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subject : Cure Schedule for Stycast 2651/Catalyst 9

Executive Summary

The Emerson & Cuming technical data sheet (TDS) for Stycast 2651/Catalyst 9 lists three alternate cure schedules for the material, each of which would result in a different state of reaction and different material properties. Here, a cure schedule that attains full reaction of the material is defined. The use of this cure schedule will eliminate variance in material properties due to changes in the cure state of the material, and the cure schedule will serve as the method to make material prior to characterizing properties. The following recommendation uses one of the schedules within the TDS and adds a "post cure" to obtain full reaction. The two-step recommended cure schedule is as follows:

1. 2 hours @ T=65C
2. 2 hours @ T=100C

These times and temperatures are what the Stycast 2651/Catalyst 9 material must experience. Thus if material temperature lags oven temperature, this should be accounted for. Ramp rates to temperature are not specified and are not critical assuming there is not significant heating due to the reaction exotherm.

Introduction

The Emerson & Cuming technical data sheet (TDS) for Stycast 2651/Catalyst 9[1] lists three alternate cure schedules for the material:

1. 16-24 hours @ T=25C
2. 4-6 hours @ T=45C
3. 1-2 hours @ T=65C

A "post cure" of the material for 2-4 hours at the highest expected use temperature is also suggested.

Since there is no explicit mention of differences in the resulting material after the listed cure schedules, one might be tempted to assume that all schedules result in the same product and use whichever one is most convenient for a particular process. On the other hand, the suggestion of a "post cure" implies that none of the recommended schedules result in full cure. It turns out that the three recommended cure

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[1] June 2009 revision, see Appendix II

schedules do not result in the same product. The differences in the product after each of the three cure schedules listed above will not be explicitly shown here. Rather, the focus of this work will be on the state of the material after the cure schedule in #3: 2 hours at T=65C. It will be shown that the material does not reach a full extent of cure under these conditions. Rather, the material vitrifies during cure at T=65C and will never reach a full extent of reaction at this temperature. Methods of attaining a full extent of reaction in the material will then be demonstrated. Finally, a recommendation on the cure schedule to be used will be made.

Experimental

The polymerization reaction that occurs in the Stycast 2651/Catalyst 9 material is exothermic and enables an evaluation of the cure schedule using calorimetric techniques. In this case the focus will be on the heat produced during the polymerization reaction and on the temperature at which the glass transition of the material occurs after the reaction process. These two quantities enable an assessment of when the reaction is occurring/completed and the glass transition temperature (T_g) of the material, respectively. In all work below, the material was mixed according to the recommendations in the TDS,[2] placed in an aluminum pan, and tested on a Q2000 differential scanning calorimeter (TA Instruments) as soon as possible after mixing. Tracking the heat flow during reaction at T=65C for two hours gives the results in Figure 1.

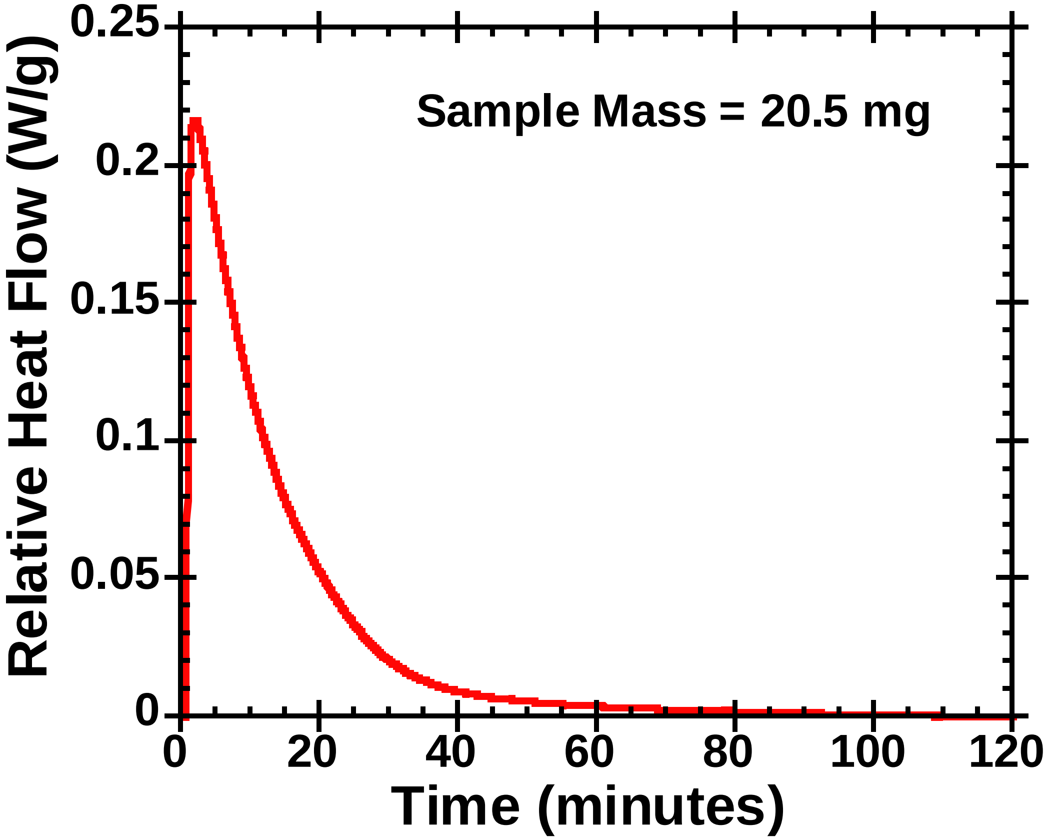

Figure 1. Heat flow versus time during reaction of Stycast 2651/Catalyst 9 at T=65C. Temperature is equilibrated to T=65C as quickly as possible upon initiating the test. The value of the heat flow at 120 min (0.007477 W/g) is subtracted from all values (assumption of a small non-zero "baseline").

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[2] 100:7 parts by weight mix ratio of Stycast 2651:Catalyst 9

The reaction does appear to have stopped within the allotted 120 minutes at T=65C (i.e., the measured heat flow, which is proportional to the rate of reaction, is very small if not zero by 120 minutes). However, upon heating the material above this reaction temperature, it is noted that remaining reaction potential does exist. This is denoted in Figure 2 below.

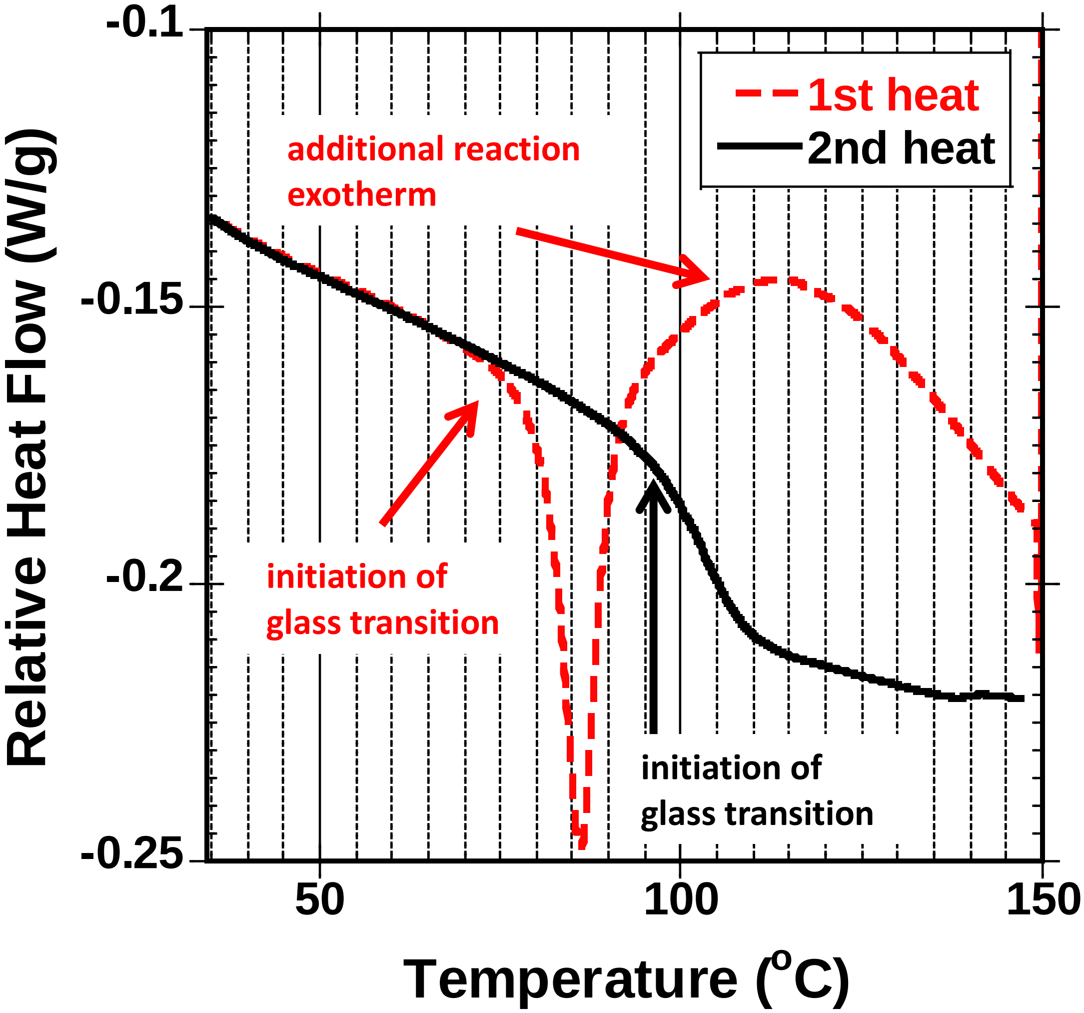

Figure 2. Heat flow versus temperature for Stycast 2651/Catalyst 9 during a heating ramp after cure at T=65C for 2 hours. The heating ramp is performed at 10C/min after cooling the material as quickly as possible once the two hours at T=65C is completed. The red curve is the response during the initial heating and the black curve is the response after cooling the same sample to T=25C at 10C/min and reheating at 10C/min.

During a temperature ramp after the two hour cure at T=65C, the material begins to go through a glass transition at about T=75C. At temperatures above this transition, the uncured reactants regain mobility and continue to react, resulting in the exothermic peak at high temperatures. Upon cooling and reheating in the same fashion, the glass transition initiates approximately 20C higher than it did after the T=65C cure alone. This is due to the additional reaction that occurred during the first heating. No further reaction exotherm is noted during the second heating.

Since the material vitrifies during cure at T=65C, it will also vitrify during cure at T=25C and T=45C. This will result in a material with a different cure state and different material properties after the three recommended cure cycles in the TDS. Because the TDS does not provide a specific "post cure" process that would achieve a fully cured product, experiments were performed to define a cure schedule that would result in full reaction. The specific tests performed examined the following "post cures" (following cure at T=65C for two hours):

1. 1 hour @ T=100C
2. 16 hours @ T=100C
3. 16 hours @ T=130C

The initial heating curves after these cure cycles, along with the heating curve after cure at T=65C for two hours, are shown in Figure 3.

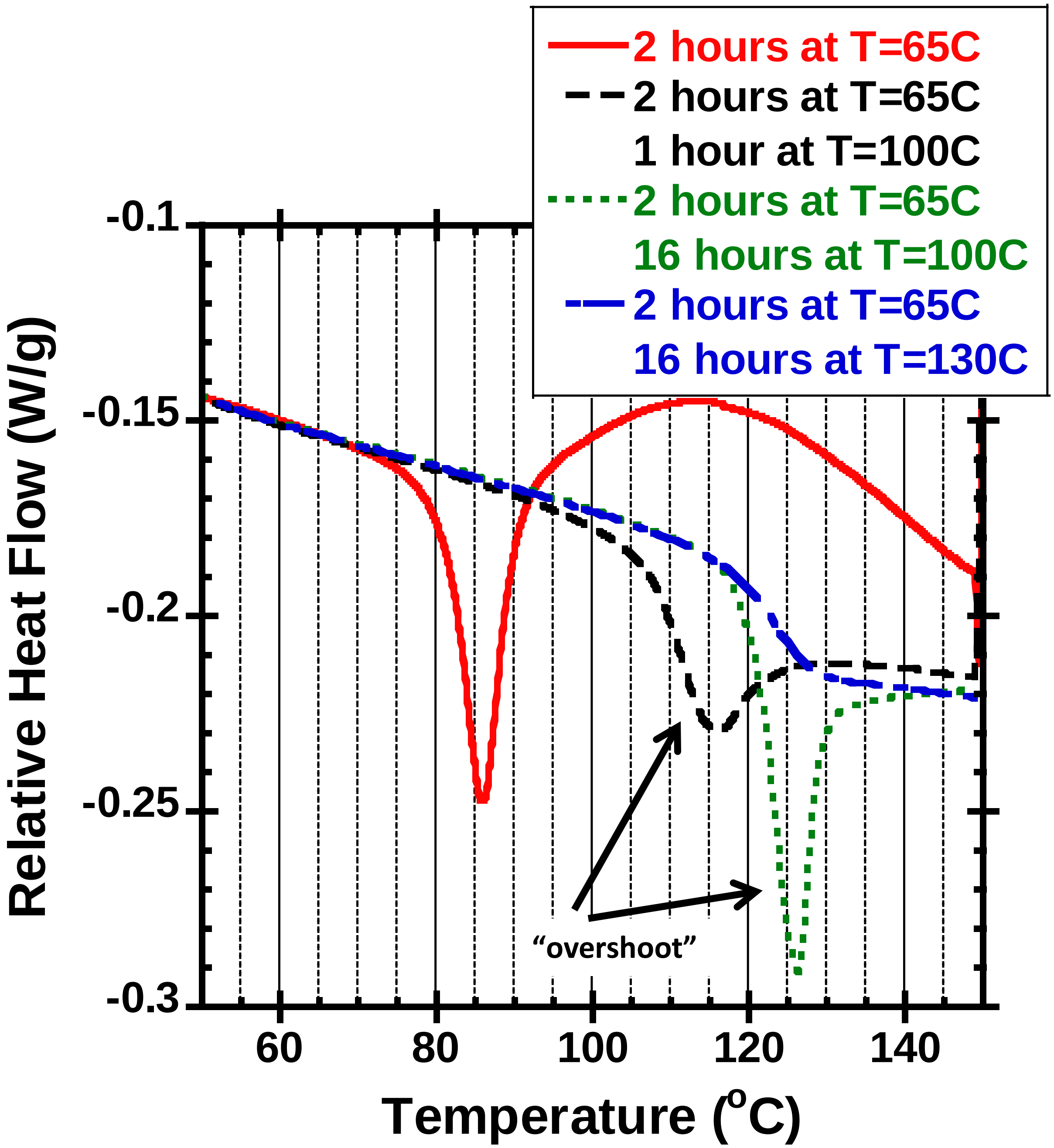

Figure 3. Heat flow versus temperature for Stycast 2651/Catalyst 9 during a heating ramp after the defined cure schedules. The heating ramp is performed at 10C/min after cooling the material as quickly as possible after the reaction.

There is a clear difference in the temperature at which the glass transition occurs after the T=65C cure schedule versus after the "post cure" schedules. Smaller differences exist amongst the "post cure" cases. The T_g measured during this heat ramp is influenced both by partial cure of the material (after the T=65C cure) and physical aging of the material (during the T=100C "post cure"). These influences can be eliminated by comparing the second heating curves, since remaining reaction potential is exhausted and physical aging effects erased at temperatures above T_g during the initial heating. The second heating curves are shown in Figure 4.

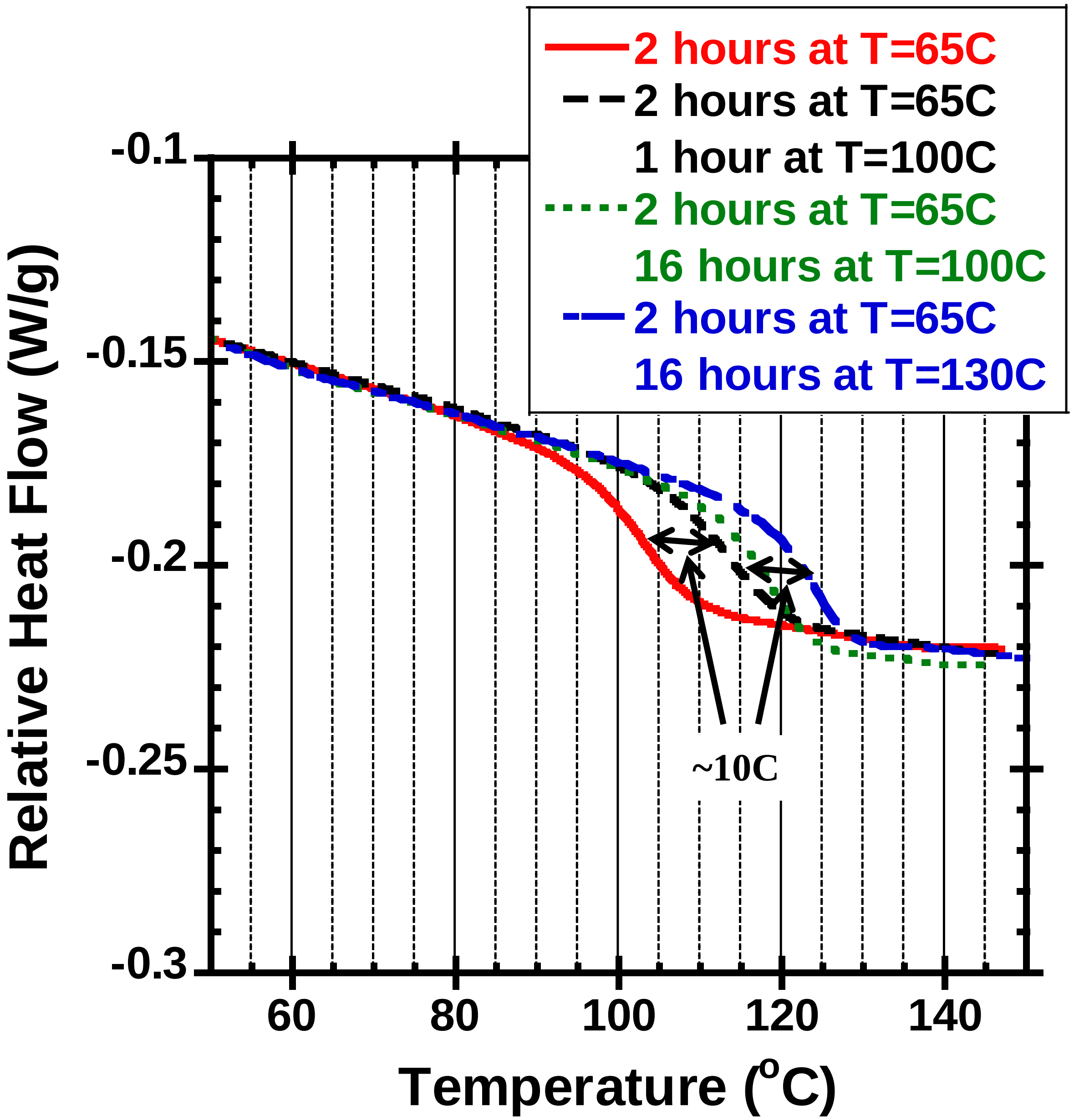

Figure 4. Heat flow versus temperature for Stycast 2651/Catalyst 9 during a second heating ramp after the defined cure schedules. The heating ramp is performed at 10C/min after cooling the material at 10C/min following the initial heating cycle.

From Figure 4 it appears that how full cure is attained may have an impact on the ultimate T_g of the material. Replicate samples have not been tested to establish the experimental variability of these measurements, but it appears that T_g increments by approximately 10C between "post cure" during a temperature ramp and "post cure" at T=100C as well as between "post cure" at T=100C and "post cure" at T=130C. Thus choosing one process for the "post cure" will produce the most consistent results.

Another observation that can be made from Figures 3-4 is the difference between curing at T=100C for different times (1 hour versus 16 hours). The T_g observed during the second heating (Figure 4) is not significantly affected by the time of “post cure” at T=100C. On the other hand, both the observed T_g and the depth of the “overshoot” of the rubbery response depend on cure time at T=100C during the initial heating (Figure 3). The “overshoot” is thought to be associated with physical aging[3] of the material as it sits at T=100C. Physical aging also increases the observed T_g. The sample that experienced 16 hours at T=100C demonstrated both a deeper “overshoot” and higher T_g during the initial heating (versus the sample that experienced one hour at T=100C). After annealing above T_g, the onset T_g for the sample that experienced 16 hours at T=100C decreased. These observations are consistent with a physical aging explanation. Whether physical aging has any impact on how the material will perform in the application is unknown.

Discussion and Recommendation

It is desired to use the Stycast 2651/Catalyst 9 material in such a way that material properties are known and do not vary amongst batches and/or products. Defining a cure schedule that attains full reaction of the material will help achieve this. The data in Figures 2 and 3 demonstrate that even the highest temperature cure recommended in the TDS does not attain full reaction of the material. This led to the evaluation of multiple “post cures”.

The two “post cure” temperatures tested appear to give a different ultimate T_g, suggesting final properties depend on the cure history of the material. Thus keeping cure history constant will produce the most consistent results. Since there are multiple advantages of keeping the temperature lower, performing the “post cure” at the lower temperature, T=100C, is recommended. The cure time at T=100C must be long enough to complete the reaction. In the experiments carried out here, in which very small quantities of material were held at isothermal conditions, one hour at T=100C appears to sufficiently complete the reaction when it follows 2 hours at T=65C.[4] In cases where isothermal conditions do not exist (e.g., even though an oven is at T=100C, it may take a while for the material in a large part to reach the oven temperature), it is important that that the Stycast 2651/Catalyst 9 material be at T=100C for at least one hour. Thermocouples placed in the Stycast 2651/Catalyst 9 during the production process could verify this. Else, conservative cure times (> 1 hour) can be used. One possible disadvantage of extending the cure time at T=100C is that physical aging of the Stycast 2651/Catalyst 9 will be faster at T=100C than at lower temperatures. Since the material vitrifies during cure at T=100C (ultimate T_g > cure temperature), physical aging will occur during the cure schedule (this would not be the case if the cure temperature was above T_g, like it is at T=130C). However, the implication of physical aging on the performance of the final product is unknown. And if physical aging does become a concern, annealing of parts can be done above the T_g of Stycast 2651/Catalyst 9 to erase physical aging history. Indeed, parts for which Stycast 2651/Catalyst 9 is currently being considered as an encapsulant will experience post encapsulation processing at T=150C. The T=150C processing will complete any small amount of remaining reaction potential and erase any physical aging history the encapsulant may have after “post cure” at T=100C. With these considerations, a buffer above the 1 hour cure time is suggested without making the cure times at T=100C excessively long. A two hour cure at T=100C is suggested to follow a two hour cure at T=65C for Stycast 2651/Catalyst 9.

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[3] Physical aging is a process by which the glassy material compresses, or becomes denser, with time

[4] In Figure 3, all that is shown is that there is little-to-no exotherm upon heating the material after a one hour “post cure” at T=100C. Other evidence of the reaction being sufficiently complete is given in Appendix I. Figure A1 plots heat flow versus time at T=100C (after 2 hours of cure at T=65C). The plot suggests the exothermic reaction is complete, or at least significantly slowed, in less than 1 hour. Figure A2 shows the T_g does not significantly change between the first and second heating after a one hour “post cure” at T=100C.

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Appendix I

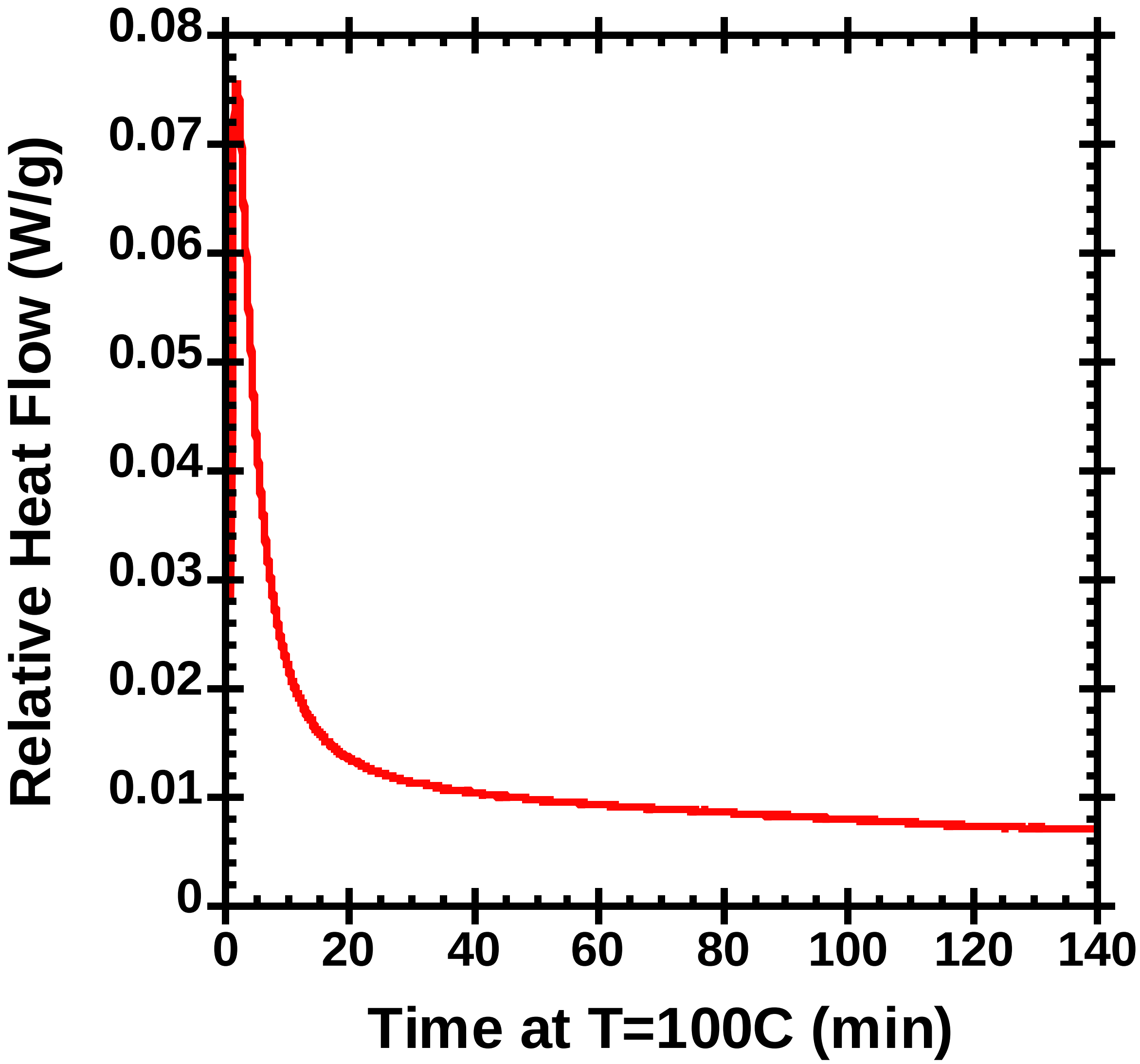

Figure A1. Heat flow versus time for Stycast 2651/Catalyst 9 during isothermal cure at T=100C after two hours of isothermal cure at T=65C. The exothermic peak appears to be completed in less than 60 minutes. The long “tail” in the data is not thought to be associated with reaction.

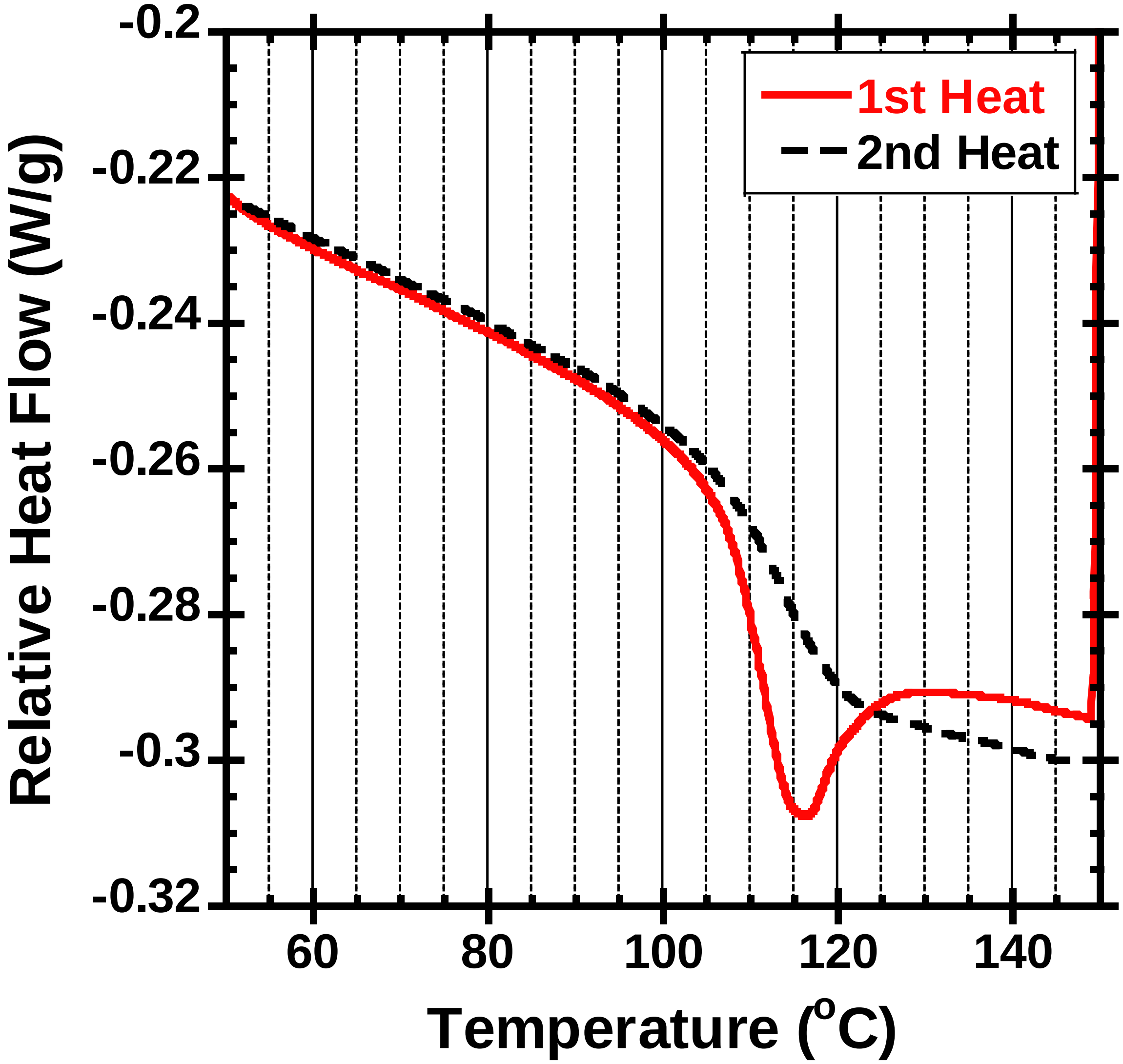

Figure A2. Heat flow versus temperature for Stycast 2651/Catalyst 9 after cure at T=65C for 2 hours and T=100C for 1 hour. The first heating ramp is performed at 10C/min after cooling the material as quickly as possible once the cure cycle is completed. The second heating ramp is performed at 10C/min after cooling the material at 10C/min following the initial heating cycle. There is no clear exotherm after T_g during the initial heating. If there is a small exotherm after T_g during the initial heating, it does not significantly affect the onset of T_g between the first and second heating.

Appendix II

Technical Data Sheet

STYCAST™ 2651™/Catalyst 9™

June 2009

PRODUCT DESCRIPTION

STYCAST™ 2651™/Catalyst 9™ provides the following product characteristics:

Technology	Epoxy
Appearance (Resin)	Black
Components	Two component - requires mixing
Mix Ratio, by weight - Resin : Hardener	100 : 7
Mix Ratio, by volume - Base : Hardener	100 : 11.5
Product Benefits	• General purpose • Excellent adhesion • Excellent electrical properties • Thermally conductive • Excellent chemical resistance • Good physical strength
Cure	Room temperature cure
Application	Encapsulant
Operating Temperature	-40 to 130 °C

STYCAST™ 2651™/Catalyst 9™ is a dielectric grade epoxy encapsulant designed for general purpose and has excellent adhesion to a wide variety of substrates.

STYCAST™ 2651™/Catalyst 9™ passes NASA outgassing standards.

TYPICAL PROPERTIES OF UNCURED MATERIAL

Part A Properties *2651™*

Viscosity, Brookfield , 25 °C, mPa·s (cP):	
Speed 5 rpm, # 7	225,000
Specific Gravity	1.65
Shelf Life @ 25°C, months	6
Flash Point - See MSDS	

Part B Properties *Catalyst 9™*

Viscosity @ 25 °C, mPa·s (cP)	80 to 105
Flash Point - See MSDS	

Mixed Properties

Mixed Viscosity, mPa·s (cP)	32,000
Specific Gravity	1.56
Working Time, 100 g mass, @ 25ºC, minutes	45
Flash Point - See MSDS	

TYPICAL CURING PERFORMANCE

Cure Schedule

16 to 24 hours @ 25°C or
4 to 6 hours @ 45°C or
1 to 2 hour @ 65°C

Post Cure

Post Cure: 2 to 4 hours at the highest expected use temperature

The above cure profiles are guideline recommendations. Cure conditions (time and temperature) may vary based on customers' experience and their application requirements, as well as customer curing equipment, oven loading and actual oven temperatures.

TYPICAL PROPERTIES OF CURED MATERIAL

Physical Properties:

Coefficient of Thermal Expansion TMA:		
Below Tg, ppm/°C		43.3
Thermal Conductivity, W/mk		0.66
Hardness, Shore D		88
Water Absorption24 hours, %		0.25
Compressive Strength, psi		17,100
Flexural strength , ASTM D790	N/mm^2 (psi)	77 (11,100)
Tensile Strength, psi		6,500

Electrical Properties:

Dielectric Strength, volts/mil	450
Volume Resistivity @ 25ºC, ohm-cm	5×10^{15}
Dielectric Constant @ 1mHz	3.9
Dissipation Factor @ 1mHz	0.05

Outgassing Properties:

Total Mass Loss, %	0.37
Collected Volatile Condensable Material, %	0.03

GENERAL INFORMATION

For safe handling information on this product, consult the Material Safety Data Sheet, (MSDS).

DIRECTIONS FOR USE

1. Complete cleaning of the substrates should be performed to remove contamination such as oxide layers, dust, moisture, salt and oils which can cause poor adhesion or corrosion in a bonded part.
2. Some separation of components is common during shipping and storage. For this reason, it is recommended that the contents of the shipping container be thoroughly mixed prior to use.
3. Accurately weigh resin and hardener into a clean container in the recommended ratio.
4. Blend components by hand, using a kneading motion, for 2 to 3 minutes and scrape the bottom and sides of the mixing container frequently to produce a uniform mixture.
5. If possible, power mix for an additional 2 to 3 minutes. Avoid high mixing speeds which could entrap excessive amounts of air or cause overheating of the mixture resulting in reduced working life.
6. To ensure a void-free embedment, vacuum deairing should be used to remove any entrapped air introduced during the mixing operation.
7. Pump-down or pull vacuum on the mixture to achieve an ultimate vacuum or absolute pressure of 1 to 5 torr or mm Hg. The foam will rise several times in the liquid height and then subside.
8. Continue vacuum deairing until most of the bubbling has ceased. This usually takes 3 to 10 minutes.
9. To facilitate deairing in difficult to deair materials, add a few drops of an air release agent, such as ANTIFOAM 88 into 100 grams of mixture.
10. Gentle warming will also help, but pot life will be shortened.
11. Pour mixture into cavity or mold.
12. Gentle warming of the mold or assembly reduces the viscosity. This improves the flow of the material into the unit having intricate shapes or tightly packed coils or components.
13. Further vacuum deairing in the mold may be required for critical applications.

Storage

Store product in the unopened container in a dry location. Storage information may be indicated on the product container labeling.

Optimal Storage: 25 °C

Material removed from containers may be contaminated during use. Do not return product to the original container. Henkel Corporation cannot assume responsibility for product which has been contaminated or stored under conditions other than those previously indicated. If additional information is required, please contact your local Technical Service Center or Customer Service Representative.

Certain resins and hardeners are prone to crystallization. If crystallization does occur, warm the contents of the shipping container to 50 to 60°C until all crystals have dissolved. Be sure the shipping container is loosely covered during the warming stage to prevent any pressure build-up. Allow contents to cool to room temperature before continuing.

Not for product specifications

The technical data contained herein are intended as reference only. Please contact your local quality department for assistance and recommendations on specifications for this product.

Conversions

(°C x 1.8) + 32 = °F
kV/mm x 25.4 = V/mil
mm / 25.4 = inches
N x 0.225 = lb
N/mm x 5.71 = lb/in
N/mm² x 145 = psi
MPa x 145 = psi
N·m x 8.851 = lb·in
N·m x 0.738 = lb·ft
N·mm x 0.142 = oz·in
mPa·s = cP

Note

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Reference 0.1