Wavelength-Shift Fluorescent Probes for Cure Monitoring of Resins

Francis W. Wang, Robert E. Lowry
Biomaterials Group, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

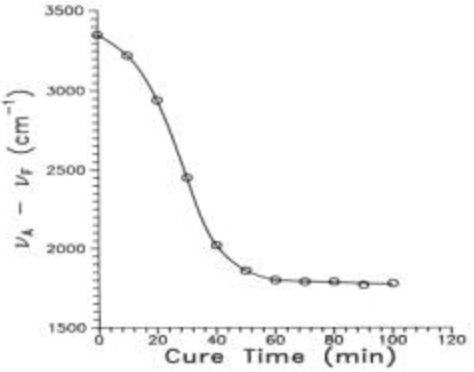
Intoduction: Fluorescence techniques are useful for cure monitoring because they are sensitive and adaptable to *in-situ* monitoring. The peak fluorescence wavelengths of some fluorescent probes dissolved in resins are sensitive to changes in the polarity and the local viscosity that occur during polymerization. This paper presents the results of a study designed to examine the feasibility of using wavelength-shift fluorescent probes for cure monitoring of an epoxy resin, an acrylic resin, and a dental resin.

Experimental: The amine hardener, 4, 4'-methylene-bis(cyclohexylamine) [Aldrich[#]], was distilled under reduced pressure. The epoxy resin, diglycidyl ether of bisphenol A (DGEBA) with an epoxy eqivalent mass of approximately 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. Each probe was dissolved in DGEBA by stirring the resin at 50 ^{o}C for several hours. 3.8 g of DGEBA containing a fluorescent probe at a concentration of 10^{-5} mol/L was mixed (at 50 ^{o}C and in an atmosphere of nitrogen) with the amine hardner to give a value of 3.4 for the mass ratio of DGEBA to the hardner. The mixture was transferred to a glass fluorescence cell, which was blanketed with nitrogen, and placed in a cell holder at 60 ^{o}C. At time intervals, the fluorescence and excitation spectra of the probe were taken on a spectrofluormeter. After 100 min in the cell holder, the epoxy resin was post-cured for 16 h at 130 ^{o}C . The fluorescence and excitation spectra of the post-cured resin at 60 ^{o}C were then measured.
Purified methyl methacrylate (MMA) containing $5x10^{-5}$ 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 ^{o}C. The fluorescence spectrum of DHASP-PS was measured at the excitation wavelength of 485 nm.

Results: The figure herein gives the Stokes' shift (the difference between the peak wavenumbers, ν_A and ν_F, of the absorption and the fluorescence spectra) of 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 caused an additional decrease of 350 cm^{-1}. 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. 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[1]. 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 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} 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 methyl methacrylate and other resins by measuring λ_{em} of a wavelength-shift fluorescent probe.

Reference:

1. K. Komatsu, F. W. Wang (1998) *J Dent Res Special Issue B* 77:808.



[#] **Disclaimer.** Certain commercial materials are identified in this work for adequate definition of the experimental procedures. In no instances does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or that the material and the equipment identified is necessarily the best available for the purpose.