

## Kinetic analysis of a fast reacting thermoset system

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### Abstract

Many thermosets are rapidly mixed and processed to quickly and efficiently effect a bond or produce a protective coating or a finished part. These processes are often characterized by non-linear time–temperature profiles. While it is often desirable to model the cure it can be challenging with such highly reactive systems in rapid processes. Described here is a hybrid approach to determine the kinetic equation for such a system. DSC multiple heating rate, isothermal and simulated process methods were combined with time–temperature superposition methodology to generate a master curve for the chemically controlled cure. Analysis of the master curve showed that it could be described by a second-order kinetic equation, consistent with polyurethane cure and permitting the complete kinetic description of the system.

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### 1. Introduction

The thermosetting system that is the subject of this study may be characterized as fast reacting. It is mixed and cured in less than 4 min in a pultrusion process where it is heated rapidly to nearly 180 °C and allowed to cool, as illustrated in Fig. 1. The goal of this study was to develop a model for the reaction kinetics of this system and to use the model to predict the evolution of cure during the production process. Isothermal DSC was the preferred method but presented challenges due to the highly reactive nature of this system. Note that above about 80 °C, almost 100 °C below the maximum process temperature, isothermal DSC measurements cannot be made due to the very short reaction times. Also note that vitrification does not occur during the process and therefore care must be taken to avoid it during isothermal cure so that all kinetic data are obtained while the reaction is under chemical control. The following approach was taken to measure the cure kinetics in the absence of vitrification

over a broad temperature range that includes actual process temperatures:

1. Assume the cure process can be described by a constant activation energy, and measure activation energy from the Ozawa multiple heating rate method.
2. Measure  $T_g$  and conversion after selected times at temperatures between 30 and 80 °C. Construct a master cure curve of conversion versus reduced time using the measured activation energy.
3. Measure  $T_g$  and conversion after DSC cures, which simulate process profiles and add these results to generate a total master cure curve.
4. Fit the master cure curve to an analytical model for cure and determine the pre-exponential factor, completing the kinetic analysis.

### 2. Experimental

#### 2.1. Materials

The two-part system consisting of a urethane resin and a cross-linker was provided in divided syringes along with

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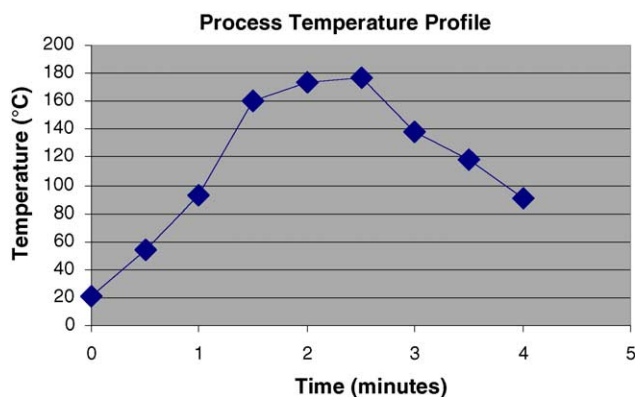


Fig. 1. Temperature profile for typical pultrusion process.

a 16 cm mixing tip. A fresh syringe of material was used for each experiment. The material initially dispensed from the syringe contained uneven amounts of the urethane and cross-linker and the first 15 ml of material forced from the syringe was discarded. Once the mix was uniform, roughly 3 ml were dispensed into a weighing dish. This deposit was stirred vigorously with a small flat wooden stick for exactly 20 s. (Several trials without this extra mixing step produced segregation of the components and large data variability.). A dot of the mixed components – roughly 5–10 mg – was placed in an aluminum liquid DSC pan using the tip of a round wooden stick. The pan was weighed, capped, placed in the DSC, and the temperature program started. The total time from dispensing the 3 ml into the pan and starting the run was about 1.75 min; from the kinetic model developed in this study <1% conversion occurred in this step.

### 2.2. DSC analysis

A TA Instruments 2920 DSC was used in this study. The program for the multiple heating rate experiments was as follows. The cell was pre-cooled to 10 °C. As soon as the sample and lids were in place, the sample was ramped at either 5, 10, or 20 °C/min to 250 °C. The sample was held at 250 °C for 5 min and cooled at 10 °C/min to –100 °C. A modulation was then applied, with an oscillation amplitude of  $\pm 1$  °C and a period of 60 s. The sample was ramped at 2 °C/min to 200 °C to measure the glass transition temperature. For this work,  $T_g$  is measured as the peak in the derivative of the temperature modulated DSC (TMDSC) heat capacity versus temperature curve. Heats of reaction were obtained by drawing a straight baseline under the reaction exotherm and integrating the area under the curve in accordance with the instrument software.

For the isothermal measurements, the cell was pre-heated to the respective isothermal temperature: 30, 45, 60, or 80 °C. As soon as the sample and lids were in place, a 20 or 45 min isothermal program was started. At the end of the isothermal program, the sample was cooled to –60 °C at 10 °C/min, held for 1 min, and heated from –60 to 250 °C at 10 °C/min to measure  $T_g$  and conversion.  $T_{g\infty}$  was measured for each

of these samples with a TMDSC run from –125 to 200 °C at 2 °C/min. The oscillation amplitude was  $\pm 1$  °C and the period was 60 s.

For the DSC runs which simulated pultrusion profiles, the cell temperature was initially at ambient. As soon as the sample and lids were in place, the sample was heated to either 130 or 160 °C at 40 °C/min, held at temperature for 1.5 min, and cooled to 25 °C at 20 °C/min. It was held at 25 °C for 30 min. These samples were subsequently heated to measure  $T_g$  and conversion.

## 3. Results and discussion

### 3.1. Activation energy

A common multiple heating rate method, which yields a simple relationship between the activation energy  $E$ , the heating rate  $\phi$  and isoconversional temperature  $T_i$ , is based on the work of Ozawa [1,2], and Flynn and Wall [3,4]:

$$E \cong \frac{-R \Delta(\ln \phi)}{1.052 \Delta(1/T_i)} \quad (1)$$

A more accurate value of  $E$  may be obtained by recalculating the constant 1.052 from tables in [5]. Several authors have observed that the extent of reaction at the peak exotherm is constant and independent of heating rate for several thermosetting systems [6], and that is the assumption made here.

Fig. 2 shows DSC at 10 °C/min heating rate for the uncured system. Note the onset of the cure exotherm near room temperature, which necessitated rapid mixing and sample preparation, and chilling of the DSC cell prior to measurement. While a small secondary exotherm was noted near 200 °C it was decided to ignore this because it was small and possibly due to errors in mixing. Nonetheless, it does suggest a possible complexity in the cure of this system. The heat of reaction, taken as the average of measurements at 5, 10 and 20 °C/min, was  $\Delta H_{Rxn} = 214$  J/g. A plot of heating rate versus peak temperature according to Eq. (1) gave an approximate activation energy of 58.9 kJ/mol (14.1 kcal/mol) and from the Doyle tables a revised value of 60.2 kJ/mol (14.4 kcal/mol) was obtained.

### 3.2. $T_g$ -conversion relationship and version 1 master curve

Samples were cured isothermally in the DSC between 30 and 80 °C, followed by a 10 °C/min heat to measure  $T_g$  and conversion from the residual heat, and a third TMDSC run to measure  $T_g$  for the fully cured thermoset,  $T_{g\infty}$ . An average of six measurements yielded a value of  $T_{g\infty} = 94$  °C. The isothermal cure data in Table 1 was observed to follow the well-known  $T_g$  - conversion relationships [7–9]. At higher conversions where  $T_g$  was more reliable than the residual exotherm, the following empirical relationship was established from the measured  $T_{g\infty}$  and the data in Table 1 in

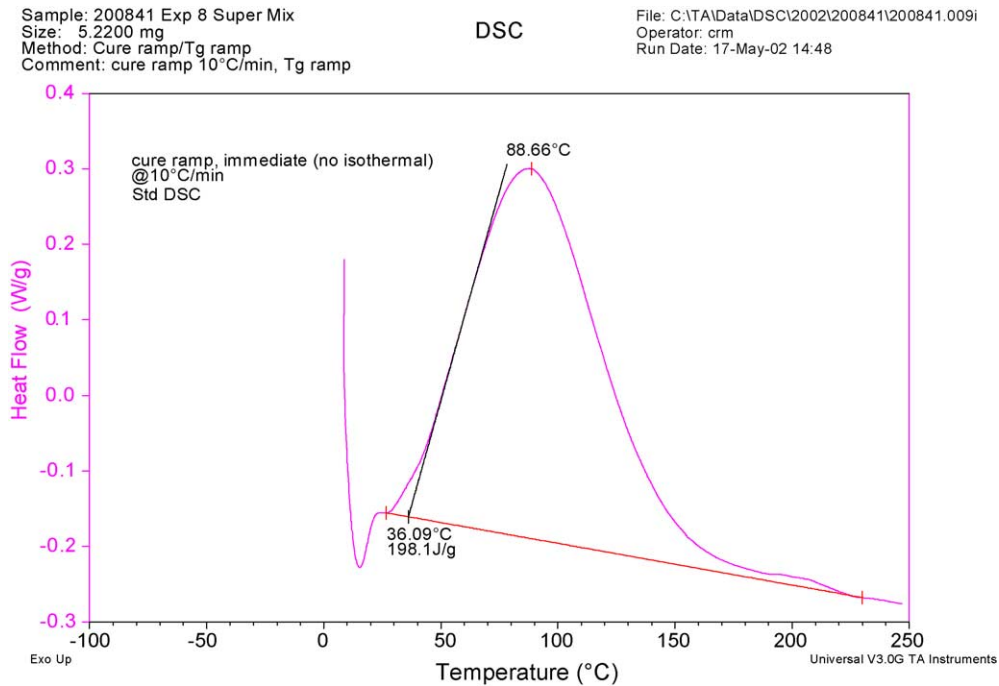


Fig. 2. Standard DSC of uncured polyurethane at 10 °C/min.

order to convert  $T_g$  to conversion:

$$\text{Conversion (\%)} = 44.1 + 0.719T_g - 0.0013T_g^2 \quad (2)$$

Fig. 3a shows the isothermal cure data measured at 30, 45, 60 and 80 °C. Table 1 and Fig. 3b show the same data shifted to a reference temperature of  $T_2 = 80$  °C, according to Eq. (3) using the measured activation energy of 60.2 kJ/mol [6,10,11], to form a master curve:

$$t_2 = t_1 \exp \left[ \frac{E(T_1 - T_2)}{RT_1 T_2} \right] \quad (3)$$

Note that the highest conversion reached on isothermal cure is 90%. Values closer to 100% conversion are required for the master curve to be truly representative of the entire cure process. The difficulty in achieving high conversions with isothermal cures is two-fold: the interference of vitrification at lower cure temperatures and the increasing error in recording the initial reaction with increasing cure temperature. Since the profile temperature quickly rises above  $T_{g\infty} = 94$  °C, vitrification does not occur during cure but only

Table 1  
 Isothermal cure data and cure times shifted to 80 °C using Eq. (3)

Temperature (°C)	Time (min)	$T_g$ (°C)	Conversion (%)	Time at 80 °C (min)
30.3	20	-21	29	0.7
45.5	20	1	43	2.2
60.3	20	35	70	6.0
60.3	45	53	76	13.4
80.5	20	63	86	20.6
80.5	45	76	90	46.3

when the temperature cools below  $T_g$  at the end of the cycle. For this reason vitrification must also be avoided in the modeling. To extend the master curve to include data closer to complete conversion, two data points were obtained from DSC cure profiles, which simulated the pultrusion process. The goal was to achieve one conversion level just below 90% to overlap with the isothermal results and the other between 95 and 100% to represent full cure.

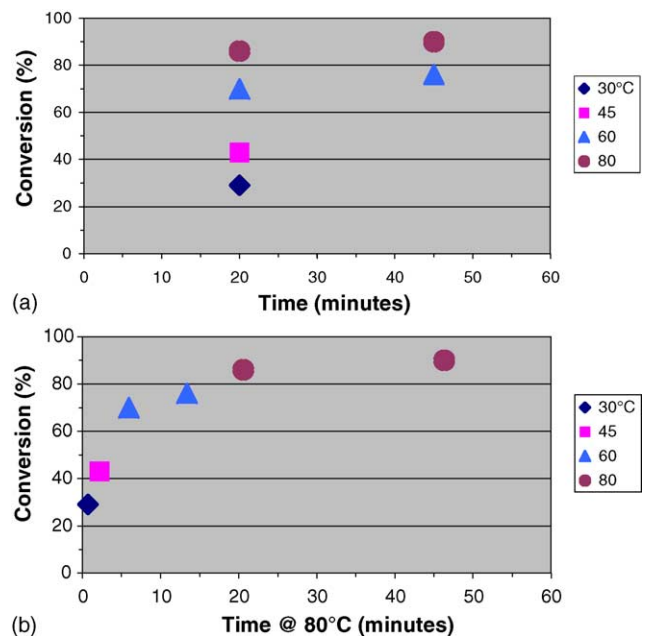


Fig. 3. (a) Isothermal conversion–time data. (b) Master curve formed from isothermal conversion data shifted to times at 80 °C by means of Eq. (3).

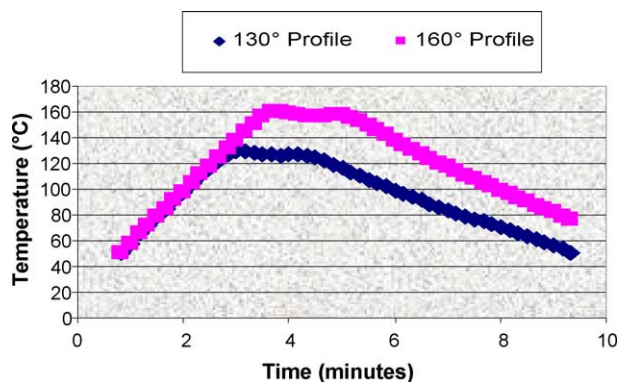


Fig. 4. DSC profiles that simulate the pultrusion process.

### 3.3. DSC time–temperature profiles

DSC profiles were designed which would give equivalent isothermal times at 80 °C ( $EIt_{80^{\circ}\text{C}}$ ) of  $\sim 35$  and  $\sim 125$  min, where  $EIt$  is computed by summing along the time–temperature profile as indicated below [6,10]. Note that for the process profile shown in Fig. 1  $EIt_{80^{\circ}\text{C}} = 115$  min can be computed:

$$EIt_{80^{\circ}\text{C}} = \sum t_{80^{\circ}\text{C}} = \sum t_i \left[ \frac{E(T - 80)}{R(T + 273)353} \right] \quad (4)$$

Fig. 4 shows the DSC profiles. Samples were cured according to these profiles and their conversions determined from subsequent DSC scans as shown in Table 2.

### 3.4. Version 2 master curve

The two data points for the DSC profile cures shown in Table 2 were added to the isothermal data to give the master curve shown in Fig. 5. Both autocatalytic and  $n$ th order

Table 2  
Measurements and computations from DSC profile studies

Maximum temperature (°C)	Equivalent isothermal time at 80 °C (min)	$T_g$ (°C)	Conversion (%)
130	37	63	86
160	133	87	97

Conversion was measured from  $T_g$  by means of Eq. (2).

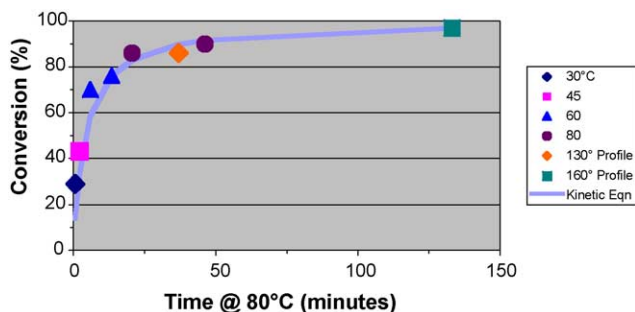


Fig. 5. Version 2 master cure curve with model from second-order kinetic equation.

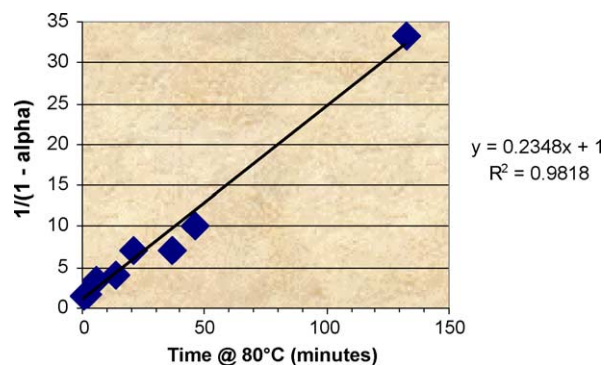


Fig. 6. Data of Fig. 5 plotted according to the integrated form of the second-order rate equation, Eq. (7).

reaction kinetics were examined. The lack of an inflection in the conversion time data of Fig. 5 plus the absence of a characteristic peak in the isothermal DSC curves eliminated autocatalytic kinetics. An attempt to fit the data to the first-order rate equation was unsuccessful. However, as shown in Fig. 6, a very good fit to the second-order rate equation:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^2 \quad (5)$$

was observed. This result is reasonable since second-order kinetics is typical of polyurethane cure, which involves the reaction of isocyanate with alcohol to form a urethane linkage. In Eq. (5)  $\alpha$  is conversion,  $t$  the time and  $k$  the rate constant. The temperature dependence of the rate constant is contained in the Arrhenius equation:

$$k = A \exp \left[ \frac{E}{RT} \right] \quad (6)$$

where  $A$  is the pre-exponential factor,  $E$  the activation energy (already determined to be 60.2 kJ/mol = 14.4 kcal/mol),  $R$  the gas constant and  $T$  the absolute temperature.

The master curve data of Fig. 5 were fit to the integrated form of the second-order rate equation:

$$\frac{1}{1 - \alpha} = 1 + kt \quad (7)$$

as shown in Fig. 6. The slope, which is the 80 °C rate constant  $k_{80}$ , was found to be 0.235 min<sup>-1</sup>. Rearranging Eq. (7), the 80 °C master curve can be described as:

$$\alpha_{80} = \left( \frac{k_{80}t}{1 + k_{80}t} \right) = \frac{0.235 (\text{min}^{-1})t}{1 + 0.235 (\text{min}^{-1})t} \quad (8)$$

This relationship is shown in Fig. 5 as ‘Kinetic Eqn’. Table 3 compares measured isothermal data with calculations from Eq. (8). Agreement is poorest for the low conversion data which were taken at the lowest temperatures, but improves to give good agreement for conversion >75%. Based on the good fit of the data in Fig. 6, including the low conversion data, we feel that these data are well represented by second-order kinetics. Taking the measured activation energy as an estimate it was observed that better agreement at low

Table 3  
Isothermal cure data compared with calculations from Eq. (8)

Temperature (°C)	Time (min)	Conversion (%)	
		Isothermal and profile DSC	Eq. (8)
30.3	20	29	14
45.5	20	43	33
60.3	20	70	59
60.3	45	76	76
80.5	20	86	82
80.5	45	90	91
130 Profile		86	90
160 Profile		97	97

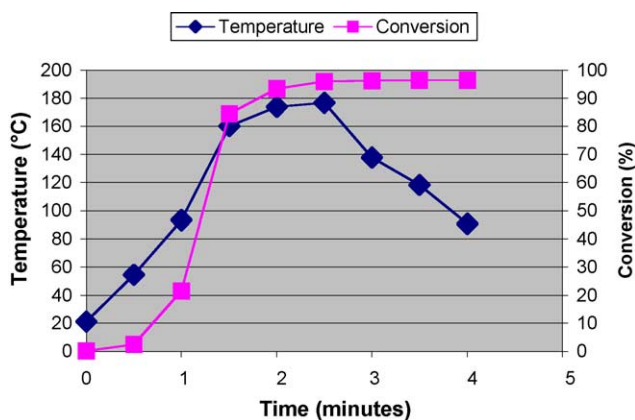


Fig. 7. Process temperature profile and development of conversion along the profile.

conversion could be obtained with a lower activation energy with a relatively small effect at high conversions. However, a lower activation energy also resulted in a lower correlation coefficient for the fit to second-order kinetics (see Fig. 6). This approach was not pursued since accuracy at high conversions was an important factor in this study. We suggest that an initially lower activation energy that increases to approximately that measured in this work may give a good fit at all conversions. Based on the original assumption of a constant activation energy and noting the possible complexity in the reaction observed in Fig. 2, we conclude that our hybrid approach gives a good estimation of the kinetics for this fast reacting thermoset system.

The temperature dependence of  $k$  ( $\text{min}^{-1}$ ) becomes

$$\begin{aligned}
 k_T &= k_{80} \exp \left[ \frac{E(T - 80)}{R(273 + 80)T} \right] \\
 &= 0.235 \exp \left[ \frac{14400(T - 80)}{702T(K)} \right] \quad (9)
 \end{aligned}$$

Eq. (9) allows computation of the master curve at any temperature. A value for the pre-exponential factor of  $2.88\text{E}-10$  can be calculated by incorporating the value for  $k$  at  $80^\circ\text{C}$  of  $0.235 \text{ min}^{-1}$  into Eq. (6).

Fig. 7 shows conversion along the process profile. This was accomplished by calculating the cumulative EIt for times and temperatures along the process profile from Eq. (4) and then using those results to compute conversion from Eq. (8). Conversion for this system cured according to the process profile with  $\text{EIt} = 115 \text{ min}$  at  $80^\circ\text{C}$  can be estimated at 96–97%.

#### 4. Summary

This thermosetting system is fast reacting, difficult to mix without significant reaction taking place, and exhibits some possible complexity in its cure. A variety of DSC techniques were employed to elucidate the cure mechanism and kinetics. Multiple heating rate DSC was used to measure the activation energy for cure, while isothermal and simulated process DSC were used to generate conversion–time data. Time–temperature superposition techniques were used to generate master curves for the chemically controlled cure. The polyurethane system was found to follow second-order kinetics, consistent with the polyurethane cure reaction. Master cure curves were constructed and analytical expressions developed to describe the conversion–time–temperature relationship.

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