

The Cure Reactions, Network Structure, and Mechanical Response of Diaminodiphenyl Sulfone-Cured Tetraglycidyl 4,4'-Diaminodiphenyl Methane Epoxies*

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Synopsis

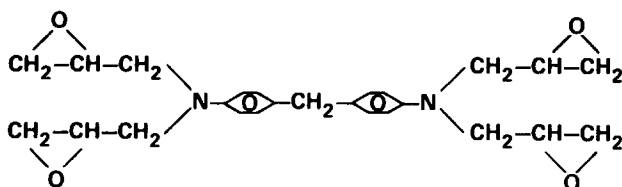
The cure reactions, chemical structure, and network topography of diaminodiphenyl sulfone (DDS)-cured tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) epoxies are reported. Systematic Fourier transform infrared (FTIR) spectroscopy studies of the cure and degradation reactions of TGDDM-DDS epoxies in the 100–300°C temperature range as a function of DDS and boron trifluoride monoethylamine, $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ catalyst concentrations are presented. FTIR studies indicate TGDDM epoxide homopolymerizes in the 175–250°C range via epoxide-hydroxyl (E-OH) chain extension reactions. The hydroxyl groups are initially present as α -glycol impurities or are formed by epoxide isomerization and/or oxidation. Three principal cure reactions occur at 177°C for TGDDM-DDS epoxies, namely primary amine-epoxide (PA-E), secondary amine-epoxide (SA-E) and E-OH reaction with the PA-E reaction being an order of magnitude faster than the other two cure reactions. The PA-E reaction dominates the early stages of cure and, hence, composite processing conditions. The three cure reactions are catalyzed to similar extents by $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$. FTIR and molecular modeling studies indicate that the E-OH and SA-E reactions can occur intermolecularly to form crosslinks or intramolecularly to form non-cross-linked internal rings. The complex degradation reactions of TGDDM-DDS epoxies in the 177–300°C range are reported. The principal degradation reactions involve (1) dehydration and/or oxidation to form ether crosslinks and (2) decomposition of the EOH cure reaction products to form propanal. Based on a knowledge of the cure reactions, together with molecular modeling, the chemical structure and network topography of TGDDM-DDS epoxies are reported.

INTRODUCTION

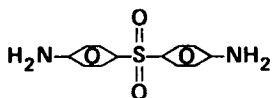
Diaminodiphenyl sulfone (DDS)-cured tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) epoxies are the most common composite matrices utilized in high-performance fibrous composites. The structures of the unreacted TGDDM epoxide and DDS monomers are illustrated in Figure 1. The TGDDM epoxide monomer is a liquid at 23°C, whereas the DDS monomer is a crystalline powder with a m.p. of 162°C. The commercially available prepreg resins such as Narmco 5208,[†] Fiberite 934 and Hercules 3501-A, all primarily consist of the TGDDM-DDS epoxy; the latter two systems also contain boron trifluoride catalysts.¹

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[†] Reference to company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.



Tetraglycidyl 4, 4' diaminodiphenyl methane epoxy TGDDM
(liquid at 23°C)



4, 4' diaminodiphenyl sulfone DDS
(crystalline solid, mp 162°C)

Fig. 1. The structure of TGDDM and DDS monomers.

To manufacture reproducible C fiber-TGDDM-DDS epoxy composites with well defined lifetimes in service environment requires a knowledge of the parameters that affect composite processing conditions and the resultant structure of the epoxy within the composite. The cure reactions directly control the composite processing and the final epoxy network structure and mechanical response. Hence, it is important to understand the cure reactions and the variables that affect such reactions. In previous studies we have reported: (1) the relations between the physical structure, the modes of deformation and failure, and mechanical properties of TDDDM-DDS epoxies;² (2) how specific combinations of moisture, heat, and stress affect their physical and mechanical integrity;³ (3) the effects of inhomogeneous physical mixing of the TDDDM-DDS epoxy components and their degree of chemical purity on the resultant epoxy chemical and physical structure,⁴ and (4) nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) studies of the chemical characterization, environmental sensitivity and catalytic activity and mechanisms of cure of the BF_3 : amine catalysts.^{5,6}

In this paper we report systematic Fourier transform infrared spectroscopy (FTIR) studies of the cure reactions of TGDDM-DDS epoxies. We report cure and degradation reactions of TGDDM-DDS epoxies up to 300°C as a function of DDS and boron trifluoride monoethyl amine ($\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$) catalyst concentrations. The effects of the starting material impurities on the cure reactions are also considered. For modeling studies the resultant chemical structure and network topography of the TGDDM-DDS epoxies are discussed.

EXPERIMENTAL

Materials

The components of the TGDDM-DDS epoxies were obtained from the following sources: TGDDM (MY720, Ciba Geigy); DDS (Eporal, Ciba Geigy) and ($\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$) (Harshaw). Pure TGDDM (99.5%) purified by liquid chromatography, was kindly supplied by G. L. Hagnauer, Army Materials and

TABLE I
Chemical Constituents in C Fiber-TDGGM-DDS Prepregs


Constituent	Fiberite 934 wt%	Narmco 5208 wt%
TGDDM	64	71
DDS	25	21
Diglycidyl orthophthalate epoxy (DGOP)	11	0
Glycidyl ether of a <i>bis</i> -phenol A Novolac (SU-8, Celanese)	0	8
BF ₃ : NH ₂ C ₂ H ₅	0.4	0

Mechanics Research Center. The reported composition of C fiber-TGDDM-DDS commercial prepregs are summarized in Table I.¹ Our NMR studies identified the BF₃ : amine catalyst in Fiberite 934 as BF₃ : NH₂C₂H₅.⁵

Starting Materials: Impurities

The commercially available TDGGM, DGOP, DDS and BF₃ : NH₂C₂H₅ all contain impurities, some of which may act as catalysts toward the cure reactions.

FTIR studies indicate that MY720 contains 15–20% less epoxide groups than the pure tetrafunctional TGDDM epoxide molecule.⁷ Liquid chromatog-

raphy studies indicate that the missing —CH₂— CH  —CH₂ epoxide groups are replaced by (1) —CH₂—CH(OH)—CH₂(OH), (2) —CH₂—CH(OH)—CH₂Cl, (3) —H, (4) —CH₃, and (5) —CH=CH—CH₂Cl groups with the α-glycol being the predominant impurity species.^{8–11} In addition, higher oligomers and homopolymer species may also be present. Pearce et al.⁹, Hagnauer and Pearce,¹⁰ and Scola¹² report that the epoxide groups in TGDDM can hydrolyze to the α-glycol species and that such species catalyze homopolymerization reactions.

The commercial DGOP (Glycel-A-100) is also far from pure with a reported equivalent weight per epoxide group of 155¹³ compared to the expected value of 139 for the pure material.

Commercial DDS also contains a small percentage of a crystalline impurity as indicated by a DSC endotherm at 77°C whose heat of fusion is 3% of the total heat of fusion associated with the pure DDS m.p. at ~ 165°C.⁶

¹H, ¹⁹F, and ¹¹B NMR studies indicate the chemical compositions of commercial BF₃ : NH₂C₂H₅ samples were highly variable (2–90% BF₃ : NH₂C₂H₅) from one manufacturer to another with BF₄⁻NH₃⁺C₂H₅ and BF₃(OH)⁻NH₃⁺C₂H₅ salts together with other unidentified highly reactive species being the principal impurities.⁵ The BF₃ : NH₂C₂H₅ commercial sample from Harshaw used in this study consisted of ~ 90 mol% BF₃ : NH₂C₂H₅, ~ 9 mol% BF₄⁻NH₃⁺C₂H₅, and ~ 1 mol% BF₃(OH)⁻NH₃⁺C₂H₅.

Sample Preparation

For FTIR studies, the TGDDM epoxide was heated up to 75°C and the DDS was added slowly while the mixture was stirred. This mixture was then

held at 74°C for 3 h, periodically stirred, and poured into vials and stored at -20°C. TGDDM-DDS mixtures were prepared in the 0 to 35 wt% DDS range. The $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalyst was introduced into the TGDDM and TGDDM-DDS mixtures in the 0-5 wt% range by two procedures. (1) The BF_3 catalyst was dissolved in the TGDDM at 90°C prior to the introduction of DDS. (2) The BF_3 catalyst and the TGDDM-DDS mixture (or the TGDDM alone) were both individually dissolved in acetone and then mixed together with the further addition of acetone. The acetone was evaporated from these mixtures under vacuum 23°C.

Experimental Techniques

The TGDDM-DDS- $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ epoxy mixtures were placed between NaCl crystals that were separated by a 0.5 mm spacer for FTIR studies of the cure reactions. The epoxy mixtures were cured between the NaCl crystals in an oven, allowed to cool slowly to 23°C and then introduced into a Nicolet FTIR spectrometer (Model No. 7199) at 23°C and the infrared spectra recorded. The spectra were obtained from 100 scans at a resolution of 1 wavenumber (cm^{-1}). (Between cure cycles the NaCl-epoxy specimens were stored in a desiccator at 23°C.) Spectral stripping, which reveals differences in the spectra recorded at different stages of cure, was utilized to monitor the disappearance of the reactants and the formation of the products during cure.

Molecular modeling of potential cross-linked structures of the epoxy networks were conducted utilizing Leybold-Heraeus (West Germany) models.

RESULTS AND DISCUSSION

TGDDM Epoxide Homopolymerization

The homopolymerization reactions of impure TGDDM (MY720) in the presence and absence of a $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalyst and, also, pure TGDDM were monitored by FTIR as a function of cure temperature from 177 to 300°C. The intensities of the epoxide, hydroxyl, ether, and carbonyl bands at

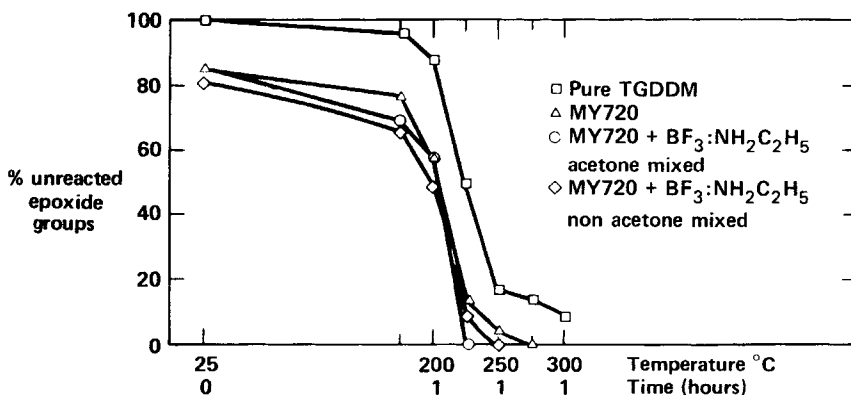


Fig. 2. Percent of unreacted epoxide groups vs. cure conditions for pure TGDDM (\square), MY720 (Δ), MY720 + 0.4 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ -nonacetone mixed (\diamond), MY720 + 0.4 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ -acetone mixed (\circ).

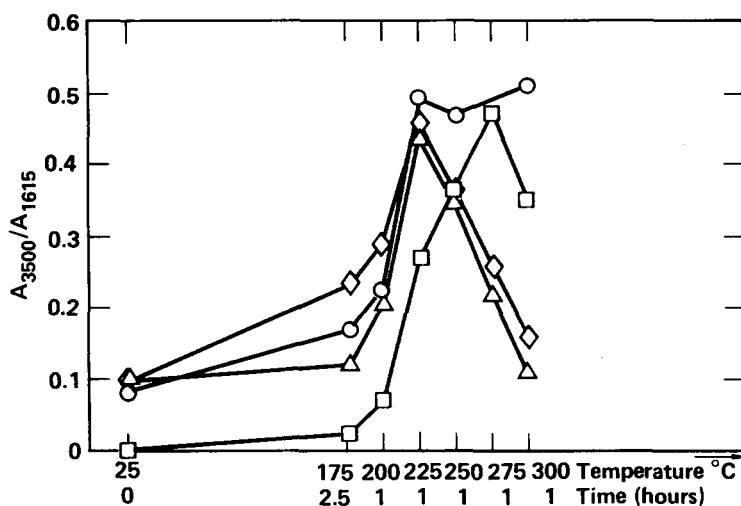


Fig. 3. Hydroxyl group IR intensity (A_{3500}/A_{1615}) vs. cure conditions for pure TGDDM (□), MY720 (Δ), MY720 + 0.4% BF₃:NH₂C₂H₅-nonacetone mixed (◇), MY720 + 0.4% BF₃:NH₂C₂H₅-acetone mixed (○).

906, 3500, 1120, and 1720 cm^{-1} , respectively, were determined from spectral differences and are plotted as a function in cure conditions in Figures 2 through 5, respectively. The 906, 1120 and 1720 cm^{-1} band intensities were normalized to the 805 cm^{-1} band and the 3500 cm^{-1} to the 1615 cm^{-1} band. The 805 and 1615 cm^{-1} bands are associated with the phenyl group which is assumed to be chemically unmodified during the homopolymerization reac-

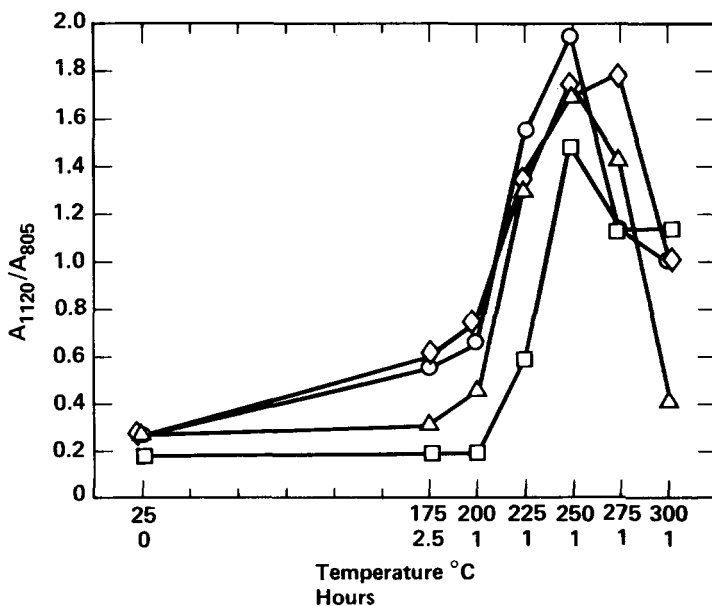


Fig. 4. Ether group IR intensity (A_{1120}/A_{805}) vs. cure conditions for pure TGDDM (□), MY720 (Δ), MY720 + 0.4% BF₃:NH₂C₂H₅-nonacetone mixed (◇), MY720 + 0.4% BF₃:NH₂C₂H₅-acetone mixed (○).

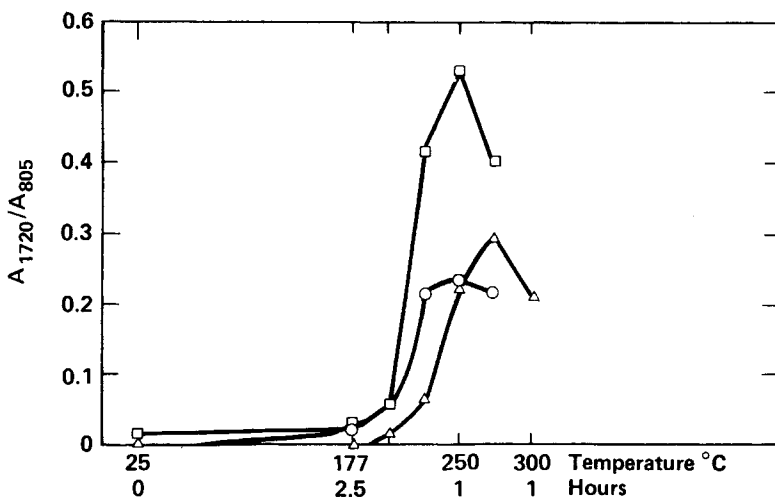


Fig. 5. Carbonyl group IR intensity (A_{1720}/A_{805}) vs. cure conditions for pure TGDDM (\square), MY720 (Δ), MY720 + 0.4% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ -acetone, and nonacetone mixed (\circ).

tions. The IR band assignments were made utilizing standard IR reference books.^{14,15}

Epoxide consumption, Figure 2, primarily occurs in the 175–250°C range with the rate of epoxide consumption being MY720- $\text{BF}_3:\text{N}_2\text{C}_2\text{H}_5 > \text{MY720} > \text{pure TGDDM}$. In agreement with the previous observations,^{9,10,12} the impurities in MY720 enhance epoxide consumption relative to pure TGDDM. No difference in epoxide consumption as a function of cure conditions was observed within experimental scatter between the MY720- $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ -acetone mixed and nonacetone mixed samples. At 177°C, the $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ accelerates the homopolymerization reactions of MY720 by a factor of 2. However, $> 200^\circ\text{C}$ the $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ has no detectable effect on the rate of MY720 homopolymerization. These phenomena may be caused by either $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalyst deactivation and/or the homopolymerization products acting as the predominant catalytic species.

Ether, hydroxyl, and carbonyl band intensities (Figs. 3–5) simultaneously increase in the same temperature range as the epoxide band intensity decreases (Fig. 2). The carbonyl band appears to be directly correlated to epoxide consumption rather than general oxidation reactions because the carbonyl band intensity does not increase once the epoxide groups are all consumed. The intensities of the ether, hydroxyl, and carbonyl bands decrease with increasing temperature in the 225–300°C range as a result of network degradation.

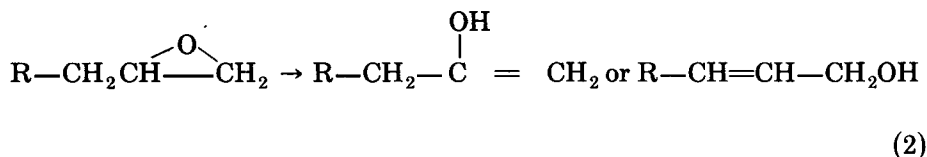
In the 177–300°C temperature range studied, epoxide isomerization, oxidation, and homopolymerization can occur, followed by complex degradation reactions. There have been numerous studies on the homopolymerization of epoxides including the effects of catalysts, alcohols, cure temperature, and epoxide-amine ratio on the chain extension reactions.^{9,10,16–27} The appearance of hydroxyl, ether, and unsaturation have been reported during homopolymerization of epoxides.^{16,18,19}

There is considerable evidence in the literature that chain extension reactions can occur between epoxide and hydroxyl groups and that this reaction (1) is enhanced in the presence of tertiary amines.^{17,19,21-27} In the case of TGDDM

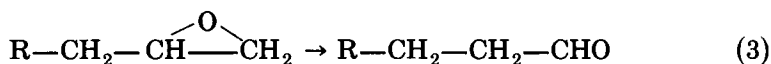


homopolymerization, hydroxyl groups are present in the impure TDGGM (MY720) as α -glycol groups and further hydroxyl groups can form in the 177–300°C range as a result of isomerization and/or oxidation of the epoxide groups. The presence of the tertiary nitrogen NR_3 groups in the TGDDM molecule should enhance the epoxide-hydroxyl (E-OH) reaction. The hydroxyl groups present in MY720 accelerate the rate of epoxide consumption compared to pure TGDDM, which indicates that the E-OH reactions rather than epoxide-epoxide (E-E) reactions are the predominant chain extension reactions for TGDDM.

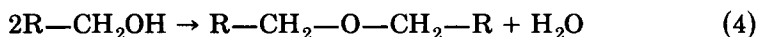
A number of workers have reported epoxides isomerize to allylic alcohols (2).^{16-20,28,29} Epoxide isomerization to



allylic alcohols and also to an aldehyde (3) is consistent with simultaneous appearance of hydroxyl and carbonyl groups upon epoxide consumption. The absence of a methyl



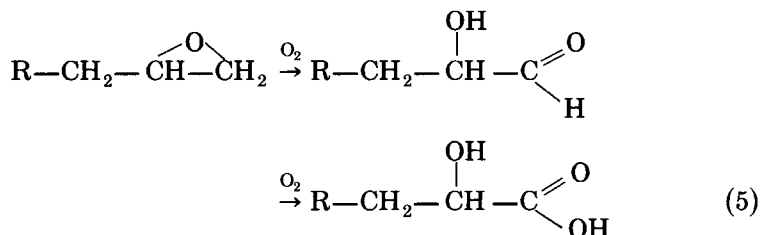
group in the IR spectra indicates isomerization to an aldehyde rather than a ketone is preferred. Although, we do observe the hydroxyl formation, which we can associate with epoxide isomerization of allylic alcohols, we found no evidence of associated unsaturation in the IR spectra. We suggest these reactive double bonds could be oxidized or water could be generated from the dehydration of two alcohol groups to form an ether linkage (4) (see section on TGDDM-DDS cure reactions).



Molecular models indicate that steric constraints are too severe to allow polymerization via unsaturated allylic alcohols.

In addition to isomerization, some of the epoxide groups could be oxidized to hydroxyl aldehyde and then carboxylic acid groups (5).³⁰ These oxidation

reactions would also be consistent with our FTIR observations.



Hence, the most plausible explanation of our FTIR observations of the simultaneous appearance of hydroxyl, carbonyl, and ether groups upon TGDDM epoxide consumption is epoxide isomerization and/or oxidation followed by epoxide-hydroxyl chain extension reactions.

At the higher temperature range of our studies (225–300°C) degradation reactions of the polymerized network will occur. Previous studies on the degradation of epoxies indicate dehydration will be the principal degradation mechanism in the 225–300°C temperature range over time periods of hours^{17,31–33} which is consistent with the observed decrease in hydroxyl band intensity with increasing temperature in this range.

We now consider the chemical structure produced upon TGDDM homopolymerization from analyses of the normalized IR band intensities of the reaction products together with molecular modeling studies. In our IR analyses we normalized the OH and ether IR band intensities relative to the initial epoxide band intensity by the following expression, illustrated in this case for the OH band intensity, (R_{OH}), where IOH_T , $\text{IOH}_{23^\circ\text{C}}$, $\text{IE}_{23^\circ\text{C}}$

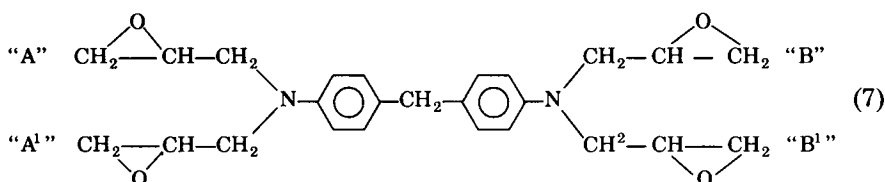
$$R_{\text{OH}} = \frac{\text{IOH}_T - \text{IOH}_{23^\circ\text{C}}}{\text{IE}_{23^\circ\text{C}} \times (\text{m.f.})_{\text{TGDDM}}} \quad (6)$$

and $(\text{m.f.})_{\text{TGDDM}}$ are the normalized OH band intensities at cure temperature T and 23°, epoxide band intensity at 23°C and the mole fraction of epoxide groups relative to pure TGDDM, respectively. The R_{ether} and maximum R_{OH} values in the 225–300°C range are 1 and 0.5, respectively, for both MY720 and pure TGDDM. From our studies on the TGDDM-DDS- $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ (25% wt% DDS) system in which all the epoxide groups are consumed at 177°C (see section on TGDDM-DDS reactions) the R_{OH} and R_{ether} values are 1 and 2, respectively. For this TGDDM-DDS system 28%, 20%, and 52% of the epoxide groups are consumed by primary amine-epoxide (PA-E), secondary amine-epoxide (SA-E), and E-OH reactions, respectively. The PA-E and SA-E reactions produce one OH group per epoxide group, whereas the E-OH reaction produces one ether group per epoxide group. From these R values we estimate for homopolymerization that 25% of the epoxide groups form OH groups, 25% of the epoxide groups react to form ether groups via E-OH chain extension reactions, and the remaining 50% epoxide groups isomerize to aldehyde groups. Based on these R-value estimates, and assuming a statistically random isomerization/oxidation of the epoxide groups on the tetrafunctional TGDDM molecule then the spatial distribution of (1) nonisomerized/oxidized epoxides (E), (2) allylic alcohol/carboxylic acid groups

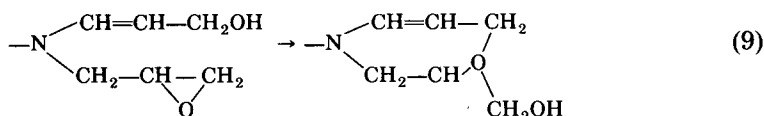
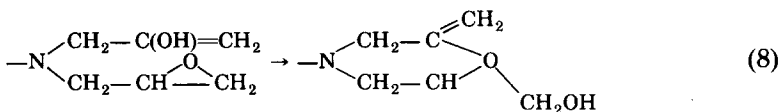
TABLE II
Spatial Distribution of Adjacent Pair Groups
in Isomerized TGDDM Prior to Homopolymerization

Adjacent pair combinations	Concentration of each pair (%)
(E), (E)	9
(E), (OH)	9
(E), (C=O)	18
(OH), (OH)	9
(OH), (C=O)	18
(C=O), (C=O)	36

(OH), and (3) aldehyde groups (C=O) in the A, A¹ and B, B¹ adjacent pair positions (7) is shown in Table II. (Molecular model studies indicate all such



spatial pairs are sterically feasible.) Our study found 36% of adjacent pairs on the TGDDM molecules are (C=O), (C=O) pairs which are inactive during the E-OH chain extension reactions and 54% of adjacent pairs will polymerize with groups on neighboring TGDDM molecules by E-OH chain extension via (E), (E); (E), (C=O); (OH), (OH) and (OH), (C=O) pair combinations. The 9% (E), (OH) adjacent pairs could either chain extend with neighboring molecules or internally cyclize by E-OH reactions (8) and (9). Molecule models indicate the rings



formed by cyclization are sterically admissible, with the six-membered ring being more energetically stable. The formation of rings structures from either cyclization of diepoxides via E-E reactions^{20, 34, 35} or cyclization of epoxide-hydroxyl moieties via E-OH reactions³⁶ have been reported in the literature.

TGDDM-DDS Reactions

In this section we report FTIR studies of the cure reactions of TGDDM-DDS-BF₃ : NH₂C₂H₅ epoxy systems as a function of cure conditions

(100–300 °C) and DDS (0–35 wt%) and $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ (0–5 wt%) concentrations. The principal cure and degradation reactions that occur are then discussed. We monitored by FTIR difference spectra the disappearance of the epoxide and PA groups and the appearance of the SA, ether, and hydroxyl groups. The IR bands at 1630 and 3410 cm^{-1} were assigned to the PA and SA groups, respectively,^{14,15} and their intensities were normalized relative to the 1516 cm^{-1} band associated with the phenyl group. The intensity of the SA group was further normalized against the O=S=O band from the DDS structure ($I_{\text{NH}:\text{SO}_2}$) which we assume does not change in intensity during cure. This normalization allows comparisons of SA changes independent of the effects of DDS concentration.

Cure reactions at 177 °C for the TGDDM-DDS (25 wt% DDS; 0.4 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$) Epoxy as a Function of Cure Time

The disappearance of the epoxides and the PA's in %'s and the appearance of the SA's, OH's, and ethers in the form of $I_{\text{NH}:\text{SO}_2}$, R_{OH} and R_{ether} values, respectively, are plotted in Figure 6 as a function of cure time at 177 °C, for a TGDDM-DDS (25% wt% DDS: 0.4 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$) epoxy system. After

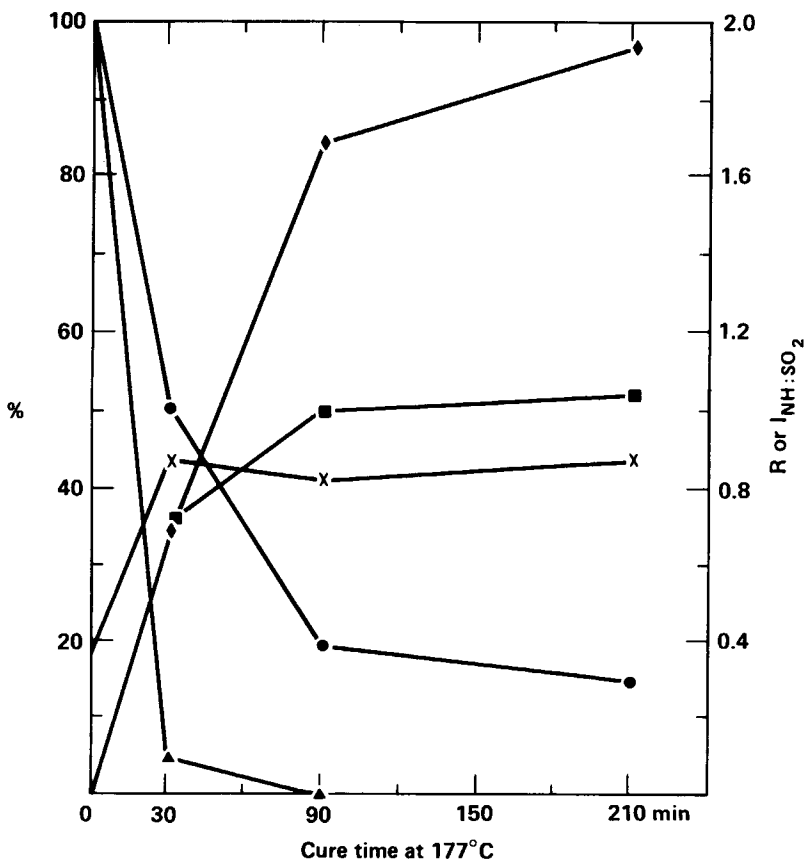


Fig. 6. Epoxides (●) and PA's (▲) (% of unreacted groups), R_{OH} (■), R_{ether} (◆), $I_{\text{NH}:\text{SO}_2}$ (X) vs. cure time at 177 °C for TGDDM-DDS (25 wt% DDS; 0.4 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$) epoxy.

210 min at 177 °C, 85% of the epoxide groups are consumed. At later stages of the cure the epoxide consumption rate is evidently hindered by steric restrictions. The PA-E reaction dominates the early stages of cure. After 30 min at 177 °C, 95% of PA groups and 45% of the epoxide groups have reacted; 28% of these epoxide groups are consumed by the PA-E reaction. From FTIR and DSC studies of the cure of a non-BF₃:NH₂C₂H₅-catalyzed TGDDM-DDS at 177 °C Moacanin et al.³⁷ and Gupta et al.³⁸ have concluded the PA-E reaction dominates the early stages of cure. Also, chemical titration and liquid chromatography studies³⁹ indicate epoxide consumption is linear with time during the early stages of cure which is also consistent with the predominance of the PA-E reaction.

In the 30–90 min cure time range there is a 30% increase in the R_{OH} intensity, despite 95% of the PA's being consumed after 30 min. This increase could be caused by ~ 25% of the SA's reacting with 7% of the epoxides via SA-E addition reactions. The I_{NH:SO₂} intensity decrease associated with the SA-E reaction would be difficult to detect because the PA-E reaction simultaneously causes an increase in this intensity. After 90 min of cure the R_{OH} and I_{NH:SO₂} values remain constant with increasing cure time which indicates the SA-E reaction does not occur during the later stages of cure probably because of network steric restrictions. The SA-E reaction rate constant for aromatic amines with structures similar to DDS, such as methylene dianiline, have been reported to be 7–12 times slower than for the PA-E reaction.⁴⁰

The increase in the R_{ether} throughout the cure is associated with the E-OH reaction which consumes ~ 50% of the total epoxides.

Cure Reactions for TGDDM-DDS (25 wt% DDS) Epoxy in the 100–177 °C Range as a Function of BF₃:NH₂C₂H₅ Concentration

FTIR was utilized to monitor the cure reactions of TGDDM-DDS (25 wt% DDS) epoxy as a function of cure temperature (100–177 °C) and BF₃:NH₂C₂H₅ concentration (0–5 wt%). The disappearance of the epoxides and PA's in %'s and the appearance of the SA's, ethers, and OH's in the form of I_{NH:SO₂}, R_{ether}, and R_{OH} values, respectively, are plotted in Figure 7, as a function of cure conditions and BF₃:NH₂C₂H₅ concentration.

The sharp decrease in the NH₂ group concentration at lower cure temperatures further supports that the PA-E reaction is the predominant cure reaction in the earlier stages of cure. The epoxide and NH₂ group consumptions are enhanced and shifted to lower cure temperatures with increasing BF₃:NH₂C₂H₅ concentration, which indicates the PA-E reaction is catalyzed by the BF₃:NH₂C₂H₅.

The I_{NH:SO₂} intensity increases with cure temperature in the 100–150 °C range for all BF₃:NH₂C₂H₅ concentrations. The I_{NH:SO₂} intensity is shifted to lower temperatures for the epoxy that contains 5 wt% BF₃:NH₂C₂H₅, which further suggests that the PA-E reaction is catalyzed by the BF₃:NH₂C₂H₅. At the later stages of cure at 177 °C the I_{NH:SO₂} intensity remains constant with cure time which indicates the SA-E reaction does not occur in this cure regime.

Ether formation is enhanced with cure temperature and time and BF₃:NH₂C₂H₅ concentration (Fig. 7), thus indicating BF₃:NH₂C₂H₅ en-

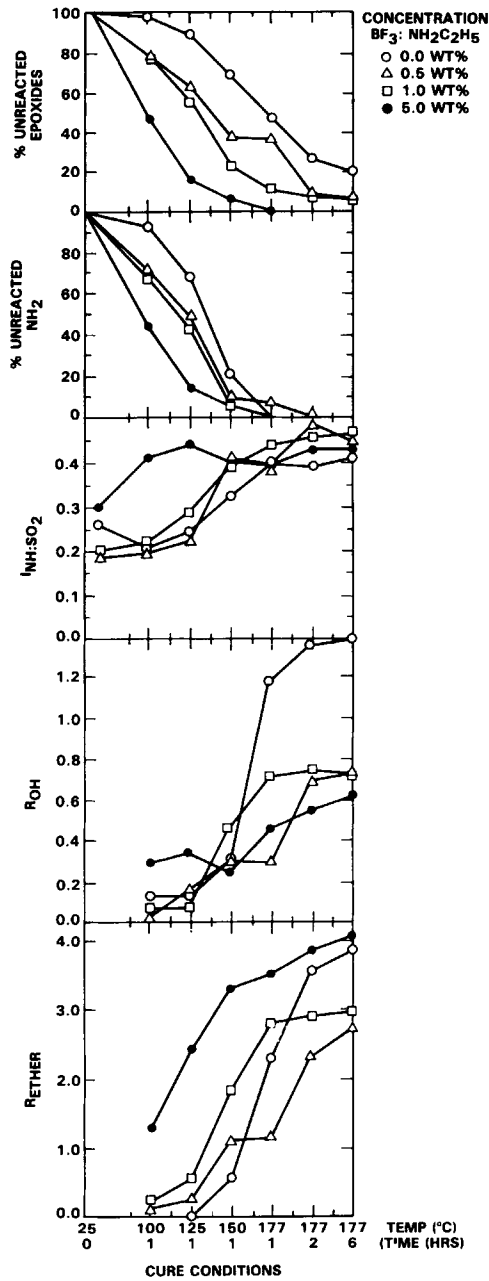


Fig. 7. Percent of unreacted epoxide and PA groups, $I_{NH:SO_2}$, R_{ether} , and R_{OH} values vs. cure conditions and $BF_3:NH_2C_2H_5$ concentration for TGDDM-DDS (25 wt% DDS) epoxy.

hances the E-OH reaction. The TGDDM-DDS (0 and 5 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$) epoxy systems exhibit anonymously high R_{ether} values of ~ 4 , which is twice the value we observe for systems directly "ramp-cured" to 177 °C.

The R_{OH} values, in Figure 7, at lower cure temperatures are enhanced with increasing $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ concentration, which is consistent with acceleration of the PA-E reaction by $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$. The R_{OH} values remain constant during the latter stages of cure, with the exception of the TGDDM-DDS (0 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$) system which exhibits an anomalous large increase in R_{OH} above 150 °C ultimately resulting in R_{OH} value nearly twice that of the $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ -catalyzed epoxy systems.

For the TGDDM-DDS (0 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$) system the simultaneous increase in the hydroxyl and ether group concentrations and decrease in the epoxide concentration when nearly all the NH_2 groups have been consumed, and the $I_{\text{NH}:\text{SO}_2}$ intensity remains constant, suggests the occurrence of an additional reaction other than the PA-E, SA-E, and E-OH reactions. In light of our observations on the homopolymerization of TGDDM, we suggest for this non- $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ -catalyzed system that the epoxide groups undergo isomerization and/or oxidation at 177 °C resulting in OH formation which enhance ether formation via E-OH reactions. The isomerization and/or oxidation of the epoxides is presumably shifted to lower temperatures relative to the TGDDM homopolymerization temperatures by PA-E, SA-E, and E-OH reaction products. This isomerization/oxidation would be less prevalent at 177 °C for the $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ -catalyzed systems, because of their lower concentration of unreacted epoxides at this temperature. The appearance of a C=O IR band after cure at 177 °C for the TGDDM-DDS (0 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$) system further supports epoxide isomerization/oxidation occurs. Furthermore, Cizmecioglu and Gupta⁴¹ observed from DSC studies for a TGDDM-DDS (0 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$) system that the cure reactions are shifted to higher temperatures and the order of these reactions decrease with increasing scan rate. A decrease in the order of the reaction is consistent with the occurrence of epoxide isomerization/oxidation.

The high R_{ether} values for the TGDDM-DDS (0 and 5 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$) epoxy systems in this study could be explained by oxidation of unreacted epoxide groups for the non- $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ -catalyzed system and $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ catalyzed oxidation of the cured network for the 5 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ system. For this cure study the TGDDM-DDS epoxies were exposed above 100 °C to longer cure times of 9 h vs. 2.5–3.5 h for our other cure studies, described earlier in this section. This longer cure time could enhance oxidation reactions.

Cure Degradation Reactions in 177–300 °C Range for TGDDM-DDS Epoxies as a Function of DDS Concentration (0–35 wt%)

The cure degradation reaction of TGDDM-DDS epoxies in the 177–300 °C range are reported in this subsection as a function of DDS concentration (0–35 wt%). Three series of epoxies were studied containing (1) 0 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$, (2) 0.4 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$, and (3) 0.4 wt% $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ -acetone mixed. The disappearance of the epoxide and PA groups and the appearance of SA ether, and OH groups were monitored by FTIR.

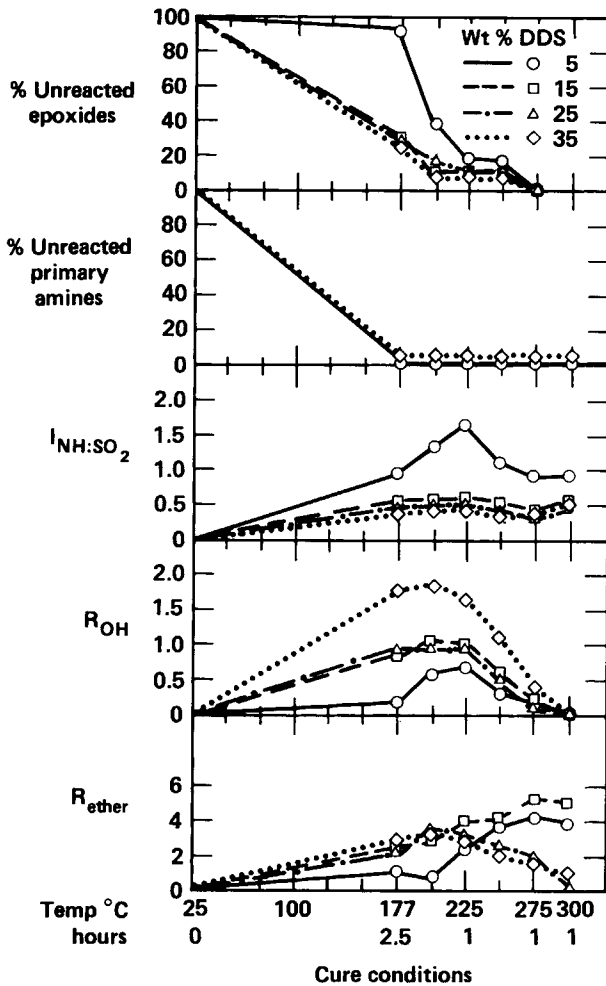


Fig. 8. Percent of unreacted epoxide and PA groups, $I_{NH:SO_2}$, R_{ether} , and R_{OH} values vs. cure conditions in the 177–300°C range and DDS concentration for TGDDM-DDS (0 wt% $BF_3:NH_2C_2H_5$) epoxies.

In Figure 8 we illustrate data for a TDGGM-DDS epoxy series (0 wt% $BF_3:NH_2C_2H_5$) in which the disappearance of the epoxides and PA's in %'s and the appearance of the SA's, OH's, and ethers in the form of $I_{NH:SO_2}$, R_{OH} , and R_{ether} values, respectively, are plotted as a function of DDS concentration and cure conditions. Similar plots were generated for the other two $BF_3:NH_2C_2H_5$ epoxy systems.

All PA groups are consumed at 177°C after 2.5 h for all TDGGM-DDS epoxy systems studied that contained < 35 wt% DDS. For TDGGM-DDS (35 wt% DDS) epoxies, however, 5% of PA's remain unreacted even at 300°C, which suggests that these unreacted groups become inaccessible to epoxide groups during the later stages of cure because of network topography constraints.

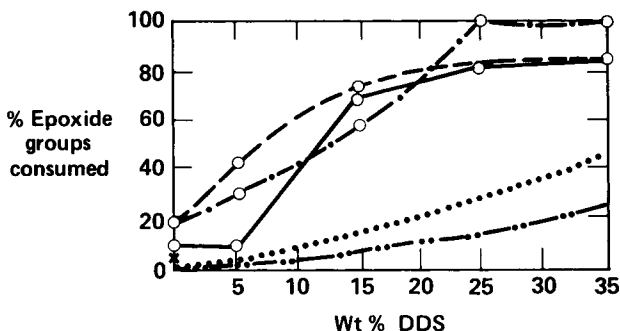


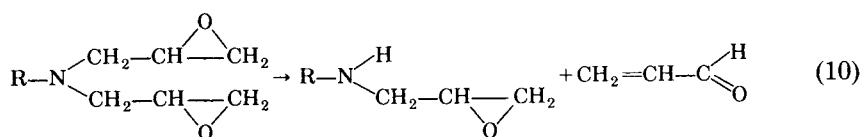
Fig. 9. Percent of epoxide groups consumed at 177°C after 2.5 h vs. wt% DDS for (1) TGDDM-DDS (0 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$) (—); (2) TGDDM-DDS (0.4 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$)-non-acetone mixed (---); (3) TGDDM-DDS (0.4 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$)-acetone mixed (-·-·-); (4) 100% pure TGDDM (×); (5) 100% completed PA-E reaction (·····) and (6) 50% completed SA-E reaction (-·-·-).

In Figure 9, plots of epoxide consumptions at 177°C after 2.5 h vs. wt% DDS for all TGDDM-DDS systems studies are illustrated. From these data and similar plots at higher cure temperatures we conclude: (1) at 177°C for a 2.5 h cure for TGDDM-DDS (0–5 wt% DDS) epoxies, the $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalyst enhances epoxide consumption 2–4 times. (2) At cure temperatures in the 200–225°C range, we found no definitive evidence that the $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalyst enhances epoxide consumption for all systems studied, which suggests the principal catalytic species, the $\text{BF}_4^-\text{NH}_3^+\text{C}_2\text{H}_5$ salt,⁵ is deactivated in this temperature regime. (3) At 177°C for TGDDM-DDS (15–35 wt% DDS) epoxies the $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalyst generally enhances epoxide consumption, but does not always produce a fully cured system. The larger scatter in epoxide consumptions, 60–100%, from a number of experiments for the TGDDM-DDS (15–35 wt% DDS) epoxies suggests there is considerable variability in the $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalytic activity. From our DSC and NMR studies of $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalytic activity,^{9,10} we attribute the epoxide consumption data scatter to variability in inherent $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ chemical composition and its particle size distribution within the epoxy, and also nonuniform mixing of this small concentration of catalyst in the epoxy. (4) From two completely independent series of acetone and nonacetone mixed epoxies we found no difference in epoxide consumption within experimental scatter. (5) The epoxide consumption is enhanced with increasing DDS concentration to a greater extent than that associated with 100% completed PA-E and 50% completed SA-E reactions (Fig. 9). The hydroxyl products of the PA-E and SA-E reactions enhance epoxide consumption via E-OH reactions. Consistent with this observation, DSC studies by Mijovic et al.⁴² suggest the cure reactions of TGDDM-DDS epoxies are autocatalytic.

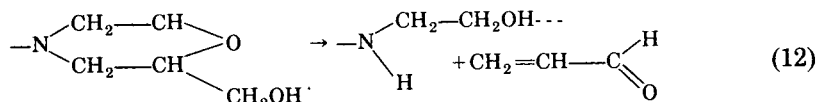
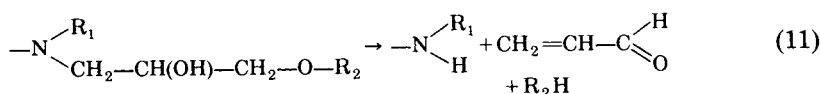
The $I_{\text{NH}:\text{SO}_2}$ intensity after 2.5 h cure at 177°C decreases with increasing DDS concentration for the three TGDDM-DDS systems studied. For a TGDDM-DDS (25 wt% DDS, 0 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$) epoxy the $I_{\text{NH}:\text{SO}_2}$ intensity is 30–40% lower than the maximum intensity observed at lower DDS concentrations, thus suggesting at least $\sim 1/3$ of the SA groups do

react with epoxide groups in commercial prepreps under standard cure conditions.

The $I_{\text{NH}:\text{SO}_2}$ intensity increases in the 177–225°C region despite the completion of the PA-E cure reaction that would result in formation of additional SA groups. This $I_{\text{NH}:\text{SO}_2}$ intensity increase is more pronounced for lower DDS concentration systems. From vaporization gas chromatography/mass spectroscopy studies Grayson and Wolf⁴³ report propenal is the principal degradation product of a TGDDM-DDS (21 wt% DDS, 0 wt% $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$) epoxy system in the 125–215°C region. Propenal was not observed, however, when MY720 was heated in the same temperature region,⁴⁴ which discounts propenal was formed by unimolecular decomposition of unreacted epoxide groups (10)



Propenal and SA group formation must form from decomposition of the PA-E, SA-E, and E-OH cure reaction products. However, because we observe the SA group formation is most prevalent for low DDS concentration TGDDM-DDS epoxies which contain higher concentrations of E-OH cure reaction products, then we suggest propenal and SA group formation most likely occurs by decomposition of noncyclized (11) and cyclized (12) E-OH reaction products (see section on chemistry of cure reactions).



Similar decomposition mechanisms have been proposed by David⁴⁵ and Grayson and Wolf.⁴⁴

The hydroxyl band intensities, plotted in the form of R_{OH} values decrease with increasing temperature above 200°C for epoxies containing 15–35 wt% DDS, which indicates these epoxies dehydrate in this temperature regime. For epoxies containing 0–10 wt% DDS, dehydration is not evident until above 250°C because isomerization of unreacted epoxide groups causes an increase in the concentration of OH groups in the 177–250°C temperature range. The R_{OH} value for a 177°C, 2.5 h cure increases with increasing DDS concentration, because of the enhancement of the PA-E and SA-E cure reactions with increasing DDS concentration. No significant differences in the dehydration processes were observed for the three TGDDM-DDS epoxy series that were studied.

Ether formation can occur from the E-OH reaction. The R_{ether} value for a 177°C, 2.5 h cure increases with increasing DDS concentration in the 0–15 wt% DDS range because of the enhanced availability of OH groups from the PA-E and SA-E addition reactions. For > 15 wt% DDS concentrations, ether

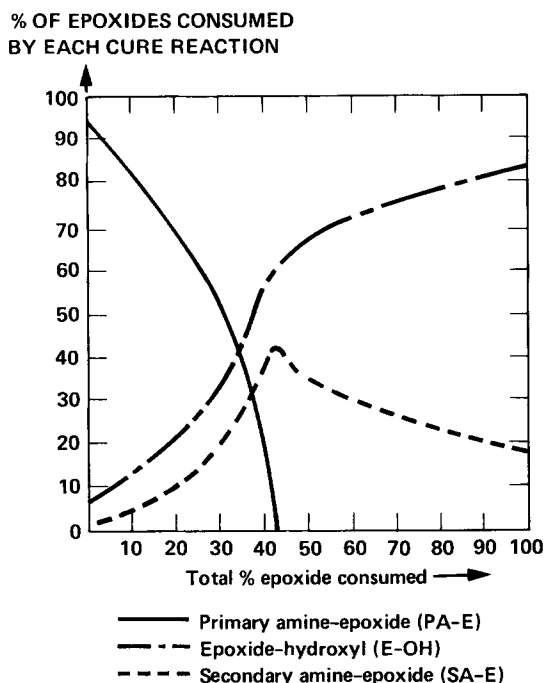


Fig. 10. Percent epoxide consumed by each cure reaction vs. total % epoxide consumed for a TGDDM-DDS (25 wt% DDS) epoxy.

formation is not enhanced with increasing DDS concentrations because the competing epoxide-amine addition reactions consume the available epoxide groups. At 0 wt% DDS, the $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ catalyst enhances ether formation ~ 5 times, but in > 0 wt% DDS epoxies, the $\text{BF}_3 : \text{NH}_2\text{C}_2\text{H}_5$ catalyst has no detectable effect on ether formation for a 177°C , 2.5 h cure. At higher cure temperatures from 177 to 300°C R_{ether} values increase with increasing cure temperature as a result of dehydration (4), and/or network oxidation and resultant formation of ether crosslinks.

Rates of Cure Reactions of TGDDM-DDS Epoxies at 177°C

From our FTIR studies of the cure reactions of TGDDM-DDS epoxies we assume that there are three principal cure reactions at 177°C for TGDDM-DDS epoxies, namely the PA-E, SA-E, and E-OH reactions.

The rate constants for the SA-E and E-OH reactions are 10 times slower than the rate constant for the PA-E reaction. The SA-E rate constant for aromatic amines similar to DDS, such as methylene dianiline, have been reported to be 7–12 times slower than the PA-E reaction.⁴⁰ From FTIR and DSC studies Moacanin et al.³⁷ report the E-OH reaction is 10 times slower than the PA-E reaction at 177°C . In Figure 10, a plot of the % of epoxies consumed by each cure reaction as a function of the total % epoxide consumed for a TGDDM-DDS (25 wt% DDS) epoxy is illustrated. The PA-E reaction dominates the early stages of cure, until all the PA is depleted. The E-OH reaction dominates the later stages of cure. The regeneration of the OH

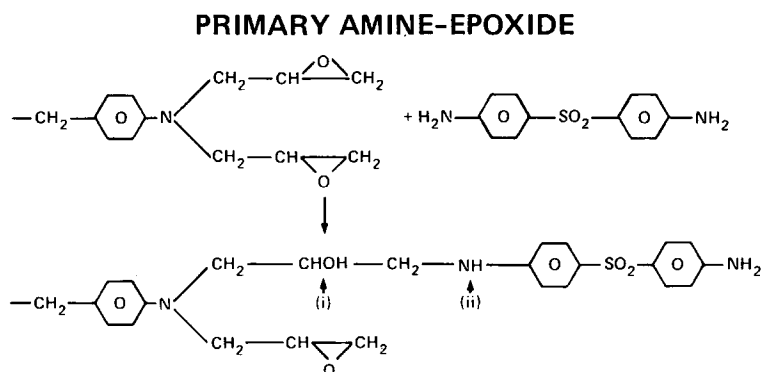


Fig. 11. Primary amine-epoxide (PA-E) reaction for TGDDM-DDS epoxies (i) and (ii) sites for E-OH and SA-E reactions, respectively.

groups in the E-OH reaction together with the permanent consumption of the SA groups in the SA-E reaction cause this domination of the E-OH reaction during the later stages of cure. About 70% of the SA groups are consumed upon 100% epoxide consumption.

TGDDM-DDS Epoxy Chemical Cure Reactions at 177°C

The chemistry of the PA-E addition cure reaction for the TGDDM-DDS epoxy system is illustrated in Figure 11, with the sites for further cure reactions via the (1) E-OH and (2) SA-E reactions indicated by arrows. The E-OH and SA-E reactions can occur (a) intermolecularly to form crosslinks and (b) intramolecularly to form non-cross-linked internal rings, as illustrated in Figure 12. Molecular models indicate that both the 6 and 8 member rings formed intramolecularly from the E-OH and SA-E reactions, respectively, are sterically possible, with the 6-member morpholine ring being less strained and energetically more favorable. From both molecular modeling studies and

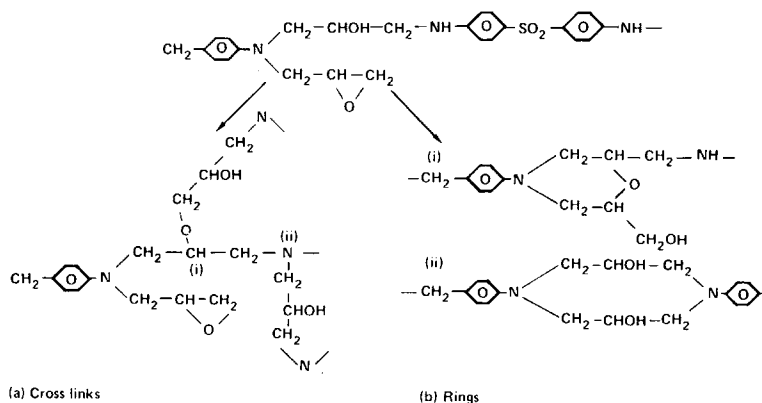


Fig. 12. (i) Epoxide-hydroxyl (E-OH) and (ii) secondary amine-epoxide (SA-E) reactions that form (a) intermolecular crosslinks and (b) intramolecular rings in TGDDM-DDS epoxies.

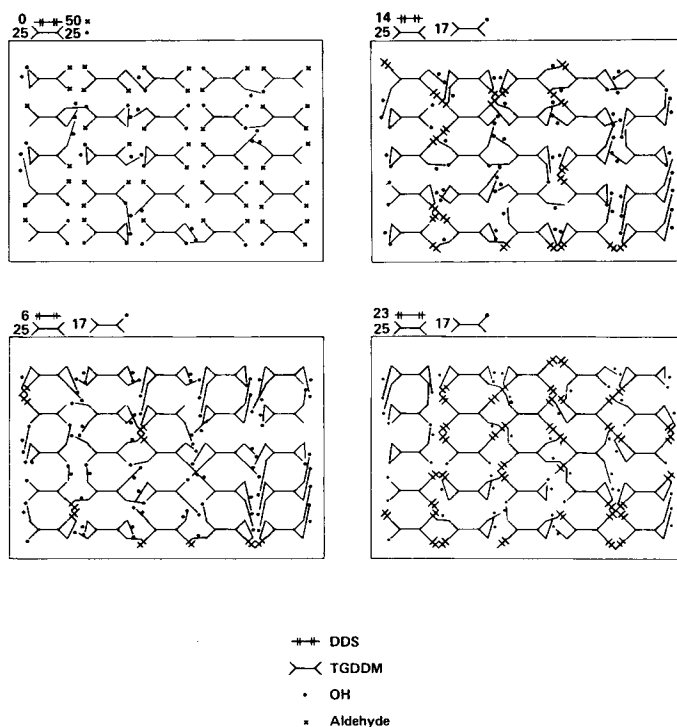


Fig. 13. Models of network structures TGDDM-DDS (0, 12.5, 25, and 35 wt% DDS) epoxies.

statistical probabilities of the reactive groups being in the appropriate relative positions for reaction, we estimate $\sim 75\%$ of the E-OH and SA-E reactions occur intramolecularly to form rings. At the later stages of cure, when the viscosity is higher, diffusion restrictions will further limit the E-OH and SA-E intermolecular reactions, but not the intramolecular reactions.

Network Topography from Modeling

Based on our understanding of the chemical cure reactions we modeled the network growth and structure of TGDDM-DDS epoxies containing 0, 12.5, 25, and 35 wt% DDS.

We start with an array of 5 by 5 TGDDM molecules (Fig. 13) in which 17 of the 100 epoxide groups have been hydrolyzed to α -glycols. (The relative dimensions of the molecules in these network arrays are schematically equivalent to their molecular sizes.) A number of simplifying assumptions were made in this modeling. Each of the 100 epoxide or α -glycol groups are designated a number 1 through 100 and are assumed to react in a random sequence as determined from tables of random numbers. The PA-E reaction is assumed to be 10 times faster than the SA-E and E-OH reactions. Equal probabilities are assumed for (1) the SA-E and E-OH reactions and (2) their inter- and intramolecular reactions. For the TGDDM homopolymerization we assume 25% of the epoxide groups isomerize to form OH groups, 50% of the epoxide groups isomerize to aldehyde groups and 25% of the epoxide groups react to form ether groups via E-OH reactions. We also assume that cure

reactions only occur (1) between adjacent groups in the same TGDDM molecule that are designated at the A, A' and B, B' pairs in Eq. (7) (section on TGDDM Epoxide Homopolymerization) (molecular models indicate internal reactions between other pairs within the same TGDDM molecule are not sterically feasible) or (2) "intermolecularly" between groups that are immediately adjacent to one another in the network. The reaction between an epoxide group and adjacent neighboring reactive groups that are positioned above, below or to the side of the epoxide group are assumed to have equal probabilities of reaction. All probabilities in this network growth model were determined from throwing dice. If a designated reaction is not possible at a specific epoxide group site a series of clockwise or anticlockwise paths are transversed through the network array until a site is reached at which the designated reaction is feasible.

The networks generated from this modeling for TGDDM-DDS (0, 12.5, 25, and 35 wt% DDS) epoxy systems are illustrated in Figure 13. All networks possess numerous defects and are complex. Network interconnectivity is similar for the TGDDM-DDS (25 and 35 wt% DDS) epoxy networks, but decreases for the TGDDM-DDS (12.5 wt% DDS) epoxy network. Consistent with these observations, we have observed that the T_g and mechanical response are only slightly dependent on DDS concentration in the 20–35 wt% DDS range but deteriorate rapidly below 20 wt% DDS.²

The ultimate ductile extensibility of an epoxy glass depends on its network extensibility and inherent defects. We have observed that the ultimate glassy-state extension for amine-cured diglycidyl ether of *bis*-phenol A (DGEBA) epoxies is a maximum at stoichiometry and decreases either side of stoichiometry as more defects are introduced into the network in the form of unreacted groups.⁴⁶ The presence of unreacted groups and their associated unconnected, nonload-bearing segments results in higher loads being imposed under stress on those segments that are incorporated into the network. The higher segmental stresses enhance stress-induced chain scissions at lower network extensibilities. The critical concentration of chain scissions associated with crack initiation will be attained at increasingly lower network extensibilities as the initial concentration of unreacted groups in the network increases. Hence, we expect the network defects present in the TGDDM-DDS epoxies will limit the ultimate extensibilities of these glasses when the glassy-state free volume is high enough to allow network segmental flow. We have observed after a 177°C, 2.5 h cure that TGDDM-DDS (23 wt% DDS; 0.4 wt% BF₃:NH₂C₂H₅) epoxies exhibit an order of magnitude greater ductility in the T_g 50°C range than TGDDM-DDS (23 wt% DDS; 0 wt% BF₃:NH₂C₂H₅) epoxies that contain considerably more network defects in the form of unreacted groups.⁴⁷

CONCLUSIONS

TGDDM epoxide undergoes homopolymerization in the 175–250°C temperature range, which is initiated by epoxide isomerization and/or oxidation which produce hydroxyl groups. These hydroxyl groups react with epoxide groups via chain extension reactions to form ether linkages. The polymerized epoxide resin dehydrates in the 225–300°C temperature range. α -glycol im-

purities and/or $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalyst accelerate the TGDDM homopolymerization.

There are three principal cure reactions at 177°C for TGDDM-DDS epoxies, namely PA-E, SA-E, and E-OH reactions, with the PA-E reaction being an order of magnitude faster than the other two cure reactions. The PA-E reaction dominates the early stages of cure, and hence, composite processing conditions; whereas the E-OH reaction dominates the later stages of cure. The three cure reactions are catalyzed to similar extent by $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$. The E-OH and SA-E reactions can occur intermolecularly to form crosslinks or intramolecularly to form non-cross-linked internal rings. At the later stages of cure, diffusion restrictions should favor ring formation.

TGDDM-DDS epoxies undergo complex degradation reactions in the $177\text{--}300^\circ\text{C}$ range. The principal degradation reactions involve (1) dehydration and/or oxidation to form ether crosslinks and (2) decomposition of the E-OH cure reaction products resulting in propenal formation.

Molecular modeling studies, based on the chemistry and rates of the cure reactions, indicate TGDDM-DDS epoxy networks possess irregular topographies and contain numerous defects in the form of unreacted, hydrated, oxidized, and/or isomerized epoxide groups.

A $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ catalyst enhances TGDDM-DDS epoxy cure and produces networks with fewer defects. The $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$ -catalyzed epoxies exhibit superior high temperature mechanical properties with ductilities an order of magnitude greater than the noncatalyzed epoxies.

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