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Self-referencing fluorescence sensor for monitoring conversion of nonisothermal polymerization and nanoscale mixing of resin components

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Abstract

Fluorescence sensor techniques have been developed for monitoring nonisothermal polymerization reactions as well as for mixing of resin components both at the nanoscale and macroscale. A polarity-sensitive probe, 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DANS), was used to monitor the cure of an industrially relevant epoxy resin system through a fluorescence emission intensity ratio, which is self-referencing and independent of excitation intensity and monitoring geometry. The ratio demonstrated significant sensitivity to cure, increasing by a factor of 5.9 over 80% conversion. It was shown that the spectral shape, and thus the intensity ratio, was independent of temperature at a given state of cure. This insensitivity to temperature makes practical monitoring of nonisothermal reactions much simpler than many fluorescence techniques whose measurable is a function of both extent of reaction and temperature. In addition, the solvatochromatic nature of DANS was utilized to monitor nanoscale mixing of epoxy resin components, with spectral shape showing significant sensitivity to well-mixed resin composition. Fluorescence nonradiative energy transfer, which involves a nanoscale dipole–dipole interaction between excited-state donor and acceptor chromophores, has also been shown to be useful for monitoring molecular scale resin mixing. Further, a method of multiple, directly excited fluorescence probes was introduced to monitor overall stoichiometry in epoxy resin systems through spectral shape, showing sensitivity to changes of ± 1% in composition.

Keywords: Fluorescence; Self-referencing sensor; Nonisothermal polymerization

1. Introduction

The use of photophysical methods for monitoring resin cure or fractional conversion in a polymerization process has been studied since the 1980s [1–34]. Luminescence methods allow for contactless, nondestructive, in situ monitoring of cure or conversion and for complementary measurement of other properties such as mold filling during resin transfer molding [34,35]. This makes photophysical approaches the equal of or better than other methods for cure monitoring, including dielectric response [36–38], infrared and Raman spectroscopy [39–41], ultrasonics [22,42], and various reflectance spectroscopies and electrooptic methods related to refractive index [43–47]. While many classes of photophysical chromophores have been studied for use in cure monitoring, including molecular rotors [1–3,20], excimer-forming probes [5,8,20], reactive dye labels [14–16,18,20], and intramolecular charge transfer probes [6,11–15,28], the most commonly employed approach has involved monitoring fluorescence intensity, which is often observed to rise with conversion due to a reduction in nonradiative processes associated with an increase in resin microviscosity. While this offers the benefit of simplicity, it suffers from several practical problems: the increase in intensity often displays little or no sensitivity over a portion of the conversion range, and measurement of intensity at a single wavelength is subject to irreproducibility associated with excitation source fluctuations and monitoring geometry.

Recently, there has been great interest in developing self-referencing fluorescence sensors [27,31,34,48–50] for monitoring a variety of phenomena, including resin cure or conversion during polymerization. Such a self-referencing system eliminates issues associated with signal irreproducibility due to the fact that an intensity ratio or another parameter associated with the change in shape of the

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fluorescence spectrum is correlated to resin cure or conversion; such parameters are generally unaffected by excitation source fluctuations or monitoring geometry. Here we demonstrate that a self-referencing fluorescence probe system, 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DANS) which is a well-known solvatochromatic fluorescence probe, not only can provide for a sensitive, correlative, in situ measure of conversion in a polymerizing system, a point made previously by others [13–15], but that it yields a measurable quantity, e.g. an intensity ratio, that within error is independent of polymerization temperature. Thus, the fluorescence sensor described here is not only self-referencing but also applicable to nonisothermal polymerizations (without need for measuring temperature at the monitoring location) such as those commonly found in reactive processing, e.g. resin transfer molding.

We also address the utility of fluorescence sensors for monitoring resin-component mixing, in terms of both stoichiometry and effectiveness of mixing at the nanoscale. Development of end-use properties of resins cured via reactive processing requires control of resin composition as well as molecular-scale mixing of the resin components in order to ensure uniform conversion and homogeneity in composition throughout the resin. While a number of photophysical methods have been used to monitor nanoscale mixing and/or diffusion at polymer–polymer interfaces [51–61] as well as to monitor selective sorption and solvation behavior in mixtures of chromophore-labeled polymers and binary solvents [62], there has been no report regarding the application of fluorescence for in situ monitoring of resin-component mixing, either for stoichiometric balance or at the nanoscale. Here we compare the utility of three self-referencing fluorescence methods for providing quantitative details associated with mixing of resin components and demonstrate that the solvatochromatic dye found to be useful as a self-referencing probe for in situ monitoring of conversion in nonisothermal cure is also effective as a self-referencing probe of stoichiometric balance and nanoscale mixing of resin components.

2. Experimental

2.1. Materials

The epoxy resin components used in this study were diglycidyl ether of bisphenol A (DGEBA) and methyltetrahydrophthalic anhydride (MTHPA) with methylimidazole (MI) as an accelerator. All were obtained from TCI America and used as received.

In cure monitoring experiments, the extrinsic probe 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene was used as received from Kodak. Additional probe molecules for mixing studies included pyrene, anthracene, and 1,8-diphenyl-1,3,5,7-octatetraene (DOT) which were obtained from Aldrich and used as received, while 4-tricyanoethylene-*N*-(2-hydroxyethyl)-*N*-ethylaniline (TC1) was synthesized by Jacob Hooker according to a procedure by McKusick et al. [63]. When dissolving chromophores in DGEBA, an elevated temperature (~60 °C) was used due to its high viscosity. Chemical structures of the probes and resin components are shown in Fig. 1.

2.2. Fluorescence measurements

Measurements of steady-state fluorescence emission spectra were made with a SPEX Fluorolog-2 DM1B in front face mode, with a 22.5° angle between excitation and emission to minimize the effects of scattered light. Excitation and emission slit widths of 1.25 mm were used, allowing a 2.25 nm bandpass. The integration time was 1 s at each wavelength. No correction was made for the wavelength dependence of the grating efficiency.

2.3. Fluorescence cure monitoring experiments

DANS was dissolved in MTHPA at 0.065 wt%. Components were thoroughly mixed at a ratio of DGEBA/MTHPA/MI 100:85:2 by weight, yielding ~1–1 molar ratio of DGEBA to MTHPA. Resin was loaded into a $1 \times 1 \times 4\ \mathrm{cm}^3$ quartz cuvette and held at reaction temperature (65 or 80 °C) via a water bath circulating through the cuvette holder. The reaction is exothermic, but at the cure temperatures used here, reaction is sufficiently slow to ensure isothermality, which was confirmed by use of a thermocouple. Emission ($\lambda_{\mathrm{excitation}} = 475$ nm) spectra were obtained over times

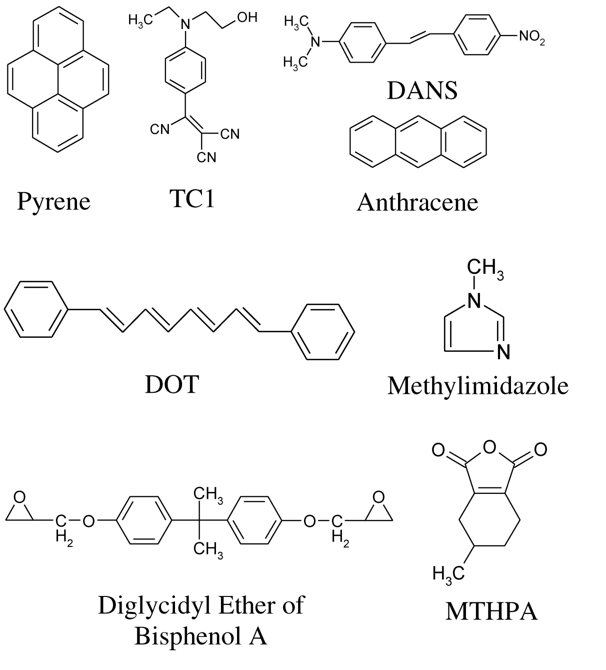

Fig. 1. Chemical structures of the epoxy resin components and extrinsic fluorescence probes used in this study. DANS = 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene, TC1 = 4-tricyanoethylene-*N*-(2-hydroxyethyl)-*N*-ethylaniline, DOT = 1,8-diphenyl-1,3,5,7-octatetraene MTHPA= methyltetrahydrophthalic anhydride.

exceeding that for complete attainable conversion according to differential scanning calorimetry (DSC). Each spectrum required ~2 min to acquire; since the reaction time was long (~150 min at 80 °C and ~300 min at 65 °C), each spectrum may be considered representative of an instant in time.

2.4. DSC measurements

Conversion-time data were obtained with a Perkin–Elmer DSC-7 differential scanning calorimeter. A 50 mg sample of reaction mixture was placed in a stainless steel, hermetically sealed sample pan. In order to achieve isothermal reaction, the temperature was ramped at 40 °C/min to the reaction temperature, where it was held until the reaction was completed and the exotherm returned to its baseline value. The rate of reaction was assumed to be proportional to the differential power supplied to the sample holder. The area between the exotherm and a linear baseline was used to calculate the extent of reaction. Since the resin does not react to completion at the temperatures used here, this value was adjusted using the following equation

$$X_{\mathrm{actual}}(T,t) = X_{\mathrm{relative}}(T,t)[\Delta H_{\mathrm{rxn}}(T)/\Delta H_{\mathrm{rxn}}] \quad (1)$$

where X_{actual} is the real fractional conversion at a given reaction temperature and time based on DSC measurements, X_{relative} is fractional conversion obtained at a given reaction temperature and time relative to the maximum conversion obtainable at that reaction temperature, $\Delta H_{\mathrm{rxn}}(T)$ is the full heat of reaction observed at temperature T, and ΔH_{rxn} is the complete heat of reaction. The complete heat of reaction was obtained by running a temperature scan at 10 °C/min until the exotherm returned to the baseline value and then integrating the area under the curve. The glass transition temperature, T_g, of the fully cured material was determined to be 145 °C using a scanning rate of 10 °C/min and the one-half ΔC_p method. A more complete explanation of the characterization of the epoxy resin conversion via DSC is given in Refs. [34,64].

3. Results and discussion

3.1. Cure/polymerization monitoring

Fig. 2 shows the evolution of the fluorescence emission from the DANS probe during the 80 °C cure of the epoxy resin. The DANS fluorescence is sensitive to both local mobility and polarity, resulting in a dramatic change in both intensity and shape of the emission spectrum as a function of cure. (The resin used in this study is of interest for high-performance composites and has been shown to react through an anionic active site generated by the ring opening of the epoxide [65,66]. While this mechanism is quite different from typical epoxy resins using an amine hardening agent, for which reaction proceeds via step growth, the change in resin polarity accompanying conversion is not unlike that found in typical epoxy resins.) Peak intensity increases by a factor of 37 while the peak wavelength experiences a shift of 62 nm on going from 0 to 80% conversion, which is the limiting conversion obtained at the 80 °C cure temperature. The change in peak shape and location is due to the solvatochromatic character of DANS and the evolution of local polarity experienced by the probes during the epoxy resin cure. Simply stated, in the context of fluorescence, solvatochromism relates to the shift in emission spectral location and/or spectral shape of a chromophore because of a change in local medium polarity or dielectric constant. The sensitivity to medium polarity results from the fact these probes, which contain both an electron-donating moiety and an electron-accepting moiety, exhibit significant intramolecular charge separation in their excited state. Emission maxima undergo shifts to higher wavelength or lower energy as the local medium polarity is increased because the dipolar excited state is more effectively stabilized in polar solvents [13].

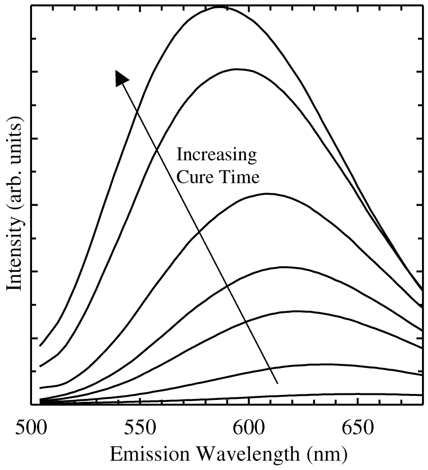

Fig. 2. Fluorescence emission spectrum of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene in epoxy resin as a function of cure time at 80 °C. Excitation wavelength = 475 nm.

There are several options available for correlating spectral shape to conversion. Among these include the use of peak wavelength and the use of a ratio of intensities at two wavelengths (588 and 684 nm), I_{588}/I_{684}. Both options were examined, and the results are plotted as a function of conversion in Fig. 3. On the whole, each parameter shows significant sensitivity to cure that appears to increase as the reaction proceeds. However, as is typical with polarity-sensitive fluorescence probes, the emission peak was broad, making precise determination of the wavelength at maximum emission difficult. As a result, there were ranges of conversion over which the use of peak wavelength yielded little sensitivity to conversion. In contrast, I_{588}/I_{684} exhibits nearly a factor of 6 increase from 0 to 80% conversion, with a smooth, precise relationship between intensity ratio and conversion at all conversion levels which grows increasingly sensitive at higher conversion. (The particular

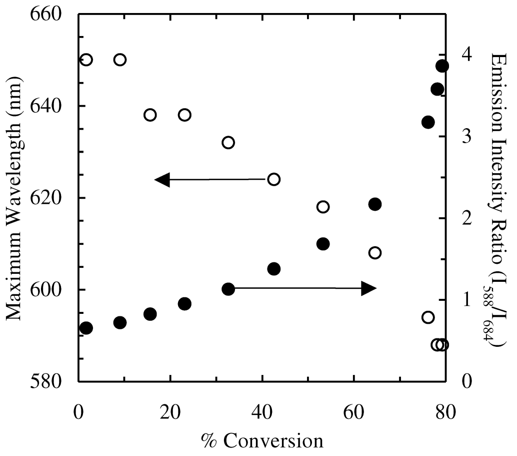

Fig. 3. Fluorescence emission intensity ratio and peak wavelength of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene as a function of epoxy resin conversion at 80 °C. Excitation wavelength = 475 nm.

wavelengths of 588 and 684 nm were chosen simply because they were on opposite sides of the emission maximum at zero conversion and provided substantial intensities throughout the conversion range studied. As long as these conditions are satisfied, a ratio of any two emission wavelengths should yields results qualitatively similar to those shown in Fig. 3 for I_{588}/I_{684}. It is coincidental that at the highest conversion obtained in Fig. 2, 588 nm was the wavelength at the emission maximum.)

Fig. 4 shows the normalized fluorescence spectra at three temperatures, 35, 75, and 125 °C, of a resin sample cured to 90% conversion. Also provided is the normalized emission spectrum of the unreacted resin mix at room temperature. The 90% conversion-state was obtained by reacting the resin at 135 °C for a period of 1.5 h. Based on DSC measurements, a limiting conversion of 90% is obtained using these reaction conditions. There are several noteworthy points regarding the fluorescence spectra shown in Fig. 4. First, the intensity ratio, I_{588}/I_{684}, for the 90% conversion resin sample is 4.9, indicating that the DANS probe continues to provide excellent sensitivity to cure at conversion levels between 80 and 90%. A second and more interesting point is that the spectral shapes of the 90% conversion sample obtained at the three monitoring temperatures are, within error, identical. This indicates that the fluorescence from DANS probes can be used to monitor the state of cure under nonisothermal reaction conditions, without the need to determine polymerization temperature either as a function of cure time or position in the sample undergoing cure. This is in sharp contrast to other fluorescence monitoring approaches, such as intensity at a single wavelength and excimer-to-monomer intensity ratios, that are normally very strong functions of temperature, requiring that temperature be simultaneously monitored during a nonisothermal polymerization and that a complex set of conversion/temperature/fluorescence-measurable calibration curves be obtained.

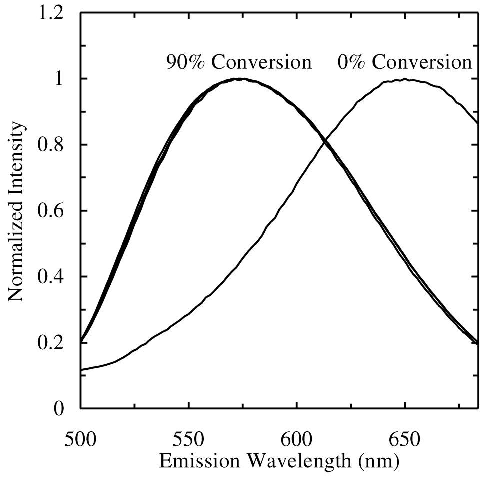

Fig. 4. Normalized fluorescence emission spectrum of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene in unreacted epoxy resin at room temperature and in epoxy resin reacted to 90% conversion at 125, 75, and 35 °C. Nearly complete overlap in 90% conversion spectra prevents distinction between the curves. Excitation wavelength = 475 nm.

Further confirmation of the ability of solvatochromatic probes such as DANS to allow for simple cure monitoring using a single calibration curve independent of temperature is shown in Fig. 5. This figure compares the values of I_{588}/I_{684} as a function of conversion at two cure temperatures, 65 and 80 °C. Excellent correspondence is observed between the lower and higher cure temperature to within ~1% of the ultimate conversion (~60%) at the lower cure temperature. It should be noted that the time frame required to go from unreacted resin to 59% conversion at 65 °C is ~5 h. The fluorescence at the 65 °C cure condition was monitored over a total period of 7 h. According to DSC measurements, within error no more than 0.5% of the limiting conversion that occurs at 65 °C takes place between 5 and 7 h of annealing and the T_g of the resin cured to limiting conversion at 65 °C is ~65 °C. Thus, with the exception of long-time annealing (from 5 to 7 h), there is a one-to-one

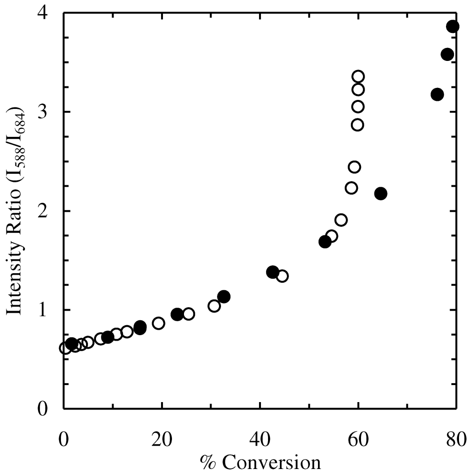

Fig. 5. Fluorescence emission intensity ratio of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene as a function of epoxy resin conversion at 80 °C (closed symbols) and 65 °C (open symbols). Excitation wavelength = 475 nm.

correspondence of the measured intensity ratio and conversion, independent of cure temperature, once the resin has cured to the point where its T_g is nearly identical to the polymerization or annealing temperature.

Fig. 6 shows a more detailed view of the evolving spectral shape and intensity during the long-time annealing, from 5 to 7 h, of the resin cured at 65 °C. While there is an increase in maximum intensity by ~20% and a blue shift of ~10 nm of the emission maximum with increasing annealing time, the spectral width at half-maximum remains unchanged within error, meaning that the latter measurement is not useful for characterizing the spectral evolution of this sample. The exact causes of the spectral changes observed in Fig. 6 are at present unclear. While other studies [67–69] have shown that fluorescent rotor probes provide sensitive measures of physical aging in polymers below T_g and more complex relaxation behavior associated with temperature jumps in polymers above and below T_g, it is not expected that similar sensitivity should be evident when polymers are annealed at T_g. Past experiments have demonstrated an invariance of rotor probe fluorescence emission with annealing time at T_g [67–69] while a recent study, in which DANS is doped in polystyrene, demonstrated an invariance of fluorescence spectral shape after equilibration at a temperature range of T_g to $T_g + 10$ °C [70]. Finally, Lenhart et al. [71] reported on the fluorescence of DANS covalently grafted to a glass surface as well as the fluorescence of DANS freely doped into a bulk resin, and they made no comment suggesting any of the unusual behavior seen with the DANS probe in this study. While further study of this interesting phenomenon is warranted, this by no means limits the use of DANS fluorescence to monitor conversion. The fact that DANS fluorescence otherwise provides a one-to-one correspondence with conversion that is invariant with cure temperature makes DANS an excellent choice as a self-referencing sensor dye for monitoring conversion.

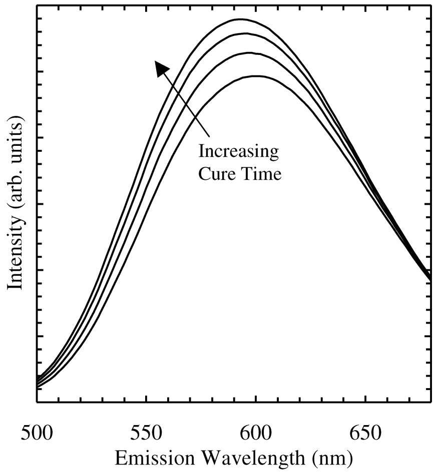

Fig. 6. Fluorescence emission spectrum of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene at high epoxy resin conversion (>99.8% of limiting conversion at 65 °C). The spectra span the final 90 min of 467 min total data collection time. Excitation wavelength = 475 nm.

3.2. Monitoring nanoscale mixing

Several options exist for monitoring the mixing of resin components using photophysical components. When using a solvatochromatic probe such as DANS, all that is required is that there exists a sufficient difference in the dielectric constant of each resin component. If DANS were dissolved in one component, one would expect a shift in the observed emission spectrum as the chromophore comes into intimate contact with other resin components during mixing. Because a polarity-sensitive probe is only sensitive to its immediate environment, the complete shift in fluorescence should not be observed until mixing is achieved at the molecular scale.

Fig. 7 shows the normalized emission spectra of DANS in pure MTHPA, pure DGEBA, and a stoichiometric mixture (100 parts DGEBA to 85 parts MTHPA, by weight). There is a substantial shift in emission as a function of composition that can be characterized by a ratio of intensities at 575 to 685 nm, I_{575}/I_{685}. (The choice of wavelengths for the ratio is made for the same reasons as described in Section 3.1.) Fig. 8 shows in detail how this ratio changes as a function of resin composition in well-mixed resin samples. There is a monotonic increase in the intensity ratio with increasing DGEBA content, indicating that spectral shape is a responsive gauge of molecular-scale mixing. At compositions of 40 wt% DGEBA and higher, the data show significant sensitivity to differences in composition of less than ±3%. In an actual monitoring situation where only one component would initially contain the DANS probe before mixing, it would be advantageous to

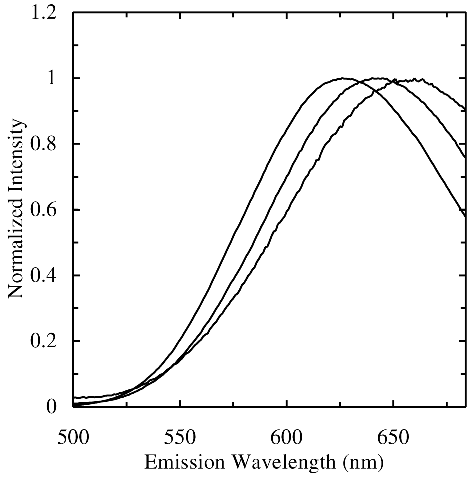

Fig. 7. Monitoring molecular scale mixing using a solvatochromatic dye. The curves are emission spectra of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene at 0.05 wt% in (from left to right): diglycidyl ether of bisphenol A (DGEBA), a 100 to 85 by weight mixture of DGEBA and methyltetrahydrophthalic anhydride (MTHPA), and MTHPA. Excitation wavelength = 475 nm.

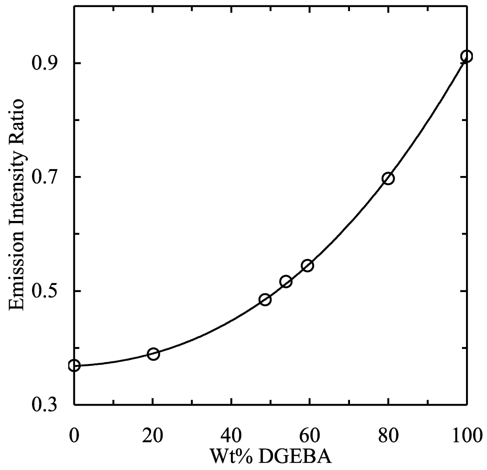

Fig. 8. Emission intensity ratio (I_{575}/I_{685}) of DANS as a function of composition in a mixture of diglycidyl ether of bisphenol A and methyltetrahydrophthalic anhydride. The DANS concentration is 0.05 wt% and the excitation wavelength = 475 nm. The curve is drawn to guide the eye.

mix DANS into DGEBA in order to yield the maximum sensitivity to mixing; this is evident because of the nonlinearity of the data in Fig. 8.

A potential limitation of this method for monitoring resin-component mixing at the nanoscale could result from diffusion of the probe molecule. In a worst case scenario, one could imagine a circumstance in which the two components of interest do not mix at all, but the probe molecule diffuses to equal concentrations in each. It is unlikely the ensemble emission spectrum would be identical to that obtained from a well mixed sample due to the greater heterogeneity of environments in the unmixed case (leading to a broader emission spectrum in the unmixed system) and due to the different quantum yields of DANS in the two components (influenced by differences in component viscosities). However, if the emission spectra were similar in the two systems, the concern of whether mixing or probe diffusion is being monitored can be eliminated by choice of a chromophore that is larger than or comparable in size to the resin components, meaning that the chromophore would diffuse more slowly than the resin components. (The impact of probe size and shape relative to solvent molecule size on probe self-diffusion is described in Refs. [72,73].) For instance, DANS is larger than MTHPA and is comparable in size to DGEBA, eliminating the concern that DANS emission may reflect diffusion of DANS between resin components instead of intimate mixing of the resin components.

Besides the use of a solvatochromatic probe such as DANS, a second option for monitoring resin-component mixing at the nanoscale involves the use of fluorescence nonradiative energy transfer (NRET). The NRET method [51,52], also called fluorescence resonance energy transfer, involves a short-range dipole–dipole interaction between two appropriately chosen chromophores, one a donor probe and the second an acceptor probe. The excited-state energy of a donor molecule has a high probability of being nonradiatively transferred to an acceptor chromophore as long as the excited-state donor molecule and the acceptor molecule are within a Förster radius of each other, typically 2–4 nm for a well-chosen donor–acceptor pair. (The Förster radius is the distance at which there is a 50% probability for NRET between the excited-state donor and the acceptor.) NRET is strongly sensitive to the separation distance between excited-state donor and acceptor; due to the dipole–dipole nature of the interaction, the efficiency of energy transfer scales with the separation distance to the inverse sixth power. By dissolving the donor in one resin component and the acceptor in the other, the potential thus exists to measure intimate mixing on the size scale of several nanometers.

Fig. 9 shows the impact of the presence of an acceptor probe, TC1, on the overall fluorescence spectrum of pyrene–TC1 donor–acceptor pair well mixed into the epoxy resin system. The pyrene–TC1 system was chosen because of the high absorbance and fluorescence quantum yield of pyrene and because the pyrene–TC1 system was previously used successfully in NRET studies of probe molecule diffusion in polymers [52]. Pyrene was dissolved in MTHPA (0.035 wt%), and TC1 was dissolved in DGEBA (0.16 wt%). Fig. 9 shows emission spectra for two mixtures. In one case, pyrene/MTHPA was mixed with pure DGEBA (without TC1), and in the other pyrene/MTHPA was mixed with TC1/DGEBA; both were stoichiometric mixtures. TC1 is not directly excited under the conditions used here. Instead, TC1 is excited through NRET from the excited-state pyrene, resulting in a reduction of pyrene fluorescence and the growth of TC1 fluorescence at long wavelengths (fluorescence maximum at ~600 nm, see inset in Fig. 9

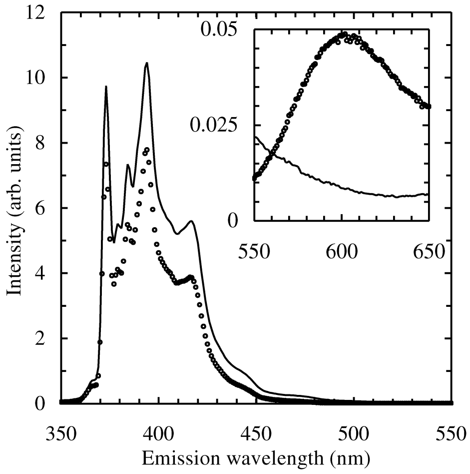

Fig. 9. Potential for using fluorescence NRET to measure mixing at the nanoscale. Emission spectrum for pyrene dissolved in an epoxy resin mixture with (∘∘∘∘∘∘∘) and without (—) the presence of fluorescence probe TC1. The inset plot is expanded to show the emission due to TC1. Excitation wavelength = 338 nm. (See text for probe concentrations).

necessitated by the strong pyrene fluorescence and the weak TC1 fluorescence).

An expression for the efficiency of energy transfer, $E(\gamma)$, between donor and acceptor chromophores randomly distributed throughout a sample as a function of acceptor concentration was derived by Bennett [74] and experimentally confirmed by Deppe et al. [52]

$$E(\gamma) = \pi^{1/2} \exp(\gamma^2)(1 - \mathrm{erf})(\gamma)) \quad (2)$$

where $\gamma = C_A/A_0$, with C_A being the acceptor concentration and A_0 related to the Förster radius, R_0, and Avagadro's number, N_A, by:

$$A_0 = 3000[2N_A R_0^3 \pi^{3/2}]^{-1} \quad (3)$$

At the TC1 concentration in the mixture, Eq. (2) yields a predicted energy transfer efficiency of 0.30. In good agreement with the prediction, the data in Fig. 9 yield a value of $E = 0.27$, which was obtained from analysis using the following expression

$$E(\gamma) = [I(0) - I(\gamma)]/I(0) \quad (4)$$

where $I(\gamma)$ and $I(0)$ are the steady-state fluorescence intensities of pyrene in the presence and absence of TC1, respectively. Intensity at the peak emission wavelength of pyrene at 394 nm was used although other choices give similar results.

By taking advantage of the fact that both pyrene and TC1 fluoresce, it is possible to construct a ratio of emission intensities that is sensitive to donor–acceptor mixing. By choosing the ratio of emission intensities at 380 to 600 nm, I_{380}/I_{600}, a dramatic change in value is obtained with mixing. This ratio yields a value of 84 when TC1 is present in the mix at the concentration employed in this study and a value of 640 when TC1 is absent, a difference of nearly a factor of 8. Thus, by characterizing the NRET response of the pyrene–TC1 system with an intensity ratio, a self-referencing fluorescence sensor system is achieved that is strongly sensitive to nanoscale mixing. The NRET approach is robust in its ability to monitor mixing of resin components at the nanoscale. However, in contrast with the use of a solvatochromatic probe such as DANS, NRET is not generally well suited for use in providing a self-referencing sensor method for monitoring resin cure and cannot provide a measurable that is independent of polymerization temperature or the nonisothermality of the polymerization.

3.3. Monitoring mixture composition

If there is an interest in monitoring resin component composition at the macroscale, that is, to determine if the appropriate level of resin components have been mixed together, it is possible to achieve this goal by using multiple fluorescence probes, one for each resin component, where each fluorescence probe may be directly excited by the excitation source. For ease of monitoring, the emission spectra of the multiple fluorescence probes must not completely overlap. Variation in the ratio of components then results in different concentrations of each chromophore in the resin mixture that in turn alters the relative observed fluorescence intensities contributed by each probe and thus the shape of the composite spectrum.

In the simplest circumstance, one may expect that a linear relationship may be developed between composition and intensity ratio. However, two factors generally complicate the relationship. Resin components typically have quite different viscosities, so that mixtures with different component ratios do not have equal viscosity. Differences in chromophore fluorescence quantum yield associated with differences in resin component viscosity may introduce nonlinearity into the intensity ratio–composition relationship. Similarly, if one or more probe molecules are solvatochromatic, related nonlinearity effects are introduced. While the effects of local viscosity and polarity complicate the relationship between spectral shape and resin composition, it in no way prevents the implementation of such a monitoring system.

Fig. 10 shows two conditions under which monitoring of overall stoichiometry of the resin mix may be accomplished. Fig. 10(a) shows the results of varying resin component ratios with the addition of 0.31 wt% anthracene to MTHPA and 0.025 wt% DOT to DGEBA. Both chromophores are directly excited at 355 nm; the fluorescence of anthracene appears at lower wavelengths and that of DOT at higher wavelengths with little overlap. By modestly varying composition, a substantial change in spectral shape was observed, giving the potential for detecting fluctuations in macroscopic stoichiometry as small as approximately ± 1%. In particular, an emission intensity ratio of I_{520}/I_{406} increases from 0.80 to 1.01 (26% change) when the amount of DGEBA was increased by 20% from stoichiometric proportions. The ratio decreases to 0.62 (23% change) upon decreasing the amount of DGEBA by 20%.

Another possible scenario utilizes the intrinsic fluorescence of one resin component. Fig. 10(b) shows the intrinsic fluorescence of the resin reaction mixture in the presence and absence of DGEBA. It is apparent that the observed fluorescence is due to MTHPA and that the addition of DGEBA merely dilutes the source of intrinsic fluorescence. (It has been shown [34] that in this epoxy resin system the intrinsic fluorescence is caused by adventitious impurities present at trace levels in MTHPA. Further, for the previous case shown in Fig. 10(a) involving two directly excited chromophores, it must be noted that anthracene and DOT absorb strongly enough that any fluorescence due to impurities in MTHPA was negligible.) Since the spectral shape does not change with composition, a trace amount of a chromophore must be added to DGEBA whose fluorescence emission does not significantly overlap with that of the impurities of MTHPA. Fig. 10(c) shows the consequence of varying the resin composition when DANS was dissolved in DGEBA at 0.015 wt%. A variation of wt DGEBA/wt MTHPA of ± 0.2 from stoichiometric balance yields

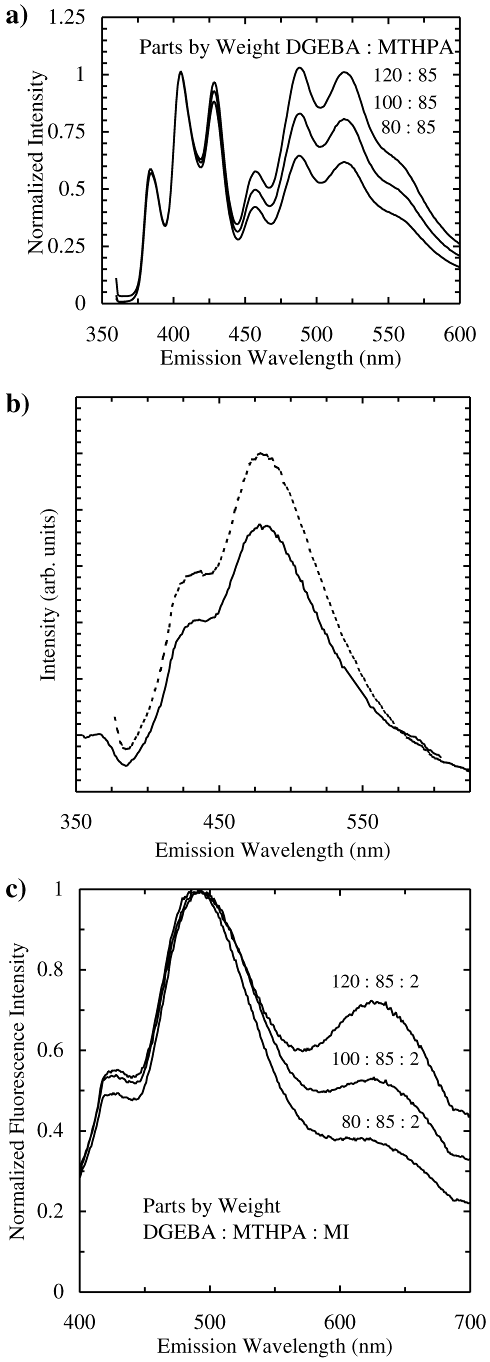

Fig. 10. (a) Stoichiometric mix monitoring with multiple extrinsic fluorophores. Methyltetrahydrophthalic anhydride (MTHPA) contains 0.31 wt% anthracene and diglycidyl ether of bisphenol A (DGEBA) contains 0.025 wt% 1,8-diphenyl-1,3,5,7-octatetraene. Spectra were normalized to the emission intensity at 406 nm. Excitation wavelength = 355 nm. (b) Emission spectrum of reaction mixture in the presence (DGEBA/MTHPA/MI 100:85:2 by weight) (—) and absence (0:85:2) (- - -) of DGEBA. Excitation wavelength = 350 nm. (Emission is due to intrinsic fluorescence from adventitious impurities in resin components [34].) (c) Stoichiometric mix monitoring of epoxy resin with one component that fluoresces. Pure methyltetrahydrophthalic anhydride (MTHPA) and methylimidazole (MI), were mixed with diglycidyl ether of bisphenol A (DGEBA) containing 0.015 wt% 4-(N,N-dimethylamino)-4′-nitrostilbene (DANS). Spectra were normalized at 493 nm. Fluorescence intensity at 425 nm, in increasing order: 100:85:2, 120:85:2, 80:85:2. Excitation wavelength = 355 nm.

substantial changes in the shape of the emission spectrum. (The fluorescence from MTHPA occurs at shorter wavelengths while that due to DANS occurs at longer wavelengths.) Increasing the amount of DGEBA by 20% from a 1 to 1 stoichiometric balance increases an appropriately chosen intensity ratio (I_{630}/I_{495}) by 37%; decreasing the amount of DGEBA by 20% decreases the intensity ratio by 30%. As with the incorporation of two directly excited chromophores, the results in Fig. 10(c) show that the macroscopic resin mixture composition can be measured to a sensitivity of ± 1% in stoichiometry.

The preceding examples illustrate the flexibility of fluorescence probe techniques for monitoring macroscopic mixing of epoxy resin components. While several options are available for monitoring macroscopic mixture composition, by employing a fluorescence sensor dye such as DANS it is possible to monitor not only mixture composition but also the quality of nanoscale mixing of the resin components at the outset of the curing process as well as conversion as a function of time during a nonisothermal polymerization.

4. Conclusions

This study has shown that, in addition to being extremely sensitive to cure, the spectral shape of the solvatochromatic chromophore DANS is nearly insensitive to temperature at a particular state of epoxy resin cure. While this may appear to be a subtle point, it has not been significantly addressed in the literature, and it has substantial ramifications in the practical implementation of fluorescence cure monitoring. Other fluorescence monitoring schemes involving the use of single chromophores whose sensitivity to cure is expressed by fluorescence intensity alone or via an excimer-to-monomer intensity ratio result in the fluorescence measurable being a function of conversion and temperature, making in situ monitoring difficult at best in nonisothermal polymerization or curing reactions. The use of multiple fluorescence chromophores can yield sensitivity to cure in terms of spectral shape, but that shape can also be a function of temperature. This can severely complicate the ability to employ fluorescence, requiring many isothermal experiments to obtain spectral shape as a function of both temperature and conversion. In contrast, the temperature insensitivity of the fluorescence spectral shape of DANS eliminates the need for extensive calibration and represents a major simplification in applying fluorescence cure monitoring techniques. Thus, the use of a single solvatochromatic chromophore such as DANS can yield a powerful, self-referencing method for monitoring conversion during nonisothermal cure of resins that exhibit a shift in polarity with conversion.

The solvatochromatic nature of DANS has also been shown to be useful in monitoring nanoscale mixing of resin components, provided their dielectric constants are different. Since the spectral shape is determined by the properties of the solvent shell around the individual DANS molecules, an intensity ratio provides a measure of composition at a molecular scale. If a significant variation of polarity is not present, it has been shown that fluorescence NRET can potentially be used to monitor nanoscale mixing. Given that NRET relies on a nanoscale interaction that is strongly dependent on local acceptor concentration, an intensity ratio of donor to acceptor fluorescence can be used to measure the extent of mixing at the molecular level. A method for monitoring overall stoichiometry of epoxy resins via fluorescence was also introduced, utilizing a directly excited probes (intrinsic or extrinsic) dissolved in each component. An intensity ratio showed sensitivity to changes in overall composition of about ± 1%. The fluorescence mix monitoring techniques developed in this study, both for assessing the quality of nanoscale mixing and the macroscale composition, denote a new level of control that can be applied to reactive processing of polymers and polymer composites.

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