PRODUCT NOTE

Differential Scanning Calorimetry

Key Features

- Power compensated DSC has the ability to hold stable isothermals and compensate for any heating caused by curing or UV radiation.
- HyperDSC® allows the measurement of weak Tg's from highly cured thermo sets
- Due to its fast equilibration time, the DSC 8500 is ideal for studying fast reactions like UV curing

UV/DSC Study on New Double Furnace DSC

Introduction

The major benefit of ultraviolet (UV) curing is that it is a cure-on-demand process. The photo-sensitive material will not cure until the UV light hits it, and when that occurs, it takes only a short time to cure. The process is fast, solvent free, and economical. The UV curing brings many benefits to product manufacturers. Among these are ease of use, process consistency and flexibility, reduced environmental considerations and the availability of high performance materials. The application of UV curing material is very broad. It includes adhesive, clear protective coatings, inks, dental material and pharmaceutical material. Cure conditions can favorably impact the performance properties of many UV-curing material. Both undercuring and overcuring should be avoided. DSC, together with the UV accessory can be used effectively to study UV curing reaction. It can be used to study curing time, curing enthalpy, the effect of light source (wavelength, intensity), photo initiator concentration, curing temperature, and purge gas (nitrogen or oxygen). The new PerkinElmer double furnace power controlled DSC is the ideal tool for the UV curing study because of its unique features compared with conventional heat flux DSC. It can perform true isothermal operation so that it can keep the sample temperature constant during UV curing reaction. It has fast response time so that it can capture the fast reaction of UV curing. It also measures the energy directly for accurate enthalpy result. This note will use a UV curing resin used in removable dental appliances as an example to demonstrate this application on the new power controlled DSC 8000/8500. Some experimental details like sample preparation, method setup, data process and system optimization will be discussed. The effect of light intensity and isothermal temperature on curing will be studied.

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For the Better

Experiment

The instrument used is the new PerkinElmer power controlled DSC 8000/8500. The cooling accessory is Intracooler III which is a new mechanical refrigerator for DSC 8000/8500. It offers -100 ˚C as the lowest program temperature and can remove heat efficiently from UV experiments. As a general rule, the cooling block temperature should be at least 30 ˚C lower than the isothermal temperature at which the curing is to be carried out. The UV light source is OmniCure 2000. It comes with a 200 W mercury lamp and a bandwidth filter of 250 nm to 450 nm. For the DSC 8500/8000, the intensity range can be varied from approximately 2 mW/cm2 (~1% iris opening) to about 180 mW/cm2 (~70%). The light source is connected to the computer through a relay box which can be triggered by Pyris software.

The sample is a fiber filled dental resin, which is a translucent, pink paste (Figure 1). Another optical adhesive sample with faster curing and higher curing energy is used for comparison purpose.

The curing experiment is conducted under isothermal conditions. A typical method is shown to the right (Figure 2). A key part of the method is to use the "trigger an external event" actions to switch the external channel used by the OmniCure 2000 curing system On and Off, to open and close the lamp shutter. Four switch external channel actions must be included in the method to trigger the lamp shutter to open and close at the end of the irradiation time. In the method here, a 10 minute isothermal holding was used. During isothermal period, the lamp shutter was opened and UV curing started at 1 minute. The shutter was closed at 8 minutes for a 7 minute UV curing experiment.

Figure 1. Picture of the fiber filled dental resin used for the UV curing experiment

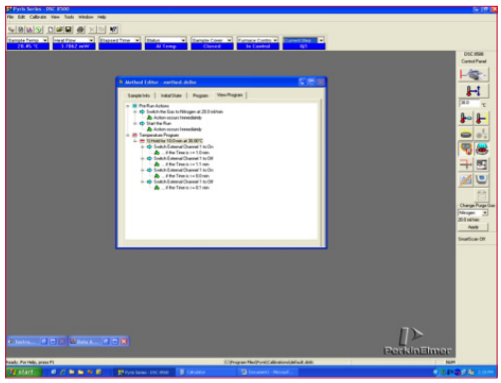

Figure 2. A typical UV curing method window

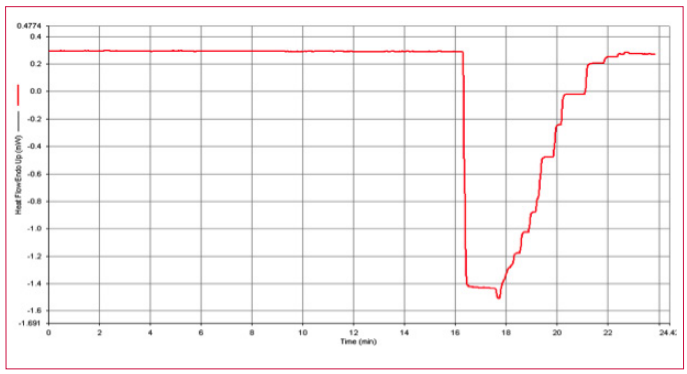

Figure 3. Adjust the heat flow baseline using the thumbscrews

Results

The sample weight must be optimized for each individual sample type depending on the kinetic of the curing reaction and the energy released during the curing. The greater the energy conversion and the faster the reaction, should result from a smaller sample. 1 mg or less is recommended for samples like lacquers, printing inks and other fast-reacting systems with a high energy conversion. Several mg's is appropriate for dental fillings or similar materials. In this experiment, about 3 mg sample was used. Since the sample is a paste, it needs to be spread as evenly as possible over the bottom of the sample pan. The thickness of the layer has a significant influence on the analysis results and reproducibility.

The heat flow signal will be changed when the shutter is open. In order to minimize this effect, the heights of the sample and reference light guides need to be adjusted to give a near zero heat flow change on irradiation. As can be seen below, there was a large baseline shift when the shutter opened. By using the thumbscrews to raise or lower the light guides, the heat flow can be brought back to the original level (Figure 3).

As a general rule, the light intensity should increase with the opacity of the sample and the thickness of the layer. The light intensity can be adjusted by opening the iris on the OmniCure 2000 system. Since the DSC 8000/8500 measures energy directly, it is possible to estimate the light intensity by using a graphite disk to adsorb the light energy. For such measurement, the graphite disks are inserted into the sample side and reference side. During irradiation, the reference side is covered with a piece of white paper. Figure 4 shows the results with the iris open 5%, 10% and 15%. With iris 15% open, the heat flow change is about 6 mW. This value, divided by the surface area of the graphite disk (approximately 0.39 cm2), gives the value of the light intensity of 15.4 mW/cm2. The translucent sample, with an iris opening (15%) was used for the curing experiment.

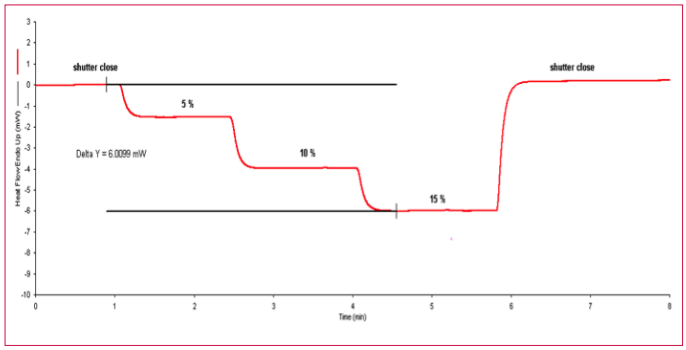

Figure 4. Light intensity determination by graphite disks

For best results, two measurements under identical conditions are recommended in order to offset the baseline shift due to the light irradiation. The first run records the UV curing reaction. The second run helps to confirm if the curing reaction is complete (no exothermic peak observed) and establish the baseline shift due to light irradiation. Subtraction of the second run from the first run can eliminate any possible baseline shift and give an accurate calculation of curing energy (Figure 5). For all the following UV curing data, subtraction of a second run was performed.

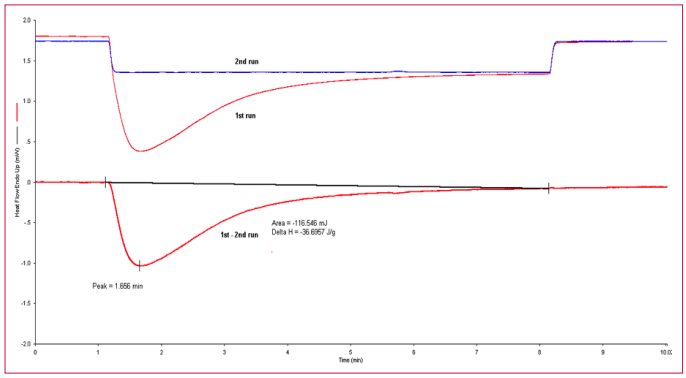

Figure 5. UV curing data process for the dental resin sample

The raw dental material has a subambient glass transition temperature. The glass transition (Tg) was determined by running a heating scan from -80 ˚C to 30 ˚C at 50 ˚C/min. The data shows a Tg at -27 ˚C (Figure 6).

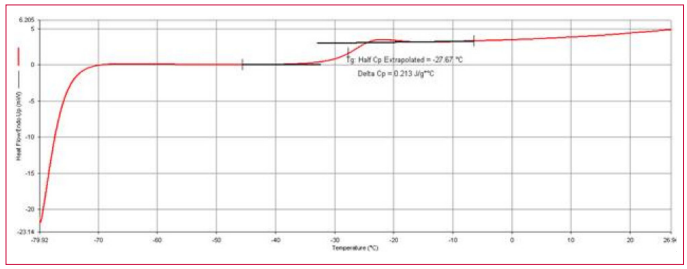

Figure 6. Raw dental material showing a Tg at -27 ˚C.

Different UV curing material may have quite different curing kinetics/energy based on their application. The dental resin needs to be cured relatively fast and low curing energy is desirable. The UV curable optical adhesive is designed to cure very quickly and high energy is released to give a tough resilient bond. UV/DSC experiment can be used easily to show the different curing behaviors. Figure 7 demonstrates the different curing profile of dental resin and optical adhesive at 30 ˚C with 15% iris opening. The optical adhesive is cured faster than dental resin and has much more energy released (189 J/g vs. 44 J/g).

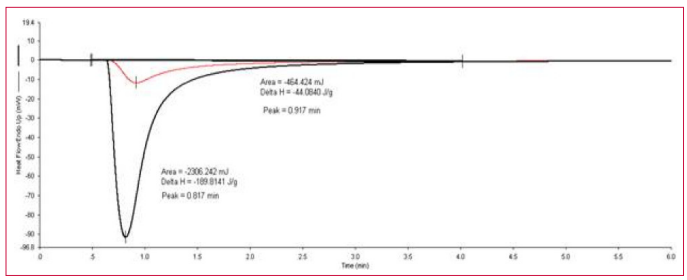

Figure 7. UV curing data at 30 ˚C with 15% iris, dental resin (red) vs. optical adhesive (black) showing different peak time and energy.

The curing reaction will change the Tg behavior. With the increasing curing time, the curing degree will increase and the original Tg of raw material will diminish. A partial UV curing experiment was conducted on dental resin with the curing time of 0, 0.1, 0.2, 0.3, 0.5, 1, 2 and 4 min. The original Tg was checked after each UV curing time. Seen in Figure 8, the Tg diminishes quickly with increasing UV exposure time.
After 0.5 min curing, the Tg has become difficult to see.

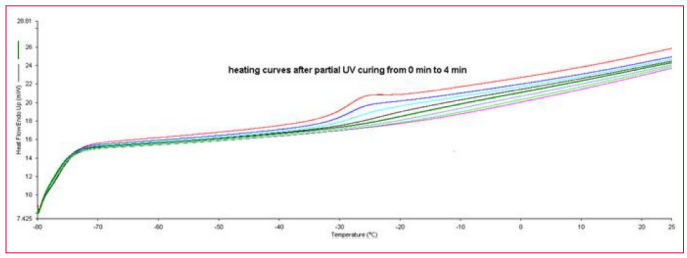

Figure 8. Heating curve after partial UV curing for 0, 0.1, 0.2, 0.3, 0.5, 1, 2 and 4 min, showing the diminishing Tg of raw material after UV curing. Note the Tg gets weaker with increasing degree of cure.

After the dental resin was UV cured fully at 30 ˚C, a heating scan from -80 ˚C to 145 ˚C was performed (Figure 9). The subambient Tg of raw resin has disappeared. The "1st Heating" shows a residual curing above the UV curing temperature and finally a small Tg around 128 ˚C of the cured resin. The "2nd Heating" curve indicates no residual curing and the Tg of cured resin as expected.

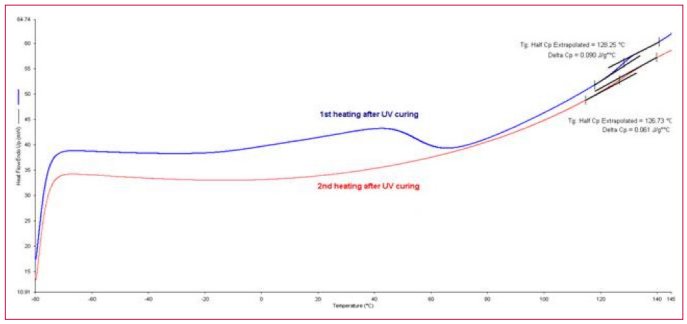

Figure 9. 1st and 2nd Heating curves after UV curing, showing residue curing, followed by Tg.

Two important parameters for UV curing experiments are light intensity and isothermal temperature under which the UV curing is conducted. Their effects on curing behavior of dental resin are studied. The effect of light intensity was studied by adjusting the iris opening from 5% to 25% (Figure 10) and three isothermal temperatures 10 ˚C, 30 ˚C and 50 ˚C were used to study its influence on curing profile (Figure 11). Clearly both factors have a large effect on the curing profile. Increasing light intensity or isothermal temperature will shorten the UV curing time and increase curing degree.

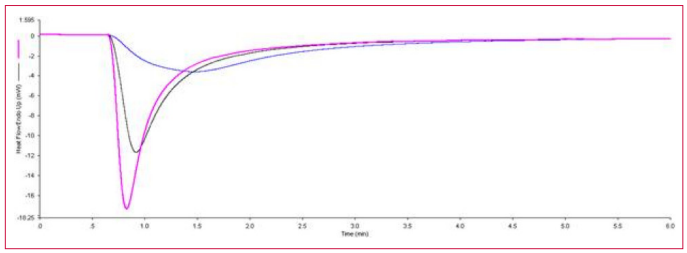

Figure 10. Effect of light intensity with iris opening at 5% (blue), 15% (black) and 25% (pink) at 30 ˚C on dental resin.

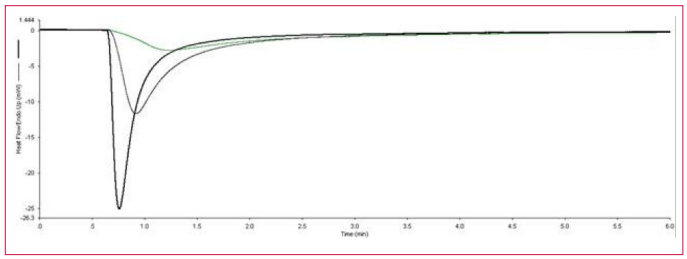

Figure 11. Effects with isotemp at 10 ˚C (green), 30 ˚C (blue), 50 ˚C (black) on dental resin curing with 15% iris opening.

The residual curing of dental resin was checked after curing at 10 ˚C, 30 ˚C and 50 ˚C. The residual curing occurred after 40 ˚C for both UV curing experiment at 10 ˚C and 30 ˚C, probably because the resin was kept at room temperature. However, the residual curing moved up to higher temperature after UV cured at 50 ˚C and the exothermic peak seemed to be reduced. All three runs resulted in a similar Tg at high temperature which is the Tg after heating cured.

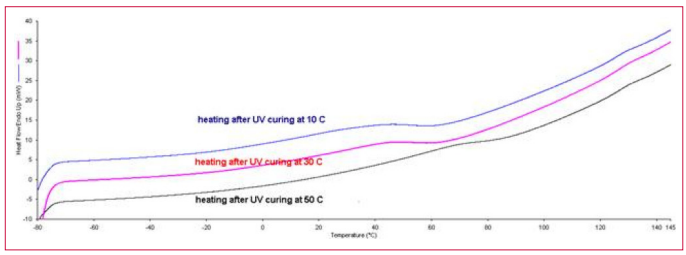

Figure 12. Heating curves after UV curing at 10 ˚C, 30 ˚C and 50 ˚C. heating rate 50 ˚C/min.

Since curing is a kinetic event, fast scanning experiments up to 750 ˚C/min were attempted after UV curing, trying to suppress the residual curing and detect a Tg before the residual curing. However, even at 750 ˚C/min, no Tg was detected and residual curing can not be suppressed (Figure 13).

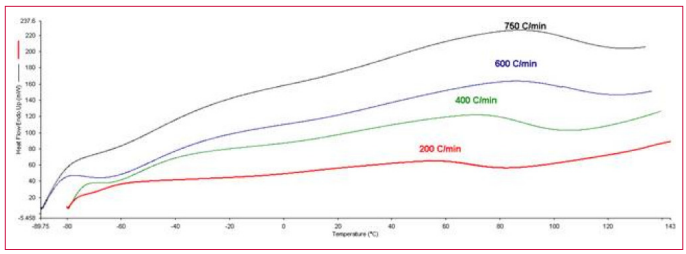

Figure 13. Heating curves after UV curing at different rates 200 ˚C/min, 400 ˚C/min, 600 ˚C/min and 750 ˚C/min.

Summary

The UV curing of the dental resin can be studied on the new DSC 8000/8500 with UV accessory. Since UV curing reaction is fast usually, a fast response DSC is needed to capture the curing process. Direct energy measurement and true isothermal operation are essential to the successful UV curing experiment. The light source can be easily controlled by Pyris software. The double furnace power controlled DSC 8000/8500 with UV accessory is the ideal tool to study the UV curing process and to characterize the material properties before and after the UV curing.

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