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Analytical Series:

Comparison of Viscosity Build to Fluorescence Probe Wavelength Shift for Characterizing Cure of Epoxy Resin

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Fluorescence occurs when a molecule (fluorophore) in an excited singlet electronic state returns to the ground electronic state by emission of a photon. Fluorescence is a type of photoluminescence, where a substance emits light after absorption of a photon, as is phosphorescence.

The electronic transitions that give rise to fluorescence are shown in a Jabłoński diagram in *Figure 1*. Absorption of a photon, generally in the UV-visible region of the spectrum, generates an excited singlet electronic state that rapidly relaxes ($\leq 10^{-12}$ s) to the first excited state before fluorescence emission occurs. The relaxation occurs by internal conversion from higher energy singlet states to the first excited singlet state and vibrational relaxation to the ground vibrational state in the excited singlet electronic state. The transition from an excited singlet electronic state to ground state is spin-allowed, so the fluorescence lifetime (τ) is generally in the range of 1–10 ns. The energy of an emitted fluorescence photon is lower energy than the absorbed photon due to internal conversion and vibrational relaxation; this effect is known as the Stokes shift. Internal conversion and vibrational relaxation also makes the fluorescence emission relatively insensitive to the wavelength of the absorbed photon so that, in general, the fluorescence emission spectrum appears as a longer wavelength mirror image of the absorption spectrum. An example of absorption and emission spectra obtained from 4-dimethylamino-4'-nitrostilbene (DMANS) dissolved in methylene chloride is seen in *Figure 2*.

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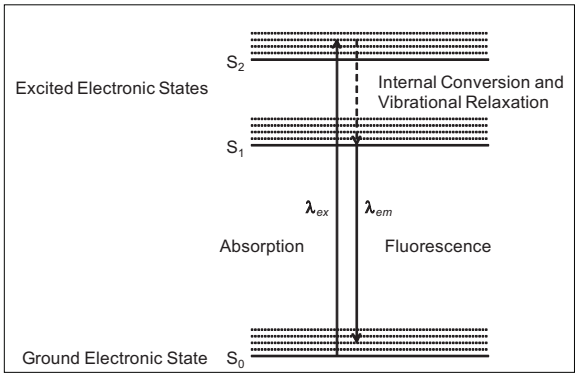
Fluorescent molecules (fluorophores) may be sensitive to a variety of environmental conditions, such

as solvent polarity, micro-viscosity, and pH that affect changes in the emission spectrum. For example, the Lippert Equation describes the effect of solvent polarity on the degree of the Stokes shift.[1] With an appropriate fluorophore, fluorescence spectroscopy is a useful technique for monitoring the degree of cure in polymer films and coatings due to its non-destructive and non-invasive nature. Fluorescence has long been used to study polymer dynamics using fluorophore adducts or probe molecules.[2] Fluorescent dyes have been used as probes to monitor polymer cure by measuring the wavelength shift of the emission spectrum due to changes in the polarity and micro-viscosity of the polymer matrix. Vatanparast has shown correlations between the fluorescence wavelength shift, differential scanning calorimetry (DSC), and infrared measurements of curing in epoxy and polyurethane systems.[3,4] Neckers has reported a method using an intensity ratio to measure the fluorescence emission wavelength shift of probe molecules and correlate it to the degree of cure in polymers determined by DSC and infrared measurements.[5,6]

FIGURE 1—Simple Jabłoński diagram showing electronic transitions that produce fluorescence.



Monitoring the degree of cure of a resin coating can be transferred from the laboratory to the field due to the current availability of small, inexpensive spectrometers with LED excitation sources and fiber optic probes.

Rheology is the branch of science studying the flow and deformation of materials. Rheological measurements have become essential tools for characterizing component materials and final products, monitoring process conditions, as well as predicting product performance.[7] Coatings, which are complex structured fluids, need to be characterized by their structures and flow properties to be applied successfully. Rheological phenomena are found in almost every coatings operation. The study of flow behavior during the application, curing, and drying process of coatings has always been of great interest in rheology. Viscosity and modulus are often the macroscopic flow characteristics obtained from rheological measurements, which can be used to study the microscopic structure of coating systems such as crosslinking chemistry, cure kinetics, drying mechanism, etc.[8,9] Dynamic mechanical analysis (DMA) is one of the widely used tests in rheological measurement of materials.

Thermosetting polymers are an important branch in the coatings industry. Typically, thermosets consist of a mixture of resin and hardener, and catalysts are sometime present to accelerate cure. Unlike thermoplastics, thermosets such as epoxy, unsaturated polyester, polyurethane, vinyl ester, and many others undergo chemical reactions during their use. Because of these reactions, the viscosity of the thermosets increases, and ultimately crosslinking occurs. The cure phenomenon, which is the crosslinking process, normally starts with the growth and branching of chains. With the reaction taking place, the increase in molecular mass also becomes faster, causing a decrease in the total number of molecules and an increase in viscosity. Numerous chains are ultimately connected together into a network formation of infinite molecular mass, and,

FIGURE 2—Comparison of absorption and emission spectra of DMANS in methylene chloride solutions.

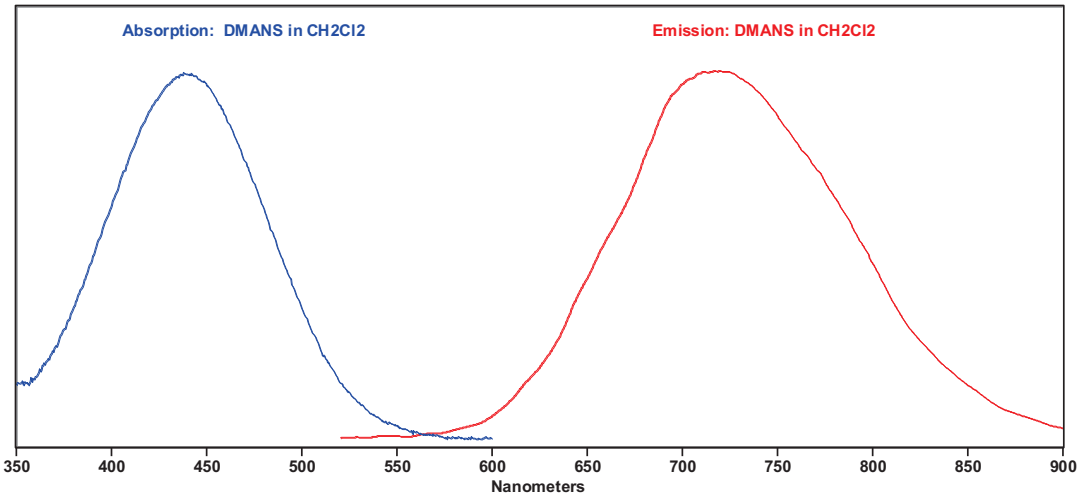


FIGURE 3—Diagram of fluorescence setup with temperature controlled sample stage.

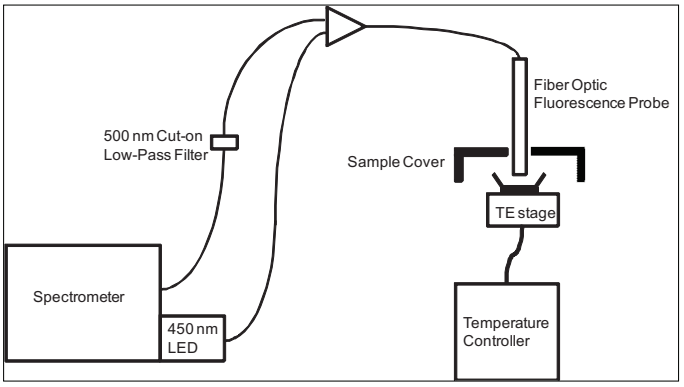


TABLE 1—Epoxy Coating Formulation

COMPONENT	WEIGHT (GRAMS)	FUNCTION
EPON™ 828*	4.5	BISPHENOL A EPOXY RESIN
ANCAMINE® 2089M	1.9	ALIPHATIC AMINE CURATIVE
EPODIL® 748	0.5	MONOFUNCTIONAL REACTIVE DILUENT

*Contains 250 ppm DMANS

TABLE 2—Least Squares Slope, Intercept, and Correlation Coefficient at Cure Temperatures

CURE TEMPERATURE, °C	SLOPE	INTERCEPT	CORRELATION, R^2
30	0.4674	0.1403	0.9992
40	0.4236	0.2873	0.9992
50	0.3964	0.3849	0.9990

therefore, the mobility of individual polymer chains consequently diminishes. Once the materials are crosslinked, they turn into an insoluble and infusible rigid part.

In-situ monitoring of the cure process will provide information about the cure process in real time. Characterization, design, and optimization of the cure process will help control and predict the cure cycle of the materials. Previous studies have shown that there are various methods that can be utilized to monitor the cure process in real time including infrared spectroscopy (IR), Raman spectroscopy, DMA, and ultrasonic methods.[10,11] However, correlation and comparison between DMA and the vibrational spectroscopy method was not well studied and established. In this study, using rheological measurement (DMA) to in-situ characterize cure reaction and monitor cure process by tracking the viscosity change of an epoxy cure system and its correlation with fluorescence wavelength shift will be presented.

SAMPLE PREPARATION

A representative epoxy coating formulation consisting of Epon™ 828 resin, Ancamine® 2089M curative, and Epodil® 748 reactive diluent was used to compare the fluorescence wavelength shift to the viscosity build of the epoxy formulation as a function of time at three temperatures: 30, 40, and 50°C. A 250 ppm solution of the fluorescent dye, 4-dimethylamino-4'-nitrostilbene (DMANS, CAS 4584-57-0), in Epon 828 resin was prepared by heating a weighed amount of the resin to 110°C and stirring in a weighed portion of the dye until all the solids dissolved. The resin with DMANS was allowed to cool to room temperature before use. The weights of resin, curative, and reactive diluent used in the coating formulation are shown in *Table 1*. The components were weighed into a Flaktac™ mixing cup and mixed for 2 min in a Flaktak mixer. Portions of the mixed coating formulation were transferred to a sample cup for fluorescence and parallel plates on RDA-III rheometer for rheology measurements. There was a 2-min delay between the end of mixing and starting both the fluorescence and rheology measurements.

FLUORESCENCE

The fluorescence spectra were obtained with an Ocean Optics USB-4000-FL spectrometer equipped with a 450 nm LED excitation source (USB-LS-450). An Ocean Optics fiber optic fluorescence probe (QF600-8-VIS/NIR) was used to excite and collect the fluorescence signal in a 180° configuration (see *Figure 3*). A low pass optical filter (Thor Labs, FEL0500) with a 500 nm cut was placed between the fiber optic probe and the spectrometer to block reflected light from the excitation LED. A cover was placed over the sample during data collection to prevent interference from room lights. The samples were placed in an aluminum cup attached to a Peltier temperature controlled stage (Sensortek BFS-3TC) with heat-conductive paste. A spectrum was obtained at 1-min intervals during resin cure to correspond to the rheology measurements. OceanView software from Ocean Optics was used to acquire the fluorescence spectra, and all spectrum processing was done using GRAMS/AI from Thermo Fisher Scientific.

RHEOLOGY

Rheological measurements were performed using a TA Instruments RDA-III Rheometer and 25 mm disposable parallel plates. The samples were prepared using the supplied ratio described earlier. The plates were zeroed at desired cure temperature and the sample was loaded. The gap was in the range of 1 to 1.3 mm. Dynamic time sweep at desired cure temperature was carried out with measurement taken every 60 sec using a frequency of 6.28 rad/sec. TA Orchestrator software was used for data processing.

RESULTS AND DISCUSSION

Examples of florescence emission spectra from an epoxy cure at different times after initial mixing are shown in *Figure 4*. The regions indicated on the spectra by vertical lines indicate the emission intensities used to calculate the emission wavelength

FIGURE 4—Examples of fluorescence spectra obtained from different times during an epoxy cure showing the frequency shift of the spectra. Dashed vertical lines indicate regions used to calculate the emission wavelength shift parameter.

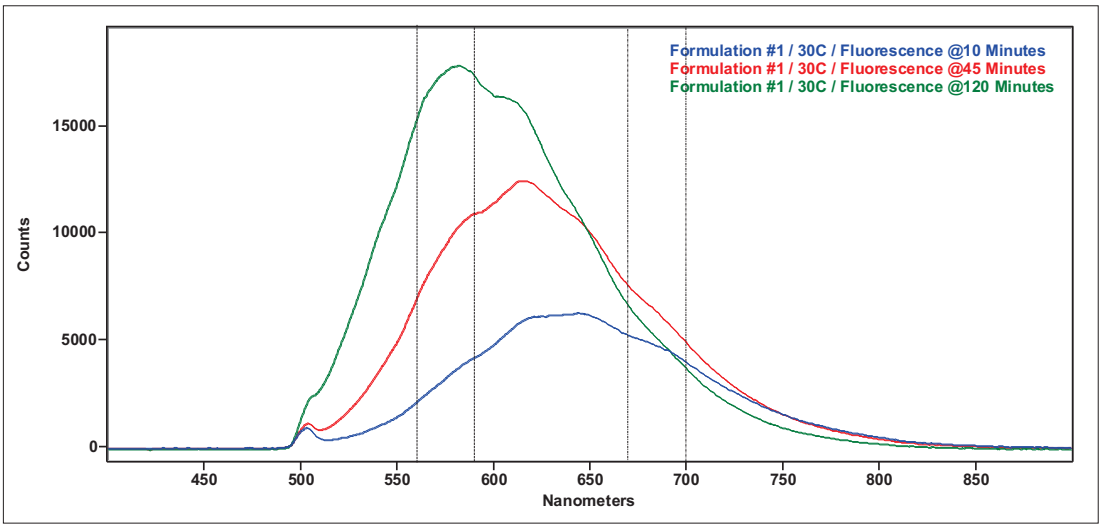


FIGURE 5—Standard deviation of intensity normalized fluorescence spectra obtained during epoxy cure monitor as a function of wavelength.

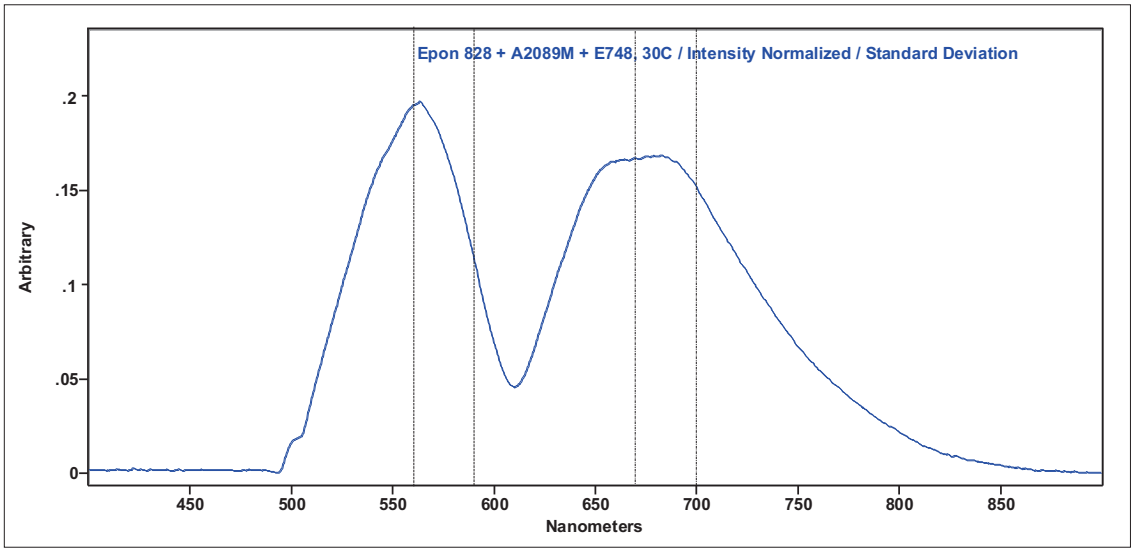
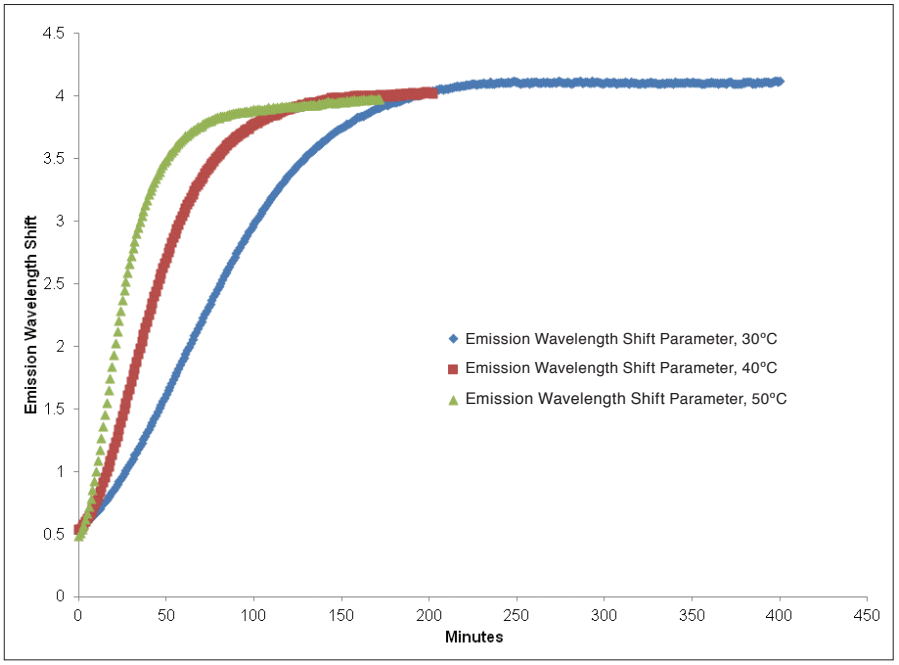


FIGURE 6—Fluorescence emission wavelength shift parameter versus time for epoxy coating formulation cured at 30, 40, and 50°C.



shift parameter, S, for each spectrum, given by: $S = I_S/I_L$, where I_S is the short wavelength intensity in the range of 560–590 nm, and I_L is the long wavelength intensity in the range of 670–700 nm. The short and long wavelength regions were selected by intensity normalizing each spectrum obtained during the cure monitor and then selecting the I_S and I_L in regions containing maxima in the standard deviation of the spectra over the active cure time, as shown in *Figure 5*. The intensity normalization prior to calculating the standard deviation rejects fluorescence intensity changes due to the polymer cure and photo-bleaching of the DMANS from the excitation light. Using intensity ranges allows transfer of the method to a two-channel filter photometer that would be more robust, portable, and inexpensive than a conventional grating spectrograph with a CCD detector.

The fluorescence emission wavelength shift parameter, S, as a function of time for the epoxy coating formulation cured

FIGURE 7—Log(Viscosity) versus time for epoxy coating formulation cured at 30, 40, and 50°C.

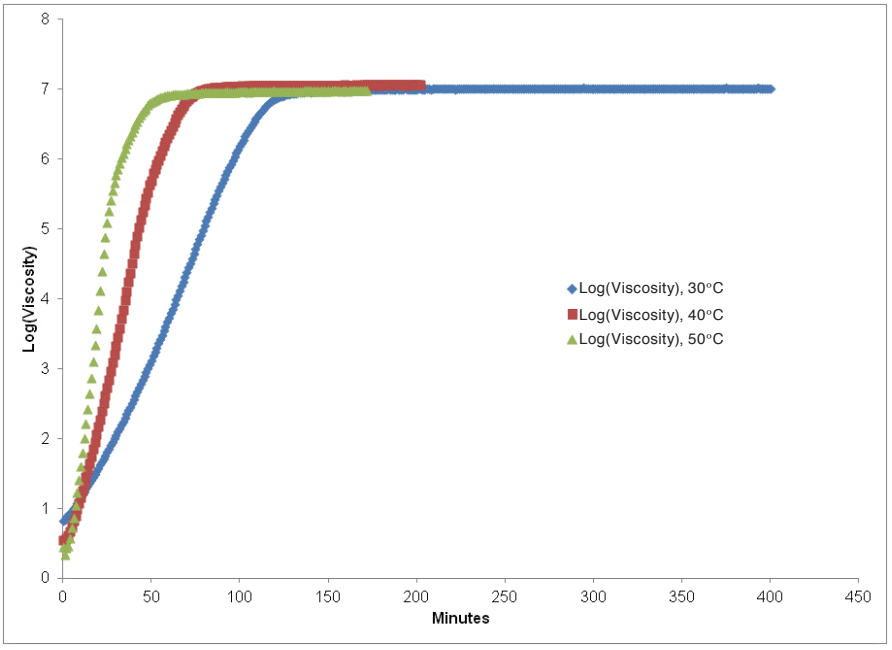
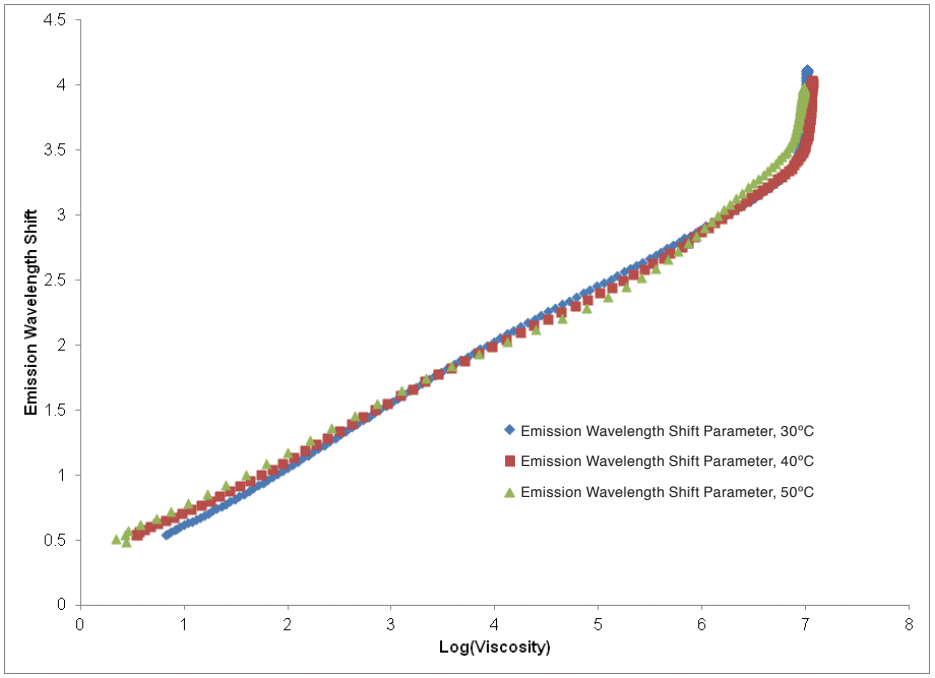


FIGURE 8—Fluorescence emission wavelength shift parameter versus Log(Viscosity) for resin cure at 30, 40, and 50°C.



at 30, 40, and 50°C are shown on the same scale in *Figure 6*. As expected, the shift parameter shows the fastest rise and plateau in the 50°C cure, followed in order by the 40 and 30°C cure profiles. Also note that the profiles plateau at about the same value, indicating the epoxy network is approaching full cure. *Figure 7* displays overlay plots of Log(Viscosity) as a function of time for the epoxy formulation cured at 30, 40, and 50°C. With cure temperature increase, the rate of cure also increases, and the time to reach viscosity plateau value decreases. As shown in *Figure 7*, the times to reach the viscosity plateau (or the instrument measurement limit of 10^7 poise) for the epoxy formulation cured at 30, 40, and 50°C are around 60, 80, and 120 min. Before reaching the plateau, the viscosity build was provoked by the crosslinking reaction that produces the formation of molecular species with growing weight and decreasing mobility.

FIGURE 9—Fluorescence emission wavelength shift parameter versus Log(Viscosity) for resin cure in linear region at 30, 40, and 50°C.

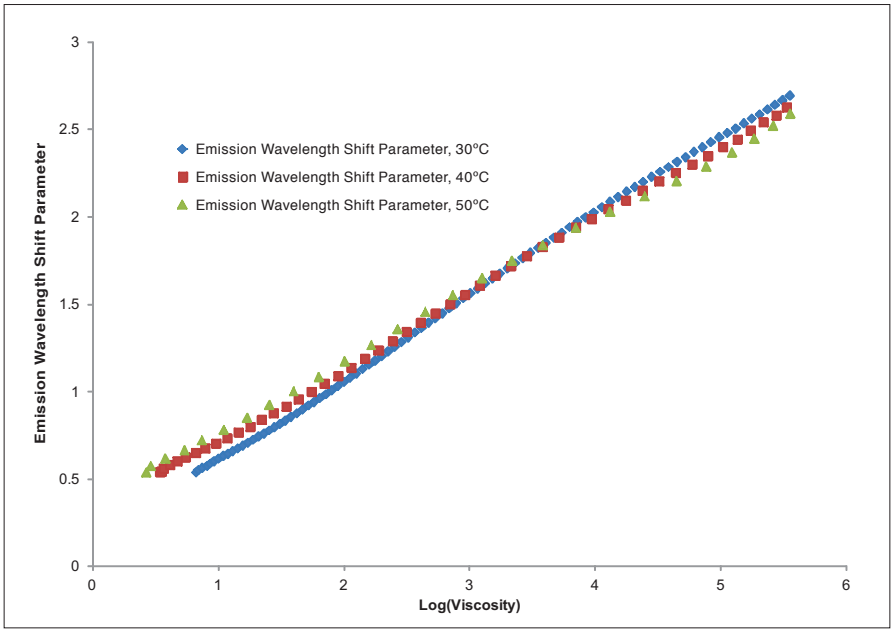
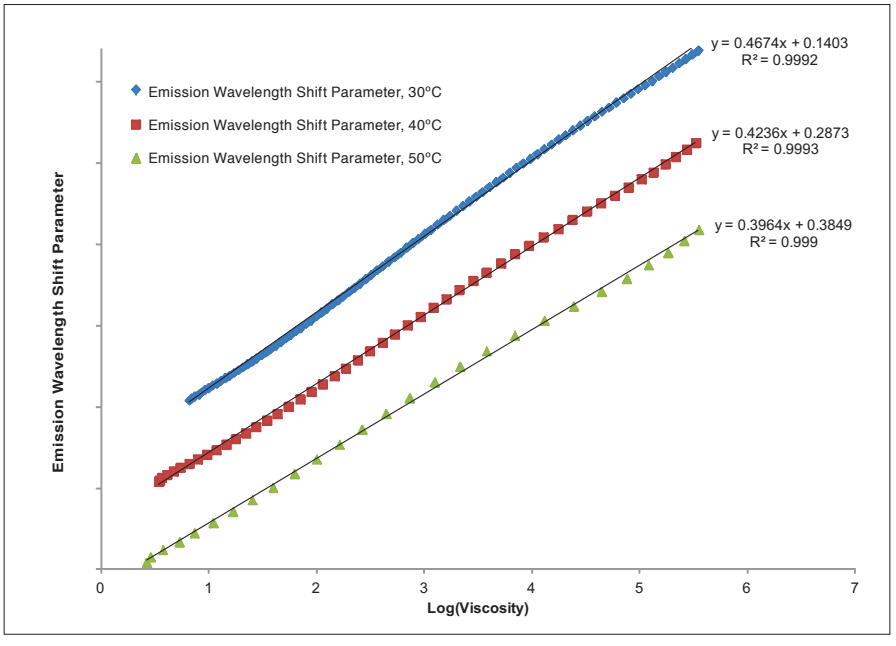


FIGURE 10—Fluorescence emission wavelength shift parameter versus Log(Viscosity) for resin cure in linear region at 30, 40, and 50°C with least squares trend lines. The ordinate scales are offset for clarity.



The results of plotting the fluorescence emission wavelength shift parameter as a function of Log(Viscosity) for the epoxy coating formulation cured at 30, 40, and 50°C are shown on the same scale in *Figure 8*. The plots show the relationship between the wavelength shift parameter and Log(Viscosity) is relatively linear from the start of the cure until between 106 and 107 poise, where the correlation breaks down. The correlation breaks down in this range possibly because the rheometer is approaching its upper measurement limit, and the response could become nonlinear. Plots of the fluorescence emission wavelength shift parameter vs Log(Viscosity) values in the linear region are shown in *Figure 9*. The plots also show the correlation slope has some dependence upon the cure temperature. Individual plots of fluorescence emission wavelength shift parameter vs Log(Viscosity) for the cures at 30, 40, and 50°C are shown in *Figure 10* with least squares fit trend lines labeled with the slope, intercept, and correlation coefficient (R^2). Note that the ordinate scales have been offset to clearly show the data. The slope, intercept, and correlation coefficient (R^2) of the least squares fit trend lines for each cure temperature are also listed in *Table 2*.

The results show that using the wavelength shift in the fluorescence emission spectrum of a probe dye molecule is a viable way to monitor the degree of cure in an epoxy coating formulation that can be directly correlated to the viscosity build measured by DMA. In essence, a calibrated fluorometer/probe dye system is an inexpensive, field-portable alternative for a laboratory-based rheometer. The fluorescence method does not have the measurement range limitation of a rheometer that performs DMA, so it can obtain a more representative endpoint of a thermoset coating.

ACKNOWLEDGMENTS

The authors would like to express our gratitude to Peter Lucas at Air Products and Chemicals, Inc. for the representative epoxy coating formulation and to Prof. Tom Betts at Kutztown University for recommending DMANS as a fluorescent probe for epoxy cure monitoring. ❄

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