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Quasi-isothermal DSC testing of epoxy adhesives using initial fast heating rates

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ABSTRACT: Three major factors decrease the accuracy of the cure measurement in standard-isothermal testing using differential scanning calorimetry (DSC). First, cure occurs during the heating step. Second, data are lost during the stabilization period between the dynamic and isothermal step. Third, the baseline selection requires a modification to the protocol. An alternative, which is explored in this study, is the use of fast ramps, which decrease the heating time, but this has been avoided due to overshoot that occurs between the dynamic and isothermal step, which is troublesome for systems with autocatalytic kinetics. By mitigating these factors, a quasi-isothermal protocol was developed. Therefore, more complete cure kinetics were captured with the implementation of fast DSC to decrease the ramp time and through the optimization of furnace parameters to decrease stabilization time and temperature overshoot. The data suggested this quasi-isothermal analysis more accurately measured the isothermal curing kinetics of a commercial epoxy adhesive at 110, 115, and 120 °C for fast ramps of 175, 350, and 500 K/min compared to the traditional ramp of 5 K/min. The enthalpy spike at the dynamic to isothermal transition remains an issue; however, an empirical shift can be used to compensate for the enthalpy signal lag. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2017**, *134*, 45425.

INTRODUCTION

Understanding cure kinetics of thermosets, including epoxies, is critical to continue the advancement of lightweight manufacturing with prepreg materials.[1–3] Spectrochemical,[4–9] mechanical,[10–14] and thermal[15–19] analyses have all been used to monitor curing reactions. One of the most common, which dates back to the 1960s is differential scanning calorimetry (DSC), which measures the heat released during the exothermic reaction[20–22] from which both the cure rate and the degree of cure as a function of time and temperature can be determined.

There are numerous protocols for isothermal DSC,[16,18,23–25] one of which was developed at the Polymer Engineering Center by Hernandez-Ortiz and Osswald in 2002.[26,27] This method was based on the principle that the behavior of a thermoset under an isothermal state can be assessed by combining results from nonisothermal and isothermal DSC scans. The method was

further improved by Restrepo-Zapata et al.,[28–31] which will be the starting point of this work and referred to as the "core" method. One unifying aspect of all these methods is how to address the reaction that occurs during the nonisothermal period. For example, Fava placed the sample and increased the temperature manually as quick as possible to reach a constant temperature,[20] and Restrepo-Zapata et al. used nonisothermal tests to account for the reaction that occurred in the ramp regime.[29]

With state-of-the-art heat-flux DSC technology, ramps of 500 K/min are possible,[32] which allows for a new solution to this problem. The ramp time from 25 to 125 °C can be decreased from 20 min for a heating rate of 5 K/min to 12 s, which is two orders of magnitude smaller. However, fast DSC has been hampered by temperature overshoots and long stabilization times at the transition between the dynamic and isothermal step, which offsets the gains of a short ramp time.

Therefore, applications of fast DSC for polymeric materials have been limited to crystallization kinetics.[32–37]

This study explores an improvement of the core protocol for isothermal DSC scans using initial heating rates of up to 500 K/min. With modifications to the furnace control parameters, the issues of stabilization time and temperature overshoots were nearly fully mitigated, which produced quasi-isothermal cycles by eliminating the loss of data during the heating step. The elimination of the baseline to calculate the exothermal reaction (degree of cure) was evaluated as well. An epoxy film was analyzed with both the core method and for fast ramp rates of 175, 350, and 500 K/min to determine the benefits of the new approach. A practical application of the method outlined here can be found in another publication,[38] where the kinetics and processing window of two commercially available thermoset adhesives are fully characterized in the time–temperature–transformation (TTT) diagram.

METHODS

Materials

A heat activated epoxy film, DA 409, manufactured by Adhesive Prepreg for Composite Manufacturers (A.P.C.M. LLC), Plainfield, CT, typically used to bond composites, metal onto metal and honeycomb structures was the only resin analyzed.[38] It has an open thermoplastic knit for bond-line thickness control, as seen in Figure 1.

Based on the MSDS, adhesive DA 409 had a content by weight of 90% epoxy resins (bisphenol A), 6% cyan guanidine and 4% amines, the last two acting as hardeners. Cyan guanidine, or dicyandiamide (DICY) is typically used as a powder-dispersed hardener in thin films because of its high exothermic effect. It is typically used as a hardener for high temperature curing resins between 160 and 180 °C, resulting in a long curing process. DICY forms crystals with a melting point around 210 °C. The reaction of bisphenol-A (DGEBA) and the amines is the typical network formation of epoxy resins, where epoxy and amine groups are linked (see Figure 2).

Adhesive DA 409, as most commercially available adhesives, come with a filler, in the form of reinforcement (fibers), or a thermoplastic knit for bond-line thickness control. A protocol, provided in the next sections, was developed to eliminate the influence of the filler in the characterization of the thermoset.

Sample Preparation

Circular samples were cut from the film adhesive (in a precuring stage—prepreg stage) inside a freezer at −18 °C (0 °F), with the mass kept between 5 ± 0.2 mg. Samples were then placed into Netzsch Concavus pans with pierced lids, and weighed. Before testing, each sample was equilibrated at room temperature (22 °C) over a 2 h period, then weighed again to control and eliminate measurement errors due to varying initial temperature and moisture influence. The tests were performed within the first two months of the 12-month shelf life of the adhesive to eliminate precuring stage variations. All the following tests were executed on a NETZSCH DSC Polyma 214.
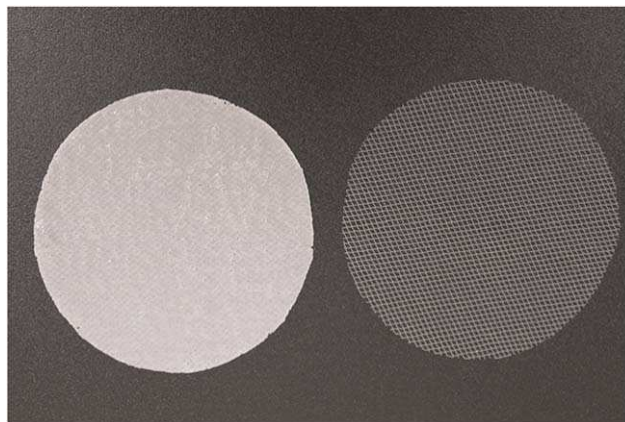

Figure 1. Epoxy film adhesive DA 409. From left to right adhesive with the inseparable knit, and thermoplastic knit after dissolving the epoxy in acetone.

Filler Content

To quantify the mass content of filler (thermoplastic knit, member of the nylon family), 50 mm samples were cut, weighed, and placed in a sealed container filled with acetone for 15 min. Once the epoxy dissolved completely, the knit was dried and measured (see Figure 1). A nylon knit content of 1%–1.5% by weight was measured, which agreed with the manufacturer's value of 1%. The specimen mass was corrected in the DSC software to compensate for the thermoplastic knit

A thermal characterization of the knit was performed. Two consecutive heating and cooling scans were executed as following: first, the sample was heated from 30 to 280 °C at a rate of 10 K/min, then cooled to 30 °C at a rate of 20 K/min. This procedure was repeated. The thermoplastic knit showed a melting temperature, T_m, of 222.0 °C and a crystallization temperature, T_c, of 175.4 °C. These temperatures were outside of the range of the isothermal scans but would have influenced the nonisothermal scans if the mass correction for filler was not applied. Endothermic and exothermic peaks shift in the direction of increasing/decreasing ramp when using fast heating/cooling ramps. The endothermic peak, T_m, shifts to higher values with increasing heating rates. The exothermic peak, T_c, occurs later with an increase of the cooling rate (shifting to lower temperatures), and the faster the thermoplastic is cooled the less time it has to form crystals, leading to lower enthalpy values (heat released).[32] This also prevented the filler from being present in the dynamic scans studied.
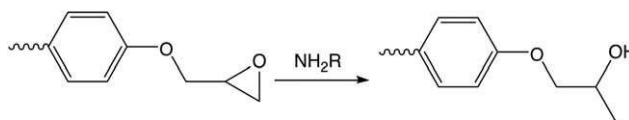

Figure 2. Formation of bonds during curing of epoxy resins using amine.[39]
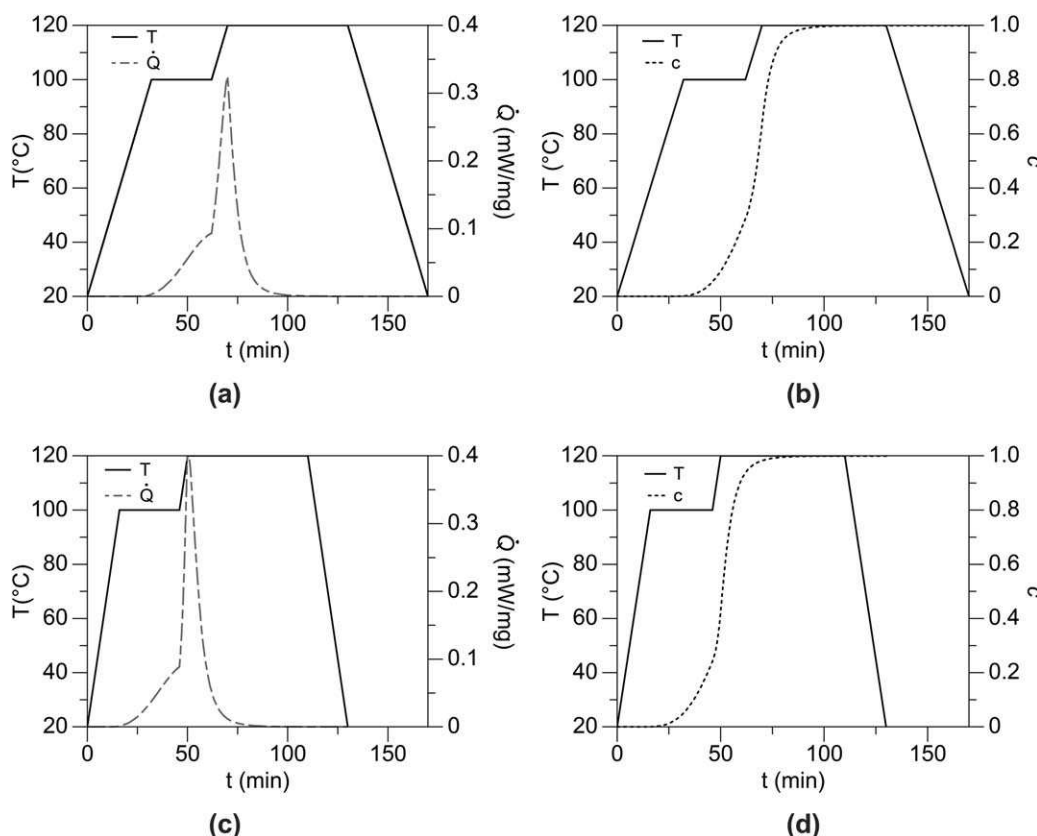
Figure 3. Manufacturing cycle used to produce thin parts with epoxy DA 409: (a) $\dot{Q}$ and (b) c during a 2.5 K/min heating/cooling ramp, and (c) $\dot{Q}$ and (d) c during a 5 K/min heating/cooling ramp.[40]

Core DSC Protocol

Samples were first tested using nonisothermal scans. Based on the analysis of the nonisothermal results, uncured adhesive samples were tested under a nonisothermal/isothermal cycle. The method was based on two consecutive DSC scans. The first scan—heating, dwell time, heating, cooling—heated the uncured sample to the isothermal state, and quantified the exothermal reaction and the residual cure. The second scan followed immediately. It used the same thermal cycle of the first scan, but in the fully cured sample giving the exact baseline at the conditions tested.

Nonisothermal Scans. Nonisothermal scans were performed at four heating rates 1, 2.5, 5, and 10 K/min in triplicate. These heating rates were selected based on the recommended manufacturing cycles used to produce thin plates as seen in Figure 3[40]—this analysis neglected the influence of processing pressure [recommended as 2 bar (30 psi)], and the results are not valid for thick parts. In the first scan, samples were heated from 30 to 270 °C and cooled to 30 °C at a rate of 20 K/min. The second scan followed immediately using the same thermal cycle. These results were used to quantify four parameters: the total heat released during the reaction, Q_T, the dependency of Q_T on the heating rate, the isothermal interval to be tested, and the loss of data during a ramp cycle before reaching the isothermal state.

Isothermal Scans. Samples were tested at three temperatures 110, 115, and 120 °C, which were selected based on the nonisothermal analysis. In the first heating scan, samples were heated from 30 to 110, 115, or 120 °C at 5 K/min. The samples were held at a constant temperature for 1 h, then heated to 270 °C at 5 K/min (to quantify the residual cure), and cooled to 30 °C at 20 K/min. The second heating scan followed immediately using the same thermal cycle. Figure 4 shows a diagram of the core method for the isothermal cure of DA 409 at 110 °C using an initial heating rate of 5 K/min. The first cycle captures:

1. The heating ramp (possible loss of information).
2. The exothermal reaction (degree of cure).
3. The residual cure.

And the second cycle captures:

1. The baseline for the heating ramp step.
2. The baseline for the exothermal reaction.
3. The baseline for the residual cure.

Improved DSC Protocol

For the fast DSC, the only modification to the protocol was increasing the ramp rate for the two heating steps to 175, 350, or 500 K/min. In theory, if a quasi-isothermal state is reached, no data is lost during the initial heating ramp, and a baseline is
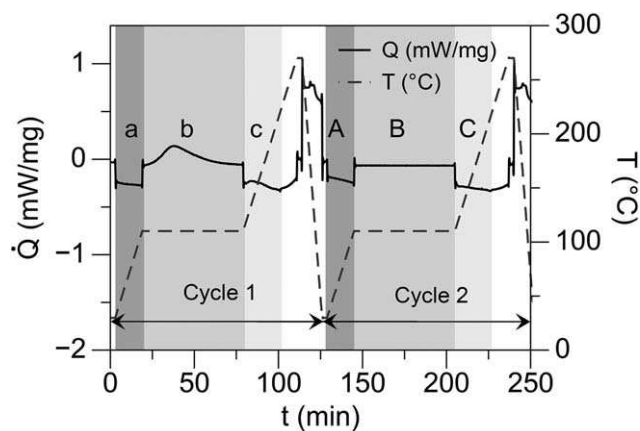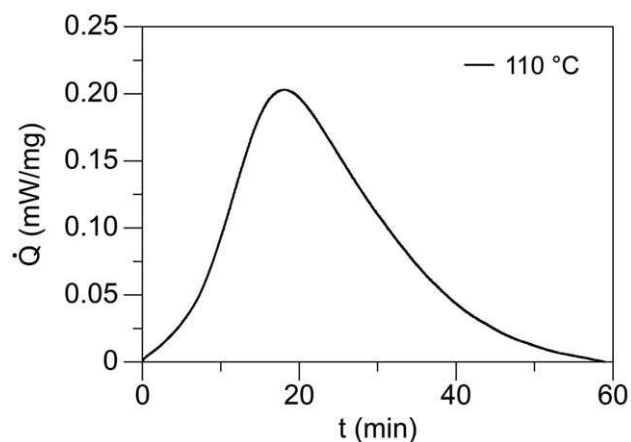
Figure 4. Isothermal cure reaction of epoxy film DA 409 at 110 °C: (a) core method with an initial heating rate of 5 K/min, and (b) $\dot{Q}$ versus t after baseline subtraction (region B subtracted from region b).[38,40]
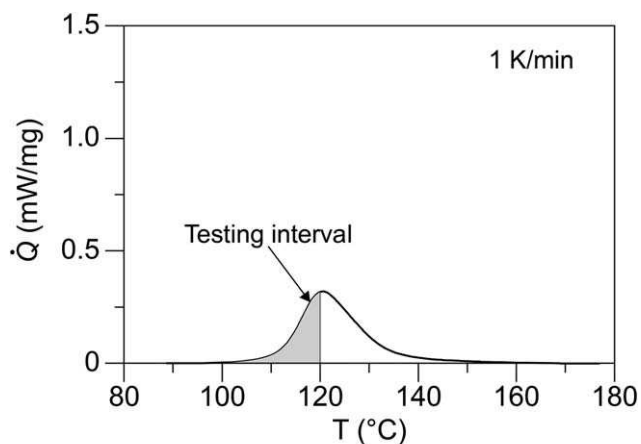

Figure 5. Selection of temperatures for the isothermal scans based on nonisothermal tests: (a) isothermal testing interval and (b) data lost during the heating step.

not needed. This means that the nonisothermal scans and the second cycle could be eliminated.
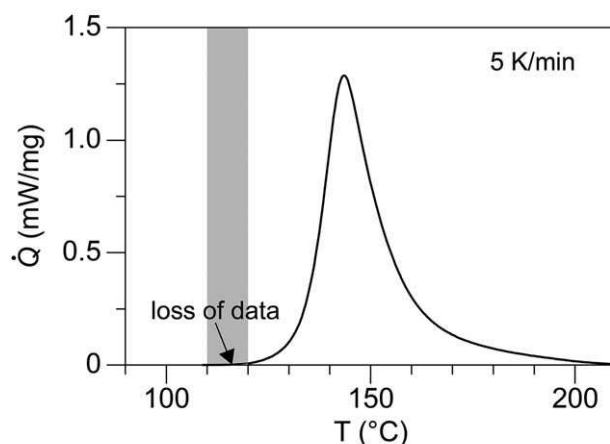
RESULTS AND DISCUSSION

Core Protocol

Nonisothermal Scans. The total heat released, Q_T, was 295 ± 8 J/g at the four heating ramps tested. Q_T showed a slight linear increase with the increase of the heating rate. To simplify the analysis of the results, Q_T was considered constant. The results from the heating scan at 1 K/min were used to select the temperatures tested in the isothermal protocol as seeing in Figure 5(a).[41] Over the first third of the area under the curve $\dot{Q}$ versus T was covered.[41] From this area, three temperatures were selected for the isothermal scans, 110, 115, and 120 °C. These temperatures are important in the manufacturing cycle since the end of the reaction occurs at these temperatures (refer to Figure 3).

An initial heating rate of 5 K/min for the isothermal scans was selected based on the manufacturing cycle shown in Figure 3.[42] The instantaneous heat, Q, from 30 to 110, 115 or 120 °C at 5 K/min was 0.017, 0.034, and 0.28 J/g, respectively. This

corresponded to a degree of cure, c, of 3.7 × 10^{-5}, 0.014% and 0.1%. Epoxy film DA 409 exhibited a c of less than 1% during this initial ramp for the three temperatures tested [see Figure 5(b)]. Since less than 1% of data are lost during the initial
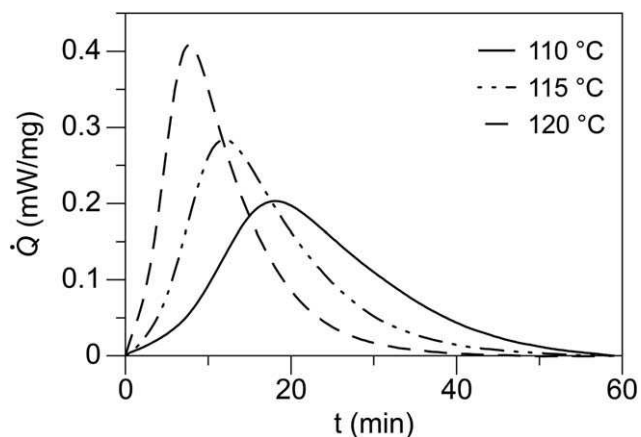

Figure 6. $\dot{Q}$ versus t using an initial heating rate of 5 K/min.
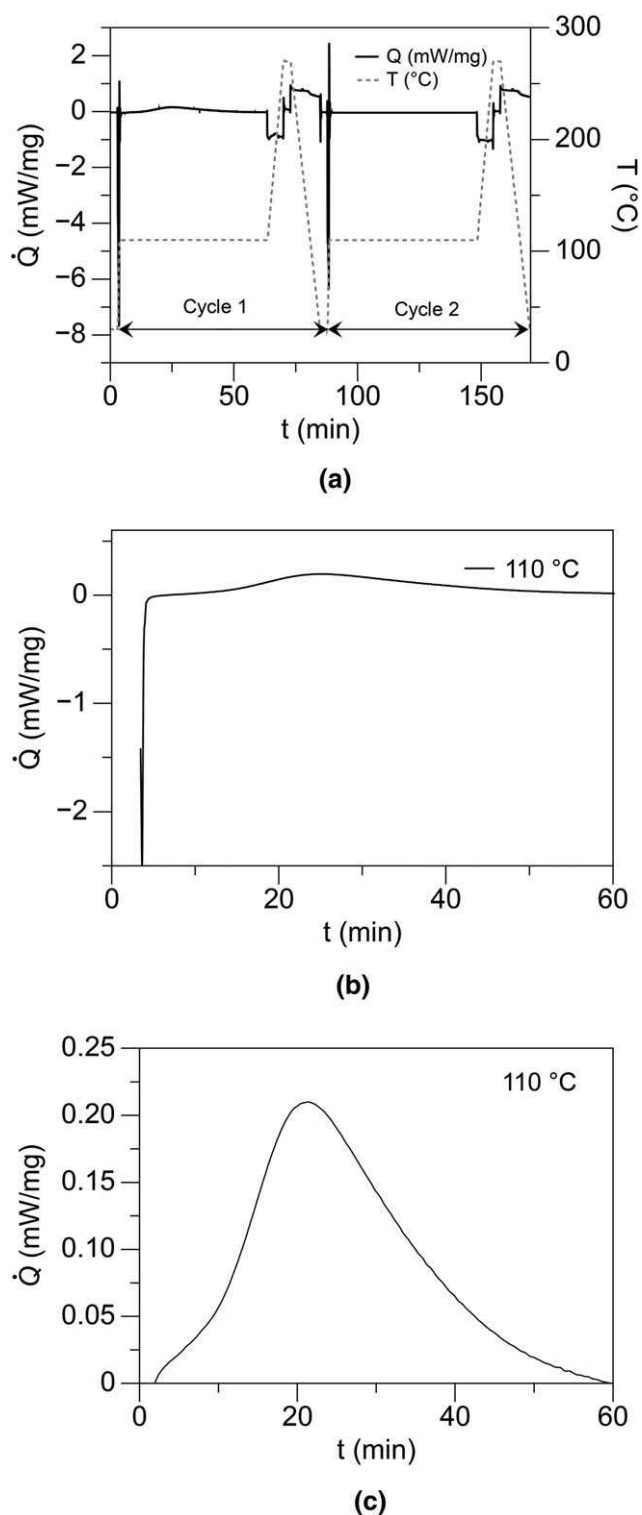
Figure 7. Isothermal scan at 110 °C with an initial heating rate of 175 K/min: (a) modified DSC cycle with an initial fast ramp, (b) $\dot{Q}$ versus t after subtracting the time of enthalpy stabilization, and (c) $\dot{Q}$ versus t after baseline subtraction.[38,40]

ramp, epoxy DA 409 is an ideal candidate to test the differences between slow and fast initial heating rates. The differences will be mainly due to the protocol itself and not to the reactive behavior of the material.

Table I. Furnace Parameters Used to Eliminate Temperature Overshoot in the NETZSCH DSC Polyma 214 During the Testing Film Adhesive DA 409

Parameter	Definition	Furnace	Sample
X_p	Proportional part	4.5	3.75
T_n	Reset time	4.0	4.0
T_v	Derivative time	4.0	3.5
STC		Off for all heating ramps	
Auto cooling		Off	

This small c quantified during the ramp period of an isothermal scan is not the rule for many thermosets. Highly reactive systems can exhibit a significant c in a 19 min time of temperature rise at a 5 K/min rate. A consequence is that a significant part of the reaction occurs in the nonisothermal state, leading to the incorrect isothermal calculation of c and the incorrect selection of processing conditions.

Isothermal Scans. The first cycle was baselined using the second cycle, and the data was then normalized choosing the initial time as the time when the constant temperature was reached. Figure 6 shows the results for the three temperatures tested after subtracting the 16–18 min of the initial ramp time and shifting the initial time to zero. Notice that between 1 and 108 s of information were lost in the core protocol during the baseline subtraction, and during signal stabilization.

Only the scan at 110 °C exhibited a residual cure of 9% (27 J/g) since this temperature was below the glass transition temperature at the fully cured state, T_{g_1} (111.3 °C).[38,40]

Isothermal Scans Using Initial Fast Ramps
The core isothermal method depends on nonisothermal DSC scans to select the temperatures tested and to measure the loss of data during the initial heating rate. It also needs a second cycle to baseline the data. Two options to shorten and improve the protocol are the use of initial fast ramps or the preheating of the furnace to the desired temperature before placing the sample and reference pan. Fast ramps are avoided due to temperature overshooting during the transient state before the instrument stabilizes at a constant temperature. This overshoot accelerates the reaction, which leads to incorrect cure data. Figure 7 shows the results for a 110 °C scan using the method proposed here.

Elimination of Temperature Overshoot. When using fast or very slow heating/cooling rates the electronic parameters of the DSC furnace are modified to eliminate temperature delay or overshooting. This calibration varies with the application, material and rates tested. Table I summarizes the regulation parameters used to optimize the transition from fast heating to the isothermal state for epoxy DA 409. The parameters X_p, T_n, and T_v are PID electronic variables that regulate the response time to temperature changes for the furnace and sample in the transition region tested.
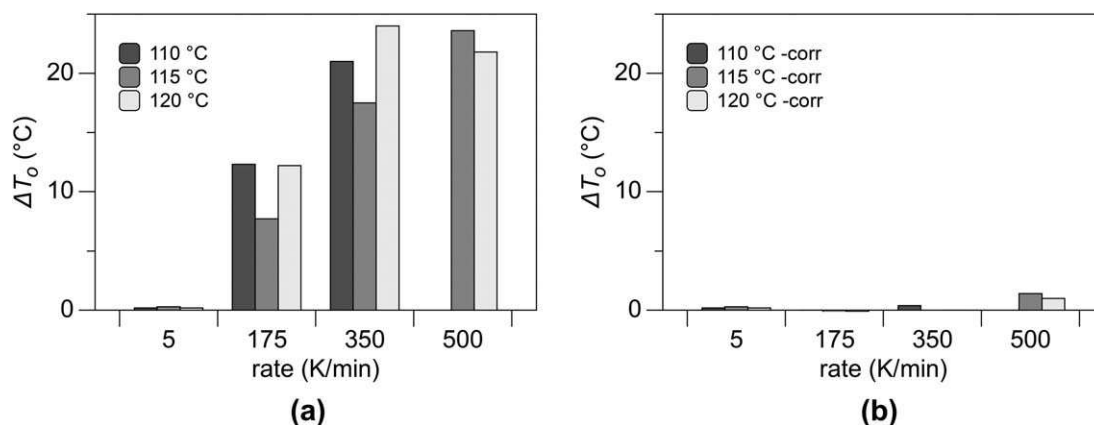
Figure 8. Temperature overshooting, ΔT_o, in the transition from heating to the isothermal segment: (a) no optimization was applied and (b) optimization of the furnace electronic parameters was applied.

Figure 8(a) shows the effect of the temperature overshooting, ΔT_o, if the parameters optimization is not applied. It was validated that with the proper optimization of furnace and sample parameters, the temperature overshoots produced during fast ramps were greatly reduced, as seen in Figure 8(b).

Enthalpy and Heating Rate Adjustments. Figure 7(a) shows a spike in the enthalpy signal during an initial fast ramp. After the enthalpy stabilizes, it is difficult to choose the initial point where the data is valuable. The alternative was to use the second cycle to baseline the data. But this effect cannot be completely eliminated with the baseline, as seen in Figure 7(b). This residual enthalpy spike is related to the specific heat capacity, C_p, and the stabilization time of the DSC system. C_p is slightly lower for uncured than for fully cured thermosets, and this is scaled up using high heating rates. In this method, samples are uncured during the first scan and fully cured during the second scan (baseline), causing the residual enthalpy peak observed.

The stabilization time for the enthalpy signal is also different for the first and second cycle. One can attempt to solve this

problem by performing a C_p calibration with a standard material such as sapphire for different thicknesses. However, the differences in the thermal behavior of sapphire and epoxies will add another error into this calibration higher than the second cycle correction.

Figure 9 shows the stabilization time, t_s, of the system. It was found that the need for the second cycle to baseline the data remains if the appropriate enthalpy and heating rate optimization is not found. t_s ranged between 40 s and 2 min, limiting this method to systems that do not exhibit a significant reaction during the first 1–2 min. t_s increased with the increase of the heating rate as seen in Figure 9. If fast ramps are used, the heating rate should be selected based on the influence of t_s on the data collection and degree of cure.

One criterion to assess the reliability of t_s is to compare Q_T during the reaction. If this point is chosen correctly, Q_T of the isothermal scans using initial slow and fast ramps will agree. Figure 10 shows Q_T for the different heating rates tested. Comparing the results of Q_T with the 5 K/min tests, the difference ranged from 0.5% to 7%.
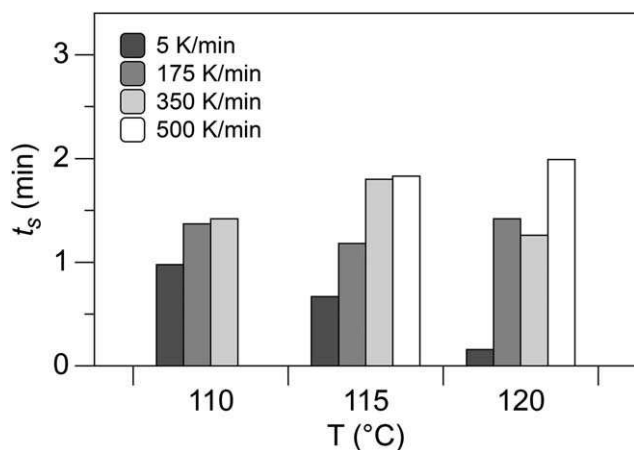

Figure 9. Stabilization time, t_s, of the DSC system for the different heating rates and temperatures tested.
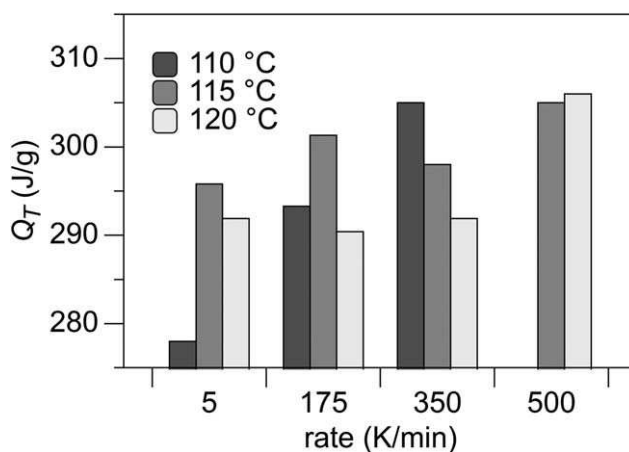

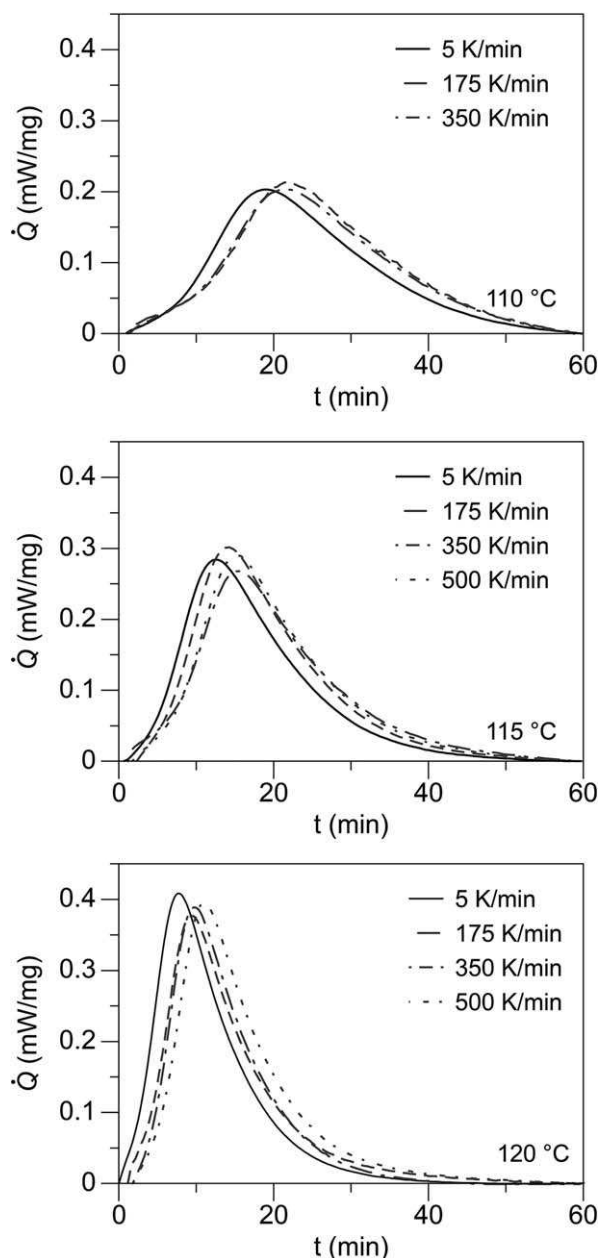**Figure 10.** Q_T for the different temperatures at the ramps tested.

Figure 12. t_p for the different temperatures at the different heating rates tested.

Figure 11. $\dot{Q}$ versus t for the different temperatures and rates tested.

Data Normalization. For the remaining analysis, we first baselined the data using the second cycle, and subtracted the time for stabilization of the enthalpy instability, t_s, which differed for every case, as seen previously in Figure 9. Figure 11 summarizes the results after the normalization. Notice that the 500 K/min ramp was not included for the 110 °C results. NETZSCH DSC Polyma 214 has a minimum step time of 10 s. A change in temperature of 80 K (from 30 to 110 °C) at 500 K/min cannot be tested because it will happen in 9.6 s.

Figure 11 shows that the enthalpy signal for the fast ramps lagged the slow ramp scan. Every DSC device has a time lag when capturing sample's changes, due to the tolerances of electrical components.[43] To get accurate results a tau-R correction,
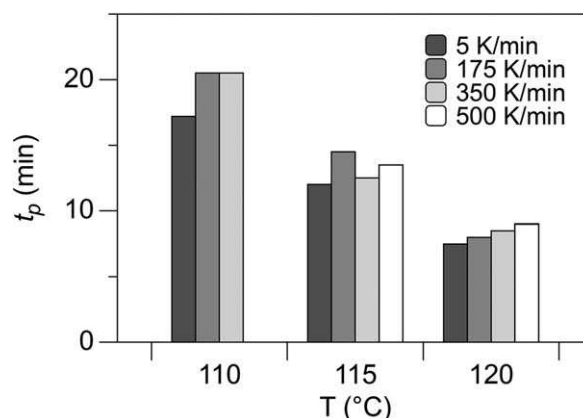
the correction of the time constant and the thermal resistance between, sensor, pan, and sample are implemented. Here, when the program temperature is reached after the fast ramp, the sample, the pan, and the furnace's lag to the sensors is increased. This affects the enthalpy signal in the testing of thermosets. An additional thermal resistance of the system is the nonideal contact between sample and pan especially with adhesives that have a high porosity. In this study, the time at which the maximum heat flow value, $\dot{Q}_{\text{peak}}$, is reached, t_p, was used to shift the enthalpy signal. Figure 12 shows t_p for the different heating rates.

Figure 13 shows the data after shifting the scans with an initial fast ramp (see Figure 10) using t_p of the initial heating rate of 5 K/min. A small difference was observed at the beginning of the reaction, but overall the data agrees for all cases. Figure 14 summarizes the results for the degree of cure. A good agreement is shown when defining the degree of cure for the three temperatures tested at different heating rates proving the validity of the method for the kinetic analysis of thermosets.

The stabilization and peak times can be used to selected appropriate heating rates and temperatures of analysis. The ideal fast ramp will give the shortest stabilization time and thermal shift. For the material and conditions tested, the recommend fast ramp lays between 175 and 350 K/min. The data for these two heating ramps had an excellent agreement for temperatures above T_{g_1}. Although a more detailed analysis is required for testing below T_{g_1}, excellent results were achieved in a kinetic analysis below T_{g_1} of two commercially available thermoset adhesives, fully characterized in the time–temperature–transformation (TTT) diagram.[38]

CONCLUSIONS

A novel method to analyze thermoset adhesives in a quasi-isothermal state was developed and evaluated. Initial heating rates up to 500 K/min were used. The results were compared to a core method that uses an initial heating rate of 5 K/min. In the core method, the material takes between 17 and 19 min to reach the isothermal conditions. With a fast ramp, the
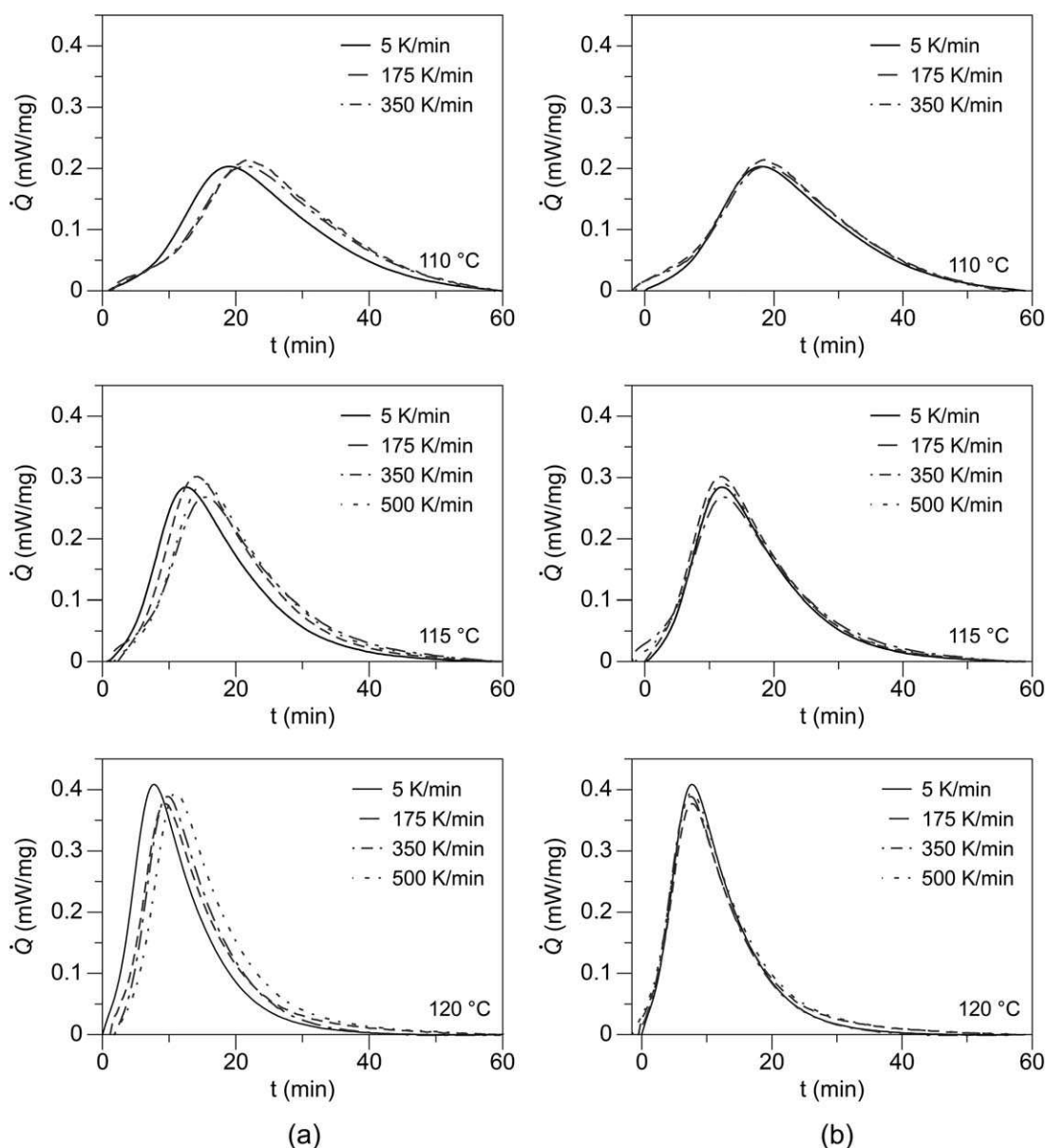
Figure 13. Comparison of the exothermal response using slow ramps (5 K/min) versus fast ramps (up to 500 K/min) at the beginning of isothermal scans: (a) data after baseline subtraction and (b) data shifted using t_p of the 5 K/min test.

isothermal condition was reached between 10 and 31 s. The results showed that with the proper optimization, initial fast heating rates could be used to characterize a thermoset reaction in a quasi-isothermal state.

The optimization of electronic parameters of the furnace for the adhesive and conditions tested eliminated temperature overshooting. The problem of an enthalpy spike was not eliminated. The use of a second thermal cycle on a fully cured sample was still needed to find the correct baseline. Even after the baseline subtraction, a residual enthalpy spike remained. This is due to differences in C_p for uncured and fully cured material, combined with the stabilization time of the system. However, this can be accounted for with an empirical data normalization. The stabilization time t_s was used to choose

the beginning of the data eliminating the residual enthalpy spike. A thermal lag of the enthalpy signal was observed for the fast ramp method. The time at which Q_{max}, for the 5 K/min tests was reached was used to normalize the enthalpy signal. This empirical shift worked for the adhesive under study. After the optimizations and postprocessing of the data, the scans using an initial slow and fast ramp showed excellent agreement.

Future work will include the study of slower rates, between 50 and 150 K/min. A new study looks for the possibility to preheat the furnace before placing the reference and sample pan. The goal is to obtain a quasi-isothermal state and evaluate the possibility to eliminate instabilities in the enthalpy signal and the need for a baseline (second cycle). Future work also includes a
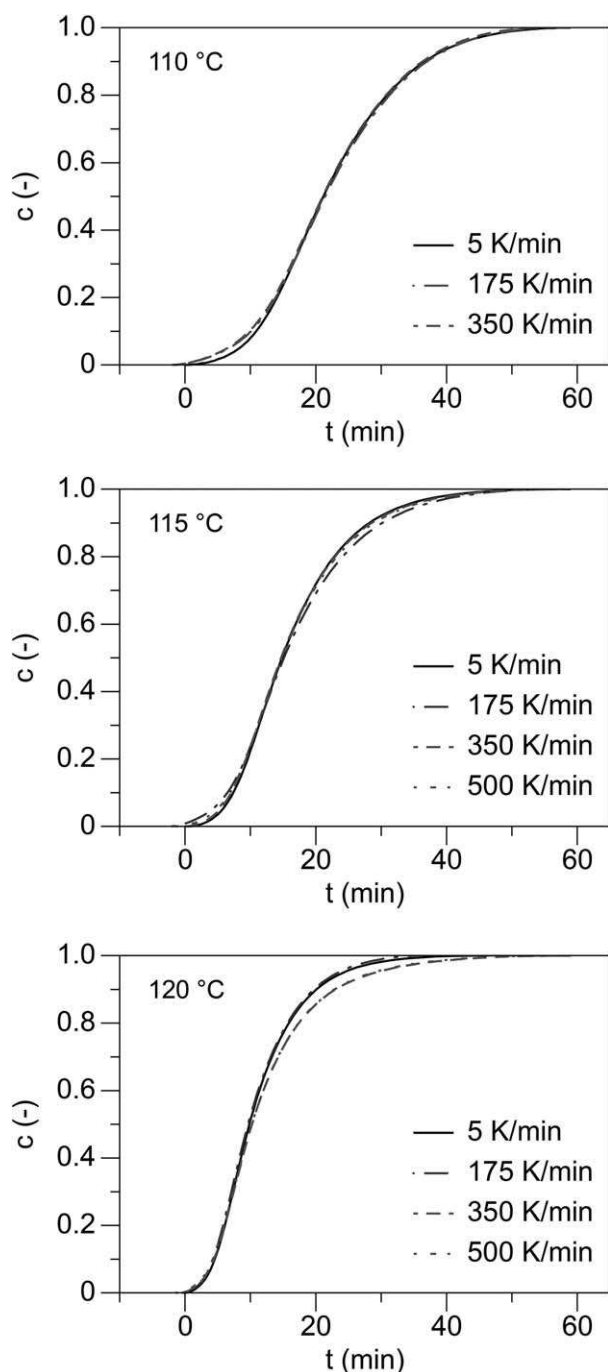
Figure 14. Comparison of the degree of cure using slow ramps (5 K/min) versus fast ramps (up to 500 K/min) at the beginning of isothermal scans.

transient energy balance to quantify the stabilization time of the geometry and conditions tested.

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