

Leading Thermal Analysis ■

# Study of UV Curing Behavior by Photo-DSC and In-situ Dielectric Analysis (DEA)

Dr. Yanxi Zhang, Technical Sales Support  
NETZSCH Instruments North America, LLC



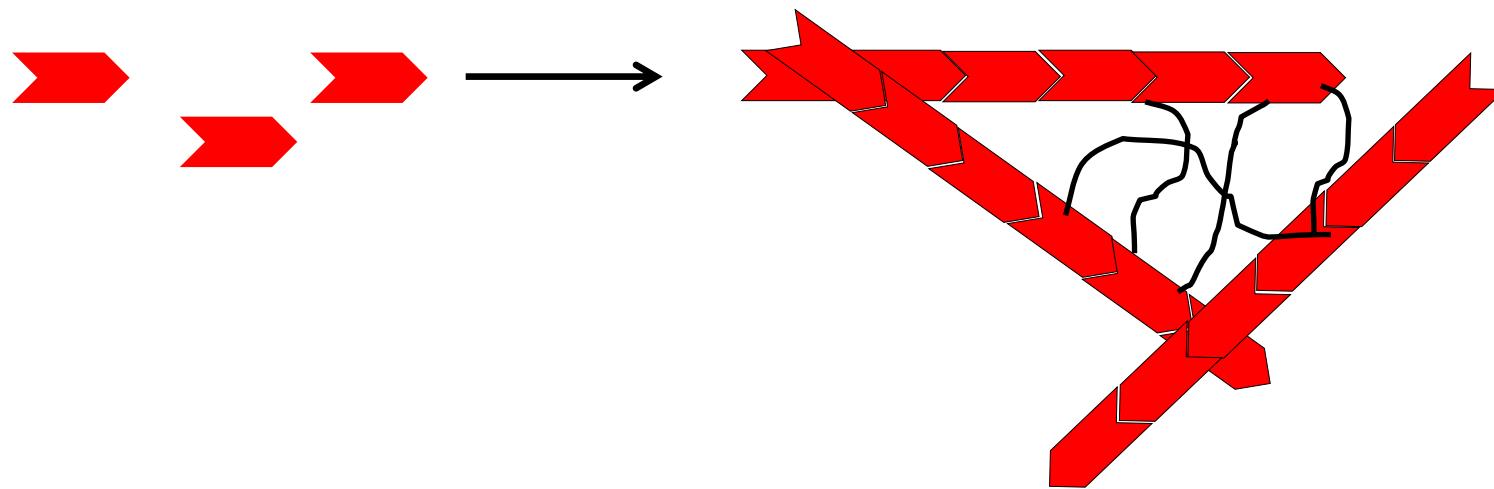
**NETZSCH Instruments North America, LLC  
Burlington, MA USA  
Sales, Service and Lab**

- Introduction to UV Curing and Thermal Analysis
- DSC - Differential Scanning Calorimetry
  - Basics
  - Photo-DSC & Applications
- DEA - Dielectric Analysis
  - Basics
  - Photo-DEA & Applications
- Summary

# What is Curing of Polymers?

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**Curing** refers to an increase in polymer length through the linkage of oligomers and the toughening or hardening of a polymer material by cross-linking of polymer chains. It can be promoted by chemical additives, heat, ultraviolet (UV) radiation or an electron beam.



## Advantages of UV Curing

- High speed (high throughput)
- Low energy (no heating)
- No solvents (ecological aspect)



## Different Types of UV Curing

- Free radical UV systems (very fast)
- Cationic UV systems (fast)
- Dual cure systems (UV + heat)



## Different Types of UV Adhesives

- UV pressure sensitive adhesives (PSA)
- Constructive UV adhesives
- UV laminating adhesives

- When does UV curing start?
  - When is the best flow behavior (lowest viscosity)?
  - What's the reactivity of the reaction?
  - Where is the glass transition temperature after curing?
  - Is there a potential for post curing?
  - What's the optimum UV curing process?
- 
- ✓ Quality Control (QC) of incoming raw materials
  - ✓ Quality Assurance (QA) of bonded parts and components
  - ✓ Optimization of the UV curing process



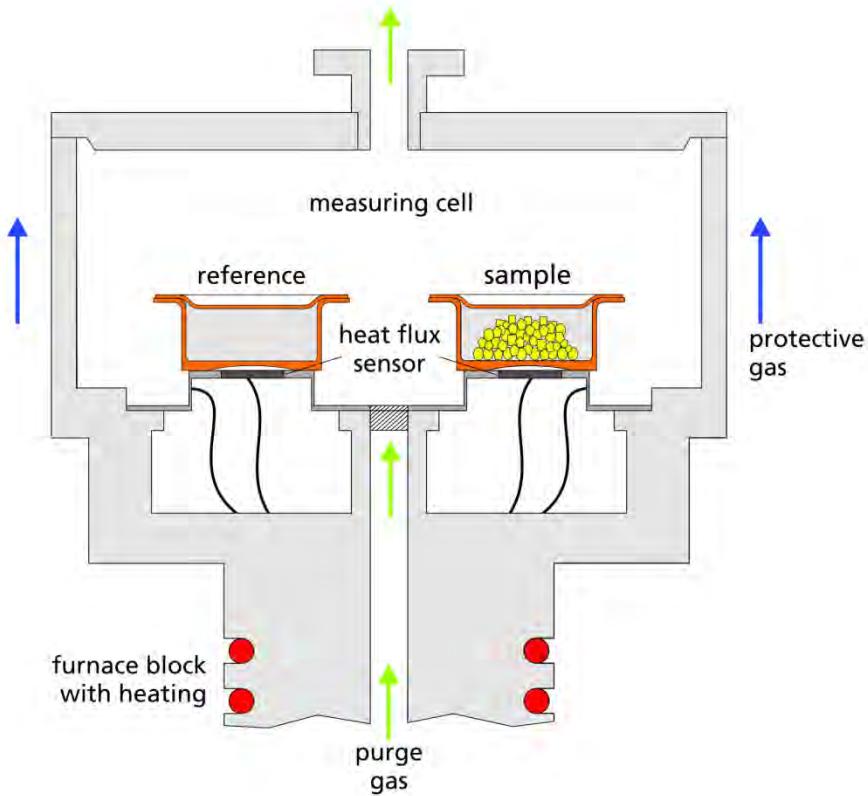
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**Method:** Measurement of energy difference between a sample and a reference material following a controlled temperature program.

→ HEAT-FLOW [mW/mg]

1 furnace for  
both sample & reference  
heating & cooling

For polymers  
reference pan is empty  
Aluminum, pierced lid  
Polycondensation, autoclave pan



## Direct thermal values:

Glass transition temperature  $T_g$

Specific heat  $c_p$

Melting temperature  $T_m$

Crystallization temperature  $T_c$

Reaction temperature  $T_r$  (e.g. curing)

Endothermal heat of melting  $\Delta h_m$

Exothermal heat of crystallization  $\Delta h_c$

Exothermal heat of reaction  $\Delta h_r$

## Further information:

Degree of crystallinity, degree of curing  
(correlations to mechanics - strength,  
toughness)

Distribution of molecular weight (shape  
of the melting peak)

Crystallization behavior (influence of  
nucleation agents)

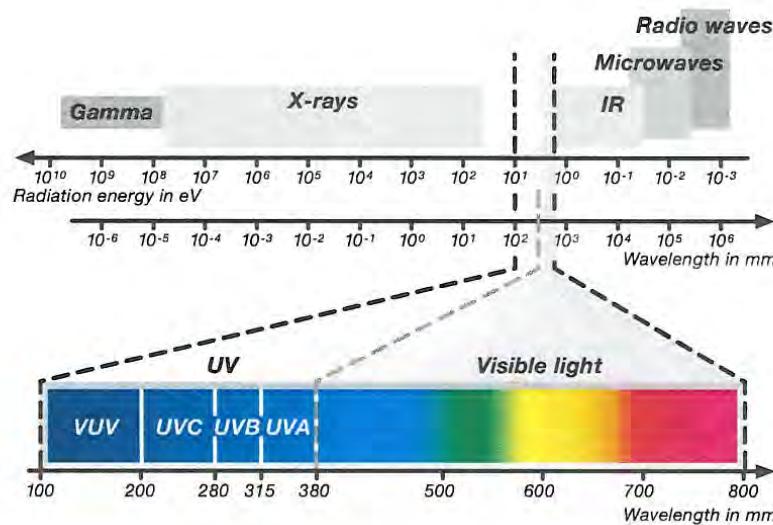
Oxidative stability (oxidation induction  
time, O.I.T. e.g. according to DIN EN  
728 or ASTM D 3895)

# Possible Light Sources for Photo-Curing

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HG-lamp



LED-lamp

**HG-lamps:** can select wide and narrow ranges with filters

UV-A Range 280 – 315 nm/ UV-B range 315 – 500 nm

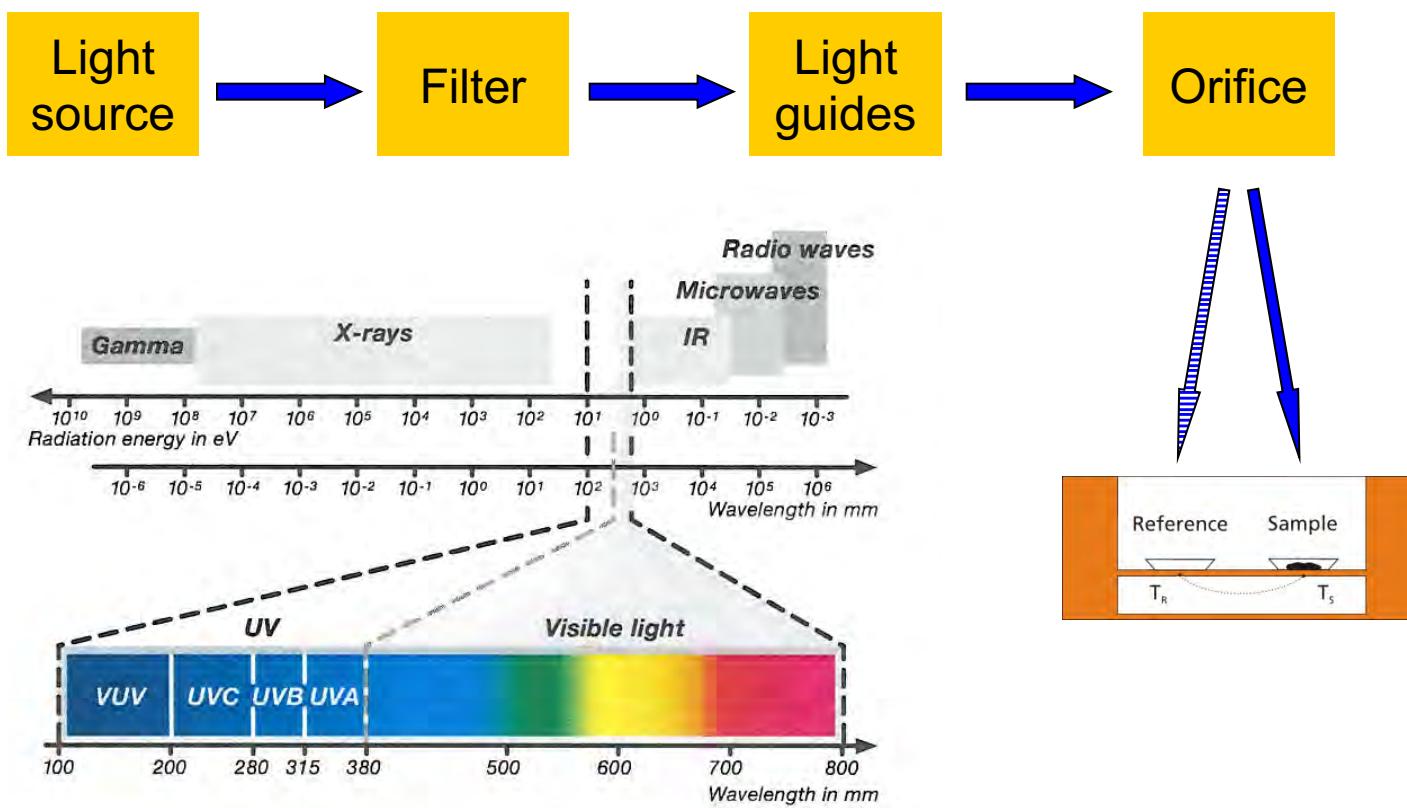
**Diode Laser Systems:** Defined wavelength for optimized curing, e.g. 447 nm

**High-power LED:** Defined wavelength for optimized curing, e.g. 365 nm, 400 nm or 460 nm

Wave length range:  
280 / 315 nm ... 500 nm



2/0  
4/0  
8/0  
  
2/2  
4/4  
8/8



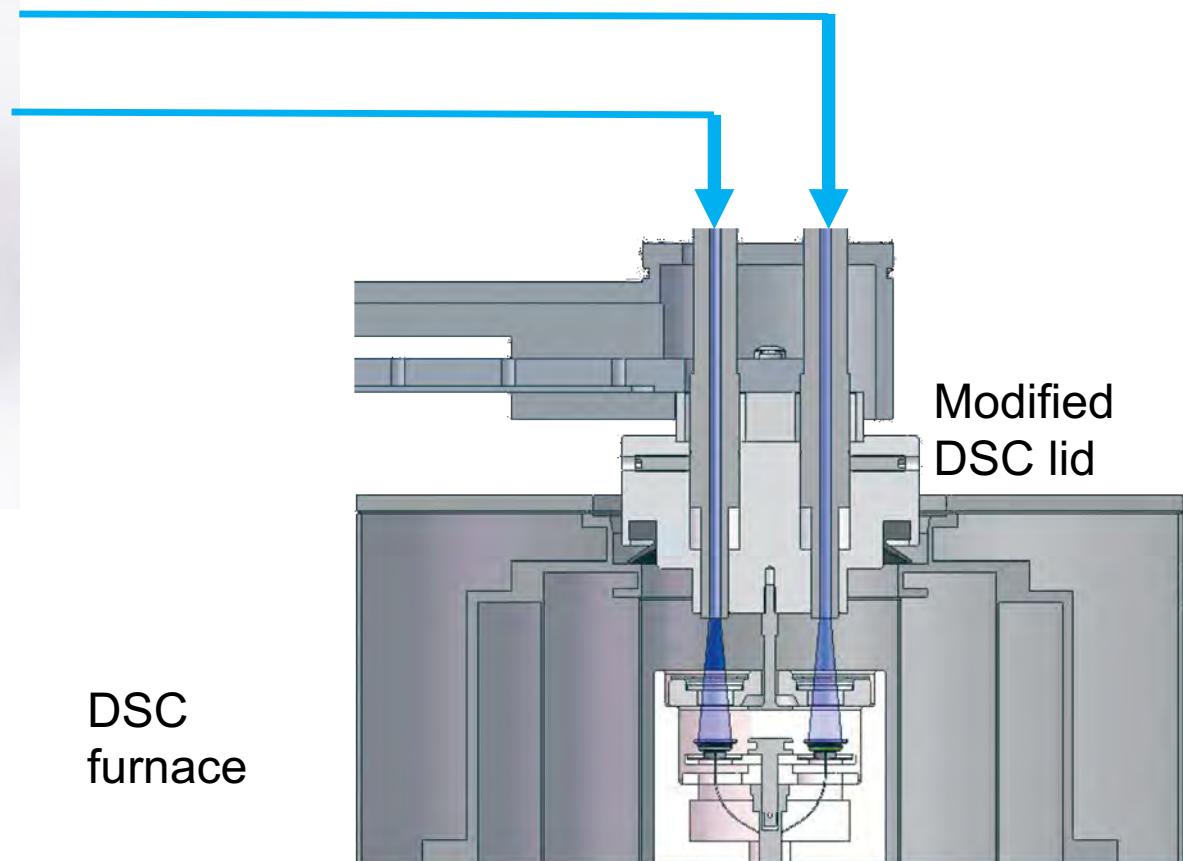
# Operation Principle of a Photo-DSC

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Light source



Light guides



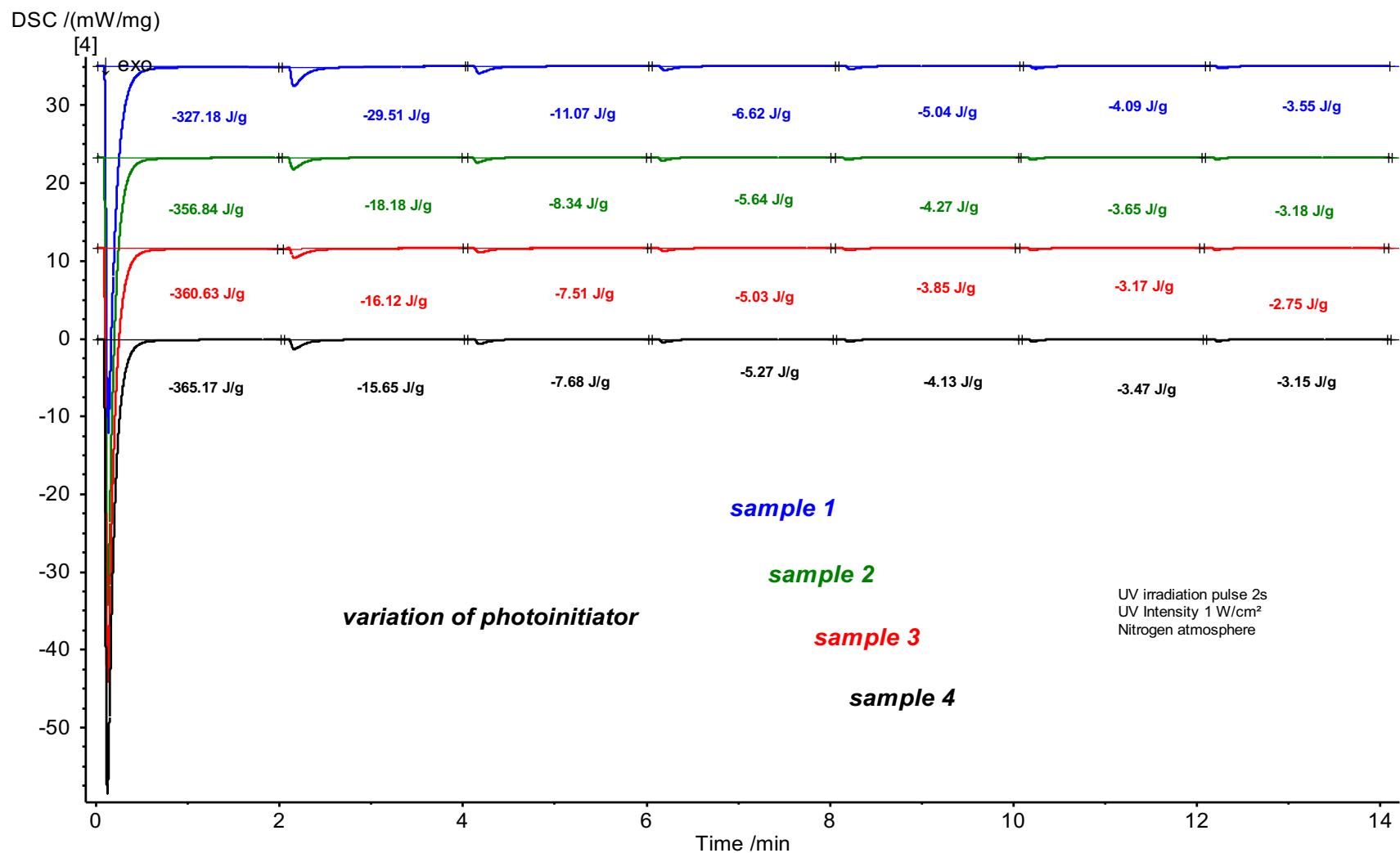
DSC  
furnace

DSC sensor with sample and reference

# DSC: Curing of UV-Coatings

Variation of Photoinitiator with Irradiation Time: 7 x 2 s

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# DSC: Curing of UV-Coatings

## Calculation of Total Curing Enthalpy

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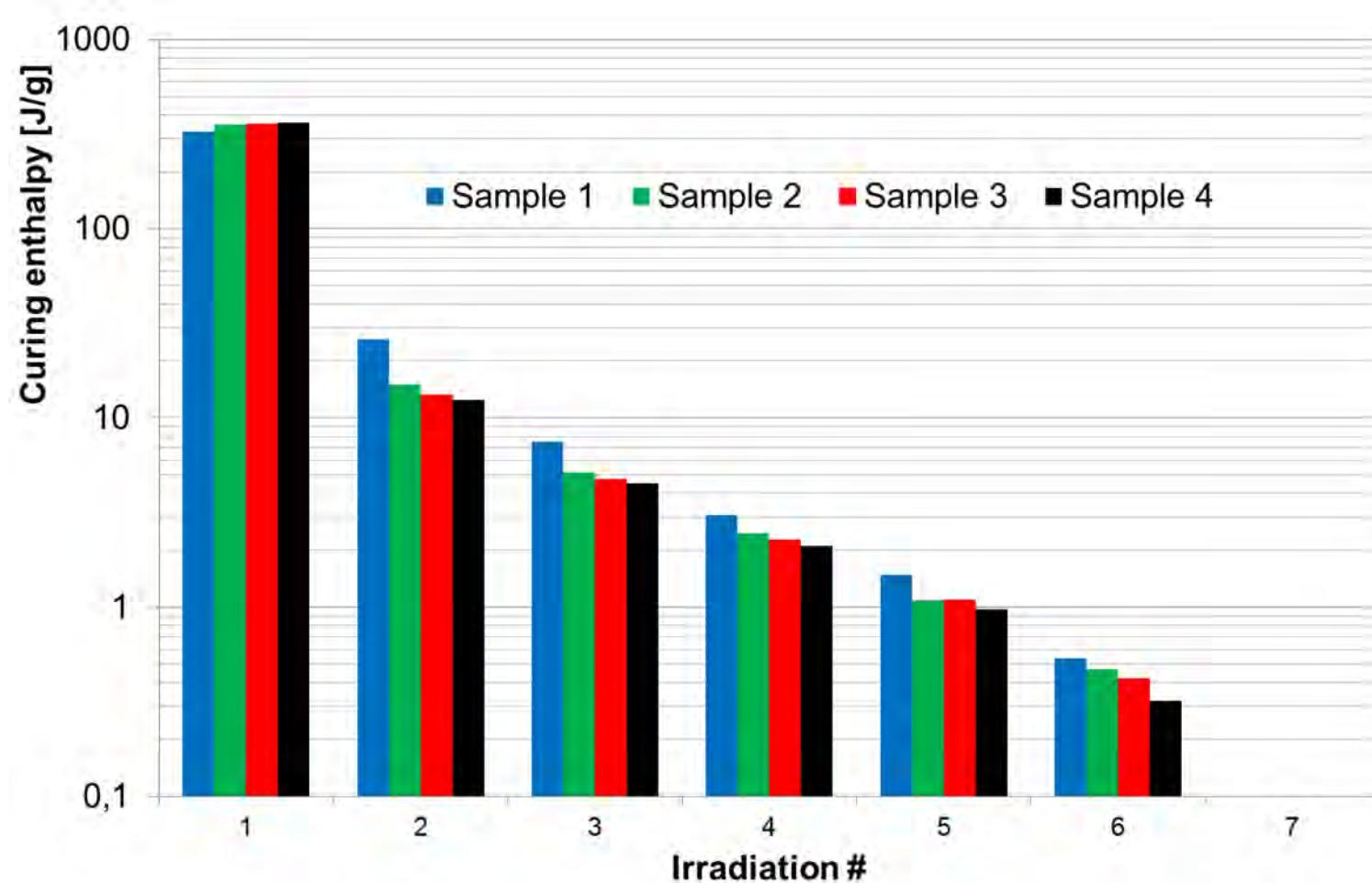
The exothermal peaks in the DSC :

1. Enthalpy of curing
2. background heating by other sources, e.g. light source

**total curing enthalpy [J/g] = Sum of peak enthalpies – background heating**

Pulse #	Sample 1		Sample 2		Sample 3		Sample 4	
	Measured	Corrected	Measured	Corrected	Measured	Corrected	Measured	Corrected
	J/g	J/g	J/g	J/g	J/g	J/g	J/g	J/g
1	-327,18	-323,63	-356,84	-353,66	-360,63	-357,88	-365,17	-362,02
2	-29,51	-25,96	-18,18	-15	-16,12	-13,37	-15,65	-12,5
3	-11,07	-7,52	-8,34	-5,16	-7,51	-4,76	-7,68	-4,53
4	-6,62	-3,07	-5,64	-2,46	-5,03	-2,28	-5,27	-2,12
5	-5,04	-1,49	-4,27	-1,09	-3,85	-1,1	-4,13	-0,98
6	-4,09	-0,54	-3,65	-0,47	-3,17	-0,42	-3,47	-0,32
7	-3,55	0	-3,18	0	-2,75	0	-3,15	0
Total Curing Enthalpy		<b>-362,21</b>		<b>-377,84</b>		<b>-379,81</b>		<b>-382,47</b>

Logarithmic scaling of y-axis

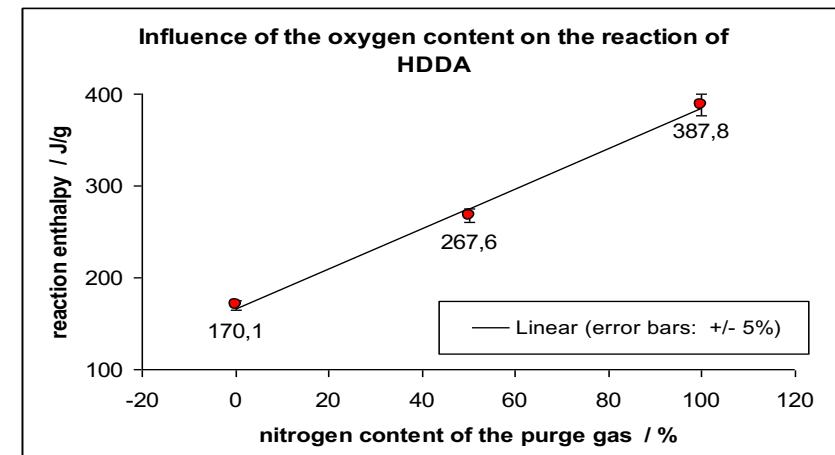
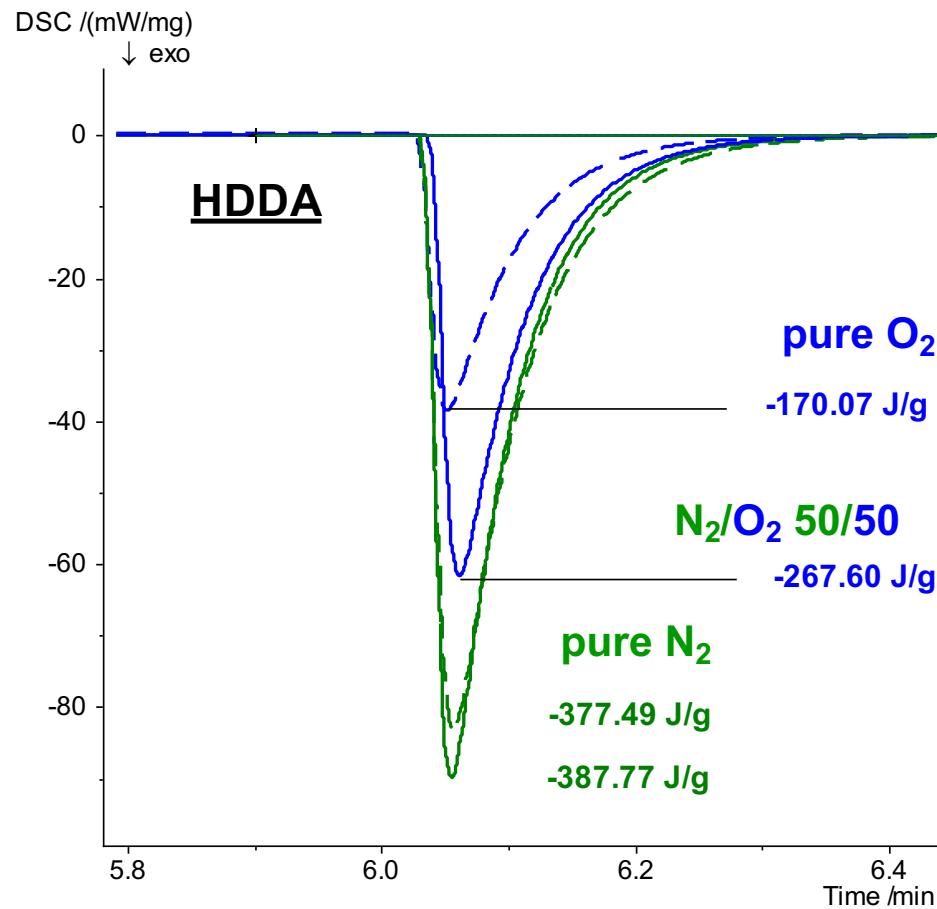


# DSC: Curing of Acrylate Paint

## Influence of the Atmosphere on the Radical UV Curing

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Oxygen inhibits the radical curing reaction of 1,6 Hexandiol Diacrylate (HDDA)



# DSC: Comparison of Hg-Lamp vs. Laser

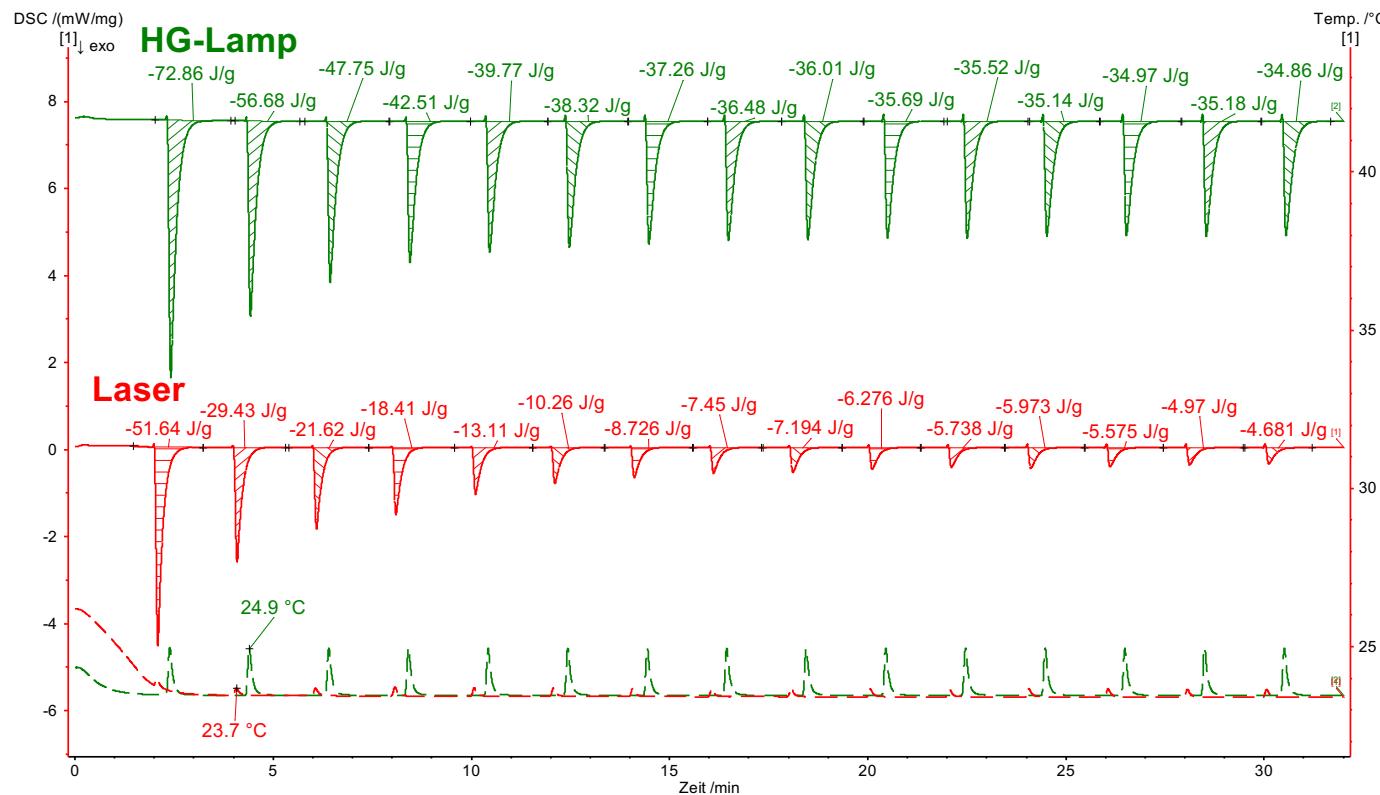
With Suitable Initiator, Laser Enables a Higher Curing Enthalpy

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Formulation: polyethylene glycol diacrylate (PEGDA) + 1% camphorquinone and DMPT (N,N-dimethyl-p-toluidine)

**HG-Lamp: 320-500nm, 10 W/cm<sup>2</sup> → Total curing enthalpy: Lamp: 96 J/g**

**Laser: 447 nm, 0.74 W/cm<sup>2</sup> → Total curing enthalpy: Laser: 131 J/g**



# UV Curing of an Adhesive Based on Acrylate

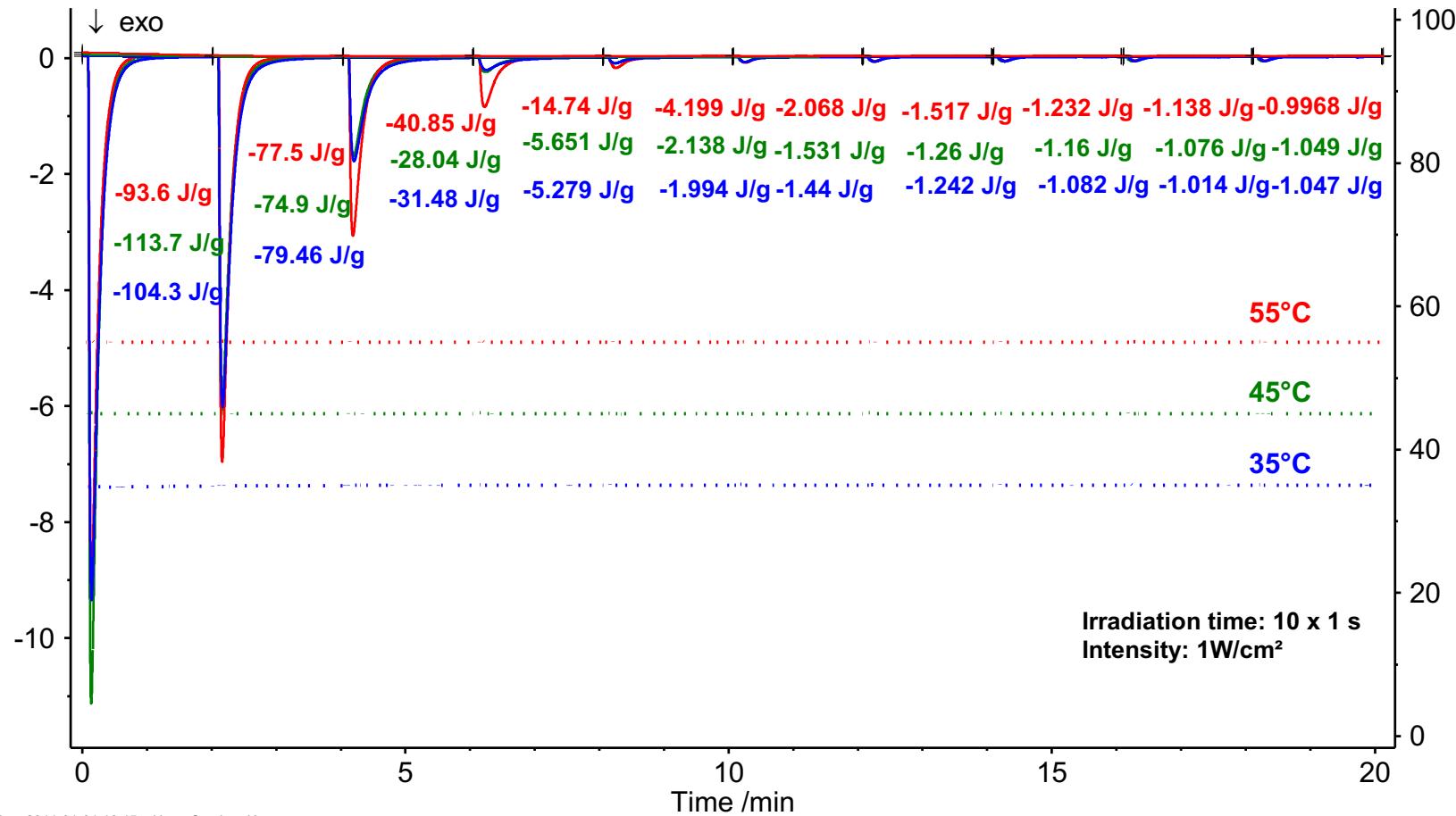
Irradiation Time: 10 x 1 s; Temperatures of 35, 45, 55°C

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DSC /(mW/mg)

*The influence of the temperture is evident*

Temp. /°C



# Curing Enthalpies at Different Temperatures with an Irradiation Time of 10 x 1 s

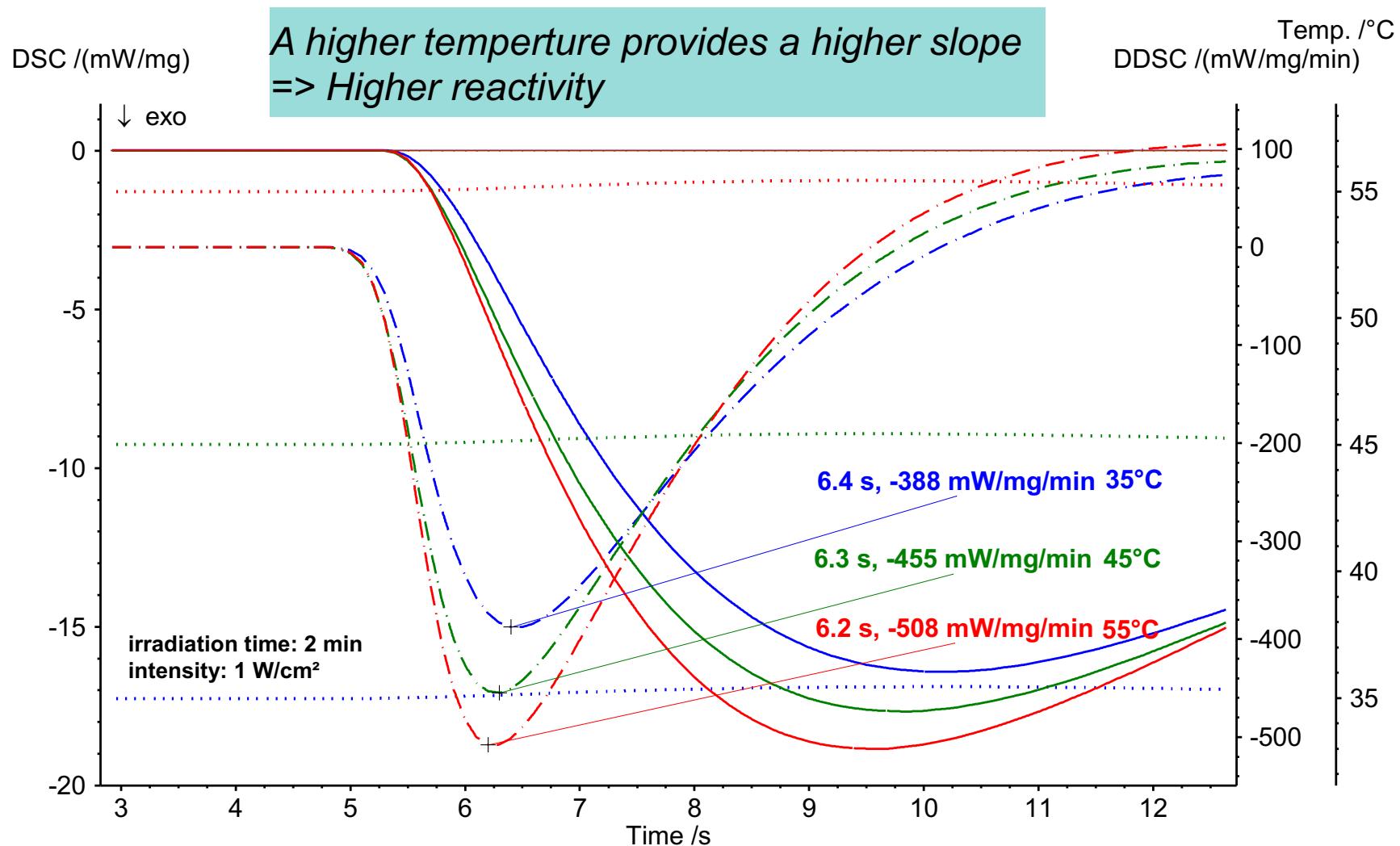
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*The highest temperture provides the highest enthalpy*

Irradiation time [s]	Curing enthalpy [J/g] at different temperatures		
	35°C	45°C	55°C
1	104.32	113.65	93.60
2	79.46	74.90	77.50
3	31.48	28.04	40.85
4	5.28	5.65	14.74
5	1.99	2.14	4.20
6	1.44	1.53	2.07
7	1.24	1.26	1.52
8	1.08	1.16	1.23
9	1.01	1.08	1.14
10	1.05	1.05	1.00
Total curing enthalpy [J/g]	228.35	230.46	237.85

# Reactivity of an Adhesive Based on Acrylate at Different Temperatures by DDSC (Derivative)

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# Curing Enthalpies at Different Irradiation Ways

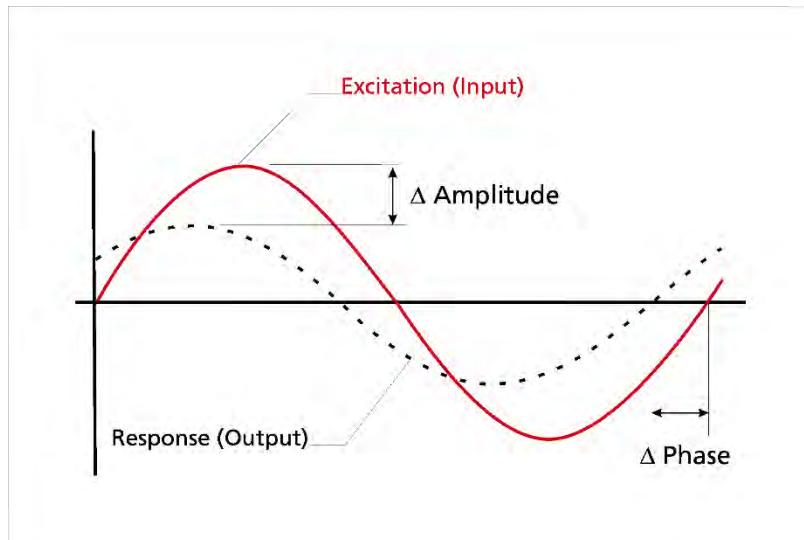
Main Question: Is  $1 \times 5 \text{ s} = 5 \times 1 \text{ s}$  ?

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*There is no difference in the total curing enthalpy at 35°C*

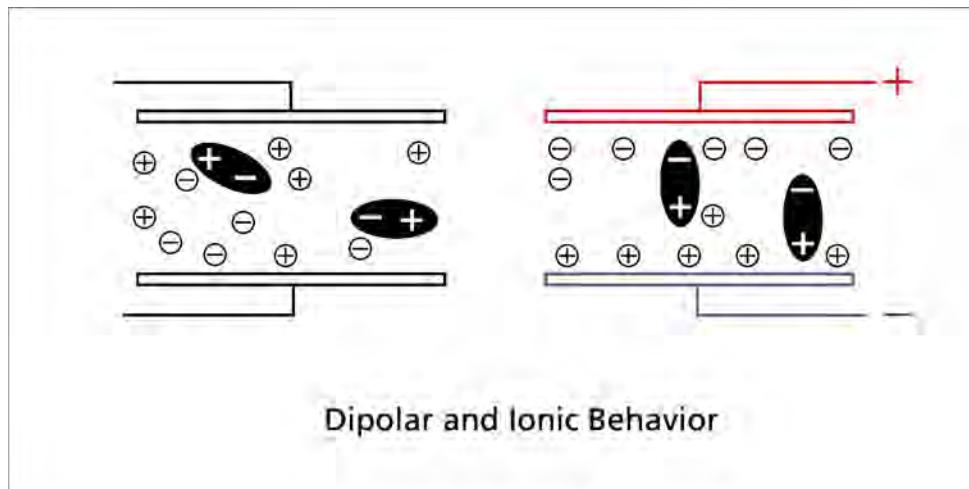
Irradiation time [s]	Curing enthalpy [J/g] at isothermal 35°C	Curing enthalpy [J/g] at isothermal 35°C
1	104.32	
2	79.46	
3	31.48	
4	5.28	
5	1.99	222.89
<b>Total curing enthalpy [J/g]</b>	<b>222.53</b>	<b>222.89</b>

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A low voltage AC signal (*input*) is applied at one electrode

The response signal detected at the other electrode (*output*) is attenuated and phase shifted



Dielectric Sensor:  
• Alignment of dipoles  
• Mobility of ions

$$C = \epsilon_r C_0$$

$$\epsilon_r = \epsilon_r' - i \epsilon_r''$$

$$\text{Capacity } \mathbf{C} = \epsilon_r * \mathbf{C}_0$$

$$\text{with } \epsilon_r = \epsilon_r' - i \epsilon_r''$$

$\epsilon'$  = Permittivity (Dielectric constant)

A measure of the alignment and number of dipolar groups in a material.

$\epsilon''$  = Loss factor =  $\epsilon''_{\text{Ion}} + \epsilon''_{\text{Dipole}}$

A measure of total energy lost due to the work performed aligning dipoles and moving ions in a material.

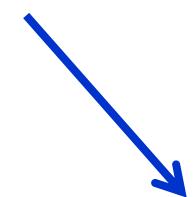
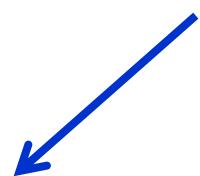
$\tan \delta$  = Dissipation factor =  $\epsilon''/\epsilon' = \tan (90^\circ - \varphi)$ ,

$\varphi$  = phase shift

### Ionic Conductivity

$$\sigma = \epsilon'' * \omega * \epsilon_0$$

$$[\text{S} / \text{m}] = [1 / \Omega\text{m}]$$



### Loss Factor

$$\epsilon'' = \frac{\sigma}{\omega * \epsilon_0}$$

[ $\cdot$ ]

### Ion Viscosity

$$\rho = \frac{1}{\sigma}$$

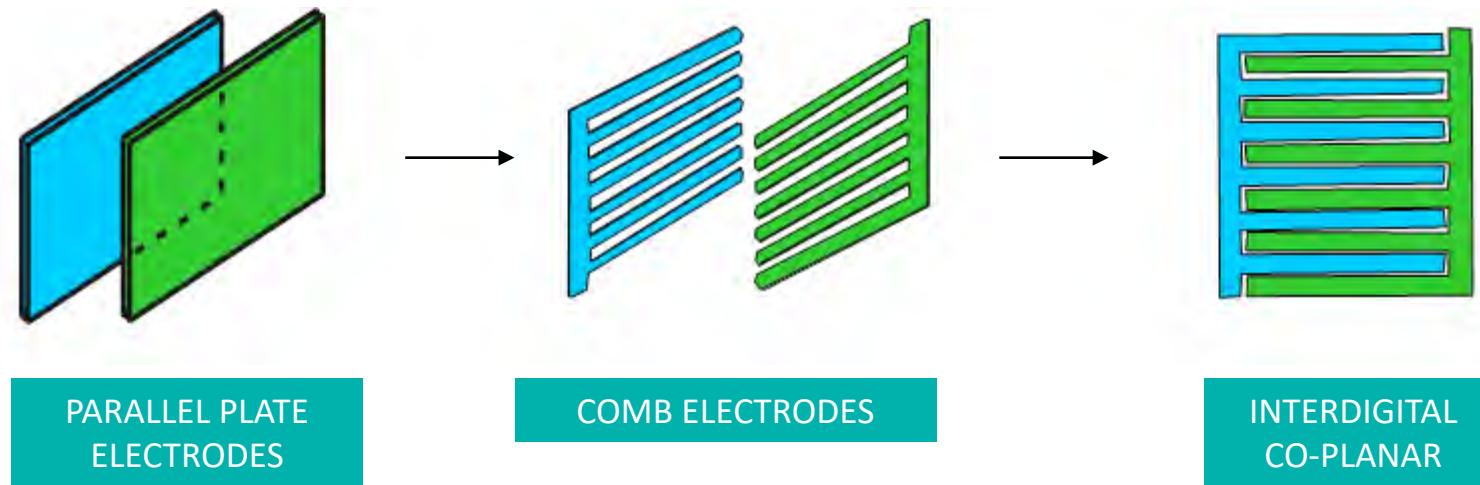
$[\Omega * \text{cm}]$

$\omega$  = Angular frequency =  $2\pi f$

$f$  = Frequency [Hz] = [1 / s]

$\epsilon_0$  = Permittivity of free space =  $8.854 * 10^{-12}$  F/m

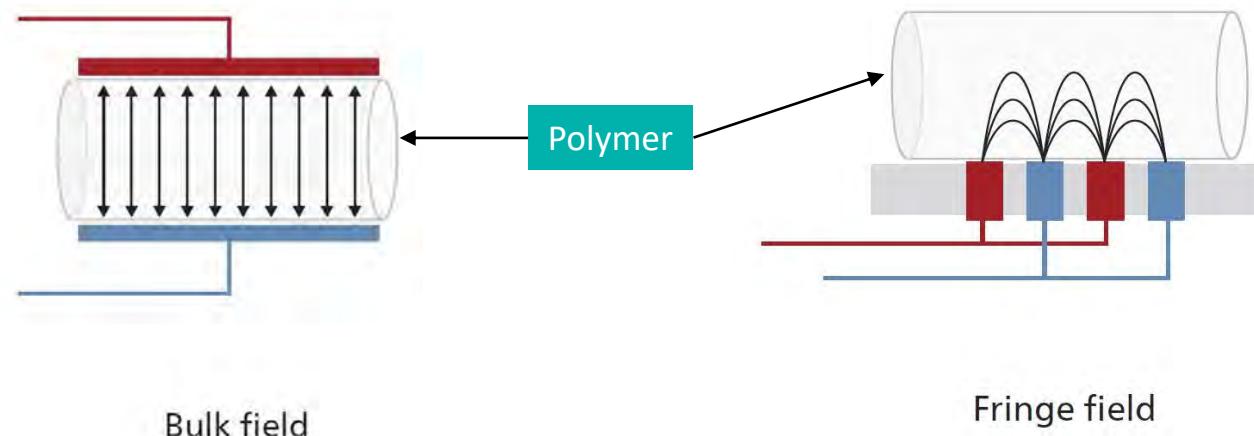
[F / m] = [C / Vm] = [As /  $\Omega\text{Am}$ ] = [s /  $\Omega\text{m}$ ]



PARALLEL PLATE  
ELECTRODES

COMB ELECTRODES

INTERDIGITAL  
CO-PLANAR



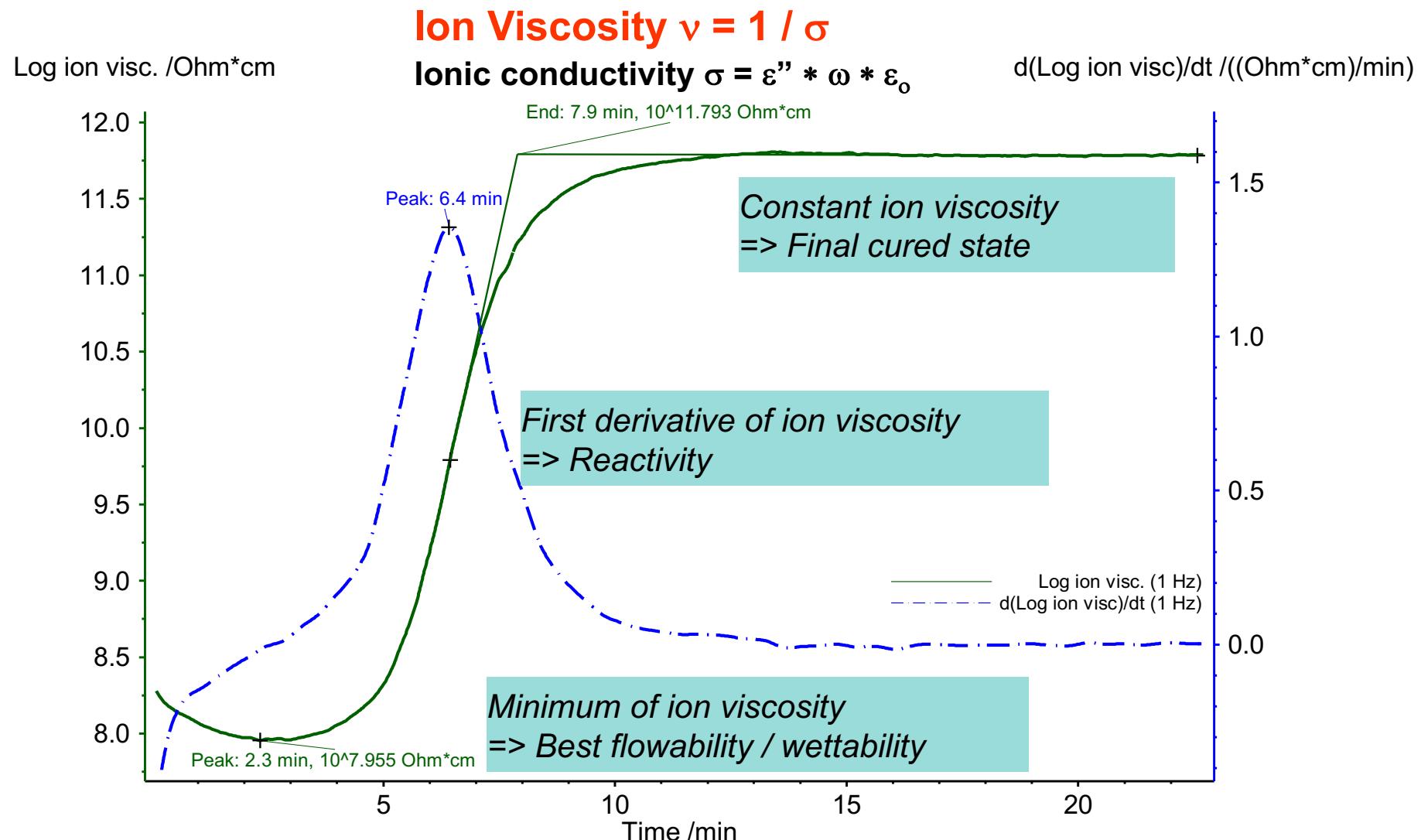
Bulk field

Fringe field

# Cure Monitoring by Dielectric Analysis

## Curing of a 2K Epoxy resin (at room temperature)

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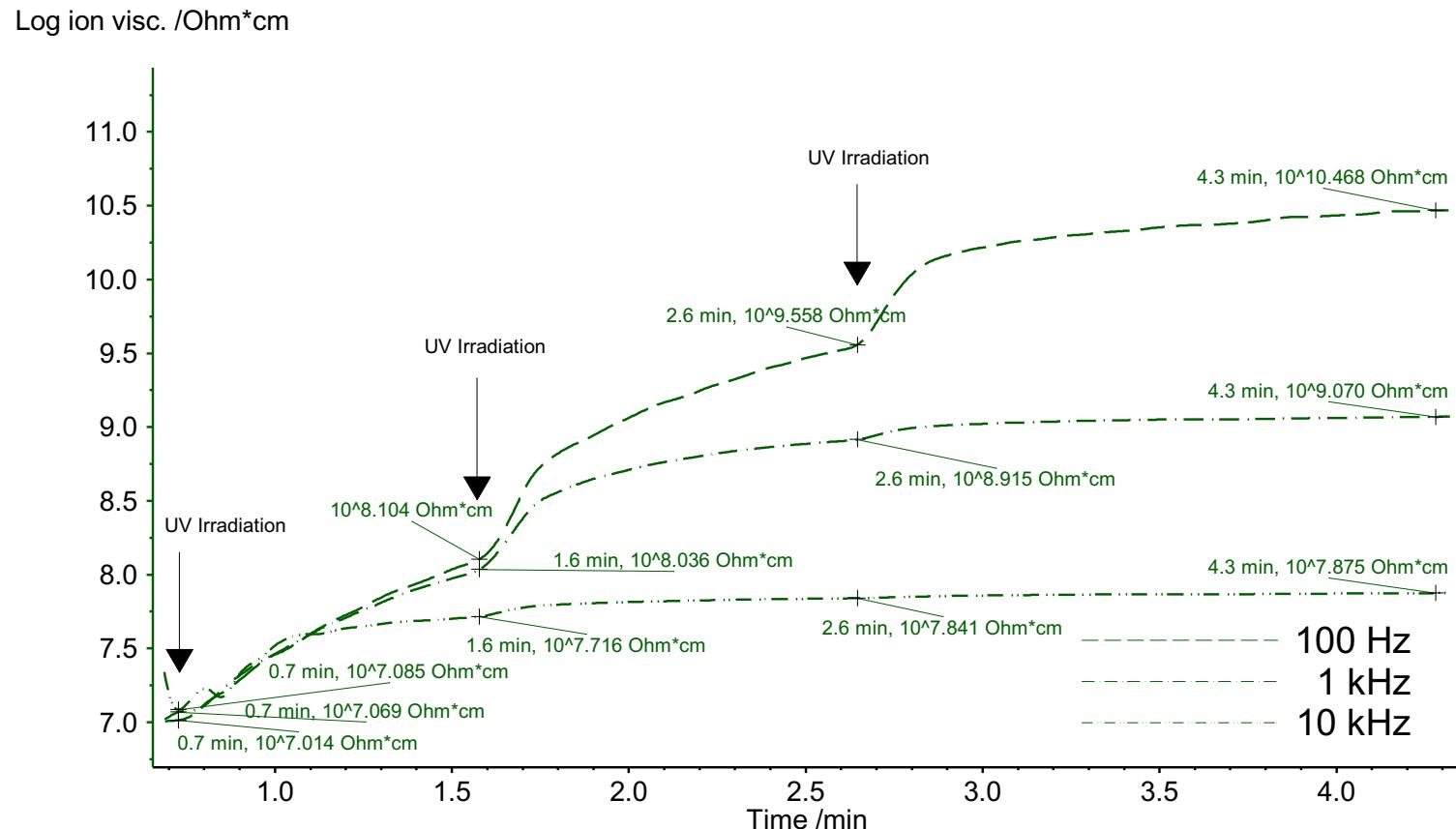
# DEA-Measurement on Acrylate-Coating

Multifrequency - 100, 1000 und 10000 Hz

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DEA 288 Epsilon with IDEX-Sensor at room temperature

Radiation time 3 x 2s



# DEA: UV-Measurement on Acrylate-Coating

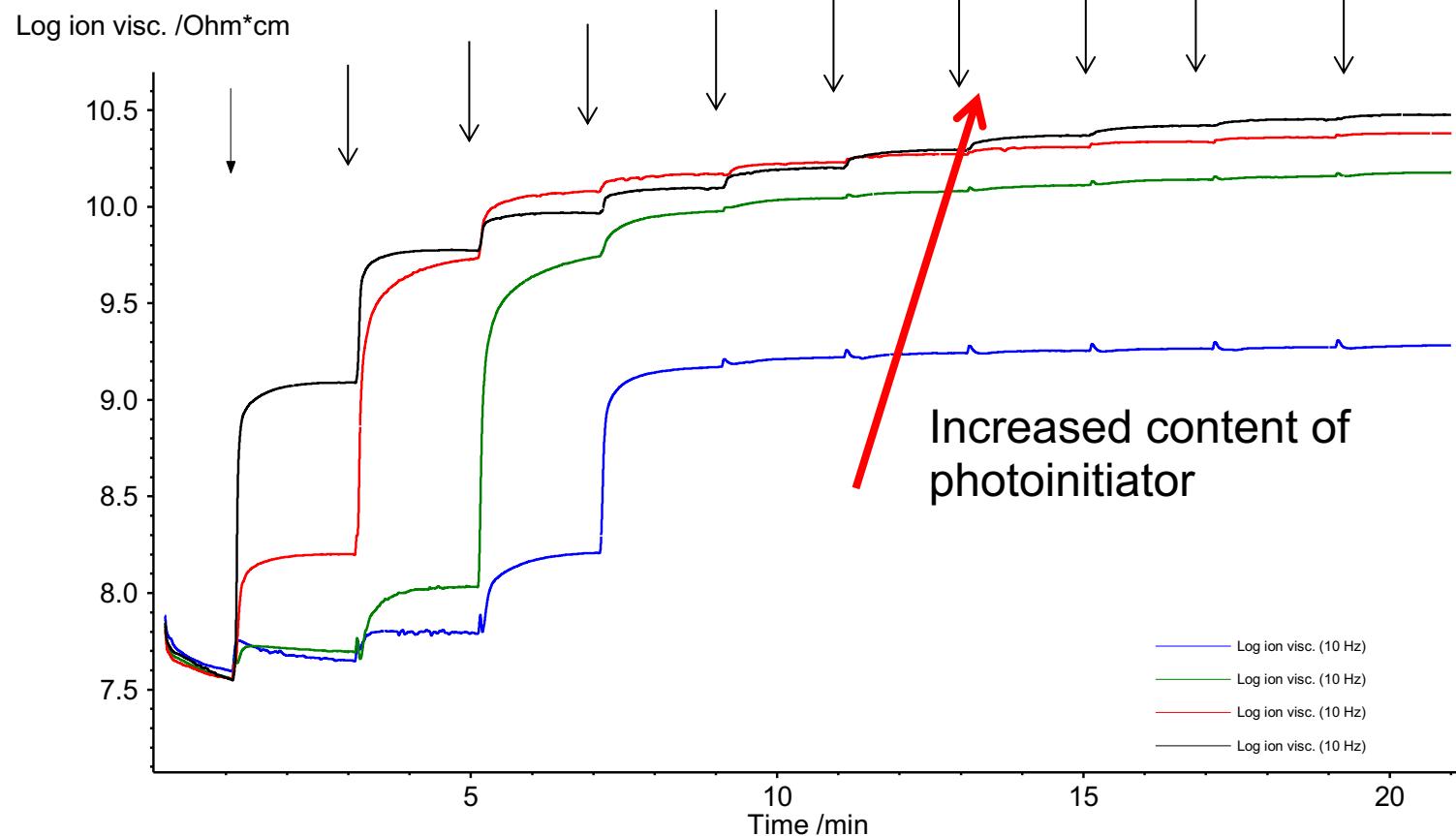
## Variation of photoinitiator content

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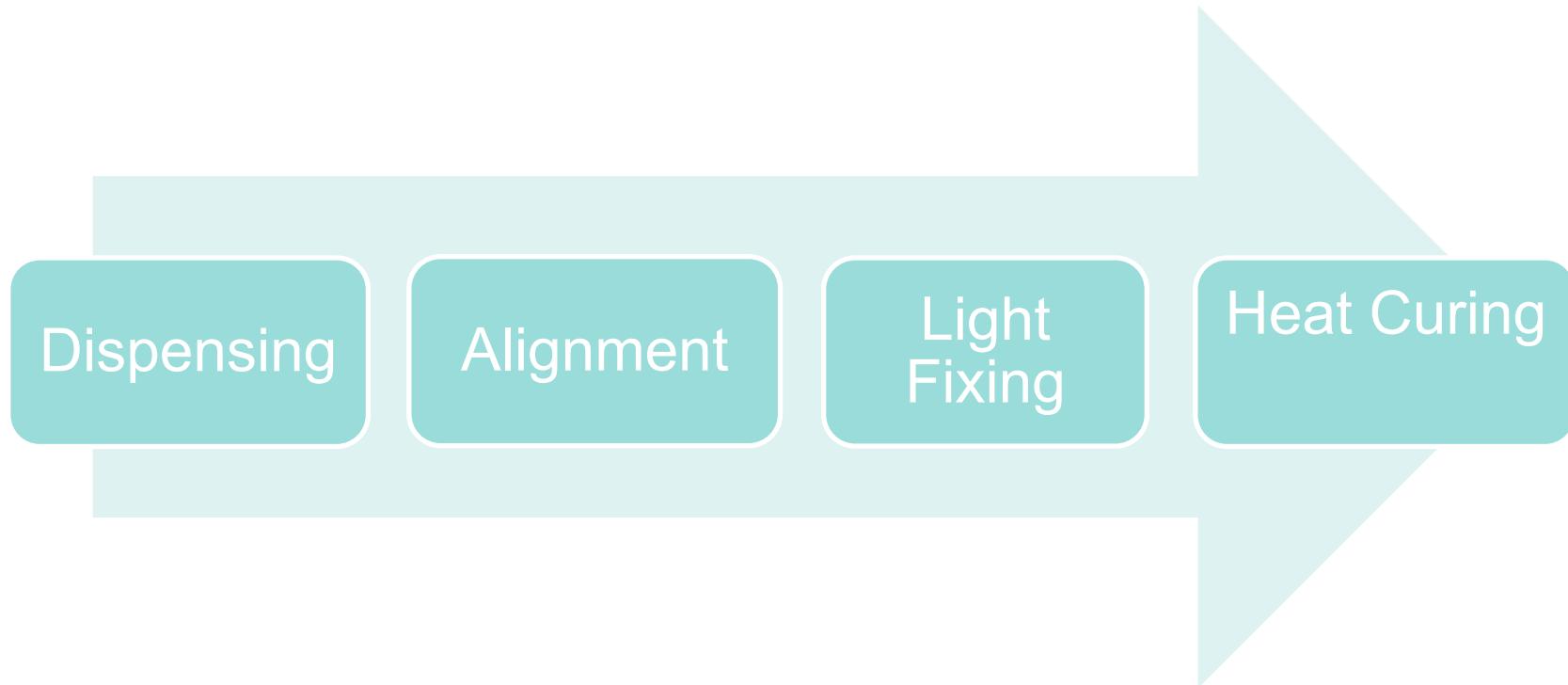
10 Hz, Room temperature

Irradiation time 10 x 3s

UV Irradiation



1. Light fixing is very fast
2. Heat curing leads to the final curing state



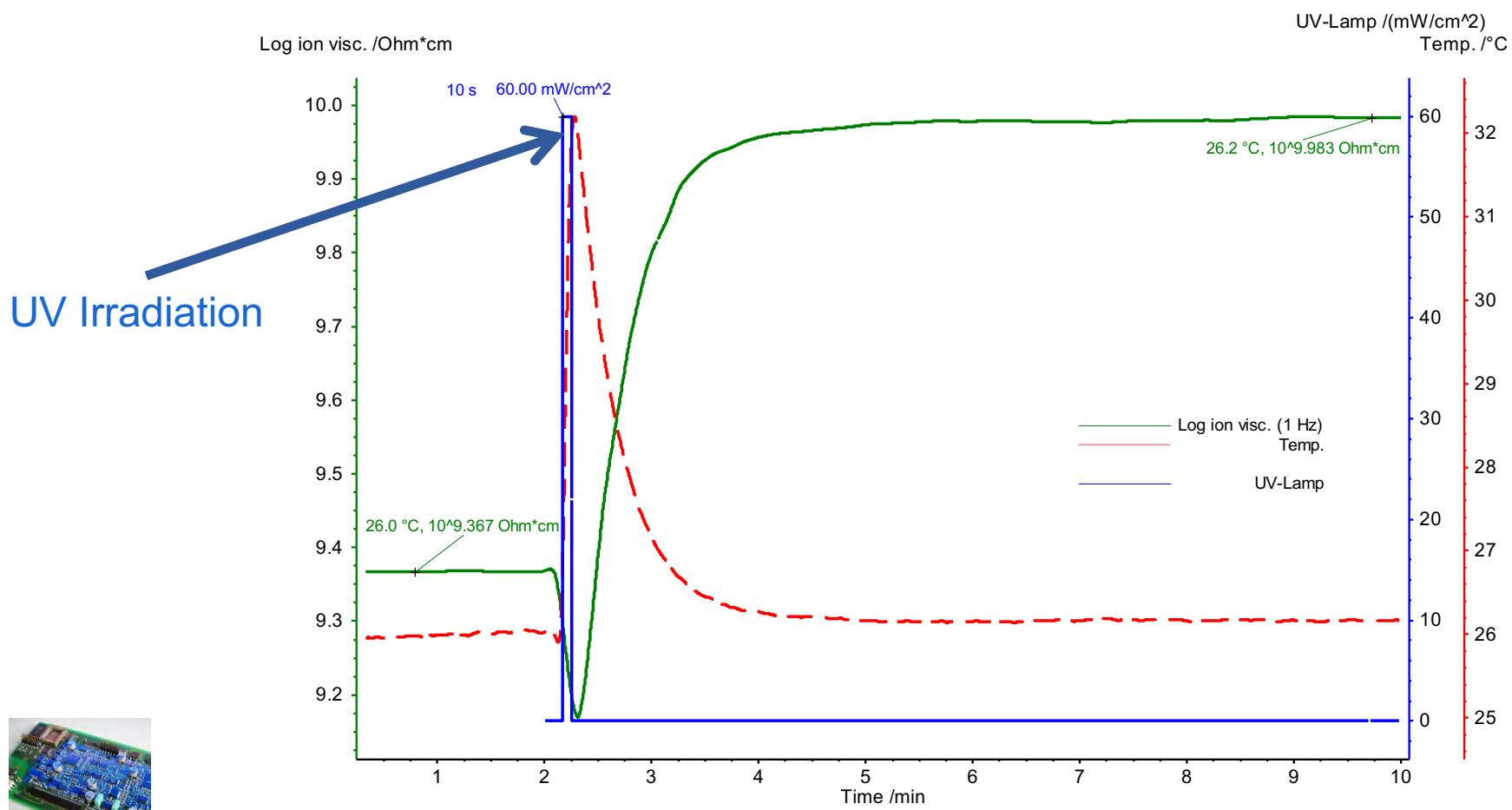
# DEA-Measurement on Dual Curing Adhesive

1<sup>st</sup> step: UV irradiation for 10 s

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DEA 288 *Epsilon* with IDEX 115 with Thermocouple

IDEX-Sensor, 1 Hz at 23°C



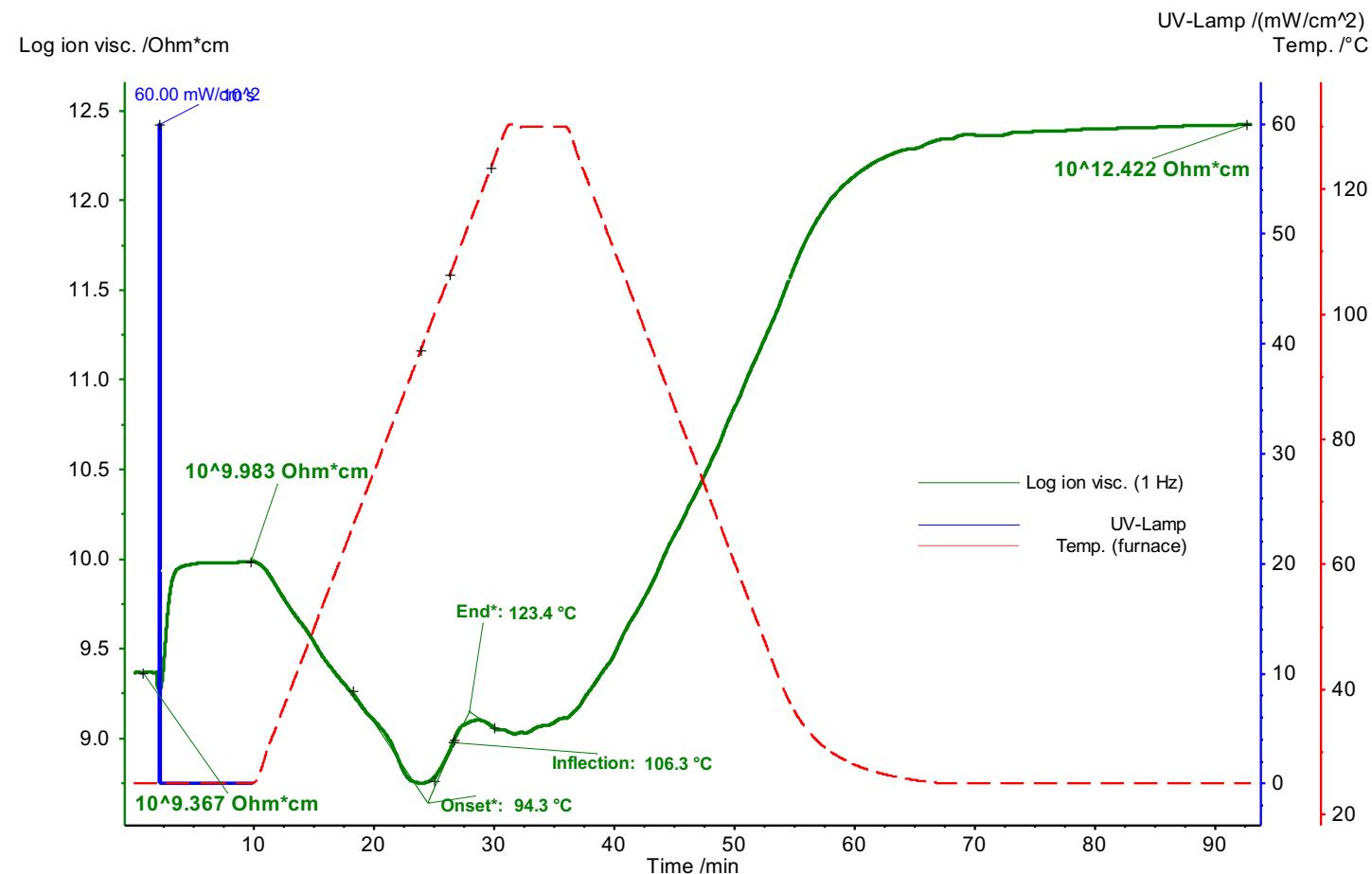
# DEA-Measurement on Dual Curing Adhesive

2<sup>nd</sup> step: thermal curing @130 °C

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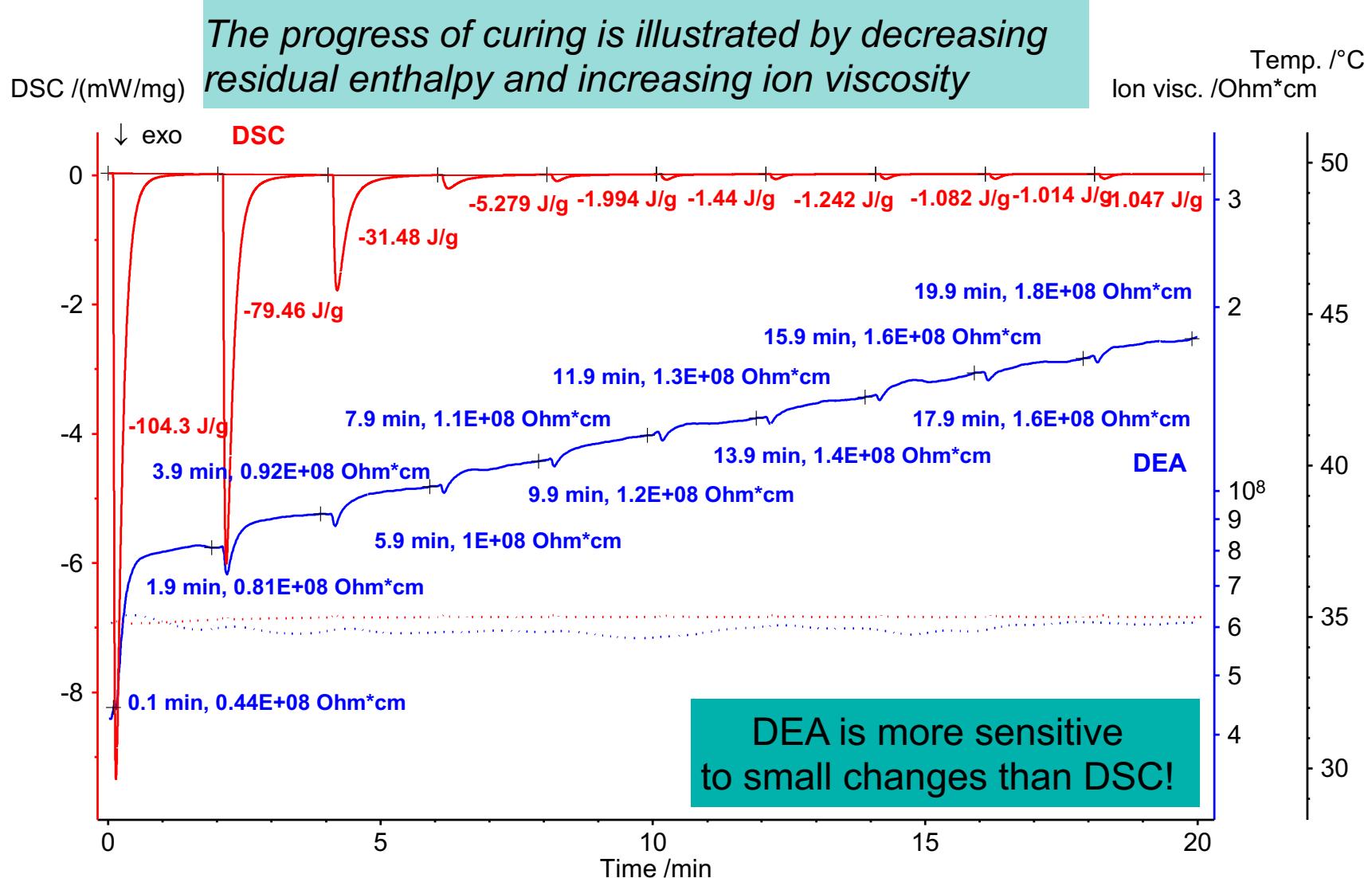
DEA 288 *Epsilon* with IDEX 115 with Thermocouple

Heating to 130 °C, Curing, Cooling to 23 °C



# Comparison of DSC and DEA for the UV Curing of an Acrylate Adhesive (Irradiation Time 10 x 1 s)

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# Complementary Thermal Techniques for Testing and Optimizing UV Curing

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Parameter	Photo-DSC	DEA	DMA
UV irradiation time	+	+	(+)
UV intensity	+	+	(+)
Temperature	+	(+)	+
Atmosphere/moisture	+	+	(+)
Frequency	-	+	+
Force	-	-	+
Deformation	-	-	+
Layer thickness	(+)	+	+

**+** ideal

**(+)** possible  
impossible

- NETZSCH Analyzing & Testing offers the advanced Photo-DSC for investigation of UV curing in the lab environment.
  - Versatile DEA system with different sensor types is ideal for fast UV cure monitoring - even in-situ.
  - Photo-DSC and DEA are complimentary techniques for the UV curing process.
-

Thank you for your attention!

**NETZSCH**

**Dr Yanxi Zhang**  
Technical Sales Support

NETZSCH Instruments North America, LLC  
BU Analyzing & Testing  
Phone: +1 781 418 1840  
Cell: +1 781 547 1371  
E-mail: [Yanxi.zhang@netzschi.com](mailto:Yanxi.zhang@netzschi.com)  
[www.netzschi-thermal-analysis.com](http://www.netzschi-thermal-analysis.com)