Simultaneous DSC-Raman analysis of the curing of an epoxy thermoset

Benefits at a glance
- Real-time monitoring of an industrially important chemical and thermal transformation
- Non-invasive tandem spectral and thermodynamic data acquisition
- Molecular-structural investigation of a curing process

Introduction

Epoxy thermoset resins are important industrial polymers in applications involving the molding of a three-dimensional shape by techniques including injection, extrusion, and compression. Their particular advantages over other similar materials include superior mechanical and electrical properties and superior substrate adhesion. Effective monitoring of the curing process, in which the polymeric material is irreversibly hardened into its final form, is important for ensuring that the material properties of the final product meet the thermal, electrical, and structural properties required for the product's intended application.

Spectral DSC is a term used to describe the combined technique of DSC with either near-infrared (NIR) or Raman spectroscopy. This technique yields both chemical-structural and heat-flow information simultaneously for materials that undergo thermally induced solid-phase transitions. Vibrational spectroscopy can provide information on the chemical or structural changes that are occurring in the material, and this information complements the heat flow data measured by the DSC.

In this study, the curing of an epoxy thermoset resin was quantified using simultaneous thermodynamic and chemical-structural data obtained by tandem differential scanning calorimetry (DSC) and Raman spectroscopy. The results demonstrate that real-time Raman spectroscopy can be used to track the curing process in a simple two-part epoxy and can also be used to investigate the specific chemical process involved.

Methods and results

A simple two-part epoxy consisting of a resin and a hardener was used in these investigations. DSC data were collected on a TA Instruments Q2000 differential scanning calorimeter with an attached RCS90 refrigerated cooling system. A TA Instruments Universal Optical Accessory interface was used to support the optimized Raman fiber-optic probe (TA-DSC-Probe-785) and position it over the sample in the DSC (Figure 1). An incorporated thumbwheel drive was used for fine adjustment of the Raman probe height so as to obtain optimum signal strength. The Raman probe has, as standard, a 5 meter cable length that enabled the base unit of the Raman analyzer to be positioned at a convenient location elsewhere on the lab bench.

Figure 1: DSC-optimized Raman probe interfaced to the Q2000 DSC

Approximately equal quantities of resin and hardener were mixed, and a small amount was placed in the center of a DSC pan without a lid (conducting

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

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the experiment in an open-pan mode is a requirement for Spectral DSC as the light must interact with the sample under investigation). This pan was then placed in the DSC, and a method was executed that first equilibrated the cell at −25°C and then ramped the temperature to 50°C at a rate of 2°C/min. The DSC results are shown in Figure 2 (plotted versus time). The peak has been integrated to measure the heat evolved during the reaction.
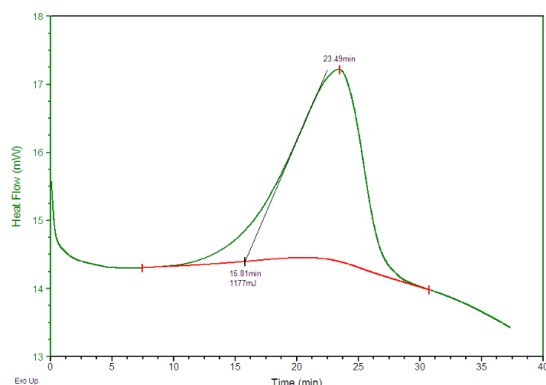

Figure 2: Cure exotherm for epoxy as captured by DSC

Simultaneous Raman data were collected with a Raman analyzer equipped with a DSC-optimized Raman probe (TA-DSC-Probe-785). The spectral range of the Raman instrument was 150–3425 cm^{-1} with a laser emission of ~70 mW (25% full power) from an Invictus 785 nm diode laser. The standard shutter of the analyzer was removed during operation so as to avoid oscillatory laser heating of the sample that is typical in competing systems and further complicates the experiment and experimental determinations.

The Raman analyzer was set up to collect data every two minutes; each resulting spectrum was an average of three accumulations. When analyzing spectral data, it is common to look for shifts in peak positions or changes in peak intensities. As the cure progressed during this experiment, a reduction of the intensity of a peak centered at 2577 cm^{-1} was evident.

The resin is a typical mixture of epichlorohydrin and bisphenol-A. The hardener is a proprietary substance,
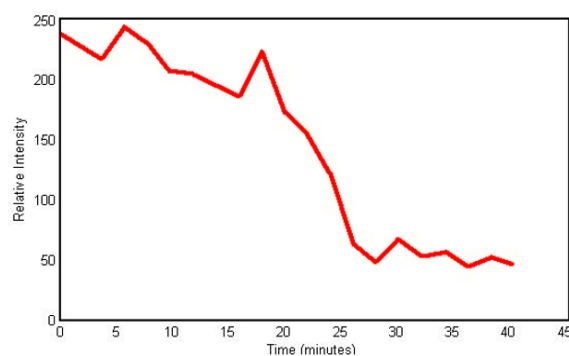

Figure 3: Plot of peak height versus time of Raman peak centered at 2577 cm^{-1}

but its chemical nature is a thiolamine blend. Thiols are organosulfur compounds containing a sulfur–hydrogen (S–H) bond, and Raman peaks between 2560 and 2590 cm^{-1} are typically due to the S–H stretching vibration. Thus it is reasonable to conclude that the changes in the 2577 cm^{-1} peak track the chemical conversion of hardener due to the curing process.

Figure 3 contains a plot of the peak height versus time of the 2577 cm^{-1} peak amplitude and confirms the reduction in amplitude. The data compares well with is the DSC results in Figure 2 regarding the onset and end of the transition.

Conclusions
The data presented here illustrate the utility of spectral DSC in investigating the chemical and thermal processes involved in the curing of a two-part epoxy system. The DSC data provide information on the heat evolved and thus could be used to determine percent cure, while the Raman data allow the nature of the chemical change to be investigated. The specificity of chemical information obtained with Raman spectroscopy is significantly greater than that from NIR, because Raman spectroscopy is sensitive to the chemical backbone of the hardener. The tandem application of thermal and spectroscopic analysis therefore provides a powerful tool for acquiring detailed molecular-level understanding of industrial thermosetting processes.

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