Network Structure in Diamine-Cured Tetrafunctional Epoxy by UV–Visible and Fluorescence Spectroscopy

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ABSTRACT: Network structure in a nearly stoichiometric mixture of diamine (diaminodiphenyl sulfone, DDS)-cured tetrafunctional epoxy (tetraglycidyl diaminodiphenylmethane, TGDDM) was investigated by *p,p*-diaminoazobenzene (DAA), which mimics the reactivities of the diamine curing agent by UV–visible, fluorescence, and IR spectroscopic techniques. UV–visible spectra show red shifts due to the reaction of DAA with epoxide to produce tertiary amines. The deconvolution of UV–visible spectra provides the cure composition including the amount of the tertiary amine species of DAA, which is at least equal to that in a stoichiometric mixture of diepoxide–diamine epoxy. Fluorescence intensity, which is mostly due to the tertiary amine, gives more evidence for the substantial amount of the tertiary amine in diamine-cured tetrafunctional epoxy. Even though a part of the tertiary amines can be a cyclic ring product, a significant amount is expected to contribute to the network structure either as a cross-link or a branch point. The fluorescence emission maxima of DDS curing agent also shows red shifts, indicating formation of tertiary amine species. IR spectra confirm the overall reaction of epoxide with diamine but indicate that ether formation becomes significant only late in the cure. Before ether formation becomes important, cure composition data are analyzed on the basis of independent epoxide reactivity in TGDDM, and a similar reactivity is found between the primary amine and the secondary amine with epoxide. The extent of DAA reaction is found to be fairly close to the extent of epoxide reaction.

Introduction

Network formation due to cross-linking in polymers is a complex process. Furthermore, its insolubility and infusibility makes the characterization of cross-linked polymers such as epoxy network difficult after gelation. Recently, we used a reactive labeling technique to follow the cure process even after gelation in epoxy networks based on diepoxides and tetrafunctional diamines.[1] In this technique, the reactive label is designed to have similar reactivities as the curing agent (diamine) and to exhibit spectral changes in the region of UV–visible absorption and fluorescence spectra where the epoxy matrix has little absorption or emission. Since the reactivities of the label and the curing agent may not be exactly matched, the difference in rates between them can be corrected by using a calibration curve.[1] When the diamines react with diepoxides, we found that a reactive label, *p,p*-diaminoazobenzene (DAA), showed significant red shifts in UV–vis spectra and drastic enhancement of fluorescence intensity due to the formation of tertiary amine groups in DAA. Thus, the deconvolution of UV–vis absorption spectra provided the estimates of the fraction of each cure species.[1a] The intensity of fluorescence emission[1a] as well as excitation[2] was also used to quantify the fraction of each cure species, assuming certain kinetic schemes.

Even though we applied the reactive labeling technique using tailored chemical sensors to other polymers such as polyimides,[3] polyurethanes,[4] and polyamides,[5] we report in this work the extension to a tetrafunctional epoxide system cured with a tetrafunctional diamine. Tetraglycidyl diaminodiphenylmethane (TGDDM) is often used as the matrix resin for high-performance composites with carbon fibers for reinforcement. This tetrafunctional epoxy is often cured with diaminodiphenyl sulfone (DDS), but the curing reactions between TGDDM and aromatic diamines can be more complex than the diepoxide–diamine system. While little cyclization is known to occur in a stoichiometric mixture of diepoxide and diamine in the absence of catalyst,[6,7] the formation of cyclization products is quite feasible due to the proximity of the epoxide rings, as shown in Scheme I. Reactions 1 and 2 are analogous to the formation of secondary and tertiary amines, respectively, which are the major reaction products with diepoxide. At least two different types of the cyclic structures may form with TGDDM; the epoxide may form intramolecular cyclic ether as in reaction 3 or the secondary amine may open the epoxide to form a cyclized tertiary amine product as in reaction 4. Reaction 3 is known to be facilitated by the catalytic effect of the tertiary amines in the TGDDM molecule.[8] In addition, intermolecular ether can be formed as shown in reaction 5.

Recently, Matejka and Dusek carried out careful studies on the mechanisms and kinetics of curing between TGDDM and an aromatic diamine, using model systems.[8a,b] They found a positive substitution effect of epoxy groups and a considerable tendency to cyclization. After one epoxide group in one end of TGDDM has reacted to form hydroxyl group, the reactivity of the adjacent epoxide is catalyzed by such a neighboring hydroxyl group, which is referred to as a positive substitution effect. In model systems, they also found that intramolecular and intermolecular etherification become possible at a later stage of the reaction, after all the amine groups have reacted. Intramolecular cyclic ethers were found to be the main product. Using NMR and model compounds, Attias et al. also confirmed that the intermolecular etherification did not either occur or occurred only very slowly.[9] Matejka and Dusek also showed the formation of a cyclic ring containing tertiary nitrogen (reaction 4) at the beginning of the reaction, accounting for about 15% of the total reaction products. In spite of these side reactions, they proved that the main reactions are the additions between epoxide and amine to form secondary and tertiary amines (reactions 1 and 2). In fact, they found the reaction rate of the secondary amine with an epoxide to form the tertiary amine is about one-half of the reaction rate of the primary amine with an epoxide. This finding proposes the presence of a substantial amount of the tertiary amines even in TGDDM–DDS epoxy. However, some previous studies such as by Morgan[10a] and Gupta et al.[10d] reported that the

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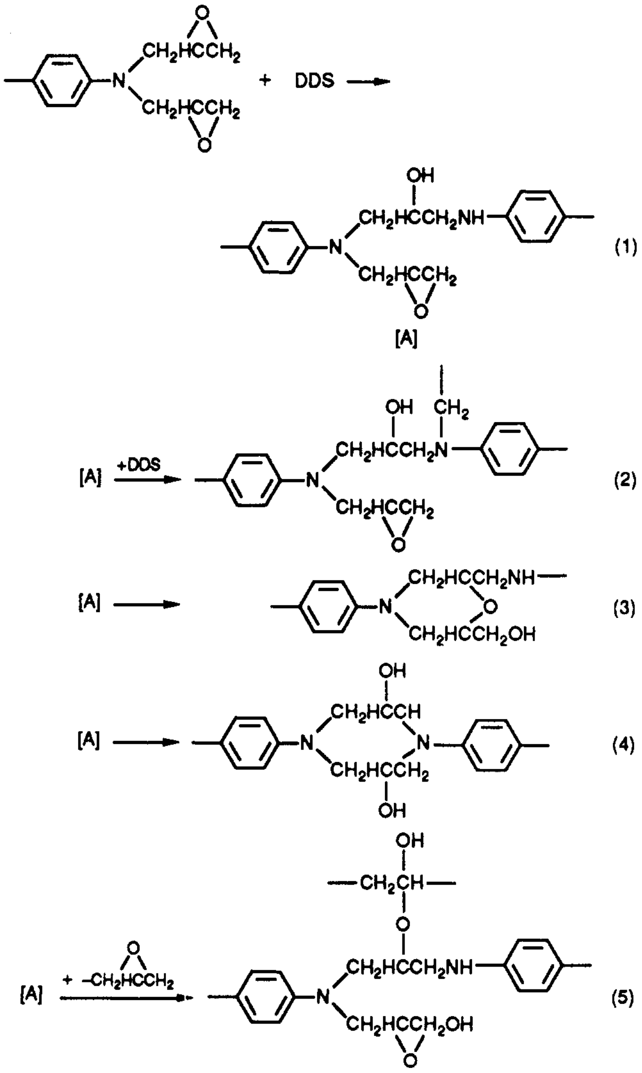
Scheme I
Various Chemical Reactions Involved in the Cure of Tetrafunctional Epoxy with a Diamine (DDS)



primary amine–epoxide reaction is 10 times faster than the secondary amine–epoxide reaction. These studies predicted a network structure where cross-linkers are mainly formed by the intermolecular ether linkages and the curing agents remain mostly as the secondary amines.[10b,d]

This study is designed to shed light on these conflicting proposals on the network structure in a tetrafunctional epoxide–diamine system. In this study, a small amount of DAA is used as a reactive label in TGDDM–DDS epoxy to characterize cure by UV-vis, fluorescence, and IR spectroscopic techniques. Since it is difficult to identify or quantify the tertiary amines by IR, we used UV-vis and fluorescence techniques that have been demonstrated to provide clear evidence for the presence of the tertiary amines. We will attempt to analyze the results by taking the complex reactions into account.

Experimental Section

As TGDDM, Ciba Geigy's Araldite MY721 was used. When analyzed by reverse-phase HPLC using varying amounts of acetonitrile/water mixture with IBM C_{18} columns, it was found to have a purity of 94% TGDDM. Most of the impurities are known to contain oligomers having functionalities higher than tetrafunctional epoxide.[10c] We cured MY721 (6.3 g) without further purification in a stoichiometric ratio with DDS (3.7 g) corresponding to 37% by weight for DDS. To this mixture, DAA was added at 1% by weight as a label for UV-visible analysis and 0.1% for fluorescence analysis. The procedures for making samples and spectral analyses are described in detail in our previous paper.[1a] UV-vis and fluorescence spectra were obtained by using a Perkin-Elmer diode array (Model 3840) and a Perkin-Elmer MPF-66 spectrometer, respectively, with a separate Model 7500 data station.

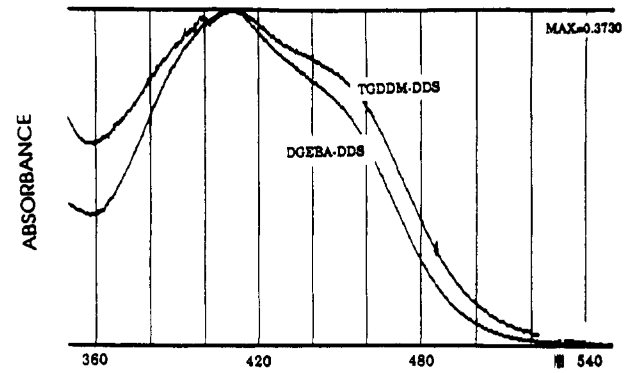


Figure 1. UV-vis spectra of *p,p'*-diaminoazobenzene, DAA, in TGDDM–DDS in comparison with DAA in DGEBA–DDS at zero cure time. DAA concentration is 1% by weight in both epoxy–diamine matrices.

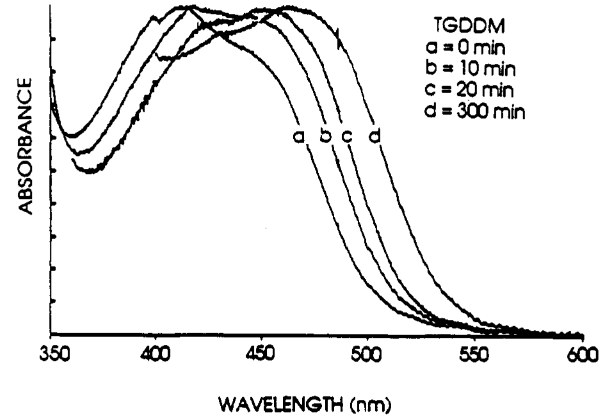


Figure 2. UV-vis spectra of DAA in TGDDM–DDS matrix as a function of cure time at 160 °C.

IR spectra were taken with a Nicolet 60SX FT-IR spectrophotometer. A heated IR cell was preheated to the reaction temperature before placing the unreacted sample in the cell.

Results and Discussion

1. Cure Composition from UV-Vis Studies. Figure 1 compares UV-vis spectrum of the TGDDM–DDS epoxide system containing 1% DAA label before cure to that of the DGEBA–DDS diepoxide system containing the same amount of DAA label. It is noted that while the absorption maxima due to DAA occurs at the same position, the spectrum for TGDDM–DDS is broader than the diepoxide system, probably due to more polar nature of TGDDM epoxy. TGDDM epoxy having two tertiary amines per molecule is more polar than DGEBA, leading to greater water absorption.[11] The tertiary–tertiary amine of DAA has been examined in different solvents, and it was found that the band becomes broader when the polarity of the solvent increases.[12] Figure 2 shows UV-vis spectra of a TGDDM–DDS system containing 1% DAA as a function of cure time at 160 °C. The general trend shown in Figure 2 displays red spectral shifts as previously observed in the DGEBA–DDS system. The red shifts are due to the formation of the secondary and the tertiary amines, which have the absorption maxima at longer wavelengths since they are more electron-donating than the primary amine of DAA.[1] Similar trends were observed

Table I
Positions of λ_{max} in UV-Visible Spectra and the Relative Fluorescence Intensity for Model Compounds of DAA and GPE

model compd[a]	λ_{max}, nm	$\Delta\lambda$	rel fluorescence int
pp	410	0	1
ps	420	10	9
ss or pt	445	35	18 or 700
st	460	50	1100
tt	470	60	1400

[a] Designation for p, s, and t means primary, secondary, and tertiary amine, respectively.

Table II
Composition[a] of Cure Products in TGDDM-DDS Epoxy as a Function of Cure Time at 160 °C

cure time, min	cure product					extent of amine reaction (ξ_a)
	pp	ps	ss	st	tt	
0	62	20	10	8	0	16
5	49	29	16	6	0	19
10	40	24	26	10	0	27
20	17	19	32	28	4	46
30	1	11	30	39	19	66
45	0	2	18	62	18	74
60	0	3	20	49	28	75
90	0	3	23	46	28	75
150	0	2	24	45	29	76
210	0	1	24	49	26	75

when cure was carried out at 140 and 180 °C. In our previous study,[1] we determined the positions of the absorption maxima for various model species of DAA with epoxide as summarized in Table I.

The extinction coefficients are found to remain constant even when the primary amines change to the secondary and tertiary amines. The UV-vis spectra such as shown in Figure 2 have been deconvoluted by using the peak positions of the model species and assuming a Gaussian peak in order to obtain cure product composition. Because of the band broadening in TGDDM-DDS, we used Gaussian peaks with half-widths about 5 nm larger than those used for the DGEBA-DDS system. Broader peaks as well as spectral overlap between different species increase the error in the deconvolution. We estimate this error to be as large as 15%, especially at intermediate cure stages.

The cure composition after cure at 160 °C determined by deconvolution is summarized in Table II, which shows increased concentration of tertiary amine species as cure time proceeds. The overall extent of DAA amine reaction, ξ_a, is defined by the following equation:

$$\xi_a = [A_{ps} + 2A_{ss} + 3A_{st} + 4A_{tt}]/4 \qquad (1)$$

Even before cure, some reactions have taken place due to heating at 100 °C during mixing of the reactants. In comparison to the cure composition for DGEBA-DDS cured at the same temperature (see Table III in ref 1), the cure reactions seem to proceed a little faster, leading to a slightly greater extent of reaction in TGDDM-DDS at cure times over 100 min. In DGEBA-DDS, the extent of amine reaction reaches about 68% while it reaches about 75% in TGDDM-DDS before vitrification. This trend can be explained by the catalytic effect of the tertiary amines in TGDDM structure as well as the faster reaction rate of the second epoxides in TGDDM-DDS as demonstrated by Matejka and Dusek.[8] These two effects, which are absent in DGEBA-DDS, are also reflected in the virtual disappearance of the primary-primary (A_{pp}) and the primary-secondary (A_{ps}) species of DAA after reaction over 45 min in TGDDM-DDS. In contrast, at least 20% of DAA remained as the sum of A_{pp} and A_{ps} species in DGEBA-DDS at comparable times of cure. Also, we note that the combined fraction of A_{st} (secondary-tertiary) and A_{tt} (tertiary-tertiary) species after 150 min of cure at 160 °C is greater for TGDDM (about 74%) than for DGEBA (about 56%). The amount of overall tertiary amines in the TGDDM-DDS matrix is about 51% (one-half of A_{st} plus A_{tt} species), which is greater than 42% for DGEBA-DDS. These trends clearly support the formation of tertiary amine species as well as a slightly faster cure in TGDDM.

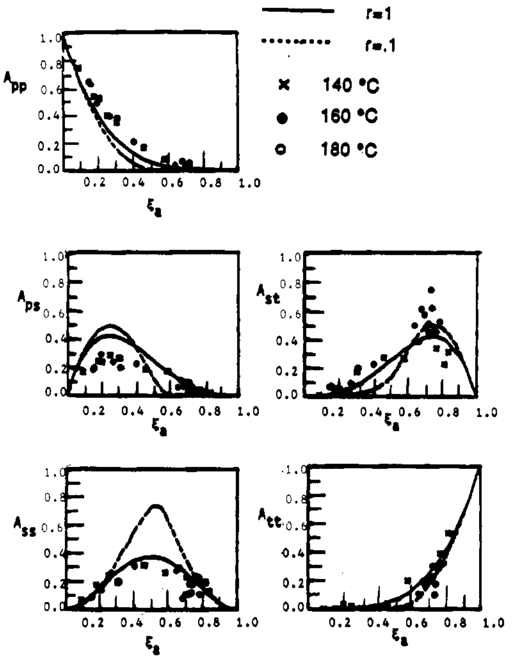


Figure 3. Experimental composition of cure species by UV-vis deconvolution in TGDDM-DDS as a function of amine reaction, ξ_a. Two lines show predictions for reactivity ratio of either 0.1 or 1.

As illustrated in Scheme I, not all of the tertiary amine species contribute as branch points or cross-linkers. For example, the nitrogen ring compound as a result of reaction 4 contains a tertiary amine. This product is known to form at early stages of cure, accounting for 15% of the total products in model compound studies.[8] If we assume that the same amount of the nitrogen ring product was formed in our TGDDM before vitrification, the fraction of the tertiary amines that contribute to the branch points or the cross-linkers is only about 36%. This value is similar to that for the DGEBA diepoxide system. Our results supporting the presence of the tertiary amines as cross-linkers and branch points are in agreement with the predictions of Matejka and Dusek[8a,b] but in contrast to the network structure proposed by Morgan[10a] and others.[10b]

Now, we can attempt to extract some kinetic parameters from the cure composition results. Figure 3 illustrates the fraction of each cure product as a function of the overall extent of DAA reaction (ξ_a) when cure was carried out at three temperatures (140, 160, and 180 °C). At 140 and 180 °C as well as at 160 °C, the formation of tertiary amines (A_{st} and A_{tt} species) is also noted.

Matejka and Dusek demonstrated in model studies that ether formation occurs after all the amines are reacted in a stoichiometric mixture.[8a,b] As discussed in a later section on IR studies, the ether formation seems negligible up to 40 min of cure at 160 °C. Therefore, we can assume that the major reactions are between epoxide and amine up to about 40 min of cure. From Table II, we note that the overall extent of amine reaction or the cure composition remain rather constant after 45 min.

In TGDDM, after one epoxide group in either end of the molecule has reacted with amine to form hydroxyl group, the reactivity of the other epoxide with amine is catalyzed by such an adjacent hydroxyl group.[8] However, the ratio of the rate constant for the first reaction to the second catalyzed reaction is 0.5, meaning that the catalyzed reaction is only twice as fast when reacted with the primary amine. In the reaction with the secondary amine, the analogous ratio is close to unity.[8b] In view of these rather small catalytic effects, we would assume that the reactivity of the epoxide in TGDDM is independent as a first approximation. We will also assume that two amino groups in DAA are relatively independent of each other. This assumption may not be valid in view of the conjugation through the azo group in DAA if the secondary or the tertiary amine on one end of DAA affects the reactivity of the other amine on the opposite end of the molecule. However, even among more strongly conjugated compounds such as aminobenzene, (methylamino)benzene, and (dimethylamino)benzene, the Hammet constant on the para position to the amino groups is known to change only slightly.[8c] In other words, the reactivity at the para position to the amino group is expected to increase only to a small extent when it is a secondary or a tertiary amine instead of a primary amine. Therefore it is reasonable to assume the independence of amino groups in DAA, even though the data on Table II on cure composition show some departures from this assumption. This departure may be caused by the inherent experimental error (up to 15%) involved in the deconvolution of closely overlapping peaks. Thus, we may use the solutions in eqs 2–6 for the

$$A_{\mathrm{ps}} = 2p({A_{\mathrm{pp}}}^{q} - A_{\mathrm{pp}}) \qquad (2)$$

$$A_{\mathrm{ss}} = p^2(-2{A_{\mathrm{pp}}}^{q} + A_{\mathrm{pp}} + {A_{\mathrm{pp}}}^{\gamma/2}) \qquad (3)$$

$$A_{\mathrm{pt}} = -2p{A_{\mathrm{pp}}}^{q} + \gamma p A_{\mathrm{pp}} + 2{A_{\mathrm{pp}}}^{1/2} \qquad (4)$$

$$A_{\mathrm{st}} = p^2[(\gamma + 2){A_{\mathrm{pp}}}^{q} - \gamma A_{\mathrm{pp}} - (2-\gamma){A_{\mathrm{pp}}}^{1/2} - 2{A_{\mathrm{pp}}}^{\gamma/2} + (2-\gamma){A_{\mathrm{pp}}}^{\gamma/4}] \qquad (5)$$

$$A_{\mathrm{tt}} = P^2[-\gamma {A_{\mathrm{pp}}}^{q} + (\gamma^2/4)A_{\mathrm{pp}} + (\gamma/p){A_{\mathrm{pp}}}^{1/2} + {A_{\mathrm{pp}}}^{\gamma/2} - (2-\gamma){A_{\mathrm{pp}}}^{\gamma/4} + (\gamma/2-1)^2] \qquad (6)$$

kinetic differential equations to find the best fit value of the reactivity ratio, $\gamma = k_2/k_1$ where k_2 and k_1 represent the rate constant for the reaction of epoxide with the secondary amine and the primary amine, respectively,[1a,13] and where $P = 1(1 - \gamma/2)$ and $q = (1 + \gamma/2)/2$.

The value of the reactivity ratio has a strong effect on many structural parameters such as gelation and molecular weights as demonstrated by the theories of Bidstrup and Macosko[14] and Dusek.[13] To find the best-fit value of γ, two theoretical curves according to the eqs 2–6 are shown, corresponding to γ of 0.1 (dotted line) or 1 (solid line). In spite of experimental error, the experimental data, especially in A_{ss} profile, seem to support the reactivity ratio (γ) of 1 rather than 0.1. In fact, the reactivity ratio in the range of 0.5–1 seems to fit the data reasonably well, given the experimental error involved. A similar conclusion was reached in two different diepoxide–diamine systems.[1a] In the model reactions, Matejka and Dusek reported the reactivity ratio of about 0.5, for the reaction with the first epoxide. Our value of γ is closer to the value by Matejka and Dusek[8b] than the value of 0.1, reported by Morgan et al.[15] based on IR studies. In IR spectra, it is known that quantitative analyses of epoxide and primary amine only are possible, while it is difficult to quantify the amount of ether, secondary and tertiary amine, and hydroxyl groups unambiguously, due to either poor resolution (hydroxyl group) or broad overlapping peaks (amino and ether groups).[9,16] Matejka and Dusek carried out model studies using HPLC and GPC methods, by which low molecular weight compounds can be well separated. Therefore, their results do not seem to suffer from the ambiguities inherent in IR studies.

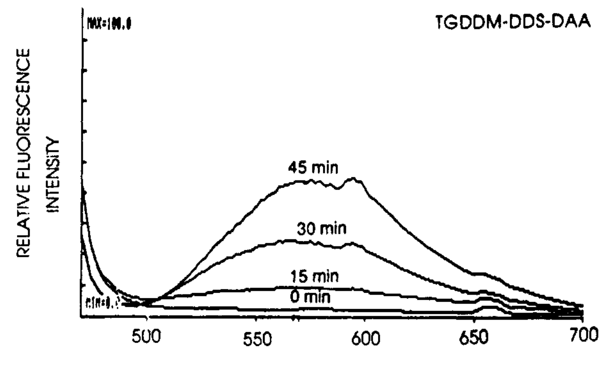


Figure 4. Fluorescence spectra of DAA in TGDDM-DDS as a function of cure at 160 °C (excitation wavelength at 456 nm).

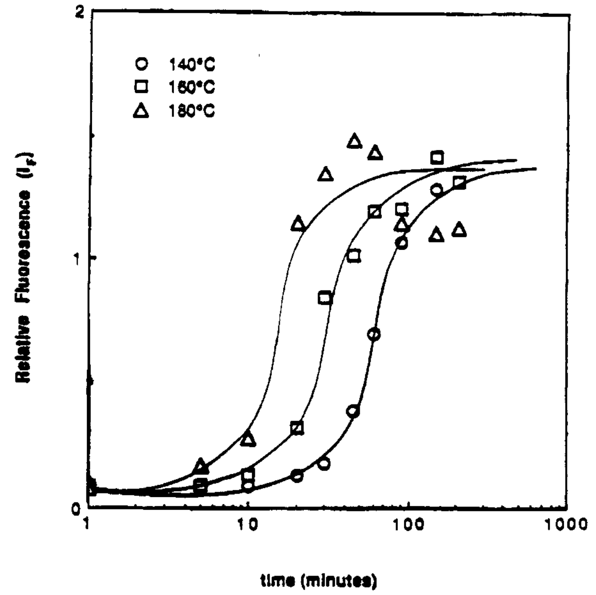


Figure 5. Relative fluorescence intensity at 575 nm as a function of cure time at three cure temperatures for TGDDM-DDS.

2. Fluorescence Studies. When the DAA label is excited at 456 nm, a strongly cure-dependent behavior of fluorescence intensity is observed in TGDDM-DDS matrix as shown in Figure 4. With increasing cure time, fluorescence with a broad emission peak around 575 nm increases, while DAA showed fluorescence emission around 565 nm at long cure times. This red shift of about 10 nm in TGDDM-DDS matrix is probably due to the more polar nature of the TGDDM matrix in comparison to DGEBA matrix.

When the intensity at the emission maxima from Figure 4 is plotted as a function of cure time in TGDDM-DDS, Figure 5 is obtained at three temperatures (140, 160, and 180 °C). All three lines are S-shaped, as observed in DGEBA-DDS matrix, indicating a sharp increase after a certain cure time. This enhancement in fluorescence intensity is due to the formation of the tertiary amines of DAA since it is known to have a much greater fluorescence

Table III
Transition Time[a] Observed from Fluorescence Intensity as a Function of Cure Time

temp, °C	DGEBA-DDA	TGDDM-DDS
140	100	90
160	50	40
180	20	15

[a] Defined as the intersection where a tangential line to the inflection point crosses a line extrapolated from the upper part of the curves in Figure 5.

quantum yield, as summarized in Table I. This sharp increase in fluorescence is a clear indication for the presence of the tertiary amine products in TGDDM-DDS, a trend in agreement with UV-vis results. In DGEBA-DDS matrix, we defined a transition time as the intersection where a tangential line to the inflection point crosses a line extrapolated from the upper part of the curve, at each cure temperature. These times were found to be close to the gel times obtained by a T-T-T (temperature-time-transformation) diagram.[17] When similar transition times are found from Figure 5, they seem to occur a little faster than for the DGEBA-DDS matrix as summarized in Table III. This trend in TGDDM-DDS matrix is also supported by UV-vis results, as discussed in the preceding section.

It will be useful to estimate the cure composition and the extent of cure reaction from the fluorescence intensity values. Up to a certain time of cure, we can neglect the other reactions except for the epoxide-amine additions. Thus, we proceed by using the same solutions of cure kinetics used for UV-vis analysis and assuming that the fluorescence intensity is a sum attributed by all the cure species in proportion to their relative quantum yield. We have shown in our previous paper[1a] that the total fluorescence intensity can be expressed by the following equation:[7]

$$I_f = C(A_{pp} + 9A_{ps} + 18A_{ss} + 700A_{pt} + 1100A_{st} + 1400A_{tt}) \quad (7)$$

In eqs 2-6, which are solutions of the kinetic equations assuming only epoxide-amine reactions, the fraction of cure composition is expressed as a function of A_{pp}. Therefore, we substitute A_{ps}, A_{ss}, A_{pt}, A_{st}, and A_{tt} by A_{pp} in eq 7 and obtain eq 8. Equation 8 shows that at certain

$$\begin{aligned} I_f = c\{&A_{pp} + 18p(A_{pp}{}^{q} - A_{pp}) + 18p^2(-2A_{pp}{}^{q} + A_{pp} + \\ &A_{pp}{}^{\gamma/2}) + 700(-2pA_{pp}{}^{q} + \gamma p A_{pp} + 2A_{pp}{}^{1/2}) + \\ &1100p^2[(\gamma + 2)A_{pp}{}^{q} - \gamma A_{pp} - (2-\gamma)A_{pp}{}^{1/2} - 2A_{pp}{}^{\gamma/2} + \\ &(2-\gamma)A_{pp}{}^{\gamma/4}] + 1400p^2[-\gamma A_{pp}{}^{q} + (\gamma^2/4)A_{pp} + \\ &(\gamma/p)A_{pp}{}^{1/2} + A_{pp}{}^{\gamma/2} - (2-\gamma)A_{pp}{}^{\gamma/4} + (\gamma/2 - 1)^2]\} \end{aligned} \quad (8)$$

values of γ and C, there is a one-to-one relationship between I_F and A_{pp}. We assume γ to be 1, based on the cure composition data from UV-vis analysis, and the C value was estimated to be 0.0015 by comparing cure composition from UV-vis data with the fluorescence intensity. With these values of γ and C, A_{pp} was estimated for a given I_F by using eq 8. Once A_{pp} values are calculated, the fraction of other cure species are determined according to eqs 3-6, as illustrated in Figure 6. In comparison to the cure composition obtained by the deconvolution of UV-vis of spectra, the results by fluorescence analyses show reasonable trends up to 40 min of cure. Beyond 40 min of cure, the solutions for the kinetic equations, eqs 2-6 are no longer valid since ether formation is not negligible. Consequently, eq 8 is applied only up to 40 min of cure.

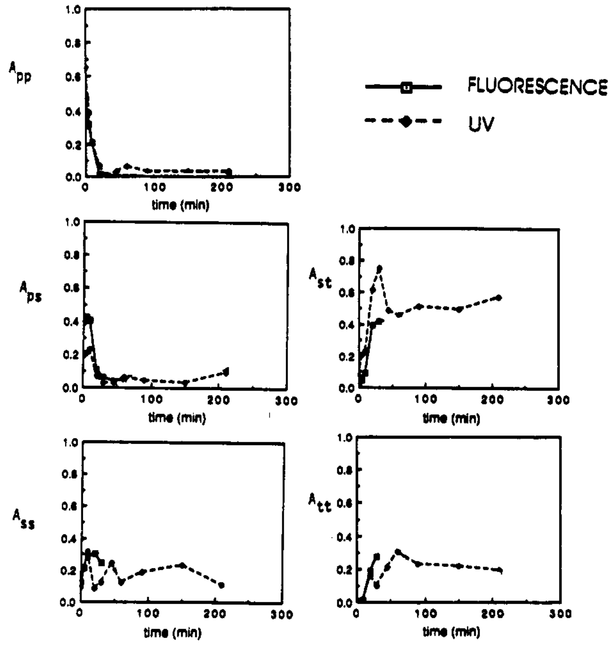


Figure 6. Comparison of cure composition by UV-vis deconvolution and by fluorescence intensity.

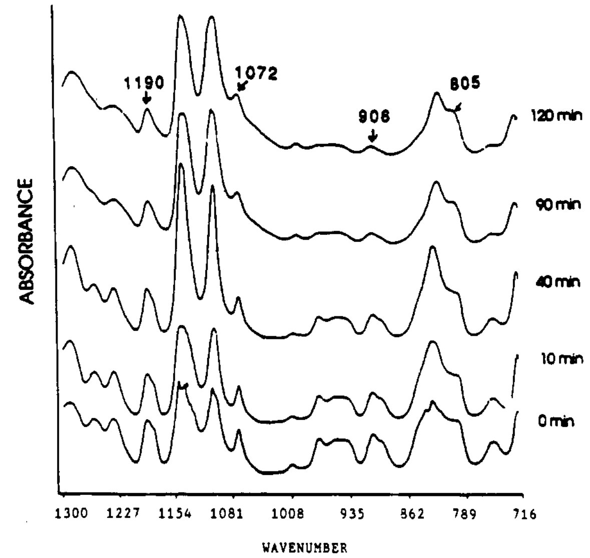


Figure 7. FT-IR spectra of TGDDM-DDS containing 1 wt % DAA as a function of cure at 160 °C.

3. IR Studies. Figure 7 shows IR spectra of TGDDM-DDS as a function of cure time at 160 °C. We note that the peak at 906 cm^{-1} due to epoxide ring decreases with cure time. Therefore, the extent of epoxide ring reaction (ξ_b) can be determined by using the peak height at 906 cm^{-1} in reference to the shoulder at 805 cm^{-1}, which is due to para-disubstituted aromatic ring C-H bending vibrations from TGDDM.[18] Figure 8 plots the extent of epoxy reaction, ξ_b for TGDDM-DDS and DGEBA-DDS, as defined by the eq 9.

$$\xi_b = 1 - \frac{A_{915\text{cm}^{-1}}(t)}{A_{805\text{cm}^{-1}}(t)} \frac{A_{805\text{cm}^{-1}}(0)}{A_{915\text{cm}^{-1}}(0)} \quad (9)$$

When cured at 160 °C, the extent of epoxide reaction is faster in TGDDM-DDS than in DGEBA-DDS. This trend, which is also observed at 180 °C, is consistent with the results obtained by UV-vis studies.

To compare the extent of DAA amine reactions to epoxide reactions, we plotted the extent of DAA amine

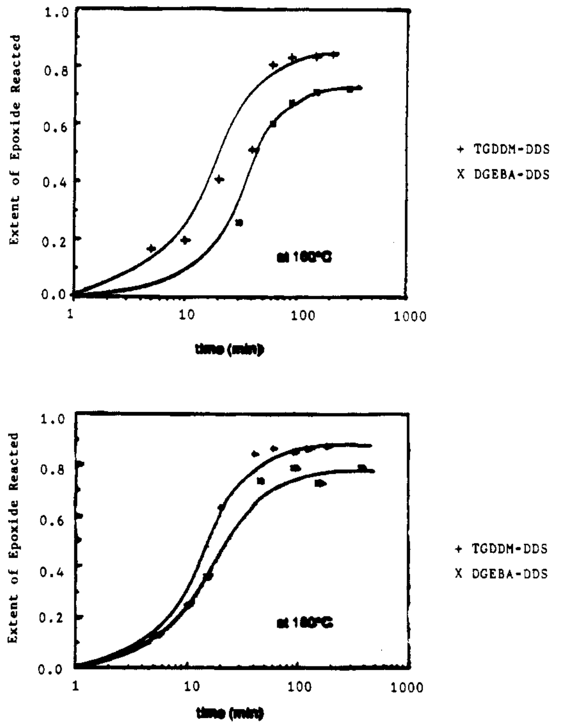


Figure 8. Extent of epoxy reaction as a function of cure time at 160 and 180 °C in TGDDM–DDS (solid line) versus DGEBA–DDS (dotted line).

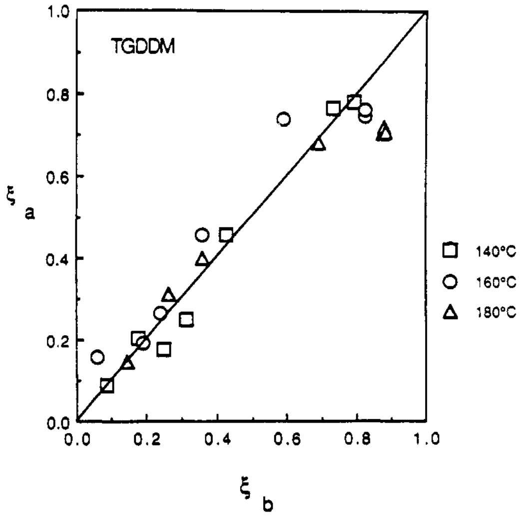


Figure 9. Extent of DAA reaction (ξ_a) as a function of epoxy reaction (ξ_b) in TGDDM–DDS.

reaction, ξ_a, via UV–vis deconvolution vs ξ_b for three cure temperatures in Figure 9. The straight line in Figure 9 shows the slope of 1, which corresponds to the case where ξ_a is equal to ξ_b. The data points fall close to this line, indicating that the extent of DAA amine reaction is similar to that of the curing agent DDS since epoxide reacts mostly with DDS. This tendency is in contrast to the case for DGEBA–DDS, where ξ_a for DAA was somewhat greater than ξ_b, meaning faster consumption of DAA amine than of the overall epoxide. Such a trend may be due to the catalytic effect of the tertiary amines in TGDDM epoxide, by suppressing the reactivity differences between DDS and DAA. The type of correlation as in Figure 9 can be used to correlate the cure extent monitored by DAA label to that of the matrix resin.

In regard to the presence of ether peaks, Smith et al. used the 1070-cm^{-1} band as representing ether groups.[19] However, even in pure DDS, this peak is prominently present. Also, as can be seen in Figure 6, this peak is clearly visible at 0 min of cure after mixing DDS and TGDDM. The ratio of the peak at 1072 cm^{-1} to that of the aromatic internal standard at 1190 cm^{-1} appear to remain rather constant up to 40 min of cure at 160 °C. Only after 40 min of cure, the ratio seems to increase, qualitatively suggesting the formation of ether groups. To obtain quantitative analysis of the percentage ether unambiguously is known to be difficult at best.[16] On the basis of the FT-IR spectra, we can assume that etherification occurs only at later stages of cure, which is consistent with the results of model compound studies of Matejka and Dusek.[8a,b]

Summary

For diamine-cured tetrafunctional epoxy matrix such as TGDDM–DDS epoxy, IR spectroscopy was the main tool used to elucidate the network structure in previous studies.[10a,d] Since only epoxide and primary amine can be quantified by IR, it was not possible to quantify the amount of ether, the secondary amine or the tertiary amines by IR technique. In fact, no direct evidence exists for the presence of the tertiary amine, which could be either branch point/cross-linker or cyclic ring by IR.

This study is designed to probe the presence of the tertiary amines as well as other cure species by UV–vis and fluorescence spectroscopic methods relying on a DAA cure sensor. The cure sensor, DAA, is designed to mimic the reactivities of the diamine curing agent, DDS. IR technique was also used to complement UV–vis and fluorescence methods. A nearly stoichiometric mixture (0.94) of TGDDM–DDS epoxy was studied by curing isothermally at 140, 160, and 180 °C.

The IR technique shows that the epoxide consumption is slightly faster in the TGDDM–diamine system compared to a diepoxide–diamine system (DGEBA–DDS). Also IR spectra do not indicate a significant formation of ether groups until about 40 min at 160 or 180 °C.

UV–visible absorption spectra of DAA in the TGDDM–DDS matrix clearly show red shifts attributable to the presence of the tertiary amine species, as a function of cure. Deconvolution of absorption spectra based on those of model cure species provides the fractions of each cure species. The amount of the tertiary amine is slightly greater in TGDDM–DDS than in DGEBA–DDS. Cure composition results before etherification is significant were analyzed by assuming only epoxide–amine reactions and independent reactivity of the epoxide rings. Similar reactivity between the reactivity of the primary amine with epoxide and that of the secondary amine with epoxide is found from the analysis.

Fluorescence spectra also support the presence of the tertiary amine species of DAA. When the fluorescence intensity is analyzed on the basis of the same assumptions applied for the cure composition data from UV–visible spectra, the quantitative amount of the cure composition including the tertiary amine content is estimated. There was reasonable agreement in cure composition data between UV–vis deconvolution results and fluorescence analysis.

There was indication from all three techniques that the cure is slightly faster in TGDDM–DDS than in DGEBA–DDS, a trend probably due to the catalytic effects of the amine groups of TGDDM. An almost linear relationship has been established between the extent of DAA amine reaction and the extent of epoxide reaction in TGDDM–DDS.

In summary, the network structure of nearly stoichiometric TGDDM–DDS indicates the presence of a substantial amount of tertiary amines. A part of this could exist as a cyclic ring compound, but the rest is expected to contribute to the network as cross-linkers and branch points. There is some qualitative indication for the formation of ether groups later in the cure reaction. The fluorescence emission maximum of DDS curing agent also shows a red shift of about 15 nm from about 352 nm after cure with a stoichiometric amount of either TGDDM or DGEBA, thus providing independent support for the presence of tertiary amine species in the network.[20] This red shift was also observed even when TGDDM was about twice as much as DDS, which was the composition studied by others.[10a,d]

During cure of amine–epoxide, especially in air, some oxidation and degradation products can be formed, resulting in color. These colored species absorb below 400 nm and fluoresce around 460 nm. Therefore, they do not interfere with the spectral properties of either DDS curing agent or DAA probe.

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