

Experiment 1: Thermal Characterization of Resins - Transitions & Cure

Objective:

- Study the glass transition and melting or crystalline transition for various thermoplastic polymers.
- Determine the exotherm and kinetics of cure with the help of DSC for a thermosetting vinyl-ester resin at various temperatures.

Background:

The differential scanning calorimeter (DSC) is an analytical tool that measures the heat flux to a material sample as it is maintained at a constant temperature or along a linear temperature ramp. The DSC operates by comparing the heat transfer to the sample pan with the heat transfer to a reference pan. From this heating data, physical properties such as melting point, glass transition point, and reaction kinetics can be determined. In this experiment the DSC is used (a) in an isothermal mode to determine the cure kinetics of a thermoset resin and (b) in the varying temperature mode to identify the thermal transitions of various thermoplastic polymers.

Experimental Guide:

This experiment is divided into two parts.

The first part involves using the DSC to study transitions in thermoplastic materials.

- Test two different polypropylenes, one a homopolymer and the other a copolymer, and Nylon 6-6. The materials should be tested using a heating rate of 5^oC/min.

The second part involves using the DSC in isothermal mode to study cure-kinetics of thermoset resins.

- The SMC paste must be examined using at least three different temperatures between 90 and 120^oC, isothermally. The goal of this study is to explore and identify the exotherm and cure kinetics of the thermoset resin.

Materials:

Thermoplastics:

Nylon 6-6

Polypropylenes

Thermoset:

SMC paste containing unsaturated polyester resin

BPO initiator emulsion in a tube (has 40 wt% BPO)

Equipment:

TA Differential Scanning Calorimeter (DSC) with TA Q10 Controller and finned air-cooling system (FACS)

I. Operation of DSC

1. Make sure the nitrogen supply is on, and the rotameter reading is close to 80 (equivalent to a flow rate of 50 ml/min). If it is not, notify the TA.
2. The DSC and computer power should be on.
3. Double click on the **TA Q-Series Explorer** icon to open the DSC software.

II. DSC Sample Preparation

Note: Always handle the aluminum sample pans using forceps.

1. Weigh the aluminum pan on the analytical balance. Tare it, load it with sample, and reweigh. Normally, sample weight in DSC experiments is in the range of 5 to 20 milligrams. Use larger sample sizes at slower heating rates, smaller sample sizes at higher rates.

Type of Measurement	Sample Size (mg)	Heating Rate (°C/min)
Glass transition	10 to 20	10 to 20
Melting point	2 to 10	5 to 10

2. After loading the sample on the pan, crimp the pan using the procedure posted near the DSC workstation. Have the TA demonstrate the technique the first time.
3. The procedure to make the thermoset paste sample has been posted at the DSC workstation. Consult TA if you have any questions.

Loading/Unloading a Sample

1. Remove the cover from the heating chamber of the DSC
2. Carefully place the sample pan on the right front raised platform (4 o'clock position) and the reference pan on the left rear platform (10 o'clock position). Centering the pans within the grid will ensure that they are centered on the platforms.
3. Replace the cover.

III. Setting up the experiment

In the TA Q-Series Explorer screen, there are three panes. The leftmost pane is the Sequence pane, in which experimental Runs can be scheduled. In the middle pane, there are three pages: Summary, Procedure and Notes; in these pages, the information to set up the experiment needs to be specified. The rightmost pane has additional information about setting up the test.

III-A. Setting Up a DSC Ramp Procedure for thermoplastic resin analysis

DSC ramp experiments heat or cool the material at a constant rate.

1. Select *Create New Sequence* (blank page) icon on the **Sequence** (leftmost) pane. You should see a red arrow pointing at *Run 1*.
2. Select **Summary** page
3. Enter the following information
 - 3a. **Mode:** *Standard*
 - 3b. **Test:** *Ramp*
 - 3c. Enter *Sample Name*, *Sample Size* (mass), *Comments*
 - 3d. Enter *Data File Name*, and specify the path using Browse icon. A sample Ramp test has been saved in \\Bucks\ta\Data\DSC\Thermoplastic-Analysis\Resin-Transitions. You can model your test based on this template. All data should be saved in the **DSC** folder; you can create additional folders, e.g., Group-Name, etc. in this directory.
4. Select **Notes** page
5. Enter *Operator name*, *Pan Type* (Aluminum), any comments in the *Extended Text* field. *Purge Gas Information*, by default should be *Nitrogen*, and *50 ml/min*.
6. Select **Procedure** page
 - 6a. Verify that the **Test** is *Ramp*.
 - 6b. By default, *Use Current Temperature* should be selected.
 - 6c. Enter *Heating Rate*
 - 6d. Enter *Final Temperature*. The final temperature should be high enough to cover the temperature at which the transition is expected to occur.
7. Click the **Apply** button at the bottom of the page to save the data.

8. Once the procedure is saved, double click on the red arrow in the **Sequence** (leftmost) pane to start the test. Wait for test completion.

III-B. Setting Up a DSC Isothermal Procedure for thermoset cure analysis

The isothermal procedure will be used to analyze the cure kinetics of thermoset resins. In this test, the sample needs to be quickly elevated to the test temperature, and maintained at that temperature for times long enough to cover the expected transitions.

1. Select *Create New Sequence* (blank page) icon on the **Sequence** (leftmost) pane. You should see a red arrow pointing at *Run 1*.

2. Select **Summary** page

3. Enter the following information

3a. **Mode:** *Standard*

3b. **Test:** *Custom*

3c. Enter *Sample Name*, *Sample Size* (mass), *Comments*

3d. Enter *Data File Name*, and specify the path using Browse icon.

A sample Ramp test has been saved in \\Bucks\ta\Data\DSC\Thermoset-Analysis\Isothermal-Cure. You can model your test based on this template. All data should be saved in the **DSC** folder; you can create additional folders, e.g., Group-Name, etc. in this directory.

4. Select **Notes** page

5. Enter *Operator name*, *Pan Type* (Aluminum), any comments in the *Extended Text* field. *Purge Gas Information*, by default should be *Nitrogen*, and *50 ml/min*.

6. Select **Procedure** page

6a. Verify that the **Test** is *Custom*.

6b. Enter brief information about test-methodology in the *Notes* field.

6c. Specify *Name* for the method

6d. Click on the *Editor*, to the right of the Name field. It should open a *Method* dialog box.

6e. In the *Method* dialog box, click on the *Create New Method* (blank page) icon to clear any prior information. Also, you should see a *Segment List* on the

rightmost pane, this list contains several standard templates available in the software that can be added to the method.

6f. From the *Segment List*, double click on *Ramp*. This will transfer *Ramp* into the *Method* dialog box.

6g. Enter *Heating Rate* (30°C/min) and *Final Temperature* (this is the test temperature at which the isothermal cure will be carried out). This *Ramp* segment ensures rapid heating of the sample to the test temperature.

6h. From the *Segment List*, double click on *Isothermal*. This will transfer *Isothermal* into the *Method* dialog box.

6i. Enter *Isothermal Time*. This time should be long enough (60-100 min) to cover the cure time.

7. Click the **Apply** button at the bottom of the page to save the data.

8. Once the procedure is saved, double click on the red arrow in the **Sequence** (leftmost) pane to start the test. Wait for test completion.

IV. Analysis of data

Double click on the TA Universal Analysis icon to open the analysis software. Open the file that you need to analyze using the *Browse* button. Click *OK* on *Data File Information* dialog box.

IV-A. Glass Transition

1. Use the **Glass Transition** menu item from the *Analyze* menu to calculate the onset, end, inflection, and signal change of a glass transition in the curve. When you select the above option, markers will be displayed on the graph.

2. Right click to display the *Analyze* pop-up menu, and then select Point 1 to activate the first marker. Position the vertical bar of the active marker where you want the data for the tangent line to begin.

3. Right click to display the *Analyze* pop-up menu again, and then select Point 2. Position the second marker where you want the tangent line to end.

4. Repeat steps 2 and 3 for Points 3 through 6 until all six markers have been placed.

5. Right click to display the *Analyze* pop-up menu. Select *Accept Limits*.

The program draws the tangent lines, calculates and displays the onset, midpoint, and end.

IV-B. Melting Point

1. Use the ***Integrate Peak*** menu item from the *Analyze* menu to calculate and report the following: Start and stop temperatures, onset temperature, peak maximum temperature (melting point), peak area (heat of transition)
2. The peak is integrated with respect to time between the start and stop baseline limits. You select type of baseline used from the menu.
3. Select *Linear* from the *Analyze/Integrate Peak* menu to perform a peak integration using a linear baseline. A linear baseline is defined as a straight line drawn between the selected start and stop limits. It is used when the baseline varies directly (linearly) with time. Markers will be displayed on the graph.
4. Double click at the intersection of the curve where you want the baseline to begin, which will position the first marker.
5. Double click at the intersection of the curve where you want the baseline to end, which will position the second marker.
6. Right click to display the *Analyze* pop-up menu, and then select *Accept Limits* (or press *Enter*). The peak integration analysis results are displayed.

IV-C. Analysis of cure transition for thermoset materials

The thermoset material investigation involves studying the cure kinetics. The important quantities in this study are rate of heat generation, the amount of heat generated in time t , and the degree of cure. This analysis can be easily performed using EXCEL. To transfer the data to EXCEL, select *View*, after opening the file in the *TA Universal Analysis* window. Select *Data Table*, and then select *Spreadsheet*. In the Spreadsheet dialog box, select All Data Points. This will open an EXCEL file. Save this spreadsheet to carry out further analysis.

The rate of heat generation is related to the rate of heat flow by the following equation:

$$\frac{dQ}{dt} = \rho_c H_R \frac{d\alpha}{dt}$$

dQ/dt = Rate of heat generation

H_r = Heat of reaction

ρ_c = Density of composite

$$d\tilde{\alpha}/dt = \text{Rate of reaction}$$

The amount of heat generated in time t at a constant curing temperature T is the area under the rate of heat generation curve up to the desired time and is expressed as:

$$H = \int_0^t \left(\frac{dQ}{dt} \right) dt$$

where, H = amount of heat released in time t .

The total amount of heat generated during a cure cycle, H_R , is found when $t = t_f$ (final time). The degree of cure at any time is defined as:

$$\alpha_c = H / H_R$$

The degree of cure is found by dividing the partial area of the heat generation curve by the total area to obtain the degree of cure at the desired time. This procedure is based on the assumption that the physical properties of the resin (i.e. density and thermal conductivity) do not vary during the cure cycle. A degree of cure vs. time curve plot is then constructed and the rate of cure is then found. A rate of cure vs. degree of cure plot can then be made.

Estimate parameters in the following rate expression for this reaction.

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

$$(m + n) = 2$$

Here k_1 and k_2 are rate constants that follow the Arrhenius relation with cure temperature. The exponents m and n , denote the order of the reaction with respect to the cured and uncured polymer fraction, respectively. Note that the total order of the autocatalytic curing reaction is taken to be 2. In the differential method, the values of k_1 , k_2 , m , and n can be determined by nonlinear least-squares curve fit to the rate data or $d(\alpha)/dt$ vs. α data. Alternatively, we can use an integral method. If $k_2 \gg k_1$, the above equation may be simplified for $\alpha > 0.05$ say to

$$\frac{d\alpha}{dt} = k \alpha^m (1 - \alpha)^n$$

where k_2 is renamed k .

$$\left(\frac{1}{\alpha} - 1\right)^{m-1} = (1-m)k_2 t$$

Plot $\log((1/\alpha) - 1)$ vs. $\log t$. With $m < 1$ typically, the slope of this log-log plot will turn out to be negative and equal to $[1/(m-1)]$. Note, however, this equation does not satisfy the initial condition of a finite rate at $t=0$ and $\alpha=0$. So the plot can only have data above some small conversion.

The values of k and m can also be determined by a nonlinear least-squares curve fit. Nonlinear least squares fit can be accomplished by either ZXMARQ in IMSL or the Solver function in Excel.

The activation energy, E_a , and Arrhenius constant, A , are found by making a plot of $\ln k$ vs. $1/T$. A regression line is then found with $(-E_a/R)$ being the slope and A being the y-intercept. The slope can be determined by the slope function in Excel. The Arrhenius equation, as well as the procedure for the non-linear least squares fit method, should be explained in detail in the final lab report. Consult the TA if help is needed in describing/understanding the non-linear least squares fit method.

Discussion Questions

Besides the calculations and questions listed on the previous pages:

1. Were the T_g and/or T_m 's of all thermoplastic materials close to the values found in literature? Why or why not?
2. How are the observed transitions in the PP homopolymer different from those of the PP copolymer? Explain.
3. What is an autocatalytic reaction? When you used the log-log plot to estimate the value of m at each temperature, were the values of m close? Should these values be the same? Comment.
4. Was the plot for $\ln k$ versus $1/T$ fairly linear or not? Why or why not? What is a good way of estimating/determining how "linear" a data set actually is?
5. Were the values for "k" and "m" (or "n") comparable to ones found in literature, as well as to each other? Why or why not?
6. If the value of m were in error by 10 percent, how much error would be incurred in estimating a demolding time?

References

1. P.K. Mallick, Fiber Reinforced Composites, Marcel Dekker, Inc. (1988), p 320-328
2. D.S. Lee and C.D. Han, "A chemorheological model for the cure of unsaturated polyester resin," *Polymer Eng. Sci.* 27, 955-963 (1987)
3. G.L. Batch, T. de Boom and C.W. Macosko, "Modeling of Crosslinking Free Radical Polymerization," *SPE ANTEC90*, p. 957-960, (1990)
4. R.L. McCullough and V.M. Nadkarni "Design of Cure Cycles for Thick Section Composites," 1991 (module on reserve in Eng Library)