# Fluorescence Method for Monitoring Isothermal Curing and Shelf Life of an Epoxy–Anhydride System

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**ABSTRACT:** A fluorescence technique with seven fluorescent probes was applied to monitor the curing and shelf life of an epoxy resin. As isothermal curing proceeded, the fluorescence emission bands of the probes exhibited blue shifts because of microviscosity and micropolarity changes. An intensity ratio method was applied in which ratios of the lowest and highest intensity changes in the emission bands were used to determine the degree of isothermal curing. A smooth and, in some cases, a linear correlation was found between the fluorescence intensity ratio and the degree of cure. This method enables the degree of cure to be monitored and allows comparable results from different types of probes to be monitored during the same curing process. The fluorescence technique and the ratio method offer the possibility of monitoring the precuring and the shelf life of the epoxy polymer. The method can be used to compare the kinetics of various monomers and resin formulations under constant curing conditions. Thus, the method would be useful for developing new resin formulations and technologies and could be applied to a variety of commercial and industrial uses of epoxy resins. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2607–2615, 2001

**Key words:** fluorescence; probe; curing of polymers; shelf life; epoxy; fluorescent

## INTRODUCTION

### Epoxy Polymers

Crosslinking occurs primarily through the hydroxyl groups of the epoxy resin and is considered dependent on the structure and the anhydride used as a crosslinking agent. During the reaction, the curing agents, cyclic anhydrides of dicarboxylic acids, combine with the epoxy to form half-esters. The newly formed carboxyl groups react quickly with other epoxy groups and form additional esters and free hydroxyl groups.[1] The initiation of a curing reaction of epoxy requires a compound that contains an active proton donor. In the presence of proton-donating solvents (e.g., water, methanol, ethanol), the reaction is greatly accelerated, and the sigmoidal form of the rate curve disappears. During curing with anhydrides, the reaction between the hydroxyl and epoxy groups occurs as a side reaction, especially at higher temperatures.[2]

The performance of advanced composites based on epoxy resins is sensitive to the cure cycle of the matrix resin. In epoxy-based composites, the extent of the epoxy cure may vary from part to part or among different locations within the parts. This is because of the exothermic nature of the reaction coupled with poor thermal conductivity and nonuniform geometry. In particular, parts with different shapes and thicknesses are often cured in the same operation. A general approach

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is to overcure most of the parts; this increases the cost because of slower manufacturing-cycle times. Variations in starting materials and changes in storage conditions also contribute to the irreproducible cure of epoxies.

Most of the monomers or polymer formulations have a definite *shelf life,* which is defined as the maximum time that the formulation can be stored. Mixtures of epoxy resins and pure anhydrides are very stable and have a long shelf life because carboxyl groups that act as catalysts are formed only during the reactions at higher temperatures. Often anhydrides are not very pure and contain varying amounts of free carboxyl groups that act as catalysts and react with hydroxyl groups and form esters. Water is also liberated as a result of this condensation. Furthermore, water may also be present in the resin either as a residue of the synthesis process or as a subsequent impurity. Water reacts with an anhydride in the same way as the hydroxyl functions of the resin, which results in the formation of dicarboxylic acid that participates in a crosslinking reaction.[2]

Variations in the amounts of impurities present in most formulations require different curing times. One batch of resin can differ significantly in from another batch, depending on the monomer suppliers, the storage times before application, and the reproducibility of its composition. Thus, it would be advantageous to have a method to immediately detect and adjust the curing process and also provide reproducibility in product quality and optimize the overall cure cycle. Cure monitoring of epoxy resins has been investigated with a number of different online monitoring techniques including microdielectrometry;[3] viscosity-sensitive fluorimetry;[4–7] and acoustic,[8] optical,[9] and chemiluminescence techniques.[10] Other, mostly offline measurements, such as infrared absorption[11–13] and thermal,[14,15] dynamic mechanical,[16,17] and Raman spectroscopy[18] have also been used. However, most methods are difficult to adapt for online monitoring (e.g., fiber-optic IR has a serious limitations for epoxy monitoring because of absorption of the light by the optical fiber below 2300 $cm^{-1}$, where many important epoxy bands are present). Recently, fluorescence techniques have been used to examine the curing characteristics of epoxy resins with intrinsic,[19,20] extrinsic,[21,22] and labeling[23–25] methods.

## Fluorescence Probe Technology

The fluorescence of many fluorophores is sensitive to the polarity of the environment because of the re-orientation of the solvent molecules around the changed dipole moments of excited fluorophores. For example, the fluorescence of para-substituted benzene derivatives are highly sensitive to the solvent polarity because of the localizations of the positive and negative charges on donor and acceptor, which cause a large change in the dipole moment on excitation.[26–29]

Fluorescence spectroscopy has gained considerable interest as a tool for monitoring the curing of polymers because of its high sensitivity, selectivity, and nondestructive characteristics.[30–34] Interactions between the fluorophore molecules and their surroundings are known to affect the energy difference between the ground and excited states.[35] The Lippert equation[35] is often employed to estimate general solvent effects on the emission spectra of the fluorophores. Fluorescence probes are widely used in chemistry for monitoring the specific properties of a medium in which they are incorporated. Some fluorescent compounds exhibit a shift in fluorescence emission with changes in the microviscosity and micropolarity of the medium in which they reside.[36–38]

When such a probe is incorporated in a polymerizing medium, its fluorescence changes with the conversion of monomers into a polymer. As polymerization progresses, the fluorescence spectrum generally exhibits a blue shift. As an epoxy resin cures, its refractive index increases and its dipolar mobility decreases, and as a result, the dye molecules fluoresce from progressively less relaxed states.[39] Therefore, one of the significant features of some fluorescent dyes is that they display a fluorescence wavelength shift as the resin cures. The shift itself cannot be used as an indicator of the progress of polymerization because the spectral shifts between the monomer and the polymer states are in most cases only a few nanometers. In some cases, the intensity of the fluorescence can be used directly as an indicator of the polymerization progress, but it cannot be used for most of the probes and polymers.[40]

Recently Neckers et al.[38,41–44] reported the use of fluorescent probes for monitoring the curing process with an intensity ratio method. In a previous report,[40] we introduced an improvement of the intensity ratio method, lowest and highest intensity change (LHIC), which can be used to obtain comparable results from different types of

**Table I Formulation of Epoxy 1509**

| Name | First Composition | Second Composition |
|---|---|---|
| Epoxy 1509 | Diglycidyl ether of Bisphenol A modified with an cycloaliphatic epoxided alcohol (55.1 wt %) | Acid anhydrydic (methyl nadic) with a latent accelerator (44.9 wt %) |

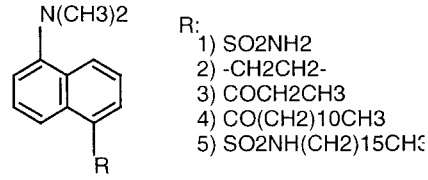
probes and polymers. This article presents the results of a recent study in which the intensity ratio method was applied to seven fluorescent probes to test its suitability for an evaluation of the curing of an epoxy polymer. Remote sensing was achieved through the use of fiber-optic cables to transmit optical signals to and from a polymerization system in real time. Our results indicate that the technique is versatile and has a general applicability in a variety of curing of the epoxy resins.

## EXPERIMENTAL

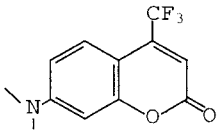
### Materials and Samples

Two components of an epoxy, coded as Epoxy 1509, were obtained from GAIRESA Co. (Ferrol, Spain; Table I). The epoxy polymer has an intrinsic fluorescence emission around 350–500 nm, which depends on the excitation wavelengths. The emission itself was not suitable for study of the curing process because of small changes in its intensity during the curing process. After a process of selection, seven intramolecular charge-transfer probes were chosen and tested to determine their suitability for monitoring the curing process of the epoxy polymer at different temperatures. The probes contain both an electron donor and an electron acceptor, linked by an aromatic chromophore, which often exhibits intramolecular charge-transfer properties with large Stokes shifts or dual fluorescences. Because both twisting and charge separation are involved in the formation of the intermolecular charge-transfer states, the fluorescence emission of the probes is sensitive to both the solvent polarity and medium microviscosity. To monitor the curing of polymers, fluorescent probes with a high fluorescence quantum yield and a large Stokes shift offer reduced possible interference between the intrinsic fluorescence of the polymer and the fluorescence signal of the probe. The structures of the chosen probes and the abbreviations used in this report are shown in Figure 1.

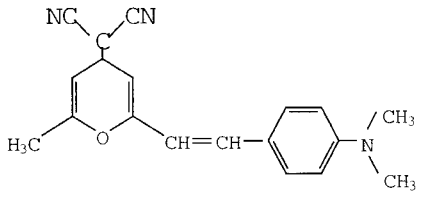
*N*-(5-dimethylaminonaphthalene-1-sulfonyl)-aziridine (DAZ), 7-(dimethylamino)-4-(trifluoromethyl)coumarin (CO152), and 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (4HP) were purchased from Aldrich (YA-Kemia Oy, Helsinki, Finland). 1,6-Propionyl-2-dimethylaminonaphthalene (PRODAN),




1) 5-[dimethylamino] naphthalene-1-sulfonamide, **[DAM]**
2) N-(5-dimethylamino naphthalene-1-sulfonyl) aziridine **[DAZ]**
3) (1,6-propionyl-2-dimethylamino naphthalene) **[PRODAN]**
4) (10,6-dodecanoyl-2-dimethylamino naphthalene) **[LAURDAN]**
5) N-(5-dimethylamino naphthalene-1-sulfonyl) hexadecylamine **[DHDA]**




(7-(dimethylamino)-4-(trifluoromethyl) coumarin) **[CO152]**




4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran **[4HP]**

**Figure 1** Chemical structures and abbreviations of the seven probes that were used to monitor the curing of Epoxy 1509.

10,6-dodecanoyl-2-dimethylaminonaphthalene (LAURDAN), *N*-(5-dimethylamino naphthalene-1-sulfonyl)hexadecylamine (DHDA), and 5-(dimethylamino)naphthalene-1-sulfonamide (DAM) were purchased from Molecular Probes (Biofellows OY, Helsinki, Finland). All the probes were spectroscopic grade and used as received without further purification.

Polymer–probe mixtures were prepared and curing was monitored as follows: the fluorescence probes were doped ($0.25 \times 10^{-3}$ mol/dm$^3$) into the first component, the epoxy resin. This was mixed subsequently with the second component, the anhydride. The mixtures were sandwiched (0.05 mg) between two glass plates, and the thickness of the mixtures was controlled by a double-coated tape (92 $\mu$m). The recommended temperatures for isothermal curing of the epoxy were 90, 100, and 120°C. The shelf life of the mixture of the epoxy and the anhydride was checked by monitoring the precuring of the mixture at the room temperature.

### Instrumentation and Experiments

Fluorescence was recorded with a Spex Fluorolog 3 spectrofluorometer (Jobin Yvon, S.A., Longjumeau Cedex, France) in front-phase mode for the polymeric films. Remote measurements were carried out with a fiber-optic cable attached to the excitation and emission monochromators. The excitation light was injected into an optical fiber, which carried the light to the measurement site. The measurement site included a sample fixed in a sample holder inside an oven. The sample was fixed at an angle in the sample holder to protect the emitted light from reflection of light from surface of the glass plate. The fluorescence emitted by the sample on irradiation with the excitation beam was picked up by another set of the optical fibers. When an optical fiber is used in a measurement system, a number of factors can affect the observed fluorescence intensity ($I$). These factors include temperature, optical alignment, excitation area, and background fluorescence level of the optical fiber. A fiber-optic fluorimeter has a background fluorescence level that results from an elastically scattered incident radiation and luminescence from the fiber itself.[23]

A differential scanning calorimeter (model 821, Metler Instruments, Oy G.W. Berg, Espoo, Finland) was used to follow the overall curing process. Conversions of Epoxy 1509 were determined at temperatures of 90, 100, and 120°C and at room temperature with the enthalpy and the glass-transition temperature ($T_g$) changes of the curing processes.

## RESULTS AND DISCUSSION

### High-Temperature Curing

The curing of Epoxy 1509 was monitored by measurement of the broad fluorescence emission bands of the selected probes as a function of the curing time at constant temperatures of 90, 100, and 120°C. The probes produced fluorescence emission at different wavelengths and behaved differently depending on the temperature. There were no pronounced changes in the shapes of the fluorescence spectra, which indicated that there were no significant specific interactions among the seven fluorescence probes with Epoxy 1509. The observed shifts of the fluorescence bands to shorter wavelengths were consistent with the predictions of the Lippert equation.[35] The refractive index of an epoxy resin usually increases with the extent of cure,[45] whereas the dielectric constant decreases,[46] which leads to a decrease in the Stokes shift. The changes in the wavelengths for each of the probes are listed in Table II.

The probes exhibited significant blue shifts on polymerization. The largest spectral shifts were observed for DAZ and 4HP. The magnitude of the shift increased with a decrease in the polarity of the environment. This caused the main changes in the emission band positions. However, the blue shifts observed in probe–polymer systems under investigation could not be used alone as reliable indicators of the degree of cure.

When the crosslinking of a polymer matrix increases, intramolecular charge-transfer probes are expected to increase their $I$s.[41] The emission spectra of DAZ during the curing of Epoxy 1509 at 90°C are shown in Figure 2, where the arrows show the evolution of the spectra during the curing process. The behavior of the DAZ was the same at different temperatures because of the same environmental changes in Epoxy 1509. At higher temperatures, changes occurred more rapidly because of the higher rate of the curing process. Five probes, DAZ, DAM, DHDA, 4HP, and CO152, showed the same behavior, namely, an increase in $I$ during the curing process.

Two probes, PRODAN and LAURDAN, exhibited similar behavior. The emission spectra of PRODAN during the curing of Epoxy 1509 at

**Table II Wavelength Changes of Emission Maxima During Curing at 90, 100, and 120°C and the Wavelengths That Were Chosen for Calculation of the LHIC Ratio**

| | Epoxy 1509 | | | | | |
|---|---|---|---|---|---|---|
| | Wavelength Changes of the Emission Maxima During the Curing Process (nm) | | | Wavelengths Chosen for the LHIC Ratio (nm) | | |
| Probe | 90°C | 100°C | 120°C | 90°C | 100°C | 120°C |
| DAM | 23<br>504 → 481 | 29<br>502 → 473 | 19<br>501 → 482 | 599/453 | 603/458 | 627/458 |
| DAZ | 32<br>507 → 475 | 33<br>508 → 475 | 25<br>492 → 467 | 618/456 | 612/448 | 649/460 |
| DHDA | 23<br>492 → 469 | 23<br>493 → 470 | 18<br>491 → 473 | 591/447 | 610/444 | 635/447 |
| 4HP | 36<br>603 → 567 | 32<br>598 → 566 | 33<br>598 → 565 | 744/533 | 743/534 | 739/539 |
| CO152 | 19<br>489 → 470 | 18<br>485 → 467 | 20<br>487 → 467 | 689/443 | 687/432 | 699/430 |
| PRODAN | 22<br>452 → 430 | 20<br>452 → 432 | 20<br>451 → 431 | 495/397 | 497/397 | 497/399 |
| LAURDAN | 23<br>454 → 431 | 20<br>452 → 432 | 16<br>448 → 432 | 505/394 | 494/399 | 489/391 |

90°C is shown in Figure 3. This probe showed a decrease in emission intensity during the curing process that could not be attributed to the changes in viscosity or mobility as polymerization proceeded.[47–49] A decrease in emission intensity as the crosslinking of a polymer matrix increases is not a generally observed phenomenon. This behavior is, however, consistent with the work of Loutfy et al.,[50] who showed that environmental factors resisting the internal molecular rotation of donor–acceptor dyes led to a decrease in nonradiative decay and, consequently, to an increase in the fluorescence yield. To enable a comparison of the various sets of measurements, the *I*s were normalized to the same initial value by application of eq. (1):

$$\text{Normalized } I = \frac{I}{I_0} - 1 \tag{1}$$

where $I$ is the fluorescence intensity at any degree of the cure and $I_0$ is the fluorescence intensity before the cure. In Figure 4, the normalized *I*s of

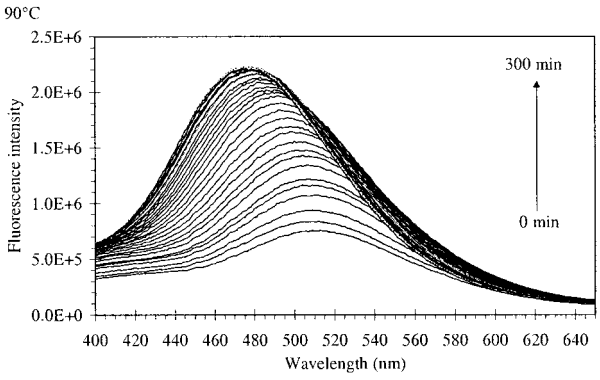



**Figure 2** Fluorescence emission spectra of DAZ during the curing of Epoxy 1509 at 90°C. The arrows show the order of the spectra during curing.

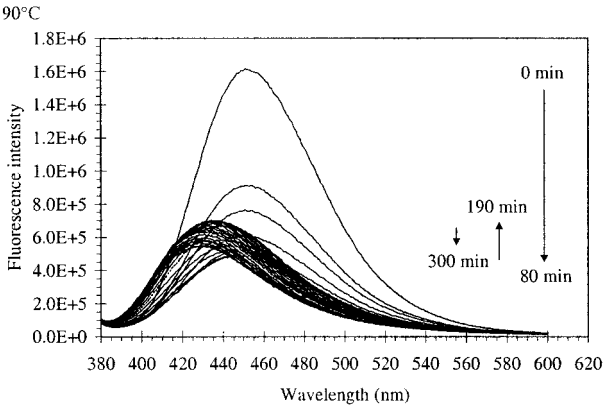



**Figure 3** Fluorescence emission spectra of PRODAN during the curing of Epoxy 1509 at 90°C. The arrows show the order of the spectra during curing.

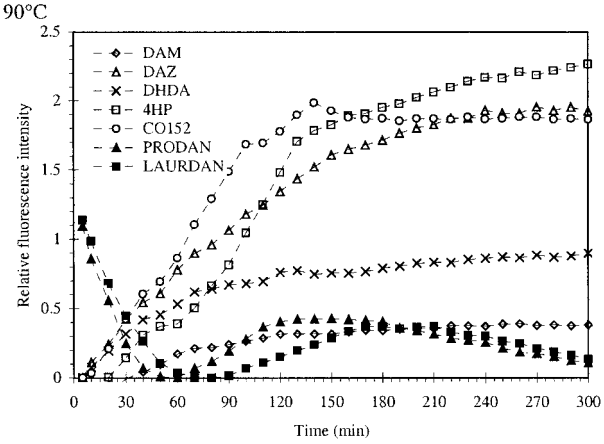



**Figure 4** Relative *I*s of the emission maxima of the probes as a function of the curing time of Epoxy 1509 at 90°C.

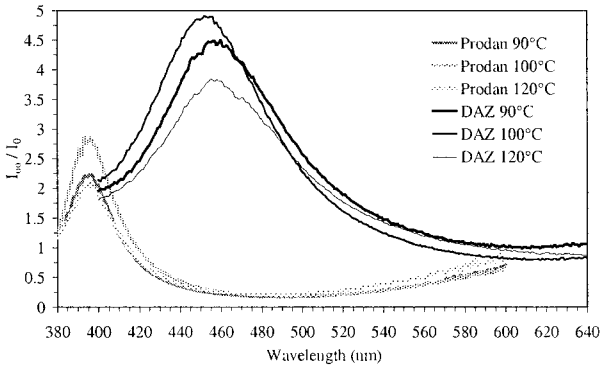



**Figure 5** $I_\infty/I_0$ for DAZ and PRODAN during the curing of Epoxy 1509 at 90, 100, and 120°C as a function of the wavelength.

the emission maxima for each probe are presented as a function of curing time for Epoxy 1509. The lowest $I$ was chosen instead of $I_0$ for PRODAN and LAURDAN. The relative intensities of the probes were determined 5 min after placing the samples in the oven to take into account the increase in temperature of the samples in the oven during the first 5 min of the process. As the temperature of the mixture increased, the *I*s decreased because the decrease in the viscosity of the mixture led to an increase in the nonradiative decay rates.

The *I*s of the probes DAZ and 4HP could be used directly to monitor the curing process. These two probes exhibited an increase in $I$ during the curing process. The $I$ remained constant or decreased when a conversion of more than 90% was reached. A comparison of the conversion curves measured by differential scanning calorimetry (DSC) with the curves of $I$ changes in emission maxima for each of the probes demonstrates that the $I$ changes varied depending on the probe–polymer system. Different probes in the same curing environments exhibited different behaviors, and thus, the $I$ for a given probe could not necessarily be correlated directly with the conversion percentage.

External factors such as temperature, optical alignment of the system, optical fiber position, excitation area, thickness of the sample, and input light intensity could contribute to the differences in the observed *I*s.[35,51,52] It was, therefore, necessary to have an internal reference with which the intensity could be normalized irrespective of the external variables affecting the intensity fluctuations. Thus, an LHIC ratio ($R$)[40] was used to determine the degree of curing. This method is independent of the probe type and also of the experimental conditions. In the LHIC method, the emission spectrum of the cured polymer, measured at the end of the curing process, is divided by the emission spectrum of the mixed monomers at the outset of the curing process. Thus, the intensity changes are obtained as a function of the wavelengths, and the low-intensity changes and the high-intensity changes can be found. The results for DAZ and PRODAN are presented in Figure 5. The chosen wavelengths for each of the probes when the $R$ method was applied are listed in Table II. Figure 5 and Table II show that the wavelengths that had the LHICs covered certain areas of the wavelengths for each probe. Thus, when the method was applied, two

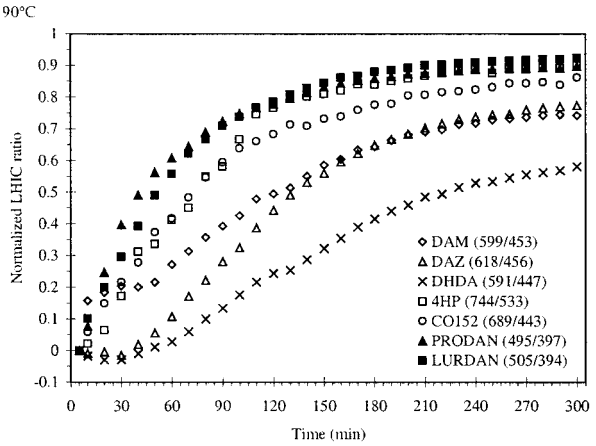



**Figure 6** Normalized *R*s of the probes during the curing of Epoxy 1509 at 90°C as a function of the curing time.

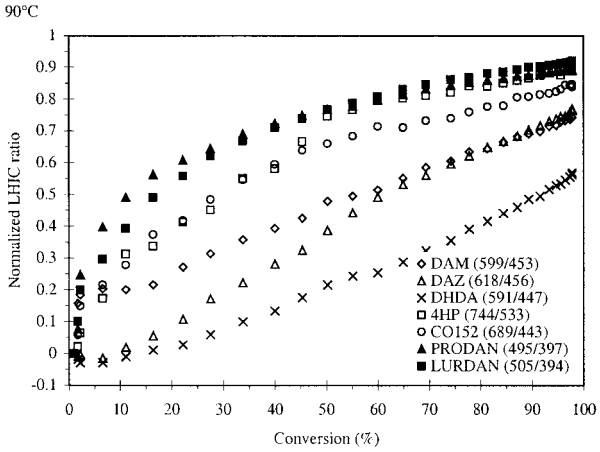



**Figure 7** Normalized *R*s of the probes during the curing of Epoxy 1509 at 90°C as a function of the conversion measured by DSC.

wavelength regions could be chosen for each of the probes.

LHIC curves were obtained by the division of the intensities at a given wavelength in the longer wavelength region by the intensities of a given wavelength in the shorter wavelength region at all times during the curing process. The ratios were normalized with eq. (2) to their initial values before curing to enable comparison between the various sets of measurements:

$$\text{Normalized } R = 1 - \frac{R}{R_0} \qquad (2)$$

where $R$ is the LHIC ratio at any degree of the cure and $R_0$ is LHIC ratio before the cure. The normalized *R*s of the selected probes are shown in Figure 6 as a function of curing time. As shown, by application of the $R$ method, similar behavior could be observed for all the probes.

The correlation between the normalized *R*s and the conversion percentages measured by DSC are shown in Figure 7. As shown, it was possible to obtain a similar correlation for all probes. The differences in the slopes reflect some useful information, such as the sensitivity of the probes to environment changes. In all cases, there was a continuous smooth change of the ratio with the degree of cure. A linear relationship was observed in all cases and in the main part of the process. Once the relationship between $R$ and the degree of cure was established, it could be used to predict the degree of curing. The suitability of all the probes for monitoring the whole curing process at higher temperatures could be confirmed by comparison of the *R*s with the $T_g$ curves. The results show that the $R$ method provides a general method for monitoring and calibrating the curing of the epoxy polymers.

## Shelf Life

The shelf life of the mixture of epoxy resin and anhydride was monitored with seven probes at room temperature. The changes in the wavelengths of the emission maxima for each of the probes are presented in Table III. A blue shift occurred because of the precuring process. The change in the intensity of the spectra during the measurements was caused by changes in the instrumental factors and the excitation area of the sample. Thus, the original intensities could not be used directly, and a calibration was required. The conversion percentage and $T_g$ of Epoxy 1509 were determined by DSC at room temperature.

To determine the degree of precuring, $R$ was applied. For each of the probes, the wavelengths

**Table III Wavelength Changes of Emission Maxima During Curing at Room Temperature and the Wavelengths that Were Chosen for Calculation of the LHIC Ratio**

| | Epoxy 1509 | | | | | | |
|---|---|---|---|---|---|---|---|
| Probe | DAM | DAZ | DHDA | 4HP | CO152 | PRODAN | LAURDAN |
| Wavelength changes of the emission maxima during the curing process (nm) | 15<br>508 → 493 | 19<br>523 → 502 | 8<br>500 → 492 | 19<br>599 → 580 | 9<br>490 → 481 | 10<br>448 → 438 | 11<br>446 → 435 |
| Wavelengths chosen for the LHIC ratio (nm) | 619/454 | 644/457 | 600/456 | 659/484 | 604/433 | 456/358 | 458/382 |

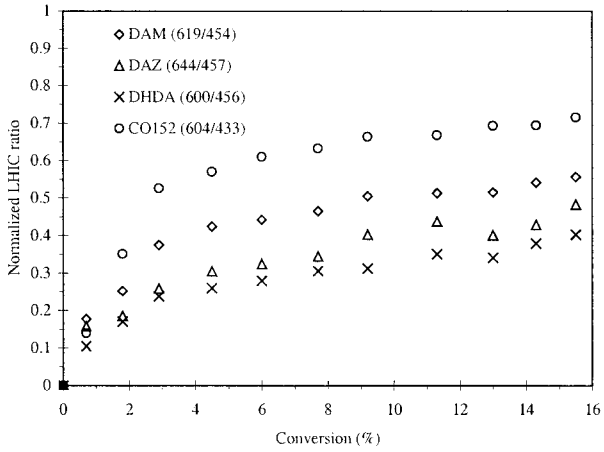



**Figure 8** Normalized *R*s of the probes during the curing of Epoxy 1509 at room temperature as a function of the conversion measured by DSC.

at which the *R* method was applied are listed in Table III. A smooth change of *R* and similar behavior could be observed for all the probes when the LHIC method was applied. The suitability of all the probes for monitoring the precuring or shelf life of Epoxy 1509 could be confirmed by comparison of the *R*s with the $T_g$ curves. The $T_g$ of Epoxy 1509 changed over a period of 11 days during the measurements, whereas the intensity ratios of three probes 4HP, PRODAN, and LAURDAN remained constant by 7 days. This demonstrates that the three probes, 4HP, PRODAN, and LAURDAN, were not sufficiently sensitive for monitoring precuring after the 7th day. The *R*s of the selected probes as a function of conversion are shown in Figure 8.

Thus, the results indicate that to find suitable probes, it is necessary to confirm the results obtained with reference to $T_g$ curves. As shown, it is possible to obtain similar correlations for most of the probes. In the main part of the process, a linear correlation between *R* and the conversion percentage could be found for some of the probes. The results show that the *R* method is a good method for monitoring the precuring and shelf life of the epoxy polymers. It also provides a calibration method for avoidance of the influences of any other changes (e.g., in the measuring area of the sample, the sample thickness, or the lamp intensities during the curing process).

It should be noted that for the purpose of quality and curability control of different supplies of the same resin formulation, all of the measurement parameters, including the excitation wavelength, the ratio of the monitoring wavelengths, the sample thickness, the excitation beam intensity, and the temperature, should always be held constant. Obviously, a set of measurement parameters can be determined for the cure monitoring of every probe–polymer system whenever necessary.

## CONCLUSIONS

The results show that fluorescence spectroscopy is a quick, effective, reliable, and nondestructive measurement method for monitoring the curing or shelf life of epoxy polymers. As the curing process proceeds, the fluorescence emission spectra of the probes exhibits blue shifts because of changes in the matrix microviscosity and micropolarity. With appropriate selection and concentration of the probe and the optimization of the monitoring parameters, the degree of the cure can be monitored simultaneously. A correlation between the ratios of the *I*s, selected from the wavelength ranges representing the LHICs, and the degree of the polymerization was obtained. The *I* ratio method eliminates the effect of intensity variations that arise because of external factors such as lamp intensity, optical alignment, probe location, excitation area, and temperature variation. The advantage of the *R* method is that it enables changes in composition to be monitored throughout the curing process independent of the probe. Application of cure monitoring with the *R* method offers the possibility to precisely control the parameters of the curing process and provides quantitative control of the quality and curability of the starting materials. The fluorescence cure sensing technique based on the *R* method can be applied *in situ* for the monitoring of polymerization in a variety of commercially and industrially used polymers.

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