

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.

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 minutes in a pultrusion process where it is heated rapidly to nearly 180°C and allowed to cool, as illustrated in Figure 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

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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 vs. 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.

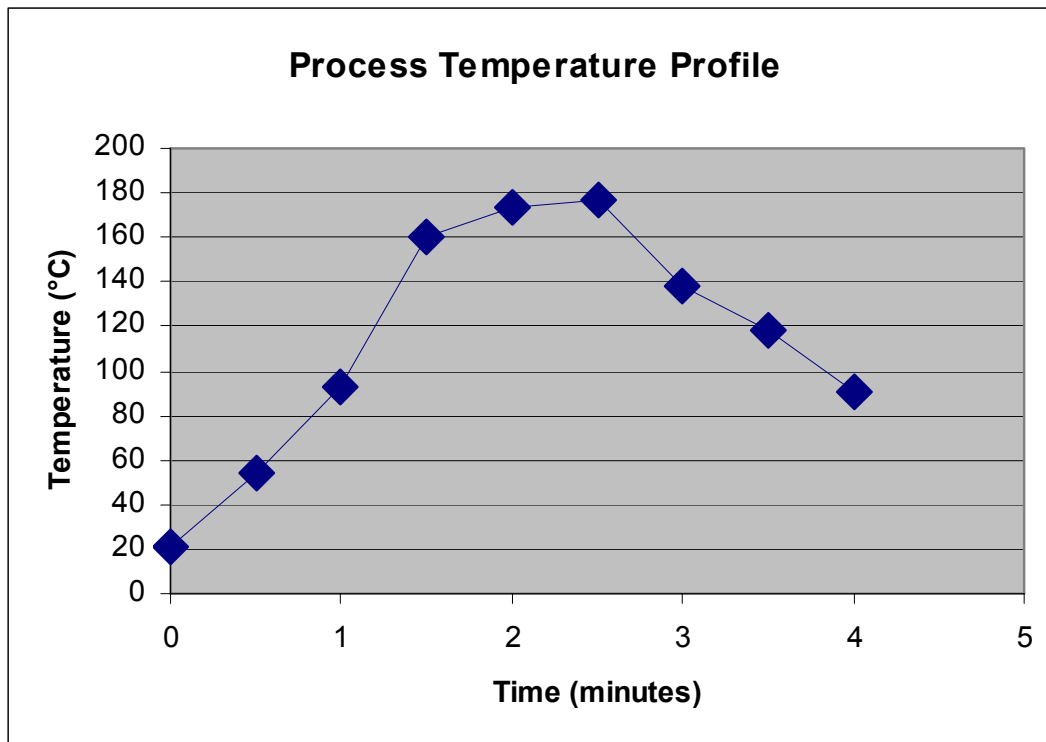


Figure 1. Temperature profile for typical pultrusion process.

EXPERIMENTAL

Materials. The two-part system consisting of a urethane resin and a cross-linker was provided in divided syringes along with 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 seconds. (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 minutes; from the kinetic model developed in this study <1% conversion occurred in this step.

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/minute to 250°C. The sample was held at 250°C for 5 minutes and cooled at 10°C/minute to -100°C. A modulation was then applied, with an oscillation amplitude of $\pm 1^\circ\text{C}$ and a period of 60 seconds. The sample was ramped at 2°C/minute 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 vs. 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 minute isothermal program was started. At the end of the isothermal program, the sample was cooled to -60°C at 10°C/minute, held for one minute, and heated from -60°C to 250°C at 10°C/minute to measure T_g and conversion. $T_{g\infty}$ was

measured for each of these samples with a TMDSC run from -125°C to 200°C at $2^{\circ}\text{C}/\text{minute}$. The oscillation amplitude was $\pm 1^{\circ}\text{C}$ and the period was 60 seconds.

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°C or 160°C at $40^{\circ}\text{C}/\text{minute}$, held at temperature for 1.5 minutes, and cooled to 25°C at $20^{\circ}\text{C}/\text{minute}$. It was held at 25°C for 30 minutes. These samples were subsequently heated to measure T_g and conversion.

RESULTS AND DISCUSSION

Activation Energy. A common multiple-heating-rate method, which yields a simple relationship below between the activation energy E , the heating rate ϕ and isoconversional temperature T_i , is based on the work of Ozawa (1,2), and Flynn and Wall (3,4).

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

A more accurate value of E may be obtained by recalculating the constant 1.052 from tables in Doyle (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.

Figure 2 shows DSC at $10^{\circ}\text{C}/\text{min}$ 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 $20^{\circ}\text{C}/\text{min}$, was $\Delta H_{\text{Rxn}} = 214 \text{ J/g}$. A plot of heating rate vs. peak temperature according to Eq. (1) gave an approximate activation energy of 58.9 kJ/mol (14.1 kcal/mole) and from the Doyle tables a revised value of 60.2 kJ/mol (14.4 kcal/mole) was obtained.

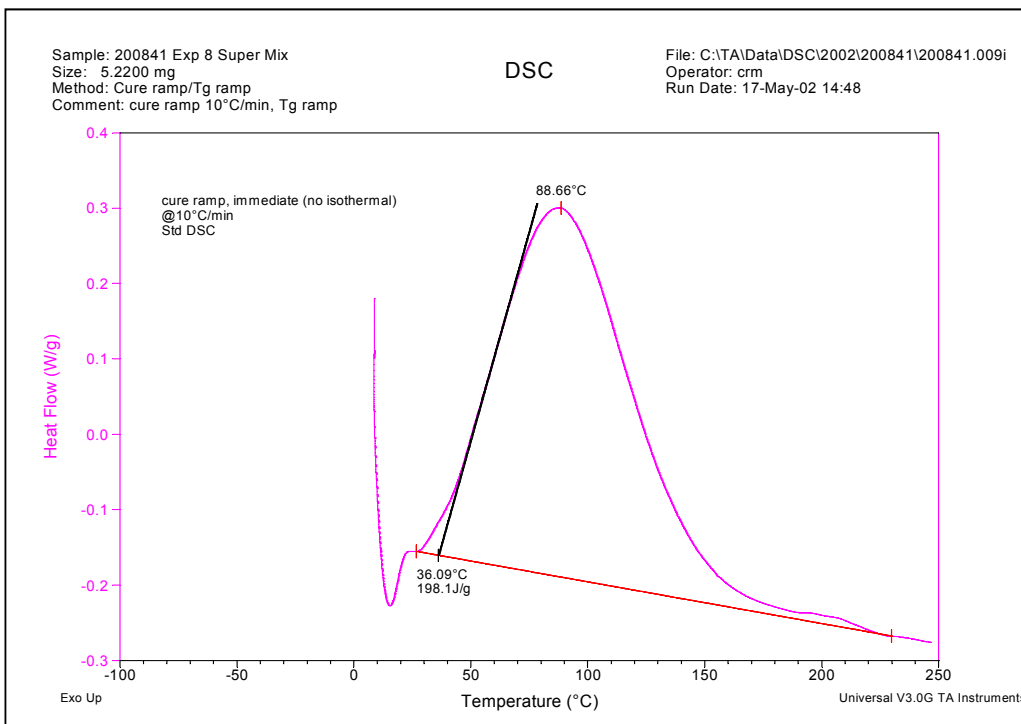


Figure 2. Standard DSC of uncured polyurethane at 10°C/minute.

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∞}. An average of six measurements yielded a value of T_{g∞} = 94°C. The isothermal cure data in Table I 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∞} and the data in Table I in order to convert T_g to conversion.

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

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

$$t_2 = t_1 \exp [E (T_1 - T_2) / RT_1 T_2] \quad (3)$$

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 twofold: 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 to above $T_{g\infty} = 94^\circ\text{C}$, vitrification does not occur during cure but only when the temperature cools to 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.

Table I. Isothermal Cure Data and Cure Times Shifted to 80°C Using Eq. 3.

Temperature (°C)	Time (minutes)	T _g (°C)	Conversion (%)	Time@80°C (minutes)
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

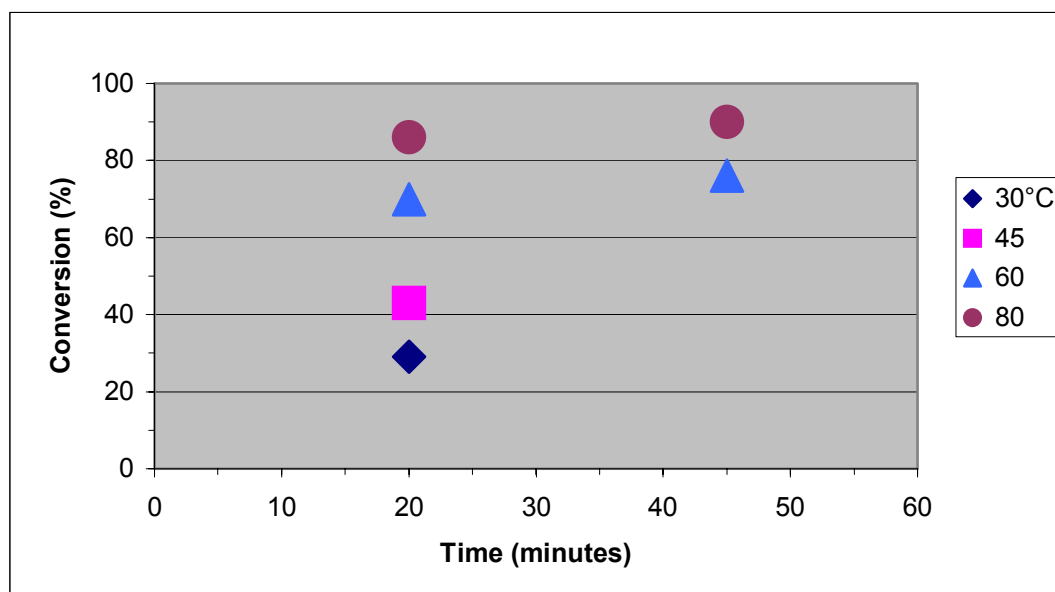


Figure 3a. Isothermal conversion – time data.

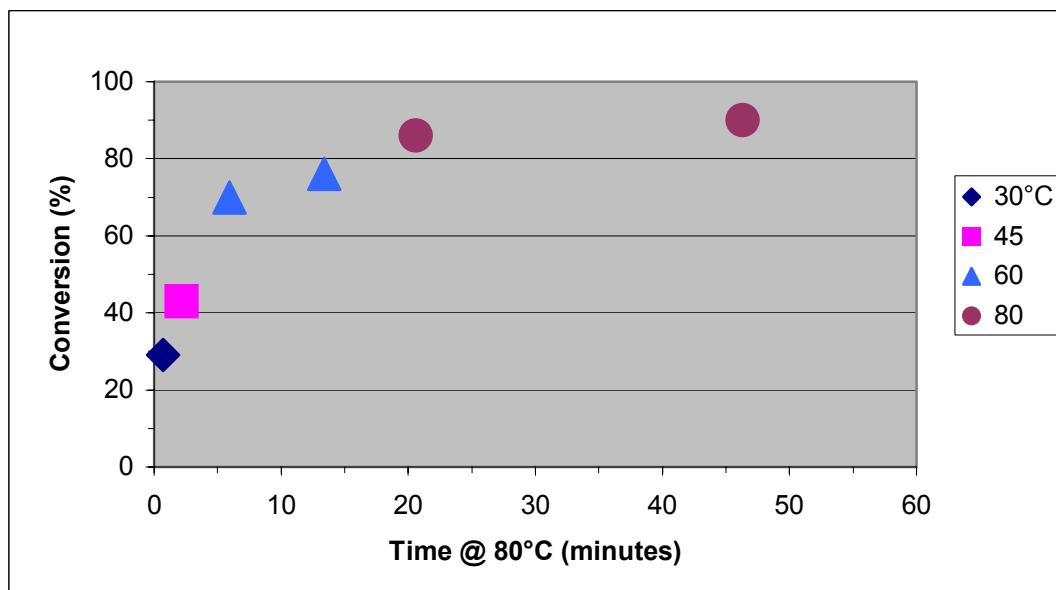


Figure 3b. Master curve formed from isothermal conversion data shifted to times at 80°C by means of Eq. 3.

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

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

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

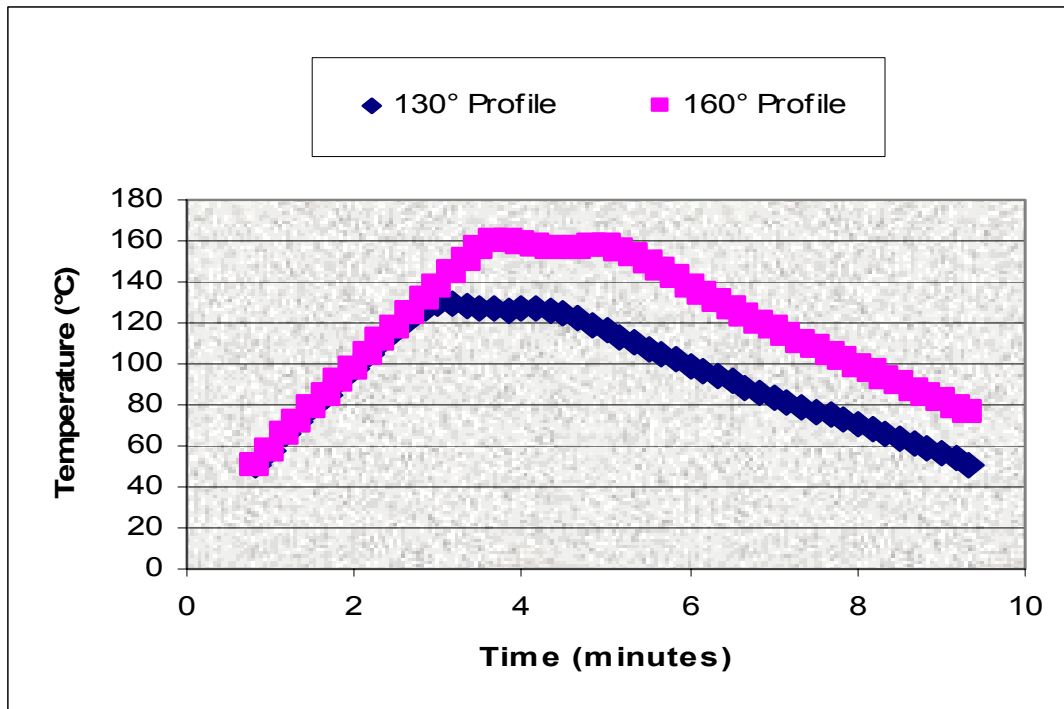


Figure 4. DSC profiles that simulate the pultrusion process.

Table II. Measurements and computations from DSC profile studies. Conversion was measured from T_g by means of Eq. 2.

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

Version 2 Master Curve. The two data points for the DSC profile cures shown in Table II were added to the isothermal data to give the master cure shown in Figure 5. Both autocatalytic and n th order reaction kinetics were examined. The lack of an inflection in the conversion – time data of Figure 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 Figure 6, a very good fit to the 2nd order rate equation,

$$d\alpha/dt = k (1 - \alpha)^2 \quad (5)$$

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 Equation 5 α is conversion, t is time and k is the rate constant. The temperature dependence of the rate constant is contained in the Arrhenius equation

$$k = A \exp[E / RT] \quad (6)$$

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

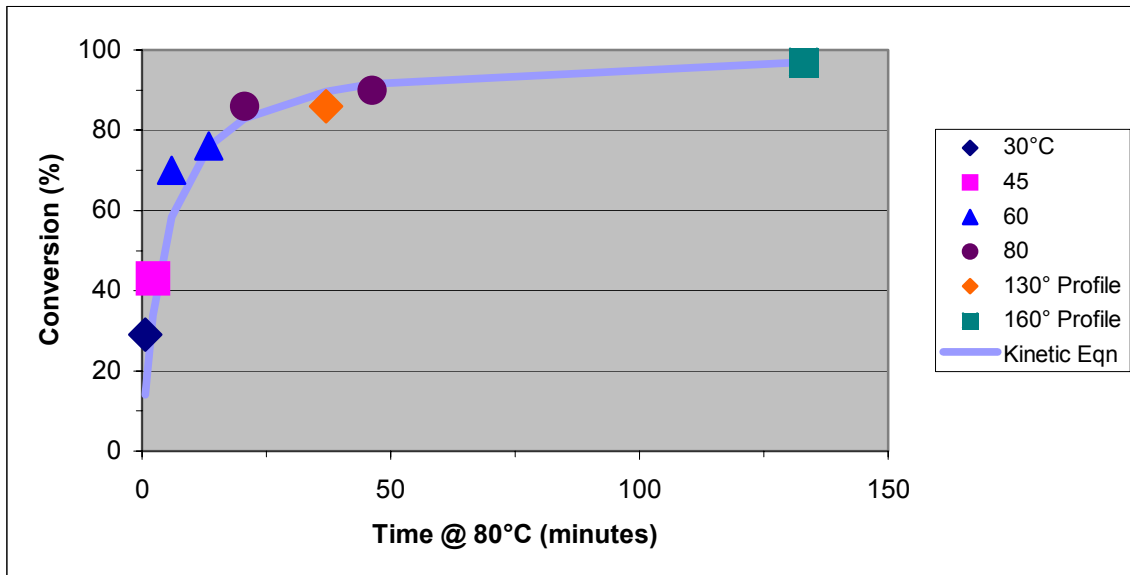


Figure 5. Version 2 master cure curve with model from 2nd order kinetic equation.

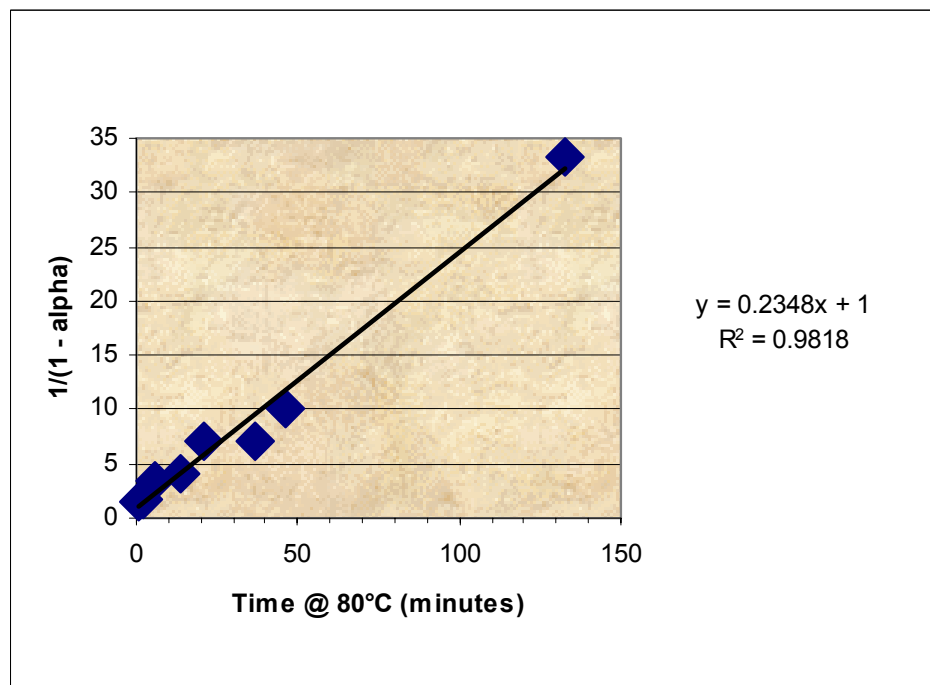


Figure 6. Data of Figure 5 plotted according to the integrated form of the 2nd order rate equation, Equation 7.

The master curve data of Figure 5 were fit to the integrated form of the 2nd order rate equation,

$$1 / (1 - \alpha) = 1 + kt \quad (7)$$

as shown in Figure 6. The slope, which is the 80°C rate constant k_{80} , was found to be 0.235 min^{-1} . Rearranging Eq. 7 the 80°C master curve can be described as

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

This relationship is shown in Fig. 5 as “Kinetic Eqn”. Table III compares measured isothermal data with calculations from Equation 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 Figure 6, including the low conversion data, we feel that these data are well represented by 2nd order kinetics. Taking the measured activation energy as an estimate it was observed that better agreement at low 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 2nd order kinetics (see Figure 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 Figure 2, we conclude that our hybrid approach gives a good estimation of the kinetics for this fast reacting thermoset system.

Table III. Isothermal Cure Data Compared with Calculations from Equation 8.

Temperature (°C)	Time (minutes)	<u>Conversion (%)</u> Isothermal and Profile DSC	<u>Conversion (%)</u> Equation 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°C Profile		86	90
160°C Profile		97	97

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

$$k_T = k_{80} \exp [E (T - 80) / R (273 + 80) T] = 0.235 \exp [14400*(T - 80) / 702T(K)] \quad (9)$$

Equation 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°C of 0.235 min^{-1} into Eq. 6.

Figure 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 $EIt = 115 \text{ min @ } 80^\circ\text{C}$ can be estimated at 96-97%.

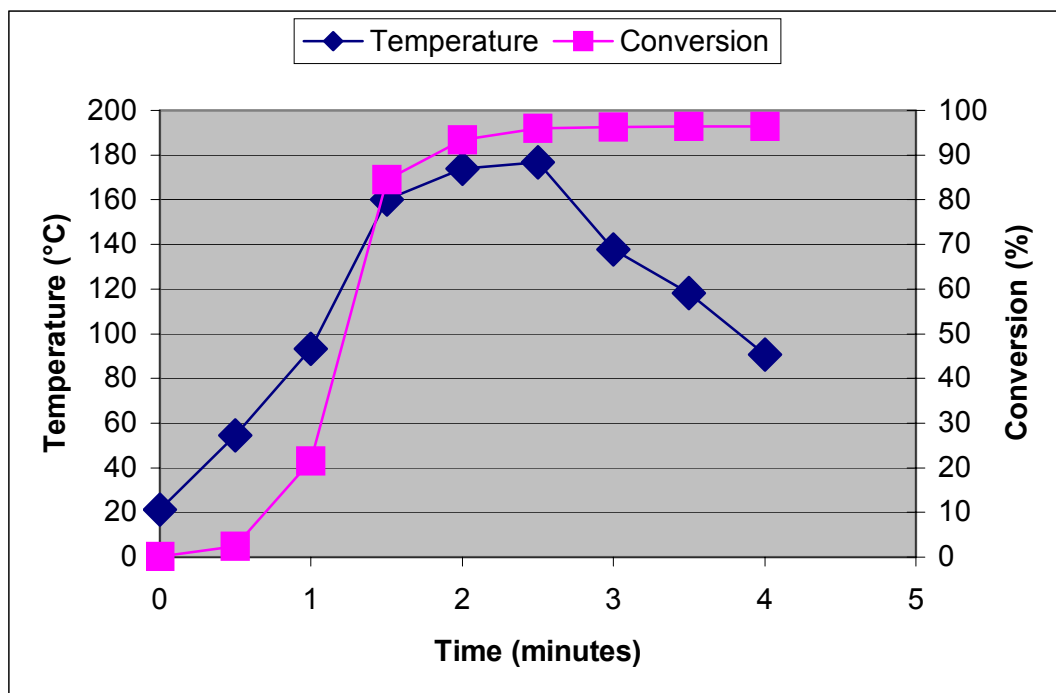


Figure 7. Process temperature profile and development of conversion along the profile.

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 2nd order kinetics, consistent with the polyurethane cure reaction. Master cure curves were constructed and analytical expressions developed to describe the conversion-time-temperature relationship.

REFERENCES

1. T. Ozawa, Bull. Chem. Soc. Jpn. 38, 1881 (1965).
2. T. Ozawa, J. Therm. Anal. 2, 301 (1970).
3. J. H. Flynn and L. A. Wall, J. Polym. Sci., Part B 4, 323, (1966).
4. J. H. Flynn and L. A. Wall, J. Res. Natl. Bur. Stand., Sect A 70, 487 (1966).
5. C. D. Doyle, Anal. Chem. 33, 77 (1961).
6. R. B. Prime, Chapter 6 “Thermosets” in Thermal Characterization of Polymeric Materials, E. A. Turi, ed., Academic Press, 1997.
7. J. P. Pascault and R. J. J. Williams, J. Polym. Sci., Part B: Polym. Phys. 28, 85 (1990).
8. A. Hale, C. W. Macosko and H. E. Bair, Macromolecules 24, 2610 (1991).
9. R. A. Venditti and J. K. Gillham, J. Appl. Polym. Sci. 64, 3 (1997).
10. R. B. Prime, Proceed. North Am. Therm. Anal. Conf. 14, 137 (1985).
11. C. M. Neag and R. B. Prime, J. Coat. Technol. 63(797), 37 (1990).