Wavelength-Shift Fluorescent Probes for Monitoring of Polymerization

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ABSTRACT: The feasibility of using wavelength-shift fluorescent probes for cure monitoring of an epoxy resin and an acrylic resin was evaluated. 4-(*N*,*N*-dihexylaminostyryl)-4′-pyridinium propylsulfonate (DHASP-PS), as well as each of other wavelength-shift fluorescent probes, was dissolved in the epoxy resin, a stoichiometric mixture of diglycidyl ether of bisphenol A and 4,4′-methylene-bis(cyclohexylamine). The fluorescence and the excitation spectra of each of the probes dissolved in the epoxy resin were then measured at various times during the cure of the epoxy resin at 60°C. The fluorescence and the excitation spectra of the probe DHASP-PS dissolved in methyl methacrylate (MMA) were also measured at various times during the cure of the acrylic resin at 55°C. Since the peak fluorescence wavelength of each of the wavelength-shift fluorescent probes decreased during the cure of the epoxy resin or MMA, these fluorescent probes can be used for monitoring the polymerization reactions of epoxy resins and vinyl resins.© 2006 Wiley Periodicals, Inc.* J Appl Polym Sci 101: 747–750, 2006

Key words: fluorescence; polymers; polymerization

INTRODUCTION

In the manufacture of a variety of products, such as polymer matrix composites and vinyl polymers, as well as in the applications of dental or medical resins, the cure or polymerization reactions of polymerizing materials must be adequately monitored and controlled to produce the desirable resultant products. Fluorescence techniques are particularly useful for cure monitoring because they are sensitive and adaptable to nondestructive, in-line, real-time monitoring. For example, Wang et al.[1] used a fluorescence technique to monitor the cure at 60°C of an epoxy resin that was a stoichiometric mixture of diglycidyl ether of bisphenol A (DGEBA) and 4,4′-methylene-bis(cyclohexylamine) (PACM). They dissolved in the epoxy resin a trace amount of 1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatraiene (DMA-DPH), which is a viscosity-sensitive fluorophore, and a trace amount of 9,10-diphenylanthracene (DPA), which is an internal standard fluorophore not sensitive to viscosity. They then measured the fluorescence intensities of the viscosity-sensitive fluorophore, DMA-DPH, and the internal standard, DPA, at various cure times. Finally, they used the ratio of these intensities, which is insensitive to the polymerization-induced shrinkage of the sample or the presence of filler particles, to monitor the cure of the epoxy resin. In US Patent No. 4,651,011, Ors and Scarlata disclosed a method to determine the extent of cure by measuring the change in fluorescence anisotropy of a fluorophore that is dissolved in a polymerizing material. Itagaki et al.[2] have reviewed fluorescence techniques for monitoring the cure of epoxy resins nondestructively.

Since it is difficult to measure the absolute fluorescence intensity of a viscosity-sensitive fluorophore when polymerizing material contains filler particles or undergoes polymerization-induced shrinkage, Wang et al.[1] dissolved two fluorophores in a polymerizing material and used the ratio of their fluorescence intensities as a measure of the extent of cure. Lin and Wang[3] described a wavelength-shift method for fluorescence cure monitoring, in which they measured the change in Stokes shift (the difference, $\nu_A - \nu_F$, where ν_A and ν_F are the peak wave numbers of the absorption and fluorescence spectra of the fluorescent probe) to monitor polarity change and gelation during epoxy cure. The wavelength-shift method is especially advantageous for *in situ*, nondestructive cure monitoring, because it eliminates an internal standard probe that is often required in methods based on measure-

Certain commercial materials and equipment are identified in this work for adequate definition of the experimental procedures. In no instances does such identification imply recommendation or endorsement by NIST or that the material and the equipment identified is necessarily the best available for the purpose.

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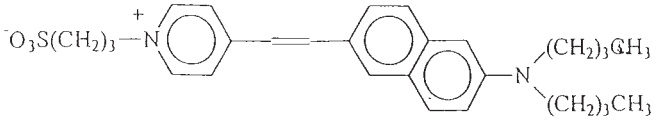
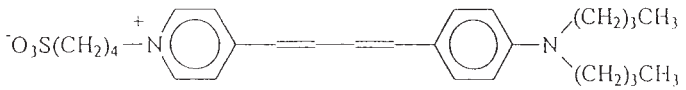
4-(N,N-dimethylamino)-4′-nitrostilbene(DANS)

6-[2-(N,N-dibutylamino)naphthyl]ethenyl-4′-pyridinium propylsulfonate(ANEPPS)



4-(N,N-dibutylanilino)hexatrienyl-4′-pyridinium butylsulfonate(AHPBS)

4-(N,N-dibutylanilino)butadienyl-4′-pyridinium butylsulfonate(ABPBS)



4-(p-dihexylaminostyryl)pyridinium propylsulfonate(DHASP-PS)

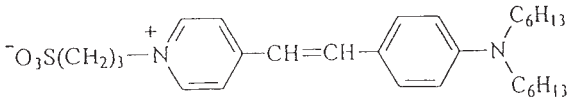


Figure 1 The chemical structures of the wavelength-shift fluorescent probes.

ments of fluorescence intensity changes, and it obviates a complex optical system that is used in methods based on measurements of fluorescence anisotropy changes. However, in some situations, the wavelength-shift fluorescent probe used by Lin and Wang,[3] DMA-DPH, has some limitations because its change in Stokes shift is moderate and its excitation wavelength is not in the visible, where the interference of impurity fluorescence from the resin and the optic fiber is less serious than in the UV. We have identified wavelength-shift fluorescent probes, which are free from these limitations. This article presents the results of a study designed to examine the feasibility of using several wavelength-shift fluorescent probes for cure monitoring of an epoxy resin and an acrylic resin.

EXPERIMENTAL

PACM (Aldrich*, Milwaukee, WI), the amine hardener, was distilled under reduced pressure and stored under dry argon. It was melted under dry argon before use. The epoxy resin, DGEBA, with an epoxy equivalent mass of ~175, was used without further purification. The wavelength-shift fluorescent probes were 6-[2-(*N*,*N*-dibutylamino)naphthyl]ethenyl-4′-pyridinium propylsulfonate (ANEPPS), 4-(*N*,*N*-dibutylanilino)-hexatrienyl-4′-pyridinium butylsulfonate (AHPBS), 4-(*N*,*N*-dibutylanilino)butadienyl-4′-pyridinium butylsulfonate (ABPBS), 4-(*N*,*N*-dihexylaminostyryl)-4′-pyridinium propylsulfonate (DHASP-PS), and 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene(DANS), all from Molecular Probes (Eugene, OR). Figure 1 shows the chemical structures of these wavelength-shift fluorescent probes.

Each wavelength-shift fluorescent probe was dissolved in DGEBA by stirring the resin at 50°C for several hours. In a typical cure-monitoring experiment, 3.8 g of the epoxy resin containing a wavelength-shift fluorescent probe at a concentration of 10^{-5} mol/L was mixed (at 50°C and under an atmosphere of nitrogen) with the amine hardener to give a value of 3.4 for the mass ratio of the resin to the hardener. The mixture was transferred to a glass fluorescence cell and placed in a cell holder maintained

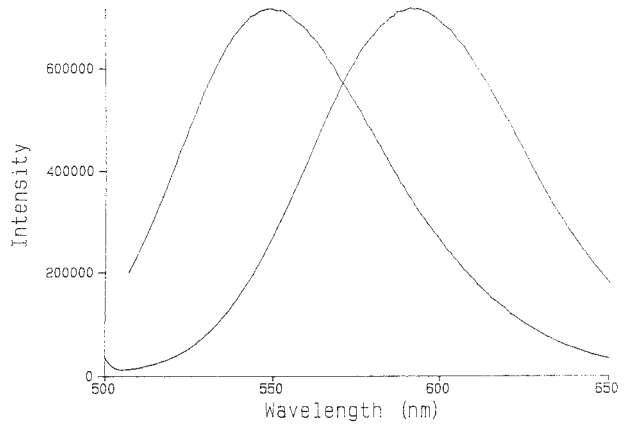


Figure 2 The fluorescence spectra of the DHASP-PS fluorescent probe in the DGEBA/PACM epoxy resin at the beginning of the cure (the spectrum to the right) and at the end of the postcure (the spectrum to the left). The fluorescence intensities are in arbitrary units and normalized to give the same peak intensity for both spectra.

at 60°C. Two small holes were drilled through the cover of the cell, one for inserting a thermocouple to measure the temperature of the resin mixture, and the other for passing a slow stream of nitrogen over the resin. At various time intervals, the fluorescence spectrum of the probe was taken on a spectrofluorometer (e.g., at an excitation wavelength of 485 nm for DHASP-PS), and the excitation spectrum of the probe was also taken (e.g., at a fluorescence wavelength of 590 nm for DHASP-PS). After 100 min in the cell holder, the epoxy resin was postcured under nitrogen atmosphere for 16 h at 130°C. The fluorescence and excitation spectra of the postcured resin at 60°C were then measured.

Purified methyl methacrylate (MMA) containing 5 $\times 10^{-5}$ mol/L of DHASP-PS and 0.01 mol/L of 2,2′-azobisisobutyronitrile was placed in a glass tube. The tube was evacuated, sealed under vacuum, and placed in a fluorescence cell that was filled with glycerol at 55°C. At various time intervals, the fluorescence spectrum of DHASP-PS dissolved in MMA was measured at the excitation wavelength of 485 nm.

RESULTS AND DISCUSSION

Figure 2 gives the fluorescence spectra of the wavelength-shift probe DHASP-PS at the beginning of the cure (the spectrum to the right) and at the end of the postcure (the spectrum to the left). At the beginning of the cure when the temperature of the resin mixture reached 60°C, the fluorescence spectrum of the wavelength-shift probe had a maximum at 592 nm, and the excitation spectrum (not shown) had a maximum at 494 nm. The peak fluorescence wavelength decreased steadily with the cure time until a plateau value of 554 nm was reached at a cure time of 60 min. As to the excitation spectrum of the wavelength-shift probe DHASP-PS, the maximum wavelength increased steadily from an initial value of 494 nm to a plateau value of 504 nm, which was reached at a cure time of 60 min. The postcure of 16 h at 130°C caused an additional decrease of 5 nm in the peak fluorescence wavelength, and an increase of 5 nm in the wavelength at the maximum of the excitation spectrum.

Figure 3 gives the Stokes shift [the difference between the peak wavenumbers, ν_A and ν_F, of the absorption (or the excitation) spectrum and the fluorescence spectrum] of the wavelength-shift fluorescent probe DHASP-PS as a function of cure time. The Stokes shift (having a sample standard deviation of 50 cm^{-1} with six degrees of freedom as an estimate of uncertainty) decreased steadily from an initial value of 3350 cm^{-1}, passed through a linear regime from the cure time of 20 min until it deviated from linearity at 37 min, and finally reached a plateau value of 1780 cm^{-1}. The post cure of 16 h at 130°C caused an additional decrease of 350 cm^{-1} in the Stokes shift. Thus, we can monitor the condensation polymerization of epoxy resins and other resins by measuring the change in the Stokes shift of a wavelength-shift fluorescent probe.

The overall decrease in Stokes shift of the wavelength-shift probe DHASP-PS (not including the decrease due to the postcure) was 1570 cm^{-1}, while Lin and Wang[3] observed an overall decrease of 1200 cm^{-1} for DMA-DPH in a stoichiometric mixture of DGEBA and diethylene triamine cured at 55°C. Thus, DHASP-

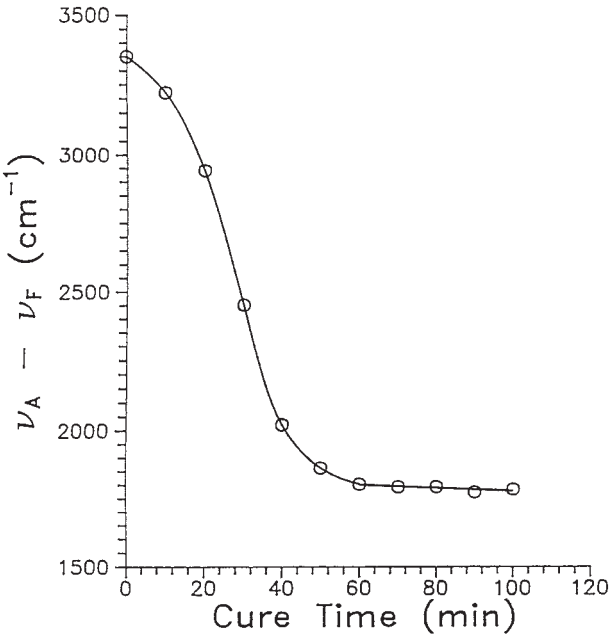


Figure 3 The Stokes shift of the fluorescence spectrum of the DHASP-PS fluorescent probe in the DGEBA/PACM epoxy resin as a function of the cure time.

PS is more sensitive than DMA-DPH. Furthermore, DHASP-PS has the added benefits of having its excitation wavelength in the visible, where the interference of impurity fluorescence from the resin and the optic fiber is less serious than in the UV. In the implementation of optical fiber cure-monitoring sensors to the manufacture of polymer matrix composites, it will be more practical to monitor the change in the peak fluorescence wave number (or the change in the peak fluorescence wavelength) than the change in Stokes shift. The overall increase in the peak fluorescence wave number of the wavelength-shift probe DHASP-PS during the cure was 1130 cm^{-1}. The postcure at 130°C caused an additional increase of 230 cm^{-1}.

In some applications, it will be more practical to monitor the peak fluorescence wavelength λ_{em} than the Stokes shift. For example, λ_{em} of AHPBS was measured to monitor the cure of a dental resin.[4] The λ_{em} for DANS, ANEPPS, AHPBS, ABPBS, and DHASP-PS in the uncured epoxy resin were 639, 650, 720, 665, and 592 nm, respectively, with an uncertainty of 2 nm when the excitation wavelengths λ_{ex} were 441, 497, 542, 528, and 494 nm. After the cure, the overall decreases in λ_{em} for DANS, ANEPPS, AHPBS, ABPBS, and DHASP-PS were 69, 61, 55, 44, and 37 nm, respectively, with an uncertainty of 3 nm. After the post cure, the overall decreases (compared to the uncured resin) in λ_{em} for DANS, ANEPPS, AHPBS, ABPBS, and DHASP-PS were 89, 68, 62, 50, and 43 nm, respectively, with an uncertainty of 3 nm.

The values of λ_{em} for DHASP-PS in MMA (with an uncertainty of 2 nm) were 592 nm before the cure, and 587 nm (a decrease of only 5 nm from the value for the uncured resin) at the cure time of 4.5 h, when the degree of conversion was 92%. After 4.5 h, the change became more rapid and λ_{em} reached a plateau value at 5.5 h; λ_{em} values were 586, 581, 566, and 555 nm at 4.8, 5.0, 5.2, and 5.5 h, respectively. Thus, we can monitor the final stage of the addition polymerization of MMA and other vinyl resins by measuring λ_{em} of a wavelength-shift fluorescent probe.

In summary, we have identified several wavelength-shift fluorescent probes, the Stokes shifts of which are sensitive to the chemical and physical changes during the cure of resins. Since the peak fluorescence wavelength of each of the wavelength-shift fluorescent probes decreased during the cure of an epoxy resin or MMA, these fluorescent probes can be used for monitoring the polymerization reactions of epoxy resins and vinyl resins. These fluorescent probes are expected to facilitate the implementation of optical fiber cure-monitoring sensors to the manufacture of polymer matrix composites, because they obviate the use of an internal standard dye or a complex optical system.

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