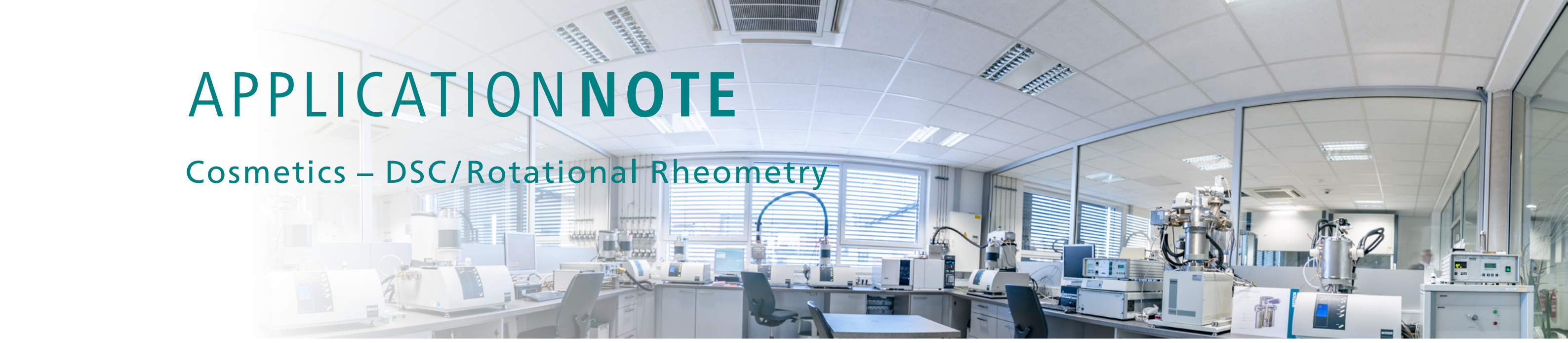

APPLICATION**NOTE**

Cosmetics – DSC/Rotational Rheometry

Thermal and Rheological Characterization of Nail Gel Curing

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Introduction

From transparent to black, including all the colors of the rainbow, the market of nail gels (those that cure) and nail polishes (those that air dry) offers a wide variety of products. Even if the first selection criteria is often an aesthetic one, the consumer also wants a product that is practical to apply giving the desired finish and performance. For that, the perfect nail gel or polish should feel relatively liquid for an easy brush application but without flowing outside the nail. The drying or curing time should be as low as possible and lead to a smooth surface for a flawless appearance. Finally, it is also desirable for the manicure to be long-lasting, without it being too difficult to remove.

Some types of nail gels require a UV-lamp for curing. These products contain a photo-initiator that will initiate the curing reaction as soon as the gel is in contact with the suitable wavelengths emitted by the lamp.

The exposure time, the wavelength and the intensity of the lamp is of great importance for the nail gel to cure in the correct way.

Experimental

The UV curing of three nail gels was characterized by two different methods:

- Differential scanning calorimetry (DSC): used to obtain information about the speed and the time of curing.
- Rotational rheometry to characterize the modulus change of the nail gel during UV exposure.

The sample colors were red, black and clear. The clear sample contained suspended glitters.

Table 1 summarizes the conditions under which the three different samples were tested.

Table 1 Measurement Conditions

DSC	Device	DSC 300 *Caliris*® with H-Module
	Sample mass	3.0 mg
	Crucible	*Concavus*® (aluminum, open)
	Temperature	30°C (isothermal)
	Atmosphere	Nitrogen (20 ml/min)
	Lamp	Omnicure® S 2000 (wavelength range: 320 to 500 nm)
	Exposure duration	180 s
Rotational Rheometry	Device	Kinexus
	Geometry	PP8 (Plate/Plate, diameter: 8 mm)
	Gap	250 µm
	Temperature	25°C
	Atmosphere	Ambient (air)
	Lamp	Omnicure® S 2000 (wavelength range: 320 to 500 nm)
	Exposure duration	30 s

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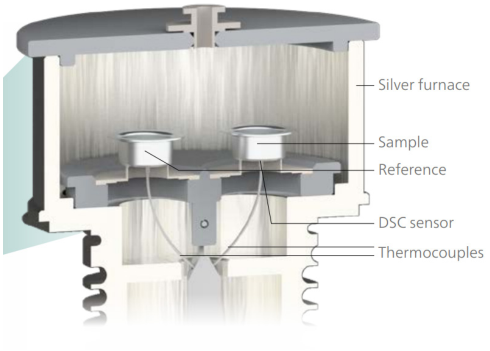


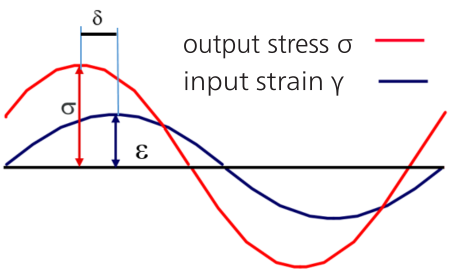
DSC – Functional Principle

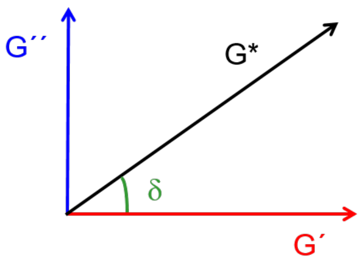
Based on ISO 11357, heat-flux DSC is a technique in which the difference between the heat flow rate into a sample crucible and that into a reference crucible is determined as a function of temperature and/or time. During such a measurement, the sample and reference are subjected to the same controlled temperature/time program and atmosphere.

Rotational Rheometry (Oscillation Measurement) – Functional Principle

The upper plate oscillates with a defined frequency f [Hz] (or ω [rad/s]) and amplitude [%] (or shear strain γ [%]), $\gamma = \gamma_o + \sin(\omega t)$.
The shear stress σ [Pa] required for this oscillation is determined: $\sigma = \sigma_0 + \sin(\omega t+\delta)$.

Result: The viscoelastic properties of the sample are determined, in particular its complex stiffness G* (|G*| in [Pa]). The "in-phase" part of G* is related to the elastic properties (→ G', storage shear modulus), the "out-phase" part to the viscous properties (→ G'', loss shear modulus) of the viscoelastic material.





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Thermal Analysis and Speed of Curing

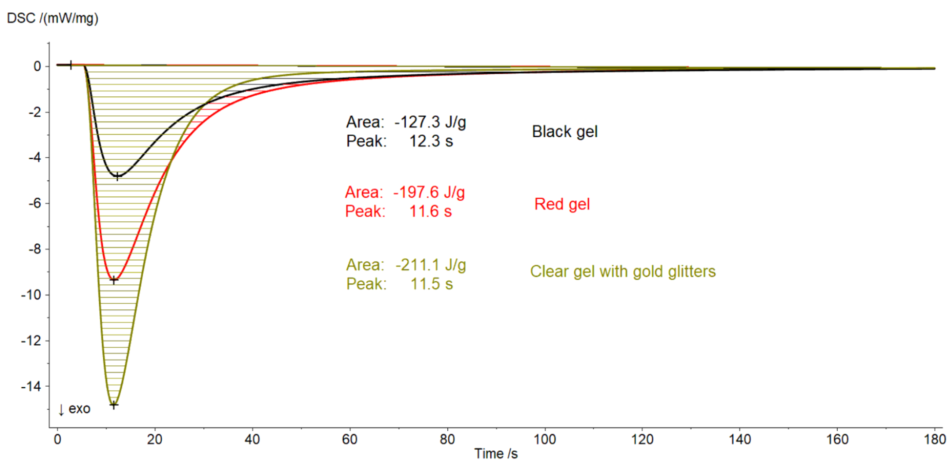
Curing effects can be observed in the DSC curves in the form of exothermic effects. The curing reaction can be initiated either by heat or by UV light, when using a DSC equipped with a UV-lamp (photo-DSC).

Figure 1 depicts the photo-DSC-curves obtained during UV exposure of the three nail gels. The peak area represents the curing enthalpy. The higher the value, the more energy is released during the reaction.

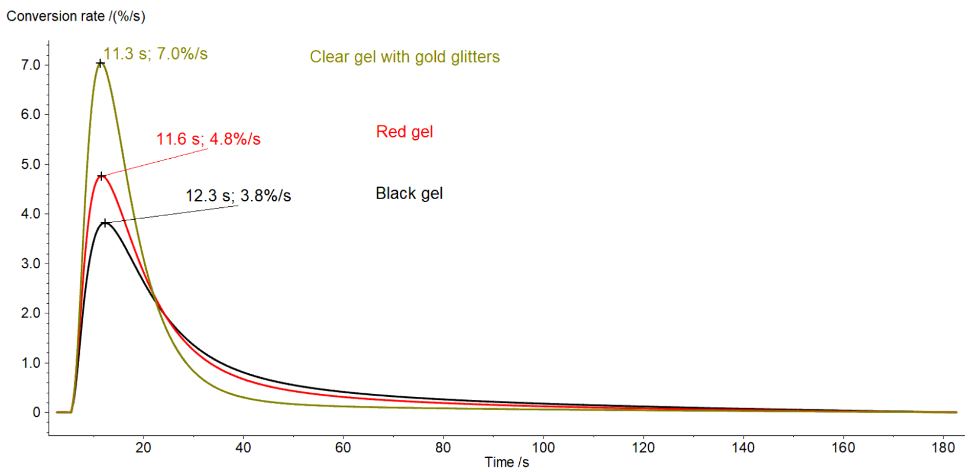
The clear sample containing glitters has the curing peak with the highest reaction enthalpy (211 J/g). That does not mean that it needs more time than the other two to finish the reaction. Actually, it is also the one that reacts most rapidly, as demonstrated by the slope of the curve before the peak maximum is reached: It is the steepest for this material. Figure 2, which depicts the conversion rate for all three samples, illustrates this result. The higher the peak maximum value and the steeper the slope before the peak maximum, the faster the conversion rate. Consequently, curing is fastest for the clear sample with glitters (peak maximum already reached at 11.5 s after exposure to UV light and associated with the highest conversion rate of 7.0%/s).

In contrast, the black sample exhibits the opposite behavior. The reaction is the slowest (a more gradual slope of the curve before peak maximum, leading to a conversion rate curve with peak maximum of 3.8%/s at 12.3 s) and is associated with the lowest energy release (127 J/g).

The red nail gel shows a curing behavior between the other two, both for the reaction speed and the curing enthalpy.



1 DSC curve resulting from UV curing of the nail gels



2 Conversion rate of the curing for the three nail gels

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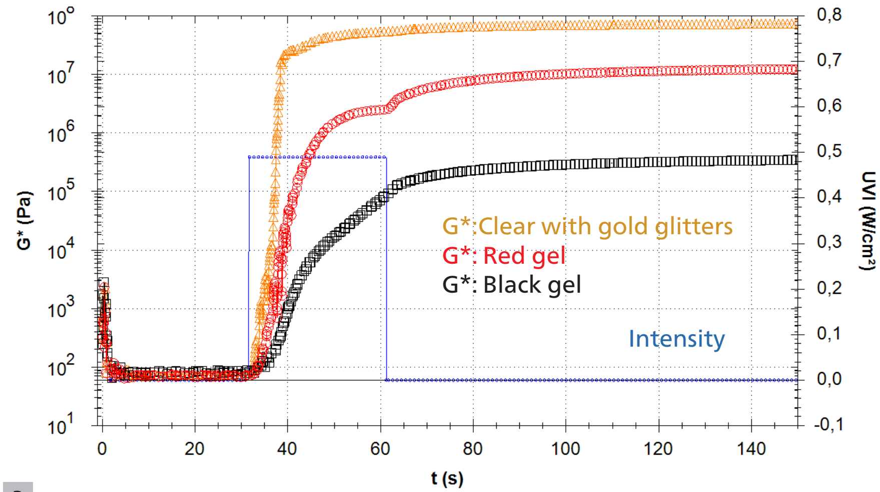
Figure 3 displays the complex modulus curves for all three samples. Before curing, all samples possess a similar stiffness of 70 - 80 Pa. The significant increase in modulus indicates curing has started. Similar to DSC, the slope of the curve is related to the reaction speed. The results correlate to those obtained with DSC: The clear nail gel with glitters cures fastest and the black sample shows the slowest curing of the three samples.

The samples differ also in their final modulus. The modulus of the clear gel with glitters increases by 6 decades during curing, vs. less than 4 decades for the black gel. This means that the clear gel reveals the highest stiffness after curing.

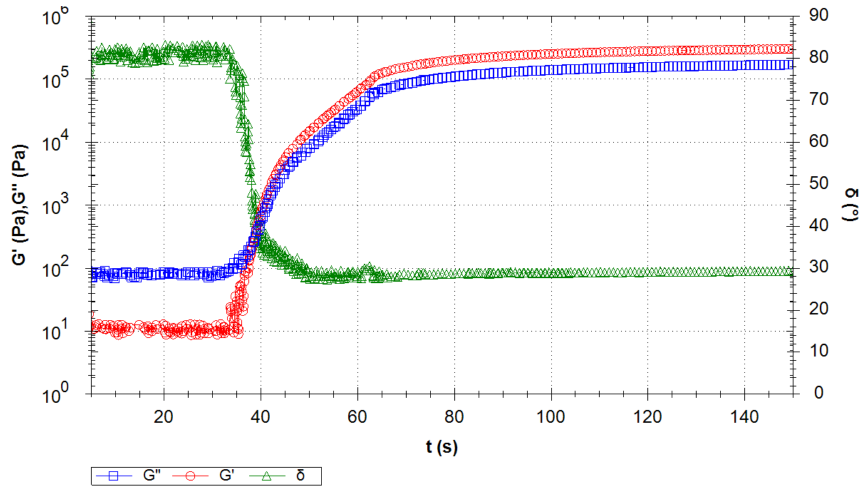
Additionally, Figure 4 shows the curves of G', G'' and δ during the curing process under UV-light of the black sample. At the beginning of the measurement, the viscous shear modulus (G", blue) is higher than the elastic shear modulus (G', red). The phase angle is high (more than 80°). This means that under these measurement conditions, prior to curing, the nail gel behaves almost like a perfect viscous liquid with only very weak elastic properties.

The curing reaction leads to an increase of both G' and G''. They crossover 7 seconds after UV exposure. In practice, the crossover means that from this time, the network built through curing is strong enough to prevent flow of the material on the time scale corresponding to 1 Hz.

At the end of the measurement, the curves of G' and G" are still increasing, even if this rise is not significant. The exposure to UV-light initiated a curing process that is able to continue despite the lamp being switched off.



3 Complex modulus of the three different nail gels



4 Curves of elastic, viscous shear modulus and phase angle obtained during UV-curing of the black nail gel

Phase Angle

The phase angle δ (δ = G''/G') is a relative measure of the viscous and elastic properties of a material. It ranges from 0° for a fully elastic material to 90° for a fully viscous material.

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Does a High Curing Speed Make the Sample Better?

A faster cure is advantageous for the consumer. However, the final properties of the manicure after application are of course also important. A post-cure amplitude sweep helps us predict the behavior of the gels after curing by providing information about their inner structure.

For that, the linear-viscoelastic region of the two extreme samples (clear with glitters and black) are compared in Figure 5.

The LVER-plateau of the black nail gel is wider with a lower modulus than that of the clear sample, indicating that the cured black gel is likely to be more flexible.

LVER – Linear Viscoelastic Region

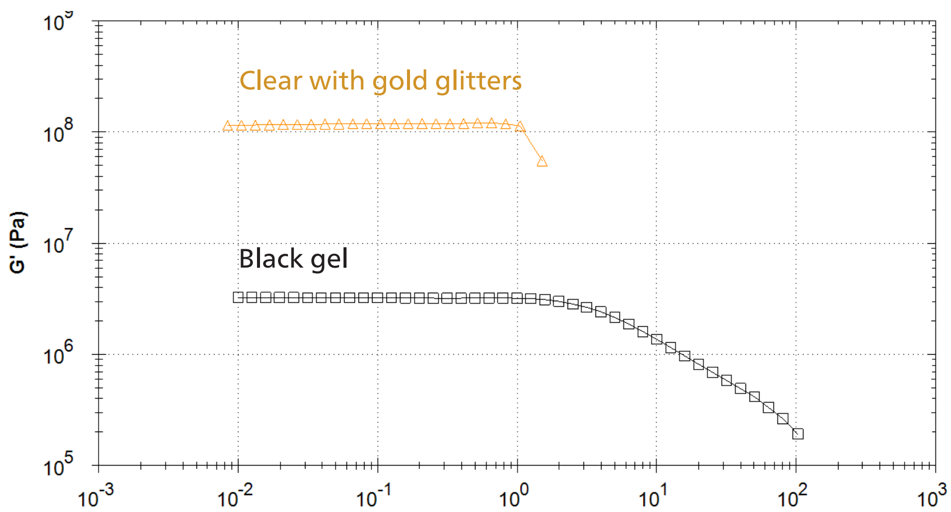
- The LVER is the amplitude range where strain and stress are proportional.
- In the LVER, the applied stresses (or strains) are insufficient to cause structural breakdown of the structure and hence, microstructural properties are being measured.

Even if the clear nail gels cures faster than the black one, it will also exhibit more brittle properties.

Conclusion

DSC and rotational rheometry are two complementary methods for the characterization of the curing of nail gels.

Both methods highlight the curing speed. The DSC 300 *Caliris*® additionally provides information about the energy released during curing, while measurements with the Kinexus compare the properties of the different products during and after curing.



5 Post-curing amplitude sweep of the black and clear nail gels

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