^{1}H, ^{19}F and ^{11}B nuclear magnetic resonance characterization of BF$_3$: amine catalysts used in the cure of C fibre–epoxy prepregs*

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^{1}H, ^{19}F and ^{11}B nuclear magnetic resonance studies are reported which characterize the complexes of boron trifluoride with monoethylamine and with piperidine, BF_3:$NH_2C_2H_5$ and BF_3:NHC_5H_{10}, respectively. These complexes are used as catalysts for the cure of high performance C fibre–epoxy composities from prepregs. The chemical compositions of commercial BF_3:amine complexes are variable and contain BF_4^- and $BF_3(OH)^-$ salts together with other unidentified highly reactive species. The BF_3:amine complexes, which are susceptible to hydrolysis, also partially convert to the BF_4^- salt (i.e. $BF_4^-NH_3^+C_2H_5$) upon heating. This salt formation is accelerated in dimethyl sulphoxide solution and in the presence of the epoxides that are present in commercial prepregs. Commercial C fibre–epoxy prepregs are shown to contain either BF_3:$NH_2C_2H_5$ or BF_3:NHC_5H_{10} species together with their BF_4^- salts and a variety of boron–fluorine or carbon–fluorine prepreg species. Considerable variation in the relative quantities of BF_3:amine to its BF_4^- salt was observed from prepreg lot to lot, which will cause variable viscosity–time–temperature prepreg cure profiles. It is concluded that the chemically stable and mobile BF_4^- salt is the predominant catalytic species, acting as a cationic catalyst for the prepreg cure reactions. During the early stages of cure the BF_3:amine catalysts convert to the BF_4^- salts in the presence of epoxides, whereas the BF_3-prepreg species are susceptible to catalytic deactivation and immobilization.

(Keywords: composite matrices; epoxies; cure; boron trifluoride; amine catalysts)

INTRODUCTION

Diaminodiphenyl sulphone (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*. Diglycidyl orthophthalate (DGOP) epoxide is a minor component in some C fibre epoxy prepregs and its structure is included in this Figure. The TGDDM epoxide monomer is a liquid at 23°C, whereas the DDS monomer is a crystalline powder with a m.pt. of 162°C. The commercially available prepreg resins such as Narmco 5208†, Fiberite 934 and Hercules 3501, all primarily consist of the TGDDM–DDS epoxy: the latter two systems also contain boron trifluoride catalysts[1–3].

To manufacture reproducible C fibre–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 final epoxy network structure. Hence, it is important to understand the cure reactions and the variables that affect such reactions. In previous studies we have reported: (i) systematic Fourier transform infra-red spectroscopy (*FT*i.r.) studies of the cure reactions of TGDDM–DDS epoxies as a function of cure conditions, DDS concentration and the presence or absence of a BF_3 catalyst[4–7]; (ii) the effects of inhomogeneous physical mixing of the TGDDM–DDS components and their degree of chemical purity on the resultant epoxy chemical and physical structure[5,7,8]; (iii) the relations between the physical structure, the modes of deformation and failure, and the mechanical properties of TGDDM–DDS epoxies[9,10] and (iv) how specific combinations of moisture, heat and stress affect their physical and mechanical integrity[9,11–13].

The cure reactions, the viscosity–time–temperature profile, the processing conditions, the resultant epoxy chemical and physical structure, and the mechanical response of a C fibre–TGDDM–DDS cured epoxy composite are modified by the presence of a BF_3-amine complex catalyst within the prepreg. These factors will also be modified by the distribution of the catalyst within the prepreg, its chemical composition and any modification of its structure and activity as a result of exposure to and/or interactions with heat, moisture and the epoxide and amine components within the prepreg.

The two most common BF_3-amine catalysts used commercially to cure epoxies are boron trifluoride-monoethylamine, BF_3:$NH_2C_2H_5$, and boron trifluoride piperidine, BF_3:NHC_5H_{10}, complexes. Such complexes

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

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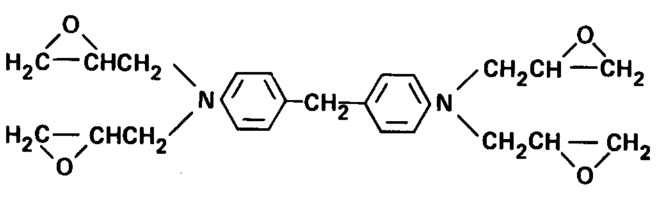
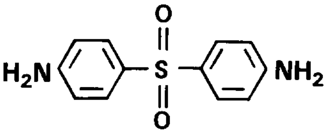
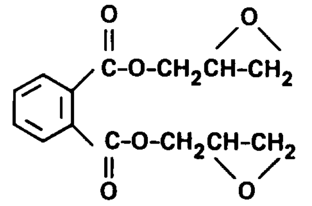


Tetraglycidyl 4, 4′ diaminodiphenyl methane epoxy TGDDM (liquid at 23°C)



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



Diglycidyl orthophthalate (liquid at 23°C)

Figure 1 Chemical structure of the TGDDM, DDS and DGOP monomers

are latent catalysts at room temperature but enhance epoxide group reactivity at higher temperatures. The catalysts have been reported to be very hygroscopic[14,15], and hydrolyse to species that are catalytically inactive[16]. Recently, Zanjana *et al.*[17] have reported the reactivity of a C fibre–TGDDM–DDS prepreg, that contains a BF_3 catalyst, decreases irreversibly after exposure to moisture. These workers suggest that the hydroxyfluoroborates formed as a result of hydrolysis of the catalyst are themselves ineffective catalysts. Also, the effect of heat upon the BF_3 catalysts and the structural form in which these complexes act as catalysts have been areas of controversy over the years. A number of workers have claimed that these complexes only become catalytically active upon their dissociation to BF_3 and the corresponding amine[16,18-21]. However, Harris and Temin[22] have presented evidence[23-25] that dissociation of the BF_3: amine complex is not a prerequisite for catalytic activity. On the contrary, they claim that epoxide group reactivity is enhanced by the non-dissociated BF_3:amine complex rather than by its dissociation products. Also, in the literature a number of mechanisms have been proposed to explain the catalytically enhanced activity of epoxide groups by BF_3:amine complexes[16,20-22,26].

In this paper we report ^{1}H, ^{19}F and ^{11}B n.m.r. studies of BF_3:$NH_2C_2H_5$ and BF_3:NHC_5H_{10} complexes, with principal emphasis on the former. Our aims were to determine: (i) the chemical composition of commercial BF_3:amine complexes, (ii) their thermal stability in the solid-state and also in solution, (iii) the effect of moisture and heat upon their composition, (iv) the nature of their interaction with the epoxide and amine components utilized in TGDDM–DDS commercial prepregs, (v) the composition of BF_3:amine complexes in commercial prepregs, (vi) their thermal stability in the prepregs and (vii) identification of the chemical structure of the predominant catalytic species of the cure reactions of the prepreg.

EXPERIMENTAL

Materials

The BF_3:$NH_2C_2H_5$ samples investigated were obtained from Alfa, Pfaltz and Bauer, Harshaw and K. and K. Chemical Companys. The C fibre–TGDDM–DDS prepregs investigated were Fiberite 934 and Hercules 3501. The reported composition[1] of these prepregs are summarized in *Table 1.*

Experimental

Model compounds and samples of the chemical constituents of the C fibre–TGDDM–DDS prepregs were dissolved in dimethyl sulphoxide (DMSO) and sealed in 5 mm glass tubes suitable for investigation by n.m.r.

For catalyst studies solutions were usually in the 0.5–1.0 M concentration range. Prepreg samples were prepared by cutting a 1.0 gm sample of prepreg material into 0.635 cm pieces, removing the backing and placing the remaining 0.79 gms into a vial equipped with an Al foil lined cap. 3 ml of dry DMSO-d6 were added and the sample was agitated on a rotary stirrer and allowed to stand overnight in order to assure complete solution of the prepreg matrix. All components of the prepreg are soluble in DMSO and we assume from our *FT*i.r. studies[4-7] that insoluble gel particles would not form during standard prepreg fabrication conditions.

Since reactive components were often present in some of these systems it was essential to use dry solvents. In order to ensure that the DMSO was dry it was allowed to stand over freshly recharged (300°C) Linde Molecular Sieve type 4X for several days with periodic stirring then decanted to a second charge of freshly recharged molecular sieve and again allowed a similar drying period. There was no readily detectable H_2O n.m.r. signal in the solvent used.

Spectra were obtained on a NT-200 Fourier Transformer NMR spectrometer using a super conducting magnet. To observe ^{1}H, ^{19}F and ^{11}B signals the spectrometer frequencies were 200.071, 188.228 and 64.190 MHz respectively. The size of the transform used was usually 16K but occasionally a 64K transform was required. A 7 μs 90° pulse was used for ^{1}H and ^{19}F spectra and a 17 μs 90° pulse for ^{11}B spectra. ^{11}B has a nuclear spin of 3/2 and is about 80% naturally abundant. Usually spectra were obtained in a few minutes except for prepreg samples

Table 1 Chemical constituents in prepreg epoxies

	% by weight	
Constituent	Fiberite 934	Hercules 3501
TGDDM (MY 720, Ciba Geigy)	64	75
DDS (Eporal, Ciba Geigy)	25	24
Diglycidyl Orthophthalate Epoxy, DGOP (Gly-Cel-A-100, Celanese)	11	0
BF_3:Amine Complex	0.4	1

where an overnight run was scheduled using a 5 s delay period between pulses and an acquisition time of 1.16 s.

For proton spectra, either an internal (TMS) reference or the residual ^1H peak from the dimethyl sulphoxide −d6 solvent were used. For ^{19}F spectra, an internal $CFCl_3$ reference was sometimes added but usually the sharp lines of the BF_4^- ion were used as a reference. The separation between BF_4^- and BF_3:$NH_2C_2H_5$ multiplets was constant and equal to 0.53 ± 0.02 ppm.

Chemical shifts refer to internal tetramethylene silane (TMS) or $CFCl_3$ references.

Precautions were taken to ensure that spectra could be interpreted quantitatively. N.m.r. peak distortions were avoided by collecting complete free induction decays at low audio frequency (AF) and radio frequency (RF) gain settings. Transform sizes were large enough to provide enough spectral points for good peak integrations.

In a Fourier transform measurement the peak intensity can be lost if the recycle time, i.e. time between stimulating RF pulses, is too short to allow return of the magnetization to its equilibrium value. A recycle time of 10 T_1's, easily fulfills this requirement, where T_1 is the spin–lattice relaxation time. This time can be reduced if a stimulating RF pulse <90° is used. In the present study 90° pulses were used and recycle times were 23 s. In a number of instances spectra taken at recycle times between 2 and 11 s did not differ significantly from each other.

Proton spectra measured before and after heating TGDDM or DDS in the absence of the BF_3:$NH_2C_2H_5$ catalyst were indistinguishable, which suggested that changes in dissolved oxygen content did not change the T_1 values. For any given series of spectra, which were monitored for differences, the data was generated under exactly the same conditions.

RESULTS AND DISCUSSION

Chemical composition

The chemical compositions of the commercial 'BF_3:$NH_2C_2H_5$' samples were investigated by ^1H, ^{19}F and ^{11}B n.m.r.

The ^1H n.m.r. spectrum of BF_3:$NH_2C_2H_5$ should exhibit peaks in three separate regions, namely, the CH_3 region at highest field, the CH_2 region at an intermediate field and the NH_2 region at lowest field. The theoretical peak intensity distribution should be 3:2:2 for the CH_3, CH_2 and NH_2 regions, respectively. In general the subspectra of two chemical components were observed. The major chemical component contributed the following multiplets: a CH_3 triplet (1.090 ppm), a CH_2 quartet (2.612 ppm) and an NH_2 signal (6.156 ppm). The intensity ratios were 3:2:2 respectively and this spectrum was assigned to the $BF_3NH_2C_2H_5$ structure. The CH_2 multiplet exhibited a broad distorted form indicative of additional spin coupling to ^{11}B. In a double resonance experiment, in which the ^{11}B n.m.r. spectrum was obtained while irradiating the protons, a sharpening of the ^{11}B multiplet lines was observed which confirmed the spin coupling. The NH_2 protons showed no indication from n.m.r. of taking part in an exchange process.

A second chemical component was evident in the proton n.m.r. spectra, characterized again by a CH_3 triplet (1.121 ppm), a CH_2 quartet (2.803 ppm) and an NH/OH peak from labile protons (7.27 to 7.63 ppm). Intensity ratios were 3:2:approximately 3. The CH_2 multiplet was sharp and showed no indications of additional spin coupling. These components of the total spectrum are attributed to (BF_4^- or BF_3OH^-)$NH_3^+C_2H_5$ species. The proton intensity measurements indicate that BF_4^- is the dominant anion.

The ^1H n.m.r. spectra for the four 'BF_3:$NH_2C_2H_5$' samples are illustrated in *Figure 2*. The two different resolved multiplets, (a) and (b), for the CH_2 group are illustrated in this Figure. The compositions of the commercial 'BF_3:$NH_2C_2H_5$' samples are summarized in *Table 2*.

The ^{19}F n.m.r. spectra of the commercial 'BF_3:$NH_2C_2H_5$' samples are illustrated in *Figure 3*. The major components identified in the ^{19}F spectra were BF_3:$NH_2C_2H_5$, BF_4^-, $BF_3(OH)^-$ and an unidentified highly reactive BF_3 species with an n.m.r. peak in the region of $BF_3(OH)^-$. The BF_3:$NH_2C_2H_5$ structure, which was identified by ^1H n.m.r., is also consistent with observed 1:1:1:1 ^{19}F and a 1:3:3:1 ^{11}B n.m.r. quartets where $J_{^{11}B,^{19}F} = 17.0$ Hz. There is a poorly resolved 2.5 Hz coupling between ^{19}F nuclei of BF_3 and CH_2 protons while ^{11}B peaks are broadened by an unresolved ^{11}B, CH_2 spin coupling. The BF_4^- species was identified by its known chemical shift[28], together with our independent measurements on $NaBF_4$/DMSO solutions.

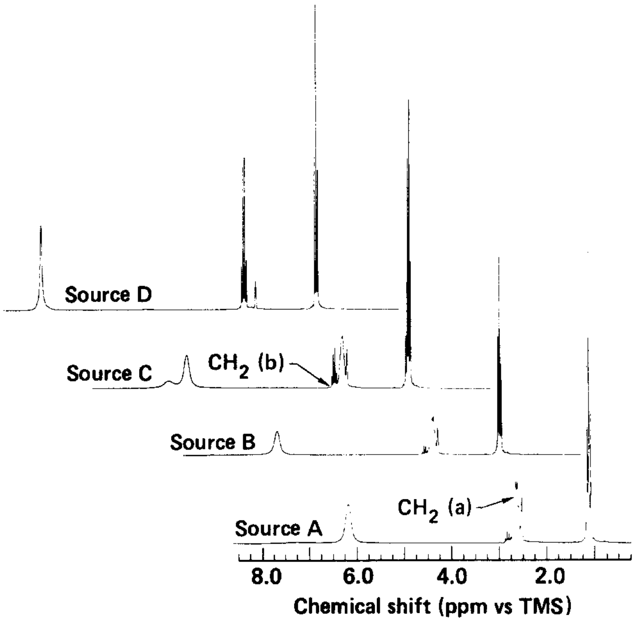


Figure 2 ^1H n.m.r. spectra of commercial 'BF_3:$NH_2C_2H_5$' samples (A-Harshaw; B-Alfa; C-K and K; D-P and B) in which (a) and (b) illustrate two different CH_2 components

Table 2 'BF_3:$NH_2C_2H_5$' compositions from ^1H n.m.r.

	% of C_2H_5 groups as	
Source	BF_3:$NH_2C_2H_5$	(BF_4^- or $BF_3(OH)^-$)$NH_3^+C_2H_5$
Alfa	91.5	8.5
Bauer	0	100
Harshaw	90.0	10.0
K and K	80.5	19.5
Chemical shift vs. TMS reference	$CH_3 = 1.090$ ppm $CH_2 = 2.6115$ ppm $NH_2 = 6.156$ ppm	$CH_3 = 1.1212$ ppm $CH_2 = 2.8026$ ppm $NH_3/OH = 7.4$ (Variable 7.63–7.27)

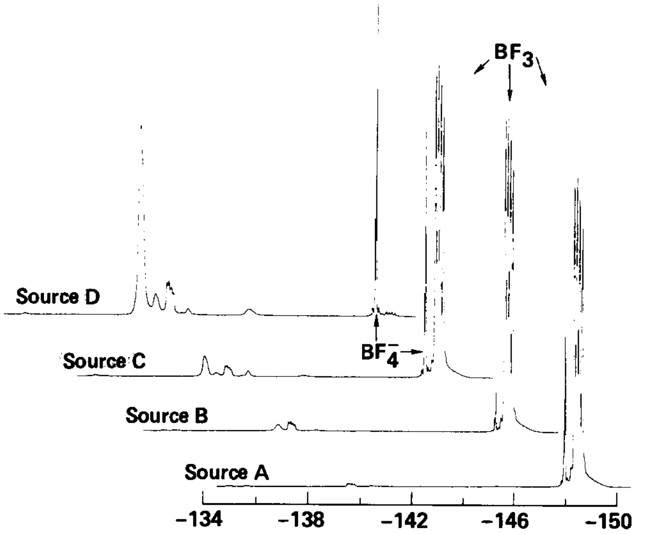


Figure 3 ^{19}F n.m.r. spectra of commercial 'BF_3:$NH_2C_2H_5$' samples (A-Harshaw; B-Alfa; C-K and K; D-P and B)

When a suitably large transform was used, a 1:1:1:1 multiplet pattern was evident with a $J_{^{11}B,^{19}F} = 1.1$ Hz[29]. The $BF_3(OH)^-$ species was identified by (i) its known chemical shift[28,30], (ii) an observed 1:3:3:1 quartet in the ^{11}B n.m.r. spectrum and (iii) the observation of its formation from the reaction of BF_3:$NH_2C_2H_5$ with H_2O (see later section 'Hydrolytic Stability').

The major ^{19}F environment in the Bauer material shows neither the sharp lines of a symmetrical BF_4^- environment, nor the well resolved 1:1:1:1 quartet patterns of amine: BF_3 adducts. Instead a single broad line (50 Hz) is observed in the region of BF_3OH^-. The ^{11}B resonance of this species is also a single broad line. Normal spin–spin coupling constants between directly bonded ^{11}B and ^{19}F nuclei range from 18 Hz in BF_3:amine complexes to 1 Hz in BF_4^- salts. ^{19}F linewidths vary from several Hz in the complexes to several tenths of a Hz in BF_4^- salts. The observation of a single 50 Hz ^{19}F peak must be interpreted as a partially collapsed ^{19}F, ^{11}B spin coupled multiplet since this width is far beyond normal values. Similarly ^{11}B linewidths are one or two Hz in BF_3:amine complexes and less than 1 Hz in BF_4^- species. The observed 55 Hz ^{11}B n.m.r. line is also consistent with a partially collapsed multiplet.

The two most likely mechanisms for multiplet collapse are quadrupolar relaxation of ^{11}B nuclei or chemical exchange with ^{19}F nuclei. However, the chemical exchange mechanism can be ruled out because no measurable temperature dependence was observed for the ^{11}B n.m.r. line width in the 23°C–80°C range. If the ambient temperature exchange rate had been comparable to the multiplet line separation, then raising the temperature, and simultaneously the exchange rate, would have sharpened the ^{11}B n.m.r. line. On the other hand, these results are consistent with a line width related to quadrupolar relaxation of ^{11}B. This relaxation is due to the fluctuating electric field gradients associated with molecular tumbling and is not markedly temperature dependant in cases where the solution viscosity is fairly constant.

A possible structure for the primary component of the Bauer material is $(C_2H_5NH_2)_2BF_2^+$ with an associated F^- or BF_4^- anion. The greater electronic asymmetry about ^{11}B for the $(C_2H_5NH_2)_2BF_2^+$ species compared to BF_3:$NH_2C_2H_5$ and BF_4^- salts would result in increased quadrupolar relaxation. No evidence of spin coupling between CH_2 protons and ^{11}B was observed in a double resonance experiment. Irradiation of protons while obtaining the ^{11}B spectrum of the Bauer material produced no change in linewidth.

We found that the primary component of the Bauer material is extremely reactive with added water. The product gives an n.m.r. spectrum characteristic of BF_3OH^-. Heating a solution of Bauer material converts it to a product having the ^{19}F and ^{11}B spectrum of BF_3:$NH_2C_2H_5$. Thus reactions (1) and 2(a,b) are proposed for the thermal- and moisture-induced reactions respectively.

$$[C_2H_5NH_2BF_2NH_2C_2H_5]^+[BF_4]^- \rightarrow$$
$$\rightarrow 2C_2H_5NH_2BF_3 \quad (1)$$
$$[C_2H_5NH_2BF_2NH_2C_2H_5]^+[BF_4]^- + H_2O \rightarrow$$
$$\rightarrow C_2H_5NH_2BF_2OH + BF_4^-NH_3^+C_2H_5 \quad (2a)$$
$$C_2H_5NH_2BF_2OH + HF \rightarrow BF_3(OH)^-NH_3^+C_2H_5 \quad (2b)$$

The fluorine species observed in the commercial samples are illustrated in *Table 3*, in which several other observed ^{19}F n.m.r. peaks are combined under the heading 'Miscellaneous'.

From these studies it was also noted that, on the n.m.r. time scale BF_3:$NH_2C_2H_5$ does not undergo rapid chemical exchange between (i) its amine protons and the protons of other amines, H_2O or NH_3^+ species and (ii) its fluorine atoms and those of BF_3 and BF_4^- species, or HF introduced as a dry gas.

The chemical composition of a 'BF_3:NHC_5H_{10}' sample was also investigated by ^{19}F n.m.r. Three fluorine containing environments were found with fluorine distributed as follows, (i) BF_3:NHC_5H_{10} (87.3%); (ii) $BF_4^-NH_2^+C_5H_{10}$ (11.5%) and (iii) $BF_3(OH)^-NH_2^+C_5H_{10}$ (0.2%). Peak assignments were based on our previous investigations of 'BF_3:$NH_2C_2H_5$'. N.m.r. parameters for

Table 3 Fluorine species in 'BF_3:$NH_2C_2H_5$' from ^{19}F n.m.r.

	% of total fluorine as				
Source	BF_3:$NH_2C_2H_5$	BF_4^-	$BF_3(OH)^-$	Reactive BF_3	Miscellaneous
Alfa	92.5	2.5	2.9	2.0	0.1
Bauer	1.9	15.3	12.4	57.3	13.1
Harshaw	89.7	8.9	0.9	—	0.5
K and K	78.1	11.1	3.1	4.8	2.9
Chemical shift vs. $CFCl_3$ reference	−140.318 ppm	−139.775 ppm	−131.676 ppm	−131.506 ppm	—

the piperidine adduct were, chemical shift (−155.17 ppm), $J_{^{11}B,^{19}F} = 18.3$ Hz.

Thermal stability

Solid '$BF_3:NH_2C_2H_5$' samples that were annealed at 85°C, 115°C or 139°C for 1 hour and then subsequently dissolved in DMSO exhibited no significant dissociation as detected by the ^1H n.m.r. spectra illustrated in *Figure 4*. These data are consistent with Harris and Temins[22] observations that BF_3:amine complexes do not dissociate irreversibly to gaseous BF_3 and amine products. (The '$BF_3:NH_2C_2H_5$' was observed to melt near 85°C during these studies.)

However, ^{19}F n.m.r. studies indicate that a small amount of the $BF_3:NH_2C_2H_5$ may slowly convert to BF_4^- and to another species which we do not detect in the ^{19}F spectrum. There is a loss of fluorine as illustrated in *Table 4*. The small % of $BF_3(OH)^-$ species present in the unannealed sample disappears after annealing for 1 h at 85°C. The loss of fluorine noted here could be the result of the formation of a gaseous product insoluble in DMSO, or could be caused by the formation of species which undergo chemical exchange at an intermediate rate on the n.m.r. time scale. For example, we have found that adding hydrogen fluoride gas to a typical dry DMSO solution of the '$BF_3:NH_2C_2H_5$' components initially provides a HF doublet at −166.1 ppm ($J_{HF} = 413$ Hz). As the amount of HF is increased both the HF doublet components and the BF_3OH^- ^{19}F quartet broaden. A further increase in the HF concentration causes the BF_3OH^- signal to become undetectable due to an intermediate rate of exchange with HF type fluorines. On the other hand ^{19}F nuclei of BF_4^- species and $BF:_3NH_2C_2H_5$ are unaffected by the addition of hydrogen fluoride. Evidence of intermediate chemical exchange rates has been reported by Mesmer and Rutenburg[30] in ^{19}F studies of similar systems at 84.67 M Hz. The relative stabilities of BF_4^- and $BF_3(OH)^-$ species have also been noted by Anbar and Gutman[27].

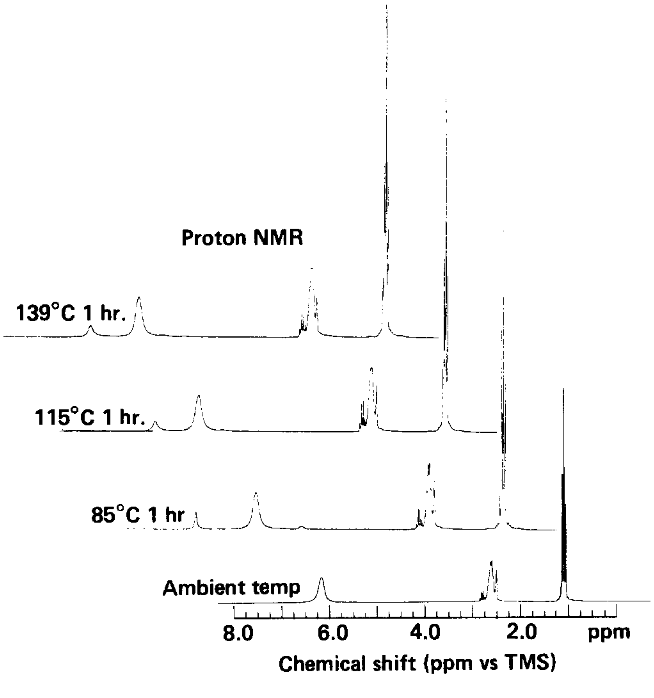


Figure 4 ^1H n.m.r. spectra of '$BF_3:NH_2C_2H_5$' as a function of annealing temperature

Table 4 Effect of thermal annealing on the fluorine species in '$BF_3:NH_2C_2H_5$' from ^{19}F n.m.r.

	% Total original fluorine as			
Anneal conditions	Fluorine loss	$BF_3(OH)^-$	BF_4^-	$BF_3:NH_2C_2H_5$
Original, unannealed solid	0	6.1	1.6	92.3
1 h, 85°C	8.1	0	11.8	80.1
1 h, 115°C	2.7	0	13.8	83.5
1 h, 140°C	9.7	0	13.7	76.6

Table 5 Effect of heating on the fluorine species in $BF_3:NH_2C_2H_5$/DMSO solution from ^{19}F n.m.r.

	% Total original fluorine as			
Heat conditions	Fluorine loss	$BF_3(OH)^-$	BF_4^-	$BF_3:NH_2C_2H_5$
Unheated solution	0	6.1	1.6	92.3
1 hr, 85°C	5.1	0	13.1	81.8
1 h, 115°C	12.9	0	34.7	52.4
1 h, 140°C	27.3	0	60.2	12.5

If $BF_3:NH_2C_2H_5$ is heated directly in DMSO the conversion to BF_4^- and the % fluorine loss is considerably greater than heating $BF_3:NH_2C_2H_5$ in the absence of the solvent, as illustrated in *Table 5*. The conversion of the $BF_3:NH_2C_2H_5$ to BF_4^- species with associated fluorine loss may occur via the same mechanism in each case but at a faster rate in solution. However, we also cannot rule out the possibility of a reaction between the $BF_3:NH_2C_2H_5$ and the DMSO solvent that enhances conversion to BF_4^- species.

$BF_3:NHC_5H_{10}$ exhibits similar thermal stability trends as $BF_3:NH_2C_2H_5$. For example, a sample with an initial fluorine distribution of $BF_3:NHC_5H_{10}$ (88.3%), $BF_4^-NH_2^+C_5H_{10}$ (11.5%) and $BF_3(OH)^-NH_2^+C_5H_{10}$ (0.24%) loses ~6% $BF_3:NHC_5H_{10}$ type fluorine and ~3% total fluorine and gains ~3% BF_4^- fluorine after annealing for 1 h at 85°C in the absence of a solvent. However, in DMSO solution the $BF_3:NHC_5H_{10}$ disappears at a considerably faster rate than $BF_3:NH_2C_2H_5$ for similar thermal exposure conditions. For example, after heating a '$BF_3:NHC_5H_{10}$'/DMSO solution for 1 h at 85°C, there is 45% BF_4^- type fluoride present and only 53% remains as $BF_3:NHC_5H_{10}$. In comparison, after exposing '$BF_3:NH_2C_2H_5$'/DMSO solutions to similar conditions, 86% of the fluorine remains as $BF_3:NH_2C_2H_5$.

Hydrolytic stability

^{19}F n.m.r. studies of '$BF_3:NH_2C_2H_5$'/DMSO solutions indicated that little change occurred in the amounts of $BF_3:NH_2C_2H_5$, BF_4^- and $BF_3(OH)^-$ species in the presence of added H_2O. For example, in a mixture of 7.7 moles H_2O + 1 mole '$BF_3:NH_2C_2H_5$' the $BF_3(OH)^-$ type fluorine increased from 0.9% to 1.8% after a period of 4 days at 23°C. However, the highly reactive $C_2H_5NH_2BF_2NH_2C_2H_5^+BF_4^-$ species reported in the chemical composition section, reacted instantaneously with H_2O at ambient conditions to form the BF_3OH^- species.

If a large (10 fold) excess of H_2O is added to the '$BF_3:NH_2C_2H_5$'/DMSO solution and the temperature raised to 85°C for 1 h, the amount of fluorine present as

BF_3:$NH_2C_2H_5$ decreased by ~50% while that present as $BF_3(OH)^-NH_3^+C_2H_5$ increases from 5% to 40%. There is an accompanying loss of ~15% fluorine. Again fluorine loss may be indicative of a reaction between $BF_3(OH)^-$ and the glass sample tube surface or the n.m.r. line is made immeasurably broad by chemical exchange.

The more stable BF_4^- species were unaffected by exposure to H_2O at 85°C.

The 'BF_3:NHC_5H_{10}' species in DMSO behaved similar to the corresponding 'BF_3:$NH_2C_2H_5$' species upon exposure to H_2O at 23°C and 85°C.

Interaction of 'BF_3:$NH_2C_2H_5$' with DDS, TGDDM and DGOP

^1H and ^{19}F n.m.r. were utilized to study the interaction of the individual resin components of the C fibre–TGDDM–DDS prepegs with 'BF_3:$NH_2C_2H_5$'. For both the 'BF_3:$NH_2C_2H_5$'–DDS and 'BF_3:$NH_2C_2H_5$' epoxide interaction studies we present first ^1H and then ^{19}F results in order to characterize the details of any reactions that occur. The ^1H n.m.r. studies were essential in detailing the reactivity of the DDS and epoxide molecules. Quantitative aspects of the catalyst reactivity were best obtained from the ^{19}F spectra where multiplet overlap was not a problem.

It was determined that the ^1H n.m.r. spectrum of DDS in DMSO does not change when BF_3:$NH_2C_2H_5$ is added at ambient temperature. 'BF_3:$NH_2C_2H_5$'/DDS/DMSO solutions were then monitored after heating for 1 h at 85°C, 115°C or 139°C. The spectrum of DDS in *Figure 5* exhibits multiplets from 2 chemically different aromatic type protons, those in H_a (7.428 and 7.472 ppm) and H_b (6.561 and 6.603 ppm) environments. The DDS amine proton peak is at higher field, 5.987 ppm. In *Figure 5* it is illustrated that upon heating 'BF_3:$NH_2C_2H_5$'/DDS/DMSO solutions, there is no shift in the position of the DDS amine proton resonance. Neither do new aromatic proton environments emerge to indicate BF_3:DDS complexes. (Concentrations were such as to provide about one DDS amine group for each $BF_3NH_2C_2H_5$ molecule.) The broad CH_2 multiplet associated with BF_3:$NH_2C_2H_5$ in the proton spectra does, however, decrease with increasing temperature exposure ultimatly resulting in a sharp CH_2 quartet which is associated with either $BF_4^-NH_3^+C_2H_5$ or $BF_3(OH)^-NH_3^+C_2H_5$ species.

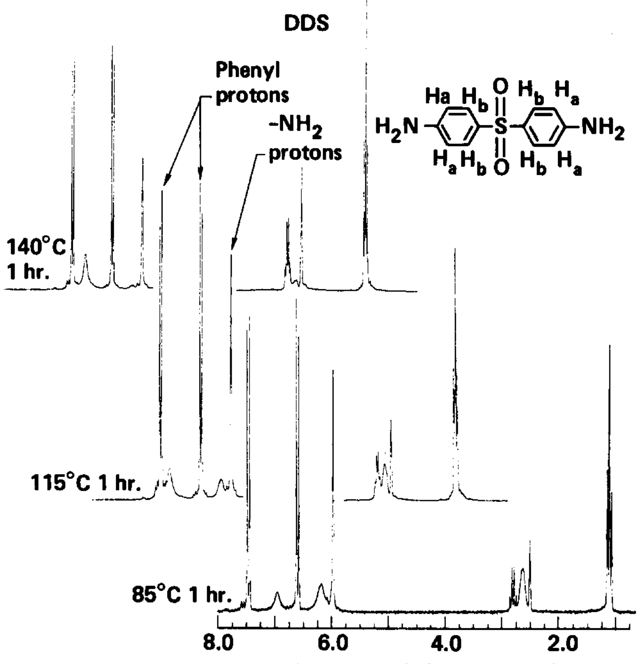
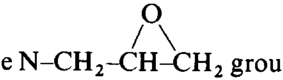


Figure 5 ^1H n.m.r. spectra of 'BF_3:$NH_2C_2H_5$'/DDS/DMSO solutions as a function of thermal exposure

^{19}F n.m.r. studies also indicate that significant changes in the BF_3 species occurs upon heating 'BF_3:$NH_2C_2H_5$'/DDS/DMSO solutions as illustrated in *Table 6*. *Table 6* shows that the BF_3:$NH_2C_2H_5$ species converts to the $BF_4^-NH_3^+C_2H_5$ salt with accompanying fluorine loss upon exposure to temperatures in the 85°C–140°C range. The degree of conversion to the BF_4^- salt, for the same thermal exposure, is similar to that observed in 'BF_3:$NH_2C_2H_5$'/DMSO solution, *Table 5*, in the absence of DDS. Hence, we have no direct evidence that DDS competes with $C_2H_5NH_2$ for BF_3 molecules or that DDS enhances BF_4^- salt formation upon heating in DMSO solution. The close proximity of the phenyl groups to the NH_2 groups in DDS lowers the electron donating power of these NH_2 groups and thus will inhibit strong complex formation with the electron acceptor BF_3 molecules.

The ^1H n.m.r. spectra of 'BF_3:$NH_2C_2H_5$'/TGDDM/DMSO solutions were investigated as a function of thermal exposure (*Figure 6*). Heating the solution for 1 hour at 85°C did not produce changes in the ^1H spectra. However, exposures to 115°C or 139°C for 1 hour did produce significant spectral changes. The unmodified TGDDM ^1H n.m.r. spectrum contains two doublets centred at 7.022 and 6.763 ppm which are associated with the two types of aromatic protons. The five different chemical proton environments associated with the  $N{-}CH_2{-}\overset{O}{CH{-}CH_2}$ group result in the series of peaks in the 2.500–3.500 ppm region. We have not attempted to assign peaks in this region to specific proton environments. The essential disappearance of the TGDDM aromatic proton doublets and the modification of the spectral region associated with the TGDDM aliphatic protons after heating for 1 hour at 115°C and 139°C confirms that $BF_3NH_2C_2H_5$ reacts extensively with the TGDDM epoxide.

^{19}F n.m.r. studies, illustrated in *Table 7*, indicate the TGDDM epoxide enhanced BF_4^- salt formation in DMSO solution. For example, after exposure to 115°C for 1 hour all the BF_3:$NH_2C_2H_5$ species have disappeared in the presence of TGDDM. However, in DMSO solution in the absence of TGDDM, 50% of the total fluorine species are still in the form of BF_3:$NH_2C_2H_5$ after 1 hour exposure at 115°C, *Table 5*.

The DGOP epoxide also reacts with the

Table 6 Effect of heating on the fluorine species in 'BF_3:$NH_2C_2H_5$'/DDS/DMSO solution from ^{19}F n.m.r.

	% Total original fluorine as			
Heat conditions	Fluorine loss	$BF_3(OH)^-$	BF_4^-	BF_3:$NH_2C_2H_5$
Unheated solution	0	6.1	1.6	92.3
1 hr, 85°C	8.8	0	18.4	72.8
1 h, 115°C	22.3	0	39.3	38.4
1 h, 140°C	27.3	0	59.6	13.1

BF_3:$NH_2C_2H_5$ catalyst because upon heating a 'BF_3:$NH_2C_2H_5$'/DGOP/DMSO solution the ^1H and ^{19}F spectra exhibited similar spectra modification as those observed in the 'BF_3:$NH_2C_2H_5$'/TGDDM/DMSO solution.

Catalyst composition in prepregs

The catalyst composition in Fiberite 934 and Hercules 3501 prepregs was investigated by ^{19}F n.m.r. The epoxy resin in these commercial C fibre–TGDDM–DDS prepregs was dissolved in DMSO.

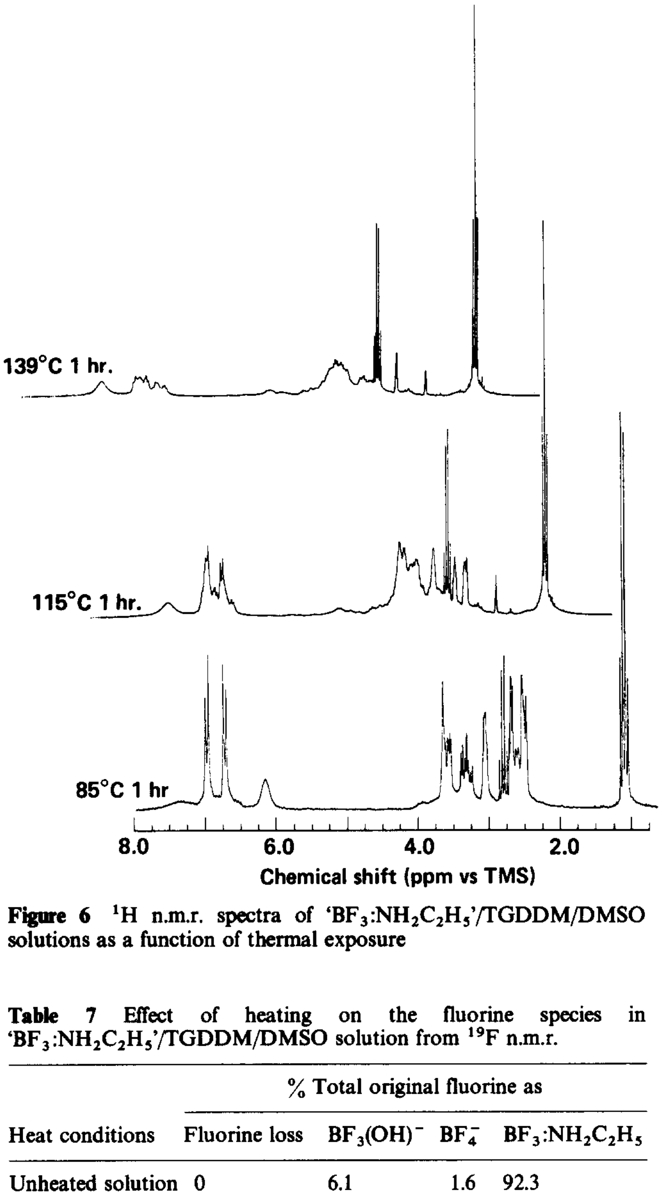


Figure 6 ^1H n.m.r. spectra of 'BF_3:$NH_2C_2H_5$'/TGDDM/DMSO solutions as a function of thermal exposure

Table 7 Effect of heating on the fluorine species in 'BF_3:$NH_2C_2H_5$'/TGDDM/DMSO solution from ^{19}F n.m.r.

	% Total original fluorine as			
Heat conditions	Fluorine loss	$BF_3(OH)^-$	BF_4^-	BF_3:$NH_2C_2H_5$
Unheated solution	0	6.1	1.6	92.3
1 h, 85°C	19.4	0	17.8	62.8
1 h, 115°C	23.0	0	77.0	0
1 h, 140°C	20.6	0	79.4	0

The fluorine species observed in five different lots of Fiberite 934 were identified and tabulated in *Table 8*. A typical spectrum is shown in *Figure 7*. The catalyst in this prepreg was identified as $BF_3NH_2C_2H_5$ by ^{19}F n.m.r. There is considerable variation in the $BF_4^-NH_3^+C_2H_5$ (14.6–60.0%) and the BF_3:$NH_2C_2H_5$ (7.2–48.6%) species from lot to lot.

We associate the various additional fluorine peaks observed in the n.m.r. spectra with principally the products of epoxide—active fluorine species reactions. The total fluorine in the form of these products is relatively constant from prepreg lot to lot (28.2–36.3%).

The epoxy resin of a Hercules 3501 sample was dissolved in DMSO and investigated by ^{19}F n.m.r. The ^{19}F peaks associated with BF_3:$NH_2C_2H_5$ were absent and the 1:1:1:1 quartet associated with BF_3:NHC_5H_{10} was found at an ^{19}F chemical shift value of -155.17 ppm. The fluorine distribution among species found in this sample was $BF_3(OH)^-$:$NH_2^+C_5H_{10}$ (2.8%); $BF_4^-NH_2^+C_5H_{10}$ (9.9%); BF_3:NHC_5H_{10} (78.3%) and epoxide–fluorine products (9.0).

The Fiberite 934 prepreg was exposed to a series of temperature–time profiles, and the soluble epoxy resin portion dissolved in DMSO and studied by ^{19}F n.m.r. The ratios of the intensity of the peak associated with BF_3:$NH_2C_2H_5$ (I_{BF_3}) to that intensity of the $BF_4^-NH_3^+C_2H_5$ ($I_{BF_4^-}$) species as a function of exposure conditions are tabulated in *Table 9*. With increasing annealing temperature the BF_3:$NH_2C_2H_5$ species con-

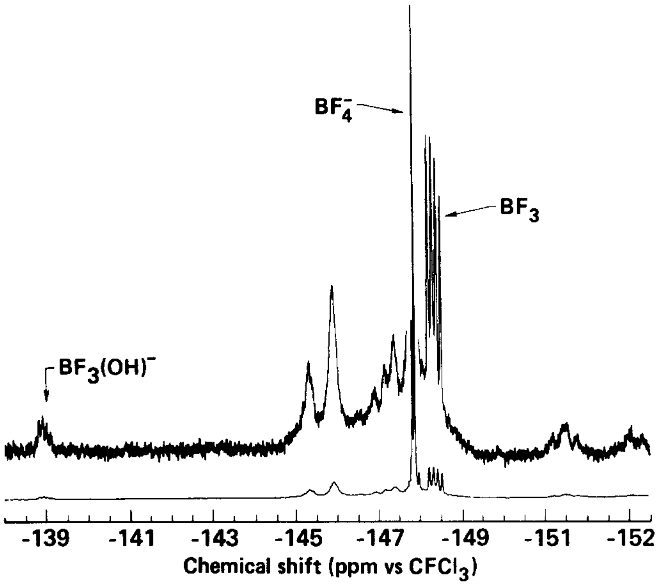


Figure 7 ^{19}F n.m.r. spectrum of DMSO extracted components from Fiberite 934 fibre composite prepreg

Table 8 Fluorine species in Fiberite 934 lots

	% of total fluorine as			
	$BF_3(OH)^-NH_3^+C_2H_5$	$BF_4^-NH_3^+C_2H_5$	BF_3:$NH_2C_2H_5$	Epoxide–BF_3 products
C2–709	3.8	38.8	25.2	32.2
C3–218	4.6	60.0	7.2	28.2
C3–389	0.5	14.6	48.6	36.3
C3–397	1.5	44.4	22.4	31.7
C3–546	1.4	49.1	18.2	31.3

Table 9 Effect of temperature, time and H_2O on the relative extractable $BF_3:NH_2C_2H_5$ and $BF_4^-NH_3^+C_2H_5$ species in Fiberite 934

Exposure conditions	$I_{BF_3}/I_{BF_4^-}$
Ambient	0.718; 0.748
50°C; 1 h	0.539
50°C; 5 h	0.554
75°C; 1 h	0.494
100°C; 1 h	0.146
100°C; 1 h+steam	0.326

centration decreases relative to the $BF_4^-NH_3^+C_2H_5$ species. The presence of steam slows the relative disappearance of the $BF_3:NH_2C_2H_5$ species.

Catalytic mechanisms and activity

Our n.m.r. studies indicate $BF_3:NH_2C_2H_5$ is slowly converted to the $BF_4^-NH_3^+C_2H_5$ salt with corresponding loss of fluorine upon heating the solid catalyst. This conversion to the salt is accelerated in DMSO solution and further accelerated in TGDDM/DMSO and DGOP-/DMSO solutions with an associated 20–30% loss of fluorine upon near complete conversion to the salt. We will now consider the catalytic mechanisms and activity of $BF_3:NH_2C_2H_5$ towards the TGDDM–DDS cure reactions in the light of our n.m.r. observations.

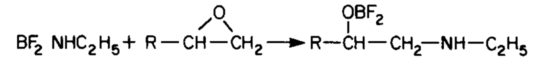
In the absence of other species, $BF_3:NH_2C_2H_5$ could disproportionate as follows

$$2BF_3:NH_2C_2H_5 \rightleftharpoons BF_4^-NH_3^+C_2H_5 + BF_2NHC_2H_5 \quad (3)$$

or

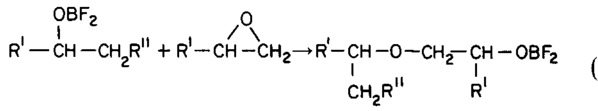
$$2BF_3:NH_2C_2H_5 \rightleftharpoons [BF_4]^-[BF_2(NH_2C_2H_5)_2]^+ \quad (4)$$

Brown[23] and Ryss and Dorskaya[25] have reported reactions similar to reaction (3) for $BF_3:NHR_2$ complexes and we have suggested reaction (4) regarding the extremely reactive species found in commercial '$BF_3:NH_2C_2H_5$' from Pfaltz and Bauer. In either case the equilibria would be shifted toward BF_4^- formation by a reaction between BF_2 species and epoxy groups, to form the monoboroester, e.g. reaction (5).



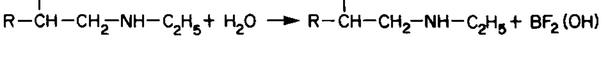
$$BF_2\,NHC_2H_5 + R{-}\overset{O}{CH{-}CH_2} \longrightarrow R{-}\overset{OBF_2}{\overset{|}{C}H}{-}CH_2{-}NH{-}C_2H_5 \quad (5)$$

Landua[21] has proposed that the monoboroester acts as a catalyst for epoxide–epoxide reactions.



$$R'{-}\overset{OBF_2}{\overset{|}{C}H}{-}CH_2R'' + R'{-}\overset{O}{CH{-}CH_2} \rightarrow R'{-}\underset{CH_2R''}{\underset{|}{C}H}{-}O{-}CH_2{-}\underset{R'}{\underset{|}{C}H}{-}OBF_2 \quad (6)$$

However, Landua[21] notes that catalyst deactivation occurs if other chains are initiated on the same boron atom by displacement of fluorine atoms. Furthermore, the monoboroester is also susceptible to hydrolysis[21] and resultant deactivation:

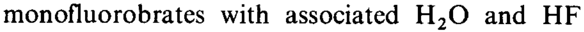


$$R{-}\overset{OBF_2}{\overset{|}{C}H}{-}CH_2{-}NH{-}C_2H_5 + H_2O \longrightarrow R{-}\overset{OH}{\overset{|}{C}H}{-}CH_2{-}NH{-}C_2H_5 + BF_2(OH) \quad (7)$$

$$BF_2(OH) + 2\,H_2O \longrightarrow B(OH)_3 + 2\,HF \quad (8)$$

$$2\,B(OH)_3 \longrightarrow B_2O_3 + 3\,H_2O \quad (9)$$

An alternative reaction path for salt formation is a direct reaction of the $BF_3:NH_2C_2H_5$ with an epoxide, resulting in HF formation.



$$BF_3:NH_2C_2H_5 + R{-}\overset{O}{CH{-}CH_2} \longrightarrow R{-}\overset{OBF_2}{\overset{|}{C}H}{-}CH_2{-}NH{-}C_2H_5 + HF \quad (10)$$

The HF generated then reacts with another $BF_3:NH_2C_2H_5$ to form the salt.

$$BF_3:NH_2C_2H_5 + HF \longrightarrow BF_4^-NH_3^+C_2H_5 \quad (11)$$

The HF from reactions (8) and (10) can also react with the components of the prepreg resulting in a variety of C–F containing species. The formation of the BF_4^- salt requires two $BF_3:NH_2C_2H_5$ molecules to be in close proximity. Hence, the formation of the BF_4^- salt will intimately depend on the dispersion of the small quantity (0.4 wt%) of the $BF_3:NH_2C_2H_5$ catalyst within the prepreg and, therefore, as such could be highly variable.

There are reports in the literature of H_2O deactivating the catalytic activity of $BF_3:NH_2C_2H_5$.[16,17] Our n.m.r. studies indicate that $BF_3:NH_2C_2H_5$ can hydrolyse to form the hydroxy fluoroborate salt, particularly at more extreme conditions (i.e. 85°C).

$$BF_3:NH_2C_2H_5 + H_2O \rightleftharpoons BF_3(OH)^-NH_3^+C_2H_5 \quad (12)$$

Mesmer and Rutenberg[30] have reported $BF_3(OH)^-$ species are less stable than BF_4^- species and can further hydrolyse to less fluorinated borates.

$$BF_3(OH)^-NH_3^+C_2H_5 \rightarrow BF_2(OH) + NH_2C_2H_5 + HF \quad (13)$$

$$BF_2(OH) + 2H_2O \rightarrow B(OH)_3 + 2HF \quad (14)$$

The more active $BF_3(OH)^-$ species could also react with the components of the prepreg. For example, the $BF_3(OH)^-$ species could react with epoxies to form monofluorobrates with associated H_2O and HF formation. However, our differential scanning calorimetry (d.s.c.) studies[31] indicate that when the $BF_3(OH)^-NH_3^+C_2H_5$ salt is substituted for $BF_3:NH_2C_2H_5$ in a TGDDM/DDS/DGOP prepreg mix the cure reactions are not modified. This suggests that the $BF_3(OH)^-NH_3^+C_2H_5$ dehydrates back to $BF_3:NH_2C_2H_5$ during the early stages of cure. If, however, a TGDDM/DDS/DGOP/$BF_3:NH_2C_2H_5$ prepreg is directly exposed to H_2O vapour at 85°C, d.s.c. studies do indicate[31] either (i) a catalytic species is poisoned (probably the monofluoroborate) and/or (ii) the $BF_3:NH_2C_2H_5$ catalyst is leached out of the prepreg.

$BF_3:NH_2C_2H_5$ catalyst deactivation could also occur as a result of the presence of impurities in the prepreg. Mica, asbestos and alkaline materials (i.e. $CaCO_3$) have been reported to deactivate the catalyst[16].

The chemical reactions, (3) through (14), indicate that all BF_3 and BF_3-prepregs species, with the exception of the $BF_4^-NH_3^+C_2H_5$ salt, are susceptible to transformation to less active or non-active catalytic species. Furthermore, our n.m.r. results indicate that the $BF_4^-NH_3^+C_2H_5$ salt does not irreversibly, chemically react with the prepreg components.

For each epoxide group to be catalysed by a BF_3

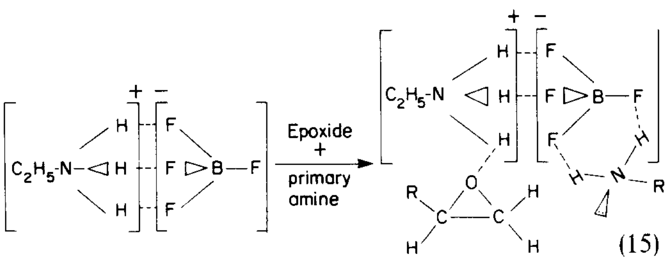
species in a prepreg containing 0.4 wt% 'BF_3:$NH_2C_2H_5$' catalyst requires each catalytic species to act as a catalyst to ~200 epoxide groups. This means each BF_3 catalytic species has to be chemically stable and mobile. Hence, we suggest that the $BF_4^-NH_3^+C_2H_5$ salt is the predominant catalytic species for the prepreg cure reactions, with the more active BF_3 species becoming deactivated and/or immobilized during the early stages of cure. Harris and Temin[22] have reported that BF_3:amine complexes and their corresponding BF_4^- salts cure epoxides in the same temperature range and cure times. This observation is consistent with the BF_4^- salt being the predominant catalytic species and the BF_3:amine complex coverting to the BF_4^- salt in the presence of epoxide groups. Our d.s.c. studies of the cure reactions of a typical TGDDM/DDS/DGOP/'BF_3:$NH_2C_2H_5$' commercial prepreg containing 0.4 wt% 'BF_3:$NH_2C_2H_5$' confirm that the $BF_4^-NH_3^+C_2H_5$ salt is the predominant catalytic species[31]. These studies indicate that the cure reactions occur (i) 50% by $BF_4^-NH_3^+C_2H_5$ catalysed reactions, (ii) 25% by BF_3:$NH_2C_2H_5$ catalysed reactions and (iii) 25% by non-catalysed reactions.

Our systematic *FT*i.r. studies of the cure reactions of TGDDM–DDS epoxies[4–7] indicate that the principal cure reactions are primary amine–epoxide, secondary amine–epoxide and epoxide–hydroxide reactions. The primary amine–epoxide reaction is an order of magnitude faster than the other reactions and dominates the first third of the cure process. A knowledge of the viscosity–time–temperature profile of the prepreg during the early stages of cure is necessary if void-free composites are to be produced, by squeezing-out excess resin and voids at low viscosity. It is critical, therefore, that we understand the parameters that control the viscosity–time–temperature profile during the early stages of cure. Our studies indicate the catalytic activity of the $BF_4^-NH_3^+C_2H_5$ salt and BF_3:$NH_2C_2H_5$ toward the primary amine–epoxide cure reaction will directly affect the processing of acceptable composite components.

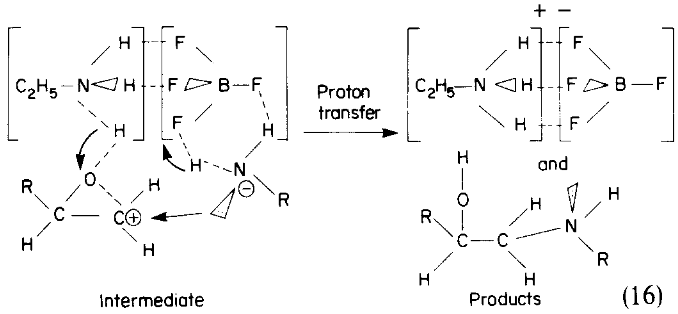
Let us consider the catalytic mechanism of the $BF_4^-NH_3^+C_2H_5$ salt towards the primary amine–epoxide reaction. In BF_3, boron has an empty outer electron orbital and as such is a strong electron acceptor (Lewis acid). However, in the case of the $BF_4^-NH_3^+C_2H_5$ salt the outer electronic orbitals of boron are full, but the ionic nature of the salt allows it to act as a cationic catalyst towards the epoxide groups during cure. The ionic $BF_4^-NH_3^+C_2H_5$ salt can be stabilized by 3 hydrogen bonds as illustrated in reaction (15). The protons of the RNH_3^+ ion can be assigned a formal $+1/3$ charge and will interact with the electronegative oxygen of an epoxide group. Also the formal $-1/4$ charges of fluorine atoms of BF_4^- make them suitable donor sites for hydrogen bonding with primary amines. Thus a stabilized catalyst molecule is able to bring into close proximity the two reactant epoxide and amine molecules as illustrated in reaction (15).

The epoxide amine condensation reaction can proceed via proton transfer reaction as illustrated in reaction (16). These reactions together with an attack by CH_2^+ on the correctly oriented N^- leads to the reaction product and a regenerated $BF_4^-NH_3^+C_2H_5$ catalyst molecule.

Arnold[20], Landua[21] and Harris and Temin[22] have previously proposed the formation of a transitory, intermediate carbonium ion for BF_3 catalysed epoxide–epoxide reactions.

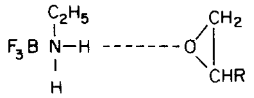


(15)



(16)

The catalytic mechanism by which BF_3:$NH_2C_2H_5$ enhances epoxide group reactivity has been considered by a number of workers[16,20–22,26]. The most plausible is that of Harris and Temin[22] in which the electronic distribution of the epoxide group is biased by the undissociated BF_3:$NH_2C_2H_5$ forming a transitory species(17).



(17)

CONCLUSIONS

^1H, ^{19}F and ^{11}B n.m.r. studies indicate the chemical compositions of commercial 'BF_3:$NH_2C_2H_5$' and 'BF_3:NHC_5H_{10}' samples are variable and contain BF_4^- and $BF_3(OH)^-$ salts together with another unidentified highly reactive species believed to be $[(C_2H_5NH_2)_2BF_2^+][BF_4^-]$.

At 85°C and above, solid BF_3:$NH_2C_2H_5$ slowly converts to the $BF_4^-NH_3^+C_2H_5$ salt with associated fluorine loss. This salt formation is accelerated in DMSO solution, and further accelerated in the presence of the TGDDM and DGOP prepreg epoxides. There is no evidence the prepreg DDS amine curing agent interacts chemically with the BF_3:$NH_2C_2H_5$.

In the presence of H_2O, BF_3:$NH_2C_2H_5$ readily hydrolyses to $BF_3(OH)^-NH_3^+C_2H_5$ at 85°C. At ambient conditions, however, this hydrolysis is slow with little detectable reaction occurring after 4 days.

In commercial TGDDM–DDS–C fibre 934 and 3501 prepregs 'BF_3:$NH_2C_2H_5$' and 'BF_3:NHC_5H_{10}' were respectively identified as the prepreg catalytic species. These catalytic species were in the form of the BF_3:amine complex, its BF_4^- salt and a variety of boron–fluorine–prepreg species. The quantities of the BF_3:$NH_2C_2H_5$ and $BF^{-4}NH_3^+C_2H_5$ species relative to the total fluorine in the prepreg varied considerably from prepreg lot to lot, i.e. BF_3:$NH_2C_2H_5$ (7–49% range) and $BF_4^-NH_3^+C_2H_5$ (15–60% range). Upon heating the prepreg the BF_3:$NH_2C_2H_5$ is converted to the $BF_4^-NH_3^+C_2H_5$ salt with associated loss of fluorine.

The chemically stable and mobile $BF_4^-NH_3^+C_2H_5$ salt is identified as the predominant catalytic species and acts as a cationic catalyst for the prepreg cure reactions. The more reactive BF_3–amine and -prepreg species are susceptible to conversion to other species with possible catalytic deactivation and immobilization during the early stages of cure.

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REFERENCES

1 May, C. A., 'Exploratory Development of Chemical Quality Assurance and Composition of Epoxy Formulations', Air Force Materials Laboratory Report, AFML-TR-76-112 (1976)

2 Carpenter, J. F., 'Quality Control of Structural Nonmetallics', McDonnell Aircraft Report, Contract No. N00019-76-C-0138 (1977)

3 Trujillo, R. E. and Engler, B. P., 'Chemical Characterization of Composite Prepreg Resins', Part 1, Sandia Laboratory Report, SAND 78-1504 (1978)

4 Mones, E. T. and Morgan, R. J. *Polym. Prepr., A.C.S.*, 1981, **22**, 249

5 Mones, E. T., Walkup, C. M., Happe, J. A. and Morgan, R. J. Proc. of 14th National SAMPE Techn. Conf., Atlanta, 1982, 89

6 Morgan, R. J. in 'The Role of the Polymeric Matrix in Processing and Structural Properties of Composite Materials', (Eds. J. Seferis and G. Nicolais), Plenum Press, 1983, 207

7 Morgan, R. J., Happe, J. E. and Mones, E. T., Proc. of 28th National SAMPE Symposium, Anaheim, 1983, 596

8 Morgan, R. J. and Mones, E. T. in 'Resins for Aerospace', A.C.S. Symposium Series 132, (Ed. C. A. May), A.C.S., Washington DC, 1980, Ch. 18

9 Morgan, R. J. and O'Neal, J. E. *Polym. Plast. Tech. Eng.* 1978, **10(1)**, 49

10 Morgan, R. J., O'Neal, J. E. and Miller, D. B. *J. Mater. Sci.* 1979, **14**, 109

11 Morgan, R. J. and Mones, E. T. *Composites Tech. Rev.* 1980, **2**, 14

12 Morgan, R. J., O'Neal, J. E. and Fanter, D. L. *J. Mater. Sci.* 1980, **15**, 751

13 Morgan, R. J. in 'Developments in Reinforced Plastics—1', (Ed. G. Pritchard), Applied Science Publishers Ltd., 1980, Ch. 7

14 Harshaw Chemical Co., Technical Bulletin, 71781, 1978

15 Carpenter, J. F., Proc. of 24th National SAMPE Symposium, 1979, **24**, 446

16 Lee, H. and Neville, K. 'Handbook of Epoxy Resins', McGraw-Hill, New York, 1967

17 Sanjana, Z. M., Schaefer, W. H. and Ray, J. R. *Polym. Eng. Sci.* 1981, **21**, 474

18 Oakes, B. and Voss, D. L. British Pat., 1959, **885**, 749

19 Lee, H. and Neville, K. *S.P.E. Journal* 1960, **16**, 315

20 Arnold, R. J. *Modern Plastics* 1964, **41**, 149

21 Landua, A. J. *Polym. Prepr., A.C.S.* 1964, **24**, 299

22 Harris, J. A. and Temin, S. C. *J. Appl. Polym. Sci.* 1966, **10**, 523

23 Brown, J. F. *J. Am. Chem. Soc.* 1952, **74**, 1219

24 Brown, C. A., Muetterties, E. L. and Rochow, E. G. *J. Am. Chem. Soc.* 1954, **76**, 2537

25 Ryss, I. G. and Donskaya, D. B., Russ, *J. Iorgn. Chem.* 1960, **5**, 1091

26 Mika, T. F. in 'Epoxy Resins', (Eds. C. A. May and Y. Tanaka), Marcel Dekker, New York, 1973, Ch. 4

27 Anbar, M. and Gutman, S. *J. Phys. Chem.* 1960, **64**, 1896

28 Kuhlmann, K. and Grant, D. M. *J. Phys. Chem.* 1964, **68**, 3208

29 Hartman, J. S. and Schrobilgen, G. J. *Inorg. Chem.* 1972, **11**, 940

30 Mesmer, R. E. and Rutenberg, A. C. *Inorg. Chem.* 1973, **12**, 699

31 Walkup, C. M., Morgan, R. J. and Hoheisel, T. H. *Polym. Prepr.* 1984, **25**, 187