DYNAMIC MECHANICAL ANALYSIS OF UV-CURABLE COATINGS WHILE CURING

Robert W. Johnson, DSM Desotech Inc., Elgin, IL 60120

Abstract

A method has been developed for following the dynamic mechanical properties of a UV-curable coating while the sample is curing. The resulting data and plots can be used to measure the material's cure speed. The precision is sufficiently high to allow small differences in cure speed between different formulations to be reliably estimated.

The sample is contained in parallel plate stress rheometer in which the usual metal bottom plate has been replaced by a UV-transparent quartz plate, allowing UV light to illuminate the sample from below. A nitrogen atmosphere is established before every run.

The instrument is set up to measure G', G", and phase angle vs. time at a frequency of 10 Hz, taking 72 data points per second. Two seconds after a run starts, the software puts out a signal for input to a relay that opens the UV shutter

Two arbitrary criteria for cure times are: 1) The time for G' to reach $2X10^4$ Pa; 2) The time for the phase angle to decrease to 45°. Typical cure times for fiber optic coatings range from 0.2 to 0.6 seconds

Introduction

One of the main uses for UV-curable coatings is to allow rapid production of fiber optic light guides for the telecommunications industry. A quartz fiber is drawn down to its final diameter (usually 0.125 mm) from a quartz preform on a very tall apparatus called a draw tower. The fiber must be covered immediately with protective layers while on the tower, because if it touches any solid object while bare, serious loss of strength will result. The fiber is covered with two liquid UV-curable layers as it moves down the tower. These layers are cured, either simultaneously or sequentially, (depending on which particular process is used) by going through one or more regions of intense UV light. The two coatings cure rapidly, the so-called inner primary coating becoming a soft rubbery material, and the outer primary coating curing to a hard solid. Only after this curing is accomplished does the fiber pass over metal capstans on its way to winding on a spool.

After a fiber is produced in the manner just described, it may be further covered with UV-curable coatings, such as colored inks and "matrix" coatings, which are used to bind 4 – 12 colored fibers in a ribbon configuration. For any of these coating processes, the speed of production is often limited by the cure speed of one of the coatings. Hence there is a need to measure cure speed of these coatings, and to use such measurements in product development.

Conventional methods for measuring the cure speed of fiber optic coatings include measuring tensile modulus as a function of fixed UV doses, and measuring the loss of acrylate unsaturation, either as a function of fixed doses or in real time, by Fourier Transform Infrared Spectroscopy (FTIR). The motive for going beyond these methods is based on the desire to more closely approximate the curing process in the end use situation, and to follow the development of mechanical property buildup in real time rather than monitor the disappearance of a chemical reactant. It is the rate of development of modulus that influences the processing speed in a coating process. Additional motives for developing a real time DMA cure speed test were 1) to achieve greater precision of the data, and 2) to obtain the data in a faster, less labor-intensive way.

References are given below[1234] to prior publications closely related to the present work. None of these methods met all of the requirements for measuring fiber optic coatings. In unpublished work[5] P. Steeman et al have constructed an instrument that not only has capabilities similar to the one described here, but also can simultaneously collect infrared data in the near-IR region, following the concentration of acrylate double bonds.

[1] Mano S. Cheema, Proc. Radtech Conf. Boston, Vol.1,626 (1992)

[2] S. A. Khan, R.A. Frantz, I.M. Plitz, Proc Radtech Conf. Boston, Vol. 2, 770 (1992)

[3] T. Renault, A.A. Ogale, M.J. Drews, Poly. Eng. Sci. Vol. 36, No. 4, 551 (1998)

[4] M.A. Zumbrum and T.C. Ward, Proc. ACS Div. of Poly. Materials, Vol. 60, 361 (1989)

[5] P. Steeman, A. Dias, D. Wienke, to be published

Requirements of a Method

The basic requirement of a method for following the development of modulus in real time is to have a dynamic rheometer (one capable of making oscillatory measurements) that can be configured to allow UV light to illuminate the sample while it is contained in the gap between the instrument's parallel plates. The second requirement, probably met by all dynamic rheometers, is that the software must have a time sweep test in the operating software. Meeting only these two requirements may be suitable for slow-curing materials, but additional features are needed for following rapid cure processes.

A third requirement is the ability to collect sufficient data points in during the early stages of curing, when the modulus is changing rapidly during fractions of a second. To meet this need, some instrument manufacturers have developed software that can estimate G', G", and the phase shift from less than one complete oscillation cycle. Evidently, the data from part of a cycle is combined with those from previous cycles to estimate the basic information of amplitude ratio and phase shift needed to calculate the rheological quantities.

The fourth requirement is that the exact time at which UV illumination begins must be known relative to the time scale of the instrument run. This is the true zero time for the curing process. One way to achieve this is to have instrument software that puts out a digital signal at a user-defined time after the run has started. The signal energizes a relay, causing a shutter in the UV source to open. Any further time delays between the signal and the actual opening of the shutter must be measured.

Equipment

The rheometer that was chosen for this application is the StressTech HR, a stress rheometer manufactured by Reologica Instruments Inc of Sweden[6]. This rheometer satisfies the four requirements given above. Stress rheometers have a configuration such that both the motor that applies the shear stress and the displacement transducer that measures angular displacement and velocity are above the sample area, leaving the region beneath the sample accessible for UV illumination. Reologica also manufactures a UV accessory, an assembly that replaces the conventional assembly beneath the sample, and allows a UV-transparent quartz plate to be mounted in place of the conventional metal bottom plate. In addition, there is a fixture for holding a light guide vertically beneath the quartz plate, allowing the sample to be illuminated from below. The light guide holder can slide vertically, allowing the UV irradiance (intensity) at the sample to be varied. The rheometer fitted with the UV accessory is shown in Figure 1.

The software that comes with the StressTech HR, RheoExplorer, has two extra capabilities mentioned above. The user can specify a number of data points to be taken in the run that corresponds to more than one data point per cycle. Also, the user can set the number of seconds after a run begins that a digital relay signal will be put out to pins in an RS232 plug on the back of the chassis. This signal with one or more relays opens a shutter, allowing UV light to pass to the sample. Another capability of the software is to increase the shear stress applied to the sample according to a prescribed polynomial as a function of time. Thus, it is possible to start a run with a shear stress appropriate for a viscous liquid, and quickly increase it to a level appropriate for a rubbery solid.

The instrument software displays the data from a run in two forms: a graph of chosen rheological quantities vs. time, and a spreadsheet with numerical data. The original data files can be saved, and data can also be exported for use in other applications.

The UV light source is the Bluepoint 2, manufactured by Dr. K. Honle GmbH, Germany[7]. It contains a metal halide doped lamp, the effect of which is to produce a spectrum that is similar, with one exception, to the metal halide lamps that are commonly used on fiber optic draw towers. The spectral output of the Bluepoint 2 has essentially zero intensity below 300 nm, while the UV lamps on draw towers have significant intensity between 250 and 300 nm. A liquid-filled light guide, 8 mm diameter and one meter long, conducts UV light from the source on the bench top to the UV accessory on the rheometer. The Bluepoint 2 contains a shutter that can be opened either by pressing a button on the front panel or by closing a circuit designed for footswitch operation. Either way, the shutter stays open for a length of time determined by rotary switches on the front panel.

---

[6] Represented In the United States by ATS Rheosystems, Bordentown, NJ.

[7] Represented in the United States by Honle UV America, Inc., Marlboro MA.

A dual-relay system converts the signal from the software to one that opens the shutter. The digital signal, about 5 VDC relative to ground, goes to a solid-state relay designed to conduct 115 volts and up to 12 amps AC through the device for an input voltage of 3-15 VDC. The 115 VAC signal goes to the coil of a small mechanical relay, and the contacts on that relay that are closed when the coil is energized are connected to the footswitch connector on the Bluepoint 2.

The UV irradiance at the sample is measured by an IL1400 radiometer paired with an SEL005 detector/filter assembly, both manufactured by International Light Inc., Newburyport MA. The irradiance is measured by placing the detector at the sample position, pressing the "on" button on the power supply, and reading the irradiance on the LCD screen of the IL1400. The vertical position of the light guide is then adjusted and further readings taken until the irradiance is in the target range.

The region around the sample can be enclosed by an oven, allowing operation at elevated temperatures and/or providing an enclosure for blanketing the region around the sample with an oxygen-free gas.

Method

The UV power supply is turned on and allowed to stabilize for at least _ hour before measuring the irradiance. The UV sensor is placed on the quartz plate, the irradiance measured, and the vertical position of the light guide tip adjusted until an irradiance of 22.0 to 22.2 mW/cm^2 is obtained. The target value is 22.0, and the bias toward the high side is chosen because the irradiance tends to drift downwards with time.

The sample is loaded by placing a drop on the center of the quartz plate, and lowering the tool (8 mm diameter) to a gap of 0.1 mm. The excess liquid is then carefully removed by using a rubber "policeman."

Nitrogen inerting starts when the clamshell oven doors are closed and nitrogen gas flow started. Seven minutes are allowed for establishing the atmosphere. (Calculations based on Fick's law diffusion for that geometry, together with the estimated diffusion coefficient for oxygen in a liquid of that viscosity range (4 - 8 Pa-sec) show that this time is not sufficient for removing the dissolved oxygen, but only for preventing oxygen inhibition of curing at the sample edges.)

Prior setup of run conditions established the following parameters: Frequency, 10 Hz; FFT size, 256 (a software setting for data treatment); Total number of data points, 360 (giving 72 data points/sec); Stress (Pa) vs. time (sec) polynomial:

$$Stress = 100 + 200t^2 + 130t^3 \qquad (1)$$

Each run was also set up to have data collection begin one second after the run starts, and the shutter relay signal to be activated two seconds after the run starts. Run durations are typically set for six seconds, since curing is nearly complete at that time, which is four seconds after the beginning of UV exposure.

Even though the run time was set to be six seconds, the process takes a little longer than that, because the computer has to do extensive calculations on the raw data in order to get rheological quantities (G', G", G*, phase shift, etc.) for time intervals that are much shorter than the 0.1 second for one cycle at 10 Hz. The total time for a run to finish completely is about 30 seconds.

The output of a measurement is a set of rheological quantities as a function of time, for time intervals of about 14 milliseconds. The software allows the results to be viewed in tabular or graphical form. Both forms of output contain a great deal of information. The question then arises as to how to extract from it one or two simple measures of cure speed, allowing these measures to be used as a basis of comparison between different formulations. This reduces to two tasks for the investigator: 1) Choose one or more criteria for cure speed, such that the time required to reach a specified condition becomes a cure speed measure: 2) Decide how to process the data so as to estimate the quantity with minimum error. The second task is not trivial for materials of very fast cure speed, which typically show marked changes after only a fraction of a second from the beginning of UV exposure. There is some scatter in the original data points, and this may be enough to obscure differences between materials.

The following two criteria for cure times have been defined:
- The time for G' to increase to 2×10^4 Pa
- The time for the phase angle to decrease to 45°

The first criterion may be preferred by the person who wants to think of curing in terms of the development of mechanical properties. The second criterion is preferred by some rheologists as a measure of gelation or the threshold of crosslinking. Either or both may be easily estimated from the tabular or graphical data output of the instrument software, without further data treatment. However, we have chosen to add additional steps to the data treatment, consisting of 1) exporting the data to a

graphing program in which the curves can be smoothed, 2) examining the smoothed curves in a magnified (zoomed) box, to determine the time for intersection of the curves with a criterion value. The StressTech software (RheoExplorer) allows the data to be exported as a "rad" file, which can be opened in the RSI Orchestrator software from Rheometric Scientific Inc. The additional steps are performed there.

It has been our practice to make three replicate runs for a sample. The reported value of cure time is the average of the three run values. This practice reduces the error (standard deviation) of the measurement by a factor of $1/\sqrt{3}$, or 0.577. Another practice for error reduction is to measure the UV irradiance both before and after each run when a series of runs are in progress and make adjustments to bring the irradiance as close as possible to the target value.

Results

Figure 2 shows the graphical output from RheoExplorer software for a cure speed measurement of a commercial fiber optic inner primary coating, 3471-1-129A, manufactured by DSM Desotech Inc. The time axis starts at two seconds, as the data collected before the UV exposure starts is of no interest. Notice that the steady rise of G' and the steady decrease of the phase angle does not start at two seconds, but at about 2.2 seconds.

Figure 3 shows the same data after transferring to RSI Orchestrator software, with all of the data points shown. Figure 4 shows a zoomed portion of Figure 3, illustrating how the intersections of curves can be determined to high accuracy. Here we make use of the fact that when the phase angle equals 45°, G' = G", and the time corresponding to phase angle = 45° corresponds to the intersection of the G' and G" curves.

The times thus determined are not what we want, which is the time to reach these criterion values since the UV began to illuminate the sample. Instead, they are the times since the beginning of the run. The signal to open the shutter was sent two seconds after the run started. However, the shutter did not open at exactly two seconds. There are two sources of delay: the inertia of the relay arm, and the inertia of the shutter inside of the UV supply. The sum of these two delay times was measured and estimated to be 0.036 seconds. Therefore, to get the true cure time by one of the criteria, 2.036 seconds must be subtracted from the intersection time found from the zoomed graph. The true cure times from this one run are:

- G' criterion: 2.326-2.036 = 0.290 seconds
- Phase criterion: 2.342-2.036 = 0.306 seconds

The average cure times calculated from three runs are:

- G' criterion: 0.308 seconds
- Phase criterion: 0.317 seconds

This method has been used to measure the cure times of many inner primary coating compositions. The results for some of these are shown in Figure 5, in the form of a box-whisker plot. The plot was prepared in Statistica software, ANOVA/MANOVA module, produced by StatSoft Inc., Tulsa, OK. Since there were three replicates in each case, measures of the measurement error can be calculated and represented as box heights and error bars (whiskers). The ANOVA procedure also provides a precise estimate of the measurement error by pooling the variances of all sample sets. The estimate of standard deviation for this data set is 0.0086 seconds. Since the 28 degrees of freedom associated with the estimate of the standard deviation is high, a 95% confidence interval for a mean cure time is given by mean ±1.96*Standard Error, or mean±0.0097.

Discussion

The method described here is rapid, easy to perform, and precise. An indication of the precision relative to differences in cure times among different formulations is visually evident in Figure 5, where the whiskers associated with different mean values often do not overlap on the vertical scale of cure time, meaning that the difference in means are statistically significant.

Acknowledgements

Figure 1. StressTech Rheometer with UV Accessory.
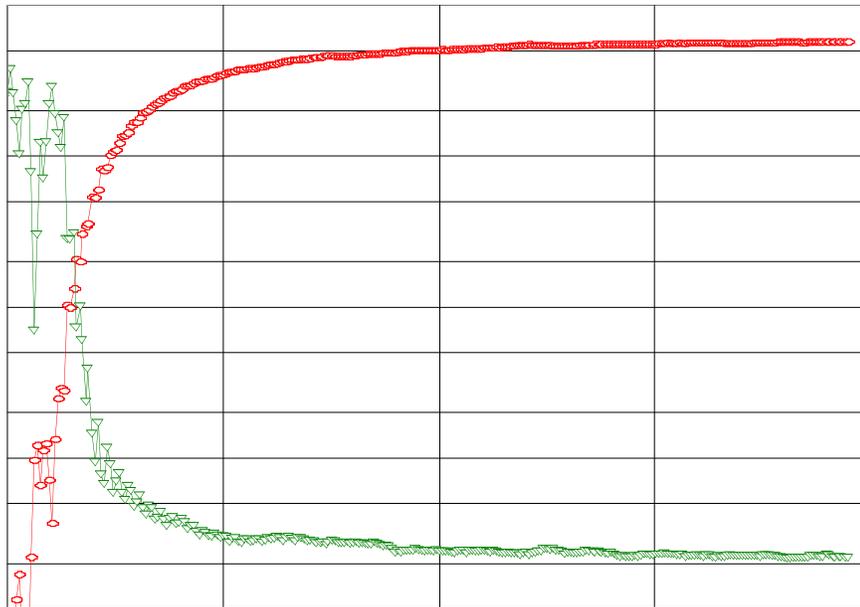
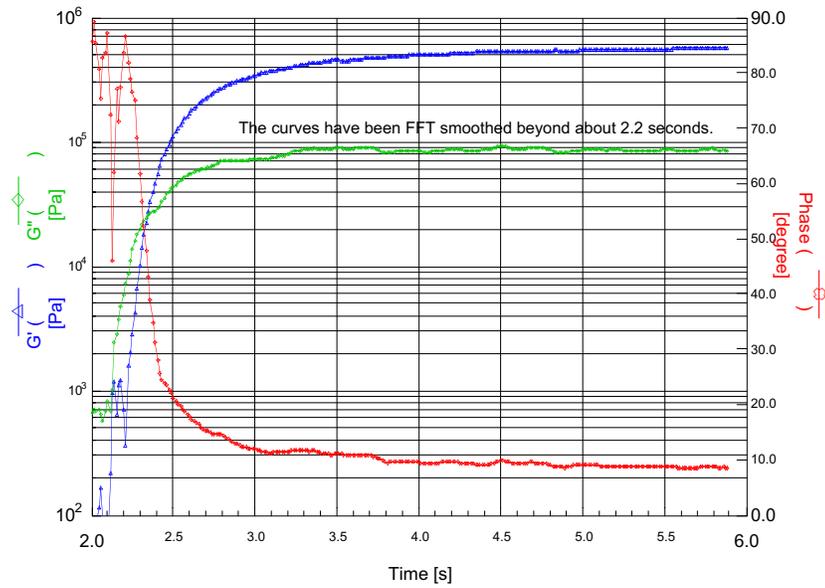**Figure 2. Fiber Optic Inner Primary Coating 3471-1-129A, 22 mW/cm^2.**

Figure 3. 3471-1-129A, 22 mW/cm^2, Run #1, in Orchestrator Software.
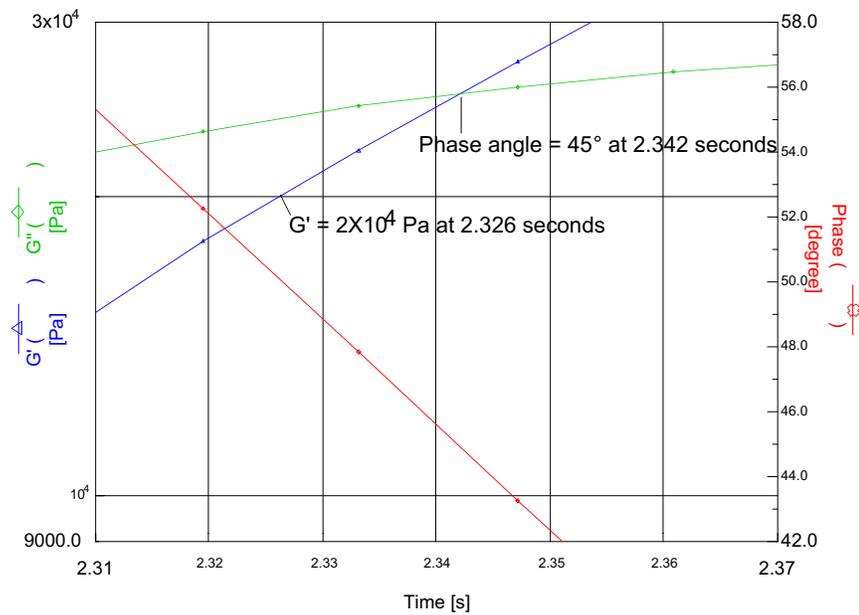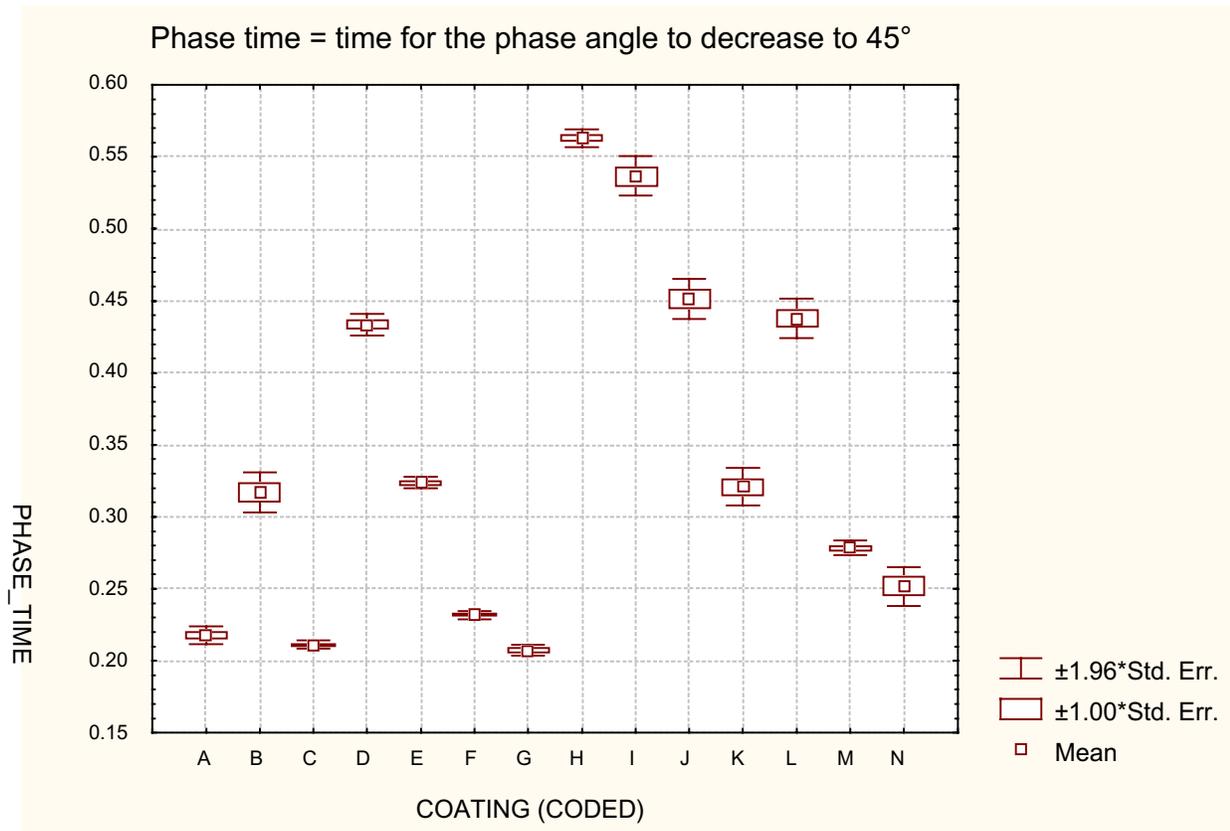

Figure 4. Zoomed View of Curve Intersection from Figure 3.

Figure 5. Categorized Plot for Variable Phase Time.