Use of the Photocalorimeter Accessory (PCA) with Tzero® DSC

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ABSTRACT

Photocalorimetry involves the introduction of an UV/Visible light to a sample while performing a DSC experiment. These experiments measure the heat released by the sample as it undergoes the light-initiated reaction. Typically, the intensity of the light is measured by an external radiometer. A new Photocalorimetry Accessory (PCA) has been developed that utilizes Tzero® technology providing several advancements over previous photocalorimetry apparatus. These include direct measurement and balancing of light intensity at the cell, dual-sample capability, and the ability to run MDSC® quasi-isothermal experiments in conjunction with the photo experiment.

INTRODUCTION

In the late 1970's several papers were published that discussed the modification of Differential Scanning Calorimeters (DSC's) to allow the introduction of ultraviolet (UV) light (1). TA Instruments (then part of The DuPont Company) commercialized the first Differential Photocalorimeter (DPC) in 1986. The design remained constant throughout the 1990's for the subsequent DSC generations. With the advent of the new Tzero® technology, a new photocalorimeter design is introduced to take advantage of the improved performance of this system.

INSTRUMENTATION

The Q Series Photocalorimeter Accessory (PCA) is based on a filter photometer design utilizing a high-pressure mercury lamp delivering light over the spectral range of 250 to 650 nm. The Light is transmitted from the instrument to the DSC cell via a one-meter long, 3-mm diameter, dual extended range, quartz light guide. The light guide attaches to the cell itself using a special adapter. A broadband filter supplied with the instrument covers 320 to 500 nm and is suitable for most UV and Visible PCA studies. Other optional filters include: 250 to 450 nm, 320 to 390 nm, 365 nm, and 400 to 500 nm. Visible longpass filters with cutoffs at 390 nm and 490 nm are also available as options. These latter filters mount at the DSC end of the light guide. The delivered intensity to the sample is adjustable by aperture control and neutral density filters over the range from 1 to 2500 mW/cm^2 (0.01 to 25 kW/m^2). The neutral density filters attached at the ends of the light guides can be easily interchanged to obtain the desired intensity output. Figure 1 shows a picture of the PCA attached to the Discovery DSC.

The PCA can be used with any TA Instruments DSC with Tzero® technology (2). The Tzero® DSC cell design (3) permits

Figure 1. PCA attached to the Discovery DSC

the independent measurement of sample and reference heat flow. It allows the use of a Refrigerated Cooling System (RCS) while doing PCA experiments. The improvements in temperature control permit experimental monitoring of the photopolymerization reactions at room temperature.

Direct Measurement and Balancing of Light Intensity at the Sample

Two key considerations when performing photocalorimetry experiments are the ability to regulate the intensity of light applied to the sample and knowledge of the light intensity. Traditionally, intensity was measured using an external radiometer. Since the intensity is related to the distance from the source, it is difficult to ensure that the intensity measured with the external radiometer is equivalent to that striking the sample. Due to the Tzero® DSC's unique ability to separately measure the sample and reference heat flow, the intensity can be measured directly at the cell with the sample and reference platforms. No apparatus or inserts are required for this measurement. Adjustment of the light guides balances intensity at the sample and the reference platforms. This minimizes the disruption to the baseline by the application of light. Figure 2 shows the sample and reference intensities after balancing, with a difference of only 0.04 mW/cm^2 (400 mW/m^2).

Dual Sample Capability

The ability to independently measure the sample and reference heat flow permits two samples to be analyzed simultaneously. The balanced light intensity ensures identical experimental conditions at the sample and reference platforms and offers productivity enhancement to the users.

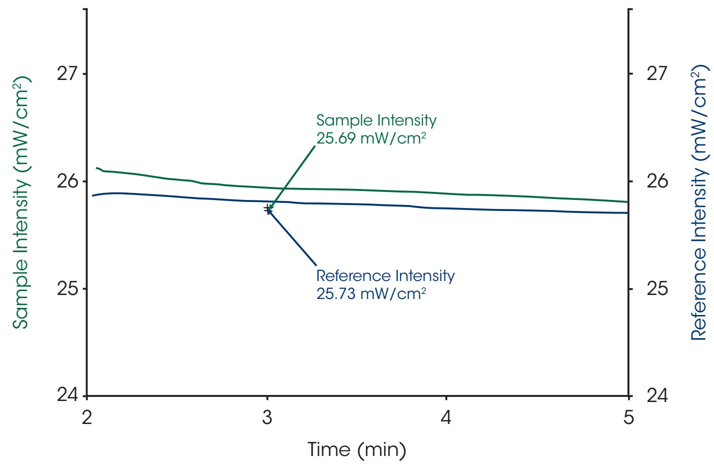

Figure 2. Sample and Reference Intensities measured with the Tzero® DSC cell

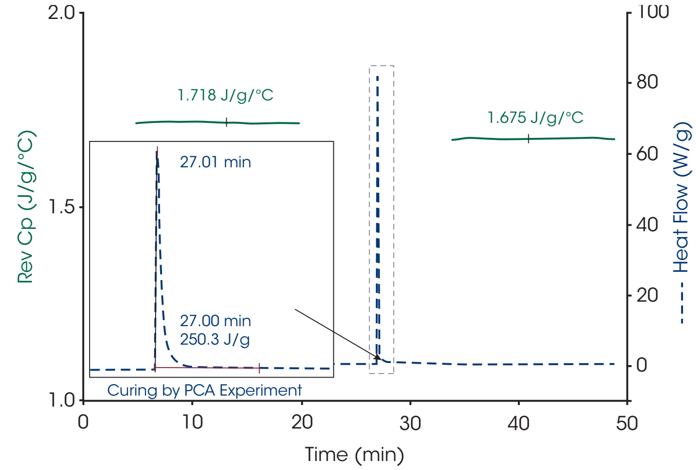

Figure 4. Data showing PCA-MDSC® Quasi-Isothermal Experiments

Figure 3 shows the results of two adhesives. Adhesive A is a fast UV curable adhesive, while Adhesive B is a general purpose UV curable adhesive with a longer cure time than experiment Adhesive A. The experiment has Adhesive A on the sample and Adhesive B on reference platforms, respectively. The samples are exposed to 25 mW/cm² light for 6 seconds beginning at 120 s. (It is common to allow a time period before light exposure to establish baseline and to use very short exposures when looking at small differences between samples.) Sample A reaches a peak maximum at 120.57 s, while Sample B takes an additional 2.0 s to reach its' peak maximum.

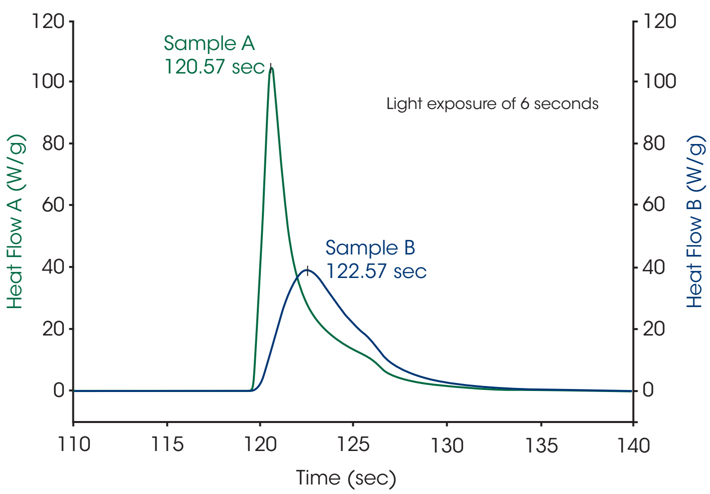

Figure 3. Data showing Dual-Sample Capability

PCA-MDSC® *Quasi-Isothermal Experiments*

In a MDSC® experiment, a sinusoidal modulation is overlaidupon a linear heating rate (4). Quasi-isothermal MDSC experiment performs this sinusoidal modulation around an isothermal temperature. It produces highly accurate determinations of heat capacity, an extremely sensitive indication of molecular mobility. As UV light is applied to a photopolymer, it undergoes a cross-linking reaction reducing molecular mobility and in turn heat capacity.

Figure 4 shows data from such an experiment. The sample is held isothermally with a temperature modulation of +/- 0.50 °C every 80 seconds to determine the heat capacity. Modulation is then turned off and a PCA experiment is performed. Here an intensity of 25 mW/cm² (250 W/m²) is applied for two minutes. Modulation is resumed to determine the heat capacity after UV exposure. Before UV exposure the sample had a heat capacity of 1.72 J/(g °C)$^{-1}$, and after UV exposure the heat capacity was 1.68 J/(g °C)$^{-1}$ for a change of 7 %.

CONCLUSIONS

Using the Photocalorimetry Accessory with a Tzero® DSC cell, permits the measurement of the light intensity directly in the DSC cell, balance the intensity at the sample and reference platforms, provides the ability to run two samples at once, and perform MDSC® quasi-isothermal experiments to determine heat capacity before and after the application of UV light. These benefits increase productivity and increase the overall accuracy and reproducibility of the results.

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