# CURE KINETICS OF THERMOSETTING BISPHENOL E CYANATE ESTER

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Resin injection repair is a common method to repair delamination damage in polymer matrix composites (PMCs). To repair high-temperature PMCs, the resin should have a very low viscosity, yet cure into a compatible adhesive with high temperature stability. Normally, thermosetting polymers with high glass transition temperatures ($T_g$) are made from monomers with high room temperature viscosities. Among the high temperature resins, bisphenol E cyanate ester (BECy, 1,1'-bis(4-cyanatophenyl)ethane), is unique because it has an extremely low viscosity of 0.09–0.12 Pa s at room temperature yet polymerizes as a cross-linked thermoset with a high $T_g$ of 274°C. BECy monomer is cured via a trimerization reaction, without volatile products, to form the high $T_g$ amorphous network.

In this study, the cure kinetics of BECy is investigated by differential scanning calorimetry (DSC). Both dynamic and isothermal experiments were carried out to obtain the kinetic parameters. An autocatalytic model was successfully used to model isothermal curing. The activation energy from the autocatalytic model is 60.3 kJ mol$^{-1}$ and the total reaction order is about 2.4. The empirical DiBenedetto equation was used to evaluate the relationship between $T_g$ and conversion. The activation energy of BECy from the dynamic experiments is 66.7 kJ mol$^{-1}$ based on Kissinger's method, while isoconversional analysis shows the activation energy changes as the reaction progresses.

*Keywords: activation energy, cure kinetics, cyanate ester, DSC*

## Introduction

Polymer matrix composites (PMC) are especially susceptible to matrix micro-cracking when subjected to repeated thermo-mechanical loadings. Often these matrix micro-cracks coalesce and lead to other damage modes including fiber/matrix debonding and ply delamination [1–5]. Low velocity impacts from events, such as a tool drop or a glancing bird strike on an aircraft, are common causes of delamination damage in fiber reinforced PMC. Currently composite parts that have been damaged in service are first inspected manually to determine the extent of damage. For critical parts this inspection may include such nondestructive testing techniques as ultrasonics, infrared thermography, X-ray tomography and computerized vibro thermography [6]. If the damage is too severe, the structural component is replaced entirely. For less extensive damage, repairs are attempted.

One common repair method is the use of adhesively bonded scarf patches. In this method, the surface material of the laminate is carefully removed to the bottom of the delamination region with a high-speed grinder at a shallow angle. Then repair plies are used to fill the removed material. Another repair method is resin-injection repair, where delamination damage is repaired by injecting resin via an evacuated access hole into the failed area. The resin-injection repair eliminates the need to remove the outer undamaged plies and can result in higher recovery strengths than repairs made by the scarf repair method. However, the use of the resin-injection repair method for high temperature PMCs (loosely defined as composites that maintain their useful properties after thousands of hours in air at 200°C) has been limited to date because of the low $T_g$'s of the cured adhesives which are available.

There are several special requirements for an ideal resin system for the resin-injection repair of high temperature PMCs: 1) low viscosity and wettability, easy to infiltrate the damage area; 2) high temperature stability – the cured resin should have a $T_g$ above the maximum temperature that the composites experience in service; 3) compatible adhesive – the cured repair resin must be a strong adhesive to the matrix and reinforcement, to bond the crack surface together and 4) long shelf-life and environmentally benign. Among these requirements, the low viscosity of the monomer resin and the high temperature stability of the resulting polymer network are critical, yet competing, properties for an ideal system for resin-injection repair applications.

Normally, a monomer which cures into a high temperature thermosetting polymer with a high $T_g$ also has a high viscosity at room temperature [7, 8]. As a general rule, the higher the cured glass transition temperature,

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the higher the viscosity of the prepolymer at a given temperature. For example, *bis*-maleimide(1,1'-(methylene-*di*-4,1-phenylene)*bis*-maleimide) resin cures into a polymer network with a high $T_g$ of above 300°C, but the temperature of the resin must be raised to 160°C for the viscosity of the resin to reach an injectable viscosity of 0.15 Pa s [7]. There is one exception to the trend: a unique type of cyanate ester monomer: bisphenol E cyanate ester (BECy, 1,1'-*bis*(4-cyanatophenyl)ethane). Compared to the more common bisphenol A cyanate ester (Fig. 1) with a melting temperature of 82°C, BECy has an extremely low viscosity of 0.09–0.12 Pa s at room temperature [9]. These processing characteristics make the BECy an excellent candidate for the resin-injection repair of high-temperature polymer composites.

The monomer of cyanate ester resins is an ester of bisphenol and cyanic acid, containing reactive ring-forming cyanate (–O–C≡N) functional groups. Cyanate ester monomers are generally polymerized via cyclotrimerization to polycyanurates (Fig. 1). The formation of substituted triazine rings via the cyclic addition of three aryl cyanates involves a series of step-growth reactions. Cyanate esters have low toxicity



Fig. 1 Cyanate ester chemical structures and cyclotrimerization reaction scheme

and no leaving groups or volatile by-products during the polymerization, which makes them less hazardous than many other high temperature polymers, such as bismaleimides. Although cyanate esters are not capable of withstanding temperatures as high as bismaleimides, they are capable of withstanding extreme temperature variations, which is a significant improvement over epoxies. Additionally, cyanate esters have excellent adhesive properties and are more resistant to moisture absorption than other thermosets. Therefore, we believe that BECy is a good candidate for the resin injection repair of high temperature composites. In this study, the cure kinetics of BECy is investigated mainly by differential scanning calorimetry (DSC). Both isothermal and multi-heating-rate dynamic cure experiments are used to obtain the cure kinetic parameters. The obtained kinetic parameters can be used as a guide to determine the processing time and temperature profile in the actual repair processes.

## Experimental

BECy monomer is obtained from BRYTE technologies, Inc. as EX1510 cyanate ester. BECy is mixed with catalyst (BRYTE technologies, Inc., supplied with EX1510 cyanate ester) in a mass ratio of 100:3 at room temperature by magnetic stirring.

Thermogravimetric analysis (TG) measurements were performed on a TG model Q50 (TA Instruments, Inc.) to determine the decomposition temperature of polymerized BECy and volatile contents during the polymerization. About 20 mg uncured resin was placed in platinum pans and heated from 25 to 800°C at a rate of 20°C min$^{-1}$ under nitrogen or air purge at 60 mL min$^{-1}$.

Differential scanning calorimetry (DSC) measurements were made on a model Q2000 DSC (TA instruments, Inc.) for isothermal and dynamic cure experiments. A helium flow of 25 mL min$^{-1}$ was used as purge gas for all the DSC experiments. Fully or partially cured solid BECy samples were sealed into standard aluminum DSC pans. The liquid samples, uncured mixture of BECy monomer and catalyst, were transferred into hermetic aluminum pans using a pipette and sealed with lids.

Uncured samples were tested first by DSC in the dynamic scan mode from –80 to 350°C at a heating rate of 10°C min$^{-1}$. This temperature scan range allowed for observation of the glass transition of BECy monomer and was below the decomposition temperature of the polymerized BECy. Integration of the exothermal peak gives the value of the total reaction heat $\Delta H_T$. A fully cured sample was also performed under these dynamic scan conditions to determine the $T_g$ of the fully cured BECy.
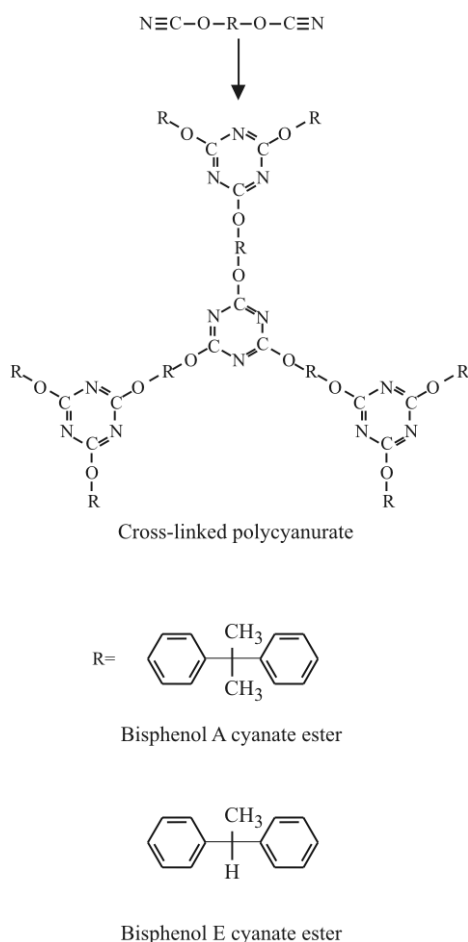
Two different methods were used to evaluate conversion *vs.* time of BECy under isothermal cure conditions. In method I, partially cured samples were prepared by pouring catalyzed BECy into silicon rubber molds followed by isothermal cure in an oven at a preset temperature ($T_c$=180, 200°C). After various curing times, ranging from 1 min to 6 h, samples were removed from the oven and quenched to room temperature with liquid nitrogen. A small piece (~10 mg) was cut from the sample for subsequent dynamic DSC evaluation from –80 to 350°C at 10°C min$^{-1}$. From these experiments both the residual reaction heat $\Delta H_r$ and $T_g$ of partially cured samples were obtained simultaneously.

To perform the isothermal curing method II, uncured BECy samples (~8 mg) were sealed in a hermetic pan with a lid and loaded into the DSC cell. The DSC cell is heated up to the cure temperature ($T_c$=160, 170, 180, 200°C) at a heating rate of 100°C min$^{-1}$, and then isothermally soaked from 1 to 6 h depending on the cure temperature used. After the first scan is finished, the DSC cell is cooled down to 25°C, and a second scan with the same temperature profile as the first is performed to obtain the baseline for analysis. Finally, the same sample is evaluated in dynamic mode from room temperature to 350°C at 10°C min$^{-1}$. The residual reaction heat $\Delta H_r$ is used to calculate the final conversion of the sample at the various isothermal cure temperatures. The cure kinetics of uncured BECy samples are also evaluated from dynamic scanning experiments at multiple heating rates of 2, 5, 10, 15 and 20°C min$^{-1}$.

## Results and discussion

### Thermogravimetric analysis

The decomposition temperature and volatile content of uncured bisphenol E cyanate ester was measured by TG (Fig. 2). The minimal mass loss below 200°C is mainly volatile content in the BECy monomer and catalyst, such as water and residual volatile solvents. At this temperature range, BECy shows very low (less than 1%) volatile content before curing. Above 400°C, the cured BECy decomposes, with 5% mass loss occurring at 438 and 437°C in nitrogen and air, respectively. In nitrogen, the decomposition rate reaches the highest value at 446°C and showed a large mass loss to about 46% of the initial sample mass by 800°C. When the sample was tested under air, it exhibited a similar sudden drop in mass. Under the air atmosphere, oxidation is involved and the entire sample is burned off by the end of the experiment. TG results confirm that the BECy does not generate significant volatile organic compounds (VOCs) and has a
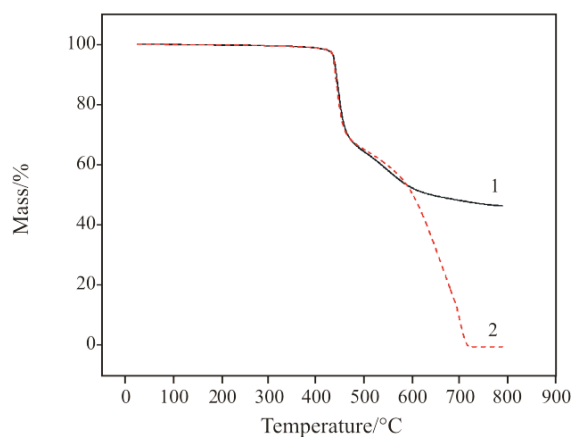


**Fig. 2** The TG curves (at 20°C min$^{-1}$) of catalyzed BECy under 1 – nitrogen and 2 – air



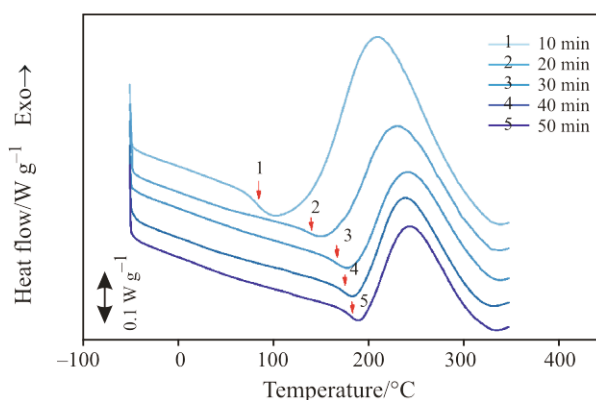**Fig. 3** Typical DSC curves for partially cured BECy samples that were cured at 180°C for various times

very high decomposition temperature, which is desirable for high temperature resin repair applications. It also indicates that the upper temperature limit for subsequent DSC experiments should be below 400°C to prevent sample decomposition in the cell.
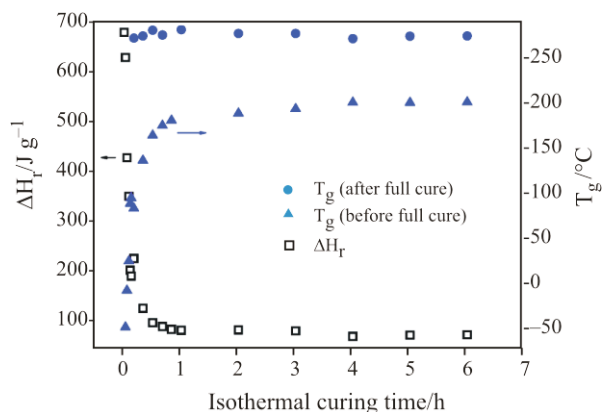
### Isothermal curing method

The isothermal curing method I allows for the calculation of residual reaction heat and determination of glass transition temperature from a single DSC scan. Typical dynamic DSC scans of BECy samples, which had first been partially cured isothermally in the oven at 180°C, are shown in Fig. 3. The $T_g$ (pointed out by arrows) of partially cured BECy increases with increasing isothermal cure time at 180°C. The exothermal peak area, which occurs after the $T_g$, represents the residual reaction heat $\Delta H_r$, and decreases with increasing isothermal cure time. The increase of $T_g$ and decrease of $\Delta H_r$ indicates how the reaction progresses with the cure time. The conversion of BECy monomer is calculated by:

$$\alpha = \frac{\Delta H_{\mathrm{T}} - \Delta H_{\mathrm{r}}}{\Delta H_{\mathrm{T}}} \qquad (1)$$
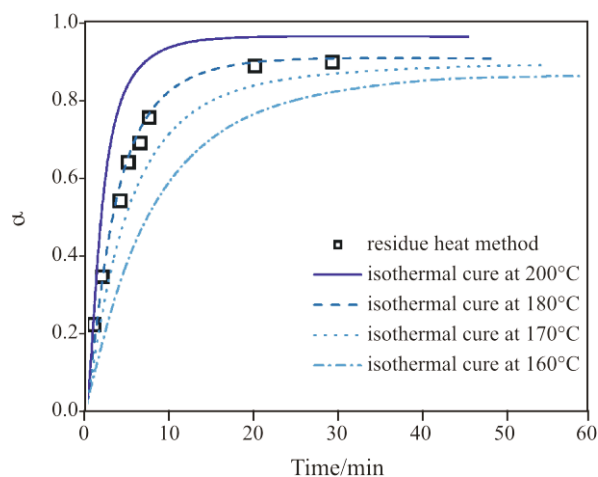
where the total reaction heat $\Delta H_{\mathrm{T}}$ is determined as 720 J g$^{-1}$ by scanning of uncured sample in the DSC cell at a heating rate of 10°C min$^{-1}$. After first scanning partially cured samples to determine $T_{\mathrm{g}}$ and $\Delta H_{\mathrm{r}}$, a second scan was performed to measure the $T_{\mathrm{g}}$ of fully cured BECy. The $T_{\mathrm{g}}$ and $\Delta H_{\mathrm{r}}$ of partially cured samples and their subsequent $T_{\mathrm{g}}$ from the second experiment are plotted *vs.* isothermal cure time in Fig. 4.

For short isothermal curing times, it is clear that the residual reaction heats, $\Delta H_{\mathrm{r}}$, decrease as the preceding isothermal cure time increases. After curing for one h at 180°C, the residual reaction heat, $\Delta H_{\mathrm{r}}$, reaches a plateau. Based on these isothermal cure experiments, the highest conversion at a cure temperature of 180°C is 91%. Therefore, a post-cure process is needed to reach the fully cured state. In Fig. 3, the exothermal peak areas, which are proportional to the residual reaction heats, have peak temperatures above the isothermal cure temperature. Additionally, the samples which cured longer than 1 h at 180°C all show peak temperatures closed to 250°C, indicating that a post-cure process should be carried out above 250°C for the samples to reach the fully cured state.

Isothermal curing method II was performed at four cure temperatures: 160, 170, 180 and 200°C, respectively. As mentioned previously, three individual scans are required to get enough information to plot conversion *vs.* time for the isothermal curing method II: (1) a first isothermal measurement of uncured BECy sample at the cure temperature for an extended period of time, (2) a second isothermal scan following the same temperature profile to obtain the baseline for data analysis, and (3) a third dynamic scan at 10°C min$^{-1}$, to measure $T_{\mathrm{g}}$ and $\Delta H_{\mathrm{r}}$ (to determine the value of final conversion). The highest possible conversions without subsequent post-cure processes were found to be 87, 89, 91 and 94% at cure



**Fig. 5** Plot of conversion $\alpha$ *vs.* time for isothermal cures of BECy at different curing temperature

temperatures of 160, 170, 180 and 200°C, respectively. The analyzed isothermal cure plot of conversion *vs.* time at different curing temperatures is shown in Fig. 5 (only the data at the beginning stage of the isothermal cure are shown). The experimental data of conversion *vs.* time obtained from isothermal cure method I (the residual heat method) is also shown in the Fig. 5, which matches very closely with the data obtained from isothermal cure method II at the same isothermal cure temperature of 180°C.

The conversion rate can be defined as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}H/\mathrm{d}t}{\Delta H_{\mathrm{T}}} \qquad (2)$$

where $\mathrm{d}H/\mathrm{d}t$ is the heat flow rate and can be measured directly by DSC. Modeling equations for the cure kinetics of thermosetting polymers generally have two categories: $n^{\mathrm{th}}$ order and autocatalytic. If more than one chemical reaction occurs during cure, the kinetic model may represent an overall process when these chemical reactions occur simultaneously [10].

For the cure of thermosetting polymers that follow $n^{\mathrm{th}}$ order kinetics, the rate of conversion is proportional to the concentration of unreacted materials:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^n \qquad (3)$$

where $n$ is the reaction order, and $k$ is the temperature dependent reaction rate constant given by the Arrhenius relationship:

$$k(T) = A\exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \qquad (4)$$

where $E_{\mathrm{a}}$ is the activation energy, $R$ the gas constant, $T$ the absolute temperature and $A$ the pre-exponential or frequency factor. Equation (3) indicates that the maximum conversion rate occurs at $\alpha=0$. The conver-



**Fig. 4** Residual reaction heat $\Delta H_{\mathrm{r}}$ and $T_{\mathrm{g}}$ of BECy samples isothermally cured at 180°C for various times

sion rate is dependent only on the amount of unreacted materials and assumes that the reaction products are not involved in the reaction.

If the reaction products are involved in the reaction, the autocatalytic model will apply:

$$\frac{d\alpha}{dt} = k'(1-\alpha)^n \alpha^m \qquad (5)$$

where, similarly, reaction rate constant $k'$ follows the Arrhenius relationship and $m$ is a component of the reaction order. According to Eq. (5), the conversion rate is zero at the beginning of the reaction and reaches a maximum value at an intermediate conversion.

To determine which models best describe the cure kinetics of BECy, a plot of conversion rate ($d\alpha/dt$) vs. conversion ($\alpha$) is made and shown in Fig. 6. As shown in Fig. 6, the conversion rate has a maximum value between 10 and 20% depending on the isothermal cure temperature ($T_c$). These characteristics indicate that the isothermal cure of BECy follows an autocatalytic model. The fitting results by the autocatalytic model are also shown in Fig. 6 as solid lines. The autocatalytic model has a good agreement to the experimental data, with the degree of fit $R^2 > 0.98$. The kinetic parameters $k$, $n$ and $m$ obtained by least squares regression are listed in Table 1. Obviously, the reaction rate constant increases with cure temperature. The isothermal cure of BECy has a total reaction order ($m+n$) of 2.4. Based on the logarithmic form of the Arrhenius relationship, a plot of $\ln k$ vs. $1/T$ (Fig. 7) gives the activation energy $E_a$ as 60.3 kJ mol$^{-1}$ and $\ln A$ as 11.2.

While the residual reaction heat, $\Delta H_r$, is difficult to measure when the reaction reaches a high degree of conversion ($\alpha > 95\%$), the $T_g$ measurably increases with cure state and serves as a more sensitive measure of conversion than residual reaction heat at the latter stages of cure. There is a one-to-one non-linear relationship between $T_g$ and conversion $\alpha$, independent of cure temperature for this high $T_g$ BECy system.
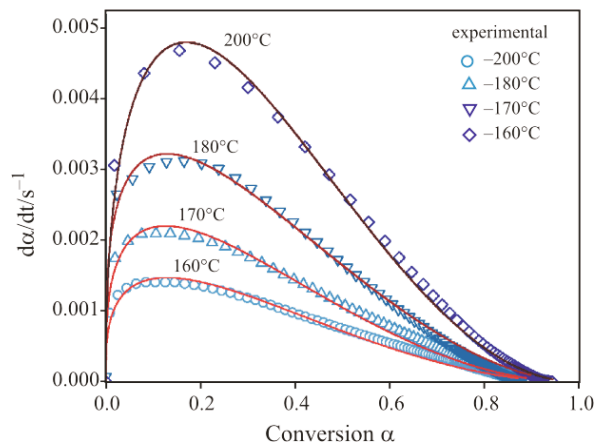
**Fig. 6** Autocatalytic modeling of isothermal cure data

**Table 1** Kinetic parameters at different isothermal cure temperatures

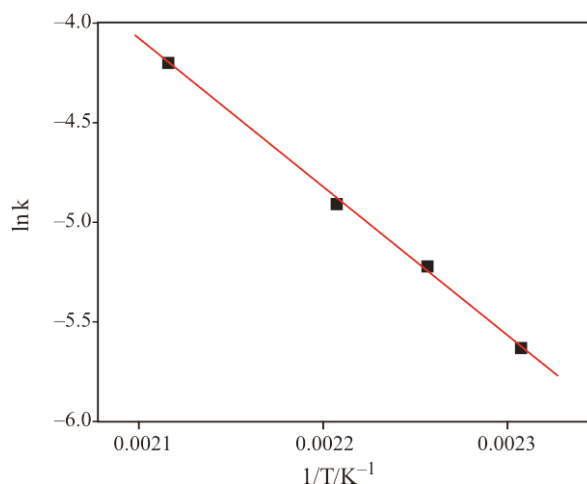| Cure temp./°C | $k \cdot 10^{-4}/s^{-1}$ | $n$ | $m$ | $n+m$ |
|---|---|---|---|---|
| 160 | 36 | 2.0 | 0.3 | 2.3 |
| 170 | 54 | 2.1 | 0.3 | 2.4 |
| 180 | 74 | 2.1 | 0.3 | 2.4 |
| 200 | 150 | 2.1 | 0.4 | 2.5 |

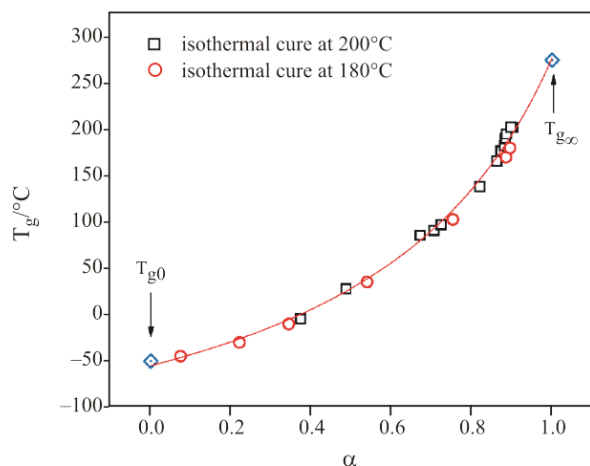**Fig. 7** Arrhenius plot obtained by autocatalytic model

Therefore, $T_g$ can be used as a primary variable to transform $T_g$ to conversion and vice versa, via the one-to-one relationship obtained from a theoretical or empirical fit of the experimental data.

To evaluate the relationship between $T_g$ and conversion, samples were prepared following the isothermal cure method I procedure: the uncured samples were isothermally cured at 180 and 200°C, respectively, for various periods of time; and then dynamic DSC scans were performed to measure the partially cured sample $T_g$ and conversion $\alpha$. A plot of $T_g$ vs. conversion $\alpha$ is shown in Fig. 8 with the $T_g$ increasing monotonically with conversion.

In Eq. (6), the empirical DiBenedetto equation, which is often used to fit $T_g$ vs. conversion data [11], is rewritten by assuming the partially cured system as a mixture of fully cured polymer and monomer:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1-(1-\lambda)\alpha} \qquad (6)$$

where $T_{g0}$ is the $T_g$ of the uncured monomer and $T_{g\infty}$ is the maximum $T_g$ for the fully cured sample. The parameter $\lambda$ is a structure dependent constant, theoretically equal to $\Delta C_{p\infty}/\Delta C_{p0}$, where $\Delta C_{p\infty}$ and $\Delta C_{p0}$ are the differences in heat capacity between the glassy and rubbery states at $T_g$ for fully cured sample and uncured sample, respectively.

**Fig. 8** $T_g$ *vs.* conversion $\alpha$ plot with DiBenedetto equation fitting



**Fig. 9** Dynamic scanning method: experimental DSC curves of uncured BECy (symbols) and model fittings (solid lines)

Taking the $T_g$ and $\alpha$ values experimentally, $T_{g0}$, $T_{g\infty}$ and $\lambda$ were determined by least squares regression as –56, 277°C and 0.32. The values of $T_{g0}$ and $T_{g\infty}$ are very close to the experimentally measured values (as shown in Table 2). The parameter $\lambda$ is difficult to measure accurately with traditional DSC techniques because of the large measurement uncertainties in $\Delta C_{p\infty}$ and $\Delta C_{p0}$; however, modulated DSC may be pursued in further experiments to experimentally measure the value of $\lambda$ and compare it with the value obtained through the model fit.
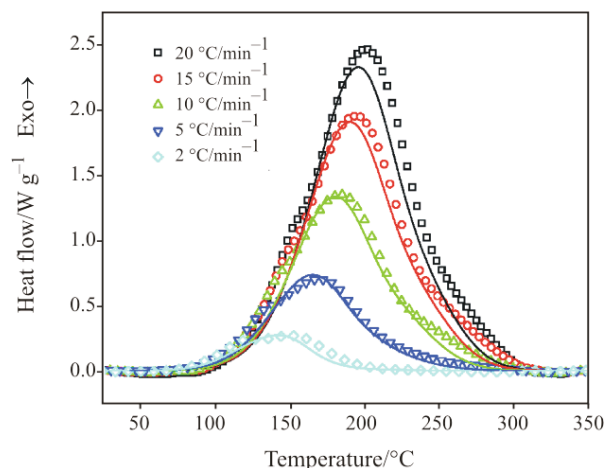
*Dynamic scanning method*

While the isothermal measurements have the advantage of a complete separation between the variables of time and temperature, dynamic scanning experiments allow for improved investigation of the kinetics at the start and end of the reaction, and the kinetic parameters can more easily be interpreted by a comparison of measurements at different heating rates [12]. Multiple dynamic DSC experiments were performed at heating rates of 2, 5, 10, 15 and 20°C min$^{-1}$, respectively, to test uncured BECy samples. Figure 9 shows the DSC scans for all of the experimental multi-heating-rate runs for the BECy samples.

The isothermal experimental data were well fit by an autocatalytic cure model. By combining Eqs (2), (4) and (5), the heat flow can be expressed as:

$$\frac{dH}{dt} = \Delta H_T A \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \alpha^m \quad (7)$$

**Table 2** Parameters for the DiBenedetto equation relating $T_g$ and conversion

|  | $\lambda$ | $T_{g0}$/°C | $T_{g\infty}$/°C |
|---|---|---|---|
| Calculated value | 0.34±0.2 | –55.9±4.1 | 276.5±5.6 |
| Measured value |  | –51.1 | 274.3 |

Using the kinetic parameters obtained from the isothermal experiments ($E_a$, $A$, $n$ and $m$) the experimental dynamic DSC data can be compared to the model, which are shown as solid lines in Fig. 9. The modeling curves fit the experimental data reasonably well throughout most of the temperature range, but deviate significantly in the high temperature regions. This deviation from the experimental data suggest that more complex cure mechanisms are involved and that BECy may not be characterized by an auto-catalytic model through the whole curing process under dynamic scanning conditions.

An isoconversional method, which assumes the activation energy and pre-exponential factor are both functions of the degree of cure, can be used to analyze the multi-heating-rate scan data [13, 14]. This makes it equally effective for analyzing both $n^{th}$-order and autocatalytic reactions.

In the analysis of experimental data from multi-heating-rate dynamic scans, there are two approaches often used to determine curing kinetic parameters: Kissinger's approach [15] and Ozawa's [16–19] approach.

The exothermal peak temperature, $T_p$, is shifted to higher temperatures with increasing heating rate. According to Kissinger's approach, the maximum reaction rate $d\alpha/dt$ occurs at $T_p$, where $d^2\alpha/dt^2=0$, and the kinetic equation can be expressed as

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (8)$$

Based on Kissinger's approach, a plot of $\ln(\beta/T_p^2)$ *vs.* $1/T_p$ gives the values of the pre-exponential factor $A$ and activation energy (where $\beta$ represents the heating rate in K s$^{-1}$). Figure 10 shows the plot of $\ln(\beta/T_p^2)$ *vs.* $1/T_p$.
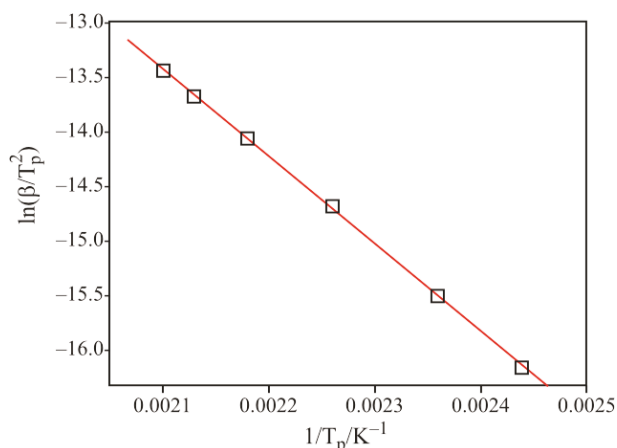
**Fig. 10** Plot used to determine kinetic parameters using Kissinger's approach

Ozawa's approach gives a simple relationship between the activation energy, the heating rate and isoconversion temperature:

$$\log\beta = -\frac{0.4567E_a}{RT_i} + A' \qquad (9)$$

where for each degree of conversion, $A'$ is a constant that can be expressed as

$$A' = \log\left[\frac{AE_a}{g(\alpha)R}\right] - 2.315 \qquad (10)$$

and $g(\alpha)$ is a function of the dependence of conversion [19]. Similarly, a plot of $\log\beta$ vs. $1/T_i$ at each degree of conversion gives a slope proportional to the corresponding activation energy $E_a$ and an intercept of the pre-exponential factor $A'$ (Fig. 11). Therefore, the relationship of activation energy and conversion can be measured through the whole reaction. The activation energy initially decreases with the increase of conversion, reaching a minimum value at around 30% conversion. It then increases, until about 70% conversion, before decreasing again at high conversions. The decrease of activation energy at the beginning may be due to the autocatalytic effect of the curing process and the subsequent increase of activation energy may be caused by the formation of the cross-linked network which restricts diffusion of the unreacted monomer. The decrease of activation energy at high conversions is still in question. At high conversions, the reaction no longer follows the autocatalytic kinetics and more complex mechanisms, such as diffusion control, are involved in the cure process. The $A'$ shows a similar trend as $E_a$ with conversion in Fig. 11. This is due to the kinetic compensation effect [20], which suggests that the value of $\ln A'$ varies linearly with $E_a$. Both Kissinger's and Ozawa's plots show a very good linear relationship between parameters based on the experimental
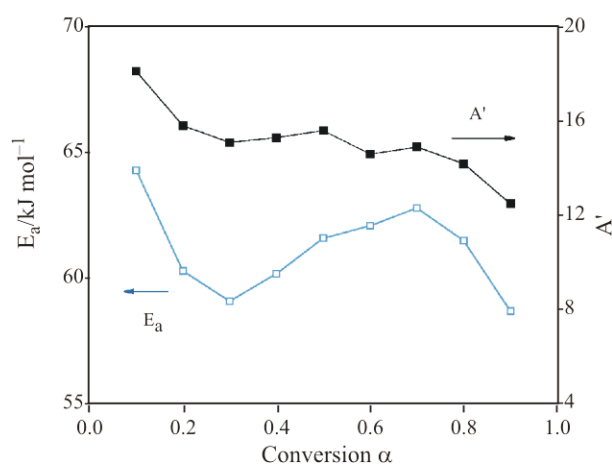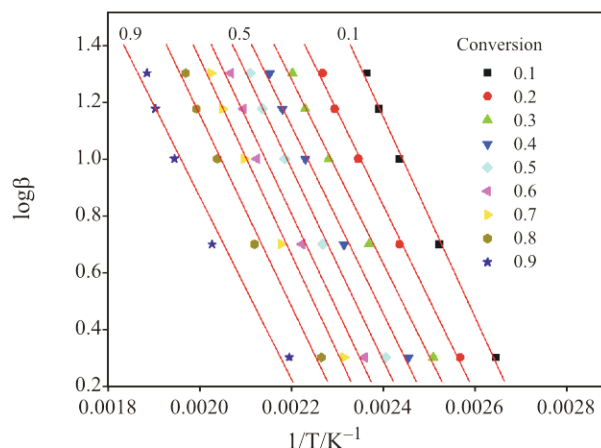


**Fig. 11** Isoconversional analysis: Ozawa's approach

**Table 3** Cure kinetic parameters calculated from Kissinger's approach

| Heating rate/ °C min⁻¹ | $T_p$/ °C | Kissinger | |
|---|---|---|---|
| | | $E_a$/kJ mol⁻¹ | $\ln A$ |
| 20 | 202.0 | 66.7±0.4 | 12.4±0.1 |
| 15 | 195.5 | | |
| 10 | 185.6 | | |
| 5 | 169.8 | | |
| 2 | 150.3 | | |

data. The calculated results based on Kissinger's approach are listed in Table 3. Ozawa approach gives an average value of 61.2 kJ mol⁻¹, which is slightly higher than the activation energy obtained from the isothermal curing method, but lower than that obtained from Kissinger's method.

Another isoconversional method is the Friedman's analysis [20]:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln f(\alpha)A - \frac{E_a}{RT} \qquad (11)$$

where $f(\alpha)$ is an unknown reaction model. Similar to Ozawa's approach, the activation energy and $\ln f(\alpha)A$ can be calculated from the slope and intercept of a $\ln d\alpha/dt$ *vs.* $1/T$ plot (Fig. 12). Friedman's analysis shows that activation energy *vs.* conversion is qualitatively similar to that found by Ozawa's method: the activation energy decreases first and then increases to a maximum value with the increase of conversion, and finally, decreases again at the highest conversion stages. Friedman's approach gives a lower average activation energy: 56.8 kJ mol$^{-1}$.

The activation energy $E_a$ of BECy is lower than the 80 kJ mol$^{-1}$ of the similar bisphenol A cyanate ester system and close to the reported value of 68.5 kJ mol$^{-1}$ calculated from a WLF diffusion-controlled model in [21]. The lower activation energy $E_a$ implies lower required cure temperatures to polymerize the resin, which is favorable for composite repair applications.
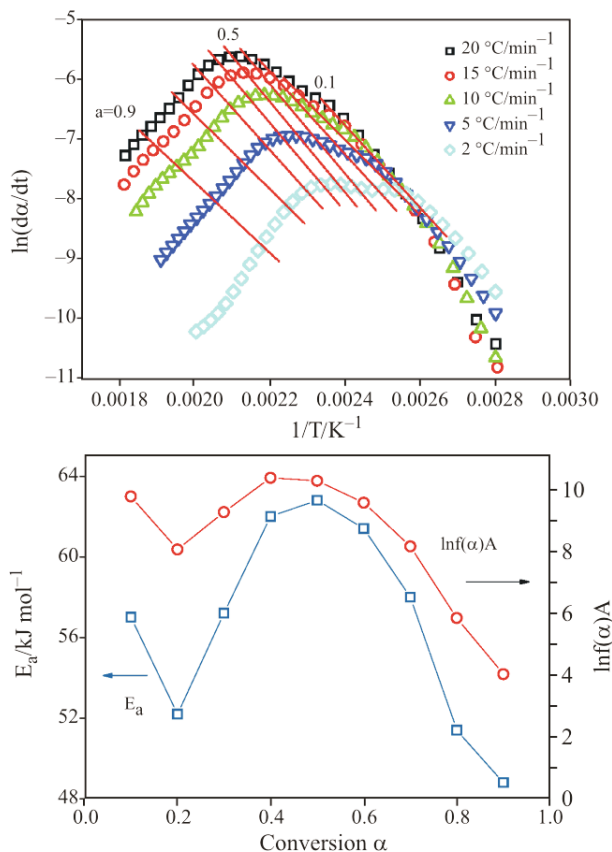


**Fig. 12** Isoconversional analysis: Friedman plot

## Conclusions

BECy has low viscosity at room temperature and can polymerize into a thermosetting polymer with a high glass transition temperature and good thermal stability. Fully cured BECy has a $T_g$ of 274°C and reaches the highest rate of decomposition at 446°C in air. The relationship of conversion *vs.* time at different isothermal cure temperatures shows how increasing the curing temperature increases the reaction rate and a post-cure process above 250°C is needed to fully cure the resin. The kinetic parameters are calculated by applying an autocatalytic model to fit the isothermal cure data. The analysis gives an activation energy of 60.3 kJ mol$^{-1}$ and a total reaction order around 2.4. Isothermal curing experiments also shows a one-to-one relationship between the $T_g$ of partially cured BECy and conversion. Multi-heating rate scans were analyzed by Kissinger's and Ozawa's approaches. The overall activation energy calculated from Kissinger's approaches is 66.7 kJ mol$^{-1}$, which is higher than the value obtained from the isothermal cure method. Ozawa and Friedman analysis give a relationship of activation energy *vs.* conversion, and an average value of 61.2, 56.8 kJ mol$^{-1}$, respectively.

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