New PCA Accessory for the Q Series™ DSC Modules

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ABSTRACT

The PCA is a compact, modular photocalorimeter accessory for the TA Instruments Q Series Differential Scanning Calorimeters with Tzero Technology™ (T_4 and T_{4P} signals), which permits samples placed inside the DSC cell to be irradiated with ultraviolet or visible light. When the samples (usually photopolymers) react to the light, the evolved heat is measured and used to study the relative reactivity and / or kinetics of reaction. The reactions studied are typically rapid and results are obtained in less than 10 minutes.

PPRODUCT DESCRIPTION

The TA Instruments PCA is based on a filter photometer design, in which radiation from a high pressure mercury source passes through broadband filter (320-500nm as supplied) and then is transmitted to the DSC cell via a one-meter long, 3-mm diameter, dual extended range (250-700 nm), quartz light guide. The light guide attaches to the cell itself using a special adapter. Figure 1 shows the DSC / PCA system.

Figure 1: QDSC / PCA System

New features of the PCA include a 200 W lamp that records the number of hours of use. Closed-loop feedback technology continuously monitors the light and automatically makes adjustments to ensure the required output level is maintained for every cure reaction in a sequence of experiments. The broad spectral lamp output (250-650 nm) and filter availability makes the PCA ideal for a wide range of applications. An

optional radiometer is available for situations where it is desired to calibrate the filter photometer itself. Because of the special Tzero Technology™ features, which allow for direct measurement of intensity at the sample and reference positions, the use of the radiometer is typically not necessary in most DSC / PCA experiments The dual quartz light guides, if used with care, offer extended operational lifetime as well as a wide range of operational temperature (-50 to 250 ºC). Further information and PCA specifications are available in the TA Instruments PCA product bulletin (PB001)[1]

The following sections provide some insight into the experimental conditions that should be considered in designing a DSC photocalorimetry experiments.

PCA EXPERIMENTAL CONDITIONS

There are several fundamental instrument characteristics that affect the quality of PCA results. Those characteristics are as follows:

- Wavelength range
- Light intensity at the DSC cell sample and reference positions
- DSC Technology
- Baseline noise
- Exposure time
- Temperature

Wavelength Range

Since the 200W high-pressure mercury lamp in the PCA provides radiation in the range 250-650 nm, it is desirable to attenuate this range as needed for a particular experiment using broad bandpass and cut-off filters. The PCA is normally equipped with a 320-550 nm broadband filter suitable for most UV and Visible PCA studies. Another broadband filter covering the UV region (250 to 450 nm) is available, as are long bandpass filters with cutoffs at 390 nm and 490 nm respectively. The latter filters mount at the DSC end of the light guide. Contact your TA Instruments representative for further details

Light Intensity

The mercury lamp in the PCA can produce a total light intensity up to 30 W/cm^2, which is more than is required for most photocalorimetry experiments, which are typically performed with intensities between 20 to 100 mW/cm^2 at the sample. The light intensity reaching the DSC cell is adjusted using a combination of aperture control at the PCA unit plus neutral density and / or cutoff filters at the end of the light guides. The light intensities at the end of each "arm" of the dual light guide must not only be regulated to the proper level, but also must also be balanced to produce minimum baseline offset.

TA Instruments QDSC Tzero ™ Technology

The Tzero Technology™ inherent in the advanced Q Series DSC modules allows the heat flows at the sample and reference platforms in the cell to be independently measured. In the absence of a sample or reference material and pans (*i.e.,* an empty cell), the heat flows observed are directly related to the light intensities at the platforms. In addition, the intensities at the sample and reference platforms can be balanced by a simple adjustment

on the cell light guide adapter. Because of this unique capability and the dual light guides, most photocalorimetry experiments using this PCA do not require the use of a radiometer. One is available however if desired for a special task.

Tzero ™ technology also provides another important advantage for PCA experiments. In addition to the above capability, it also allows the ability to perform dual sample PCA experiments in Q Series DSC analyzers operating in the T_4 or advanced T_{4P} heat flow modes.

Baseline Noise

Ideally, the light intensity delivered to the DSC cell via the light guide should be constant. However, there is always minor intensity fluctuations inherent in the output of the high-pressure mercury lamps typically used in PCA studies. The DSC cell is sufficiently sensitive to detect those small fluctuations in light intensity as noise in the heat flow baseline. Fortunately, the noise is typically less than + 100 μW/cm2 and has no effect on the heat flows associated with the photo initiated events being studied since they are several orders of magnitude larger.

Exposure Time

Photo initiated curing reactions are fast thermal events and often complete cure is achieved in a very short time frame (seconds to several minutes). This can make differentiating the curing behavior of similar materials difficult even if low light intensities are used. The ability to vary exposure time, therefore, provides an additional experimental variable that can help improve differentiation of behavior and / or provide conditions that better mimic those found in real-world processes (*e.g.*, photo curing of a film coating as the film rapidly passes under a light source). The PCA connects to the DSC cell via an event cable that opens and closes a shutter at the light source. Exposure times as short as 0.6 seconds can be selected when setting up a PCA method.

Temperature

The PCA is compatible with the TA Instruments FACS and RCS cooling devices. While most PCA experiments are run isothermally, the PCA equipped with the dual quartz light guides can be used in experiments over the temperature range –50 to 250°C. Furthermore, once the PCA experiment is complete, a standard DSC experiment can be performed on the fully / partially cured sample material over the broader temperature range covered by the selected cooling accessory by making only a few minor changes to the system.

TYPICAL APPLICATIONS

The Photocalorimeter Accessory (PCA) provides a convenient tool to assess reactions in materials initiated with UV / Visible light. Figure 2 shows a typical result from a DSC / PCA experiment where visible light was used to cure an adhesive material. The experiment is fast, with less than 3 minutes to complete cure.

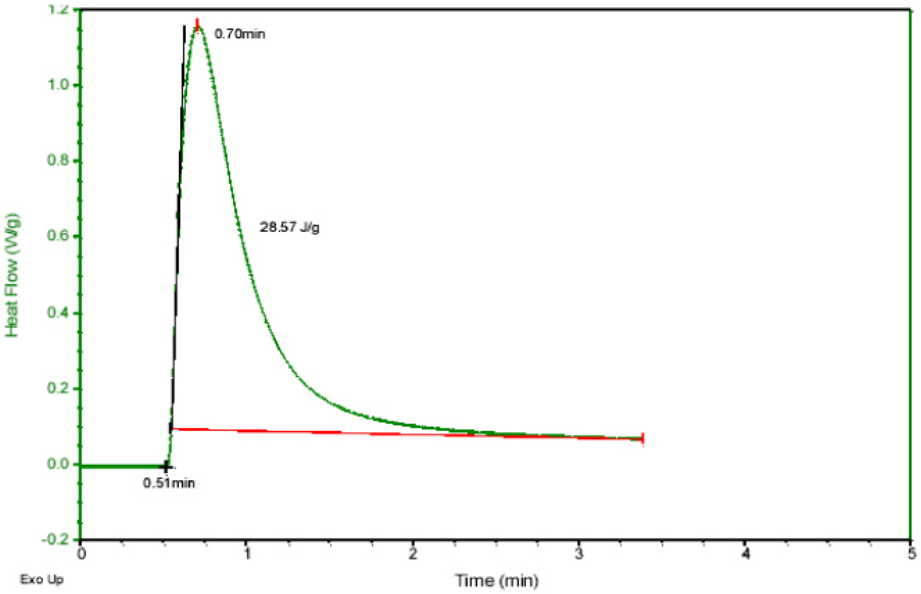


Figure 2

Figure 3 compares two different acrylic formulations under the same curing conditions. The data shows that formulation A cures rapidly upon exposure to UV radiation, while formulation B reacts slower, and has both a longer time-to-peak and lower energy. In all PCA experiments, the peak shapes and transition energies are affected by the formulation chemistry. The Universal Analysis software readily calculates the cure onset, time to maximum rate of cure and the energy involved in the cure.

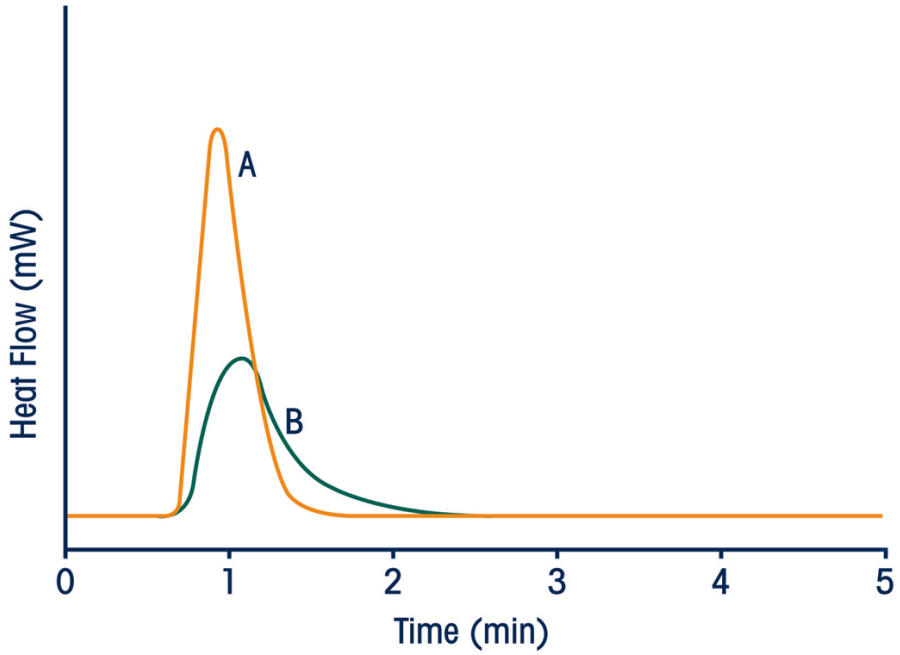
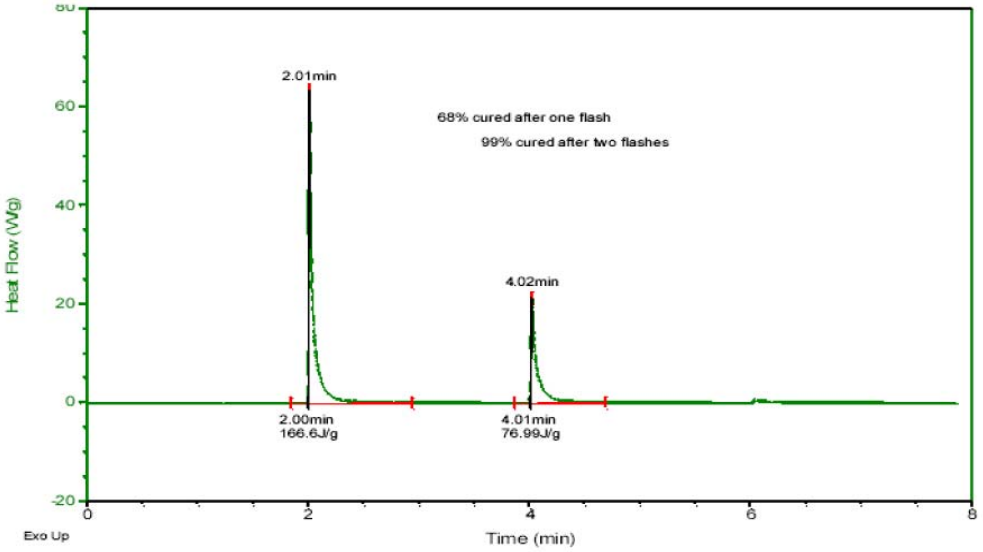


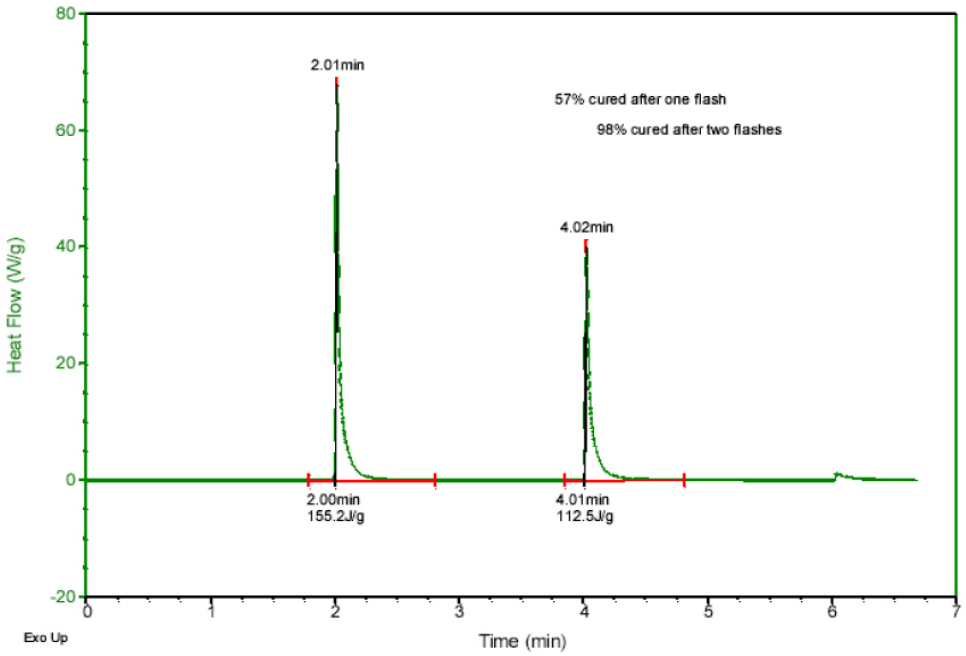
Figure 3. Acrylic Cure Comparison

Figures 4 and 5 illustrate results from "multiflash" experiments on two similar adhesives, where each was exposed to a series of short (0.6 second) "flashes" of broadband (320 - 500 nm) light. The data clearly indicates different amounts of curing with each "flash", with adhesive sample A curing faster than sample B. The evaluation of the kinetics of curing, based upon a series of photocuring experiments at different temperatures is possible using the TA Instruments DSC Isothermal Kinetics software.



Adhesive A Flash Curing

Figure 4



Adhesive B Flash Curing

Figure 5

PCA Specifications

Lamp	High Pressure 200 W Mercury Vapor
Filters - bandpass	320 – 500 nm (standard) 250-450 nm (optional)
Filters – cutoff	390 nm (optional) 490 nm (optional)
Panel Controls	Power On / Off; Mode; Adjust Up/Down; Start / Stop; Lock / Unlock
Electrical Power	100-120 VAC / 200-240 VAC; 50 / 60 Hz
Dimensions	34 cm (D)*18cm(W)*20 cm (H)
Weight	4.5 kg (9.9 lbs)
Warranty (ex lamp/light guide)	One year

Note: Spent Hg lamps must be managed in accordance with Disposal Laws.
Another version of this PCA is available for use with the ARES rheometer for photocuring studies. Contact TA Instruments for details.

REFERENCES

1. TA Instruments Product Bulletin (PB001), 2006

Keywords

DSC, PCA, Photocalorimeter, Filter Photometer,Cure

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