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Rheological Studies of UV - curable Materials

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ABSTRACT

The challenge for studying fast changing systems with rheology such as UV initiated polymerization and crosslinking is multifold. These materials react within seconds and the moduli change over 2 to 3 decades. UV light must irradiate the sample homogeneously over a short time period and fast data acquisition is required to capture the modulus change during the reaction. An option for UV curing, using parallel plate has been designed for the ARES rheometer. A fast data sampling device with a new correlator has been developed to provide up to 500 dynamic mechanical data points per second, so the modulus build up can be easily followed. Results are obtained for an acrylate-based pressure sensitive adhesive. The curing reaction is studied as a function of the sample gap, UV intensity and UV exposure time.

INTRODUCTION

UV-curable materials are widely used as coatings, inks and adhesives[1-5]. These materials contain a blend of unsaturated monomers and oligomers. Some are also blended with photoinitiators. When these systems are exposed to ultraviolet radiation, the light energy is absorbed either by the unsaturated functional groups or the photoinitiators to generate free radicals, which induce further polymerization and cross-linking. UV curing reactions are commonly conducted under ambient conditions. Most of the reaction products exhibit relatively low dimensional shrinkage. One of the distinctive characteristics of industrial UV-curable systems is the high reaction rate, which takes place under intense UV radiation. The entire reaction is usually complete in a few seconds to a few minutes. During this short period, the viscosity and moduli of the material increase up to 5 decades.

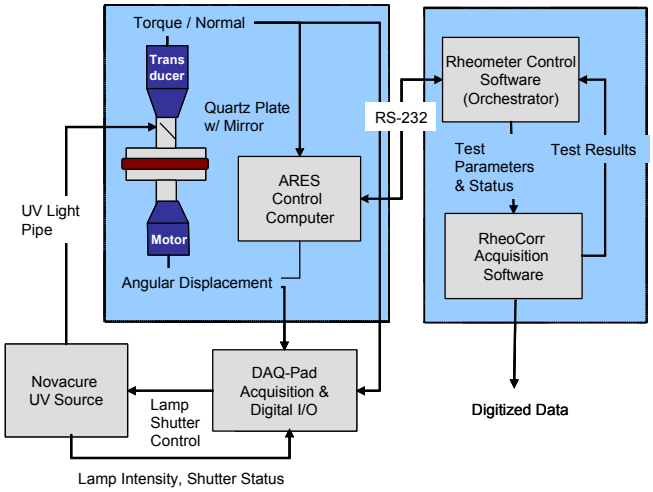

Figure 1: Experimental setup with fast data acquisition and UV curing option

However, it is a great challenge to monitor this fast changing reaction system using a standard commercial rheometer. Most of the commercial rheometers use data acquisition and correlation systems to generate dynamic mechanical tests results, capable of collecting approximately 1 data point per second regardless of the test frequency. A fast data acquisition device providing more than 100 data points in one second is necessary to monitor typical photo-induced liquid to solid transition[6-7]. In this paper, a new UV-curing test equipment for the ARES instrument is presented. The performance of this equipment was evaluated using a UV-curable pressure sensitive adhesive. The influence of geometry gap, sampling time, UV light intensity and dosage are discussed in details.

THE UV CURING OPTION

The UV curing equipment for the ARES rheometer consists of a waveform fast data acquisition, which includes a National Instruments DAQ-Pad 6020E, the "RheoCorr" correlation software, and special optical test fixtures[7]. The experimental setup is shown in Figure 1. A Novacure 2100 photometer providing the UV light, interfaces with the external DAQ pad hardware. Lamp shutter and UV intensity

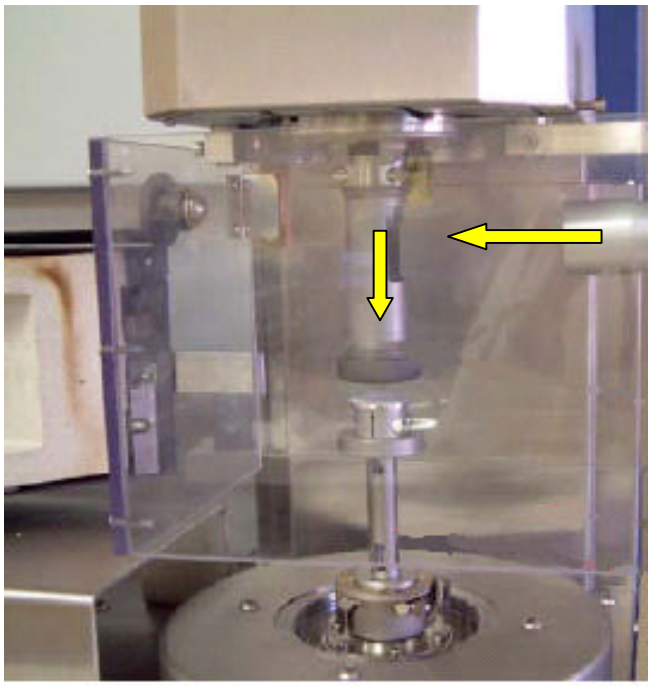

Figure 2: UV-Curing device based on ARES unit

are controlled from the instrument operation software (TAOrchestrator) during the test. Special 20mm upper disposable acrylic (or quartz) parallel plates are used to illuminate the sample with the UV light. A flexible glass fiber light guide with 5mm cross-section conducts the UV light to the UV test fixture. The radiation intensity is homogeneously redistributed over a 20mm diameter area with a collimator and then reflected onto the upper plate by a mirror built into the test fixture (Figure 2). The output UV intensity is calibrated using an external UV radiometer. The UV light shield box is installed to protect the operator from UV light exposure. UV curing experiments are performed at room tem/perature in oscillation mode.

VALIDATION OF THE UV OPTION

Figure 3 shows the dynamic moduli of a UV initiated curing reaction monitored by the ARES LS2 rheometer equipped for fast data acquisition. At a probing frequency of 200 rad/s, the ARES correlator uses several oscillation cycles and determines one data point every 5 seconds. However, for this curing reaction the G' /G" crossover, which measures the liquid-to-solid transition, happens in less than 1 second after the sample was exposed to the UV radiation. The ARES rheometer cannot collect data fast enough to monitor this gelation process (large symbols in figure 3). The "RheoCorr" external correlator, combined with the fast data acquisition measures the complex modulus and phase every 0.03 second, i.e. 33 data points per second. The G'/G" crossover time can be accurately captured within +/- 10 ms . The maximum sampling rate for the ARES fast sampling option is 500 points per second.

OPTIMUM SAMPLE GAP

Choosing an optimum sample gap is important for UV curing experiments. Figure 4 shows the influence of sample gap on the UV curing reaction rate and the modulus of the final product. For a free radical initiated polymerization or crosslinking reaction, the initial reaction rate correlates directly with the concentration of free radicals, in this case initiated by UV radiation. Large sample gaps require a large sample volume. Under the same UV radiation, the relative concentration of photo-induced free radicals decreases with increasing sample gap. Therefore, as shown in figure 4, the initial reaction rate (dG*/dt) determined from the modulus curve obtained at a large sample is lower than the initial reaction rate obtained from tests with a smaller gap. A smaller sample gap also allows a more uniform cure for samples with high turbidity. Note that below

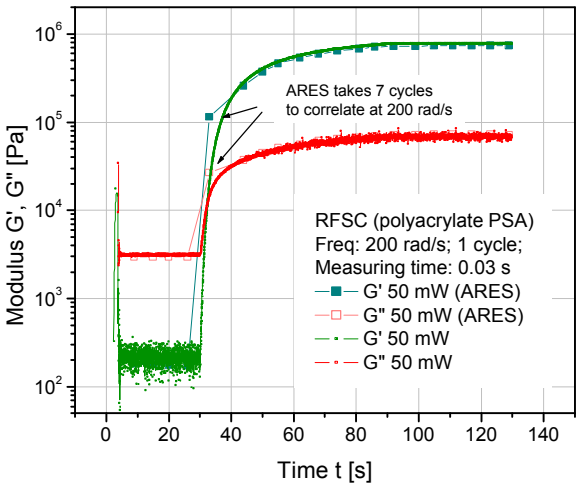

Figure 3: Monitor of UV-curing reaction on ARES LS2 rheometer. Data collected by ARES rheometer and fast sampling acquisition

a critical gap the measured final modulus decreases again (see Table 1). This is an effect of the instrument compliance.

In general a small sample gap benefits the UV curing reaction. To avoid instrument compliance effects, a large gap is preferred. As such the gap selection has to be a compromise and is different for each sample. For the specific sample used in figure 4, the optimum gap is 0.6 mm.

Gap(mm)	Reaction Rate dG*/dt [Pa/sec)]	Final Modulus G* [Pa]
0.2	3.7×10^4	7.6×10^5
0.4	3.6×10^4	9.1×10^5
0.6	3.2×10^4	9.4×10^5
1.0	2.6×10^4	9.3×10^5

Table 1: Effect of sample gap on the curing reaction

EXPERIMENTAL

An acrylate-based pressure sensitive adhesive is used in this study. The curing reaction is initiated without any external photo-initiator. Dynamic rheological UV curing experiments were carried out using a TA ARES LS2 rheometer equipped with a 2KFRTN1 transducer, the waveform fast acquisition, and the UV curing option. An optical 20mm disposable parallel plate was used as the upper geometry. The intensity of the UV output was calibrated using an external radiometer, inserted between the plates. Dynamic time sweep measurements were performed at 200 rad/s at room temperature with different UV light intensities. The UV light source was triggered on, 30 second after the test start by the software.

RESULTS AND DISCUSSIONS

Effect of UV intensity

For UV-initiated polymerization and cross-linking, the reaction rate correlates with the concentration of initiator: in this case the concentration of free radicals. The number of free radicals in the system depends on the UV radiation intensity. Figure 6 shows the influence of the UV light intensity on the curing reaction rate. As the UV intensity increases, the initial reaction rate increases. The change of the initial modulus with time dG*/dt as a function of UV intensity follows a linear relationship. For the same radiation dosage (dosage = intensity * exposure time) in figure 5, the complex modulus reaches the same final value.

Effect of UV dosage

Figure 7 exhibits a series of cure traces for the same adhesive as a function of UV exposure time. The results, here G' & G" show that for a UV radiation of 30mW, the adhesive does not reach the maximum modulus value after an exposure time of 30 s. Since the radiation dosage represents the total energy applied to the sample by the UV light source, the sample did not receive enough energy to fully complete the cure; the final modulus G* was not obtained. Figure 8 shows the relationship between UV dosage and the final modulus G' of the material. To reach the maximum G' value or full cure for this

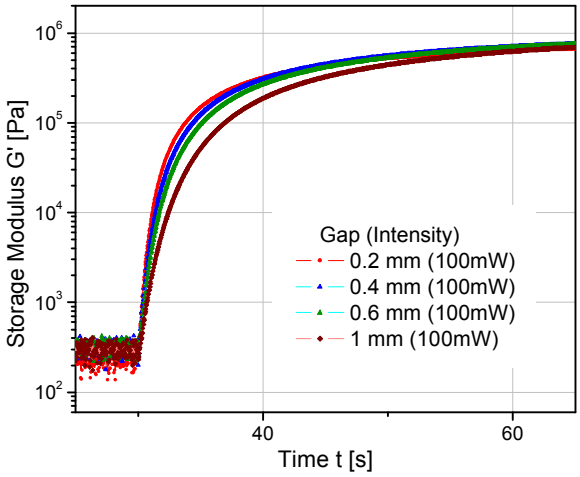

Figure 4: Effect of sample gap to the UV curing reaction

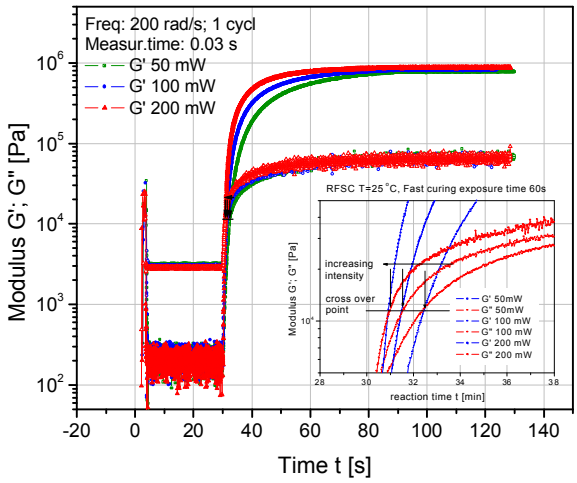

Figure 5: Influence of ultra-violet light intensity to the curing reaction. Sample modulus vs reaction time at different UV intensities

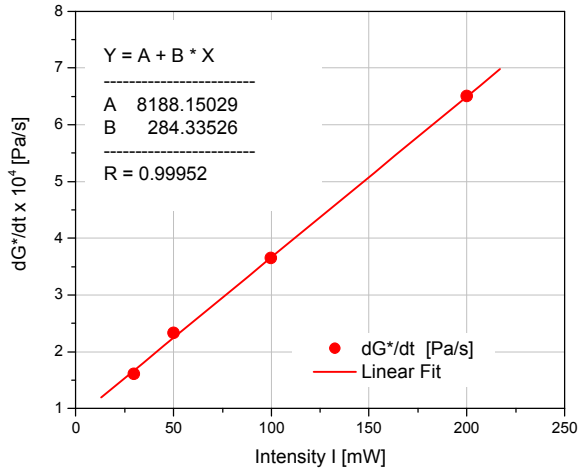

Figure 6: The reaction rate (dG/dt) vs UV exposure intensity*

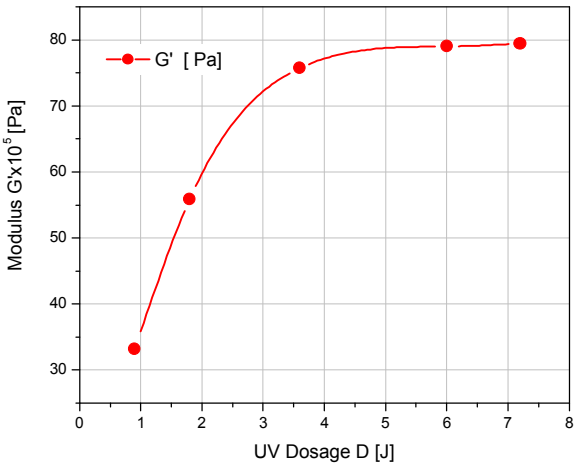

Figure 8: The influence of UV exposure dosage to the material's final modulus

specific material a dosage of 6 Joules is required. Since the UV intensity was constant during the test, the initial rate of reaction is unaffected and the cure curves superpose during the start up.

CONCLUSIONS

The ARES Rheometer equipped with the fast data acquisition and newly designed UV curing option is a powerful tool to study fast changing UV curing reactions. The fast sampling is capable of collecting a maximum of 500 data points per second. As such it is possible to monitor fast changes of material properties during UV curing reactions. The test results show high accuracy and reproducibility. The UV curing fixtures enable uniform light intensity distribution across the diameter of the plate. Results show that the influence of the UV light intensity and dosage on the curing reaction rate and the photo-induced changes in the mechanical properties can be easily studied.

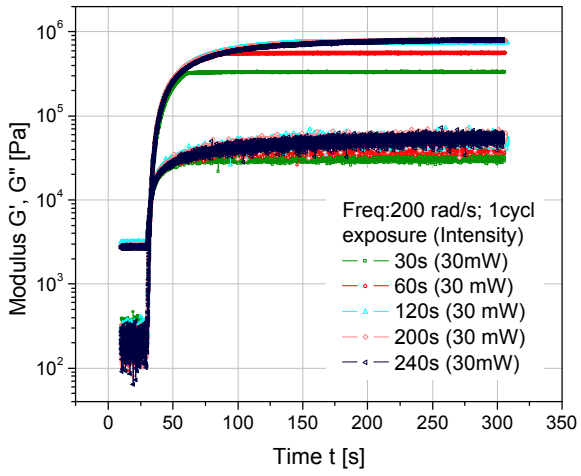

Figure 7: UV-initiated curing under 30mW intensity and different exposure time

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