental data of isothermal DSC measurements. The result shows that in the earlier stage of the curing course, the kinetic model and the modified Olivier's model have good agreement with the experimental data. But during the later stage, there is obvious deviation between α calculated by kinetic model and the experimental data. The modified Olivier's model is more accurate during the later stage, especially at high temperatures ($T \geq 90$ °C), the modified Olivier's model predicts the experimental data with excellent accuracy. Furthermore, the modified Olivier's model is simple and easy to use. For the engineering application, resin system would be usually curing at high temperatures by mould heating, so the modified Olivier's model could be applied to predict the degree of cure at isothermal temperatures well in engineering.

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