Thermal and UV-curing Behavior of Inks, Adhesives, and Coatings by Photo-, In-situ DEA and DMA.

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Introduction

The main advantages of light- (normally UV-) curing systems are their fast reaction – within a few seconds at low isothermal temperature – and their absence of solvents. Often, a combination of thermal and light curing reactions is applied to dual cure adhesives or paints. Characterization of UV-curing process is needed to optimize materials and manufacturing process. Ultraviolet (UV) light curing is a technology being applied increasingly in the fields of paints, inks, coatings, sealants, adhesives and dental composites. 1-component free radical UV systems such as acrylates can cure within some tenths of a second at room temperature. 1- or 2-component cationic epoxy resins exhibit a curing time ranging from just seconds to a few minutes. The advantages of UV resin systems are evident: Their high speed translates to high throughput, they have a low energy requirement (no heating is needed), and the lack of solvents eliminates ecological concerns. A variety of questions may arise during the UV curing process. How long does it take for the resin to begin UV curing? How high is the reactivity? How effective is the photo initiator? When is curing complete? How can the curing cycle be optimized? Is there any potential for post-curing?

The answers to questions such as these can be investigated by using Thermal Analysis Method as Photo Differential Scanning Calorimetry (UV-DSC), Dielectric Analysis (DEA) and Dynamical Mechanical Analysis (DMA), which are nowadays more and more used – not only in the laboratory environment, but also in-situ, i.e. in-process.

This paper gives an overview of the possibilities offered by these techniques in for paints, coating, Photovoltaic materials optimization.

Photo-DSC Measurement and Evaluation

By means of Differential Scanning Calorimetry (DSC) it is possible to determine phase transition temperatures as well as transition enthalpies, this is also possible for curing reactions. Usually the samples were analyzed in a crucible with pierced lid under normal pressure with a constant purge gas

flow. For investigation of photocuring reactions the differential scanning calorimetry is also used [1]. In this case the combination of an UV lamp (Fig.1.) with the NETZSCH DSC 204 ***F1*** *Phoenix*® provides a versatile tool (Fig.2).

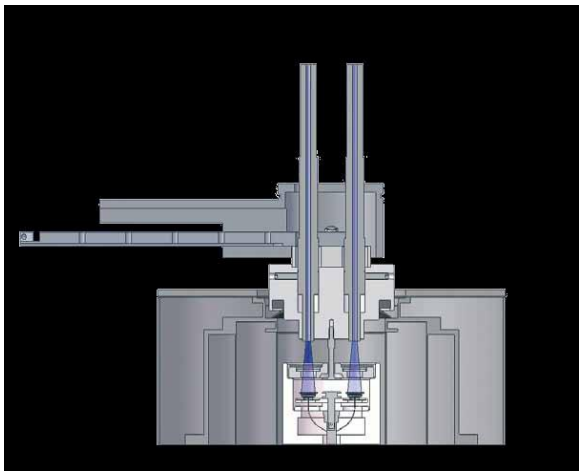

Fig. 1: Cell design of a photoDSC

Sample and reference are irradiated with UV light at a constant temperature until the sample is cured. Afterwards, the already cured sample and the reference are irradiated for a second time for the same duration and at the same temperature. Finally, the difference between the first and the second irradiation is calculated to determine the pure heat of reaction (curve subtraction).

Fig. 2: NETZSCH photoDSC 204 *F1 Phoenix*® equipped with OmniCure S2000 Lamp

The sample is prepared in an open crucible which is irradiated by UV light. The intensity and the irradiation time could by varied at a defined temperature program. Usually isothermal conditions or a dynamic temperature program can be used.

Results

Figure 3 shows the influence of the atmosphere on the Radical UV Curing of an Acrylate Paint by photo DSC. As the UV-curing of acrylate coatings is generally carried out in the presence of air, oxygen inhibition has always been a key issue. Indeed, the free radicals formed by the photolysis of the initiator

are rapidly scavenged by O2 molecules to yield peroxyl radicals. These species are not reactive towards the acrylate double bounds and can therefore not initiate or participate in any polymerization reaction. They usually abstract hydrogen atoms from the polymer backbone to generate hydroperoxides. The different ratio 0_2 versus N_2 demonstrate the existence of competitive reaction occurring during the UV curing steps

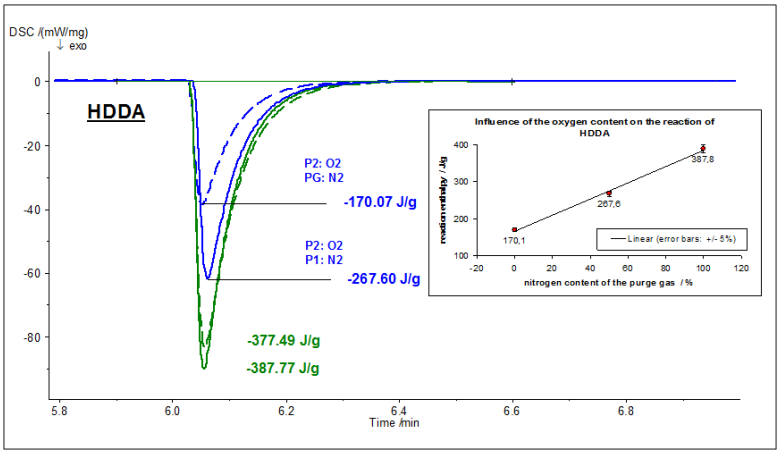

Figure 3 : influence of the atmosphere on the Radical UV Curing of an Acrylate Paint

The same method can be applied to select for screen printing ink in figure 4. UV-DSC measurements with different atmospheres were easily realised with the photo DSC by using the internal mass flow controllers for a precise purge gas flow. The results show that the enthalpy for the curing is less compared to the measurement under nitrogen atmosphere. The present oxygen acts as an inhibition agent for the UV curing process [2].

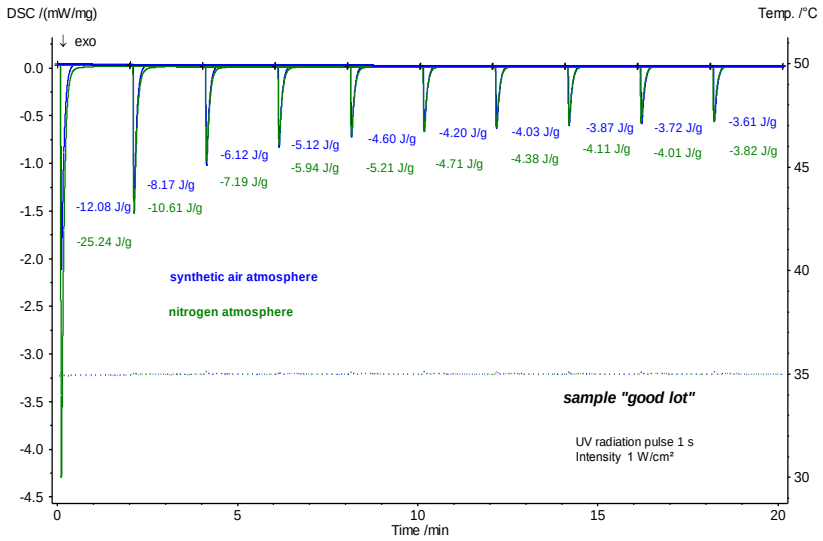

Fig. 4: UV DSC results for different atmospheres (blue synthetic air; green : nitrogen)

Figure 5 shows the photo DSC results for the curing of an acrylate based screen printing ink. In this case two samples of different lots were investigated. The experiment was carried out at constant temperature of 35 °C under nitrogen atmosphere. The irradiation was done in a pulsed manner with UV pulse of 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 no more curing takes place. The last irradiation step was subtracted from the previous steps and the enthalpy of a single step was set proportional to the total enthalpy. The conversion curve in figure 6 shows that there is a slight difference in the curing behaviour of the "good" sample compared to the "bad" sample during the first two irradiation steps. Figure 7 depicts the total enthalpies for the two inks, which have a significant difference. The "good" sample shows a higher reactivity compared to the "bad" sample

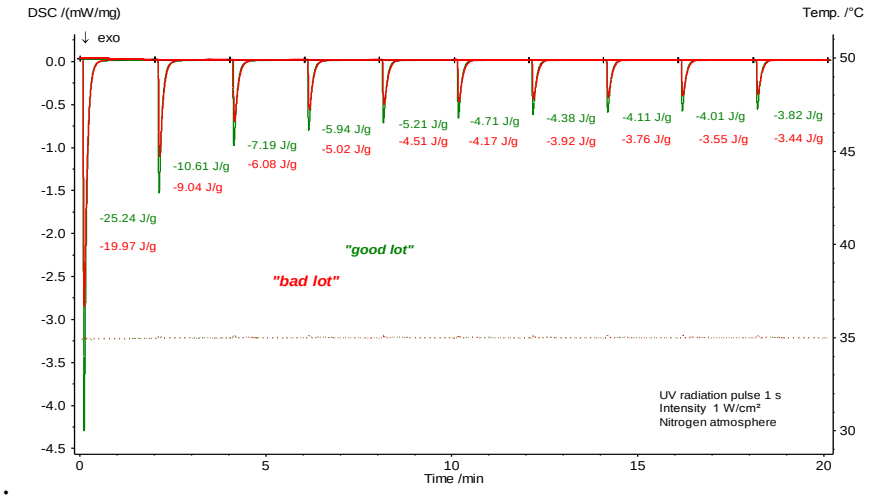

Fig. 5: UV Curing of Screen Printing Ink (green: "good lot"; red: "bad lot")

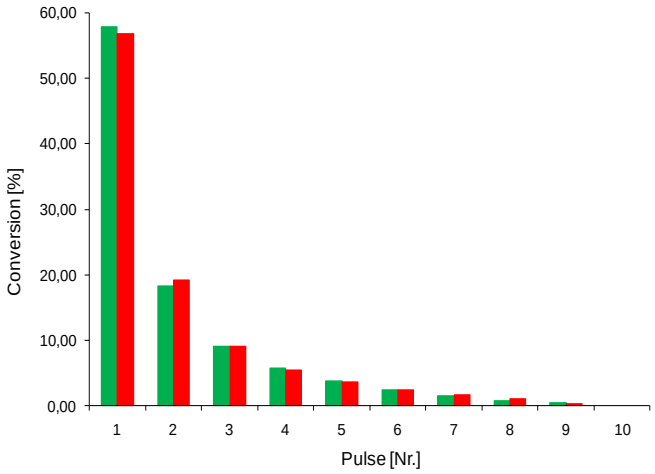

Fig. 6: Conversion of Screen Printing Ink

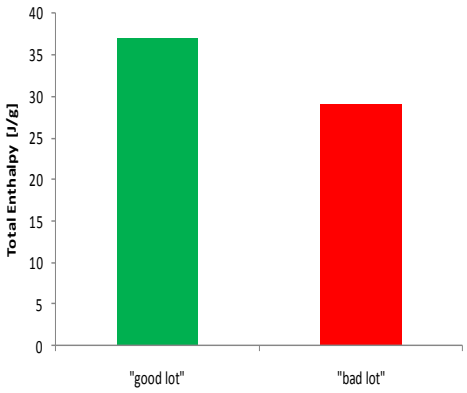

Fig. 7: Total Enthalpy of UV Curing "good lot" (green) and "bad lot" (red)

The influence of colour on the curing behaviour of inks is shown in figure 8. The blue curves represent the UV-DSC results for two blue inks and the red curves are the UV DSC results for red inks. Both blue inks (different lots) show a significant higher enthalpy for the UV curing compared to the red inks. Again also the slight differences in the curing behaviour of the two ink lots of the same colour are monitored by the UV-DSC results. Especially for the development of new formulations the UV-DSC results are a helpful tool in order to achieve formulations of different colour but with the same curing behaviour which is necessary for the later application.

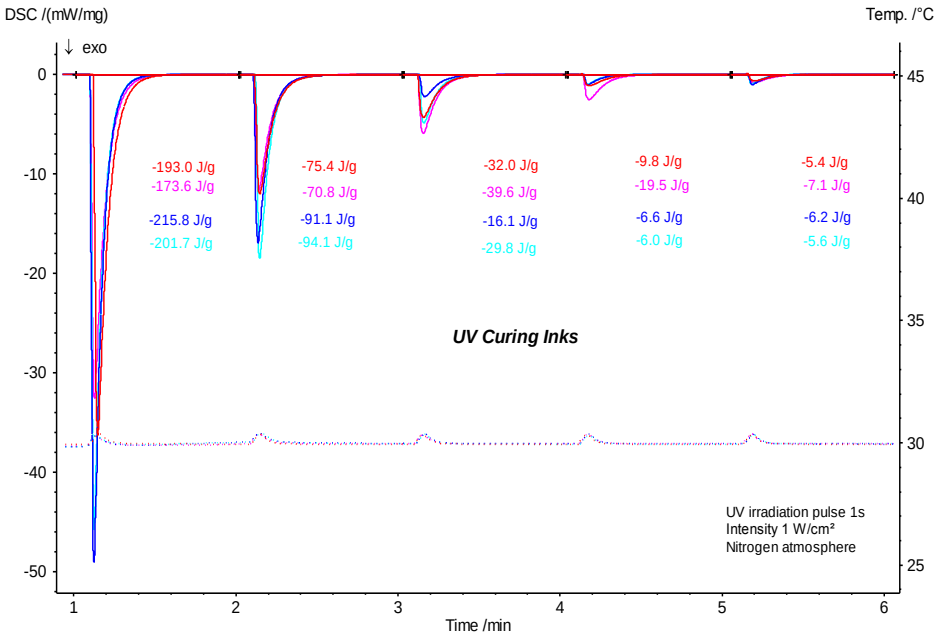

Fig. 8: UV DSC results of four UV curing Inks of different colour (two blue inks and two red inks)

Besides the investigation on systems which a single curing mechanism, the UV DSC could be also used for dual curing systems [3] like special types of adhesives. This kind of adhesives do not only cure by UV radiation, they also show a thermal post curing effect. Figure 9 shows the results for such a systems. The 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 up to 200 °C the thermal curing effect is observed at 164 °C (peak temperature) with an enthalpy of 55 J/g. This example shows clearly that the full characterization of the curing behaviour is derived from a single UV-DSC experiment.

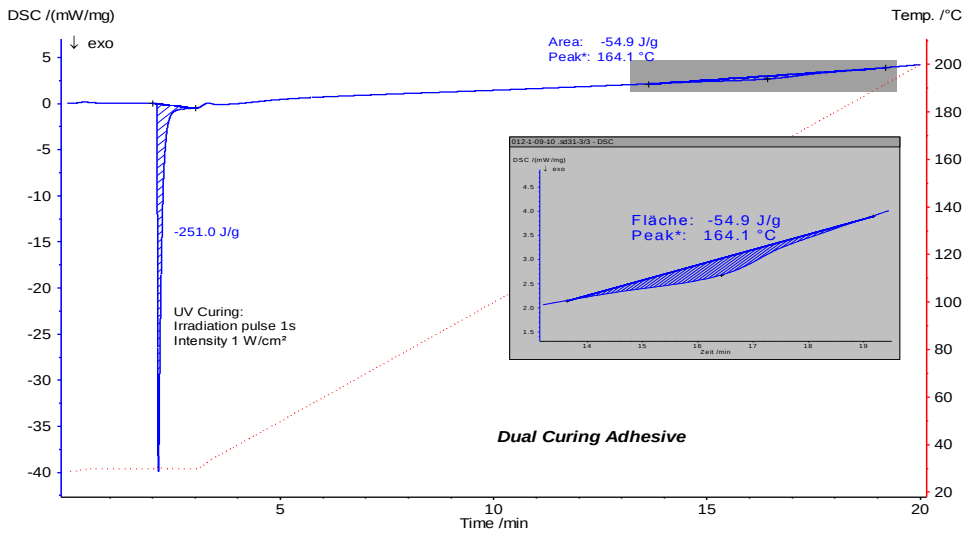

Fig. 9: UV DSC results of a Dual Curing Adhesive

Dielectric Analysis (DEA)

Dielectric Analysis (DEA), as per ASTM E 2038 and E 2039, allows for the measurement of changes in the dielectric properties of a resin during UV curing. The liquid or pasty resin must be placed in direct contact with two electrodes comprising the dielectric sensor. A sinusoidal voltage (excitation) is applied and the resulting current (response) is measured, along with the phase shift between voltage and current. These values are then used to determine the ion mobility (ion conductivity) and the alignment of dipoles. In turn, the dielectric properties of permittivity ε' and loss factor ε'' are calculated from these effects. Of primary interest with regard to curing is the ion viscosity. This is the reciprocal value of the ion conductivity, which is proportional to the loss factor. Use of the DEA technique is not limited to the lab environment; it can also be applied to in-situ curing in a mold or on a conveyor under processing conditions. For production monitoring and process control, a specific ion viscosity value can be programmed to trigger de-molding of a part or coating once it is sufficiently cured. This reduces cycle times and increases throughput, thereby lowering costs and potentially allowing lower prices to be charged for the finished product. Analysing the ion mobility of charged particles and dipole movements in an alternating electrical field allows the real-time characterisation of rapid photo-curing processes of dental composite filling materials and their post curing behaviour. The Dielectric Analysis (DEA) measurements match significantly to mechanical (DMA) and calorimetric (DSC) comparing measurements and allow much more simple sample preparations. The DEA is an easy to handle and cost efficient method to investigate curing kinetics either for dental composite material engineering as well as for quality insurance purposes.

The modular concept of the brand-new DEA 288 Epsilon allows for the study of the UV curing behaviour of adhesives, paints, inks and coatings in nearly any application. The lab version, with up to 8 channels, can be used in conjunction with a newly designed furnace for research and development, which has access to a UV lamp triggered via a light guide. The industrial versions are intended for production monitoring and process control, and are designed with up to 16 channels. As an example, the picture shows the slim version with up to two channels. The industrial devices are connected via rugged

Flexible modules and solar cells have an impressive range of applications. Instead of lying flat and rigid on roofs, flexible solar cells and modules can also be adapted to curved and non-standard building Shapes. Therefore, encapsulation must be as well flexible and trans-parent. In addition, it must protect the sensitive materials against degradation especially due to humidity and oxygen. This protection is done by bonding the cover film with low-permeation adhesives. Besides demonstrating an excellent adhesion special UV-curing sealants with a high water barrier effect are developed to guarantee a long life time.

The epoxy adhesive DELO Katiobond LP655 stands out for his low water vapor permeation and short curing time. The fast curing can observed with the DEA 288 using an IDEX-sensor (figure 10)(and applying a frequency of 1000 Hz.

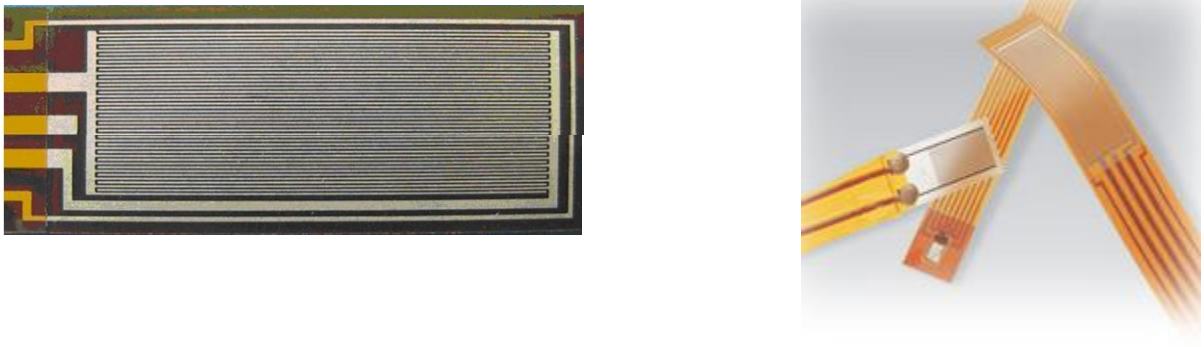

Fig.10. IDEX sensors

The UV light exposure (intensity 55 ... 60 mW/cm2) occurred 60 s on the approx. 200 mm thick sample layer at room temperature. After 17 s of light exposure curing starts what can be seen in the increase of the ion viscosity. The adhesive is completely cured after approx. 350 s.

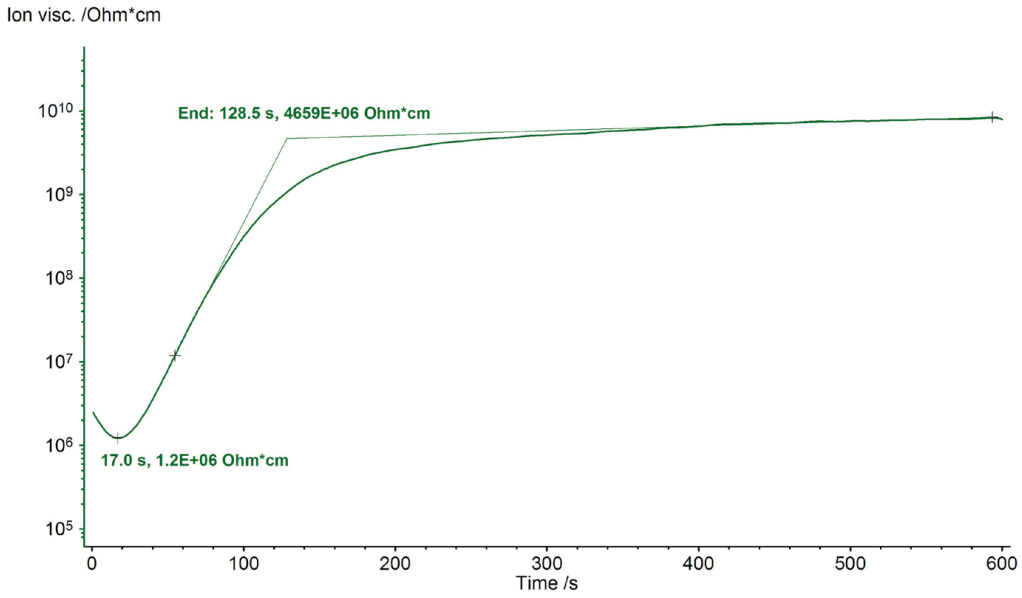

Fig. 11. DEA analysis of epoxy adhesive DELO Katiobond LP655

Figure 12 shows a comparison of two fast curing cationic epoxy systems (supplier: DELO) which are used in the electronic industry for bonding and fixing during assembly. Katiobond 1 (blue curve) shows a faster curing with an extrapolated endpoint of 8.8 s. Katiobond 2 (red curve) is slightly slower and provides an endpoint of 11.2 s but a further increase of the ion viscosity at a higher level.

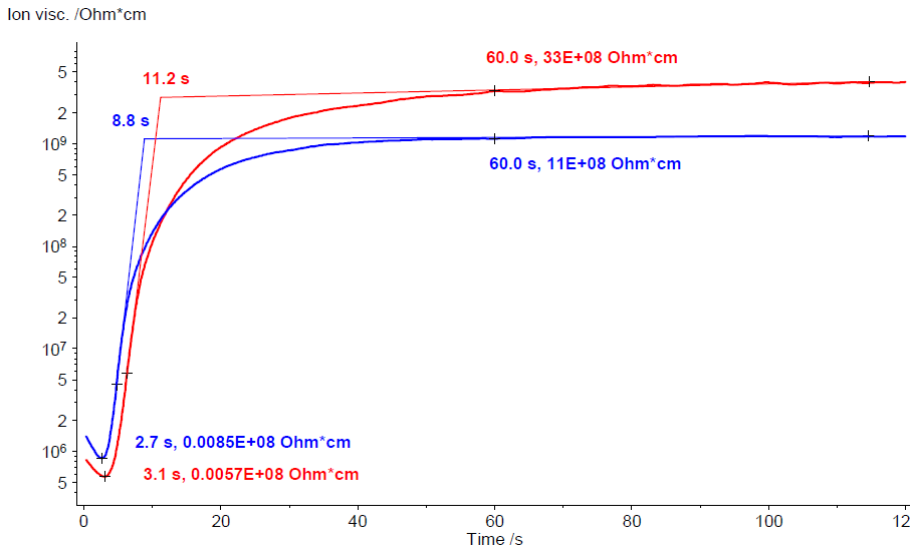

Figure 12 : Ion viscosity curves of two fast curing cationic epoxy adhesives, measured at 30°C at 1000 Hz

UV curing of the free radical adhesive based on acrylate (supplier: HENKEL) was not only investigated with DSC but also with DEA. The DEA 288 Epsilon was used together with a small lab furnace with access of UV light by the OmniCure® S2000 and one light guide. The same light intensity was applied

as with DSC: 1 W/cm². The sample was applied on the IDEX sensor and irradiated with UV pulses of 10 x 1 s, each pulse after the 2nd minute. The DEA measurement was carried out at a frequency of 1000 Hz at isothermal temperature of 35°C under sta tic air. Figure 13 shows the DSC result (red curve) in comparison to the ion viscosity curve (blue) for the acrylate adhesive. The progress of curing can be evaluated as the increase of the ion viscosity from $0.4x10^8$ cm to $1.8x10^8$ cm after the 10th UV pulse. Even the heat influence of the UV lamp can be detected by DEA since there is always a small initial decrease of the ion viscosity for each UV pulse followed by the increase for the curing process.

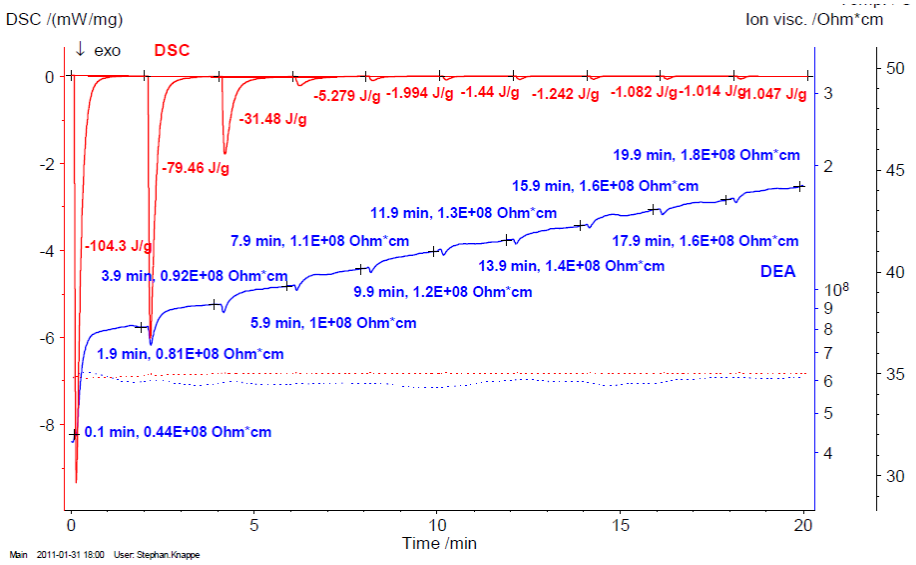

Fig. 13: Comparison of the UV curing of 10 x 1 s measured with DEA (blue curve) and DSC (red curve)

Additionally, the acrylate adhesive was measured by DEA for irradiation times of 2 x 2 min at 35°C. Figure 14 displays the increase of the ion viscosity (blue curve) in direct comparison to the DSC result (red curve).

By means of DEA it can clearly be monitored that the progress of curing continues over an irradiation time of 2 min. The level of the ion viscosity increases from $0.3x10^8$ cm to $20x10^8$ cm. In contrast to this, the exothermal DSC curve already returns to the baseline after approx. 1 min. Even the second irradiation of 2 min shows a further increase of the ion viscosity to $25x10^8$ cm. This means that DEA is more sensitive towards the end of curing. It should be mentioned that the sample thicknesses for DSC and DEA measurements are different.

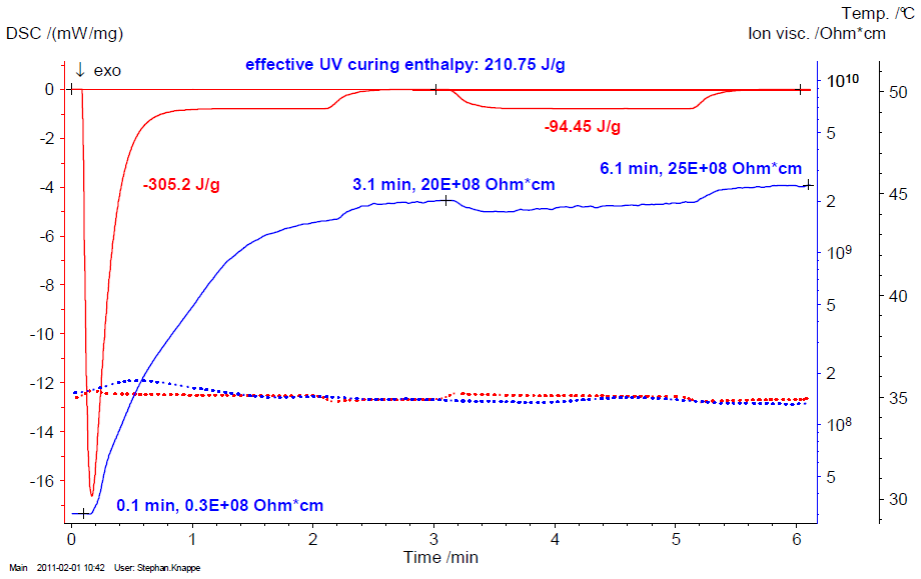

Fig. 14: Comparison of the UV curing of 2 x 2 min measured with DEA (ion viscosity, blue curve) and DSC (red curve)

Dynamic-mechanical Analysis for the viscoelastic properties of UV-cured adhesives

Dymanic Mechanical Analysis as DMA 242 (figure 15) C is mainly used for investigating the viscoelastic properties of cured films in tension and components in bending as a function of time, temperature and frequency, but can also be used to study the progress of curing itself. This is made possible by a modified DMA furnace allowing a connection to the UV light guide and a Modified compression holder. Here, two different UV Curing of Dental Composites have been investigated in Compression Mode (figure 16). The DMA allow to compare the viscoelastic properties of the two resins by the analysis of the storage modulus E' while the resins are cured.

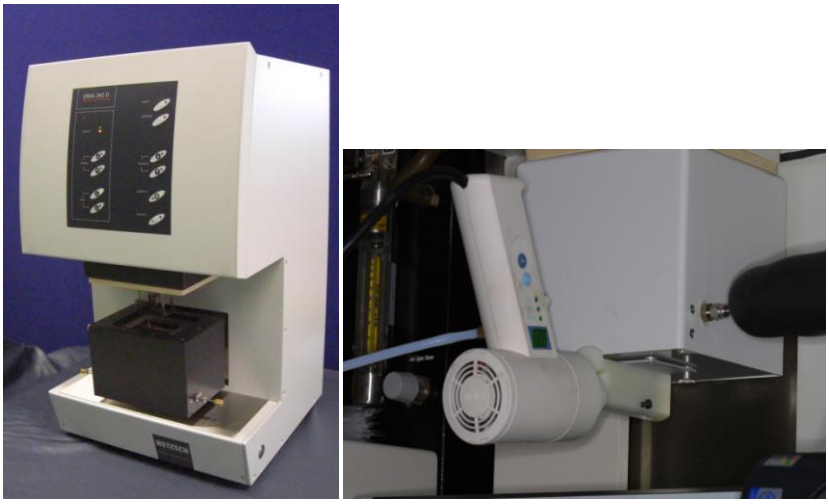

Fig. 16: Netzsch DMA 242 C and its modified furnace with UV accessory

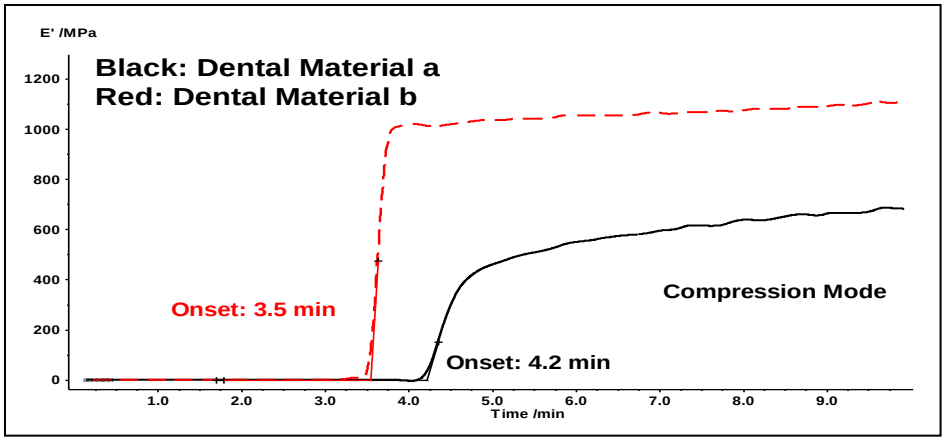

Fig. 16: Different viscoelastic properties of two dental resins, measured in the compression

Summary

Differential Scanning Calorimetry (DSC) in combination with the radiation of an UV lamp enables the investigation of curing processes of UV curing systems. it provides reliable values for the curing enthalpy and reactivity The results could be used for a better understanding of curing mechanism and the kinetics of the curing reactions. Furthermore dual curing systems were investigated within a single experiment.

DEA is not only helpful for the quality control lab but also ideal for fast cure monitoring under process parameters (in-situ). Analysing the ion mobility of charged particles and dipole movements in an alternating electrical field allows the real-time characterization of rapid photo-curing processes of dental composite filling materials and their post curing behavior. The Dielectric Analysis (DEA) measurements match significantly to mechanical (DMA) and calorimetric (DSC) comparing measurements and allow much more simple sample preparations. The DEA is an easy to handle and cost efficient method to investigate curing kinetics either for dental composite material engineering as well as for quality insurance purposes.

In general Photo-DSC and DEA are complementary techniques for an intensive investigation of the UV curing process. With practice-oriented DMA measurements of adhesive layers or of bonded parts, the performance and applications temperature range can be tested under the influences of force and frequency.

Literature:

[1]Schwalm, R., „UV coatings – Basics, Recent Developments and New Applications“; Elsevier, Amsterdam-Oxford, **2007**.

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[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“.