Fluorescence Studies of Diaminodiphenyl Sulfone Curing Agent for Epoxy Cure Characterization

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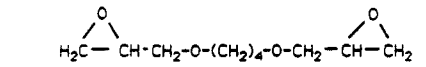
ABSTRACT: Fluorescence emission and excitation of a commonly used aromatic diamine curing agent, 4,4′-diaminodiphenyl sulfone (DDS), were studied during the curing process with a bifunctional epoxide or a tetrafunctional epoxide. As the curing proceeds, both the emission and the excitation spectra exhibit red shifts of about 25 nm for DDS due to the conversion of the primary amine groups in DDS to tertiary amine groups. Matrix effects such as the polarity decrease and the viscosity increase on the fluorescence spectra of the tertiary amino DDS (tt-DDS) were found to be small. The excitation spectra provide sharper peaks than the emission spectra, even though the overall spectral red shift in both spectra for DDS is about 25 nm. Based on the spectra of the model DDS cure species and the curing kinetics, the excitation spectra were simulated as a function of the extent of amine reaction. The result shows that the excitation spectral shift can be easily correlated to the extent of amine reaction. The extent of epoxide reaction based on IR analysis was found to be correlated almost linearly with the DDS excitation spectral shift. These results on the excitation spectra provide a basis for cure monitoring of the epoxide–diamine networks from the intrinsic fluorescence of the diamine curing agent DDS.

Introduction

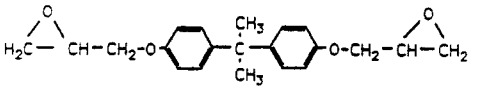
Epoxy resins are finding increasing applications in high-performance composite materials, especially for the aerospace industries. The ultimate mechanical and physical properties of epoxy materials depend to a large extent on the degree of cure, which affects the network structure of the epoxies. Thus in-situ monitoring of the curing process is essential to the optimization of the performance and the applicability of these resins.

The fluorescence technique has been shown to be effective for the cure characterization of polymers because of its sensitivity and selectivity and its capability for in-situ and nondestructive studies.[1-8] Generally, two types of fluorescence probes have been used. The first type of probes which have been extensively studied in recent years are nonreactive, viscosity-sensitive probes such as self-probe fluorescence,[2] excimer fluorescence,[3,4] fluorescence polarization,[5,6] fluorescence quenching,[7] and time-resolved fluorescence[8] probes. Although the use of nonreactive fluorescence probes can yield important information on the matrix viscosity, they are not useful for probing the curing mechanism and network structure of epoxies. The other type of probes are the reactive fluorescence probes developed in our laboratory.[9] In this case, a reactive diamine fluorophore which has a reactivity similar to that of the curing agent was introduced in small concentration to the uncured epoxy matrix as the reactive label. As the cure proceeds, bathochromic shifts of about 60 nm in the UV–visible spectra with subsequent enhancement of the fluorescence intensity of a diaminoazobenzene label (DAA) were observed. These spectral changes are essentially caused by the conversion of the primary amine groups in DAA to tertiary amine groups, following the curing process. The information about the network structure and the compositions of the cure species were obtained by spectral analyses. However, monitoring fluorescence intensity usually requires careful calibration with other internal standards for quantitative analysis,[1] since the intensity can fluctuate due to other factors such as the lamp intensity. Also, it is not very convenient to use extrinsic fluorophores in actual fabrication processes. Furthermore, the epoxy resins for composites may contain impurities with fluorescence characteristics similar to those of the extrinsic probes.[2a]

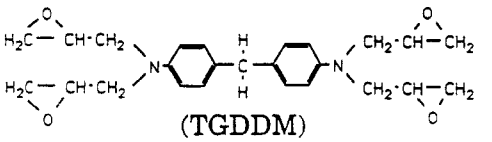
Chart I. Chemical Structures of Epoxides Used



(DGEB)



(DGEBA)



(TGDDM)

Most epoxy resins for high-performance composite materials are cured by a fluorescent aromatic diamine, 4,4′-diaminodiphenyl sulfone (DDS). However, its fluorescence behavior during the cure has not been studied in the literature. Since it emits at a shorter wavelength than the extrinsic reactive probe we had used in our previous work,[9] we expected a smaller red shift which could be related to the extent of cure. It was the main objective of this research to study the fluorescence behavior of the epoxy–DDS network and to establish the relationship between the intrinsic fluorescence due to DDS and the extent of cure of epoxy resins. For epoxides, either of two bifunctional epoxides (diglycidyl ether of butanediol (DGEB) and diglycidyl ether of Bisphenol A (DGEBA)) or one tetrafunctional epoxide (*N*,*N*,*N*′,*N*′-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM)) was reacted with DDS. Their chemical structures are shown in Chart I.

Experimental Section

1. Synthesis of Model Cure Products. The model compounds of two DDS curing species (ss-DDS and tt-DDS; see structures in Scheme I) were made by reacting DDS with a large excess (10 times) of the monoepoxide butyl glycidyl ether (BGE)

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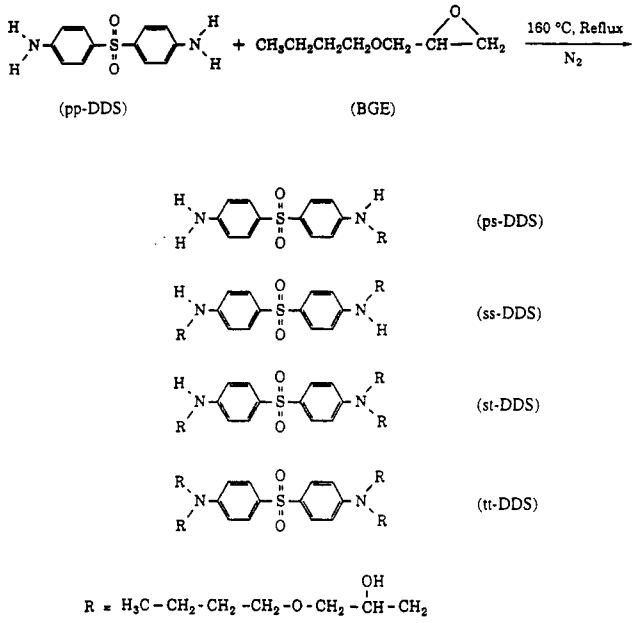
Scheme I. Various Reaction Products from 4,4′-Diaminodiphenyl Sulfone (pp-DDS) and Butyl Glycidyl Ether (BGE)



at 160 °C under nitrogen for 24 h. The excess epoxide was then removed under vacuum for 48 h. DDS and BGE were purchased from Aldrich and used without further purification. IR analysis of the reaction product indicated that all the primary amine groups were consumed, while ^{13}C NMR spectra of the product revealed the presence of the tertiary amines (54.7 ppm) and a small amount of the secondary amines (46.0 ppm), according to the assignments reported in the literature.[10] An analytical, reverse-phase HPLC system (Varian 500 LC) was used to separate the different model compounds. An Alltech Econosil column (L = 250 mm, i.d. = 4.6 mm) was used, with the mobile phase consisting of 60% H_2O and 40% THF by volume. An ultraviolet detector was set at 300 nm, while the flow rate was set at 1 mL/min.

2. Sample Preparation for Cure Reaction Studies. DGEB (98% purity) was purchased from Aldrich and used without further purification. As for DGEBA and TGDDM, Shell's Epon 825 and Ciba-Geigy's Araldite MY721 were used respectively, without further purification.[9] A stoichiometric mixture of DGEB (or DGEBA) and DDS was made by mixing 2.98 g of DGEB (or 5 g of Epon 825) with 1.825 g of DDS under constant stirring at 120 °C for 2 min. A stoichiometric mixture of TGDDM and DDS was obtained by mixing 3.15 g of TGDDM and 1.85 g of DDS in acetone. Acetone was then removed under vacuum at room temperature. The samples were cured between two quartz plates separated by two thin Mylar spacers (25 μm in thickness) on the edges at a specific preset temperature in the oven.[9]

3. Spectroscopic Analysis. The fluorescence spectra of the epoxy samples were taken after curing for a certain amount of time and cooling to room temperature. Fluorescence emission and excitation spectra were recorded on a Perkin-Elmer MPF-66 spectrofluorimeter with a Model 7500 data station. UV–visible spectra were obtained with a Perkin-Elmer diode array system (Model 3840) with a Model 7300 data station.

A Nicolet FTIR spectrometer was used to monitor the rate of disappearance of the epoxide ring of thin epoxy films which were spread between two KBr disks as a function of cure.

Results and Discussion

1. Spectra of Model Cure Products. When DDS is reacted with the epoxide, the primary amine groups in DDS are converted to secondary and tertiary amine groups. Since there are two amine groups in the para and para primed positions of DDS, we can expect four reaction products, namely, ps-, ss-, st-, and tt-DDS as designated in Scheme I. In addition, another species, pt-DDS, is

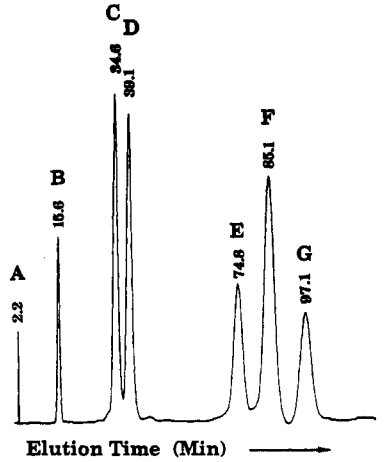


Figure 1. HPLC elution profile of the reaction products of 4,4′-diaminodiphenyl sulfone and butyl glycidyl ether.

possible. However, its concentration is known to be small, compared to the concentrations of other species.[9a] In UV and fluorescence spectra, we expect red shifts as the primary amine groups in DDS are converted to secondary and tertiary amine groups since tertiary amine groups are more electron donating. In 4,4′-diaminoazobenzene, we observed about 60 nm of spectral red shift.[9a] Figure 1 shows a typical HPLC elution profile of the reaction product of DDS with a 10-fold excess of butyl glycidyl ether (BGE). Four groups of peaks were obtained, including a singlet peak at 2.2 min (fraction A), a singlet peak at 15.6 min (fraction B), a doublet at 34.6 and 39.1 min (fractions C and D), and a triplet at 74.8, 85.1, and 97.1 min (fractions E, F, and G). The fractions corresponding to each HPLC peak were collected and dried under vacuum at 50 °C for 24 h. UV–visible spectra of each fraction dissolved in methanol were recorded. DDS before reaction (pp-DDS) shows an absorption peak at 294 nm in methanol due to the π–π^* electronic transition. Fraction A does not fluoresce and is probably due to impurities present in the starting materials. Fraction B has a major absorption peak at 306 nm (π–π^* transition) and a shoulder peak at 268 nm. Fractions C and D have identical UV–visible absorption spectra in methanol, showing a major peak at 315 nm and a shoulder peak at 274 nm. Fractions E, F, and G all show absorption peaks at 319 (π–π^* transition) and 280 nm (shoulder) in methanol, except that fractions E and G give a long-wavelength absorption peak at about 450 nm, which is probably caused by side products due to the oxidation and/or degradation of the tertiary amino DDS (tt-DDS). Thus, according to their UV–visible absorption characteristics, we assigned fractions B, C/D, and F as ss-DDS, st-DDS, and tt-DDS, respectively, as designated in Scheme I. The results of fluorescence excitation and emission spectral studies of these separated fractions in THF also showed progressive red shifts, consistent with the assignment.

Figure 2 shows the fluorescence excitation spectra of DDS model compounds in butyl diglycidyl ether solution. As expected, the excitation peak position of the most substituted tt-DDS is red-shifted in comparison with those of ss-DDS and pp-DDS. The total spectral shift obtained from pp-DDS to tt-DDS is about 25 nm. Even though some short-wavelength shoulders are observed in ss-DDS and tt-DDS, they do not influence the quantum yield of each species measured at the emission maxima. Table I summarizes the excitation spectral properties and quantum yields of DDS model compounds in butyl diglycidyl ether solution. In addition to the spectral red shift, tt-DDS is more fluorescent than ss-DDS and pp-DDS due

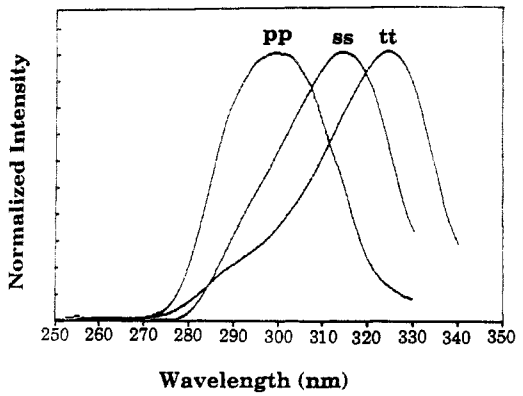
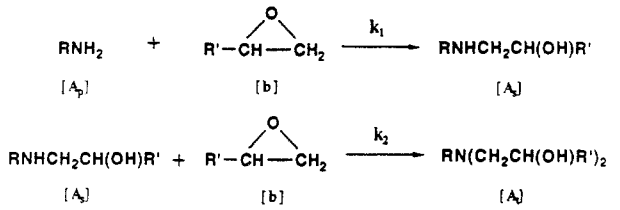


Figure 2. Fluorescence excitation spectra of the model cure compounds of 4,4′-diaminodiphenyl sulfone (DDS), namely, pp-DDS, ss-DDS, and tt-DDS, in a dilute solution of butyl glycidyl ether.

Table I. Fluorescence Excitation Spectral Properties and Relative Quantum Yields of DDS Model Compounds in DGEB

compd	λ_{max}, nm	$\Delta(\lambda_{max})$, nm	rel quantum yield (Φ_R)
pp-DDS	300	0	1
ss-DDS	315	15	1.7
tt-DDS	325	25	2.6

Scheme II. Cure Kinetics of Epoxide by Amine Addition



to its higher relative fluorescence quantum yield values (Φ_R). These spectral data of the DDS model compounds provide the basis to correlate with the extent of cure.

2. Simulated Excitation Spectra and the Extent of Amine Reaction. To establish the correlation between the fluorescence excitation peak position and the extent of amine reaction with the epoxide, the fluorescence excitation spectra of diepoxide–DDS with different extents of amine reaction have been simulated according to the procedures described below.

First, we need to know the concentration of each cure product as a function of the extent of amine reaction to simulate the spectra. Even though Scheme I shows at least four cure products, we do not have all the model compounds. Therefore, we will simplify the cure reactions so that only two cure products, namely, the secondary and tertiary amines, will be considered. In a typical stoichiometric epoxide–amine addition reaction, the primary amines are converted to secondary amines with a rate constant of k_1, and the secondary amines are consequently converted to tertiary amines with a rate constant of k_2, as shown in Scheme II. In this case, the following kinetic equations can be established.[11]

$$d[A_p]/dt = -2k_1[A_p][b] \quad (1)$$

$$d[A_s]/dt = 2k_1[A_p][b] - k_2[A_s][b] \quad (2)$$

$$d[A_t]/dt = k_2[A_s][b] \quad (3)$$

where $[A_p]$, $[A_s]$, and $[A_t]$ are the fractions of primary amine, secondary amine, and tertiary amine, respectively, and [b] is the concentration of epoxide. The solutions of

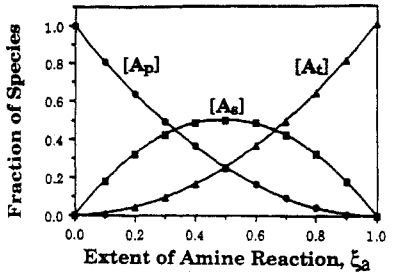


Figure 3. Fractional composition of the cure species as a function of the extent of amine reaction (ξ_a). ($[A_p]$, $[A_s]$, and $[A_t]$ stand for fractions of the primary, the secondary, and the tertiary amine, respectively.)

the above kinetic equations were given by Dusek and Bleha[11] as the following

$$[A_s] = \{[A_p]^r - [A_p]\}/(1-r) \quad (4)$$

$$[A_t] = 1 + r\{[A_p] - [A_p]^r/r\}/(1-r) \quad (5)$$

where $r = k_2/2k_1$. The extent of amine reaction (ξ_a) can be defined as

$$\xi_a = ([A_s] + 2[A_t])/2 \quad (6)$$

and substituting eqs 4 and 5 into eq 6, we can express ξ_a in terms of $[A_p]$.

$$\xi_a = 1 + [A_p](r-0.5)/(1-r) + [A_p]^r/(2r-2) \quad (7)$$

In the literature,[12] most of the reported values of r vary from 0.05 to 0.5. If $r = 0.5$, then $\xi_a = 1 - [A_p]^{1/2}$. Thus at a given ξ_a, we can obtain the concentration of each species using eqs 8–10.

$$[A_p] = (1-\xi_a)^2 \quad (8)$$

$$[A_s] = 2\xi_a(1-\xi_a) \quad (9)$$

$$[A_t] = \xi_a^2 \quad (10)$$

and a plot of the cure species composition versus ξ_a can be constructed as shown in Figure 3.

Now, the next step is to simulate the excitation spectra of DDS at each curing stage. Using the model compound spectra and the quantum yields of ss-DDS and tt-DDS to represent the secondary and the tertiary amino DDS, respectively, the fluorescence excitation spectra of DDS as a function of the extent of amine reaction (ξ_a) can be generated by adding the contributions of each model compound spectra according to the following equation.

$$(\text{Spectra})\xi_a = [A_p]\Phi_{pp}(\text{Spectra})_{pp} + [A_s]\Phi_{ss}(\text{Spectra})_{ss} + [A_t]\Phi_{tt}(\text{Spectra})_{tt} \quad (11)$$

where Φ_{pp}, Φ_{ss}, and Φ_{tt} are the relative fluorescence quantum yields for pp-DDS, ss-DDS, and tt-DDS, respectively, as summarized in Table I. $(\text{Spectra})_{pp}$, $(\text{Spectra})_{ss}$, and $(\text{Spectra})_{tt}$ are the fluorescence excitation spectra for pp-DDS, ss-DDS, and tt-DDS, respectively. Figure 4 shows the simulated excitation spectra of DDS as a function of ξ_a, where the maximum intensity was deliberately set to be the same. As expected, the spectral peak position is shifted to longer wavelengths as ξ_a increases. Again, the presence of short-wavelength shoulders does not influence the peak position. A correlation curve between the excitation peak position and ξ_a was obtained as shown by the triangles in Figure 5 for the case when k_1 is close to k_2. When $r = 0.05$, the spectra also can be simulated, and the correlation curve in that case is shown as the squares in Figure 5. It is noted that the

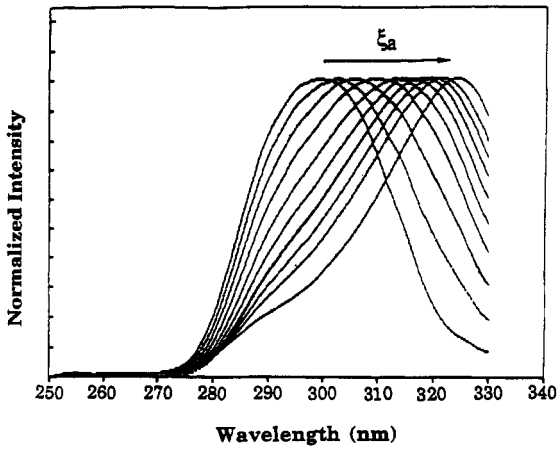


Figure 4. Simulated excitation spectra of 4,4′-diaminodiphenyl sulfone as a function of the extent of amine reaction (ξ_a) with butyl glycidyl ether. (ξ_a = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0, from left to right.)

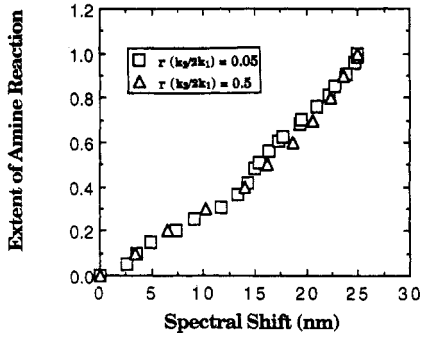


Figure 5. Correlation plot between the excitation peak position and the extent of amine reaction (ξ_a) according to two cases of simulation (r = 0.05 and 0.5).

latter case provides a more linear relationship than the former case. These two curves, which are not too different from each other, provide a basis for analyzing the extent of amine reaction from the excitation peak position.

While the overall spectral shift is about 25 nm, the spectral shift for the later stages of cure, for example, the last 20%, is only 3 nm, making the monitoring in the later stages less accurate. Therefore, this method is more sensitive for in-situ monitoring of the early and middle stages of cure. For the accurate monitoring of cure at the later stage, the phosphorescence signal which occurs at longer wavelength seems promising,[16c] even though it will not be an in-situ technique.

3. DDS-Cured Epoxies. (1) UV-Visible Absorption Studies. During the past few years, UV-visible absorption spectroscopy of several reactive labels has been used in our laboratory to study the mechanism and kinetics of the curing processes of important polymers such as epoxy,[9] polyimides,[13] polyurethanes,[14] polyamides,[15a] and polyureas.[15b] Basically, the advantage of UV-visible absorption is its ability to distinguish the different cure species due to the magnified effects of the substituent changes in the para and para primed positions of the aromatic labels. Since the tertiary amine groups are more electron donating to the aromatic ring, it was expected that the UV-visible absorption peak corresponding to the π–π^* transition in the DDS molecule will be shifted to longer wavelengths as the primary amines are converted to secondary amines and tertiary amines. The UV-visible spectra of three DDS model cure species, namely, pp-DDS, ss-DDS, and tt-DDS, obtained in methanol solution are very similar to the excitation spectra as shown in Figure 2. An overall spectral

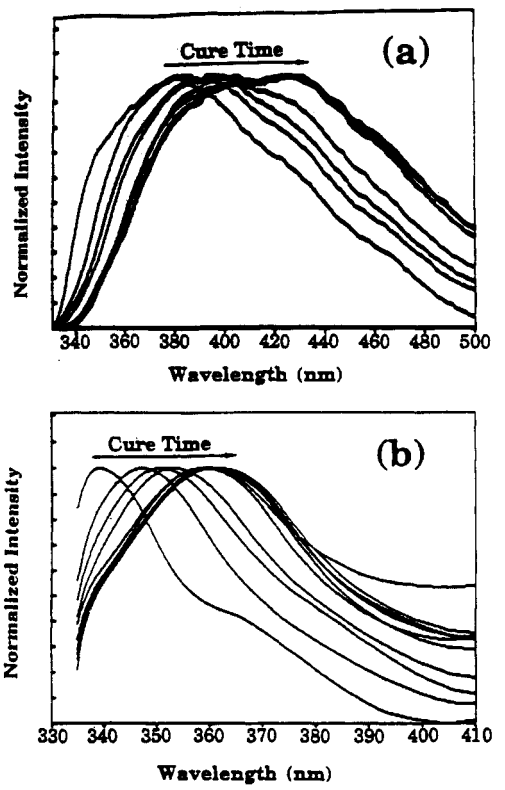


Figure 6. Intrinsic fluorescence emission spectra (a) and first-derivative emission spectra (b) of the stoichiometric DGEB-DDS epoxy as a function of cure time at 160 °C. (Cure time = 0, 10, 20, 30, 60, 90, 120, 180, and 240 min, from left to right; excitation at 315 nm.)

red shift of about 25 nm was observed between the pp-DDS and tt-DDS.

The UV-visible absorption spectral characteristics of diepoxide-DDS diamine thin film were also investigated as a function of cure. The UV-visible spectra of a very thin DGEB-DDS epoxy film as a function of cure time at 160 °C showed the absorption maximum to change progressively from about 298 to 322 nm. The overall shift of about 24 nm is also observed. The extent of epoxide reaction in DGEB-DDS cured at 160 °C for 120 min approaches about 95% since the T_g of DGEB-DDS is only about 80 °C.[9] Therefore, the overall shift of 25 nm corresponds to 95% completion of the cure reaction.

(2) Fluorescence Studies of DGEB-DDS and DGEBA-DDS Epoxies. When DGEB-DDS was excited at 315 nm, a fluorescence emission was observed with an emission maximum around 380 nm, as illustrated in Figure 6a. As the cure time increases at 160 °C, the emission maxima were shifted to longer wavelengths. A total red shift of about 24 nm was observed for samples cured for 90 min at 160 °C. After 90 min, the intensity of another emission peak around 430 nm probably due to other side reactions[16] becomes greater than that of the main DDS peak, making the emission peaks quite broad. This broadening may also be caused by environmental effects such as a distribution of the polarity surrounding the tertiary DDS molecule. Regardless of the cause for the band broadening, we find it is difficult to determine the peak position accurately, particularly at the later stages of cure.

To improve the resolution of the emission spectra, the first-derivative spectra were obtained as shown in Figure 6b, showing a significant enhancement in peak resolution. It must be noted that the peak wavelengths are much lower than the emission peaks, since they correspond to the inflection points of the emission spectra. Nevertheless,

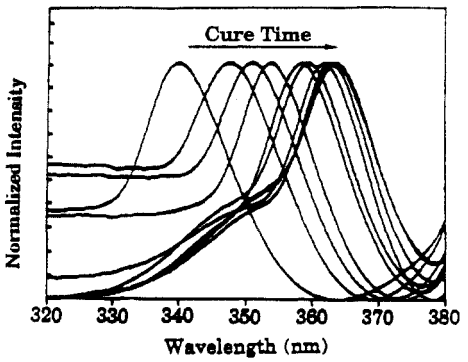


Figure 7. Intrinsic fluorescence excitation spectra of the stoichiometric DGEB–DDS epoxy as a function of cure time at 160 °C. (Cure time = 0, 10, 20, 30, 46, 60, 90, 120, 150, 180, and 240 min, from left to right; emission at 390 nm.)

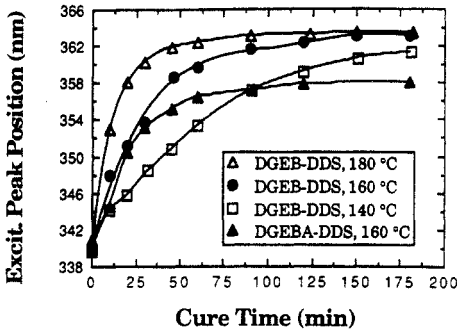


Figure 8. Plots of the DDS excitation spectral peak position as a function of cure time at three cure temperatures (T_{cure} = 140, 160, and 180 °C) for the stoichiometric DGEB–DDS epoxy and the stoichiometric DGEBA–DDS epoxy (T_{cure} = 160 °C).

the peak position of a derivative emission spectrum shows the same trend with respect to cure time as that of the corresponding emission spectrum, with the same overall red shift of about 24 nm.

Fluorescence excitation spectra corresponding to the absorption process from the ground singlet state to the first excited singlet state were obtained by fixing the emission at 390 nm. As illustrated in Figure 7, the excitation peaks are much sharper than the emission peaks, resulting in a better resolution for analysis. Figure 8 shows plots of the DDS excitation peak position as a function of cure time at three cure temperatures (140, 160, and 180 °C). It is noted that the higher the cure temperature, the faster is the spectral change, corresponding to a faster cure rate, and the greater is the spectral shift. Overall, about 24 nm of red shift was observed when cure was about 95% complete.

DGEBA is also a bifunctional epoxide, but with a much higher melting temperature and a higher viscosity than DGEB. Later stages of cure can be hindered due to vitrification[9,10] when DGEBA is cured below its maximum T_g of about 200 °C. A strong and broad emission at 380–400 nm from a stoichiometric DGEBA–DDS system was observed when it was excited at 340 nm. We monitored the excitation spectra as a function of cure time by emitting at 390 nm. Similar red shifts were obtained as shown in Figure 8 as a function of cure time at 160 °C. The total spectral red shift observed for DGEBA–DDS was only 17.8 nm, which is smaller than that for DGEB–DDS epoxy (24 nm), indicating a lower extent of amine reaction in DGEBA–DDS epoxy due to vitrification at the later stages of the cure.

(3) Studies of Matrix Effects. To investigate how much of these spectral shifts was due to the changes in the matrix such as polarity or viscosity change during the curing process, the fluorescence emission and excitation spectra of a model tertiary DDS were obtained before and after cure in a stoichiometric mixture of DGEB and an aliphatic diamine, 2,2′-(ethylenedioxy)diethylamine (EDDA). This diamine, which has no absorption or emission where the tertiary amino DDS does, can be cured easily at 120 °C. In this case, any spectral change would be due to the matrix effect since t,t-DDS cannot react further with epoxide. Only a small blue shift (3-nm blue shift in emission spectra and 2-nm blue shift in excitation spectra) was observed after a full cure. The blue shifts are probably caused by a decreasing matrix polarity due to the curing process, which has been confirmed by dielectric constant measurement of epoxy resins.[17] Therefore, we can deduce that the spectral shifts obtained in the emission and excitation spectra of epoxide–diamine systems arise mostly from the curing reactions.

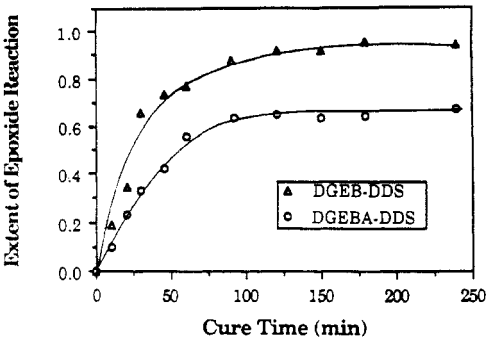


Figure 9. Comparisons of the changes of the extent of epoxide reaction as a function of cure time at 160 °C for the stoichiometric DGEB–DDS and DGEBA–DDS epoxies.

(4) Correlations between the Extent of Epoxide Reaction and the Spectral Shift. It is useful to establish the correlation between the extent of epoxide reaction (ξ_b) and the excitation peak position. We used FTIR spectroscopy to determine the rate of disappearance of the epoxide ring of the DGEB–DDS epoxy as a function of cure time. All the samples used for the IR study were prepared and cured in the same way as those used for the fluorescence studies. The extent of epoxide reaction (ξ_b) is obtained by using eq 12.

$$\xi_b = 1 - (A_{910}(t)A_{1590}(0))/(A_{910}(0)A_{1590}(t)) \quad (12)$$

where $A_{910}(t)$ and $A_{910}(0)$ are the absorbances at 910 cm^{-1} after cure times t and zero, respectively. The absorption at 910 cm^{-1} is due to the epoxide ring in DGEB, and there is no absorption at 910 cm^{-1} due to DDS. $A_{1590}(t)$ and $A_{1590}(0)$ are the absorbances at 1590 cm^{-1} after cure times t and zero, respectively. The 1590-cm^{-1} peak is due to the phenyl ring in DDS and is used as an internal standard to calibrate the thickness fluctuations during the cure.

The extent of epoxide reaction of DGEBA–DDS epoxy was obtained by using eq 13.

$$\xi_b' = 1 - (A_{910}(t)A_{1184}(0))/(A_{910}(0)A_{1184}(t)) \quad (13)$$

where $A_{1184}(t)$ and $A_{1184}(0)$ are the absorbances at 1184 cm^{-1} after cure times t and zero, respectively.[9] The 1184-cm^{-1} peak is due to C–C stretching of the bridge carbon atom in DGEBA and is used as an internal standard.

Figure 9 compares the changes of the extent of the epoxide reaction as a function of cure time at 160 °C for the DGEB–DDS and DGEBA–DDS epoxy systems, showing a trend similar to that in Figure 8. A correlation plot between the extent of epoxide reaction and the spectral shift for the two difunctional epoxide–diamine systems is given in Figure 10. The data obtained from the two epoxy

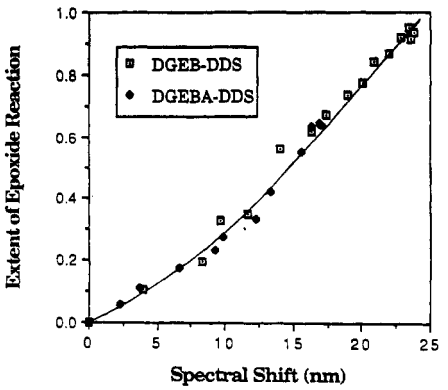


Figure 10. Correlation plot of the excitation spectral shifts versus the extent of epoxide reaction for the stoichiometric DGEB-DDS and DGEBA-DDS epoxies.

systems can be fitted to a single curve which is very similar to the correlation curve between the extent of amine reaction and the spectral shift (Figure 5). This indicates that the major reactions in the difunctional epoxide-diamine systems are the amine additions, consistent with the results of our previous work[9] and others.[11,18]

The correlation plots for the extent of epoxide reaction and the emission peak position or the first-derivative emission peak position have also been obtained, showing a trend similar to that for the extent of epoxide reaction and the excitation spectral shift (Figure 10). However, because of the higher spectral resolution, the excitation spectral results yielded better correlation than those of the emission and the first-derivative emission spectra.

(5) Fluorescence Studies of TGDDM-DDS Epoxy. This epoxy system has found widespread uses in aerospace applications where operation at high temperatures is required. Since TGDDM is a tetrafunctional epoxide where the two epoxy groups are quite close at both ends of the molecules, reactions in the TGDDM-DDS system can be quite complex and may include more etherification of cyclic (intramolecular) as well as cross-linking (intermolecular) type. Information about the cure kinetics of this system is only recently available in the literature with some controversies over the reactivities of primary amine, secondary amine, and hydroxyl group and the types of cross-linkers which are present in the cured TGDDM-DDS system.[9d,19] Figure 11a shows the emission spectra of a stoichiometric TGDDM-DDS mixture as a function of cure time at 160 °C by exciting at 315 nm. The emission spectra are very broad, ranging from 360 to 465 nm. Moreover, the emission from DDS around 360 nm is overlapped by a strong and broad emission in the range 430-465 nm, which is probably caused by the presence of some fluorescent impurities and/or some oxidation or degradation during cure.[16b] Once again, the first-derivative emission spectra were successfully employed in the TGDDM-DDS system for the enhancement of spectral resolution, which was very similar to those obtained for DGEB-DDS epoxy (Figure 6b). The excitation spectra of a stoichiometric TGDDM-DDS mixture as a function of cure time at 160 °C were obtained by fixing the emission wavelength at 410 nm (Figure 11b). The total red shift is about 20 nm, which is a little larger than that of the stoichiometric DGEBA-DDS system (17.8 nm). This means that DDS is a little more reacted in TGDDM-DDS than in DGEBA-DDS. A similar trend was observed by an extrinsic reactive fluorophore technique.[9d]

To study the effect of the content of DDS on the cure kinetics and extent of the TGDDM-DDS epoxy system, the fluorescence emission and excitation spectra were

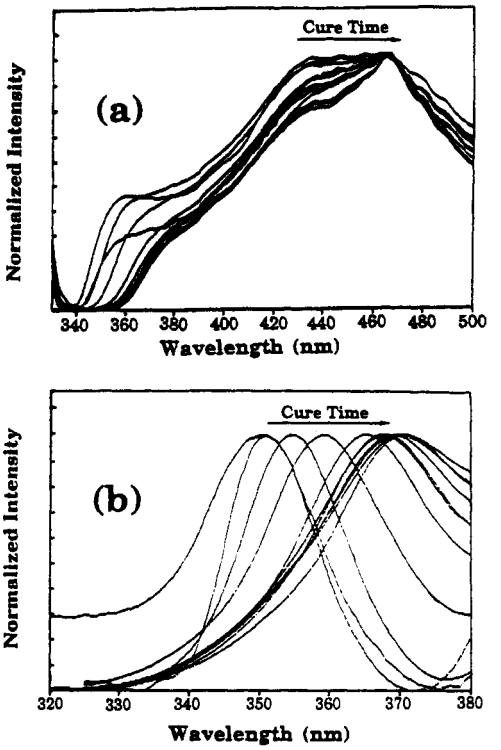


Figure 11. Intrinsic emission spectra (a) and excitation spectra (b) of the stoichiometric TGDDM-DDS epoxy as a function of cure time at 160 °C. (Cure time = 0, 10, 20, 30, 45, 60, 90, 120, 150, 180, and 300 min, from left to right; excitation at 315 nm; emission at 410 nm.)

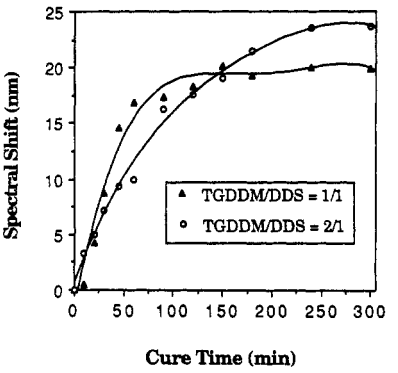


Figure 12. Comparisons of the excitation spectral shifts of two TGDDM-DDS epoxy systems with different DDS concentrations as a function of cure time at 160 °C.

obtained as a function of cure time for a nonstoichiometric TGDDM-DDS epoxy system with a 2:1 molar ratio of TGDDM to DDS. This composition is close to that of the commercial epoxy composite prepregs.[19b] The emission spectra look quite similar for the two compositions, with broad peaks ranging from 360 to 465 nm. However, the excitation spectra provide good spectral resolution as discussed before. Figure 12 compares the excitation spectral shifts of these two systems as a function of cure time. We can see that the overall spectral shift in the 2:1 system (25 nm) is greater than that of the 1:1 system (20 nm) at the same curing temperature (160 °C), indicating a higher content of tertiary amine in the 2:1 system because of the higher content of TGDDM that pushes the conversion of DDS to completion.

Summary

In this work, the intrinsic fluorescence emission and excitation of a commonly used aromatic diamine curing agent, 4,4'-diaminodiphenyl sulfone (DDS), were studied

during cure with epoxides. As the cure reaction proceeds, both emission and excitation spectra exhibit red shifts of about 25 nm for DDS due to the conversion of the primary amino DDS (pp-DDS) to the tertiary amino DDS (tt-DDS). Several model cure species were separated using analytical HPLC. Matrix effects such as the polarity decrease and the viscosity increase on the fluorescence spectra of tertiary amino DDS were found to be small. The excitation spectra provide much sharper peaks than the emission spectra, with an overall spectral shift of about 25 nm. The total excitation spectral shifts observed in DGEBA–DDS epoxy and TGDDM–DDS epoxy when cured at 160 °C were 18 and 20 nm, respectively. Based upon the excitation spectra and the relative fluorescence quantum yields of the model amine cure species and the cure kinetics, the excitation spectra of DDS–diepoxide resin were simulated as a function of amine cure extent (ξ_a). The result shows that the excitation spectral shift is easily correlated to the extent of amine reaction. The extent of epoxide reaction based on IR studies is found to have a similar correlation with the excitation spectral shift, indicating that the major curing reactions are the amine–epoxide addition reactions in diepoxides. Since no extrinsic fluorophore is required, this intrinsic cure sensing technique has been conveniently used for in-situ monitoring of the curing process of epoxide–DDS systems in actual composites with a fiber optic fluorimeter.[20] Even in composites reinforced with graphite or glass fibers, the fibers do not interfere with DDS spectra due to its high concentration, thus providing clean spectra for cure analysis.

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