

Characterization of High-Performance Adhesives and Coatings by Photorheometry

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Introduction

Photorheometry allows one to monitor typical rheological properties such as viscosity and shear modulus while a coating or adhesive material is irradiated with UV or visible light. The technique provides information about the bulk properties of the final (cured) product while also affording “real-time” measurement of the material’s shear properties during photocure. Photocuring kinetics can be measured rheometrically, complementing more traditional kinetics measurement techniques such as photo-DSC (DPC) or real-time infrared spectroscopy (RTIR). These traditional techniques measure kinetics based on sample chemistry (enthalpy change or double bond conversion, respectively), but they do not generally provide any information about physical properties such as sample viscosity, shrinkage stress, shear modulus, etc. Photorheometry, on the other hand, directly measures changes in the physical properties of the photocuring sample. Using photorheometry, one can determine with good reproducibility critical radiation cure performance parameters such as fixture time, the extent of shrinkage, and final modulus. One can also determine how these parameters are impacted by variables such as inhibitor concentrations, the presence of oxygen, film thickness, radiation dose, the lamp wavelength emission profile, and temperature.

A majority of radiation curable adhesives and sealants can be described as “viscoelastic”—i.e., they exhibit both fluid-like (viscous) and solid-like (elastic) behavior, depending on the time scale of evaluation. When a sinusoidal deformation (strain) is applied to a viscoelastic sample, it causes a sinusoidal stress that is out of phase with regards to the strain by a shift angle, δ . The key parameters that are reported for photorheometer experiments derive from the applied stress and strain and include the complex shear modulus and the damping factor. The complex shear modulus is defined as

$$\mathbf{G}^* = \boldsymbol{\tau}(t) / \boldsymbol{\gamma}(t) = \text{shear stress} / \text{shear strain};$$

the damping factor ($\tan \delta$) is the tangent of the shift angle δ and is defined as the ratio of the loss modulus to the storage modulus (i.e., $\tan \delta = G'' / G'$). For viscoelastic liquids (such as most uncured samples), $G'' > G'$, so $\tan \delta > 1$. As a sample cures and begins to behave as a viscoelastic solid, G' increases more rapidly than G'' , and $\tan \delta$ eventually decreases to some value less than 1. The sample fixture time is defined as the time at which $\tan \delta = 1.00$ and may also be described as “crossover time”, since the two moduli cross from $G'' > G'$ to $G' > G''$ at this point.¹ It has been well established that the crossover point is close to the theoretical gel point.²

The shear modulus G^* of a sample typically increases rapidly during photocure, eventually reaching a plateau value. The time required to reach the plateau G^* value may be of interest, although the time required for the sample to gel (fixture time) is more commonly reported. The plateau modulus of an adhesive sample can be used as a relative indicator of the likely “strength” of the adhesive. A low- G^* sample is likely to be more flexible (e.g., have higher elongation) but have lower strength than a

sample with a higher plateau G^* value. The plateau modulus is related to the crosslink density of a polymer according to the relation,

$$G = \nu_e RT$$

where G is the plateau modulus, ν_e is the crosslink density (defined as the number of moles of elastically effective network chains per cubic centimeter of sample), T is the temperature in $^{\circ}\text{K}$ corresponding to the modulus value, and R is the gas constant.³

In a typical photorheometer experiment such as those that will be described below, the sample is loaded as a 1 mm thick film between two 25 mm-diameter parallel plates; see Figure 1 for an illustration. The strain, angular frequency, and the force normal to the shear direction (F_N) are all specified at the start of the experiment. In addition to G^* and $\tan \delta$, other measured variables may include gap (i.e., sample shrinkage), storage modulus (G'), loss modulus (G''), and complex viscosity.

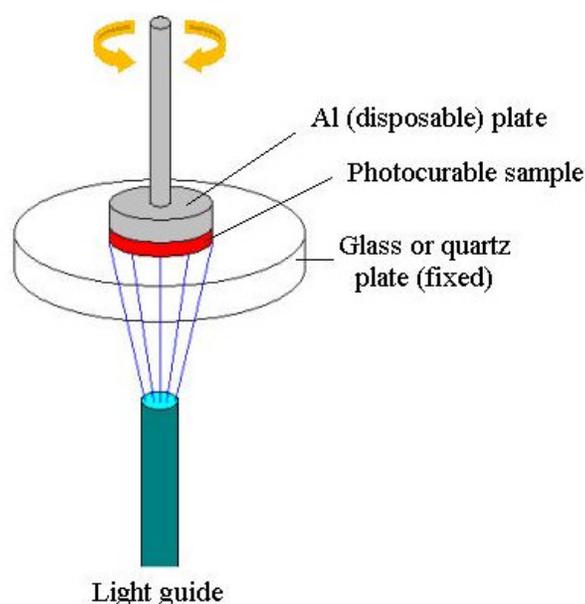


Figure 1. Illustration of photorheometer setup.

Several different types of adhesives and coatings have been evaluated with photorheometry. Select data will be presented below as demonstrations of the technique's capabilities. The examples will demonstrate the use of photorheometry to quantify the effects of radiation dose, photoinitiator concentration, and inhibitor concentration on cure; to compare cure performance of different co-initiators; and to compare the extent of shrinkage of two different samples.

Experimental

Materials: All raw materials were used as supplied, without removal of inhibitors or other purification. Compositions were 100% solids (no solvent) and were mixed using a high shear speed mixer.

Instrumentation: Experiments were carried out using parallel plates on a Physica MCR301 rheometer equipped with a Peltier plate, an environmental chamber and a UV cell. A 25 mm disposable aluminum plate was attached to the instrument's stainless steel spindle, and the bottom plate was either glass (supplied by Anton Paar) or quartz (supplied by Precision Glass and Optics). A UV wand with a high

pressure mercury arc lamp was used as the primary light source, with neutral density filters (Edmund Optics) mounted directly over the wand tip to reduce intensity when desired.

For Example 3 below, the standard UV source used with the photorheometer was fitted with a bandpass filter (“FCG459”) supplied by Melles Griot. The resulting lamp emission spectrum, measured by RPS200 and RPS380 spectroradiometers from International Light Technologies, Inc., showed a single peak centered at 450 nm, with a peak width at half height of about 9 nm.

Results and Discussion

For each photorheometer experiment described below, percent strain, frequency, and normal force were all specified. In order for the photorheometry data to be meaningful, it is essential that the strain and frequency are set within a given sample’s linear viscoelastic (LVE) range. Within the LVE range, both G' and G'' show constant plateau values when plotted as a function of strain amplitude. Outside the LVE range (e.g. at high strain amplitudes), the structure of the sample is irreversibly changed or even destroyed, making any rheometric data obtained under these conditions meaningless. One challenge in using rheometry to study photocuring kinetics is that the limits of the LVE range often change as a sample cures. It is necessary, therefore, to determine the LVE-limiting strain (γ_L) for both the uncured and cured materials prior to performing the photocuring experiment. During the photocuring experiment, then, the strain setting can be programmed to transition from a value suitable for the uncured sample to one appropriate for the cured polymer, ensuring that the sample is within its LVE range throughout the experiment.

An additional precaution necessary when performing a photorheometry experiment is related to the sample shrinkage. With a parallel plate setup, it is common to carry out experiments at a fixed gap, for example 1.0 mm. However, if the sample being studied shrinks during cure, a fixed gap will introduce errors. Sample shrinkage will have two effects on the experiment: 1) it will induce a force on the spindle of the instrument normal to the direction of oscillation, and 2) some of the photocuring material can be pulled away from the outer periphery of the sample. The first effect has not been directly observed to cause significant problems with the data; however, we have observed that removal of sample with creation of air pockets at the periphery of the plates causes significant deviations in the measured torque, modulus, etc. Sample shrinkage has been addressed in the examples that follow by using a fixed normal force ($F_N = 0$ N) in the instrument setup rather than a fixed gap. With this setting, the instrument automatically adjusts the gap between plates so that the force exerted on the spindle (normal to the oscillation direction) is maintained at zero. Thus, if the sample shrinks, the gap is decreased accordingly. Plots of the measured gap as a function of time can then be used to monitor sample shrinkage and, if appropriate, to correlate shrinkage to radiation dose, sample composition, or other variables.

The utility of the photorheometer was tested in a number of different adhesive and coating applications. Some of the applications for which photorheometric data has been found to be most useful include the following: 1) confirmation of adequate cure of a developmental product at a specified radiation dose, 2) evaluation of variables such as lamp emission profile, atmosphere (air versus nitrogen), photoinitiator concentration, etc. and their impact on the photocure performance of a typical acrylate composition, 3) selection of the best photoinitiator package for a given lamp emission profile, and 4) comparison of cure kinetics and physical properties such as modulus and shrinkage of different adhesive candidates for a specified application. The examples below are representative of some of the studies that have been carried out.

Example 1. Effect of radiation dose on cure of acrylate-functional adhesives.

A model urethane acrylate composition was prepared and irradiated under nitrogen using several different lamp intensities. Figure 2 shows a plot of complex shear modulus versus time as a function of intensity. It had been anticipated that a very low cure speed (i.e., low light intensity) would provide a cured network with superior mechanical properties, since the slow cure rate could allow for greater structural relaxation within the forming polymer. However, the data in Figure 2 were used to conclude that bulk mechanical properties were independent of cure speed for this particular adhesive composition. Photorheometry showed that whereas the fixture time varied predictably according to lamp intensity, the plateau G^* was essentially constant.

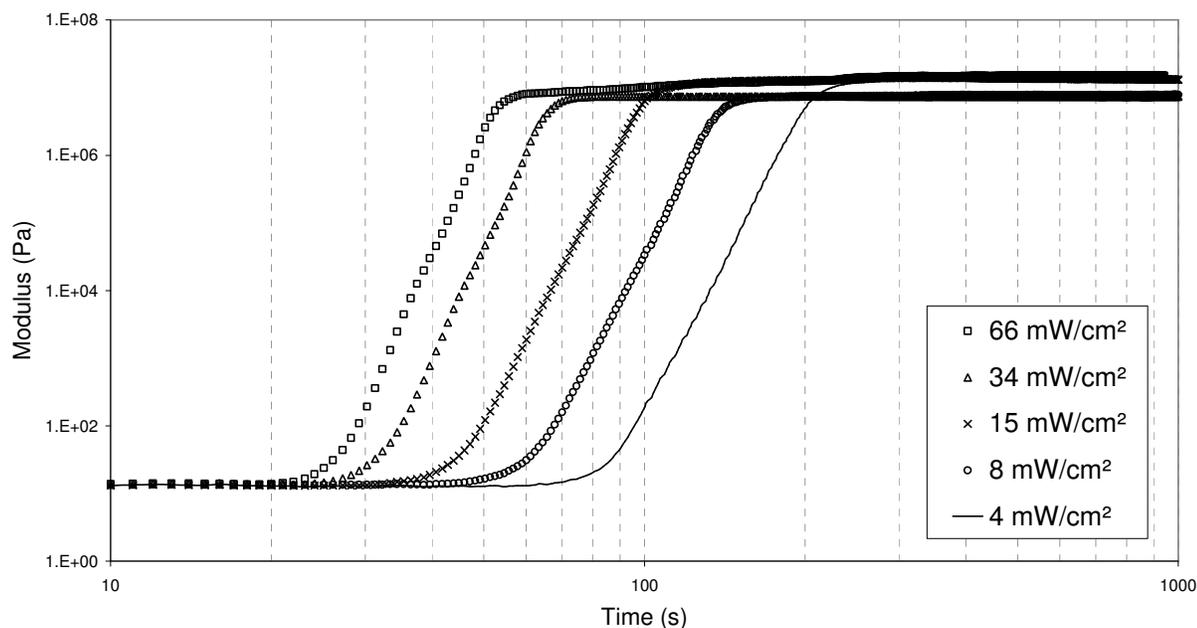


Figure 2. Comparison of shear modulus for an acrylate adhesive irradiated continuously at different incident intensities. The experiment was carried out under nitrogen with an initial gap of 1.0 mm.

A different dose study was carried out using a “photoactivated urethane” composition. This technology involves use of a photolatent base to photoactivate a stoichiometric blend of polyisocyanates and polyols, leading to a subsequent (delayed) cure. Similar compositions are disclosed in the literature.⁴ The target application demanded that the properties of the cured material be consistent regardless of fluctuations in the applied UV dose. Table 1 shows the photorheometric data for an activated urethane irradiated for different exposure times at a constant intensity of 200 mW/cm². The data confirmed that varying the exposure time produced a correlated, “tunable” crossover (i.e., fixture) time with no significant impact on the final modulus.

Table 1. Photorheometer Data for Activated Urethane Irradiated at 200 mW/cm²

Irradiation Time (s)	G* after 4 hr (MPa)	Crossover Time (s)
5	0.348	2785
10	0.366	578
30	0.367	356
45	0.326	324
60	0.487	242
120	0.332	188
180	0.41	172

Example 2. Effect of photoinitiator and inhibitor concentration

A series of model acrylate compositions were prepared with the purpose of quantifying the effect of photoinitiator and inhibitor concentrations on photocure. Photorheometer experiments were carried out using continuous irradiation at low intensity (2 – 3 mW/cm²) under a nitrogen atmosphere. The plateau modulus was found to be unaffected by changes in photoinitiator or inhibitor concentration, provided that sufficient UV dose was applied to fully cure the sample. Figures 3 and 4 show the variations in crossover time with inhibitor level and photoinitiator concentration, respectively. The results shown in Figures 3 and 4 were not unexpected in either case. However, the data confirmed that the photorheometer could be used to quantify the effect of both variables on cure speed and bulk properties.

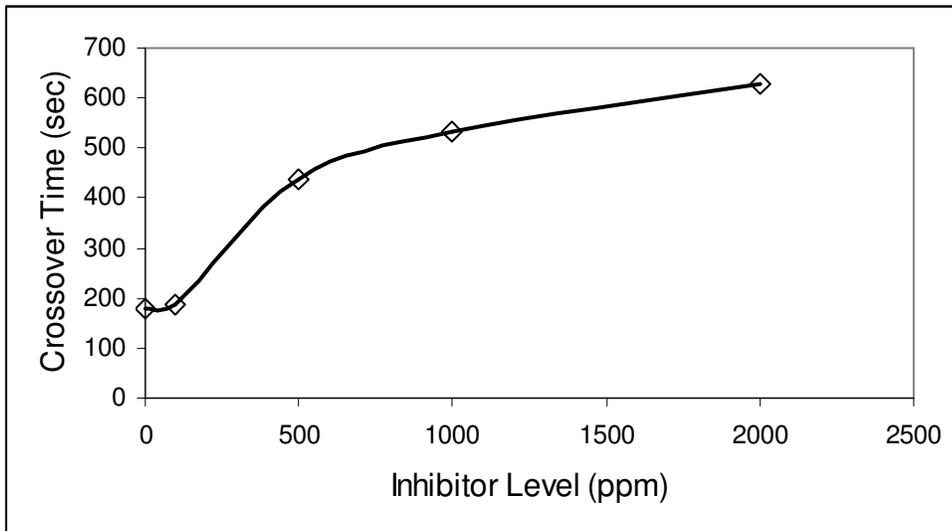


Figure 3. Effect of inhibitor level on crossover time for samples continuously irradiated under nitrogen at an intensity of 3.0 mW/cm².

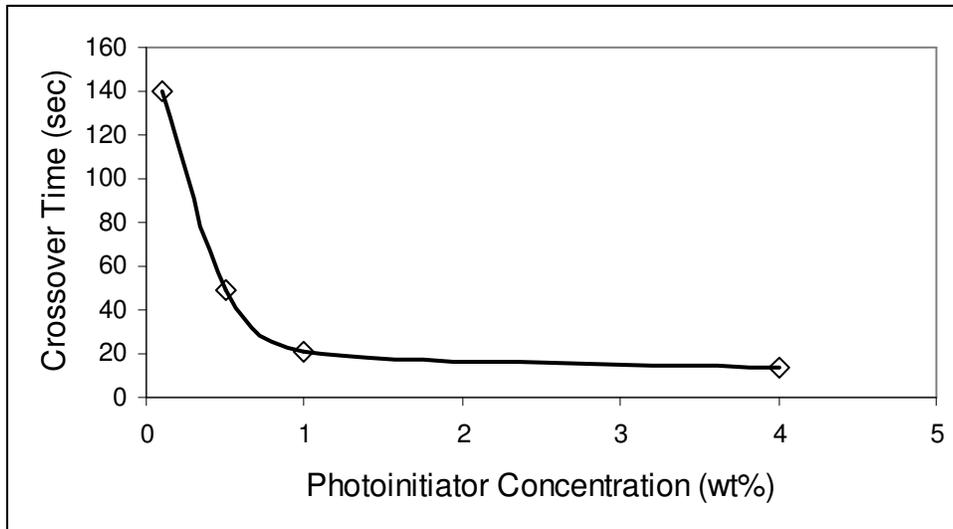


Figure 4. Effect of photoinitiator concentration on crossover time for samples continuously irradiated under nitrogen at an intensity of 1.8 mW/cm².

Example 3. Use of photorheometry to select the best co-initiator

The study described in this example was designed to select the best coinitiator to use with camphorquinone, a Type II photoinitiator; the goal was to identify a compound (or class of compounds) that would provide rapid cure response with minimal impact on final properties. Three different classes of co-initiators were evaluated, along with a control that contained camphorquinone alone. Photorheometry was carried using continuous irradiation through a 450 nm bandpass filter at an incident intensity of 21 mW/cm². Results are given in Table 2.

Table 2. Photorheometry Results for Photoinitiation by Camphorquinone with Various Co-Initiators

Sample	Crossover Time (s)	Plateau G* (MPa)
CTRL (no co-initiator)	12	2.27
Co-initiator 1	6.6	12.3
Co-initiator 2	6.7	1.24
Co-initiator 3	21	0.865

The photorheometry data indicate that both co-initiators 1 and 2 accelerated cure (i.e., provided faster fixture) relative to the control. However, whereas co-initiator 1 provided an increased final modulus, co-initiator 2 negatively impacted the bulk properties of the cured adhesive. Based on the data obtained, co-initiator 1 was identified as the best class of co-initiators for this system. Ordinarily, this conclusion would have been reached through a combination of conventional kinetics techniques (RTIR, DPC) and physical testing. The associated time requirement for specimen preparation, instrument setup, etc. would have been a few hours. With photorheometry, both kinetics and physical property data were obtained with just four 10-minute experiments.

Example 4. Shrinkage during cure of a thiol-ene versus an acrylate

Figure 5 shows a comparison of an acrylate adhesive with a thiol-ene; both contain equal concentrations of photoinitiator and equal molar concentrations of vinyl groups. Cure conditions (lamp intensity, irradiation time, temperature) were identical for both experiments. The addition-cure acrylate was found to shrink to about twice the extent of the step-cure thiol-ene (4% versus 2% reduction in gap, respectively). A thiol-ene adhesive in a geometrically confined bondline would therefore be expected to have less inherent stress than an acrylate adhesive in the same application.

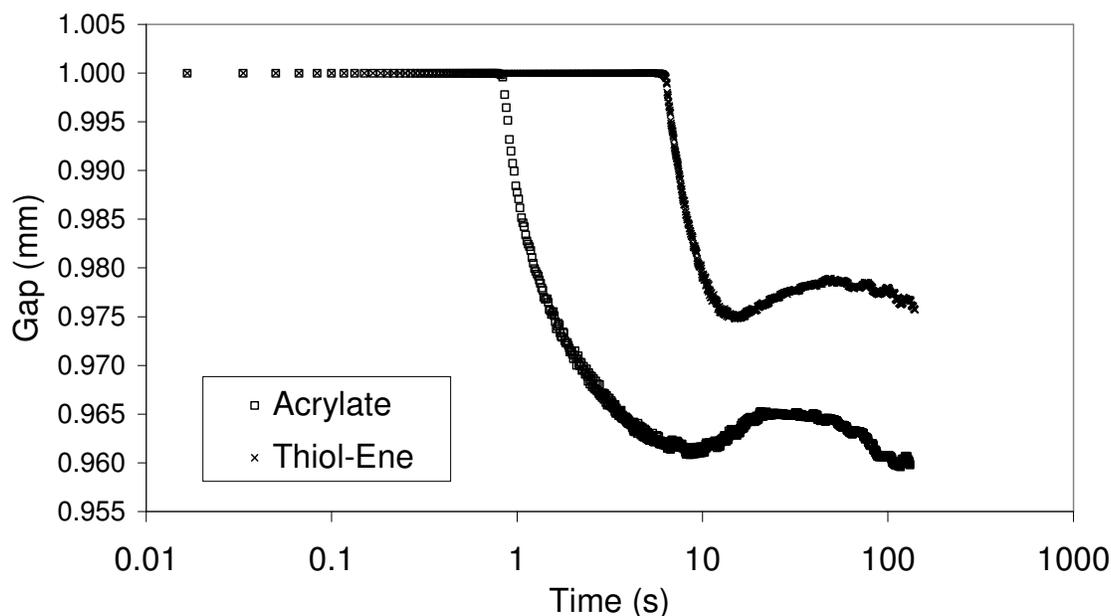


Figure 5. Gap between plates as a function of time for photocuring adhesive samples.

Conclusions

As a research team tasked with developing and characterizing new technology for radiation curable adhesives and coatings, we have found the photorheometer to be an indispensable tool. It provides simultaneous measurement of photocure kinetics and physical properties including shear modulus and extent of shrinkage. Photorheometry has proven useful for both quality control and product development purposes. While we are still identifying and developing new methods and applications for the instrument, we have so far successfully demonstrated its use for characterizing a wide array of compositions with regards to their fixture times, relative strengths (cured), anticipated shrinkage in bond lines, and the dependence of all of the above on photocuring parameters such as lamp intensity and wavelength profile.

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