Kinetic Analysis of the Storage Modulus to Predict the Thermal Post-Curing of a UV-Cured Resin System

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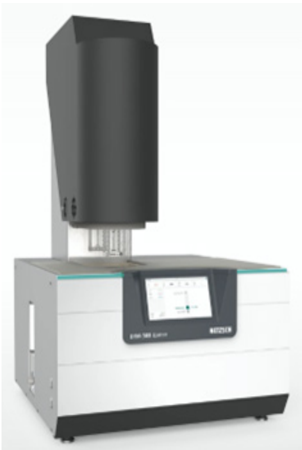

1 DMA 303 *Eplexor®*

Introduction

The resin system developed by the European Centre for Dispersion Technologies (EZD) has been meticulously designed for use in a variety of applications, including inks, coatings, and additive manufacturing. Central to its performance is an understanding of its curing behavior, which is analyzed through kinetic studies of the storage modulus. UV-curing, involving crosslinking reactions that create covalent bonds and form three-dimensional networks, is a key feature of this resin. The storage modulus, a measure of a material's stiffness during curing, provides critical insights into the curing kinetics and helps predict the resin's behavior under different conditions. By combining UV-curing with thermal post-curing, the resin system achieves optimal material properties such as hardness, elasticity, and chemical resistance. This approach not only ensures rapid and efficient curing but also enhances performance in applications across industries like printing, wood processing, automotive, electronics, medical technology, optics, aerospace, and food packaging. Kinetic analysis of the storage modulus allows for precise predictions of the resin's curing behavior.

Measurement Conditions

The samples were produced using 3D-printing at SKZ-KFE gGmbH and analyzed with a NETZSCH DMA 303 *Eplexor®* (figure 1). The most important measurement parameters are summarized in table 1.

Table 1 Measurement conditions of the DMA 303 *Eplexor®* measurement

Sample holder	3-point bending, 30-mm flexible supports
Sample thickness	Approx. 2 mm
Sample width	Approx. 10 mm
Max dynamic force	10 N
Dynamic Amplitude	50 µm
Frequency	1 Hz
Heating rate	5 K/min
Target temperature	180°C, 200°C., 210°C and 220°C
Isothermal segment	5 h, each at target temperature

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Measurement Results and Discussion

To determine the ideal curing temperature for the new resin system, the samples were heated at 5 K/min from room temperature to target temperatures of 180°C, 200°C, 210°C, and 220°C, respectively, and held isothermally for 5 h after reaching the temperature in order to analyze the possible increase in storage modulus during the holding time; see figure 2.

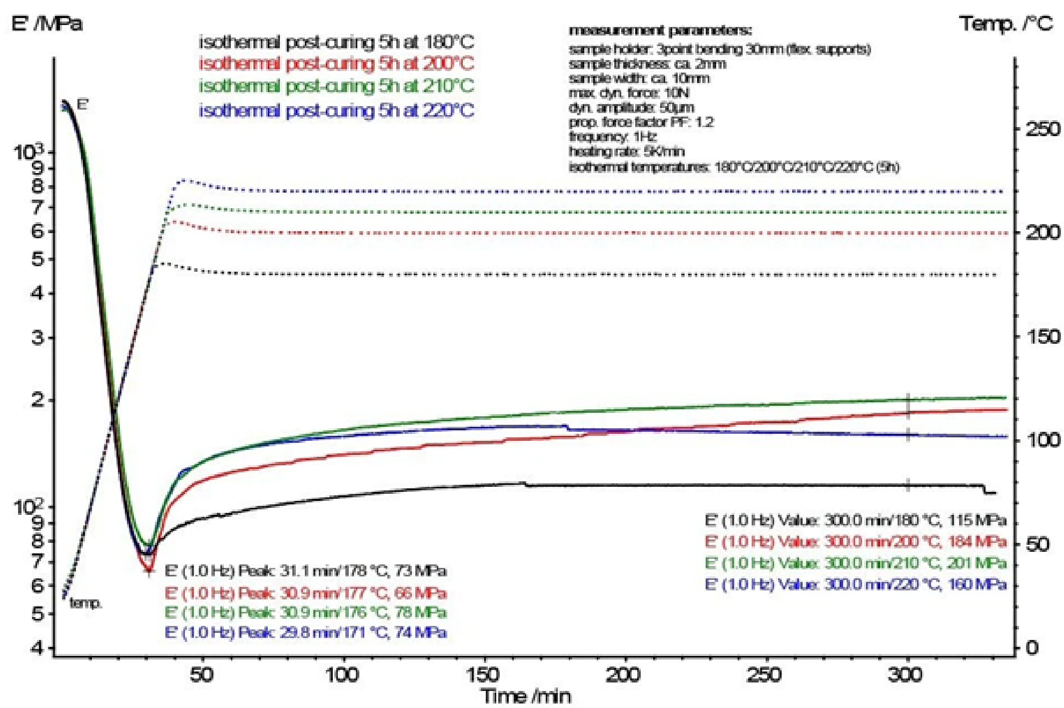
It can be seen that with increasing curing temperature (isothermal segments), higher modulus values can be achieved, and that the increase also takes place faster at higher temperatures. Only at 220°C (blue curve) does a negative effect appear. Following an initial increase in the modulus value, it begins to decline after approx. 80 minutes of the total measuring time, which is an indicator of embrittlement of the material. Thus, it can be assumed that at 220°C, material damage already occurs.

The achievable modulus values after 300 minutes show the considerable increase with temperature. However, this difference is not so significant between 200°C (red curve) and 210°C (green curve).

Kinetic Analysis of the Post-Curing Reaction

The Kinetics Neo software allows for the determination of the kinetic parameters of a chemical reaction. It also enables the prediction of the storage modulus from mechanical properties using dynamic mechanical analysis (DMA). Measurements for kinetic analysis are carried out at different isothermal temperatures and shown in figure 2.

Using these measurements, Kinetics Neo is capable of determining the number of steps describing the curing reaction. For each of those steps, the software also calculates the kinetic parameters, i.e., reaction type, activation energy and order of reaction.



2 Isothermal measurements of resins at different temperatures: 180°C, 200°C, 210°C, and 220°C.

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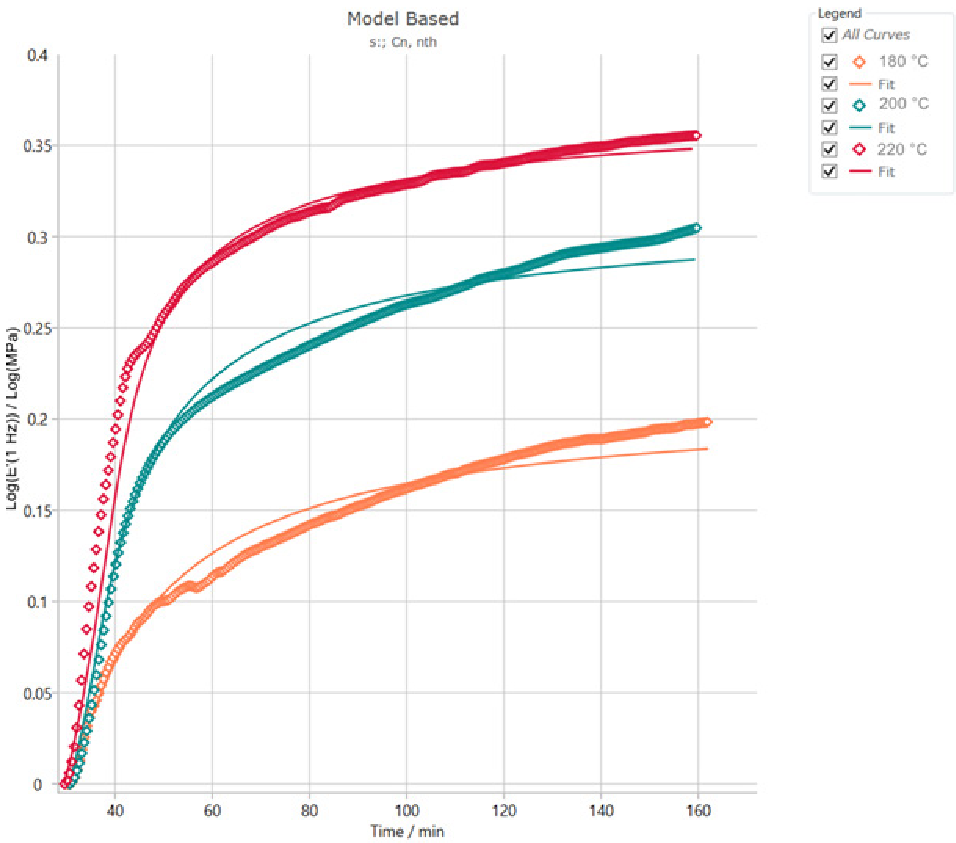
Figure 3 depicts the measurements carried out at different isothermal temperatures after baseline removal. A horizontal baseline is used starting from the point with minimal E'. Because the mechanical measurements already indicate a one-step reaction, a model with Cn, n^{th} order autocatalysis is selected for kinetic analysis.

Figure 3 displays the measured curves as symbols and the model fit as solid lines.

The model fit is calculated for the temperature used in the experiment by Kinetics Neo software. Table 2 depicts the optimal kinetic parameters used for the calculation. The deviation between the measured and calculated curves shows the differences in sample preparation. However, the high Coefficient of determination R^2 = 0.995 indicates strong agreement between the model and the experimental data.



3 Experimental data (symbols) and the model (solid lines) of the storage modulus for isothermal conditions at 180°C, 200°C, and 220°C.

Table 2 Kinetic parameters, calculated by Kinetics Neo

	Step 1 (Units)
Activation energy	50.319 (kJ/mol)
Log(PreExp)	2.591 log (s^{-1})
ReactOrder n	2.591
Log (AutocatPreexp)	0.01 log (s^{-1})
Contribution	1

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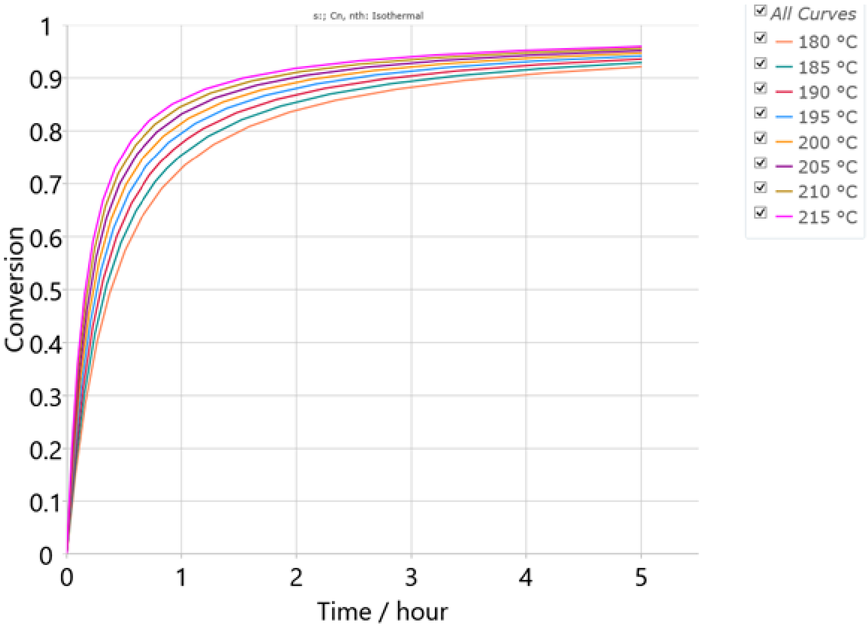
Simulation of Curing for User-Specific Conditions

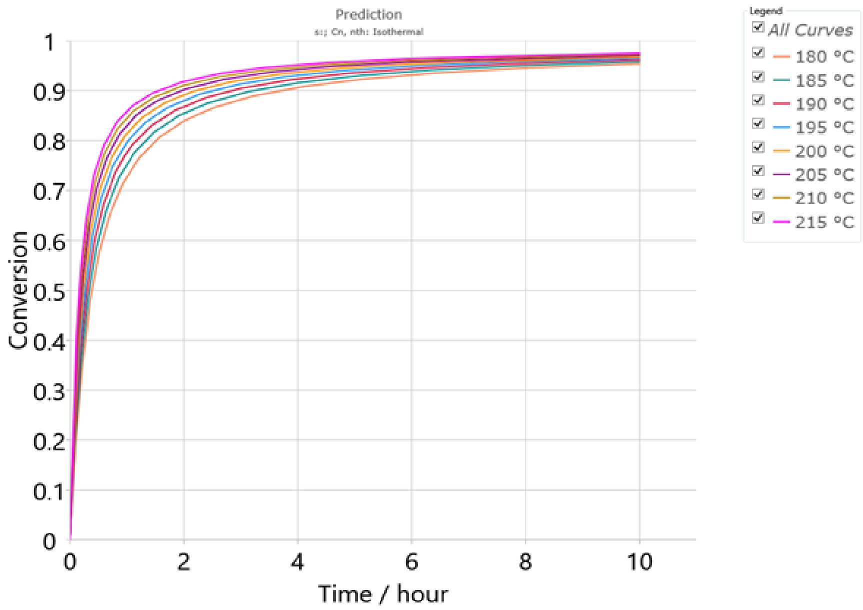
Based on the determined kinetics parameters, Kinetics Neo is capable of calculating the sample's behavior for any time/temperature condition, close to experimental temperatures.

As an example, figures 4 and 5 depict the degree of cure of the resin at different isothermal temperatures from 180°C to 215°C for 5 hours and 10 hours, respectively. As expected, curing occurs faster at higher temperatures.

A longer period is needed to ensure complete curing. For instance, after 5 hours, the degree of cure reaches 0.940, and over 16 hours, it reaches 0.972. Full curing may take several hours or days, depending on temperature.



4 Prediction of degree of cure of the resin for 5 hours at different temperatures.



5 Prediction of degree of cure of resin for 10 hours at different temperatures.

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Conclusion

The mechanical properties of a UV-cured resin system after thermal curing were evaluated using Dynamic Mechanical Analysis (DMA). Isothermal measurements were performed at different temperatures: 180°C, 200°C, 210°C, and 220°C. The data was analyzed using Kinetics Neo software, and a kinetics model was developed to predict the degree of cure. This model can be applied not only to the measured temperatures and durations but also to conditions that were not experimentally tested. As a result, it enables the identification of parameters that achieve a specific degree of cure in the shortest time or at the lowest temperature, depending on the optimization goal. This approach reduces the number of physical tests required, saving both time and costs, while accelerating the overall process for users.

Kinetic Analysis Benefits

Lower Experimental Costs

Kinetics Neo software reduces the need for numerous and costly physical trials by optimizing the number of tests required. This allows customers to save both time and money while speeding up their overall process.

Optimizing Curing Cycles

The software helps identify the optimal post-curing temperature and time to achieve the best material conversion. This ensures production efficiency, preventing issues like over- or under-post-curing.

Customization and Flexibility

Customers can adjust the curing process to meet specific application requirements, whether they need materials to be more flexible or more rigid. This flexibility ensures that the final product aligns perfectly with their needs, reducing the need for additional trials.

NGB · Application Note 339 · DE · 0125 · Technische Änderungen vorbehalten.

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