PHOTO-DSC AS A VERSATILE TOOL FOR UV CURING SYSTEMS CHARACTERIZATION

From dental mass, adhesives, coatings and lacquers to resins for additive manufacturing

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During the last decades, ultraviolet (UV)-curable resin systems have been gaining more and more market share in the coating, lacquer and other related industries due to their unique advantages including fast curing, low energy consumption and low VOC emission levels. Therefore, the UV-curable resins market size was estimated to be worth over USD 3.5 billion in 2015 and is expected to exceed USD 8.6 billion by 2023, which means an annual growth of more than 9.2%.[1]

Latest trend which is believed to be contributing to this growth, is the additive manufacturing industry. 3D printing processes such as the DLP (digital light processing) or the CLIP (continuous liquid interface production) method, which promise up to 100 times faster production times compared to other 3D printing processes, are on the verge of overturning parts of the industrial landscape.[2] Here, LED-based light sources are used for precise manufacturing where in the whole industry a change to LED-curing due to longer service life and lower energy consumption is visible.

This growth is spurred by increased availability and improved performance of the LED systems and adapted formulations. In general, one major drawback of these UV-cured resin systems however is the lack often sufficient thermo-mechanical properties and dimensional accuracy. Further development and innovation are necessary where differential scanning calorimetry in combination with a light source (Photo-DSC) is a useful tool to determine optimal cure conditions. Properties such as curing kinetics, phase transitions or influence of additives can be easily identified. The Linseis Chip-DSC10 is ideally suited as its low thermal mass of sensor and furnace allows fast heating and cooling rates and outstanding temperature control without loss in signal quality. This is especially important for fast-curing resins where significant reactions can take place in time frames of milliseconds.

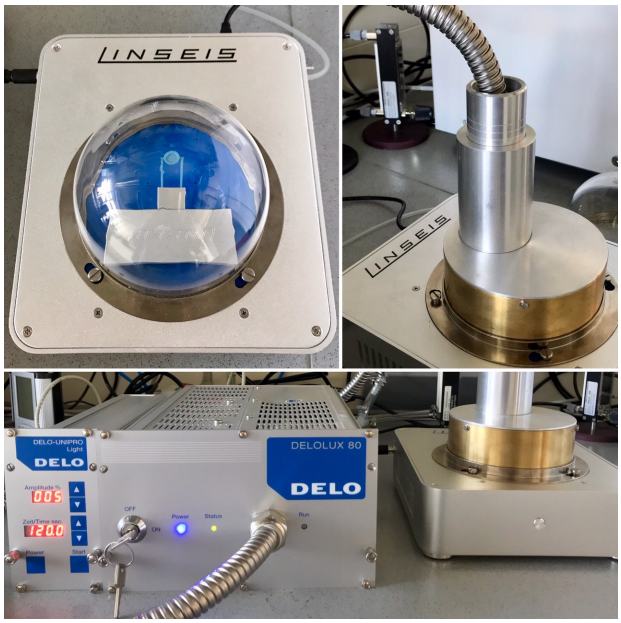

Figure 1. Linseis - Chip - DSC 10 with DELOLUX80 LED Lamp

- Temperature range: RT - 600°C (+/- 0.2°C)
- Heating Rate: 0.001 - 300 K / min

Experimental

The new Linseis ChipDSC10 was connected with a DELOLUX 80 400nm-LED-lamp (DELO Industrie Klebstoffe, Windach, Germany), where selection of temperature, atmosphere and irradiation time is easily adjustable (see Figure 1).

Dual Curing- Best of Both Worlds

Many resin formulations for additive manufacturing consist of the so-called dual cure systems with thermal and photocurable portions. Here the photocurable part allows the printing of individual layers within seconds whereas the thermal system can boost the thermal and mechanical properties of the 3D-printed part when transferred to an oven for second stage curing.[3]

In this case, a mixture of a photocurable acrylate and a thermally curable epoxy system was used, and around 10 mg of material were placed in an open crucible and irradiated with several UV light pulses (405 nm Wavelength, 100% Amplitude, lamp distance of 45mm). Each pulse lasted 1 second and was applied every minute until no change in peak area was detected. The first pulse was applied after 2 minutes to ensure the

isothermal condition of the experiment, set up at 50°C. (See Figure 2.)

The difference between the first irradiation peak and the last one, (when the area under the peak reaches a plateau, thus it is assumed that no reaction is taking place), is calculated to determine the heat of reaction for the UV-curing part, and to derive a conversion curve.

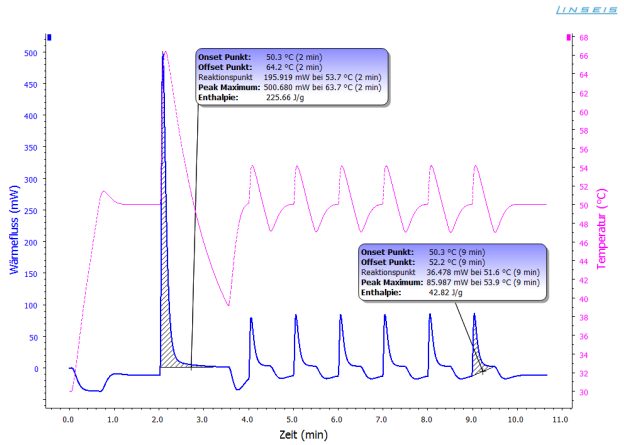

Figure 2. Determination of UV-curing enthalpy by light pulses

It can be seen in Figure 2, that the UV-curable part is almost fully cured after the first light pulse. Subsequently, the concentration and reactivity of the thermally-cured system can be determined by applying heating ramps at different rates up to 300°C/min, as shown in Figure 3 after UV irradiation.

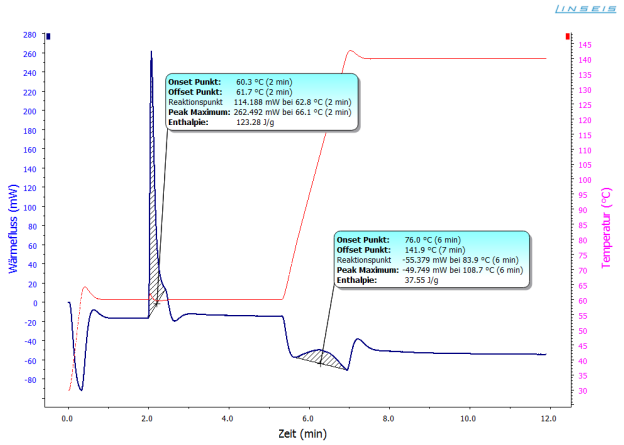

Figure 3. Determination of thermal-curing enthalpy by heating

Storage Stability – Quality Control

For a constant part quality, it is necessary to reliably qualify differences between fresh and stored products or composition of various batches. Therefore, the storage stability of a commercially available UV-curable resin system (Formlabs White V4) was observed. After one year stored in an opened container, the resin didn't show a significant drop in the total energy released as the samples were irradiated, compared with a fresh resin newly opened (see Figure 4). These results fall into the warranty given by the manufacturer, that specifies 1 year of the same performance (reactivity). Further studies are needed to determine the effect of aging, once the expiring date has passed.

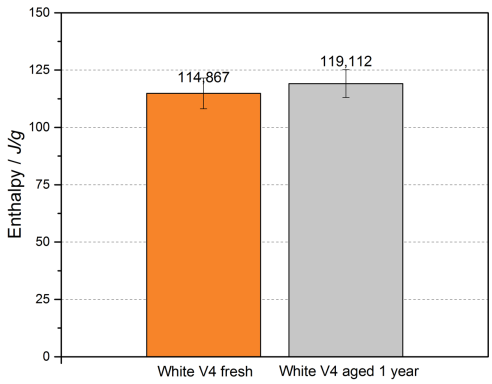

Figure 4. Comparison between fresh and aged resin reaction enthalpy

Conclusion:

The Linseis ChipDSC10 in combination with an UV/LED source is a powerful tool for the characterization of fast photo-curable resin systems. Deep insight into curing kinetics as well as into the quality of the raw materials, is possible. The technique allows experimental flexibility and the software, that accompanies the device, facilitates the evaluation of the collected data.

Your benefits at a glance:

- Linseis ChipDSC10 allows easy and fast modification to Photo-DSC within minutes.
- Instantaneous (≤ seconds) reaction initiation can be detected, as well as progress and termination of the same by simply applying pulses.
- High heating and cooling rates are available to support processability demands.
- Convenient and user-friendly software.

References:

1) UV-Curable Resins Market Size, Industry Analysis Report - Global Market Insights, **2019**
2) Tumbleston et. al., Science, 347, **2015**
3) A. Uzcategui et. al., Advanced Engineering Materials, 20, 12, **2018**

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