UV Curing Analysis Using A Rheometer

Keywords: UV Curing, kinetics, gel point, coatings, adhesives, inks

RH032

ABSTRACT

UV-curable materials are widely used for coatings, adhesives, and inks. When these materials are exposed to UV radiation, a fast crosslinking reaction occurs, typically within less than a second to a few minutes. TA Instruments has introduced two types of UV accessories for the study of the rheological behavior of materials undergoing fast UV curing reactions. One accessory uses a light guide and a reflecting mirror assembly to transfer UV radiation from an external light source, an EXFO Omnicure S2000 equipped with a high-pressure mercury lamp. This light guide system provides a broad wavelength spectrum from 220 nm to 600 nm, with a primary peak at 365 nm. Filters can be used to cut off certain wavelength range in specific applications. A second type of accessory uses self-contained light emitting diodes (LEDs). There are two LED systems currently available. These systems provide a single band wavelength at 365 nm or 455 nm, respectively. Both light guide and LED systems can be configured with temperature control to a maximum temperature of 150 °C. Accurate and reproducible monitoring of rapid curing reactions are possible using fast data acquisition.

INTRODUCTION

The UV curing reaction is a free radical initiated crosslinking reaction. Under appropriate ultraviolet radiation, free radicals are generated, and the crosslinking reaction can occur in as quickly as less than one second to as long as a few minutes [1-6]. Most curable materials, such as acrylic adhesives, coatings, and inks, start as low to medium viscosity fluids. Upon being irradiated, they undergo either partial or full curing. The mechanical properties of the materials (G′, G″ and viscosity) can increase by over six to seven decades in magnitude. A rotational rheometer is commonly used to monitor this kind of curing process and measure the modulus change of the material. In this paper, two types of UV curing accessories on TA Instruments' rheometers (AR/DHR and ARES-G2) are introduced. The light guide accessory uses a high-pressure mercury lamp as the UV light source, which provides a broad wavelength range from 220 nm to 600 nm. The LED accessory uses an array of light emitting diodes, which provides a single wavelength band. Both accessories can be used with a temperature control unit. Fast data acquisition is built into the instrument control software, which allows collecting more data points to capturing rapid reactions. The performances of these accessories have been evaluated using a UV curable adhesive and an ink material. The influences of UV light intensity, temperature and normal stress on the curing reactions are discussed in detail.

UV Light Guide Accessory

The UV light guide accessory uses an external high-pressure mercury lamp as the UV light source. Figure 1 shows a picture of the EXFO Omnicure Model S2000 light source. The EXFO Omnicure provides a broad range spectrum of wavelengths from 220 nm to 600 nm. UV filters are available from EXFO, which allow users to adjust the wavelength range for each particular application. An event cable is connected from the light source to the rheometer, enabling the rheology software to trigger it on and off.

Figure 1: EXFO Omnicure S2000, the external light source for UV light guide accessory.

Figure 2 shows the light guide accessory used on a AR/DHR model rheometer. Light is transferred from Omnicure to the bottom geometry stage through a 5mm diameter light guide. Then it was focused by a collimator onto a mirror and redirected to a 20 mm quartz (or disposable acrylic) plate where the sample resides. The optical devices are all pre-aligned to ensure uniform irradiance across the surface of the plate (shown in figure 3).

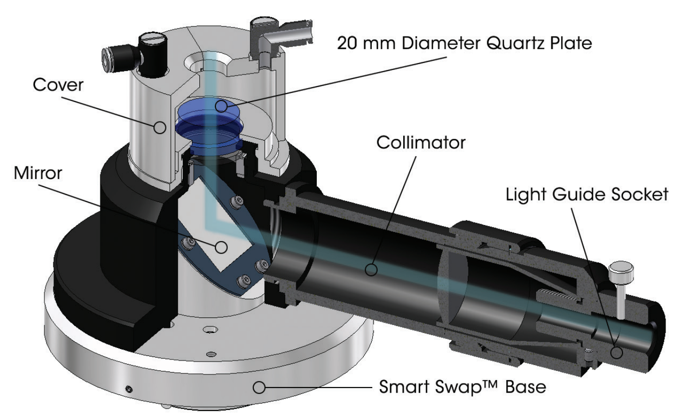

Figure 2. The UV Light Guide Accessory on AR/DHR Rheometer.

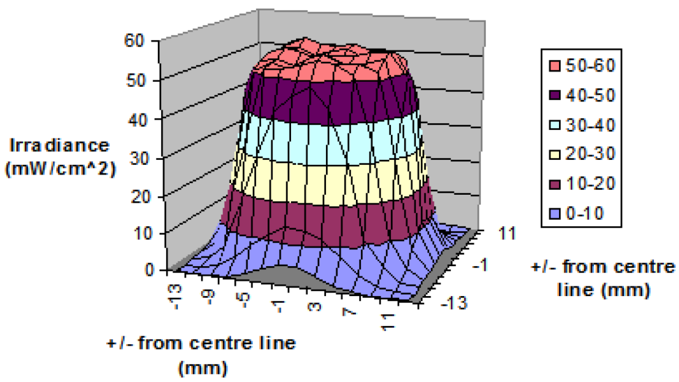

Figure 3: Irradiance distributions across 20 mm plate.

Figure 4 shows the picture of the light guide accessory used on an ARES-G2 rheometer. The UV light passes through the light guide, the collimator and then reflected onto the 20mm upper plate by a mirror built into the test fixture. The output UV intensity can be calibrated using an external UV radiometer. The UV light shield box is installed to protect the operator from UV light exposure.

Figure 4. The light guide UV accessory on the ARES-G2 rheometer.

<u>UV LED Accessory</u>

The UV LED accessory is available on AR/DHR rheometers. It uses an array of light emitting diodes (shown in Figure 5) to provide a single band wavelength UV light source. The LED array is mounted on a printed circuit board (PCB) that is fixed to a water jacket to cool the LED array. Similar to the UV light guide system, the LED's are pre- aligned to ensure uniform irradiance across the surface of the plate. Two LED accessories are available at wavelengths of 365 nm and 455 nm. These LED accessories are fully integrated with the rheometer through the smart swap connection. The users can easily program a trigger time and intensity through the rheology software.

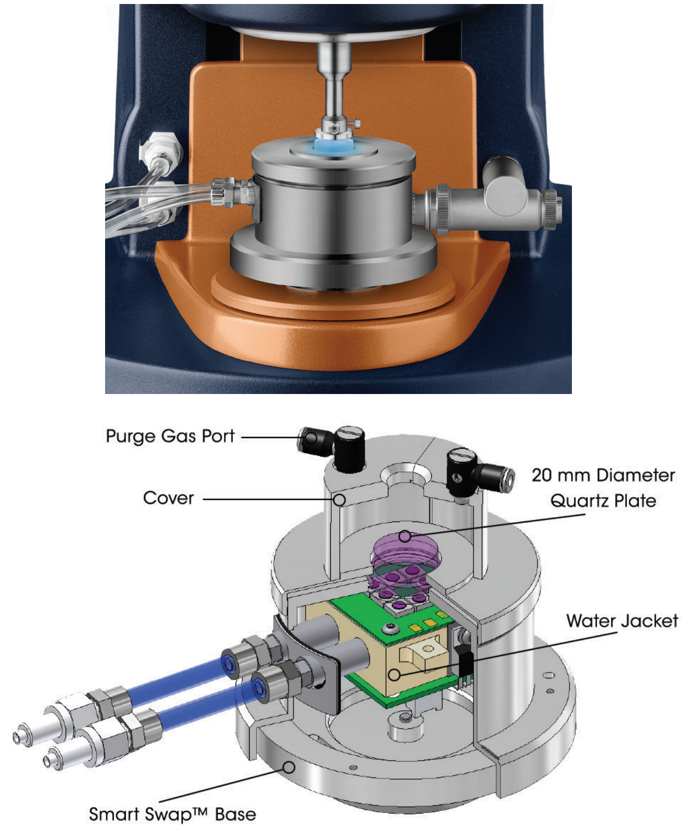

Figure 5: The UV LED accessory on AR/DHR rheometer.

EXPERIMENTAL

Two UV curable pressure sensitive adhesive samples (adhesive A and adhesive B) were analyzed using the two UV curing accessories on DHR rheometer. The UV output intensities were calibrated at the sample position using an external radiometer. For the light guide accessory, the intensity was recorded as total intensity (from 250 nm to 600 nm) without any filter. The bottom geometry was a 20 mm disposable acrylic plate and the top geometry was a 20 mm disposable aluminum plate. Dynamic time sweep experiments were used to monitor the curing process. Fast data acquisition was enabled, which allowed a data collection rate of up to 50 data points per second.

To evaluate the influence of UV intensity on curing, adhesive A was loaded on the 20 mm disposable plate with a geometry gap of 0.5 mm. An isothermal time sweep was performed at a frequency of 10 Hz and a strain of 0.5% with the fast data sampling enabled. The UV light was triggered on 30 seconds after oscillation had begun to establish an adequate baseline. UV intensity was set to 50 mW/cm^2, 100 mW/cm^2 and 150 mW/cm^2, respectively. The exposure time for all measurements was set to 30 seconds. After the light was triggered off, measurements were continued for another 60 seconds before the test was terminated.

To measure the temperature effect on curing, the TA Instruments' electrically heated upper plate (EHP) was used for temperature control. If the disposable acrylic geometry is used, the recommended maximum test temperature is 50 °C.

However, if the nondisposable quartz geometry is used, the maximum temperature can be as high as 150 °C. Dynamic time sweep tests were performed at temperatures of 25 °C and 50 °C using both light guide and LED accessories. The sample (adhesive A) was pre-measured in oscillation for 30 seconds before being exposed to the UV radiation. The UV intensity was set to 100 mW/cm^2. The exposure time for each measurement was 30 seconds and the total measurement time was set to 120 seconds.

Most polymers shrink during curing. The normal force transducer on the DHR rheometer is capable of accurately measuring sample shrinkage during curing. To monitor the sample shrinking force/stress, adhesive B was loaded to the rheometer with a fixed geometry gap of 0.5 mm. An isothermal time sweep test was performed at 25 °C. The sample was pre-measured for 20 seconds before the UV light was triggered on. The output UV intensity was set to 20 mW/ cm^2. For monitoring sample volume shrinkage, the same test was performed with the normal force control activated. The normal force was set to 0 ± 0.1 N. During the test, sample gap change was monitored.

RESULTS AND DISCUSSIONS

1. Influence of UV intensity on curing

Figures 6a and 6b shows results from curing adhesive A using both UV light guide and LED accessories. The tests were conducted with intensities of 50 mW/cm^2, 100 mW/cm^2 and 150 mW/cm^2. Before curing, adhesive A was a liquid (G″ was higher than G′). Upon exposure under UV, both the moduli and viscosity of adhesive A increased rapidly with time. The sample underwent a liquid to solid transition within 0.9 to 2.8 seconds (see Table 1). After the curing was complete, the modulus reached to a plateau and the sample behaved like a rigid solid. As can be seen from figure 6, adhesive A cured faster with higher exposure intensity. The moduli crossover time, where G′ equals to G″, is commonly used to describe a sample's transition from liquid to solid state. It is also used to compare the samples' curing rate under different conditions. Results in figure 6 show that the higher the exposure intensity, the earlier the G crossover appeared during the test. Additionally, the UV curing rate can be calculated using the slope of the complex modulus versus time (dG*/dt) [6]. The percentage of curing can be evaluated by comparing the material's initial and final modulus. Table 1 shows the comparison of curing adhesive A using both light guide and LED accessories. Since the light guide accessory provides broadband wavelength and the intensity was recorded as the total intensity from 250 nm to 600 nm, results show that sample was cured much slower using the light guide accessory compared with using the LED accessory, especially at higher exposure intensities. Adhesive A was not able to get fully cured when exposed to 50 mW/cm^2 for 30 seconds using the light guide accessory. A higher radiation dosage (i.e., a higher UV intensity and/ or a longer exposure time) is required to fully complete the curing reaction [6].

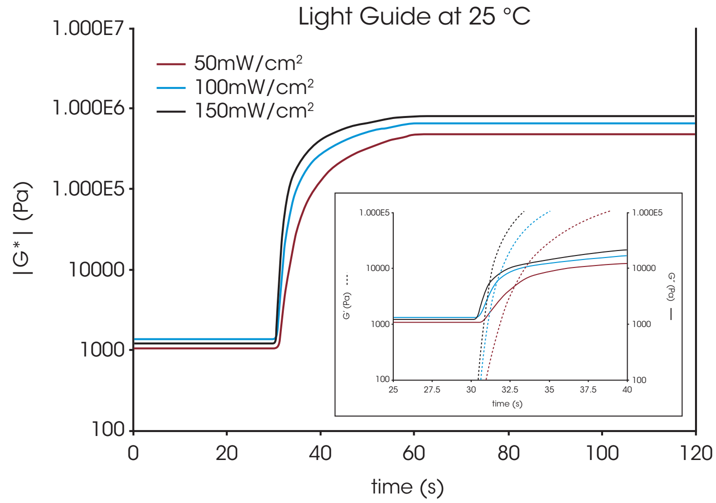

Figure 6a: UV curing at different intensities using the light guide accessory.

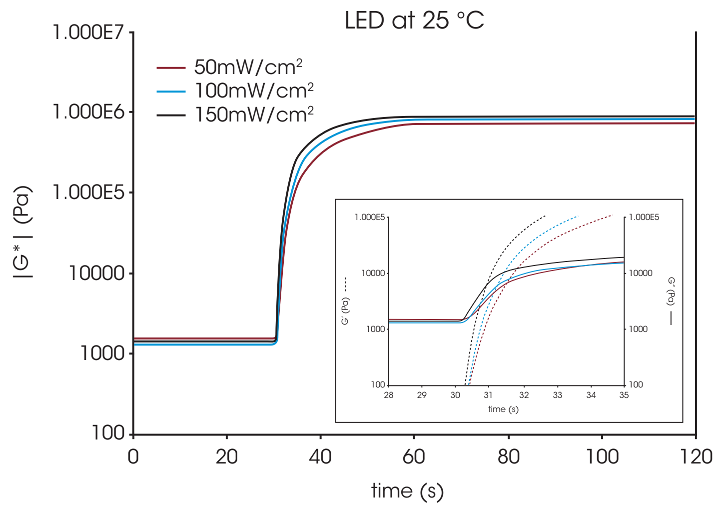

Figure 6b: UV curing at different intensities using the LED accessory.

Table 1: Comparison of curing at different exposure intensities

Light Guide:			
Intensity (mW/cm^2)	G Crossover Time t(sec)	Final Modulus G* (Pa)	Reaction Rate dG*/dt (Pa/sec)
50	2.8	4.8E5	2.1E4
100	1.6	6.6E5	2.7E4
150	1.1	8.1E5	3.2E4
LED:			
Intensity (mW/cm^2)	G Crossover Time t(sec)	Final Modulus G* (Pa)	Reaction Rate dG*/dt (Pa/sec)
50	1.5	6.9E5	3.5E4
100	1.2	7.9E5	5.1E4
150	0.9	8.5E5	6.8E4

2. Influence of temperature on UV curing

Figures 7a and 7b shows a comparison of curing adhesive A at different temperatures using the light guide and LED UV accessory. An electrically heated upper plate (EHP) was used as the temperature control system. Dynamic time sweep tests were performed at temperatures of 25 °C and 50 °C, respectively. Sample was pre-measured in oscillation for 30 seconds before being exposed to the UV radiation at 100 mW/cm^2. The UV exposure time for each measurement was set to 30 seconds and the total measurement time was 120 seconds. Results in figure 7 show that adhesive A was a liquid before curing. At 50 °C, sample shows lower initial modulus compared to that was at 25 °C. Upon applying the UV, sample cured from liquid to rigid solid in less than one minute. The higher the reaction temperature, the faster the material cures. The G crossover time appeared earlier at curing temperature of 50 °C.

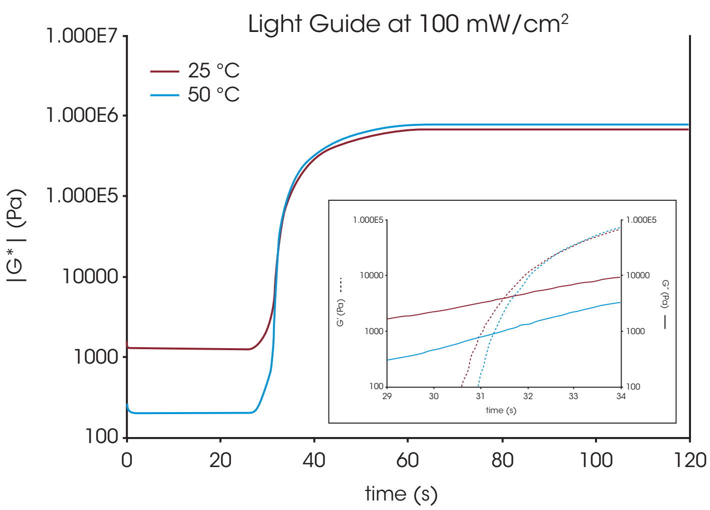

Figure 7a: UV curing at different temperatures using the light guide accessory.

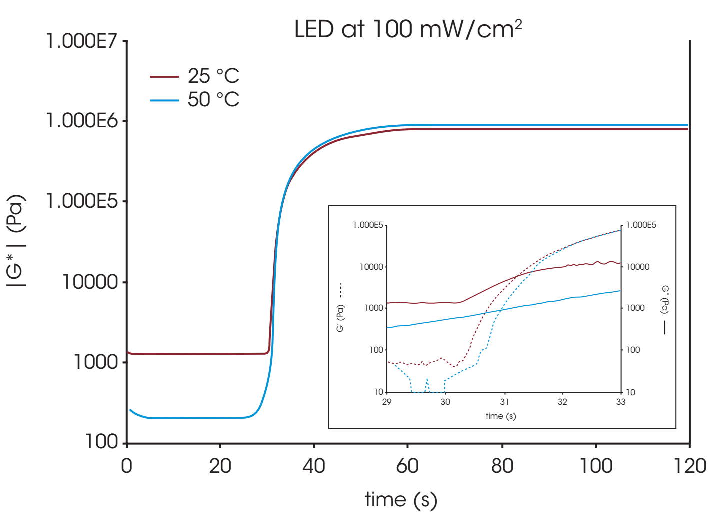

Figure 7b: UV curing at different temperatures using the LED accessory.

3. Axial force control in UV curing

Most polymer materials shrink during a crosslinking reaction. The shrinking force or amount of volume shrinkage may directly affect the performance of the final product. The normal force transducers on both AR/DHR rheometer and ARES-G2 rheometer are capable of accurately measuring sample shrinkage during curing. Figure 8a shows the results of curing adhesive B under a constant geometry gap. This sample was pre-measured in oscillation for 20 seconds before the UV was triggered on. The UV intensity was set to 20 mW/cm^2. It was observed that there was a negative axial force built up during curing, which indicates sample shrinkage. The maximum axial force was monitored to be 14.6 N across a 20 mm diameter plate. Figure 8b shows the results of curing this adhesive sample under a controlled axial force of 0 ± 0.1 N. As the shrinkage force was actively released during curing, reading the geometry gap monitored the sample volume change. Results in figure 8b show that the maximum gap change was 4% during the curing reaction.

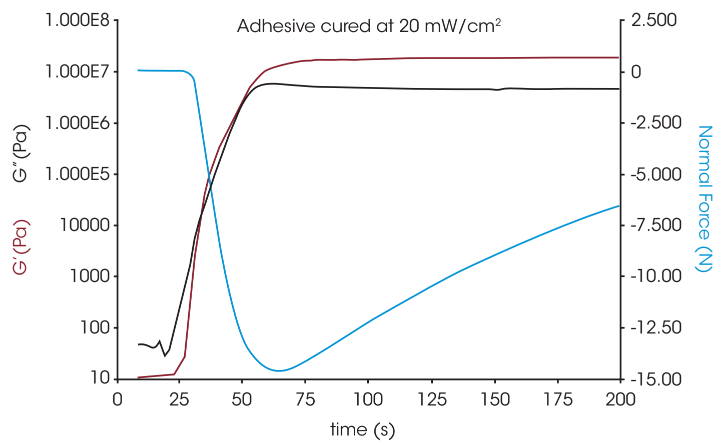

Figure 8a: UV curing analysis at a fixed gap. Sample shrinking force was monitored.

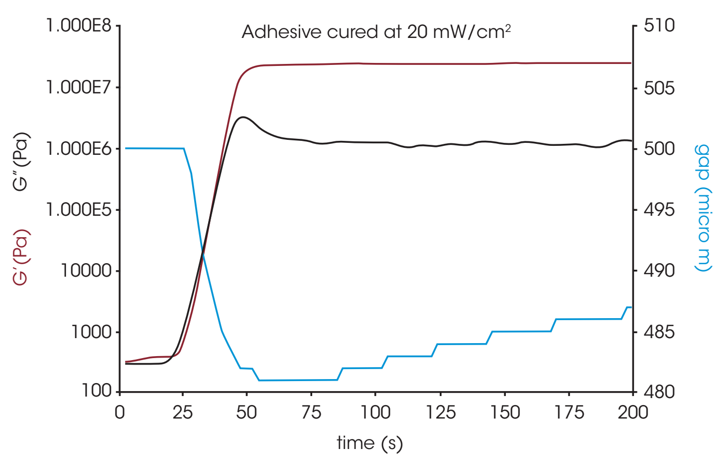

Figure 8b: UV curing analysis with active axial force control at 0 +/- 0.1N. Sample gap change was monitored.

CONCLUSIONS

TA Instruments AR/DHR and ARES-G2 rheometers, equipped with UV light guide or LED accessories, provide a powerful tool for studying UV initiated curing reactions. The UV light intensity was uniformly distributed across the area of the 20 mm diameter geometry. Curing tests can be performed under ambient conditions or other temperatures using the EHP temperature control option. Samples can be measured at different UV intensities, different exposure times, and at different geometry gaps. The normal force transducer on rheometers can also provide the capability of measuring sample shrinkage during curing.

ACKNOWLEDGMENT

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For more information or to place an order, go to http://www.tainstruments.com/ to locate your local sales office information.

REFERENCES

1. S.A. Khan, I.M. Plitz, R.A.Frantz. "In situ technique for monitoring the gelation of UV curable polymers". Rheologica Acta, 31, 151 (1992)
2. S.S. Lee, A.Luciani, JA.E.Manson. "A rheological characterization technique for fast UV-curable systems". Progress in Organic Coatings, 38, 193 (2000)
3. R.R.Eley. "Rheology in coating, Principles and Methods". Encyclopedia of Analytical Chemistry. 1-30 (2001)
4. R.J.Geiger, C.A.Henderson. "UV flexographic inks: correction between rheology and press performance". Radtech Report. July, 15 (2001)
5. B.S.Chiou, S.R.Raghavan, S.A.Khan. "Effect of colloidal fillers on the crosslinking of a UV-curable polymer: gel point rheology and the Winter-Chambon Criterion". Macromolecules, 34, 13 (2001)
6. T. Chen. "Rheological studies of UVcurable materials". TA Instruments applications notes AAN021 (2005)