APPLICATION NOTE

UV-Curing Materials – DMA

Efficient Post-Curing of Coatings and 3D-Printed Components by Means of DMA

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General

UV-curing systems have found a place in various industries and applications due to their fast processability, precision in application and versatility. Some of the most important applications to date are:

- Printing industry: UV-curing inks and paints are widely used in the printing industry. They allow for fast drying and curing of inks on paper, cardboards, plastics and other printing substrates, which increases the production speed.
- Wood processing: UV-curing coatings are used in wood processing, particularly for furniture, flooring, furniture surfaces and finishes, and wood décor. They provide fast curing and high surface quality.
- Automotive industry: UV-curing paints and coatings are used in the automotive industry for painting plastic parts, interior components and dashboards. They offer fast curing and high surface quality.
- Electronics: UV-curing materials are used in the electronic industry for the production of printed circuit boards, displays, housings, switches and other electronic components. They offer precise dosage and application, and enable fast production.
- Medical technology: UV-curing materials are used in the production of medical devices, dental products, orthopedic appliances and other medical applications. They offer high precision and biocompatible properties.
- Optics and glasses: UV-curing materials are employed for eyeglass lenses, contact lenses and optical coatings. They offer fast curing, high transparency and scratch resistance.
- Aerospace: UV-curing coatings are applied in the aerospace industry for components, housings and surface applications. They offer light weight, durability and fast curing.
- Food packaging: UV-curing coatings are used in the food packaging industry to protect packing materials, improve durability and reduce moisture penetration.

In addition to these traditional areas, they have been widely used in Additive Manufacturing for several years. UV-curing resins form the basis for Vat Photopolymerization and Material Jetting processes, and are also employed in Binder Jetting. Here, too, the properties of fast curing are relevant for 3D-printing speed; the precision and fineness are relevant for resolution and achievable layer thickness; and the wide range of formulations allow for an almost infinite combination of material properties and materials

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In some applications, the properties of inks, coatings and 3D-printed parts can even be further enhanced by curing at elevated temperatures after UV-curing. This is sometimes useful for controlling the cure depth or improving properties:

- Thickness of the coating or print film: For thick layers of UV-curing materials, the UV light may not sufficiently penetrate to ensure complete curing. Thermal post-curing is required to achieve complete cure throughout the entire thickness.
- Material composition and degree of cross-linking: Some materials require thermal post cure to achieve sufficient cross-linking and polymerization. Post-curing helps complete incomplete reactions and improve material stability.
- Optimization of material properties. The combination of UV curing and thermal post-curing allows for optimization of specific material properties such as hardness, elasticity, impact strength and chemical resistance.

A good method for optimizing thermal post-curing with regard to mechanical properties is dynamic mechanical analysis (DMA). DMA analyzes the behavior of materials at varying temperatures, frequencies, and strain. In the following example, it was used to determine the ideal post-cure temperature in terms of time, cost and performance.

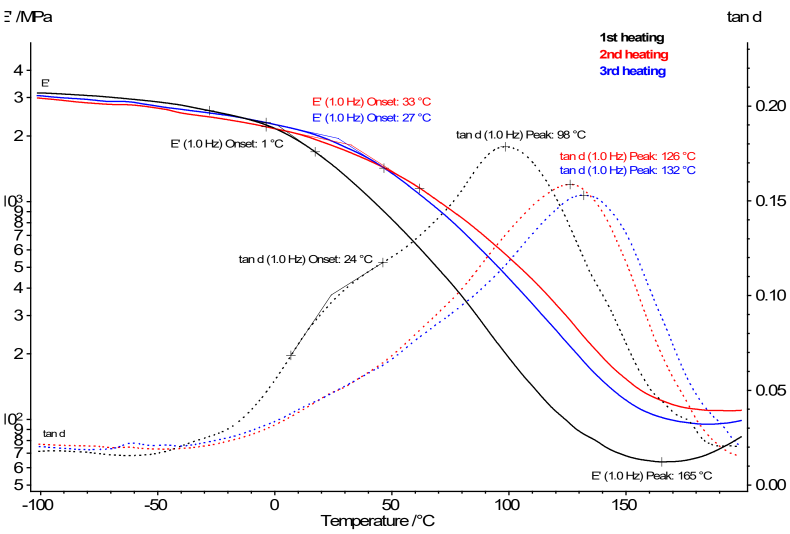
Measurement Parameter and Measurement Results

The resin system was developed by EZD for use as an ink or coating, or in additive manufacturing. The samples were produced using 3D-printing at EZD-SKZ and analyzed with a DMA 303 *Eplexor*®. The most important parameters are summarized in the following table

Table 1 Parameter of the the sample investigated

Sample holder	3-point bening, 30-mm flexible support
Sample thickness	Approx. 2 mm
Sample width	Approx. 10 mm
Maximal dynamic force	10 N
Dynamic amplitude	50 µm
Frequency	1 Hz

For an initial evaluation of the curing behavior and the mechanical behavior under the influence of temperature, a DMA measurement was performed from 100°C to 200°C at a heating rate of 2 K/min. After cooling, this cycle was repeated 2 more times on the same sample. The results are shown in figure 1. It can be seen that a difference in storage modulus occurs at temperatures above room temperature. The stiffness increases with increasing heating. In addition, the glass transition shifts to higher temperatures.



1 DMA measurement with 2 repetitions to analyze the storage modulus and tan d to determine the glass transition temperature.

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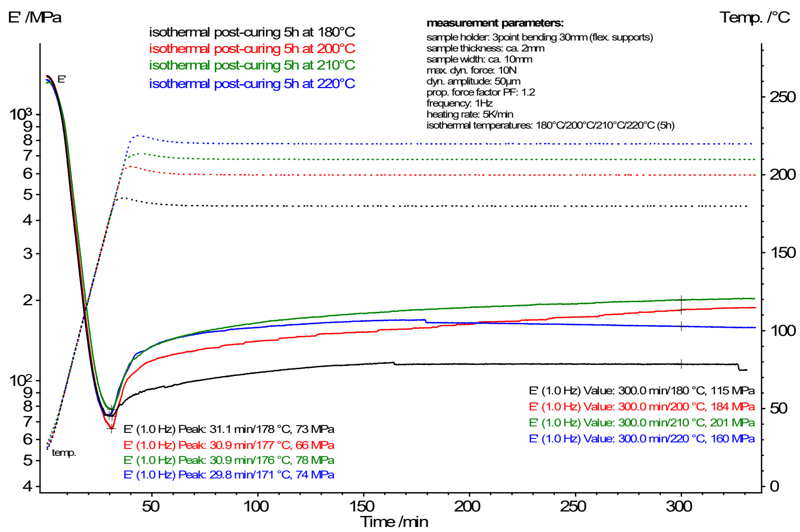
To determine the ideal curing temperature for the new resin system, the samples were heated at 5 K/min from room temperature to target temperatures of 180°C, 200°C, 210°C, and 220°C and held isothermally for 5 h after reaching the temperature to analyze the possible increase in storage modulus during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

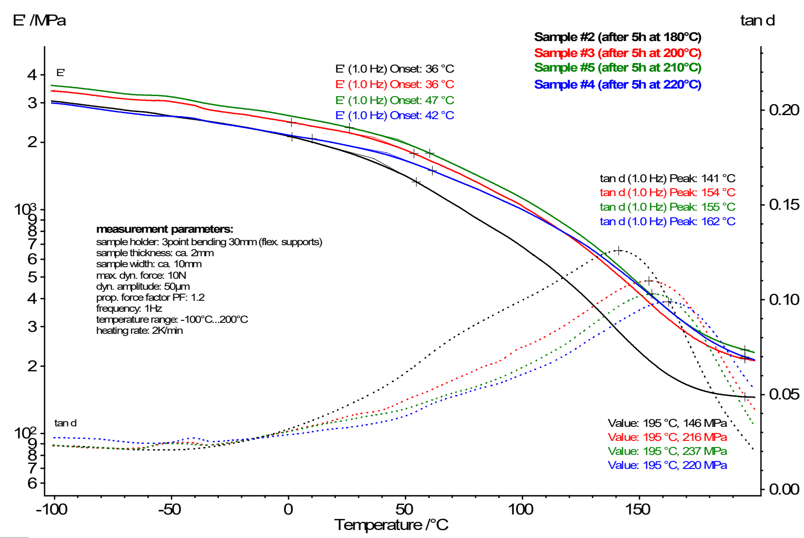
It can be seen that with increasing temperature, higher and higher modulus values can be achieved and that the increase takes place faster at higher temperatures. Only at 220°C does a negative effect appear. Following an initial increase of the modulus value, it begins to decline after approx. 80 minutes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

The achievable modulus values after 300 minutes show the considerable increase with temperature. However, this difference is no longer so large between 200°C and 210°C.

To evaluate the effect on the glass transition, all isothermally held samples are then dynamically heated from -100°C to 200°C at a heating rate of 2 K/min (figure 3).



2 Isothermal measurement on different samples at 180°C, 200°C, 210°C and 220°C



3 DMA measurement on post-cured samples, among others for determination of the T_g (peak of tan d)

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In order to be able to evaluate the effect on the glass transition, all samples held isothermally are subsequently heated dynamically from -100°C to 200°C at a heating rate of 2 K/min. The difference in the modulus values can now already be recognized at the beginning of the measurement at -100°C. It can also clearly be seen that the modulus value of the sample damaged at 220°C does not differ from the sample post-curing at 180°C. The peak of tan d, which corresponds to the glass transition (T_g) of the material, is shifted to higher values as holding temperature increases. It is also to be seen, however, that the differences increase less sharply following a post-curing at 200°C.

The results show that the highest modulus value and T_g can be achieved at a curing temperature of 210°C.

Depending on the frame conditions, different optimization decisions can now be derived:

1. In order to obtain the maximum modulus of 201 MPa, curing must be performed at 210°C for 300 min.
2. If, for example, a modulus value of 150 MPa is sufficient, this will be reached at 200°C after 160 minutes and at 210°C after 70 minutes. Depending on the furnace technology, it can be assumed that it is more energy efficient (+ time and costs) to achieve the same results in 90 minutes less at 210°C.
3. If a certain glass transition value is required, e.g., > 150°C, a curing temperature of 200°C may already be sufficient. Further isothermal hold times should be used to check whether the same T_g can also be achieved faster at higher temperatures.

Summary

This example is intended to show that depending on the target value of performance (modulus or T_g), time, cost, or energy efficiency, a few DMA measurements are usually sufficient to narrow down the result space and then verify the achievement of the target values with one to two confirmation measurements.

Therefore, DMA can be used to optimize the thermal curing of UV-curing inks, coatings and 3D-printing resins. Depending on the target value, other methods such as our UV-DSC, UV coupling on the Kinexus rotational rheometer, or UV-DEA can be employed to optimize UV curing.

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