Monitoring of Curing Process and Shelf Life of the Epoxy−Anhydride System with TICT Compounds by the Fluorescence Technique

Kati Hakala,*,† Ramin Vatanparast,† Shuyan Li,† Carmen Peinado,‡ Paula Bosch,‡ Fernando Catalina,‡ and Helge Lemmetyinen†

Institute of Materials Chemistry, Tampere University of Technology, P.O. Box 541, FIN-33101 Tampere, Finland, and Instituto de Polimeros, Consejo Superior de Investigaciones Cientificas, Calle Juan de la Cierva, 3-28006 Madrid, Spain

Received April 4, 2000; Revised Manuscript Received June 1, 2000

ABSTRACT: In this study the curing degree and the shelf life of an epoxy resin were monitored by a fluorescence method. Four extrinsic fluorescence probes, so-called TICT compounds, were used. An intensity ratio method was applied, in which ratios of the lowest and highest intensity changes in the emission bands are used to determine the degree of the isothermal curing. A smooth and in some cases a linear correlation was found between the fluorescence intensity ratio and the degree of the cure. The fluorescence technique and the ratio method enable the monitoring of the precuring and shelf life of the studied epoxy polymer.

Introduction

The performance of advanced composites based on epoxy resins depends sensitively on 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, due to the exothermic nature of the reaction coupled with the poor thermal conductivity and a nonuniform geometry. Particularly, parts with different shapes and thicknesses are often cured in the same operation. A general approach is to overcure most of the parts in order to increase the cost due to slower manufacturing cycling times. Variations in starting materials and changes in storage conditions also contribute to the nonreproducible cure of epoxies.

Most of the monomers or polymer formulations have a definite "shelf life", which means 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, since carbonyl groups that act as catalysts are only formed during the reaction at higher temperatures.

Because of variations in the amounts of the impurities present in most of the monomers used for the polymer formulations, different curing times are required for each. One batch of resin can differ significantly from another, depending on the monomer suppliers, the storage times before application, or the reproducibility of its composition. Thus, it would be advantageous to have a method to immediately detect and adjust the curing process as well as to provide reproducibility in the product quality and to optimize the overall cure cycle. Cure monitoring of epoxy resins has been investigated using a number of different on-line monitoring techniques including microdielctrometry,[1] viscosity-sensitive fluorimetry,[2−4] acoustic,[5] optical,[6] and chemiluminescence techniques.[7] Others, mostly for off-line measurements, such as infrared absorption,[8−10] thermal,[11,12] dynamic mechanical,[13,14] and Raman spectroscopy,[15] are also used. However, most methods are difficult to adapt for on-line monitoring (e.g., fiber-optic IR has a serious limitation for an epoxy monitoring due to 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 using intrinsic,[16,17] extrinsic,[18,19] and labeling[20−22] methods.

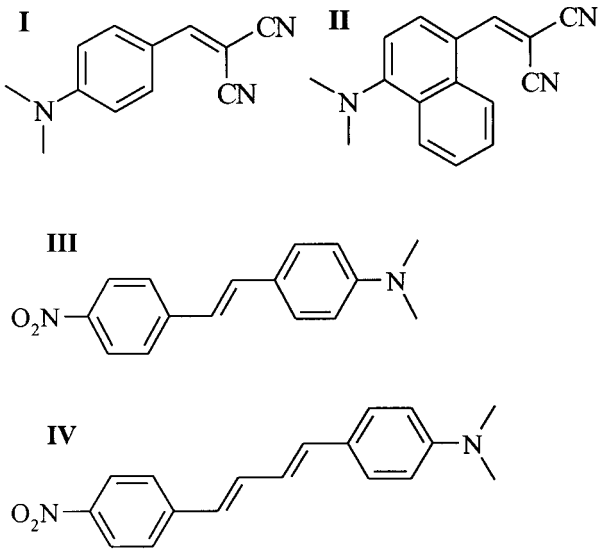
Fluorescence spectroscopy has gained considerable interest as a tool for monitoring the curing of polymers because of its high sensitivity, selectivity, and nondestructive characteristics.[23] Interactions between the fluorophore molecules and their surroundings are known to affect the energy difference between the ground and excited states.[24] 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.[25−27] When such a probe is incorporated in a polymerizing medium, its fluorescence changes with the conversion of monomers into a polymer. As polymerization proceeds, 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.[28] 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 emission can be used directly as an indicator of the polymerization progress.[29]

Neckers et al.[27,30−33] have reported the use of fluorescence probes for monitoring the curing process using an intensity ratio method. In our previous report[29] we presented also the use of an intensity ratio method, lowest and highest intensity change (LHIC), which can be used to follow the curing of different types of polymers with several probes. The present paper presents the results of a recent study in which the intensity

† Tampere University of Technology.
‡ Consejo Superior de Investigaciones Cientificas.

10.1021/ma000599n CCC: $19.00
Published on Web 07/21/2000



I 4-dicyanovinyl-N,N-dimethylaniline, (DMABM)
II 4-dicyanovinyl-N,N-dimethylamino-1-naphthalene, (DMANM)
III 4-dimethylamino-4′-nitrostilbene, (DMANS)
IV 4-dimethylamino-4′-nitrophenylbutadiene, (DMANPB)

Figure 1. Structures and abbreviations of the four probesthat were used for monitoring the curing of LAB 1509.

ratio method was applied to four fluorescent probes in order to test its suitability for an evaluation of the curing and shelf life of an epoxy polymer. Remote sensing was achieved by using fiber-optic cables to transmit optical signals to and from a polymerization system in real time and in situ. The results indicate that the technique is versatile and has a general applicability in a variety of curing processes of the epoxy resins.

Experimental Section

The studied polymer adhesive was an epoxy resin, coded LAB 1509, and its two components were obtained from GAIRESA Co., Spain. The component configurations were diglycidyl ether of Bisphenol A modified with a cycloaliphatic epoxided alcohol (55.1 wt %) and acid anhydric (methyl nadic) with a latent accelerator (44.9 wt %). The epoxy polymer has an intrinsic fluorescence emission around 350−500 nm depending on the excitation wavelengths. The emission itself was not suitable for studying the curing process due to small changes in its intensity during the curing process.

Four twisted 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 a large Stokes shift or a dual fluorescence. 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 reduce 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.

4-Dicyanovinyl-*N*,*N*-dimethylaniline (DMABM) [**I**], 4-dicyanovinyl-*N*,*N*-dimethylamino-1-naphthalene (DMANM) [**II**], 4-(dimethylamino)-4′-nitrostilbene (DMANS) [**III**], and 4-(dimethylamino)-4′-nitrophenylbutadiene (DMANPB) [**IV**] were all synthesized by ICTP. 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 ($c = 0.25 \times 10^{-3}$ mol dm^{-3}) into the first component, the epoxy resin, and then mixed subsequently with the second component, the anhydride. The mixtures were sandwiched (0.05 g) between two glass plates, and the thickness of the mixtures was controlled by a double-coated tape (92 μm). The recommended temperatures for the isothermal curing of the epoxy were 90, 100, and 120 °C. The shelf life of the mixture of the epoxy and the anhydride was studied by monitoring the precuring of the mixture at the room temperature, 20 °C, and at a low temperature, 6 °C.

Fluorescence was recorded using a Spex Fluorolog 3 spectrofluorometer. At 20 and 6 °C the fluorescence spectra were measured using a front-phase method. For higher temperatures, in-situ measurements were carried out inside an oven using a fiber-optic cable attached to the excitation and emission monochromators. The sample was fixed at an angle in a sample holder in order to avoid scattering of the emitted light from the surface of the glass plate. The fluorescence emitted by the sample upon irradiation with the excitation beam was collected 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. These include temperature, optical alignment, excitation area, and the background fluorescence level of the optical fiber. A fiber-optic fluorimeter has a background fluorescence level resulting from an elastically scattered incident radiation as well as luminescence from the fiber itself.[20]

A differential scanning calorimeter (DSC), model 821, Metler Instrument, was used to follow the overall curing process. Conversions of LAB 1509 were determined at temperatures of 6, 20, 90, 100, and 120 °C using the enthalpy and the glass transition temperature, T_g, changes of the curing processes.

Results and Discussion

The fluorescence spectrum of the probe−polymer system can be represented as

$$I_{\text{polymer-probe}}(\lambda,t) = I_{\text{probe}}(\lambda,t) + I_{\text{polymer}}(\lambda,t) + I_{\text{instrument}}(\lambda) \quad (1)$$

where λ is the emission wavelength and t is the curing time. Equation 1 shows that the monitoring precision and the reproducibility of the curing depend strongly on the magnitude and character of the intrinsic polymer fluorescence intensity. The fluorescence intensity of many polymers upon irradiation may be constant or may vary during changes in the polymer matrix. The fluorescence of LAB 1509 changes very little and is assumed to be constant during the curing process. The effect of the fluorescence of the polymer itself can be minimized by choosing probes with large extinction coefficients and long excitation wavelengths or by using high concentrations of the probes in the polymer−probe mixtures. It was found that, for monitoring to be possible, the fluorescence intensity of the probe had to exceed the intrinsic fluorescence of the polymer. If the fluorescence of the polymer is time-independent, the influence of the fluorescence intensity of the polymer is small, and all changes taking place can be considered as being due to the probe. In this situation, eq 1 can be reexpressed as follows:

$$I_{\text{polymer-probe}}(\lambda,t) = I_{\text{probe}}(\lambda,t) + I_{\text{constant}}(\lambda) \quad (2)$$

The high-temperature curing of LAB 1509 was monitored at constant temperatures of 90, 100, and 120 °C by measuring the fluorescence emission of the selected

Table 1. Wavelength Changes of Emission Maxima during the Curing of LAB 1509 at 90, 100, and 120 °C and the Wavelengths That Were Chosen for LHIC Ratio Calculation

	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
I	3 (395→392)	8 (399→391)	3 (394→397)	580/420	620/415	620/415
II	6 (415→421)	1 (419→418)	4 (418→422)	600/390	590/400	630/410
III	47 (579→626)	55 (626→571)	31 (571→602)	740/570	750/575	750/575
IV	33 (602→569)	65 (588→523)	28 (591→563)	815/620	800/627	830/650

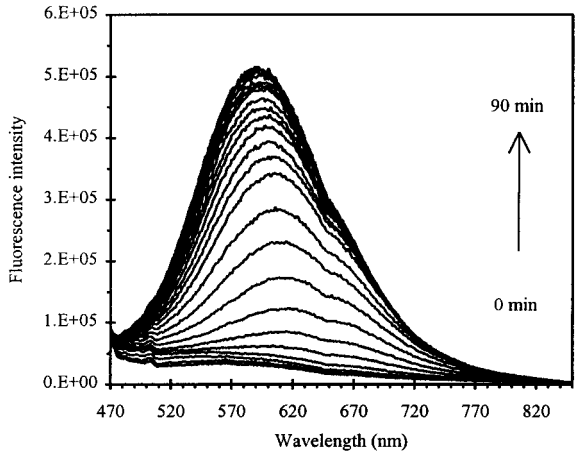


Figure 2. Fluorescence emission spectra of probe **IV** during the curing of LAB 1509 at 120 °C. The arrow indicates the order of the spectra during the curing.

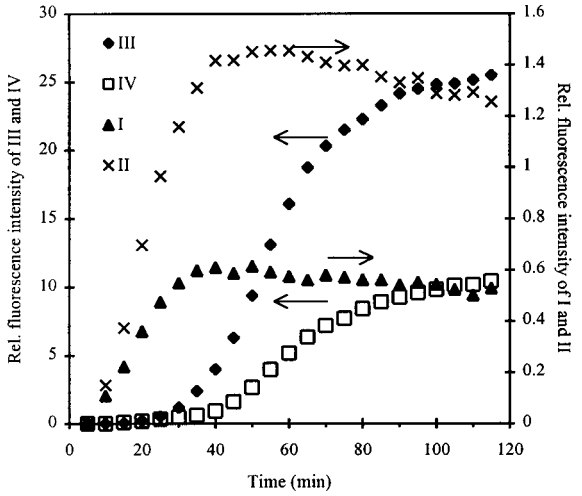


Figure 3. Relative fluorescence intensities of emission maxima of the four probes as a function of the curing time of LAB 1509 at 120 °C.

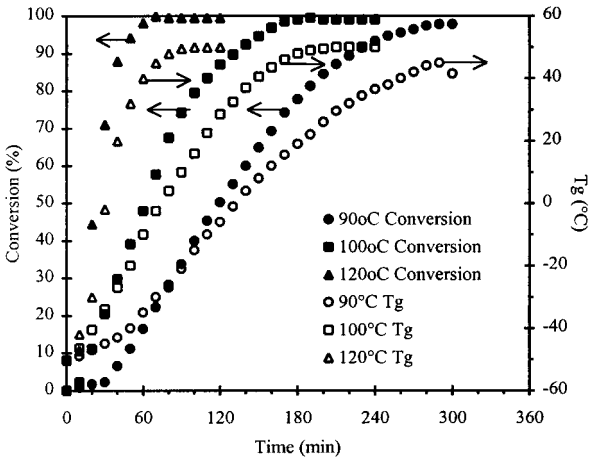


Figure 4. Conversion and T_g of LAB 1509 as a function of the curing time at 90, 100, and 120 °C.

probes as a function of the curing time. The probes produced fluorescence emission at different wavelengths and behaved differently depending on the temperature. No pronounced changes in the shapes of the fluorescence spectra were observed, indicating that there were no significant specific interactions among the four fluorescent probes with the LAB 1509. The refractive index of an epoxy resin usually increases with the extent of cure,[34] while the dielectric constant decreases,[35] leading to a decrease in the Stokes shift. The changes in the wavelengths for each of the probes are listed in Table 1.

The probes exhibit blue and red shifts upon the polymerization at different temperatures. The largest spectral shifts were observed for probes **III** and **IV**. The magnitude of the shift increases with a decrease in the polarity of the environment. This causes the main changes in the emission band positions. However, the shifts observed in the probe−polymer systems under investigation could not be used solely as reliable indicators of the degree of cure.

When the cross-linking of the polymer matrix increases, intramolecular charge-transfer probes are expected to increase their fluorescence intensity.[30] Accordingly, all the four probes showed an increasing of the intensity as the curing proceeded. As an example the emission spectra of the probe **IV** during the curing of LAB 1509 at 120 °C is shown in Figure 2 where the arrow indicates the evolution of the spectra during the curing process. The behavior of the probe **IV** was the same at different temperatures due to the same environmental changes in the LAB 1509.

To enable comparison of the various sets of measurements, the fluorescence intensities were related at $t = 0$. The relative intensities of emission maxima of the four probes at 120 °C are presented in Figure 3 as a function of the curing time. The scaling is different because the relative intensity values of probes **I** and **II** were much lower than the values of probes **III** and **IV**.

The conversion and the glass transition temperatures of LAB 1509 were determined by DSC, and the results at different curing temperatures are shown in Figure 4. Comparison of Figure 4 with Figure 3 shows that the fluorescence intensity changes vary depending on the probe−polymer system. Since the probes in the same curing environment show different behavior, the fluorescence intensity of the probes cannot necessarily be correlated directly with the conversion percentage. The same behavior was also observed in the other temperatures, 90 and 100 °C.

To determine the degree of the curing, an LHIC ratio[29] was used. This method is independent of the type of the probe and also of the experimental conditions. In the LHIC method the emission spectrum of the cured

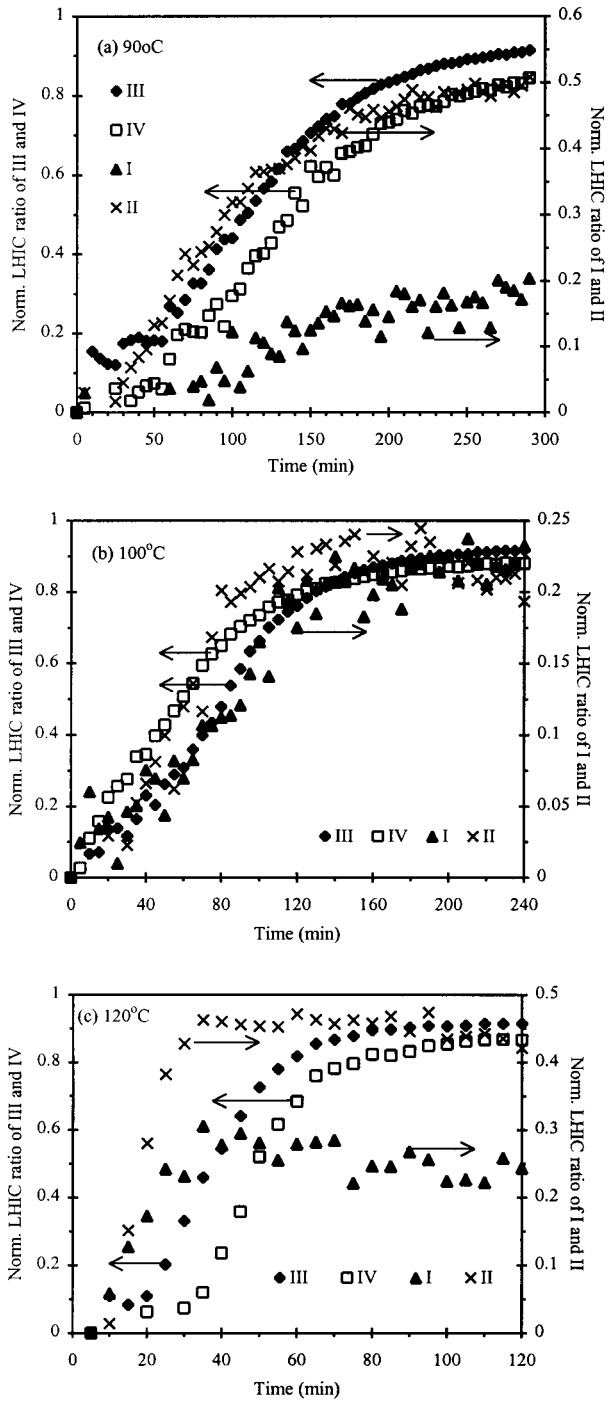


Figure 5. Normalized LHIC ratios of the probes during the curing of LAB 1509 at 90 (a), 100 (b), and 120 °C (c) as a function of the curing time.

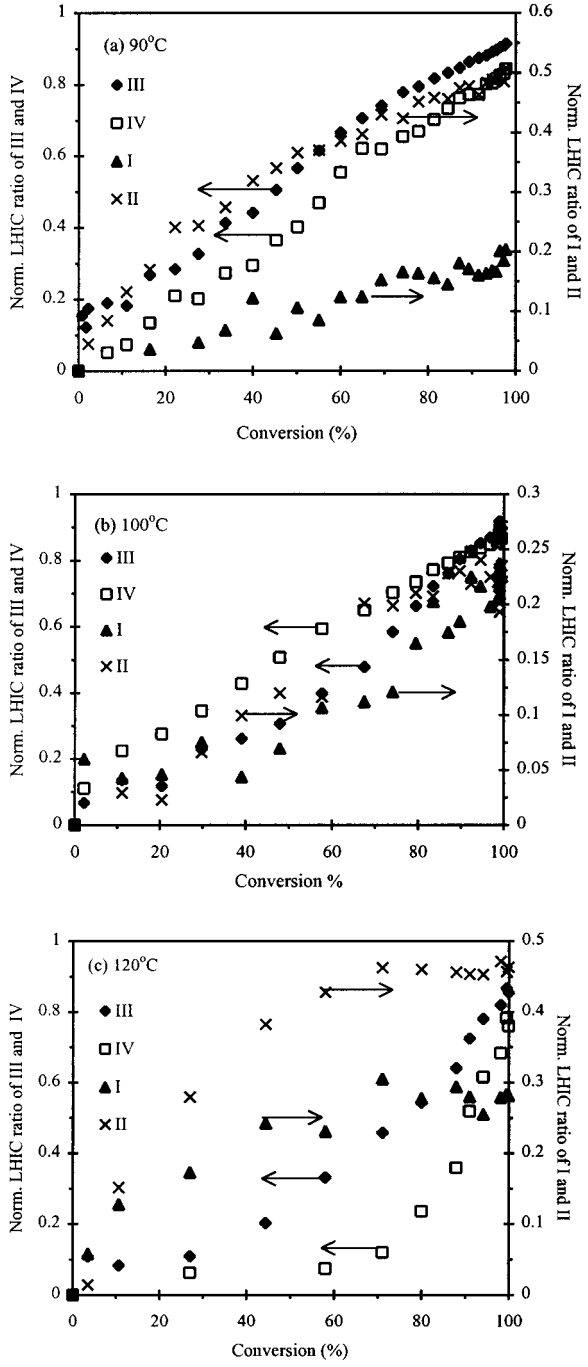


Figure 6. Normalized LHIC ratios of the probes during the curing of LAB 1509 at 90 (a), 100 (b), and 120 °C (c) as a function of conversion.

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 (LIC) and the high-intensity changes (HIC) can be found. The chosen wavelengths for each of the probes when the LHIC ratio method was applied are listed in Table 1. It can be seen from Table 1 that the wavelengths, which have the lowest and highest intensity changes, cover certain areas of the wavelengths for each probe. Thus, when the method is applied, two wavelength regions can be chosen for each of the probes.

LHIC curves are obtained by dividing 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 are normalized with eq 3 to their initial values before the curing to enable comparison between the various sets of measurements.

$$\text{normalized LHIC ratio} = 1 - \frac{R}{R_0} \qquad (3)$$

where R is the LHIC ratio at any degree of the cure and R_0 is LHIC ratio before the cure. The normalized LHIC ratios of the selected probes are shown in Figure 5 as a function of the curing time. As can be seen, by

Table 2. Wavelength Changes of Emission Maxima during the Curing of LAB 1509 at Room Temperature and at Low Temperature and the Wavelengths That Were Chosen for LHIC Ratio Calculation

	wavelength changes of the emission maxima during the curing process (nm)		wavelengths chosen for the LHIC ratio (nm)	
probe	room	low	room	low
I	0 (473→473)	0 (473→473)	575/455	534/451
II	8 (413→405)	3 (413→410)	600/385	575/384
III	48 (634→586)	42 (634→592)	680/500	680/500
IV	2 (397→395)	0 (397→397)	600/380	600/530

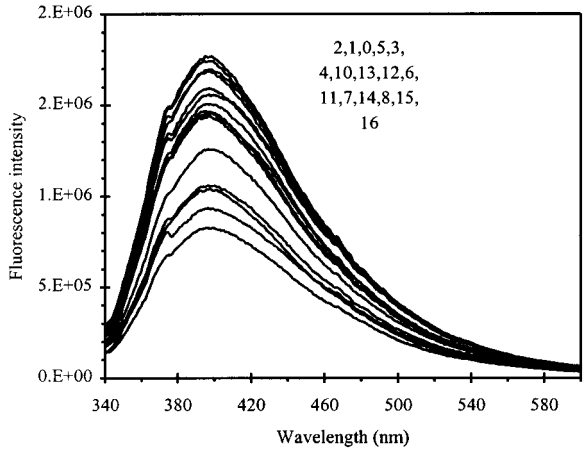


Figure 7. Fluorescence emission spectra of **IV** during the curing of LAB 1509 at room temperature (a) and at low temperature (b). Numbers indicate the order of the spectra (day) during the curing.

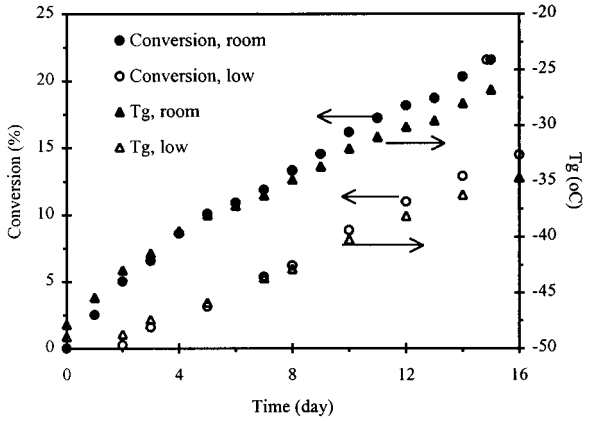


Figure 8. Conversion and T_g of LAB 1509 at room temperature and at low temperature measured by DSC as a function of the curing time.

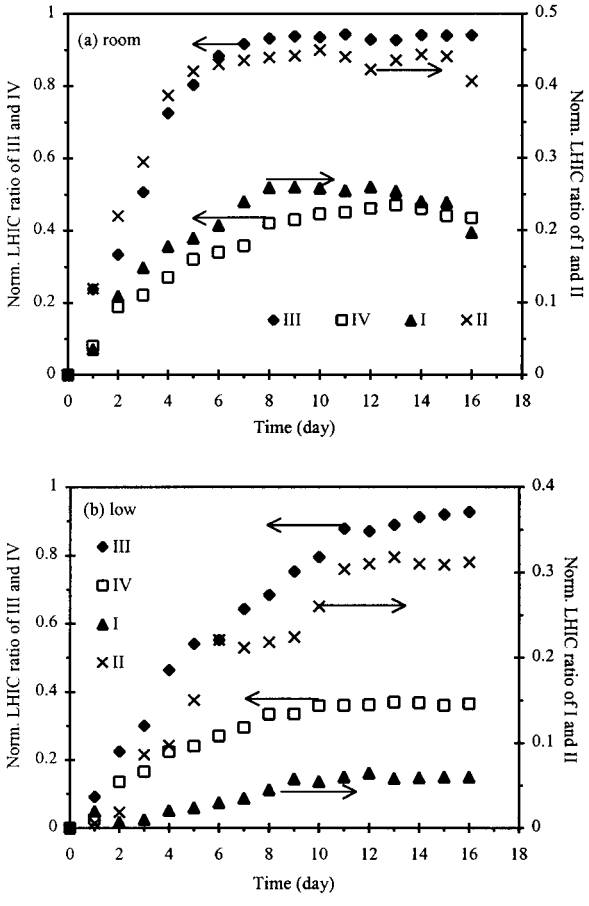


Figure 9. Normalized LHIC ratios of the probes during the curing of LAB 1509 at room temperature (a) and at low temperature (b).

applying the LHIC ratio method, similar behavior can be observed for all the probes.

The correlation between the normalized LHIC ratios and the conversion percentages measured by DSC are shown in Figure 6. Similar behavior can be obtained for all the probes. There are some differences in the slopes that reflect useful information such as the sensitivity of the probes to the environmental changes. In all cases there is a continuous smooth change of the ratio with the degree of cure. The results show that the LHIC ratio method provides a general method for monitoring the curing of epoxy polymers.

The shelf life of the mixture of epoxy resin and anhydride was monitored with four probes at room temperature, 20 °C, and at low temperature, 6 °C. The changes in the wavelengths of the emission maxima for each of the probes are presented in Table 2. The emission spectra of probe **IV** during a precuring period of 16 days of LAB 1509 at room temperature are shown in Figure 7. The numbers show the evolution of the spectra during the curing processes. The change in the intensity of the spectra during the measurements is not regular, and that is due to changes in the instrumental factors and the excitation area of the sample. Thus, original intensities cannot be used directly, and a calibration is required. Same behavior was also observed at low temperature. The conversion percentage and the glass transition temperature of LAB 1509 were determined by DSC at room temperature and at low temperature and are shown in Figure 8.

To determine the degree of precuring, the LHIC ratio was applied. For each of the probe the wavelengths at which the LHIC ratio method was applied are listed in Table 2. The LHIC ratios of the selected probes as a function of curing time are shown in Figure 9. A smooth change of LHIC ratio and similar behavior can be observed for all the probes when the LHIC method is applied. The suitability of all the probes for monitoring the precuring or shelf life of LAB 1509 can be confirmed by comparing the LHIC ratios in Figure 9 with the T_g

curves from Figure 8. At room temperature the intensity ratios of the probes were constant after 8 days and at low temperature after 9 days for probes **I** and **IV** and after 12 days for probes **II** and **III**. However, the T_g value of LAB 1509 was still changing at both temperatures 16 days after the mixing, indicating that these probes are not sufficiently sensitive for monitoring precuring during the whole process. Thus, results indicate that in order to find suitable probes it is necessary to confirm the results obtained with reference to T_g curves.

The results show that the LHIC ratio method provides a good method for monitoring the precuring and shelf life of the epoxy polymers. It also provides a calibration method for avoiding 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 some of the probes exhibited blue shifts due to 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 intensity ratios of the fluorescence intensities, selected from the wavelength ranges representing the lowest and highest intensity changes, and the degree of the polymerization was obtained. The fluorescence intensity ratio method eliminates the effect of intensity variations arising due to external factors, such as lamp intensity, optical alignment, probe location, excitation area, and temperature variation. The advantage of the LHIC ratio method is that it enables changes in composition to be monitored throughout the curing process independent of the probe. Application of cure monitoring using the LHIC ratio method offers the possibility to precisely control the parameters of the curing process, as well as providing quantitative control of the quality and curability of the starting materials. The fluorescence cure sensing technique based on the LHIC ratio method can be applied in situ for monitoring polymerization in a variety of commercially and industrially used polymers.

Acknowledgment. Financial support by the European FLUORAD project, Contract BRPR-CT97-0534, Project BE97-4472, is gratefully acknowledged.

References and Notes

(1) Senturia, S. D.; Sheppard, N. L.; Lee, H. L.; Day, D. R. *J. Adhes.* **1982**, *15*, 69.
(2) Wang, F. W.; Lowry, R. E.; Fabconi, B. M. *Polymer* **1985**, *53*, 180.
(3) Wang, F. W.; Lowry, R. E.; Fabconi, B. M. *Polymer* **1986**, *27*, 1529.
(4) Levy, R. L.; Schwab, S. D. *Polym. Sci. Technol.* **1987**, *56*, 169.
(5) Herrold, R. T.; Sanjana, Z. N. *Rev. Prog. Quantum Nondestr. Eval.* **1987**, *6B*, 1277.
(6) Afromowitz, M. A.; Lam, K. Y. *SPIE Proc.* **1988**, *986*, 135.
(7) Goerge, G. A.; Schweinsberg, D. P. *J. Appl. Polym. Sci.* **1987**, *33*, 2261.
(8) Antoon, M. K.; Zehner, B. E.; Koenig, J. L. *Polym. Compos.* **1981**, *2*, 81.
(9) Mones, E. T.; Morgan, R. J. *Polym. Mater. Sci. Eng.* **1984**, *51*, 430.
(10) Druy, M. A.; Elandjian, L.; Stevenson, W. A. *SPIE Proc.* **1988**, *986*, 130.
(11) Hagnauer, G. L.; Laliberte, B. R.; Dunn, D. A. *ACS Symp. Ser.* **1983**, *221*, 229.
(12) Mijovic, J.; Kim, J.; Slaby, J. *J. Appl. Polym. Sci.* **1984**, *29*, 1449.
(13) Wisanrakkit, G.; Gillham, J. K. In *Polymer Characterization*; Craver, C. D., Provder, T., Eds.; American Chemical Society: Washington, DC, 1983; p 143.
(14) Munns, T. E.; Seferis, J. C. *J. Appl. Polym. Sci.* **1983**, *28*, 2227.
(15) Myrick, M. L.; Angel, S. M.; Lyon, R. E.; Vess, T. M. *SPE ANTEC Tech Papers* **1992**, *38*, 2052.
(16) Paik, H. J.; Sung, N. H. *Polym. Eng. Sci.* **1994**, *34*, 1025.
(17) Dang, W.; Sung, N. H.; Sung, C. S. P. *ACS PMSE* **1990**, *63*, 512.
(18) Sung, C. S. P.; Puyn, E.; Sun, H. L. *Macromolecules* **1986**, *19*, 2922.
(19) Yu, W. C.; Sung, C. S. P. *Macromolecules* **1990**, *23*, 386.
(20) Dang, W.; Sung, N. H. *Polym. Eng. Sci.* **1994**, *34*, 707.
(21) Chin, I. J.; Sung, C. S. P. *Macromolecules* **1984**, *17*, 2603.
(22) Sung, C. S. P.; Chin, I. J.; Yu, W. C. *Macromolecules* **1985**, *18*, 1510.
(23) Zhang, X.; Kotchetov, I. N.; Paczkowski, J.; Neckers, D. C. *J. Imgaging Sci. Technol.* **1992**, *36*, 322.
(24) *Principles of Fluorescence Spectroscopy*; Lakowicz, J. R., Ed.; Plenum Press: New York, 1983.
(25) Paczkowski, J.; Neckers, D. C. *Chemtracts: Macromol. Chem.* **1992**, *3*, 75.
(26) Song, J. C.; Torres-Filho, A.; Neckers, D. C. *Proc. RadTech* **1994**, *338*.
(27) Paczkowski, J.; Neckers, D. C. *Macromolecules* **1991**, *24*, 3013.
(28) Mangion, M. B.; Johari, G. B. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 1117.
(29) Vatanparast, R.; Li, S.; Hakala, K.; Lemmetyinen, H. *Macromolecules* **2000**, *33*, 438.
(30) Song, J. C.; Neckers, D. C. *J. Polym. Eng. Sci.* **1996**, *36*, 3.
(31) Paczkowski, J.; Neckers, D. C. *Macromolecules* **1992**, *25*, 548.
(32) Paczkowski, J.; Neckers, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 841.
(33) Popielarz, R.; Neckers, D. C. *Proc. Radtech* **1996**, *1*, 271.
(34) Dannenberg, H. *SPE J.* **1959**, 875.
(35) Nass, K. A.; Seferis, J. C. *Polym. Eng. Sci., Polym. Chem. Ed.* **1993**, *31*, 841.

MA000599N