PROCESS MONITORING OF POLYMER MATRIX COMPOSITES

USING FLUORESCENCE PROBES

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INTRODUCTION

On-line process monitoring and control are prerequisites for more efficient and reliable manufacture of polymer matrix composites. The cure process involves complex chemical and physical changes that must be adequately controlled to consistently produce high quality products. Of various changes that occur, the viscosity is particularly important as it influences fiber wetting, uniformity of resin distribution and consolidation of the reinforcement plies. In the usual cure cycle, the viscosity of the resin initially decreases as the temperature of the resin rises owing to the higher temperature of the autoclave and heat released by the exothermic chemical reactions of the cross-linking process. Ultimately, the growing molecular weight of the polymer increases the viscosity beyond the range where flow will occur. If the resin viscosity becomes too low during this period, excess resin will seep out of the part producing an inferior product owing to resin deficiency. On the other hand, if the viscosity increases too fast the flow may be insufficient to achieve good consolidation of the plies.

On-line process monitoring techniques would also facilitate the introduction of modified or new resin systems. Currently, extensive off-line laboratory studies must be conducted to optimize the cure cycles before new resin systems can be introduced. On-line process monitoring of viscosity should greatly reduce the necessity of conducting time-consuming laboratory investigations.

Our approach to viscosity monitoring uses organic dye molecules that exhibit viscosity-sensitive fluorescence intensities [1]. A number of dyes have been investigated for potential as viscosity probes, and several promising dye systems have been identified [2,3]. For neat resins, conventional fluorescence spectroscopic techniques have been used to measure intensities. These techniques are generally limited in sensitivity to the surface of a reinforced specimen, particularly for opaque reinforcements. To probe the interior of a specimen, optical waveguides in the form of glass fibers may be used to transmit the excitation light into a thick specimen and to collect and transmit a portion of the emitted light to the detector. Furthermore, the optical fibers may be selectively placed in the specimen to develop an image of the viscosity profile across the specimen. The combination of fluorescence probe molecules and optical fibers shows promise as a

useful system to monitor on-line the viscosity of a curing matrix resin. In this paper, we report investigations of the use of fluorescence spectroscopy to monitor resin viscosity.

The fluorescence spectra of some organic dyes are also sensitive to chemical changes that take place during cure, or subsequent to cure owing to environmental effects, such as moisture uptake. Since the optical fibers remain in the composite part after processing they may have wider use, such as probes of moisture uptake, stress concentration [4], and macro-cracking [5]. In this report, we focus on the use of optic fibers for cure-monitoring only.

VISCOSITY SENSITIVE FLUORESCENCE PROBES

The sensitivity of the fluorescence spectra of some organic dye molecules to viscosity stems from the competition between radiative and non-radiative processes for de-excitation of electronically excited states [6]. As the solution viscosity increases, the degrees of motion of the solute dye molecules are affected to the extent that the probability of large scale movement is diminished. For example, translational modes are converted into internal modes as the probe molecule is trapped in a highly viscous medium. Inhibiting molecular mobility reduces the probability for non-radiative decay of the electronic excitation, and fluorescence is enhanced. There are molecules, however, for which the reverse is true; that is the fluorescence intensity of some bands diminishes with decreasing mobility. An example of the latter situation is the excimer-forming dyes in which mobility enhances the formation of the excited electronic states from which fluorescence occurs [7]. An example of this phenomenon is demonstrated in Figure 1 with the fluorescence spectra of 1,3-bis-(1-pyrene)propane.
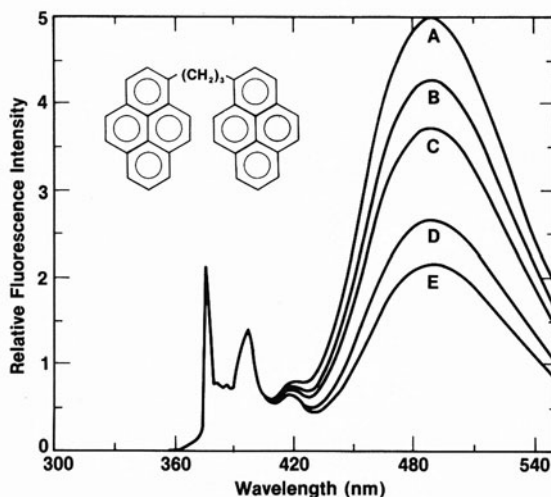

Fig. 1.   Dependence of the fluorescence spectrum of 1,3 bis(1-pyrene)propane on the solvent viscosity. All spectra are normalized to constant monomer intensity. The solvent viscosity progressively increases from A to E: A, 0.44cp; B, 0.91cp; C, 1.36cp; D, 2.81cp; E, 4.0cp.

The structure of the molecule, shown in Fig. 1, consists of two pyrene rings that are the chromophores involved in the electronic excitation. The absorption of a quantum of UV radiation produces an electronically excited pyrene moiety. The lifetime of the excited state is of the order of 100ns, meaning that after this time interval fluorescence will occur at the wavelength of pyrene emission shown as the higher frequency band envelope in Figure 1, provided that other processes of de-exciting the pyrene ring have not occurred. One such process is the formation of an electronically excited state involving both pyrene groups. In this process, termed excimer formation, the excitation is shared between the two pyrene groups. Excimer formation takes place when the two planar pyrene groups adopt a sandwich conformation, that is, parallel arrangement of the pyrene rings with a 0.3nm interplanar distance separating the ring moieties. Molecular motion about the propane linkage allows the pyrene groups to achieve a sandwich arrangement.

The importance of excimer formation to viscosity monitoring is two-fold. First, fluorescence from the excimer state occurs at a longer wavelength and is sufficiently well separated from the monomer fluorescence to permit measurement of both (see Figure 1). Second, the probability of the two chromophores adopting a sandwich conformation within the lifetime of the excited state of the pyrene group is inversely proportional to the microviscosity. As the surrounding medium viscosity (termed microviscosity) increases, the less likely is the formation of an excimer within the lifetime of the electronically excited state of the pyrene group. This is demonstrated in Figure 1 in which fluorescence spectra ratioed to constant monomer emission intensity are plotted. The decrease in excimer fluorescence with increasing solvent viscosity is evident. A particularly attractive feature of excimer-forming dyes as probes is the availability of the monomer fluorescence intensity as an internal standard. This would obviate the need for absolute intensity measurements or secondary standards.

Figure 2 shows the ratio of the fluorescence intensities from the monomer and excimer states of 1,3-bis-(1-pyrene)propane in a curing epoxy (EPON 828* and an amine hardener, 4,4'-methylene-bis-(cyclohexlamine). The ratio of fluorescence intensities clearly shows a dip corresponding to a decrease in viscosity in the initial stages of cure followed by a rapid rise. The decrease in the fluorescence intensity ratio at the initiation of cure is due to the temperature rise as the resin temperature approaches that of the mold and as heat is evolved by the exothermic chemical reactions. The slight decrease in the ratio at longer cure times relates to the onset of photochemical reactions as the dye molecules no longer possess sufficient mobility to move in and out of the excitation beam. These data were obtained using a conventional fluorimeter and a dye concentration of 10^{-5}. The low dye concentration implies that the probe will not appreciably affect resultant composite properties. The effect of the optical fibers on mechanical properties has not been addressed in our work.

*Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.
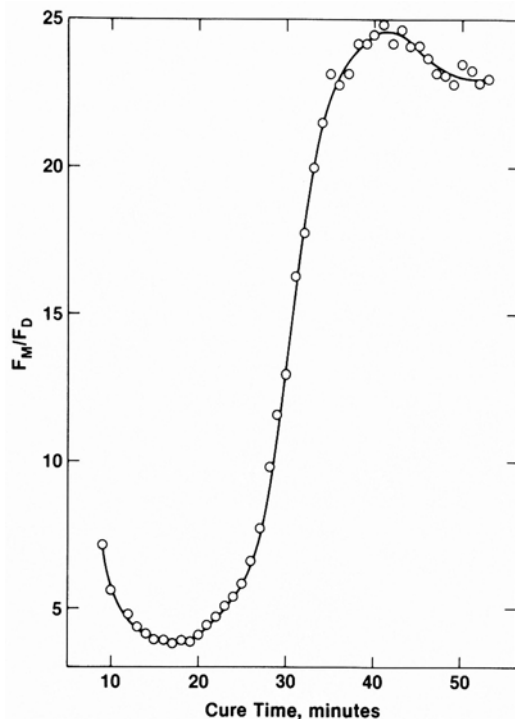
Fig. 2. The cure curve of an epoxy system [EPON 828, cured with 4,4'-methylene-bis-(cyclohexylamine)] monitored by the fluorescence ratio of the excimer dye, 1,3-bis-(1-pyrene) propane.

Owing to the lack of sensitivity of excimer-forming dyes at longer cure times we have examined other dyes as viscosity probes. The fluorescence and excitation spectra of one such dye (1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hexatriene, DMA-DPH) are shown in Figure 3, and the dependence of its fluorescence intensity with cure of an epoxy resin is shown in Figure 4. The excitation spectrum is obtained by monitoring the fluorescence intensity at the peak of the fluorescence band as the excitation monochromator is scanned. The excitation spectrum should resemble the absorption spectrum of the dye and is useful in selecting the optimal excitation frequency. This dye is attractive because its fluorescence intensity is sensitive to viscosity over a wider range of viscosities than the excimer-forming dye. However, in this case an internal standard is required. We have selected a second dye, 9,10-diphenylanthracene, DPA, as the standard since the fluorescence spectrum of this dye occurs at a different wavelength and the intensity is virtually independent of viscosity, as shown in Figure 4, lower trace.

The cure of an epoxy resin system (DER 332 cured with 4,4'-methylene-bis-(cyclohexylamine) was monitored using this dye pair and a conventional fluorimeter and the results are shown in Figure 5. To obtain this plot the probe and intensity standard molecules are excited with a xenon lamp at frequencies lying within the respective excitation band profiles and the fluorescence intensities recorded at the peak frequencies of the two dyes. The viscosity of the resin system as a function of cure time was determined by ultrasonic measurements (1), and the results are shown in Figure 5 for comparison with the spectroscopic measurements.
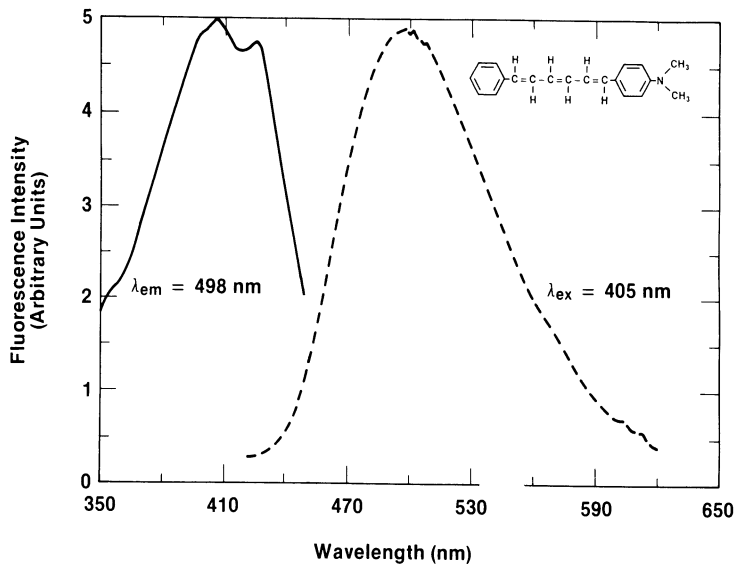
Fig. 3. The fluorescence (dashed curve) and excitation (solid curve) spectra of the viscosity-sensitive dye (1-(4-dimethyamino)-6-phenyl-1,3,5-hexatriene) in solution.
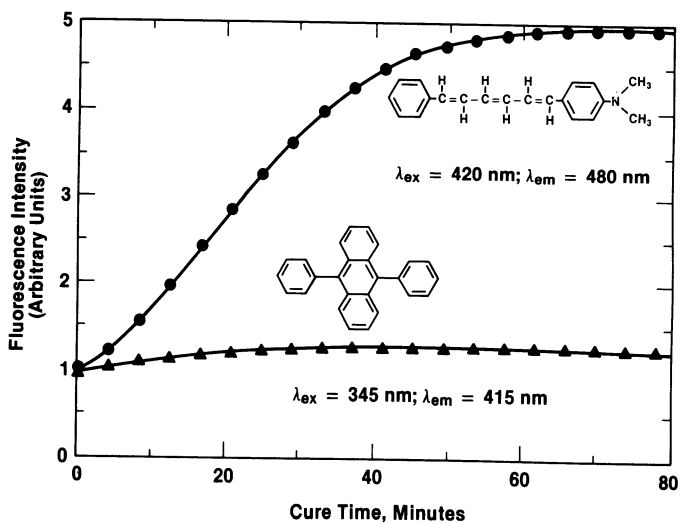

Fig. 4. The fluorescence intensity of DMA-DPH, solid circles, and DPA, solid triangle, in an epoxy system, [DER 332 cured with 4,4'-methylene-bis-(cyclohexylamine)], as a function of cure time.
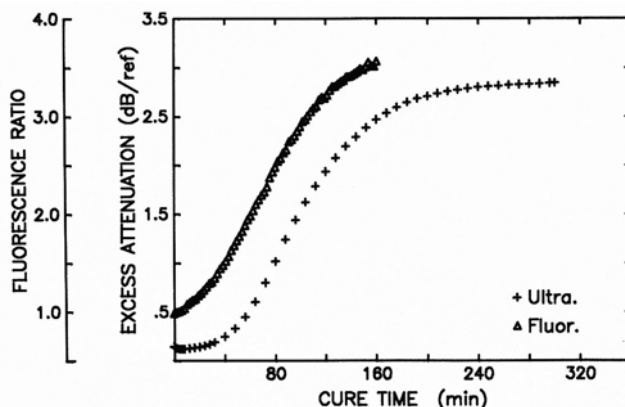
Fig. 5. The cure curves of an epoxy system [DER 332 and 4,4'-
         methylene-bis-(cyclohexylamine)]: Δ, by fluorescence
         spectroscopy using dye pair shown in Fig. 4; solid line, by
         an ultrasonics shear wave method.

OPTICAL WAVEGUIDES

     Optical waveguides have been investigated as a means of
transmitting the light into the interior of opaque specimens and
capturing and transmitting a portion of the dye fluorescence to the
detector system. The salient feature of optical waveguides is that the
electric field intensity does not vanish at the waveguide interface but
penetrates a short distance into the surrounding medium. The electric
field in the lower refractive index medium is referred to as the
evanescent wave, and the distance into the lower index medium at which
the intensity falls to 1/e of its value at the interface is called the
penetration depth. As a result of the evanescent wave, light
propagating in a waveguide fiber can excite dye molecules that are
located within the penetration depth of the fiber-matrix interface.

     The penetration depth depends on the refractive indices of the
fiber and the surrounding medium, the wavelength of light, and the
angle the propagating light makes with the waveguide-matrix interface.
A necessary condition for a guided wave is that the refractive index of
the waveguide must be higher than that of the surrounding medium. For
resins with refractive indices lower than about 1.47, ordinary glass or
high purity quartz may be used as the waveguide.

     In Figure 6 is shown the fluorescence spectrum of rhodamine-B
obtained with a glass fiber made of ordinary silica. The dye was
dissolved in the solvent mixture propanol-1 and o-dichlorobenzene, and
the volume ratio of the two solvents was selected so that the
refractive index of the solution was less than that of the glass fiber.
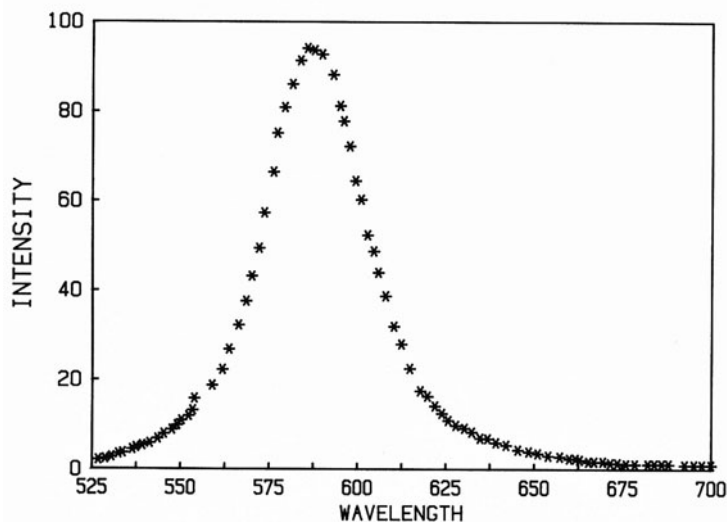
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Fig. 6. Fluorescence spectrum of rhodamine-B in propanol-1 and o-dichlorobenzene obtained with optic fiber.

The 488nm laser line of an argon ion laser was focused on one end of the fiber, and a portion of the fiber was immersed in the dye solution. The fluorescence light emerging from the other end of the fiber was directed into a double 0.25M monochromator and the spectrum recorded.

One potential advantage of our optical fiber method is that the fluorescence signal is generated along the entire length of the exposed fiber, and therefore more descriptive of the entire specimen, rather than would be the case if only a small localized volume was interrogated. This is the situation for other optical fiber designs. In these designs, one end of the fiber is imbedded in the sample, and it acts as both the illumination point and fluorescence light collector. For these designs, the sampling volume is restricted to a small region surrounding the fiber end.

We have examined the relationship between the length of the fiber exposed to the dye solution and the intensity of the fluorescence light observed at the end of the fiber. The findings given in Figure 7 show that a linear relationship exists between fiber length and fluorescence intensity. In these experiments no attempt was made to optimize the fluorescence signal so that the minimum length of exposed fiber needed to obtain good quality data has not been addressed. Other factors such as the total change in fluorescence intensity during a cure cycle, fiber characteristics (diameter, refractive index composition), laser intensity, and dye concentration will influence the limiting resolution of the system.
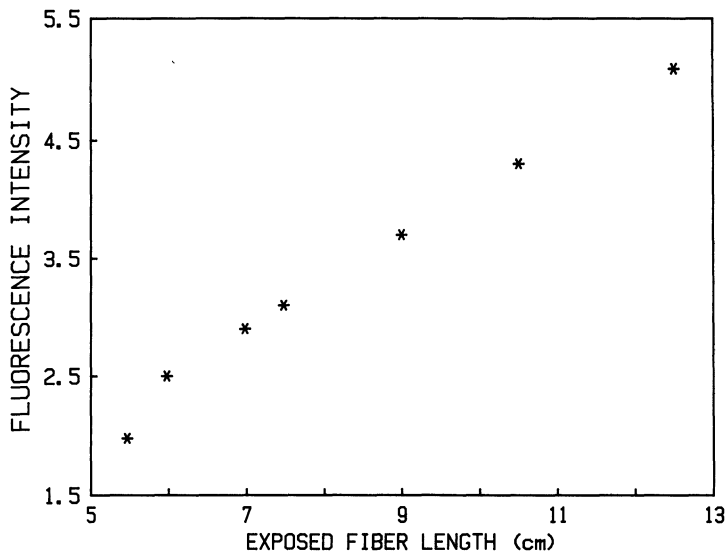
Fig. 7. Dependence of the intensity of fluorescent light collected by optic fiber on length of immersed fiber.

As the refractive indices of epoxies are in the range 1.5-1.6, one potential problem is the availability of fibers of high refractive index. It is likely that the fiber index would be close to that of the resin. For this reason we have examined the dependence of the fluorescence intensity observed with a fiber on the difference between refractive indices of the waveguide and surrounding medium. In Figure 8 is shown the fluorescence intensities observed with a glass fiber (index 1.47) immersed in rhodamine-B solutions of different refractive indices. Care was taken to ensure that the same length of fiber was exposed to the solution for each measurement. The observed fluorescence increases by three orders of magnitude when the solution refractive index is less than that of the glass fiber. The residual intensity observed with the solution index higher than that of the fiber is attributed to scattering of the propagating light at the air-liquid interface. The scattering results from a change in the minimum angle of incidence for total internal reflection when the surrounding medium refractive index increases at the air-liquid interface. The observed fluorescence intensities are also sensitive to the effects of the refractive index mismatch on the efficiency of the fiber to collect some of the fluorescence light for transmission through the fiber to the detector.

SUMMARY

Fluorescence probes have been identified that are applicable to monitoring viscosity during curing of polymer matrix composites. Optical fibers have been investigated as a means of exciting the probe molecules in the interior of a thick specimen and collecting and
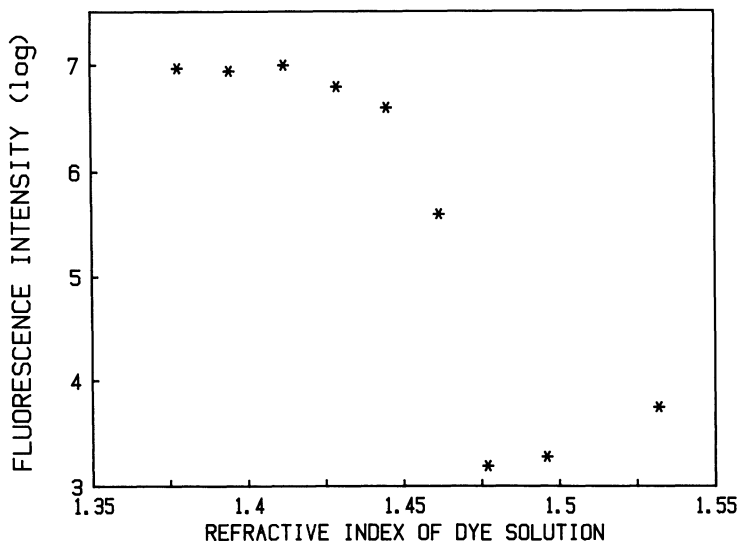
Figure 8. Dependence of the intensity of fluorescent light collected by optic fiber (index 1.47) on the medium refractive index.

transmitting a portion of the fluorescent light to the detector. It has been shown that the optical waveguide integrates the signal along its path through the specimen. This technique would permit indirect measurements of viscosity at various positions in the curing part, thereby providing a profile of the cure state throughout the part.

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