

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 09-02-2011		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE CURE CHARACTERISTICS OF TRICYANATE ESTER HIGH TEMPERATURE COMPOSITE RESINS (Preprint)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Andrew J Guenther (AFRL/RZSM), Kevin R Lamison (ERC), Matthew C Davis (NAWC), Lee R Cambrea (NAWC), Gregory R Yandek (AFRL/RZSM), and Joseph M Mabry (AFRL/RZSM)				5d. PROJECT NUMBER	
				5f. WORK UNIT NUMBER 23030521	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZSM 9 Antares Rd. Edwards AFB CA 93524-7401				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RZ-ED-TP-2011-029	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RZ-ED-TP-2011-029	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for public release; distribution unlimited (PA #10780).					
13. SUPPLEMENTARY NOTES Proceedings of SAMPE 2011					
14. ABSTRACT Highly aromatic tricyanate ester resins exhibit glass transition temperatures well in excess of 350 degrees Celsius when thermally cured to full conversion. In many cases, though, complete conversion is difficult to achieve in practice due to the highly rigid nature of the molecules. A thorough understanding of the cure process is thus important for realizing the full potential of these materials. In order to characterize the cure of these systems completely, measurements of cure kinetics were undertaken using both isothermal and non-isothermal DSC, and compared to measures of conversion obtained through IR spectroscopy and thermomechanical analysis. These measurements were performed on Primaset PT-30 (a commercially available resin), as well as a newly synthesized tricyanate with enhanced molecular chain flexibility. The effect of catalytic impurities on the cure kinetics and extent of cure was also examined. The more flexible tricyanate showed a decrease in activation energy as well as increased extent of network formation after cure temperatures ranging from 210 to 290 degrees Celsius. Although the Tg at full conversion of the flexible tricyanate was lower than that of PT-30, the increased extent of network formation enabled the flexible system to achieve Tg values nearly as high or higher than the corresponding values for PT-30 under identical cure conditions.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dr. Joseph M. Mabry
Unclassified	Unclassified	Unclassified	SAR	15	19b. TELEPHONE NUMBER (include area code) N/A

CURE CHARACTERISTICS OF TRICYANATE ESTER HIGH-TEMPERATURE COMPOSITE RESINS

Andrew J Guenther¹, Kevin R Lamison², Matthew C Davis³,
Lee R Cambrea³, Gregory R Yandek¹, Joseph M Mabry¹

¹Air Force Research Laboratory, Propulsion Directorate
Edwards AFB, CA 93524

²ERC Corporation, Edwards AFB, CA 93524

³Naval Air Warfare Center, Weapons Division, China Lake, CA 93555

ABSTRACT

Highly aromatic tricyanate ester resins exhibit glass transition temperatures well in excess of 350 degrees Celsius when thermally cured to full conversion. In many cases, though, complete conversion is difficult to achieve in practice due to the highly rigid nature of the molecules. A thorough understanding of the cure process is thus important for realizing the full potential of these materials. In order to characterize the cure of these systems completely, measurements of cure kinetics were undertaken using both isothermal and non-isothermal DSC, and compared to measures of conversion obtained through IR spectroscopy and thermomechanical analysis. These measurements were performed on Primaset PT-30 (a commercially available resin), as well as a newly synthesized tricyanate with enhanced molecular chain flexibility. The effect of catalytic impurities on the cure kinetics and extent of cure was also examined. The more flexible tricyanate showed a decrease in activation energy as well as increased extent of network formation after cure temperatures ranging from 210 to 290 degrees Celsius. Although the T_g at full conversion of the flexible tricyanate was lower than that of PT-30, the increased extent of network formation enabled the flexible system to achieve T_g values nearly as high or higher than the corresponding values for PT-30 under identical cure conditions.

1. INTRODUCTION

Polycyanurates, or “cyanate ester resins” [1-3] represent a key “next generation” material technology for a variety of aerospace applications [4], including aircraft skin components [5], airframes for missiles [6], and heat shields on spacecraft [7]. Monomers containing three or more cyanate ester groups, herein referred to as “tricyanates” for simplicity, such as the “phenol triazine” resins (Primaset® PT-30 and others) tend to form networks with a high density of physical cross-links, since the central branch point(s) in each monomer becomes an effective physical cross-link once the chemical cross-linking reaction has been substantially completed. Such a high density of physical cross-links results in values of the (dry) glass transition temperature (T_g) for tricyanates of 320-350 °C [2], with values of around 400 °C also reported [8], making these materials attractive candidates for high-temperature polymer matrix composite applications.

The most attractive thermal properties of tricyanates tend to be obtained when highly rigid molecules of a mostly aromatic character are utilized as monomers, however, the resultant rigid molecular networks typically suffer from several drawbacks that limit their performance. For

example, the combination of rigidity and a high cross-link density often leads to brittleness upon cure. In addition, limited molecular flexibility is thought to play a role in preventing complete cure of the cyanate ester groups, which must join together three at a time in cyclotrimerization. Uncured cyanate ester groups, when subsequently heated to 200 °C or above, can participate in moisture-induced degradation reactions that produce volatile by-products, creating blisters in cured parts and weakening the network [9]. The incorporation of flexible chemical linkages into these networks may mitigate these issues, however, at present there are few if any comparative reports on the properties of rigid and more flexible tricyanates.

Recently, the synthesis and properties of a number of tricyanates that incorporate more flexible chemical bonds into the network have been reported. Laskoski and co-workers [10] created oligomeric cyanate esters with highly flexible ether linkages in the backbone; these, though, had dry glass transition temperatures below 150 °C. Yameen et al. [11] synthesized tricyanates with more favorable thermal properties for high-temperature applications that were comparable in performance to the best available dicyanate monomers. Most recently, Cambrea et al. [12] reported the synthesis and properties of a tricyanate analog of Bisphenol E-based cyanate ester, with a dry T_g of 305 °C and other properties equal to or slightly better than the corresponding dicyanate. In all of these cases, the physical cross-link density was considerably lower than that of Primaset® PT-30, thus it is difficult to deconvolute the effects of molecular flexibility and cross-link density in determining physical properties.

In this paper, we report on the properties of a newly synthesized tricyanate ester with a physical cross-link density almost identical to that of Primaset® PT-30, but with flexible chemical linkages incorporated into the monomer. A comparative examination of the physical properties of both Primaset® PT-30 and the new tricyanate showed that molecular flexibility had several noticeable effects, including a lowered activation energy for cure, a higher extent of cure, lower thermo-chemical stability leading to a lower maximum use temperature under dry conditions, and similar “wet” glass transition temperatures. The details have been reported elsewhere [13]. In this paper, we focus on heretofore unreported aspects of the cure kinetics and physical properties of the flexible tricyanate, namely, the effect of impurities on cure kinetics, comparative kinetics derived from non-isothermal and isothermal differential scanning calorimetry (DSC) measurements, and comparative measures of the extent of cure based on DSC, Fourier Transform Infrared (FT-IR) Spectroscopy, and Oscillatory Thermomechanical Analysis (OTMA). Specifically, we found that impurities do increase the rate of cure while affecting the activation energy in specific ways, that non-isothermal and isothermal methods yield very similar activation energies (though with more uncertainty for non-isothermal methods), and that OTMA measurements provided qualitatively useful but quantitatively variable or limited data on the extent of cure.

2. EXPERIMENTATION

2.1 Materials

Primaset® PT-30 was kindly supplied from Lonza, Inc., stored at 4 °C under dry conditions, and used as received in a low-humidity environment. 1,2,3-tris(4-cyanatophenyl)propane, herein referred to as “FlexCy”, a tricyanate with a flexible linkage replacing the rigid linkage of Primaset® PT-30 at the central branch point, was synthesized at NAWCWD China Lake [13] and provided to AFRL for evaluation. FlexCy was supplied as a white powder with a melting point of 104 – 107 °C, in two versions. One version had been purified by re-precipitation into ethanol (EtOH), while the second version had been purified by re-precipitation into isopropanol (IPA). Precipitation into IPA was expected to more thoroughly remove impurities (at the cost of decreased product yield). No catalysts were added to these cyanate esters for the experiments reported herein. The chemical structures of the materials used are provided in Figure 1.

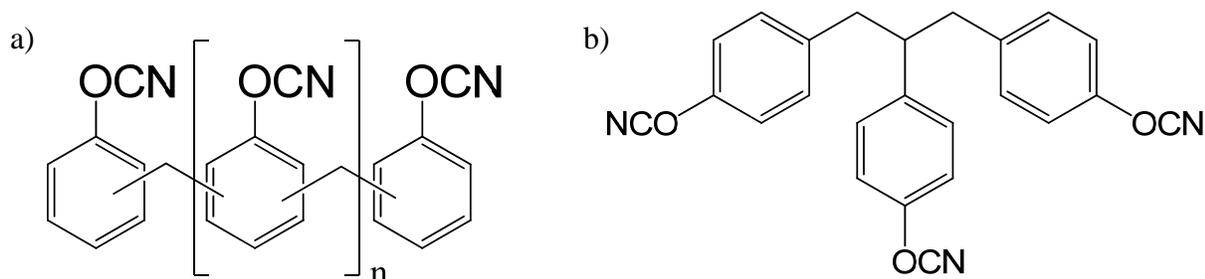


Figure 1. Chemical structures of materials tested: a) PT-30 ($n=1-2$), b) “FlexCy”

2.2 Sample Preparation

Uncured samples for DSC and FT-IR analysis were used as received. Cured samples were prepared by melting and partly de-gassing the monomers at 125 °C for 30 minutes under reduced pressure (300 mm Hg), followed by pouring into prepared silicone molds. The silicone molds (R2364A silicone from Silpak Inc., mixed at 10:1 by weight with R2364B platinum-based curing agent and cured overnight at room temperature, followed by post-cure at 150 °C for 1 hour) were prepared by de-gassing for 60 minutes at 95 °C and 300 mm Hg. To accomplish cure of the cyanate ester, the open mold and sample were placed under flowing nitrogen for 1 hour at 150 °C followed by 24 hours at 210 °C to produce void-free discs measuring approximately 11.5-13.5 mm in diameter by 1-3 mm thick and weighing 200-400 mg. The temperature ramp rate during cure was 5 °C/min. Some of these samples were subjected to a free-standing post-cure in a nitrogen-purged oven at 290 °C for 30 minutes. Additional samples were cured directly at high temperatures by transferring the de-gassed monomer into a 6 mm diameter aluminum pan and placing into a nitrogen-purged oven at either 250 °C for 2 hours, or 290 °C for 30 minutes to produce void-free discs weighing around 100 mg. Small samples weighing 5-10 mg were removed from the discs for further DSC and FT-IR analysis, while the discs themselves were used for OTMA.

2.3 Characterization Techniques

DSC was performed on a TA Instruments Q200 calorimeter with ~5 mg samples under 50 mL/min. of flowing nitrogen. For non-isothermal tests, samples were heated to 350 °C, then cooled to 100 °C and re-heated to 350 °C, at heating rates of 5, 10, and 20 °C/min. The re-heating scan was used to provide a baseline for evaluating heat flow rates. For isothermal scans, samples were heated to 120 °C at 5 °C/min, then held at 120 °C for 5 minutes to establish a reference isothermal baseline. Samples were then heated to the test temperature at 100 °C/min., held at the test temperature for 30 minutes, then quenched by cooling at 100 °C/min. to 120 °C. Following this, samples were heated to 350 °C at 10 °C/min., then cooled at 10 °C/min to 100 °C to determine the residual enthalpy of cure. Test temperatures of 210 – 290 °C in 20 °C increments were utilized. Baselines were determined using (in order of preference) the flat portions of curves obtained either before or after cure during a given heating, cooling, or hold, or the reference isothermal baseline determined at 120 °C. Comparisons of these baseline measures in cases where both were available revealed a difference of less than 0.1 mW, which typically equated to a conversion rate error of less than about 0.00003 / s.

FT-IR was performed via Attenuated Total Reflection (ATR-FTIR) spectroscopy using a single bounce diamond ATR crystal. The instrument used was a Nexus 870 FTIR spectrometer with a liquid N₂ cooled mercury cadmium telluride (MCTA) detector. Each spectrum is an average of 28 scans at 4 cm⁻¹ resolution. OTMA was conducted with a TA Instruments Q400 series analyzer under 50 mL/min of nitrogen flow. The discs were held in place via a 0.2 N initial

compressive force with the standard ~5 mm diameter flat cylindrical probe while the probe force was modulated at 0.05 Hz over an amplitude of 0.1 N (with a mean compressive force of 0.1 N) and the temperature was ramped twice (heating and cooling) between 0 °C and 200 °C (to determine thermal lag) with a final heating to 400 °C, all at 50 °C/min. The details on the method of correcting for thermal lag (which is near 20 °C at the heating rates used and therefore must be accounted for) have been published previously [14].

2.4 Analysis of DSC Data

To analyze the isothermal cure data, both the rate of conversion ($d\alpha/dt$) and the total conversion (α) were determined as follows:

$$\frac{d\alpha(t)}{dt} = \frac{\dot{Q}(t)}{Q_T + Q_R} \therefore \alpha(t) = \frac{\int_{t_0}^t \dot{Q}(t') dt'}{Q_T + Q_R} \quad (1)$$

where \dot{Q} represents the baseline corrected differential heat flow, Q_T is the total integrated heat flow (enthalpy of cure) observed during the isothermal cure period beginning at t_0 , and Q_R is the sum of all residual heat flow associated with resin cure observed on subsequent thermal cycling to 350 °C. The cure data were fitted over the range $\alpha = 0.1$ to 0.5 to the Kamal model [15], namely:

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

To fit the data, a modified form of the graphical analysis developed by Kenny [16] was used, as described in detail elsewhere [13]. To help constrain the data, the ratio of m and n for the FlexCy sample precipitated into ethanol was assumed to be the same as that found for the FlexCy sample precipitated into isopropanol. For the determination of activation energies, the values of m and n were fixed (at the mean value found from prior analysis of individual data sets) for all temperatures tested, in order to eliminate spurious effects resulting from correlations in the fitted values of the model parameters.

The non-isothermal DSC data were analyzed via the Kissinger [17], Ozawa [18], and Friedman [19] methods, as described in the recent analysis of dicyanate ester cure kinetics performed by Sheng, Akinc, and Kessler [20].

3. RESULTS

3.1 Isothermal DSC

Figures 2a and 2b compare the rate of conversion as a function of time and isothermal cure temperature for the FlexCy samples precipitated into ethanol (“FlexCy-EtOH”, Figure 2a) and isopropanol (“FlexCy-IPA”, Figure 2b). Although both samples are highly pure according to elemental and NMR analysis, precipitation into ethanol was slightly less efficient at removing trace impurities (thought to be primarily the triethyl ammonium bromide salt that is a by-product of the cyanogen bromide reaction that forms the cyanate esters from their phenolic precursors, along with incompletely cyanated phenolic precursors). Since the cyclotrimerization of cyanate esters is catalyzed by such impurities, FlexCy-EtOH was catalyzed to a higher extent, resulting in the completion of cure in just over half the time compared to FlexCy-IPA.

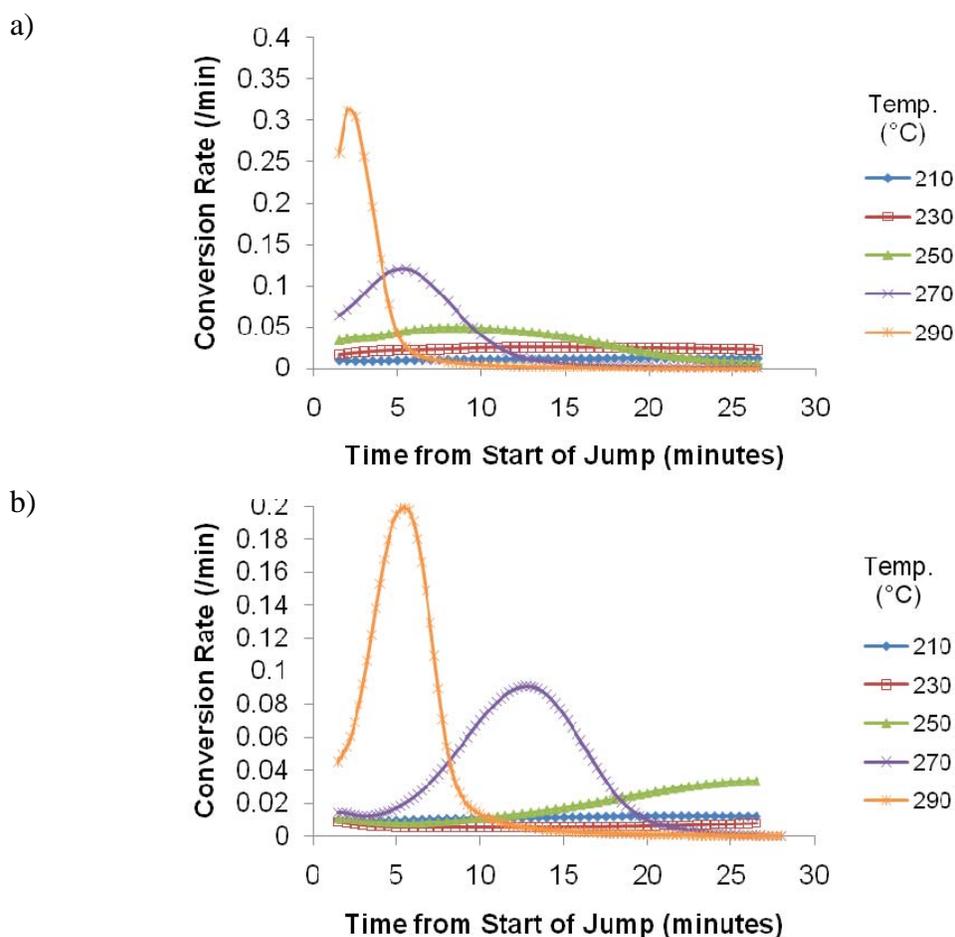


Figure 2. Conversion rates of FlexCy precipitated into (a) ethanol and (b) isopropanol obtained from isothermal DSC experiments.

More subtle differences in the cure kinetics are revealed by Figure 3, in which the conversion rate is plotted as a function of the total conversion for isothermal cure at 270 °C and 290 °C. While the peak conversion rates for the FlexCy-IPA were at a conversion of 0.5, as was the case for Primaset® PT-30 [13], those of FlexCy-EtOH were shifted to lower conversions. It is also apparent that the initial rates of conversion were substantially higher for FlexCy-EtOH, with the curves for FlexCy-EtOH resembling those of FlexCy-IPA superimposed on a tilted baseline corresponding to a decreasing conversion rate with increasing conversion. These features are entirely consistent with the Kamal model, in which the k_1 term has been associated with catalyzed cure while k_2 has been associated with auto-catalytic cure [21]. The curves for FlexCy-IPA appear to be described well by $k_1 \sim 0$, while those for FlexCy-EtOH appear to be described by the same kinetics with the addition of a significant k_1 term, corresponding to significant catalysis.

An Arrhenius plot of the auto-catalytic rate constant k_2 for FlexCy-EtOH and FlexCy-IPA over the conversion range 0.1 to 0.5 (used to eliminate any effects from gelation and initial transients in the DSC signal) is presented in Figure 4. The rate constants k_1 are much smaller and therefore subject to larger relative errors, making determination of their activation energy less reliable. Nonetheless, the results are included in Table 1, which shows the model parameters obtained for

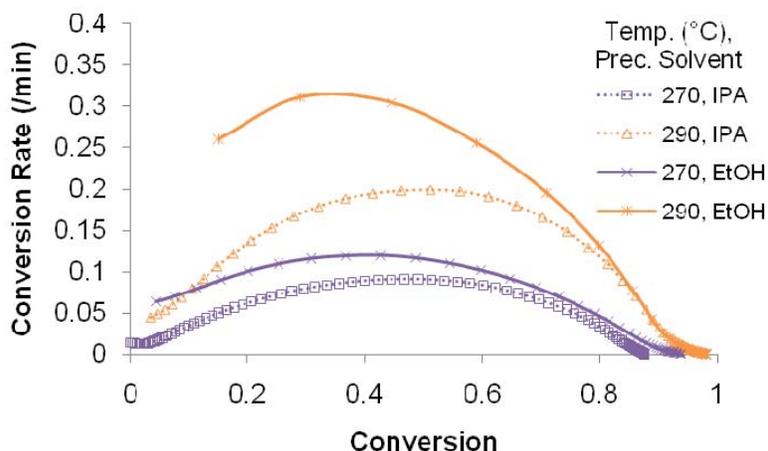


Figure 3. Conversion rates of FlexCy as a function of total conversion, isothermal cure temperature, and solvent used for purification by re-precipitation.

independent analyses at each temperature as well as for fixed values of m and n (obtained by averaging the independent values at each temperature). Note that fixed values are required for a proper determination of the activation energy. Whereas FlexCy-IPA exhibited a constant, well-defined activation energy of 110 ± 2 kJ/mol, FlexCy-EtOH showed a more variable activation energy, ranging from around 80 kJ/mol at 210 – 250 °C to around 120 kJ/mol at 250 – 290 °C, with a fitted value of 97 ± 6 kJ/mol over the entire temperature range.

The idea that the cure of FlexCy-EtOH falls into two separate regimes was supported by several other features of the data. First, both Figure 4 and Table 1 show that the rate constants for both materials are within about 10% of each other at temperatures of 250 °C and above, whereas they differ by around a factor of two at 210 °C. Note that even at 210 °C, these differences are about one order of magnitude too large to be due to imprecision in the measurements (mainly due to uncertainty in the baseline). A much more likely explanation is that the mathematical form of the coupling between the catalyzed and auto-catalytic processes assumed in the Kamal model is not completely accurate. If too much of the total cure had been assigned to the auto-catalytic process at low temperatures, where the catalytic mechanism dominates, then the features of the Arrhenius plot seen in Figure 4 would result. Moreover, the activation energies for the k_1 rate constant, though difficult to measure accurately, were also around 80 kJ/mol, in agreement with the previous work of Chen et al. [21] on Primaset® PT-30 that is evidently catalyzed (due to the much higher rates of cure compared to the work reported herein). Note that Chen et al. defined the “total” activation energy as being the sum of the individual k_1 and k_2 activation energies in order to overcome the discrepancy between their computed values and other, higher reported activation energy values for cyanate esters; we believe rather that the discrepancy is simply due to differing levels of catalysis.

In summary, isothermal DSC measurements showed an activation energy of 110-120 kJ/mol for FlexCy when the auto-catalytic process dominated, but appeared to show a lower activation energy of 80 kJ/mol when the catalytic process was responsible for a significant portion of cure. In comparison, the activation energy of Primaset® PT-30 was slightly higher (124 kJ/mol) [13] when auto-catalytic processes dominated, and about the same (80 kJ/mol) [21] when catalytic processes were present to a significant extent. Note that these results are likely applicable to systems catalyzed by phenolic or other organic impurities, but may not apply to cyanate esters catalyzed by transition metals.

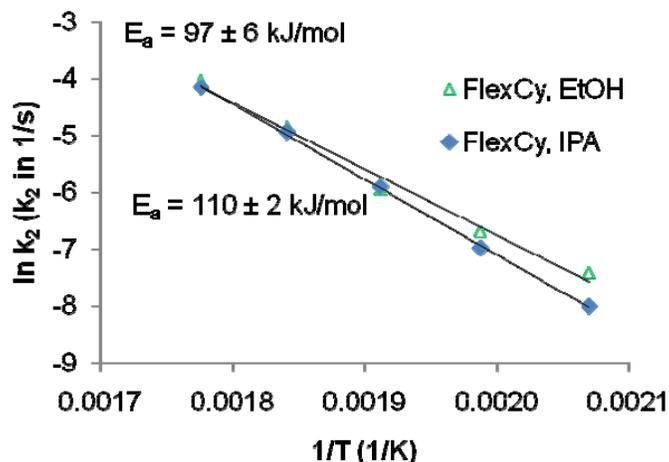


Figure 4. Arrhenius plot for FlexCy purified by re-precipitation in ethanol (EtOH) and isopropanol (IPA).

Table 1. Kamal model cure kinetics parameters for FlexCy

FlexCy - Cure Temp- erature (°C)	m, n independent of temperature				m, n fixed			
	k_1 (/s)	k_2 (/s)	m	n	k_1 (/s)	k_2 (/s)	m	n
EtOH 210	0.000163	0.000628	1.147	1.194	0.000167	0.000603	1.146	1.193
EtOH 230	0.000333	0.00137	1.198	1.247	0.000330	0.00125	1.146	1.193
EtOH 250	0.000515	0.00226	1.018	1.060	0.000580	0.00296	1.146	1.193
EtOH 270	0.00087	0.00762	1.111	1.157	0.000937	0.00781	1.146	1.193
EtOH 290	0.00343	0.0213	1.254	1.306	0.00337	0.0176	1.146	1.193
IPA 210 ^a	0.0000688	0.000332	1.128	1.174	0.0000690	0.000334	1.132	1.178
IPA 230 ^a	0.0000487	0.00109	1.247	1.298	0.0000398	0.000932	1.132	1.178
IPA 250 ^a	0.0000637	0.00307	1.232	1.283	0.0000358	0.00272	1.132	1.178
IPA 270 ^a	0.0000878	0.00663	1.052	1.095	0.000171	0.00718	1.132	1.178
IPA 290 ^a	0.000270	0.0156	1.111	1.157	0.000354	0.0157	1.132	1.178

^adata from Reference 13

3.2 Non-isothermal DSC

Despite potential issues related to determination of the appropriate baseline for measure, non-isothermal DSC has generally been considered superior to isothermal DSC for the investigation of some aspects of cyanate ester cure kinetics, owing to the fact that a significant portion of the cure can take place prior to the stabilization of temperature in an isothermal DSC experiment [22]. As is evident from Figure 2, however, the highly pure systems under study exhibit significant auto-catalysis, allowing sufficient time for temperature stabilization in almost all cases. In addition, non-isothermal DSC is mainly used for the determination of activation energies, rather than determination of a full set of kinetic model parameters. To gain further insight into these issues, we analyzed non-isothermal DSC data for both Primaset® PT-30 and FlexCy-IPA.

Figures 5, 6, and 7 present the graphical analysis that underlies the Kissinger [17], Ozawa [18], and Friedman [19] methods, respectively, of non-isothermal DSC cure for FlexCy using heating rates of 5, 10, and 20 °C/min. For the Kissinger method, the slope of a plot of the parameter $\log(\beta/T_p^2)$ versus $1/T_p$, where β is the heating rate and T_p the absolute temperature at the peak cure rate, is proportional to the activation energy. For the Ozawa method, isoconversion plots of $\ln \beta$ versus $1/T(\alpha)$, where $T(\alpha)$ represents the absolute temperature at which conversion α is achieved, are proportional to the activation energy, and for the Friedman method, isoconversion plots of $\ln(d\alpha/dt)$ versus $1/T(\alpha)$, where $d\alpha/dt$ is the conversion rate, are proportional to the activation energy. A more detailed review of all three methods is provided by Sheng et al. [20].

The activation energies for FlexCy-IPA (at conversions of 0.1 to 0.5 for comparison to the isothermal DSC analysis) were 101 ± 8 kJ/mol for Kissinger's method, 108 ± 13 kJ/mol for Ozawa's method, and 107 ± 4 kJ/mol for Friedman's method. These values agree well with the 110 ± 2 kJ/mol determined from isothermal analysis, although the standard errors are considerably larger, due mainly to errors in the determination of the individual slopes. (For the isoconversion methods, conversion intervals of 0.05, inclusive of the end-points, were analyzed).

For Primaset® PT-30, heating at 20 °C/min overwhelmed the DSC control system, resulting in instantaneous heating rates of over 50 °C/min during the main peak exotherm. Not only did such an event invalidate the assumption of a constant heating rate, it also greatly complicated any attempt to determine conversion (since the DSC baseline was also affected in a manner that cannot be measured). Using only the 5 and 10 °C/min data yielded activation energies of 114, 130, and 110 kJ/mol for the Kissinger, Ozawa, and Friedman methods, respectively. If the (undetermined) errors in the slopes were equivalent to those for the FlexCy data, then the standard errors of these measurements would have been 7, 14, and 5 kJ/mol, respectively. These values were more variable than those for FlexCy, with the Ozawa and, marginally, the Kissinger method, producing agreement with the value of 124 ± 7 kJ/mol obtained from isothermal DSC data [13]. In all cases, however, the activation energy determined for Primaset® PT-30 was larger (though not always significantly) than for FlexCy-IPA.

Figures 8 and 9 show the activation energy as a function of conversion as determined by the Ozawa and Friedman methods, respectively, for FlexCy-IPA and Primaset® PT-30. The Ozawa method produced values that were independent of conversion away from the initial and final extremes, and it can be seen that the FlexCy data was less dependent on conversion. Interestingly, the activation energy values produced by the Ozawa method at the flattest portion of each curve were 110 kJ/mol for FlexCy-IPA and 124 kJ/mol for Primaset® PT-30, in very good agreement with the values obtained by isothermal DSC. The flat portion of the curve based on the Friedman method yielded activation energies of 106 and 110 kJ/mol for FlexCy-IPA and Primaset® PT-30, respectively, both about two standard errors lower than the values obtained by isothermal DSC. Both methods resulted in qualitatively similar behavior of the activation energy as a function of conversion; the effects at high conversions could well be due to vitrification, whereas those at low conversions differ for the two materials and are not readily explained.

In summary, non-isothermal DSC enables somewhat less precise determination of the activation energy compared to isothermal DSC. Although it does not require a parametric kinetic model, it does exhibit some dependence on the choice of method. The contrast with previous work on cyanate esters [22] stems mainly from the auto-catalytic nature of the systems examined herein. In sharp contrast to catalyzed systems with a continuously decreasing reaction rate, auto-catalysis and thermal activation are mutually confounding phenomena when examined via measurement of reaction rates during heating. Furthermore, auto-catalysis significantly narrows the temperature range over which conversion takes place, essentially squeezing the useful data into a shorter time period (and therefore fewer data points), and making it difficult to maintain a constant heating rate. Ozawa's method seems to work best because it measures the way in which thermal activation compensates for time compression throughout cure, rather than for changes in the instantaneous rate of reaction (as in Friedman's method), since in auto-catalysis, the instantaneous rate of reaction can be highly sensitive to the reaction history.

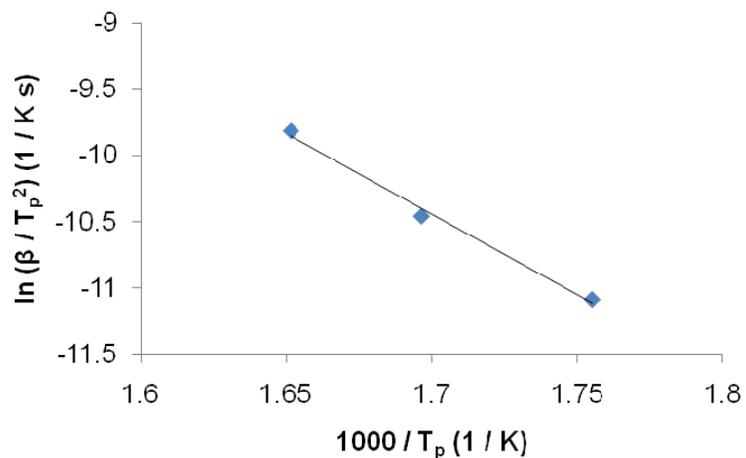


Figure 5. Plot for the determination of the activation energy of FlexCy-IPA by Kissinger's method [17]. The computed activation energy is 101 ± 8 kJ/mol.

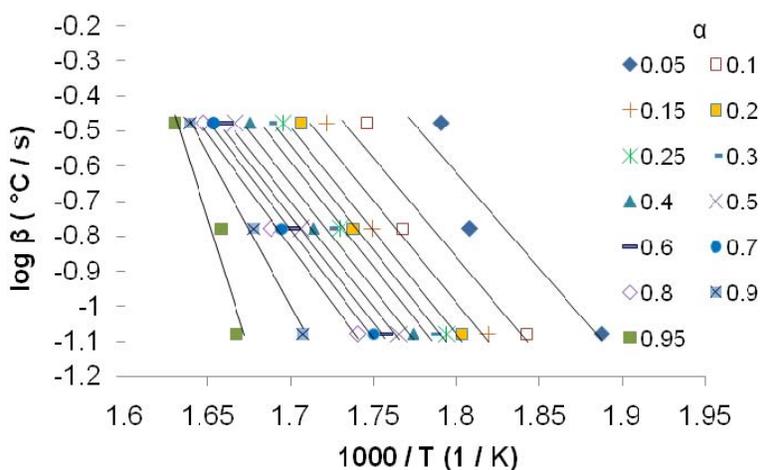


Figure 6. Plot for the determination of the activation energy of FlexCy-IPA by Ozawa's method [18]. The computed activation energy is 108 ± 13 kJ/mol.

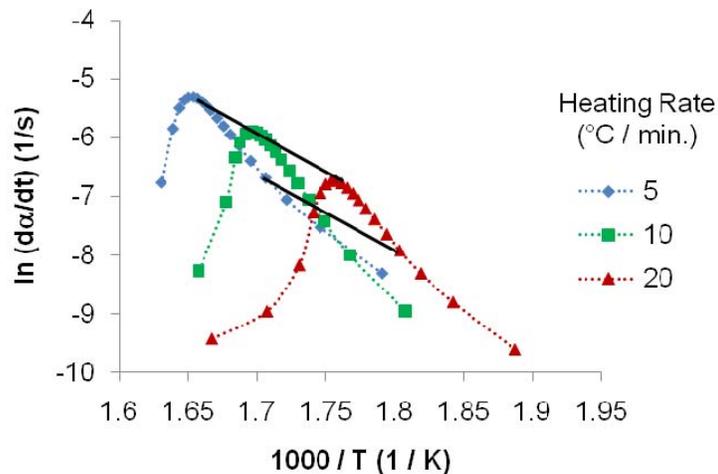


Figure 7. Plot for the determination of the activation energy of FlexCy-IPA by Friedman's method [19]. The computed activation energy is 107 ± 4 kJ/mol.

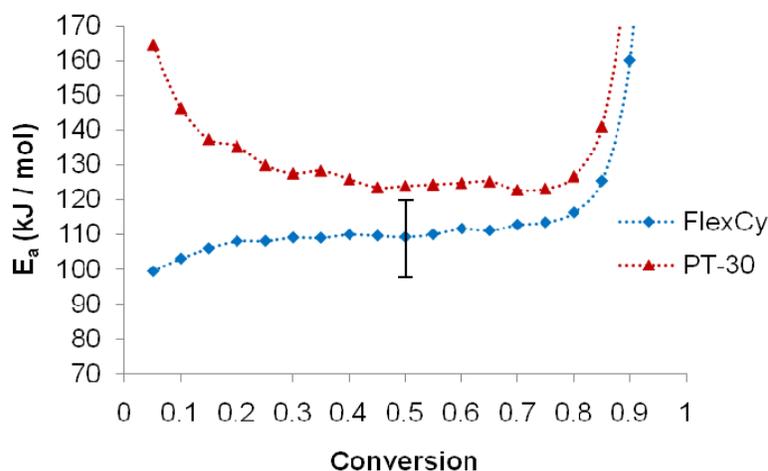


Figure 8. Activation energy as a function of conversion for FlexCy-IPA and Primaset® PT-30 based on Ozawa's method [18].

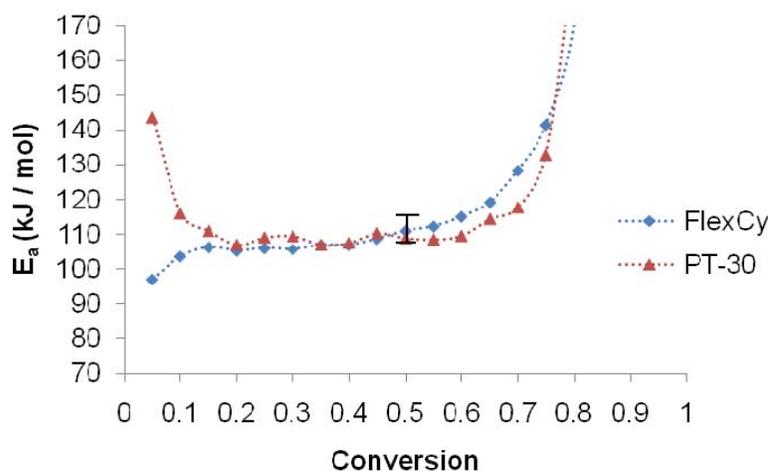


Figure 9. Activation energy as a function of conversion for FlexCy-IPA and Primaset® PT-30 based on Friedman's method [19].

3.3 Measures of Conversion

In addition to DSC, the kinetics of cyanate ester cure can be studied by more laborious tracking of conversion as a function of thermal history. The conversion is typically tracked via determination of the residual enthalpy of cure in a non-isothermal DSC experiment, or via the relative absorption of infrared spectral bands associated with the uncured cyanate ester groups in an FT-IR experiment. These studies represent an important complement to the determination of reaction rates, since rigid cyanate esters often display an inability to cure completely at temperatures low enough to prevent significant degradation.

In these situations, DSC can be of limited use in tracking conversion since it cannot distinguish additional cure from thermally-induced degradation. The issue is usually circumvented by limiting the temperatures used for DSC analysis, with the side effect that conversions must be expressed relative to their "ultimate" attainable values rather than to the true completion of reaction. While FT-IR does not suffer from the aforementioned limitation, it has been shown that changes in the solid state conformation of cyanate esters preclude quantitative conversion tracking via FT-IR unless extensive prior calibration via tracking of solution reactions coupled

with chromatography is first performed [2]. As a result, additional measures of conversion are needed to improve the quality of conversion tracking experiments for rigid cyanate esters.

Since it has been repeatedly demonstrated [2] that cyanate esters follow the diBenedetto equation [23] (which relates conversion to observed glass transition temperatures), techniques for determining the glass transition temperature (T_g) of cured samples (such as OTMA) could be especially useful in determining the ultimate attainable conversion of cyanate esters. At high conversions, the glass transition temperature is especially sensitive to small changes in conversion, increasing the utility of techniques such as OTMA.

Table 2 presents a comparison of T_g (and associated conversion values) obtained via OTMA and FT-IR for FlexCy-EtOH, FlexCy-IPA, and Primaset® PT-30. To utilize the diBenedetto equation, the T_g of both “fully cured” and uncured systems must be known. Using DSC, the T_g of the uncured systems was determined in all cases to be -17 °C. For the fully cured systems, the T_g can be determined by extrapolating DSC measurements of the T_g of co-cyclotrimerized blend systems, or, for Primaset® PT-30, from measurements of samples heated slowly in a DMTA [8]. Based on available data as described, the fully cured T_g for FlexCy and Primaset® PT-30 were estimated at 390 °C and 405 °C, respectively. Previous work [14] has shown that measurements via DSC and OTMA are comparable when the peak in loss is used as the determinant of T_g , while DMTA and OTMA data using the same determinant are typically directly comparable.

In many cases, a loss peak could not be recorded reliably prior to run termination, thus, the step change in the coefficient of thermal expansion (CTE), which normally occurs about 20 °C lower than the peak in loss, was also utilized as a determinant of T_g in the OTMA measurements. In this case, values of -37 °C were used for the initial T_g for all systems, and values of 370 °C (FlexCy) and 385 °C (Primaset® PT-30) were used for the fully cured T_g . The value of the λ parameter in the diBenedetto equation in all cases was 0.6, in accord with previous determinations [24] for cyanate ester systems, though lower values were recently estimated for flexible dicyanates by Sheng et al. [20].

Table 2. Comparison of OTMA and FT-IR Measures of Conversion

Material	Cure Temp. (°C)	Cure Time (hrs)	Tg via OTMA CTE (°C)	Tg via OTMA Loss Peak (°C)	Conversion via OTMA CTE	Conversion via OTMA Loss Peak	Conversion via FT-IR
FlexCy-IPA	210	24	310	338	0.91	0.92	0.83
FlexCy-IPA	250	2	307	>352 ^a	0.90	>0.94	0.82
FlexCy-IPA	290	0.5	>349 ^a	>349 ^a	>0.95	>0.94	0.94
FlexCy-IPA ^c	210 / 290	24 / 0.5	302	351	0.89	0.94	n/a
FlexCy-EtOH	210	24	301	317	0.89	0.88	n/a
FlexCy-EtOH	250	2	327	>354 ^a	0.93	>0.94	n/a
FlexCy-EtOH	290	0.5	301	>352 ^a	0.89	>0.94	n/a
PT-30	210	24	274	309	0.82	0.85	0.80
PT-30	250	2	309	>355 ^a	0.88	>0.93	0.91
PT-30	290	0.5	327	>352 ^a	0.91	>0.92	0.80
PT-30 ^c	210 / 290	24 / 0.5	314	>389 ^a	0.89	>0.98	n/a

^arun terminated due to thermal decomposition prior to obtaining sufficient data to confirm value

^btwo-step cure

The FT-IR conversions, when available, were computed using a baseline anchored at 2100 and 2320 cm^{-1} (points straddling the peaks associated with uncured cyanate ester groups). The uncured group concentration was assumed proportional to the peak area between 2100 and 2320 cm^{-1} , scaled to the area of the phenyl peak at 1470 – 1515 cm^{-1} . It should be emphasized that quantification of the type just described was performed only to provide a comparison to the OTMA data. We do not believe the calculated values from FT-IR measurements represent quantitatively accurate conversions.

The data in Table 2 show numerous features that indicate reliability issues with the OTMA measurements. Comparing the T_g via step change in CTE to the T_g obtained from the peak in loss, the difference in temperature ranged from 16 °C to at least 75 °C. Five out of the 11 cases exhibited at least a 40 °C difference, which is too far above the expected difference of 20 °C to be due to random variations. Possible causes for these unexpectedly large differences include: mechanical instabilities and temperature gradients in the samples that create a large amount of uncontrolled variability in the recorded step change in CTE, significant *in-situ* cure of the sample near the T_g that shifts the loss peak to higher temperatures faster than the heating rate (even though the heating rate is 50 °C/min.), and unwanted changes in the sample to probe contact in the OTMA instrument when passing through T_g for the first time. Since the heating runs typically ended in thermal decomposition of the sample, it was not possible to collect reliable data on a second heating.

Comparisons between samples also provide some insight into the reliability of the data. For instance, the two-step cure is simply the 210 °C / 24 hr cure with a 290 °C post-cure added, therefore, the observed conversions (and T_g 's) should be the same or higher for the two-step cure compared to the 210 °C cure. While for the loss peak data on all samples, the aforementioned trend was indeed seen in the data, for the step change in CTE, the Primaset® PT-30 showed an increase in conversion after post-cure while the FlexCy-IPA showed an apparent decrease. Moreover, at 290 °C, the cure kinetics of the two FlexCy materials were quite similar, yet the step change in CTE was measured at quite different temperatures. It thus seems that at least some of the step change in CTE data were too highly variable to quantitatively estimate conversions with a desirable level of precision.

Despite the limitations, some useful information did emerge from the OTMA analysis. For instance, it is clear that cure at 210 °C resulted in a higher extent of conversion, and in fact a higher T_g , for the FlexCy samples. This difference in conversion was not readily apparent from the FT-IR data, which served only to confirm that substantially less than complete conversion was achieved for both FlexCy and Primaset® PT-30 cured at 210 °C. A similar tendency toward higher conversions in FlexCy is also apparent when looking at the data sets as a whole, although the variability and lack of completely bound intervals preclude comparisons involving most of the specific cure cycles tested. Thus, the lower activation energy for cure of FlexCy does appear to have translated into the ability to achieve more complete cure, especially at lower temperatures. More complete cure is widely believed to be a desirable trait for cyanate ester resins, as incomplete cure has been cited as a cause of degradation and failure in samples exposed to wet environments and subsequently heated [9]. Moreover, the OTMA data show that, contrary to general expectations, molecular flexibility in a tricyanate ester can lead to higher T_g values due to the ability to attain a higher conversion when cured at moderate temperatures.

4. CONCLUSIONS

Comparative studies of the cure kinetics of tricyanate esters by isothermal and non-isothermal differential scanning calorimetry (DSC), infrared spectroscopy (FT-IR), and oscillatory thermomechanical analysis (OTMA) have provided important insights into the structure-property relationships of these technologically useful materials. Isothermal DSC showed that changes in the level of catalytic impurities in the tricyanate ester FlexCy altered the cure kinetics in a

manner that is consistent with the Kamal model and its interpretation relating to the relative effects of catalytic and auto-catalytic mechanisms of cure. The analyses also showed that the higher levels of catalytic impurities lowered the activation energy for cure, especially at temperatures below 250 °C. Analysis of non-isothermal DSC data produced activation energies that were quite similar, although less precise and reliable, than those found by isothermal DSC. These results (for auto-catalytic systems with a rapidly increasing initial rate of cure) are in contrast to those for catalyzed systems with a continuously decreasing rate of cure, for which non-isothermal DSC analysis is usually more appropriate. The OTMA data was often limited by either the difficulty of obtaining a verifiable peak in the loss component of the oscillatory stiffness for samples with T_g values greater than about 350 °C, or by the apparently large variability in alternate measures of the T_g such as the step change in coefficients of thermal expansion. Analysis by OTMA did, however, produce some valuable information about the relative extent of cure in FlexCy compared to Primaset® PT-30. Specifically, FlexCy was observed to exhibit a higher T_g than Primaset® PT-30 when a cure temperature of 210 °C was employed, due to its ability to attain a higher conversion, which more than compensated for the effect of reduced rigidity.

The support of these efforts by the Air Force Office of Scientific Research and the Office of Naval Research is gratefully acknowledged.

5. REFERENCES

1. Fang, Trelant and Shimp, David A. "Polycyanate esters: science and applications." *Progress in Polymer Science* 20 (1995): 61-118.
2. Hamerton, Ian (Ed.). *Chemistry and Technology of Cyanate Ester Resins*. London, UK: Chapman & Hall, 1994.
3. Nair, C. P. Reghunadhan; Mathew, Dona, and Ninan, K. N. "Cyanate Ester Resins, Recent Developments." *Advances in Polymer Science* 155 (2001): 1-99.
4. McConnell, Vicki P. "Resins for the Hot Zone Part II: BMIs, CEs, Benzoxazines & Phthalonitriles." *High Performance Composites* September 2009: 43-49.
5. Shimp, David A. "Technologically driven applications for cyanate ester resins" in Hamerton, Ian (Ed.). *Chemistry and Technology of Cyanate Ester Resins*. London, UK: Chapman & Hall, 1994, pp. 282-327.
6. Facciano, Andrew. "High-temperature organic composite applications for supersonic missile airframes." *SAMPE Journal* 36(1) (2000): 9-23.
7. Wienhold, Paul D. and Persons, David F. "The development of high-temperature composite solar array substrate panels for the MESSENGER spacecraft." *SAMPE Journal* 39(6) (2003): 6-17.
8. Marella, V., Master's Thesis, Drexel University, 2008.
9. Shimp, D. A. and Ising S. J. "Moisture effects and their control in the curing of polycyanate resins." *Polymer Materials Science and Engineering* 66 (1992): 504-505.
10. Laskoski, Matthew, Dominguez, Dawn D., and Keller, Teddy M. (2006). "Oligomeric cyanate ester resins: Application of a modified Ullmann synthesis in the preparation of thermosetting polymers." *Journal of Polymer Science Part a-Polymer Chemistry* 44 (2006): 4559-4565.

11. Yameen, Basit, Duran, Hatice, Best, Andreas, Jonas, Ulrich, Steinhart, Martin, and Knoll, Wolfgang "Polycyanurate Thermoset Networks with High Thermal, Mechanical, and Hydrolytic Stability Based on Liquid Multifunctional Cyanate Ester Monomers with Bisphenol A and AF Units" *Macromolecular Chemistry and Physics* 209 (2008): 1673-1685.
12. Cambrea, Lee R., Davis, Matthew C., Groshens, Thomas J., Guenther, Andrew J., Lamison, Kevin R., and Mabry, Joseph M. "A new room-temperature liquid, high-performance tricyanate ester." *Journal of Polymer Science Part A: Polymer Chemistry* 48 (2010): 4547-4554.
13. Guenther, Andrew J., Davis, Matthew C., Lamison, Kevin R., Yandek, Gregory R., Cambrea, Lee R., Groshens, Thomas H., Baldwin, Lawrence C., and Mabry, Joseph M. "Synthesis, Cure Kinetics, and Physical Properties of a New Tricyanate Ester with Enhanced Molecular Flexibility" in preparation.
14. Guenther, Andrew J., Yandek, Gregory R., Mabry, Joseph, M., Lamison, Kevin R., Vij, Vandana, Davis, Matthew C., Cambrea, Lee R. "Insights into moisture uptake and processability from new cyanate ester monomer and blend studies" *Proceedings of SAMPE '10*, Vol. 55. Covina, CA: SAMPE International Business Office, 2010, paper 42ISTC-119.
15. Kamal, M. R. and Sourour, S. "Kinetics and thermal characterization of thermoset cure" *Polymer Engineering and Science* 13 (1973): 59-64.
16. Kenny, José M. "Determination of autocatalytic kinetic model parameters describing thermoset cure" *Journal of Applied Polymer Science* 51 (1994): 761-764.
17. Kissinger, Homer E. "Reaction Kinetics in Differential Thermal Analysis" *Analytical Chemistry* 29 (1957): 1702-1706.
18. Ozawa, Takeo "Kinetic analysis of derivative curves in thermal analysis" *Journal of Thermal Analysis and Calorimetry* 2 (1970): 301-324.
19. Pielichowski, K. Czub, P. and Pielichowski, J. "The kinetics of cure of epoxides and related sulphur compounds studied by dynamic DSC" *Polymer* 41 (2000): 4381-4388.
20. Sheng, X., Akinc, M. and Kessler, M. R. "Cure Kinetics of Thermosetting Bisphenol E Cyanate Ester" *Journal of Thermal Analysis and Calorimetry* 93 (2008): 77-85.
21. Chen, Ching-Chung, Don, Trong-Ming, Lin, Tai-Hung, Cheng, Liao-Ping "A Kinetic Study on the Autocatalytic Cure Reaction of a Cyanate Ester Resin" *Journal of Applied Polymer Science* 92 (2004): 3067-3079.
22. Hamerton, Ian, Emsley, Alan M., Howlin, Brendan J., Klewpatinond, Paul, Takeda, Shinji "Studies on a dicyanate containing four phenylene rings and polycyanurate blends. 2. Application of mathematical models to the catalysed polymerization process" *Polymer* 44 (2003): 4839-4852.
23. Pascault, J. P. and Williams, R. J. J. "Glass transition temperature versus conversion relationships for thermosetting polymers" *Journal of Polymer Science Part B: Polymer Physics* 28 (1990): 85-95.