Novel fluorescence method for cure monitoring of epoxy resins*

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The fluorescence spectra of organic dyes dissolved in epoxy resins are sensitive to local viscosity. The excimer forming dyes are particularly useful as probes since the monomer emission can be used as an internal standard in the measurement. In this case, the probability of excimer formation is related to molecular mobility and hence to the microviscosity. This approach has been demonstrated on epoxy resins. In another approach, trace amounts of 1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene (DMA–DPH) and 9,10-diphenylanthracene (DPA) are added to an epoxy resin. The fluorescence intensity of DMA–DPH increases with the increase in local viscosity while the fluorescence intensity of DPA is insensitive to local viscosity and can be used as an internal standard. The ratio of the fluorescence intensities of DMA–DPH and of DPA has been measured to monitor the cure of epoxy resins.

(Keywords: cure monitoring; epoxy resins; excimer; fluorescence; local viscosity; polymerization; process control; spectroscopy)

INTRODUCTION

The manufacture of polymer matrix composites involves complex chemical and physical changes that must be adequately controlled to produce desirable products. Lack of adequate control during manufacturing may result in poor quality and high rejection ratios in large-volume productions. Monitoring techniques and models to correlate monitoring data to improve processing are therefore key aspects to increasing production rates and product quality.

Fluorescence techniques are particularly useful to monitor the change in local viscosity because they are sensitive, and can be easily adopted to *in situ* nondestructive monitoring. In a previous paper[1], we described how we used an excimer-fluorescence technique to monitor the polymerization of methyl methacrylate. We show here the application of the excimer-fluorescence technique to monitor the cure of epoxy resins. In addition, we describe the cure monitoring of epoxy resins with the use of two fluorescent dyes, a dye whose fluorescence intensity increases with local viscosity, and another dye which serves as an internal standard with nearly constant fluorescence intensity. This second technique is similar to the one used by Loutfy[2,3] and the one used by Levy[4]. However, to the best of our knowledge, there has been no previous report of the use of a viscosity-insensitive internal standard. The use of such an internal standard is a significant step forward in the application of fluorescence spectroscopy to cure monitoring in the factory environment. Using such an internal standard, we eliminate altogether the inconvenience of absolute measurements.

EXPERIMENTAL

Amine hardener

4,4'Methylene-bis-(cyclohexylamine) (PACM) was distilled under reduced pressure and stored under dry argon. It was melted under dry argon before use.

Epoxy resin

Diglycidyl ether of Bisphenol-A (DGEBA) was used without further purification. The resin, with an epoxy equivalent weight of approximately 175, had a weak emission band at 415 nm when excited at 345 nm. The intensity of the band increased by about 80% when the resin was fully cured with PACM. However, the resin showed negligible emission at 480 nm.

Excimer-forming probe

1,3-Bis-(1-pyrene)propane was from a commercial source and was used without further purification.

Viscosity-sensitive probe

1-(4-Dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene (DMA–DPH) was dissolved in DGEBA by rotating the resin at 45°C for several hours.

Internal standard

An internal standard, 9,10-diphenylanthracene (DPA), at a concentration of 2×10^{-5} mol l^{-1} was added to the resin–hardener mixture. At the excitation wavelength of 345 nm, the fluorescence intensity of DPA in the mixture at 415 nm was about four times that of the mixture alone.

Reaction cell

The reaction cell was made of a silicone rubber gasket sandwiched between two Pyrex cover slides 0.18 mm

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thick. The cell was pressed against the flat face of a cylindrical heater, which was proportionally controlled to within 1°C. This compression kept the resin from leaking out and provided adequate heat transfer between the heater and the cell. Two small holes were drilled at the top of the rubber gasket, one for inserting a thermocouple and the other for filling the cell.

Cure monitoring

In a typical experiment, 0.5 ml of the epoxy resin containing a probe at a concentration of 5×10^{-5} mol l^{-1} was put into a stoppered syringe kept at 40°C. The amine hardener was then rapidly mixed with the epoxy resin to give a value of 0.3 for the weight ratio of the hardener to the resin. Finally, the mixture was injected into the reaction cell which had been preheated to 60°C.

When 1,3-bis-(1-pyrene)propane was used as a probe, cure monitoring was carried out in the manner previously described in ref. 1. The sample was irradiated at 345 nm and the monomer and excimer fluorescence intensities at 377 nm and 480 nm were measured at time intervals. When DMA–DPH was used as a probe and DPA was used as an internal standard, they were excited at 420 nm and 345 nm, respectively. Uncorrected fluorescence spectra were taken on a spectrofluorometer operating in the front surface illumination mode.

RESULTS AND DISCUSSION

An excimer is formed by the association of an excited molecule with another molecule in its ground state. Such an excimer gives off a broad structureless fluorescence which has longer wavelengths than the fluorescence of the isolated excited molecule. Excimers may also be formed intramolecularly from molecules carrying excimer-forming groups. For example, excimer fluorescence has been observed in dilute solutions of pyrene-labelled alkanes such as 1,3-bis-(1-pyrene)propane and 1,10-bis-(1-pyrene)decane[5].

Figure 1 gives the chemical structure of 1,3-bis-(1-pyrene)propane and its fluorescence spectra in mixed solvents made of ethyl acetate and glycerol tripropionate. In these spectra, the structured violet fluorescence band at 377 nm is due to the emission from excited, isolated pyrenyl groups, hereafter referred to as monomers, while the broad structureless blue fluorescence band at 480 nm is due to the emission from intramolecularly formed pyrene excimers, hereafter referred to as excimers. (All spectra have been normalized to constant monomer fluorescence intensity.) The intensity of the excimer fluorescence depends on the medium viscosity because the pyrene excimer is formed by the diffusion-controlled, intramolecular reaction of an excited pyrenyl group and a pyrenyl group in the ground state. Thus, we see in *Figure 1* that the intensity of excimer fluorescence (F_D) relative to the intensity of monomer fluorescence (F_M) decreases as the viscosity progressively increases going from A to E.

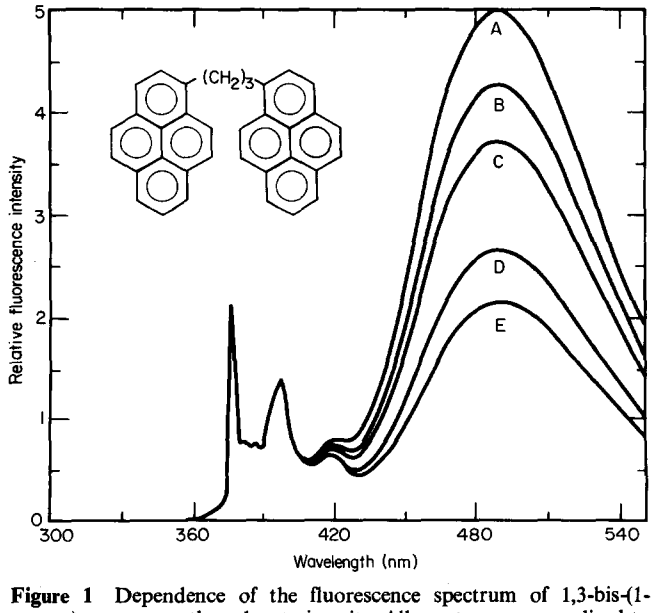

Figure 1 Dependence of the fluorescence spectrum of 1,3-bis-(1-pyrene)propane on the solvent viscosity. All spectra are normalized to constant monomer intensity. The viscosity progressively increases going from A to E: A, 0.44cP; B, 0.91cP; C, 1.36cP; D, 2.81cP; E, 4.0cP

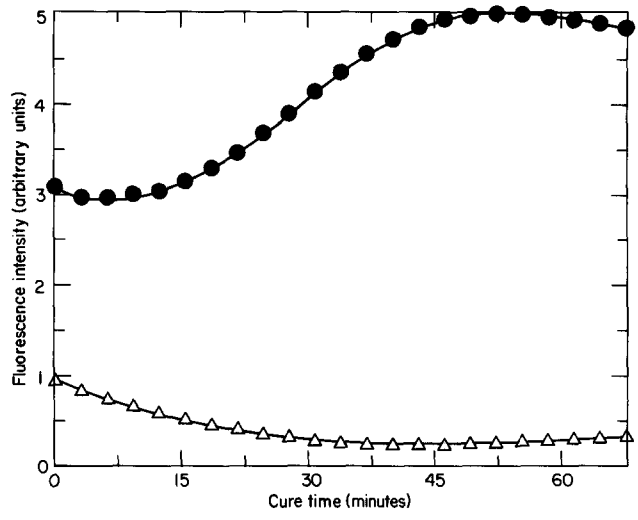

Figure 2 Fluorescence intensities of the pyrene monomer at 377 nm (●) and of the pyrene excimer at 488 nm (△) as a function of cure time

Since the intensity ratio F_M/F_D of pyrene-labelled alkanes and pyrene-labelled poly(methyl methacrylate) polymers[6] depends on the viscosity of the medium, they can act as probes to monitor the viscosity change taking place during the cure of epoxy resins.

Figure 2 gives the fluorescence intensities of the monomer at 377 nm (the upper curve) and of the excimer at 488 nm (the lower curve) as a function of cure time for 1,3-bis-(1-pyrene)propane dissolved in a stoichiometric mixture of the epoxy resin and the amine hardener. As the cure went on and the resin viscosity increased, the monomer fluorescence intensity increased while the excimer fluorescence intensity decreased. There was a slight decrease in the monomer fluorescence intensity at the beginning of the cure, because the resin viscosity decreased when it was heated to 60°C. However, the expected increase in the excimer fluorescence was too small to be detected.

We see in *Figure 2* that after 52 min of cure, there was a small decrease in the monomer fluorescence intensity and a small increase in the excimer fluorescence intensity. These small changes were most likely due to the photodegradation of 1,3-bis-(1-pyrene)propane (BPP). As the resin became more viscous, the translational diffusion of BPP molecules became slower. This reduction in the rate of diffusion, together with the photodegradation of BPP, led to a depletion of BPP molecules in that part of the resin exposed to u.v. radiation. The apparent increase

in excimer fluorescence may be attributed to the fluorescence of photodegradation products at 488 nm. This complication due to photodegradation can be eliminated by reducing the exposure of the resin to u.v. radiation with the use of an optical multichannel analyser, for example. In addition, we have capitalized on this observation to monitor the resin cure by measuring the change in the translational diffusion coefficient of a probe[7].

Figure 3 gives the change in the intensity ratio F_M/F_D as a function of cure time for 1,3-bis-(1-pyrene)propane dissolved in a stoichiometric mixture of the epoxy resin and the amine hardener. Here F_M and F_D are, respectively, the fluorescence intensity of the monomer at 377 nm and that of the excimer at 488 nm. As crosslinking proceeded, the viscosity increased owing to the growth in molecular weight and this led to an increase in the intensity ratio. After 45 min cure, there was a small decrease in the intensity ratio due to the photodegradation of the probe.

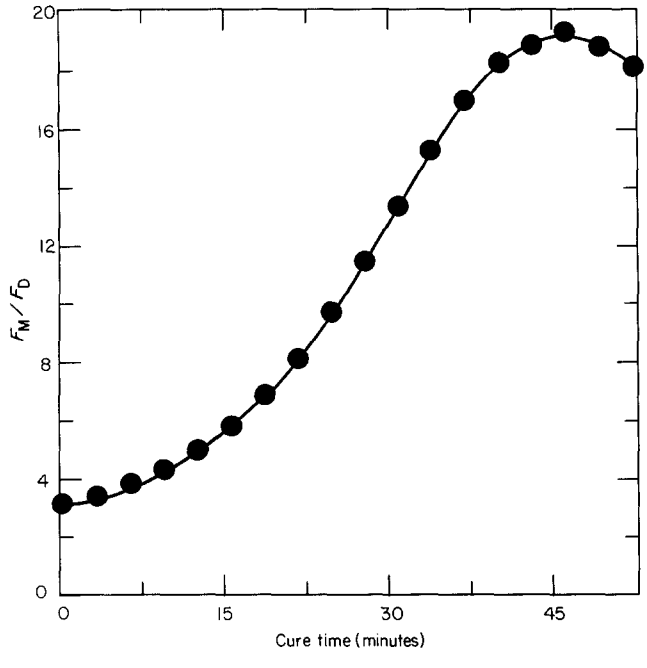

Figure 3 Ratio of monomer (F_M) to excimer (F_D) fluorescence intensities of 1,3-bis-(1-pyrene)propane in epoxy as a function of cure time

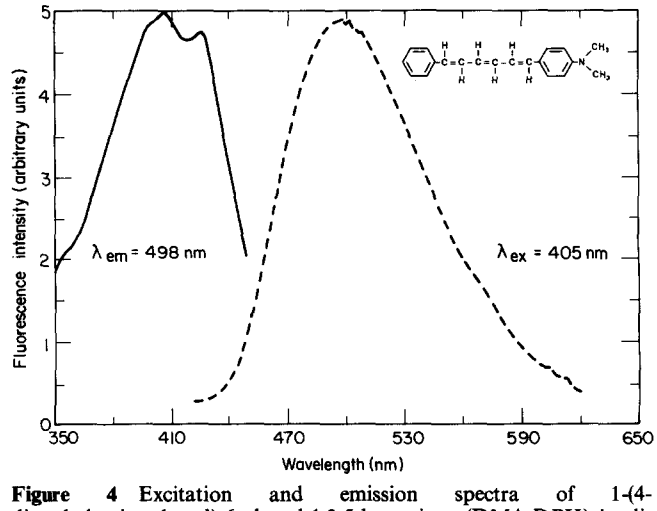

Figure 4 Excitation and emission spectra of 1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene (DMA-DPH) in diglycidyl ether of bisphenol-A (DGEBA). The excitation and emission wavelengths were 405 nm and 498 nm, respectively

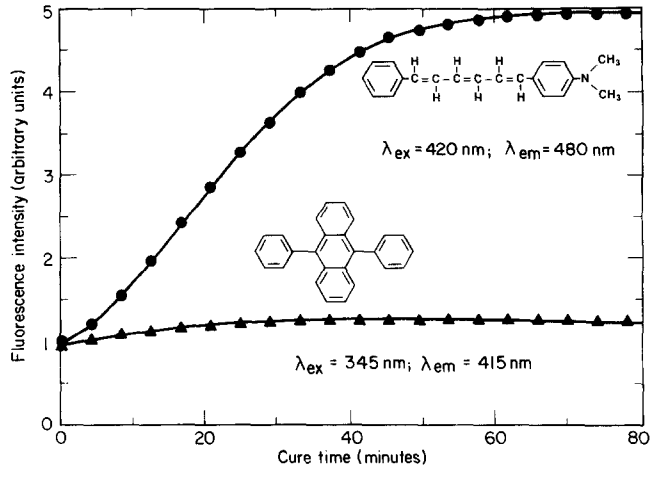

Figure 5 Fluorescence intensities of DMA–DPH at 480 nm (●) and of DPA at 415 nm (▲) as a function of cure time

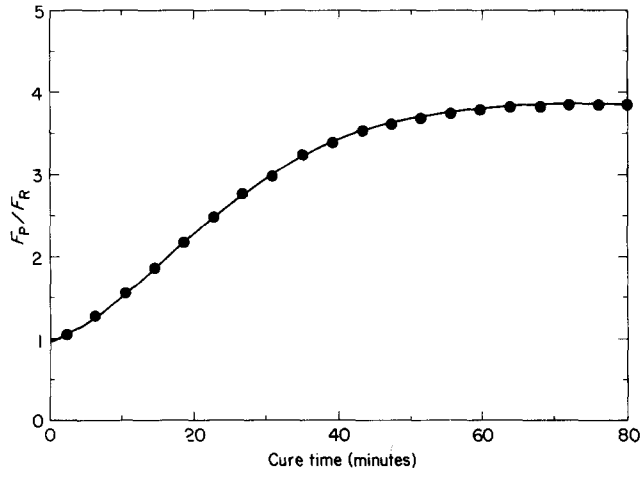

Figure 6 Ratio of the fluorescence intensity of the probe DMA–DPH (F_P) and the fluorescence intensity of the internal standard DPA (F_R) as a function of cure time

Owing to the lack of sensitivity of the BPP probe at the longer cure times, we have examined the use of other types of viscosity-sensitive probe molecules. *Figure 4* gives the excitation and the emission spectra of the viscosity-sensitive dye DMA–DPH in diglycidyl ether of bisphenol-A (DGEBA). The excitation and the emission spectra of the internal standard DPA has been published by Berlman[8].

Figure 5 gives the fluorescence intensity, F_P, of DMA–DPH at 480 nm (the upper curve) and the fluorescence intensity, F_R, of DPA at 415 nm (the lower curve) as a function of cure time for a stoichiometric mixture of the epoxy resin and the amine hardener. The fluorescence intensity of DMA–DPH increased with cure time while that of DPA remained practically the same. In *Figure 6*, we show the intensity ratio F_P/F_R as a function of cure time. The intensity ratio increased steadily with cure time and reached a plateau value at the end of the cure when the resin became rigid. This intensity ratio is not sensitive to the geometry of the sample. We can therefore measure this ratio to monitor the cure of samples which contain reinforcing fibres or particles.

CONCLUSION

We have described two fluorescence techniques for monitoring the cure of epoxy resins, one based on

intramolecular excimer fluorescence and the other based on enhancement of fluorescence intensity with the viscosity of the medium. Since both techniques are insensitive to the sample geometry, they can be adopted to *in situ* monitoring of the cure of composite structures in the factory environment.

ACKNOWLEDGEMENT

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