

### Kinetic Analysis of Photopolymer Curing Under Variable UV Light Intensities Using Kinetics Neo and DEA, Part 1

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#### Introduction

Photopolymers are light-sensitive materials that polymerize upon exposure to light, transforming liquid monomers or oligomers into solid, functional networks. Their rapid and controllable curing process makes them suitable for applications such as inks, coatings, adhesives, and 3D printing.

Next-generation additive manufacturing (AM) processes, including multiphoton lithography and fusion jetting (FJ), exploit these materials to produce high-resolution, complex geometries and multi-material parts [1]. In these processes, the curing behavior of acrylate photopolymers is strongly influenced by both UV light intensity and temperature, which significantly affect the curing rate and the final material properties. In AM processes, curing of material is done layer by layer with typical layer thicknesses around 50 to 100 µm [2,3].

The aim of this study is to investigate the curing kinetics of photopolymer diacrylates under different isothermal conditions and UV light intensities using dielectric analysis (DEA), and the Kinetics Neo software for kinetic analysis, prediction, and process optimization.

#### Measurement Conditions

DEA measurements were performed using the DEA 288 *Ionic* (figure 1) under the measurement conditions listed in table 1. The DEA curves obtained are the basis for the kinetic analysis.

Multiple sensors allow for precise measurement of temperature, ensuring optimal performance and quality.



1 DEA 288 *Ionic* Dielectric Analyzer

Table 1 Measurement conditions

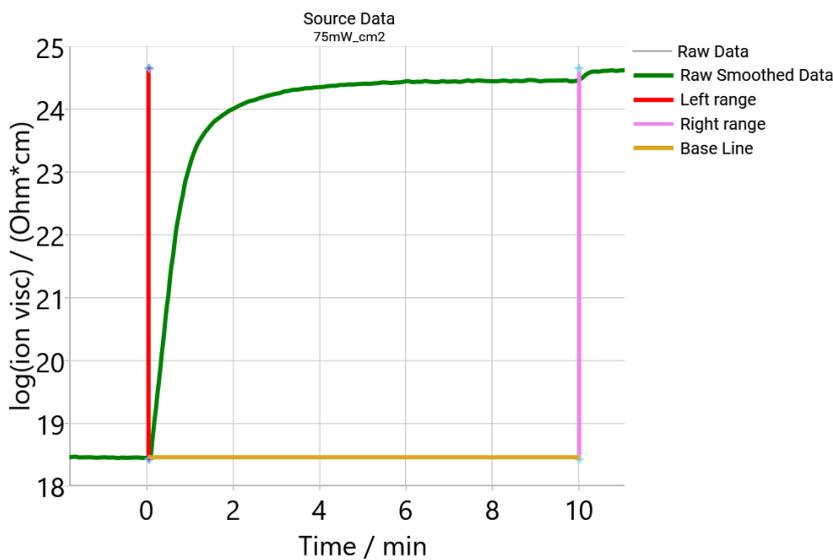
|   |  |
|---|--|
| Instrument                                | NETZSCH DEA 288 <i>Ionic</i>           |
| Material                                  | Photopolymer diacrylates (UV DLP Firm) |
| Isothermal temperature/°C                 | 30, 90 and 150                         |
| UV intensities at 30°C/mW/cm <sup>2</sup> | 36, 75, 150 and 300                    |
| Radiation time/min                        | 10                                     |
| Sensor                                    | IDEX sensor                            |
| Frequency/Hz                              | 10                                     |

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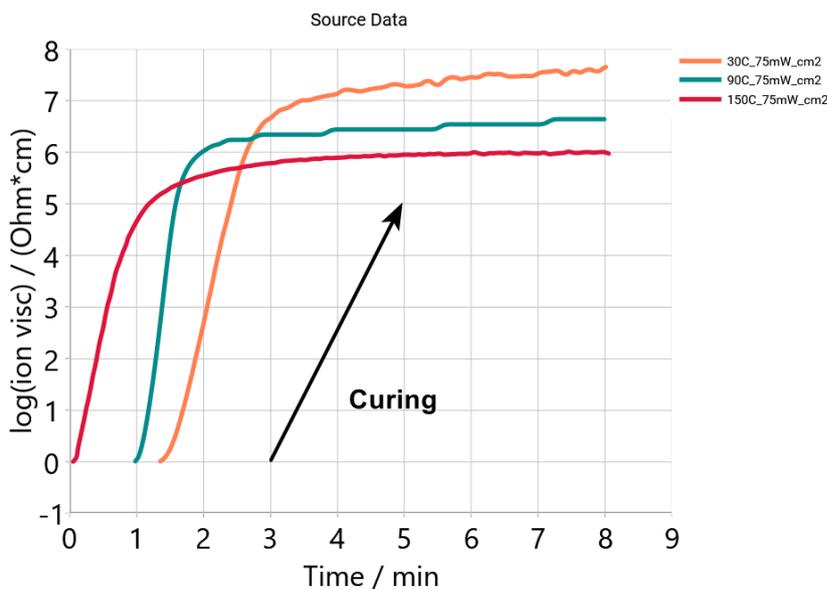
### Measurement Results and Discussion

Figure 2 shows the typical experimental data curve at 150°C under UV light exposure with an intensity of 75 mW/cm<sup>2</sup>. The horizontal baseline is set to the data point at the left cursor where the light is switched on. The initial decrease in ionic viscosity, caused by the temperature dependence of the ion viscosity during heating, was removed by this baseline correction. Time  $t=0$  is placed here at the point where the light is turned on. The curing process leads to an increasing ion viscosity which is seen after starting the UV light exposure.

Figure 3 presents the set experimental measured data at the same UV intensity of 75 mW/cm<sup>2</sup>, but different temperatures. The ion viscosity is temperature-dependent, and this is the reason for the different final experimental values at different temperatures. For a UV intensity of 75 mW/cm<sup>2</sup>, curing is not fully completed after 8 minutes at isothermal temperatures of 30°C, 90°C, and 150°C, as the ion viscosity continues to exhibit a slight increase.



2 Horizontal baseline (yellow) applied for a UV intensity of 75 mW/cm<sup>2</sup> at isothermal temperatures of 150°C.



3 DEA measurement of photopolymer diacrylates for the same UV intensity of 75 mW/cm<sup>2</sup> at different isothermal temperatures of 30, 90 and 150°C.

## APPLICATIONNOTE Kinetic Analysis of Photopolymer Curing Under Variable UV Light Intensities Using Kinetics Neo and DEA, Part 1

The measurement at the lowest temperature of 30°C shows a slower increase in the ion viscosity curve than at 90°C because the curing rate decreases as temperature declines. The reaction at 150°C is a little slower than for 90°C because at high temperature, the termination step in radical polymerization becomes faster than the polymerization step. Our goal is to create a kinetic model that depends on both the temperature and the intensity of the UV light.

Figure 4 presents the set of DEA measurements at the same temperature of 30°C for UV intensities of 75, 150 and 300 mW/cm<sup>2</sup>. The ionic viscosity increases from minimum ion viscosity, indicating the onset of curing. For all experimental curves, the ionic viscosity continues to exhibit a slight increase after four minutes. This figure demonstrates fastest curing at the highest intensity of a UV light of 300 mW/cm<sup>2</sup>, the slowest intensity of a UV light of 75 mW/cm<sup>2</sup> corresponds to the slowest curing rate.

### Kinetic Analysis

Kinetics Neo software is used to create a unified model for different temperatures and intensities of UV light.

### Degree of Conversion

The degree of conversion,  $\alpha$ , is calculated by the Kinetics Neo software from the DEA measurement,

where  $\alpha$  ranges from 0 to 1. In thermal analysis for isothermal measurements, the conversion is operationally defined as the thermoanalytical effect observed at time,  $t$ , divided by the total thermoanalytical effect. For DEA, the definition of thermoanalytical conversion is as follows:

$$\alpha = \frac{v(t) - v_0}{v_{final} - v_0} \quad (1)$$

$v_0$  is the initial ion viscosity at the point of time where the UV light is switched on

$v_{final}$  is the final ion viscosity for the cured material

$v(t)$  is the current ion viscosity at the point of time,  $t$

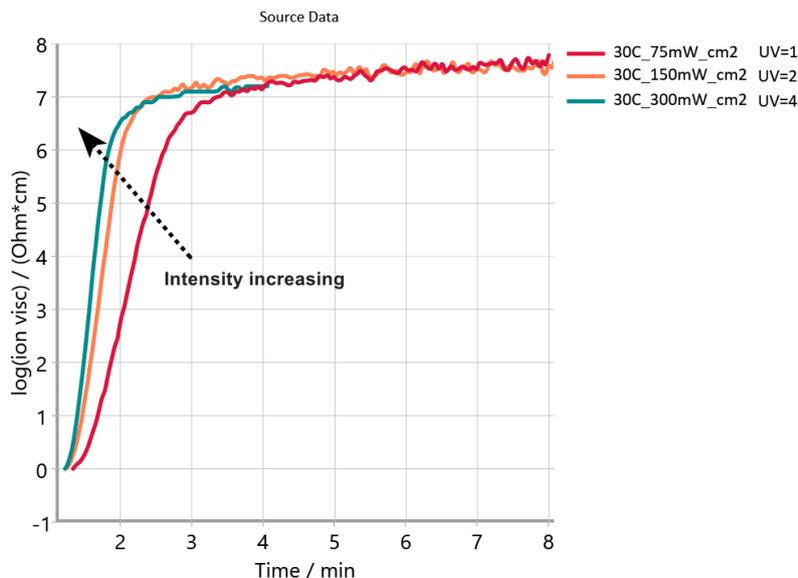
The reaction rate depends on the temperature,  $T$ , the UV intensity,  $I$ , and the reaction type,  $f(\alpha)$ :

$$\frac{d\alpha}{dt} = k(T, I) \cdot f(\alpha) \quad (2)$$

Combined  $n^{\text{th}}$  order and autocatalytic reaction model

$$f(\alpha) = (1 - \alpha)^n \cdot (1 + K_{cat} \cdot \alpha^m) \quad (3)$$

where the weight factor,  $K_{cat}$  represents the pre-exponent of the autocatalytic reaction, and  $n$  and  $m$  are the reaction orders of the  $n^{\text{th}}$  order reaction and the autocatalytic reaction, respectively [6].



4 DEA measurements on photopolymer diacrylates at an isothermal temperature of 30°C and UV intensities of 75, 150 and 300 mW/cm<sup>2</sup>.

# APPLICATIONNOTE Kinetic Analysis of Photopolymer Curing Under Variable UV Light Intensities Using Kinetics Neo and DEA, Part 1

## Effect of UV Intensity on the Reaction Rate

The influence of UV intensity on the reaction kinetics was evaluated using a power-law dependence of the rate constant on light intensity [4,5]. The rate constant,  $k$ , can be expressed as (equation 4):

$$k(T, I) = k_0(T) \cdot \left(\frac{I}{I_0}\right)^{n_{UV}} \quad (4)$$

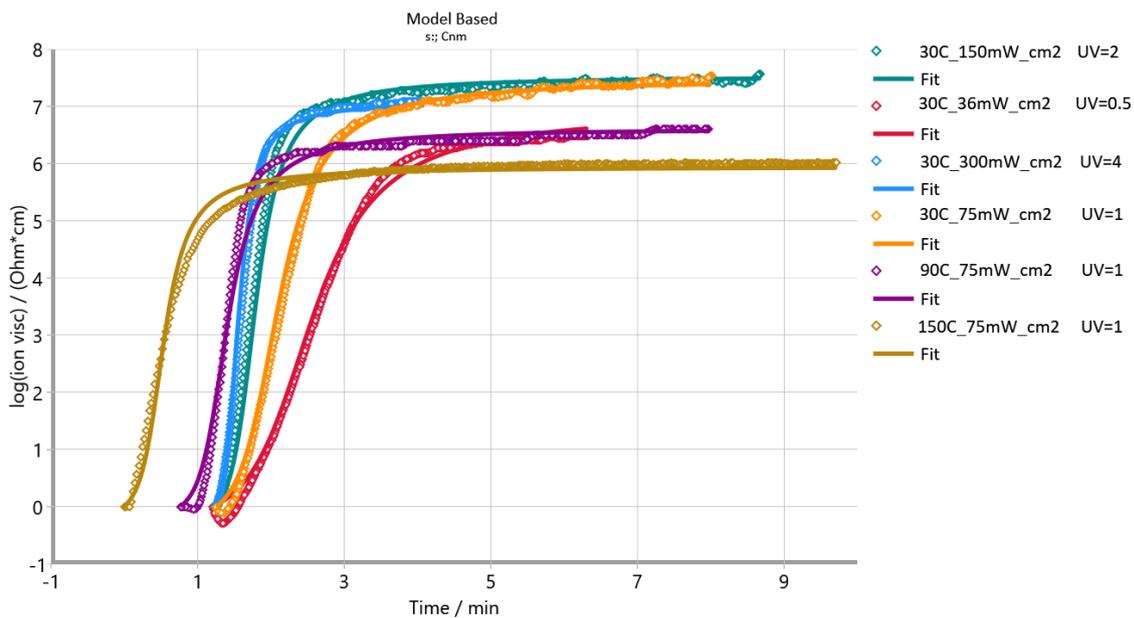
where  $k_0(T)$  is the temperature-dependent kinetic constant,  $I/I_0$  is the relative UV intensity where a relative intensity of 1 corresponds in this case to  $I_0 = 75 \text{ mW/cm}^2$ , and  $n_{UV}$  is a fitting parameter reflecting the sensitivity of the reaction rate to UV intensity.

Figure 5 illustrates the effects of temperature and UV intensity on the curing behavior of photopolymer diacrylates, measured by DEA (dielectric analysis). A common kinetic model was created using the Kinetics Neo software. The rhombus symbols represent the experimental data, and the solid lines correspond to the fitted curves. In the figure,  $UV = 1$  corresponds to  $75 \text{ mW/cm}^2$ . The kinetics parameter are detailed in table 2.

**Table 2** Kinetic parameters of photopolymer acrylates based on DEA measurements

|   |        |
|---|--------|
| Reaction step                                   | A → B  |
| Reaction type                                   | Cnm    |
| Activation energy [kJ/mol]                      | 5.174  |
| Log (pre-exponential factor) [Log (1/s)]        | -1.793 |
| Reaction order                                  | 1.724  |
| Log (Autocat pre-exponential factor [Log(1/s)]) | 1.629  |
| AutcatPower mf                                  | 1.136  |
| $n_{UV}$ Light                                  | 0.619  |
| $I_0$ [mW/cm <sup>2</sup> ]                     | 75     |
| Coefficient of determination (R <sup>2</sup> )  | 0.996  |

Cnm: Reaction of n<sup>th</sup> order with m-power autocatalysis



**5** Kinetic evaluation of photopolymer diacrylates at different isothermal conditions and UV intensities.

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## Isothermal Prediction

The kinetic model can now be applied to predict results as a function of time, temperature, and relative intensity.

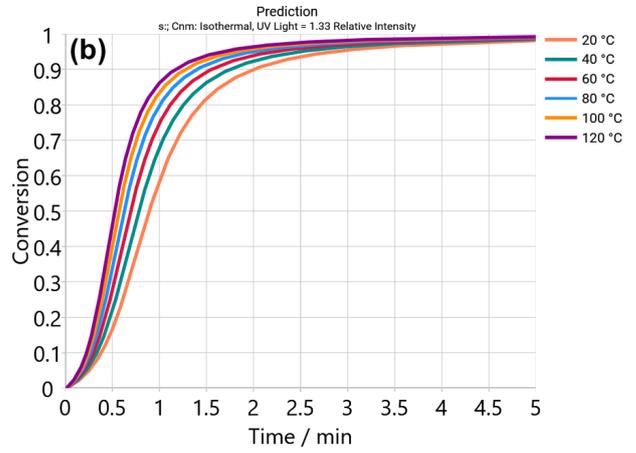
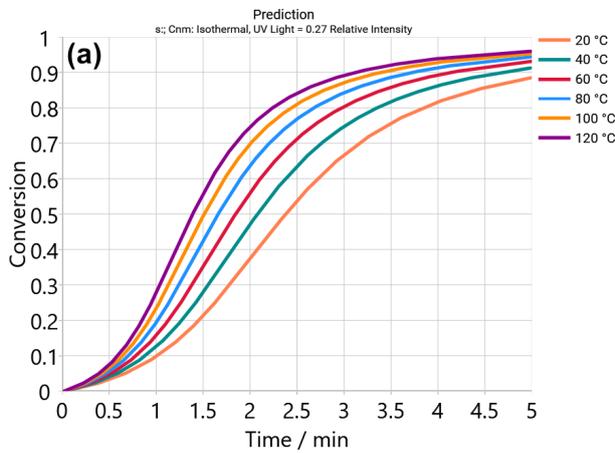
Figures 6 (a) and 6 (b) present the predicted degree of conversion of diacrylate photopolymers under isothermal conditions (20 to 120°C) at light intensities of 20 mW/cm<sup>2</sup> and 100 mW/cm<sup>2</sup>.

At a UV intensity of 100 mW/cm<sup>2</sup>, the final degree of conversion after 5 minutes ranges from 0.98 to 0.99. In contrast, at a UV intensity of 20 mW/cm<sup>2</sup>, the final

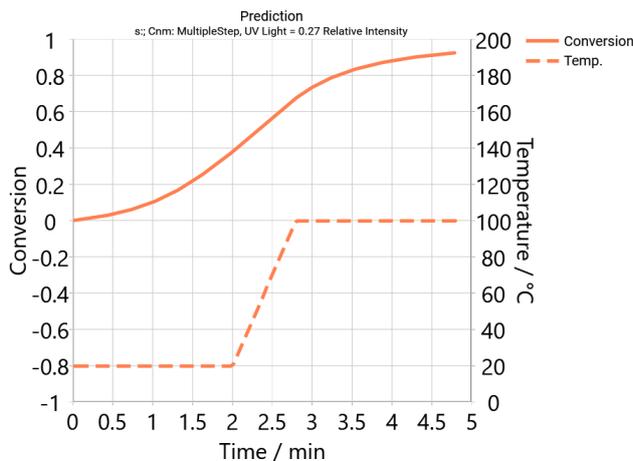
conversion after 5 minutes decreases, reaching values between 0.88 and 0.96.

## Multi-Step Prediction (Sequence of Dynamic and Isothermal Segments)

Figure 7 shows the step prediction of the degree of conversion for diacrylate photopolymers at an intensity of 20 mW/cm<sup>2</sup> under multi-step conditions (dynamic and isothermal segments). Using this temperature program, outlined in table 3, the process can be optimized to achieve the desired degree of conversion more efficiently.



6 Prediction of the degree of conversion of diacrylate photopolymers under isothermal conditions (20 to 120°C) (a) intensity (20 mW/cm<sup>2</sup>) and (b) intensity (100 mW/cm<sup>2</sup>).



7 Multiple-step prediction of the the degree of conversion of diacrylate photopolymers at an intensity of 20 mW/cm<sup>2</sup>.

Table 3 Multi-step predictions

| Start T/°C | End T/°C | H.R./K/min | Time/min |
|------------|----------|------------|----------|
| 20         | 20       | 0          | 2        |
| 20         | 100      | 100        | 0.8      |
| 100        | 100      | 0          | 2        |

## Conclusion

Dielectric Analysis (DEA) is an effective tool for monitoring UV photopolymers. It can be used not only in the laboratory but also directly on the production line. When combined with the Kinetics Neo software, DEA measurements have been proven to effectively determine kinetic parameters that are a function of both temperature and UV intensity. Termica Neo software adds significant value by simulating the thermal behavior of photopolymer layers, predicting temperature evolution, identifying potential hotspots, and enabling optimization of layer thickness and curing conditions.

## Benefits of Kinetic Analysis and Thermal Simulation

**Optimized Curing and Quality Control:** Predict and achieve the desired degree of cure, ensuring consistent material properties and reducing defects in 3D-printed or coated products.

**Faster Development and Process Efficiency:** Use kinetic models and simulations to shorten trial-and-error experiments, speeding up R&D and production setup for new photopolymer formulations or AM processes.

## Literature

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