APPLICATION**NOTE**

Investigations on UV-Curing Systems by Means of Photo-Differential Scanning Calorimetry (Photo-DSC)

Dr. Stefan Schmölzer

Introduction

Differential scanning calorimetry (DSC) allows for the determination of phase transition temperatures and transition enthalpies, also for curing reactions. The samples are usually analyzed in a crucible with pierced lid under normal pressure with a constant purge gas flow. Differential scanning calorimetry can also be used for investigation of photo-curing reactions [1]. The combination of an UV lamp with the NETZSCH DSC 204 ***F1*** *Phoenix*® (figure 1) features a versatile tool here.

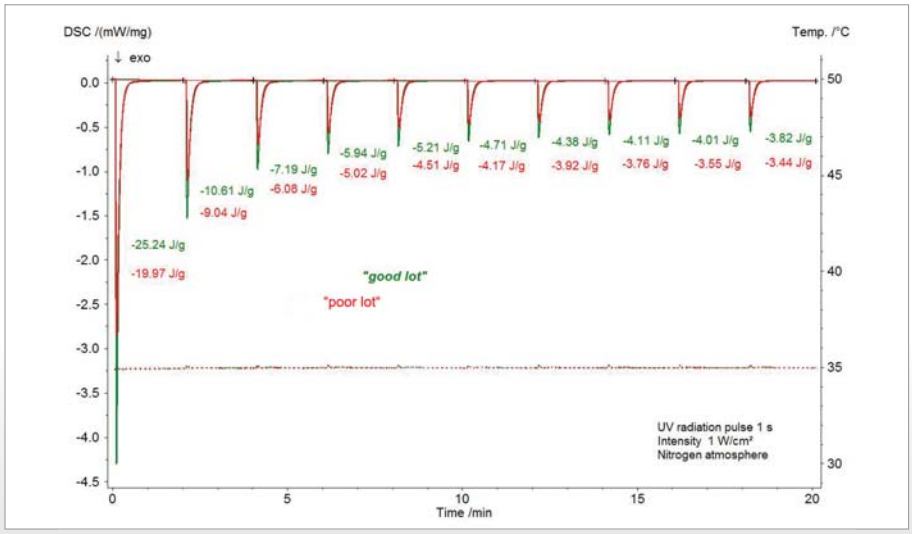
1 NETZSCH Photo-DSC 204 ***F1*** *Phoenix*® equipped with the Omnicure S2000 lamp

Results

Single-Curing Systems: Comparison "Good/Poor" of 2 Printing Inks

The sample is prepared in an open crucible which is irradiated by UV light. Intensity and irradiation time can be varied at a defined temperature program. Isothermal conditions or a dynamic temperature program are generally employed.

Figure 2 shows the results of the Photo-DSC for the curing of an acrylate-based screen printing ink. Two samples of different lots were investigated. The experiment was carried out at a constant temperature of 35°C under a nitrogen atmosphere. Irradiation took place in a pulsed manner with UV pulses with an intensity of 1 W/cm² and a pulse time of 1 s. From the measurement, the conversion curve is calculated, assuming that during the last irradiation step, curing no longer occurs. The last irradiation step was subtracted from the previous steps and the enthalpy of a single step was set proportional to the total enthalpy.

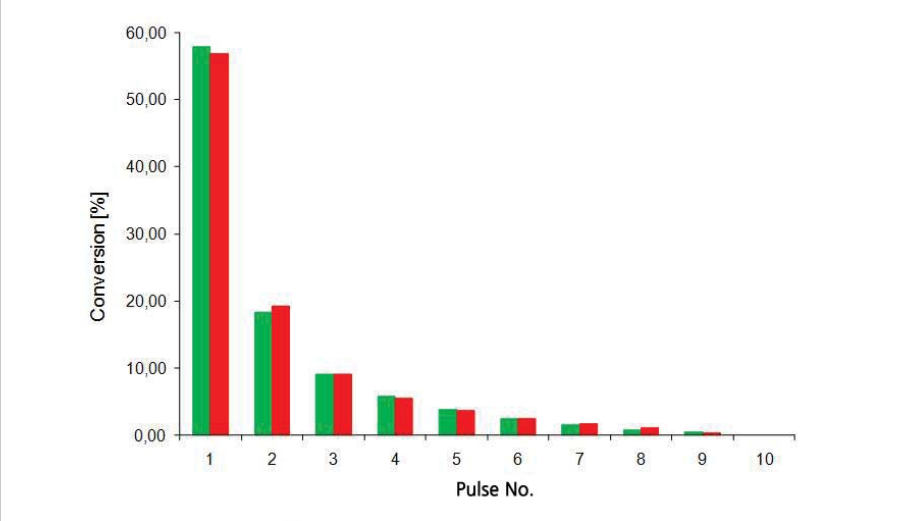


2 UV curing of a screen printing ink (green: "good lot"; red: "poor lot")

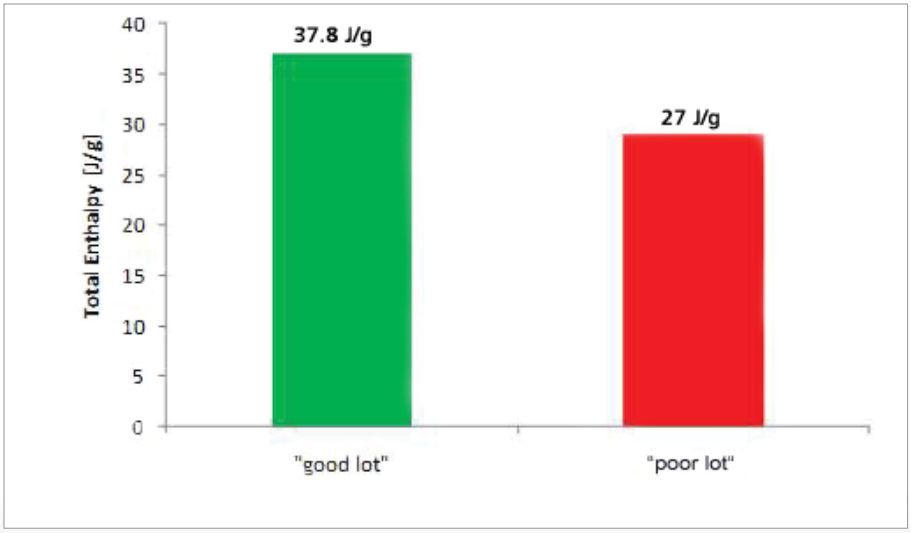
NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone +49 9287 881-0 · Fax: +49 9287 881505
at@netzsch.com · www.netzsch.com

NETZSCH

The conversion curve in figure 3 shows that there is a slight difference in the curing behavior of the "good" sample compared to the "poor" sample during the first two irradiation steps.



3 Conversion of a screen printing ink (green: "good lot"; red: "poor lot")



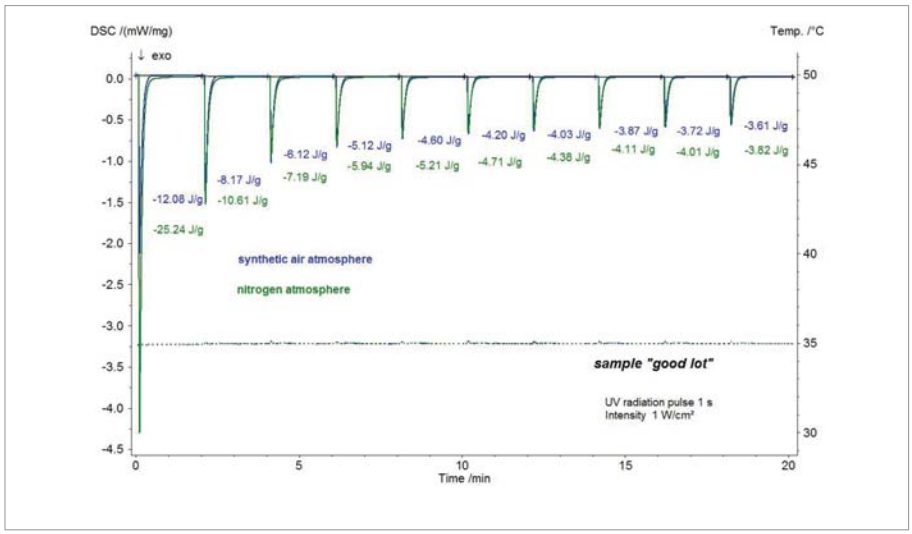
4 Total enthalpy of UV curing for "good lot" (green) and "poor lot" (red)

Figure 4 depicts the total enthalpies for the two inks which show significant differences. The "good" sample shows a higher reactivity compared to the "poor" sample.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone +49 9287 881-0 · Fax: +49 9287 881505
at@netzsch.com · www.netzsch.com

Impact of the Gas Atmosphere

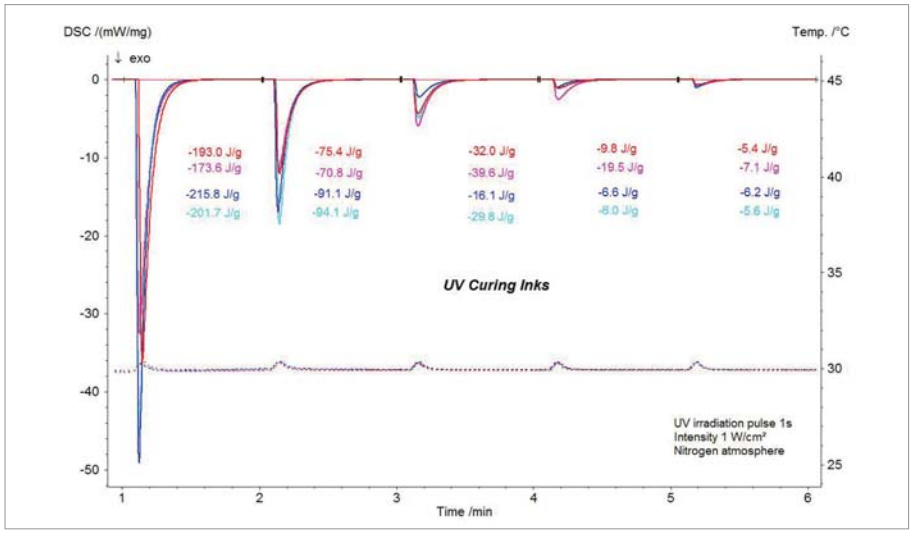
The influence of oxygen on the curing behavior is well known for acrylate systems. This is shown for the "good" screen printing ink in figure 5. UV-DSC measurements with different atmospheres could easily be realized with the NETZSCH DSC 204 ***F1*** *Phoenix*® using the internal mass flow controllers for a precise purge gas flow. The results show that the enthalpy for curing is lower compared to the measurement under a nitrogen atmosphere. The present oxygen acts as an inhibition agent for the UV-curing process [2].



5 UV-DSC curing results for different atmospheres (blue: synthetic air; green: nitrogen)

Influence of the Color on the Curing Behavior

The blue curves in figure 6 represent the UV-DSC results for two blue inks and the red curves are the UV-DSC results for the red inks. Both blue inks (different lots) show a significantly higher enthalpy for UV curing compared to the red inks. Again, slight differences in the curing behavior of the two ink lots of the same color are monitored by the UV-DSC results. Especially for the development of new formulations, UV-DSC results are a helpful tool to achieve formulations of different colors but with the same curing behavior which is necessary for the later application.



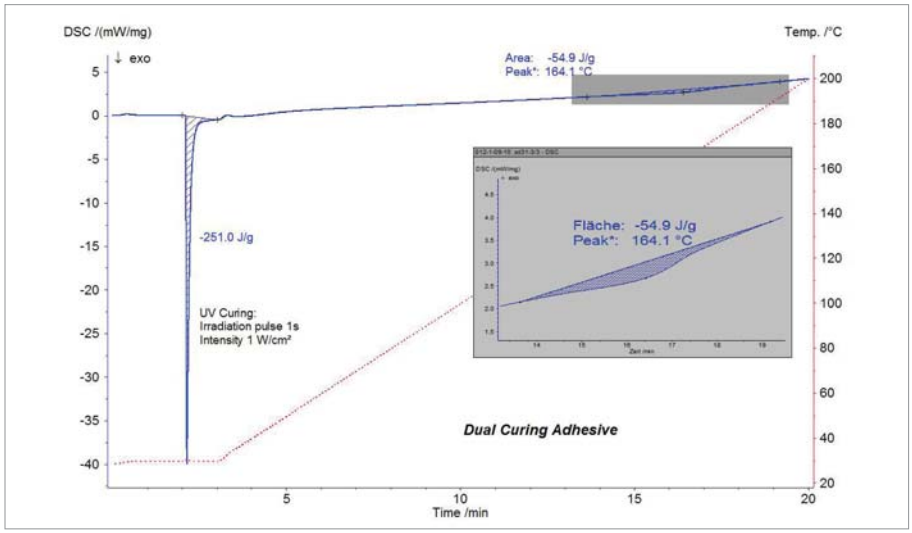
6 UV-DSC results for four UV curing inks of different colors (two blue inks and two red inks)

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone +49 9287 881-0 · Fax: +49 9287 881505
at@netzsch.com · www.netzsch.com

Results for a Dual-Curing System

Along with the investigation on systems with a single curing mechanism, the UV DSC can also be used for dual-curing systems [3] like special types of adhesives. These kinds of adhesives do not only cure by UV radiation, they also show a thermal post-curing effect.

Figure 7 shows the results for such a system. Radiation with UV light for 1 s at ambient temperature shows an exothermic curing effect with an enthalpy of 251 J/g. By heating the sample to 200°C, the thermal curing effect could be observed at 164°C (peak temperature) with an enthalpy of 55 J/g. This example clearly demonstrates that complete characterization of the curing behavior can be derived from one single UV-DSC experiment.



7 UV-DSC results for a dual-curing adhesive

Summary

Differential Scanning Calorimetry (DSC) in combination with radiation of an UV lamp allows for the investigation of curing processes of UV-curing systems. The results obtained help gain an insight into curing mechanisms and the kinetics of curing reactions. In addition, dual-curing systems were investigated within one single experiment.

Literature

[1] Schwalm, R., „UV coatings – Basics, Recent Developments and New Applications"; Elsevier, Amsterdam-Oxford, 2007.
[2] B.Vollmert, „Grundriss der Makromolekularen Chemie" Vol. I, Karlsruhe 1982, 76 ff.
[3] J.P. Fouassier (Ed.), „Radiation curing in polymer science and technology", Elsevier, 1993, Chapter 6, S. Peters, „Overview of Dual-Cure and Hybrid-Cure Systems in Radiation Curing".

NGB · Application Note 026 · E · 12/12 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone +49 9287 881-0 · Fax: +49 9287 881505
at@netzsch.com · www.netzsch.com