JULY/AUGUST 2009

RadTech Report

RADTECH INTERNATIONAL NORTH AMERICA www.radtech.org

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Prsrt Std
US Postage Paid
Cincinnati OH
Permit No 7312

The Effect of UV Intensity on the Cure Profiles of Developing Networks

A Case Study for Determining Optimized UV Curing Intensity

By Dr. Tien T. Dao, Nick Roye, Dr. Kaj Hedman and Dr. Peyman Dehkordi

UV radiation is successfully used for many photocuring applications. Determination and optimization of UV radiation is an important aspect of UV curing as it impacts material formulation, production equipment and production cost. Therefore, optical radiation parameters should be considered with the material formulation and characterization during the research and development (R&D) phase. Accurate rheological measurements have become essential in characterizing materials within analytical labs as they can quickly and accurately set and control processing conditions, optimize material performance, and/or assure material acceptance. This article looks into the impact of UV radiation intensity on the cure profiles of developing networks for a clear, colorless and low-viscosity fiber optic coating. Utilizing rheological measurements, various UV curing process conditions are experimented and an optimized UV curing setting is identified while the final material properties and performance are predicted. The rheological results, material description, optimization procedure and equipments are also described in this article.

Accurate rheological measurements have become essential in characterizing materials within analytical labs as they can quickly and accurately set and control processing conditions, optimize material performance, and/or assure material acceptance.

Material scientists and photochemists are constantly challenged to formulate and evaluate new photocured material, while optimizing product performance. The photocuring process is a function of a few important parameters such as wavelength, intensity, exposure time, etc. The optical radiation intensity is a vital photocuring parameter. The optimum intensity level should be identified in conjunction with material property and cure cycle time during the formulation and characterization phase. Dehkordi *et al.* describes how the UV curing parameters developed during the R&D phase also impact the production cycle of these products and, subsequently, the production equipment and related cost.[1] Therefore, the photocuring intensity has to be carefully evaluated and optimized for most optimum material performance, equipment cost and production cost.

Rheology is defined as the study of the flow and deformation of fluids. Accurate rheological measurements have become essential in characterizing materials within analytical labs. Scientists utilize rheological measurements on new materials to identify the process

Figure 1

The AccuCure Programmable UV Curing System

The AccuCure programmable UV curing system.

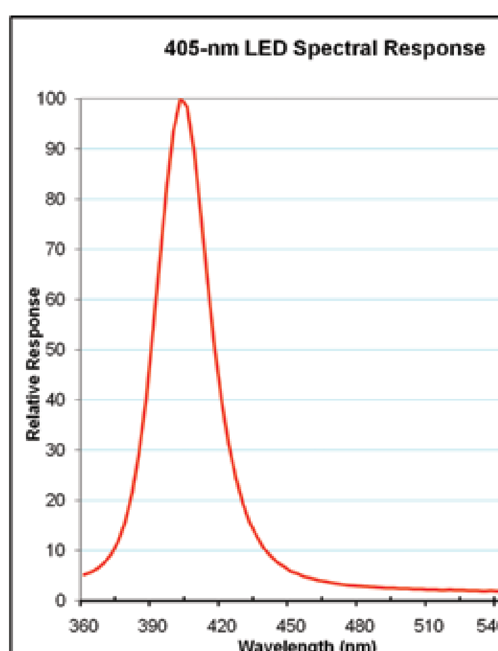
The AccuCure LED head mounted directly beneath the sample on the NOVA Rheometer.

conditions and to determine and predict final product properties and performance. Accurate measurement and monitoring of rheological properties of materials undergoing cure present a challenging and intriguing problem. Zhang *et al.* explain that this is due to several factors, including the kinetics of the reactions, building of the structure and heat transfer considerations.[2] The kinetics can have a significant effect due to the time scale at which these systems undergo the curing process. The development of structure or the evolution of a networked system, which in turn can lead to shrinkage or expansion and/or other changes in the physical appearance of the sample, can present several difficulties in measuring the rheological properties accurately. The ability to measure and fully understand these phenomena becomes a requirement within the industry to accurately characterize and/or to identify the process conditions of these materials. Accurate rheological properties measurements can help to optimize both the design and the process. This design and optimization leads to flow models which allow a user who knows the rheological properties of the systems to predict the final properties of their product.

The development of network systems has been discussed previously by many authors including Colo *et al.* and Herh *et al.*, in which they described the effect of the development of these networks during both thermal curing and curing via ultraviolet (UV) radiation.[3,4] Specifically studied was (1) the effect of shrinkage and (2) how rheometers can be used to probe the thermal transitions, including the final cure time and the shrinkage (or change in shape) during ultraviolet radiation. This article expands the study by Colo *et al.* by adding the effect of varying the UV

Figure 2

Typical spectrum for a 405-nm AccuCure programmable UV curing system



optical radiation using a new style LED source with programmable intensity.[3]

Instruments

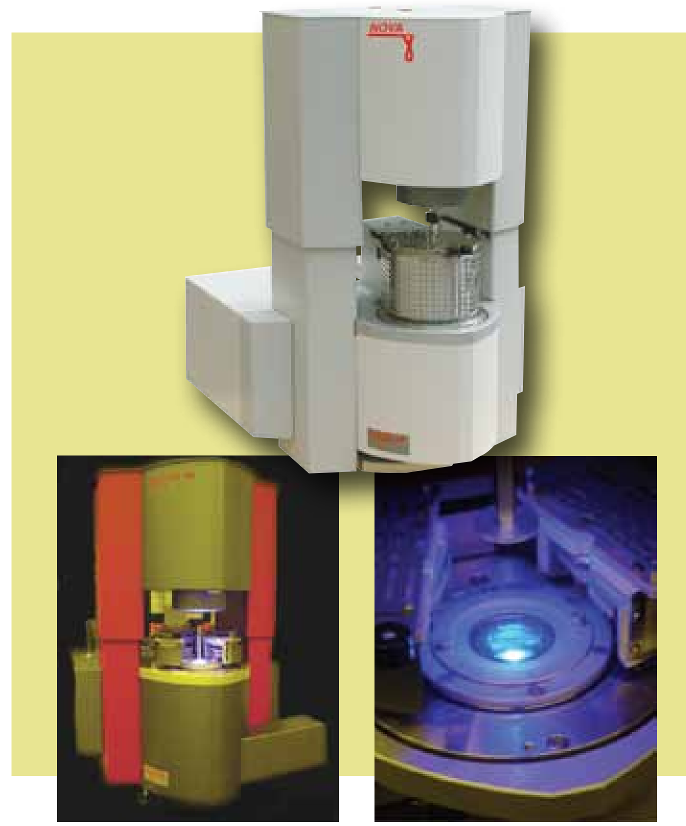
There are two instruments used to experiment and to measure the real-time rheological properties during UV curing—a Rheometer and a UV curing lighting system. The NOVA Rotational Rheometer is manufactured by REOLOGICA Instruments and the UV curing is the AccuCure system manufactured by Digital Light Lab. Together, they provide a complete turnkey solution for photo-rheology type measurements. Figure 1 shows a 405-nm AccuCure UV curing system.

The system enables the users to set the intensity in radiometric units (i.e., 0.0 to 100.0 mW/cm²) via the AccuCure software. The AccuCure system is based on LED technology providing a narrow-bandwidth optical energy with various selectable wavelength of interest ranging from UV to visible. For example, a typical 405-nm AccuCure system has a peak wavelength of 405-nm +/-5-nm with full-width-half-max (FWHM) of 15 nm as shown in Figure 2.

Figure 3 shows the NOVA Rheometer for the UV curing experiments and the AccuCure LED head is attached to the rheometer directly beneath the test sample (no light guide is required). The AccuCure system empowers the users to set the UV intensity incident on the sample, in radiometric unit (i.e., mW/cm²). The intensity level and exposure profile are set through the AccuCure software, and the actual UV intensity is monitored in the LED head and adjusted in real time to match the pre-programmed values. A proprietary "Fast Oscillation" data acquisition algorithm was used by the NOVA Rheometer to collect data at rates in excess of 500 points per second.

Figure 3

NOVA Rheometer (top) and Rheometer integrated with AccuCure UV System (bottom)



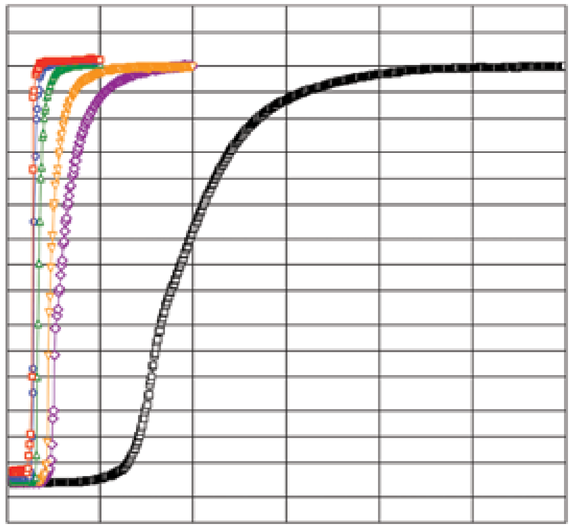
Ultraviolet Curing Experiments

For this case study, a clear and colorless, low-viscosity fiber optic coating sample with photoinitiator centered on a wavelength of 405 nm was used. The effect of different UV radiation intensities on the cure profile was investigated. The fiber optics coating sample was tested at a constant gap and temperature to study the effect of intensity. For this study, UV curing intensities of 1.0, 5.0, 10.0, 25.0, 50.0, and 100.0 mW/cm² were investigated. For all experiments shown, the UV source was activated four seconds into the experiment so a "no exposure" baseline could be obtained. The sample was clear and colorless so it would not hinder the transmittance of the UV light through the sample.

For all experiments, the sample was placed on the lower plate at room temperature and the gap was set to 0.300 mm. The "expert condition" setting within the RheoExplorer software package was used to control the gap during the experiment. The auto-tension feature was turned on once the phase angle of the sample reached a value below 45°. A phase angle of 45° was selected because the sample does not undergo consolidation until the gel point is reached. If the shrinkage is not accounted for in real time during the experiment, unwanted stresses can be built up in the sample and delamination from the plates may occur.

Figure 4

Curing profile with a 405-nm UV LED source at various intensities



P 25 ETC Gap 0.300 mm
Manual control
Frequency 1.000E+0 Hz FFT size 256
Stress=1.000E+02 + (1.000E+03 – 1.000E+02) / (1+exp((5.500E+00 – Time) /

Ultraviolet Curing Results

The cure profiles for all different intensities are shown in Figure 4. Interestingly, there is a significant difference between the intensity of 1.0 mW/cm^2 and all the other intensities. For the intensity of 1.0 mW/cm^2, the material was exposed for over 20 seconds before any noticeable curing had taken place. Also, the time to fully cure at 1.0 mW/cm^2 experiment is approximately 100 seconds. This is significantly longer than all other investigated parameters. The results suggest a UV intensity of 1.0 mW/cm^2 is not recommended for this sample.

The data are re-plotted on a shorter time scale in Figure 5 to highlight the differences for the higher intensities. The results suggest that as the intensity increases, the curing process initiation time decreases, as well as the time to a fully cured state. There is also a small difference between the curing profiles for the intensities of 50.0 and 100.0 mW/cm^2. Therefore, it can be concluded that the optimum intensity required to fully cure this material is 50.0 mW/cm^2. Any value greater does not produce a beneficial effect while it would increase the production equipment cost and complexity.

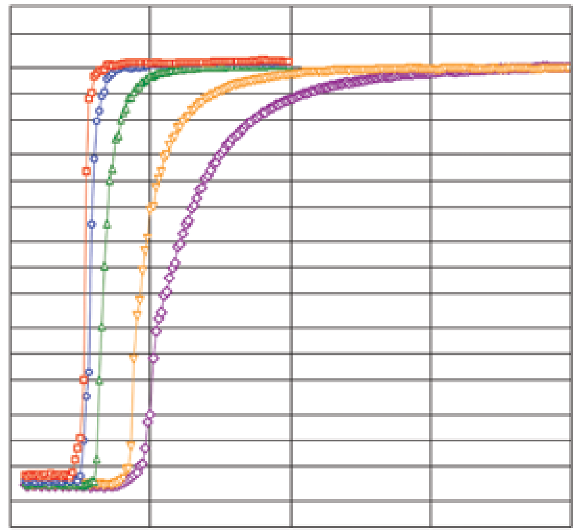
To further illustrate the effect of the intensity of the radiation on the curing time of this material, Figure 6 plots the time for the curing specimen to reach a viscosity of 180,000 Pa*s versus the intensity of the ultraviolet radiation used. There is a significant difference with small changes in the intensity at the low range with the time to reach a viscosity of 180,000 Pa*s approaching infinity as the intensity goes to zero. (See figure 6) Above an intensity of 50 mW/cm^2, there is negligible change in time to reach a viscosity of 180,000 Pa*s.

Conclusion

Significant differences in UV cure profile were observed for a fiber

Figure 5

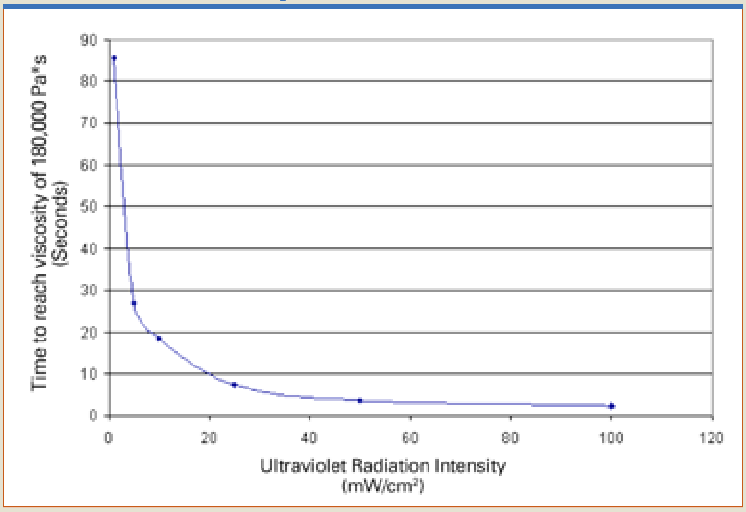
Curing profile with a 405-nm UV LED source at various intensities on a shorter time scale



P 25 ETC Gap 0.300 mm
Manual control
Frequency 1.000E+0 Hz FFT size 256
Stress=1.000E+02 + (1.000E+03 – 1.000E+02) / (1+exp((5.500E+00 – Time) /

Figure 6

Time to reach a viscosity of 180,000 (Pa S) as a function of intensity



optic coating sample exposed to UV radiation from a programmable UV LED source. An intensity of 1.0 mW/cm^2 showed poor cure characteristics when compared to intensities of 5.0 mW/cm^2 and higher. Also, there was no significant difference between 50.0 and 100.0 mW/cm^2, suggesting 50.0 mW/cm^2 is the optimum UV curing intensity for this material.

References

1. Dehkordi, Peyman; "Photo Curing Equipment Challenges: Medical Device Manufacture's Point of View," *RadTech Report,* pg. 47, November/December 2008.
2. Zhang, X.D.; Giles, D.W.; Barocas, V.H.; Yasunaga, K.; and Macosko, C.W.; "Measurement of Foam Modulus via a Vane Rheometer," *Journal of Rheology,* v. 42, pg. 871, July/August 1998.
3. Colo, Steven M.; Herh, Peter K.W.; Klein, Fred; and Hedman, Kaj; "Fast Oscillation Rheological Data Analysis for Real-Time Cure Profiling and Shrinkage Determination of Developing Network Systems," *American Laboratory,* pg. 14, June 2004.
4. Herh, Peter K.W.; Colo, Steven M.; Enns, John; Roye, Nick; and Hedman, Kaj; "Rheology of developing network systems: New techniques, capabilities, and instruments," *American Laboratory News,* June 2001.

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