

The wavelength-shift fluorophores of the invention exhibit a much larger change in the peak fluorescence wavelength than DMA-DPH. For example, the overall decrease in the peak fluorescence wavelength of DANS during the cure of a stoichiometric mixture of DGEBA and 4,4'-methylene-bis(cyclohexylamine) ("PACM") at 60° C. was 69 nm. The post-cure of 16 hours at 130° C. caused an additional decrease of 20 nm. The overall decrease of 69 nm was more than twice the overall decrease of 30 nm in the peak fluorescence wavelength of DMA-DPH during the cure at 50° C. of a similar epoxy resin which was a stoichiometric mixture of DGEBA and DETA.

Each of the wavelength-shift fluorophores of the invention also exhibits a much larger change in Stokes' shift than DMA-DPH in response to the change in polarity and mobility of its surroundings. Stokes' shift (the difference between the peak wavenumber of the absorption spectrum and the peak wavenumber of the fluorescence spectrum) provides a measure of the polarity and the mobility of the medium in which the fluorophore resides, and is discussed in Lin et al., *35 Polymer 687* (1994), which is herein incorporated by reference. Specifically, during the curing process, the electronic charge distribution, together with the dipole moment of a fluorophore, is substantially changed during an electronic transition to the excited state. After dissipation of intramolecular vibrational energy, the energy of the fluorophore molecules in the excited state is lowered by the reorientation of solvent molecules (or polymer segments) around the fluorophore molecules. The energy reduction due to solvent reorientation, together with the energy loss due to intramolecular vibrational relaxation, is observed as the Stokes' shift. For example, the overall decrease in the Stokes' shift of DANS during the cure of a stoichiometric mixture of DGEBA and PACM at 60° C. was 2349/cm. The post-cure of 16 hours at 130° C. caused an additional decrease of 638/cm. The overall decrease of 2349/cm in the Stokes' shift was nearly twice the overall decrease of 1200/cm in the Stokes' shift of DMA-DPH during the cure at 55° C. of a similar epoxy resin which was a stoichiometric mixture of DGEBA and DETA.

Further, the fluorophores of the invention all absorb light in the visible range, which is desirable when an optical fiber probe is used for measuring the extent of cure of a polymerizing material or the extent of solidification of a thermoplastic polymer (discussed in greater detail below in connection with FIGS. 2 and 3). By contrast, excitation wavelength of DMA-DPH is in the ultraviolet ("UV") range, making detection of the peak fluorescence wavelength or the Stokes' shift more difficult because of interference from impurity fluorescence of the resin and the optical fiber probe.

The shift in the peak fluorescence wavelength of each of the fluorophores of the invention, at the earlier stage of polymerization reactions, is increased by covalently attaching to the fluorophore molecules one or more moieties that take part in polymerization reactions, in such a manner that the photophysical properties of the fluorophore are not significantly altered by covalent bonding. This is accomplished using any one of the appropriate synthesis methods known in the art. For example, 4-(N-methacryloyloxymethyl-N-methylamino)-4'-nitrostilbene (hereinafter referred to as "methacryloxy-DANS") is formed by reaction of 4-(N-hydroxymethyl-N-methylamino)-4'-nitrostilbene with methacryl chloride. When dissolved in methyl methacrylate or methacrylic bone cements, methacryloxy-DANS shows a larger shift in the peak fluorescence wavelength than DANS at the earlier stage of polymerization. This is due to the fact that methacryloxy-DANS molecules continually become

incorporated into growing polymer chains and respond to the polarity and mobility of the polymer chains (which are different from the polarity and mobility of unreacted monomer molecules), while DANS molecules remain in methyl methacrylate and respond only to methyl methacrylate molecules, until the later stage of polymerization. Similarly, increases in the shift of peak fluorescence wavelength at the earlier stage of polymerization, are obtained by using 4-(N,N-dimethacryloxymethylamino)-4'-nitrostilbene as a fluorophore instead of DANS to monitor the cure of dimethacrylic dental resins, or by using 4-(N,N-dihydroxymethylamino)-4'-nitrostilbene as a fluorophore instead of DANS to monitor the formation of polyurethanes or polyesters, or by using 4-(N,N-diaminomethylamino)-4'-nitrostilbene as a fluorophore instead of DANS to monitor the formation of polyureas or polyamides.

The wavelength-shift method and fluorophores of the invention are also useful for monitoring the polymerization of vinyl monomers at the later stage of cure. Monitoring and control of the later stages of a curing process are important in many manufacturing processes and clinical processes, such as the setting of bone cements. As an example, a trace amount of the fluorophore DHASP-PS was added to methyl methacrylate which contained 0.01M of the initiator azobisisobutyronitrile ("AIBN") at 55° C. At the cure time of 4.5 hours, when the extent of cure was 92%, the peak fluorescence wavelength of the fluorophore was 587 nm, only 5 nm shorter than the peak fluorescence wavelength of 592 nm at the beginning of the cure. However, after the cure time of 4.8 hours (when the peak fluorescence wavelength was 586 nm), the peak fluorescence wavelength decreased rapidly to 581 nm, 566 nm, and 555 nm at the cure times of 5.0 hours, 5.2 hours, and 5.5 hours, respectively.

FIG. 2 shows an example of a design of an optical fiber probe **10** for use in conjunction with the method of the invention. The probe **10** is inserted into a processing machine **12** in a port **14** normally used for a temperature or a pressure probe. The optical fiber probe **10** includes a bifurcated optical fiber that contains a bundle of nineteen fibers and a window **13**. The central fiber **11** carries the excitation light of an appropriate wavelength from a light source **16** to the fluorophore molecules which are dissolved in the polymerizing material inside the processing machine **12**. The collection fibers carry the fluorescence from the fluorophore molecules to the monochromator-detector (not shown) where peak wavelength is measured. The monochromator is a wavelength-dispersing component which disperses the polychromatic fluorescence radiation into light of various wavelengths. A fluorescence spectrum is obtained when the intensity of the light from the monochromator at various wavelengths is measured with the detector and plotted as a function of the wavelength. The peak fluorescence wavelength is determined as the wavelength at which the fluorescence intensity is a maximum.

Other probe configurations may also be utilized in the method of the invention. For example, the central fiber **11** can be replaced by a large number of excitation light fibers randomly distributed among a large number of collection fibers. FIG. 3 shows another example of an optical probe **20** which operates based on evanescent-wave induced fluorescence spectroscopy. This method is particularly useful in the manufacturing of polymer matrix composites. In this arrangement, an uncoated optical fiber **21** of high refractive index that is immersed or embedded in the polymerizing material **25** carries light (shown by arrow A) from a light source **23**, such as an Argon laser, to the fluorophore molecules in the polymerizing material **25**. Fluorescence