The Use of Isothermal Microcalorimetry to Characterize the Cure Kinetics of a Thermoset Epoxy Material

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ABSTRACT

Isothermal microcalorimetry was used to investigate a thermoset epoxy system at multiple temperatures. The kinetics of the epoxy cure was calculated using Arrhenius kinetic analysis.

INTRODUCTION

Thermoset polymer precursors undergo irreversible chemical reactions to form crosslinked or cured materials. A common example of a thermoset polymer system is a two-part epoxy. The cross-linking reaction is an exothermic process and an isothermal microcalorimeter can be used to measure the heat evolved by this reaction at a given temperature. Cross-linking or curing of an epoxy can depend on many variables such as chemistry, temperature and sample mass. This study investigates the effect of temperature on curing of an epoxy resin.

EXPERIMENTAL and RESULTS

The materials used for these experiments were D.E.R. 331 epoxy resin (Dow Chemical) and Jeffamine D-230 hardener (Huntsman). Based on the manufacturer's recommendations, the two materials were mixed in a ratio of 100 parts epoxy to 32 parts hardener by mass. The epoxy was first weighed and immediately afterwards the correct amount of hardener was added and the components mixed for 30-60 s. Epoxy mixtures (5-7 g) were loaded into tared plastic ampoules in order to measure total sample weight before placing into the TA Instruments TAM Air microcalorimeter. Figure 1 shows the normalized heat flow versus time plots for 4 different samples that were collected simultaneously at 25 °C. The TAM Air has 8 calorimeters and it is possible to analyze up to 8 individual samples with corresponding references. For all experiments described, empty plastic ampoules were used as references.

The effect of temperature on the curing process is shown in Figure 2, in which the normalized heat flow versus time plot of the same epoxy was collected at five different temperatures: 25, 30, 35, 40, and 50 °C respectively. Note the change in peak shape and shift in time elapsed to reach heat flow maximum. Figure 3 is Figure 2, with the maximum heat flow signal recorded. The latter values are used as a common point at each temperature and are utilized in the Arrhenius kinetic analysis. Figure 4 shows the results as calculated from the Arrhenius analysis option from TAM Assistant software. Arrhenius kinetic analysis is used to calculate the activation energy and rate constant of a reaction. Using the labeled points (Figure 3) for kinetic analysis involves the assumption that the percent total enthalpy or conversion at this point is the same at each temperature. For more quantitative values of activation energy and rate constant it would be recommended to use curve deconvolution to more accurately calculate the time elapsed to reach the identical percent conversion. For more information on the Arrhenius kinetics calculations please refer to the experimental and technical note (1).

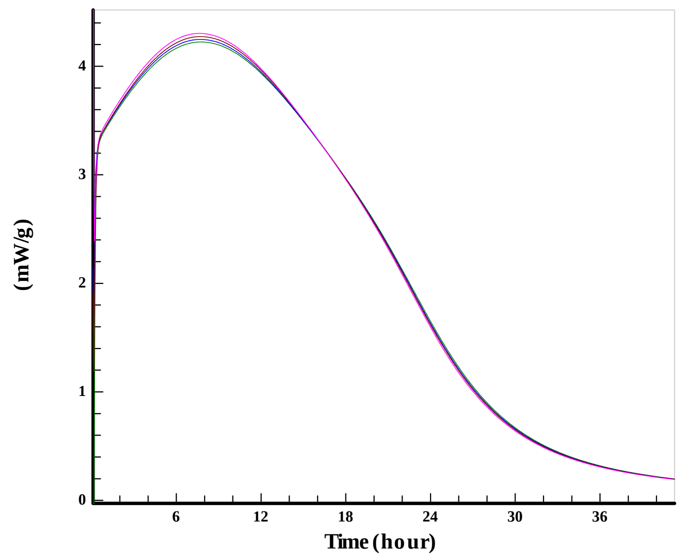

Figure 1: Normalized heat flow versus time plots of 4 epoxy samples collected at 25 °C.

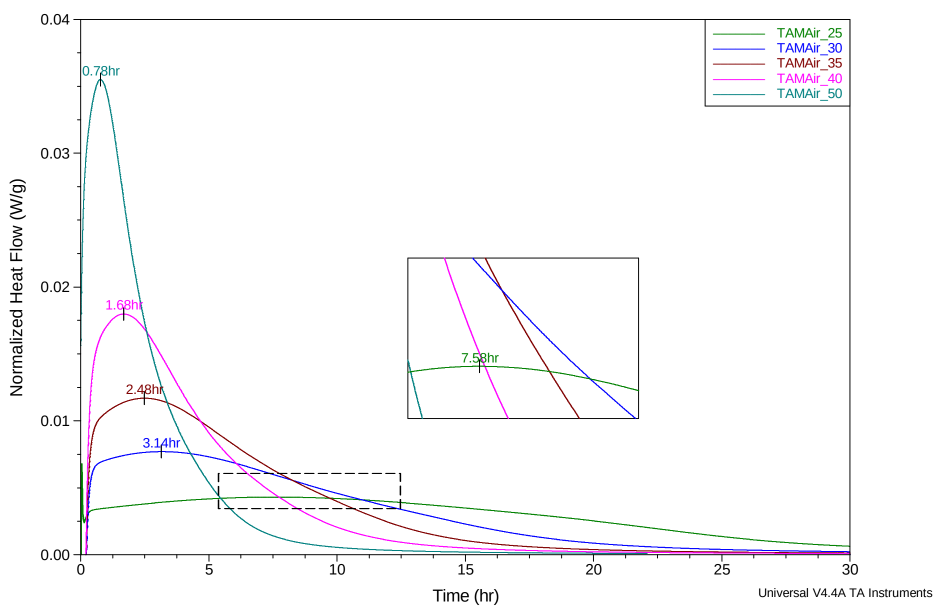

Figure 2: Normalized heat flow versus time plots of an epoxy cure at various temperatures. The time to maximum heat flow signal is indicated.

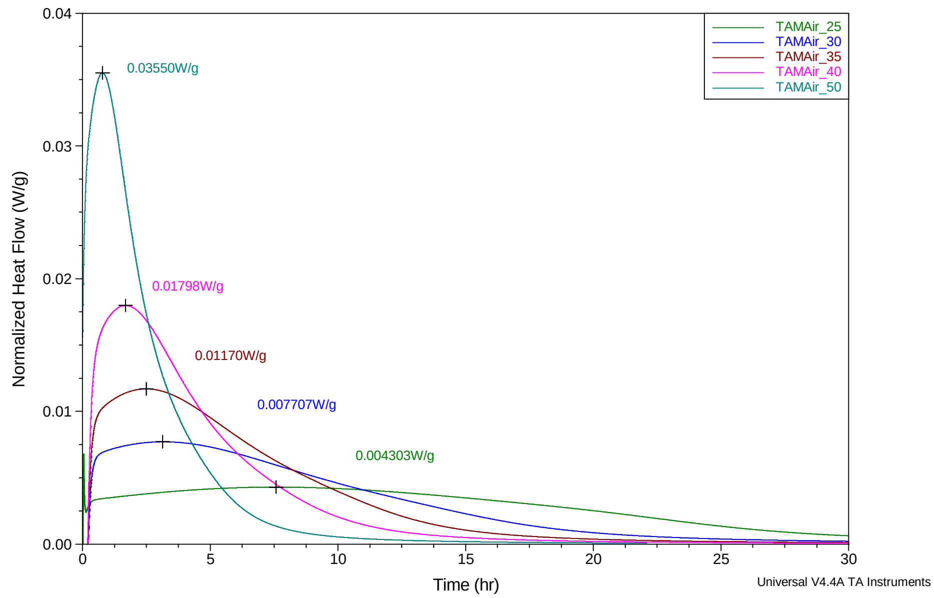

Figure 3: Normalized heat flow versus time plots of an epoxy cure at various temperatures. The maximum heat flow signal is indicated.

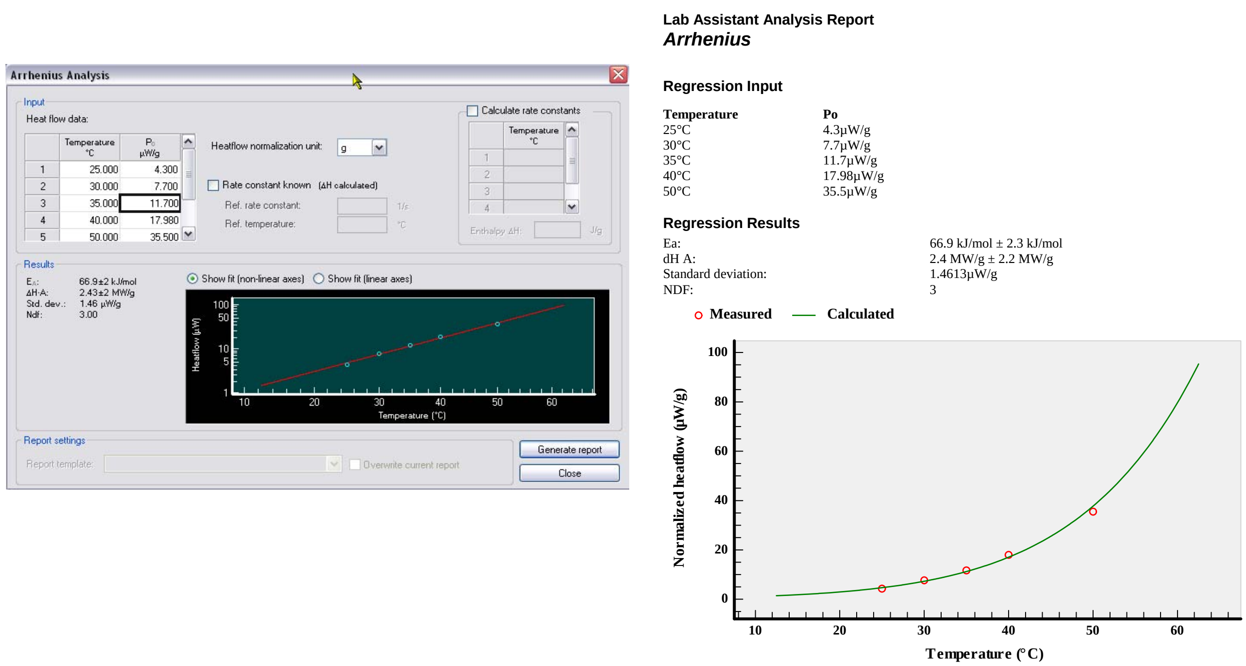

Figure 4: Arrhenius analysis window from TAM Assistant software and the report generated from the analysis.

CONCLUSIONS

Variables that effect the cross-linking or curing of a thermoset material can be investigated by isothermal microcalorimetry. The effect of temperature on an epoxy cure was measured from the TAM Air and the curing kinetic data was calculated using the TAM Assistant software.

REFERENCES

1. How to Use the Arrhenius Plot Program in Digitam, TA Instruments Experimental & Technical Note 015d

KEY WORDS

TAM Air, isothermal calorimetry, isothermal curing, thermoset, epoxy, kinetics, Arrhenius

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