The mechanism of epoxy-resin curing in the presence of glass and carbon fibres

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The crosslinking mechanisms and kinetics of carbon fibre (four samples) and glass fibre (five samples) reinforced epoxy formulations subjected to various treatments were studied by ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (liquid and solid cross-polarization/magic-angle spinning) and Fourier-transform infrared spectroscopy, differential scanning calorimetry, high-performance liquid chromatography and Calvet microcalorimetry. By comparison with the results obtained in previous work on pure matrices, it was shown that the presence of fibres does not change the reaction mechanisms or the network structure. On the other hand, it was possible to show that the nature of the fibre reinforcement, the various treatments undergone, the formulation and heat cycles led to notable differences in the reaction rate, particularly at low temperature.

(Keywords: kinetics; networks; structure; epoxy resins; prepregs; carbon fibres; glass fibres)

INTRODUCTION

Fibre-reinforced composite materials consist of a reinforcing material, such as high-tensile-strength fibres, maintained by another material. Most of the final properties will depend on the properties of each constituent, as well as on the interface between the reinforcing material and the matrix, and this is often the weakest link in the system.

Understanding of the role of the interface in the behaviour of the composite and the possibility of controlling it are just as important as the determination of structure–property relationships for the fibre and polymer. The existence of a linking phase, or interphase, whose properties are different from those of the mass of fibre or matrix, may be related to one or several parameters. The fibre may contain morphological modifications near the surface, which are often absent in the bulk. Thus, the chemical composition of surface zones can be totally different from the bulk composition. Surface treatments (oxidation, irradiation, deposit of a coating, etc.) are often carried out, giving rise to a new layer from the chemical and structural standpoints. The reactive groups on the fibre surface may also exert a catalytic effect when the network is being formed. Each of these different parameters can vary quantitatively and be manifested alone or with others in the interface zone.

The aim of the present work was to determine the effect of the reinforcing agent on the reaction mechanisms and kinetics of the epoxy–amine system, in light of results obtained using only the neat resin, both our own results[1–8] and those of others[9–17].

The system chosen for this study consisted of: (a) an epoxy polymer matrix obtained by mixing a tetraepoxy tetraglycidyldiaminodiphenylmethane (TGDDM) prepolymer and a curing agent, 4,4′-diaminodiphenylsulphone (DDS), in the proportion of 100/30; (b) reinforcing fibres, either glass or carbon fibre, whose surface characterizations have been published[18]. The fibre/matrix interface was modified by treating the fibre and/or depositing a coating.

After characterizing the prepregs by liquid ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.) and Fourier-transform infrared (FTi.r.) spectroscopies as well as high-performance liquid chromatography (h.p.l.c.), the effect of the reinforcing agent on the polymerization kinetics and network structure was studied by solid-state n.m.r., differential scanning calorimetry (d.s.c.) and FTi.r..

MATERIALS

The tetraepoxy prepolymer used in this work was supplied by CDF Chimie, under the name of Lopox 3302. We have studied this prepolymer in previous work and identified all the impurities present[5]. Its epoxy equivalent weight (*EEW*) is 119 (theoretical 107) and mean functionality, i.e. number of epoxy groups per mole of product, is 3.6 (theoretical 4). 4,4-Diaminodiphenylsulphone is a commercial product (Fluka) and was recrystallized in ethyl acetate/petroleum ether: m.p. = 176°C.

The formulation contained 30 parts of curing agent per hundred parts of resin (phr). The epoxy–amine mixture is prepared by heating the resin (between 100 and 120°C), adding the curing agent and stirring continuously until a clear mixture was obtained. The homogeneous mixture was then degassed at 100°C for 20 min. The prepregs studied in this work are listed in *Tables 1* and *2*.

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Table 1 Characteristics of glass fibre prepregs

Fibre reference	Weight of fabric ($g m^{-2}$)	Type of coating[a]	Fabric treatment	Nature and per cent of resin[b]	Surface mass ($g m^{-2}$)
A	300	PC	None	TGDDM-DDS (41.5)	511
B_1	300	Uncoated	Textile	TGDDM-DDS (44.4)	523
B_2	300	TC	Chromium methacrylate salt	TGDDM-DDS (42.4)	508
B_3	300	TC	Epoxy silane–chlorinated silane (2)	TGDDM-DDS (44)	518
B_4	300	TC	Epoxy silane (silane (1))	TGDDM-DDS (42.5)	511

[a] PC = textile–plastic coating; TC = textile coating
[b] Stoichiometry: TGDDM/DDS 100/28

Table 2 Characteristics of carbon fibre prepregs

Fibre reference	Type of prepreg	Treatment	Nature and per cent of resin[a]	Surface mass ($g m^{-2}$)
C_1	Fabric	Uncoated	TGDDM-DDS (49)	511
C_2	Fabric	Epoxy compatible coating	TGDDM-DDS (48)	563
C_4	Unidirectional	Epoxy compatible coating	TGDDM-DDS (36)	205
C_5	Unidirectional	Epoxy–polyester compatible coating	TGDDM-DDS (35)	202

[a] Stoichiometry: TGDDM/DDS 100/30

EXPERIMENTAL TECHNIQUES

Calvet microcalorimetry

Polycondensation kinetics were followed isothermally with a high-temperature model Calvet microcalorimeter in the temperature range 100–200°C. Sample weights were of the order of 2–3 g and the calorimeter was calibrated electrically. The total heat of reaction, established by differential scanning calorimetry on various samples of epoxy prepolymer/aromatic amine[8,19], was used to plot the extent of reaction as the reaction progressed.

Differential thermal analysis

Total heats of reaction and the glass transition temperatures were obtained with a Perkin–Elmer DSC 7 (heating rate 10°C min^{-1}).

^{13}C solid-state and liquid nuclear magnetic resonance

^1H and ^{13}C (liquid and solid) n.m.r. spectra were obtained using a Bruker WM 250 spectrometer, equipped with a Bruker Aspect 2000 computer (DISN 88 program) and a CPMAS (cross-polarization and magic-angle spinning) accessory.

The following conditions were employed to record the spectra in liquids: flip angle 45° (14 μ), 100 scans, digital resolution 0.925 Hz/point (0.015 ppm/point), equivalent to a spectral width of 15000 Hz for a 32K memory. Chemical shifts were calculated on the basis of tetramethylsilane (TMS) as internal standard.

Solid spectra (boron nitride sample holder) were recorded with a 1 μs contact time, 10 s between sequences and a rotation between 5 and 6 kHz. A mean of 1000 contacts is necessary to obtain spectra with good signal/noise ratio.

Fourier-transform infrared spectroscopy

Spectra were recorded with a Bruker IFS 45 spectometer. The following conditions were used: 200 scans, spectral width 400–5000 cm^{-1}, digital resolution 2 cm^{-1}, signal processing by triangular apodization. A Perkin–Elmer heating cell controlled with a chromel–alumel thermocouple temperature regulator was used in isothermal conditions and at different temperatures. Spectra were recorded at different time intervals. Attenuated total reflection (ATR) analyses were carried out with a variable-angle ATR (Specec) with a KrS_5 crystal.

High-performance liquid chromatography

Chromatograms were recorded with a Varian 5000 chromatograph. Experimental conditions are presented in the figure legends.

ANALYSIS OF RESULTS

Analysis of the prepregs

The prepregs (glass or carbon fibres) were first cut into 1–2 cm pieces. Organic constituents were separated from the reinforcing fibres by extracting either with a Soxhlet apparatus at 40°C (in methylene chloride) for 12 h, or by ultrasound treatment (in chloroform) for 2 h.

The extracts were studied directly in solutions of the extraction solvents.

Study of base products by h.p.l.c. The tetraepoxy polymer used to prepare the prepregs was analysed by chromatography using the same conditions of column and solvent as in previous work[4,8] and the chromatograms obtained were compared. The prepolymer contained the same impurities as those identified previously.

An h.p.l.c. study of the reaction mixture used to prepare the prepregs (*Figure 1*) showed various impurity peaks (impurities A and B plus homopolymers and tetraepoxy prepolymer (R)), two additional peaks corresponding to the aromatic amine (4,4′-diaminodiphenylsulphone (peak D)) and one peak (R-D) between impurities A and B, corresponding to a β stage, i.e. the opening of a first epoxy group with a primary amine (principal reaction product from the progression of the reaction).

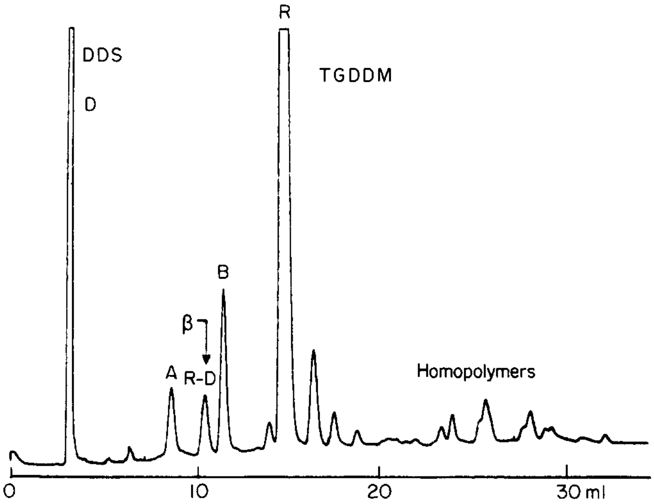


Figure 1 H.p.l.c. study of TGDDM-DDS reaction mixture (stoichiometry 100/28). Identification of different peaks. Spherisorb C18 column (5 μm). Solvents: methanol/water, 65/35% to 100% in 40 min. Flow rate 1 ml min^{-1}. Detection by u.v. at 260 nm

Study of different glass and carbon fibre prepregs by h.p.l.c., n.m.r. and FTi.r. The chromatograms obtained with the methylene chloride and chloroform extracts are shown in *Figures 2* and *3*. The chromatograms were identical regardless of solvent and extraction methods. These chromatograms were very similar to those observed with the reaction mixture (*Figure 1*). All the impurities present in the initial prepolymer were present, as was the β stage, confirming progress of the reaction to about 3–5%, depending on the prepregs studied. The β stage peak (R-D) was confirmed by heating prepreg A for 4 h at 140°C and following the reaction kinetics with samples taken at 0.5 and 4 h. The resulting h.p.l.c. chromatograms (*Figure 2*) show an increase in the intensity of this peak and the appearance of a new peak, called the γ stage (*Figure 2*). A kinetic analysis before the gel point showed that the β stage increased very little, as well as higher oligomers (γ stage). A simultaneous ^{13}C n.m.r. study (see below) showed that the 60–70 ppm and 150–160 ppm regions contained carbons characteristic of the opening of epoxy bridges by primary amines. This enables structures to be proposed (*Figure 4*) for the β and γ stages before the gel point.

All the extracts were examined by ^{1}H and ^{13}C n.m.r.; all the spectra contained lines specific to the two basic constituents TGDDM and DDS, regardless of whether the prepregs were carbon or glass fibre. Other specific lines appeared, either for β and γ stages or for impurities (*Figure 5* is an example). The liquid ^{13}C n.m.r. chemical shifts of these compounds are listed in *Table 3*.

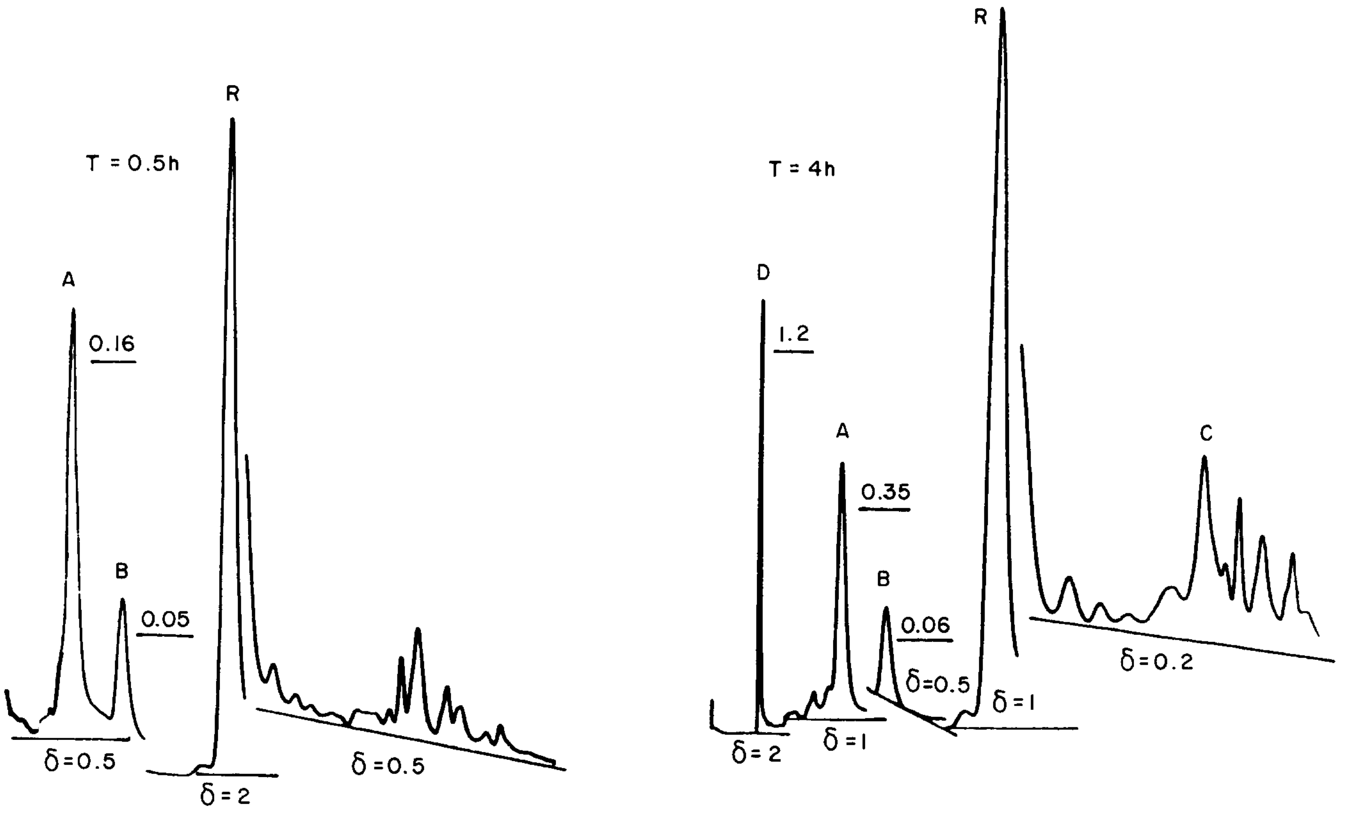


Figure 2 H.p.l.c. study of the kinetics of CH_2Cl_2 extracts of glass fibre A prepreg at 140°C for 4 h. A = β stage, B = impurities, C = γ stage; δ = sensitivity; D = DDS; R = TGDDM

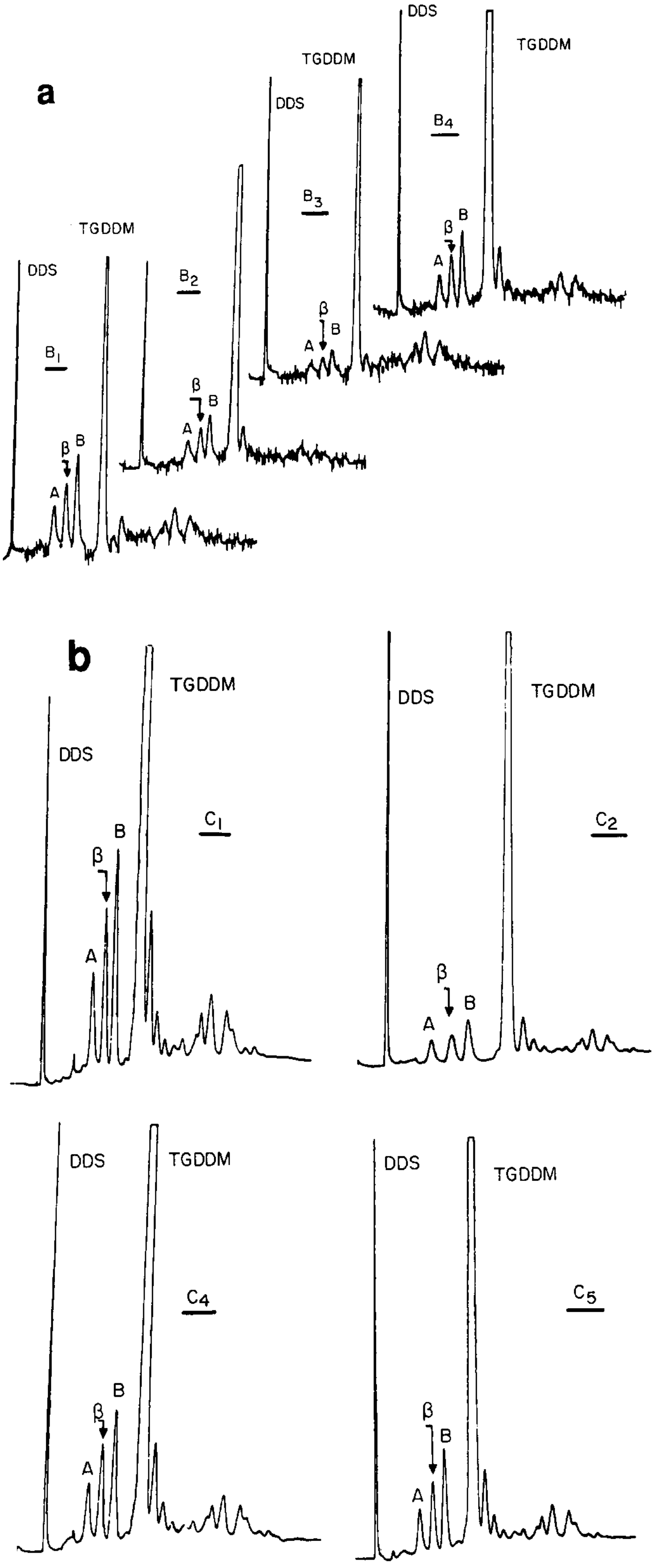


Figure 3 H.p.l.c. study of chloroform extracts of different glass fibre (a) and carbon fibre (b) prepregs $t = 0$, 25°C. Same experimental conditions as in *Figure 2*

The FTi.r. spectra of the initial reaction mixture were recorded as a film, while the prepregs were studied directly by ATR without sample preparation[20,21]. As an example, *Figure 6* shows the spectra obtained with the reaction mixture and the two prepregs (glass fibre B_1 and carbon fibre C_1) (time = 0 min). The various spectra were all very similar (*Table 4*) and consistent with published data for the monomers[17,22,23].

The d.s.c. diagrams obtained were identical to published data obtained with the neat resin[6,8,17,19]. The results (*Table 5*) indicate no notable differences among the different samples. The slight differences in enthalpy expressed as ΔH per gram of resin are consistent with the uncertainty about the true level of impregnation. Enthalpy expressed on the basis of one epoxy group is 90 kJ per mole of epoxy groups, a value consistent with that obtained using the matrix without added fibre[8,19]. This value is 107 kJ per mole of epoxy groups for pure epoxy prepolymers.

Kinetics and network structures of prepregs

Reaction mechanisms in the molten state

Thermoset cure is a complex process, which begins by formation and linear growth of chains that soon branch and then crosslink. Former approaches rely upon knowledge of the exact reaction mechanism leading to the development of structural models[1,2,6–8,15–17] (*Figure 7*).

The first reaction is the attack of a primary amine on an epoxy group (reaction I) on a side chain (β stage). This may be followed by a second step, which furnishes higher oligomers (this predominates at the beginning of the reaction, since it is the reaction with the lowest activation energy). It should nevertheless be noted that the molecule formed has three active centres (secondary amine, secondary hydroxyl and epoxy), which are in close proximity to one another.

Two types crosslinking reactions begin, intermolecular and intramolecular. The former occurs (1) via attack of the primary amine on an epoxy group, constituting the expected crosslinking nodes (reaction II_A), (2) via attack of an epoxy group on a hydroxyl group, leading to the creation of a β-hydroxylamine fragment and formation of an ether-type crosslinkig node (reaction II_B), and (3) via homopolymerization of the tetraepoxy prepolymer, catalysed by the presence of impurities in the reaction mixture. Intramolecular reactions can occur between a hydroxyl group formed (secondary alcohol in this case) and an epoxy group on the same nitrogen atom of the tetraepoxy prepolymer, leading to the creation of six-, seven- and eight-membered rings and the creation of highly reactive primary and secondary alcohols. These different reactions occur very rapidly in the reaction medium (molten) and may be autocatalysed by residual functions in the TGDDM prepolymer or by impurities present. In order to follow the kinetic and mechanistic aspects of the prepregs either in FTi.r. or solid-state ^{13}C n.m.r., we selected certain well characterized and specific spectral regions of these different reactions[6,8].

Reaction mechanisms and kinetics on prepregs

Solid-state ^{13}C n.m.r. Only glass fibre prepregs could be studied by this technique. Carbon prepregs could not be examined because parasitic currents created a poor signal/noise ratio and rendered the spectra uninterpretable.

The results shown in *Figure 8* involve the kinetics of the pure matrix at 150°C (*Figure 8a*), the kinetics of prepregs B_1 at 150°C (*Figure 8b*) and the kinetics for five samples of prepregs at the end of the heating cycle, 6 h at 150°C (*Figure 8c*).

As a result of the different chemical species expected (*Figure 7*), the broad peak at 0–70 ppm changes with time. The various chemical shifts expected on the basis of model compounds simulating the different reactions

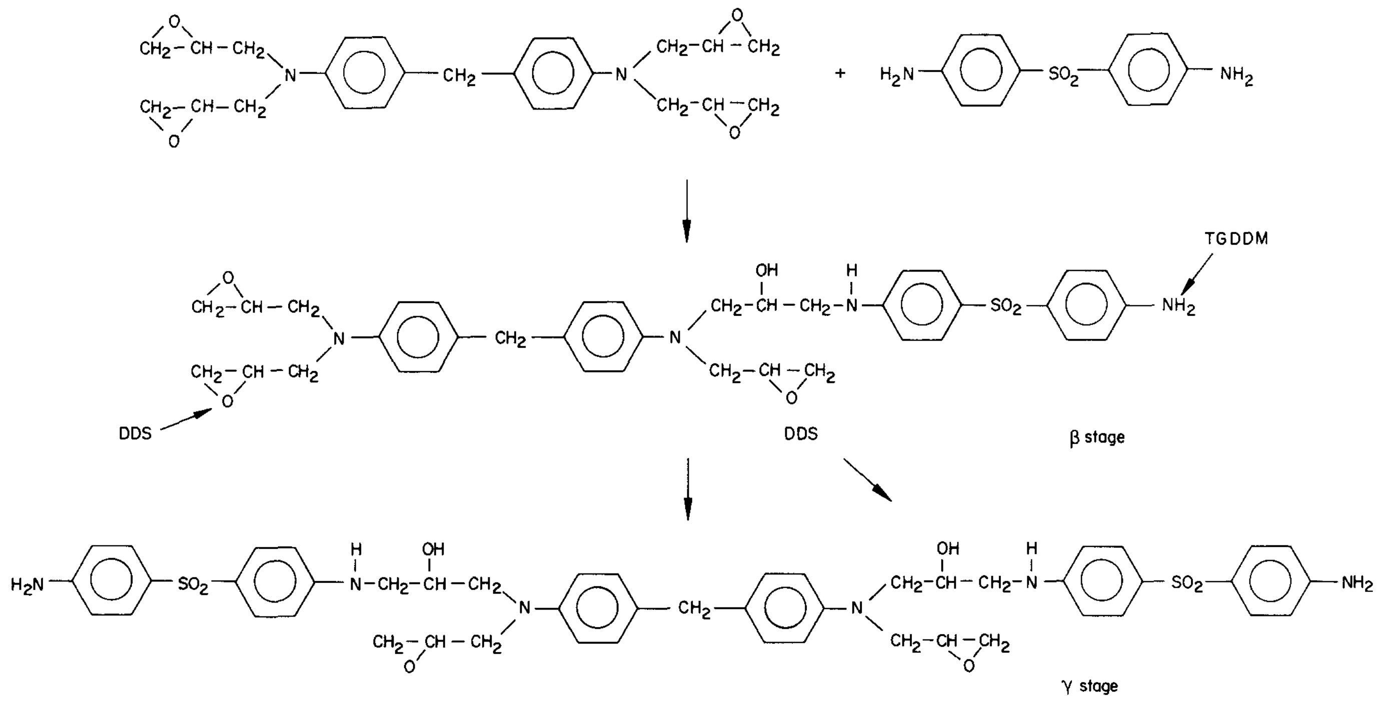


Figure 4 Chemical structures of the different products (D, T, β and γ stages in the chromatograms of *Figures 2* and *3*)

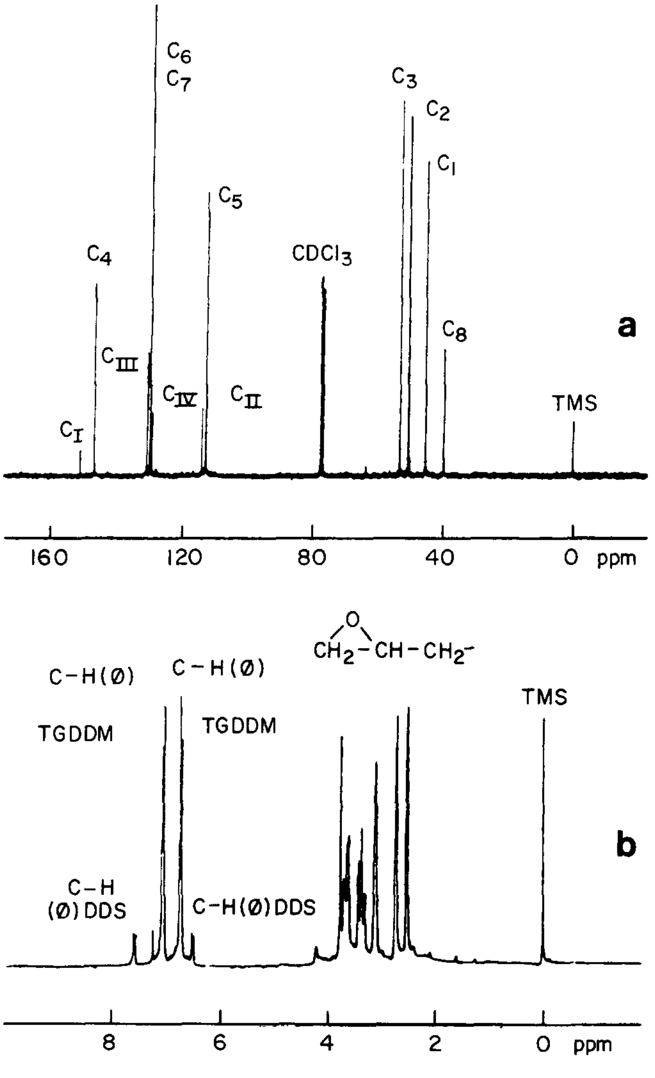


Figure 5 (a) ^{13}C liquid n.m.r. (62.89 MHz) study of the extracts (chloroform) of glass fibre B_3 prepreg. (b) ^1H liquid n.m.r. (250 MHz) study of the extracts (chloroform) of glass fibre B_3 prepregs

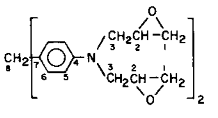
shown in *Figure 7* and published elsewhere[6,8] are listed in *Table 6*. Taking the expected number of lines into account (up to 16), if all the mechanisms are operative during the reaction in the molten state, when the solid-state ^{13}C n.m.r. spectra are compared with time 0 and polycondensed, a fairly broad band is observed characteristic of the different chemical species present. After decomposing the spectra into their basic lines[6], by using the chemical shifts in *Table 6*, it was possible to utilize five lines: residual epoxy at 45.5 ppm, primary and secondary alcohols at 65 and 68 ppm, respectively, and ethers at 74–80 ppm. The 40 ppm line characteristic of the methylene group between the aromatic rings of the TGDDM prepolymer was used as an internal standard (*Figure 8*). Similarly, in the region of 145–160 ppm, characteristic of primary (150 ppm) and secondary amines (153 ppm), it was possible to follow unambiguously the degree of crosslinking at the level of the hardener fragment (DDS). The structural results show that, if the epoxy level decreases rapidly as in the pure matrix, then there are considerable ether and intramolecular cyclization-type reactions. In addition, all the spectra obtained at the end of the curing cycle show that the networks obtained were all very similar, regardless of the surface treatment applied (*Figure 8c*).

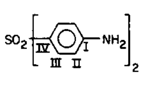
Fourier-transform infrared spectroscopy. Comparing the spectra obtained at various times with those of the prepregs at the beginning of the polymerization cycle ($t = 0$), substantial modifications can be seen (*Figure 9* and *Table 4*). In the 3200–3800 cm^{-1} region, changes in bands were caused by the disappearance of primary amines ($\nu(NH_2)$) around 3470–3380 cm^{-1} and the appearance of secondary amines around 3450 cm^{-1} and of alcohol functions represented by a broad peak around 3410 cm^{-1} (*Figure 9a*). In the 2800–3200 cm^{-1} region, epoxy functions disappeared (ν(epoxy C–H) at 2994 cm^{-1} and ν(epoxy CH_2) at 3052 cm^{-1}), causing a change in existing bands ($\nu_{as}(CH_2)$ and $\nu_a(CH_2)$ at 2992 and

Table 3 Liquid ^{13}C (62.89 MHz) and ^{1}H (250 MHz) n.m.r. (solvent $CDCl_3$, reference TMS). Chemical shifts and attributions of different lines in the spectra of prepregs. See footnotes for structures and numbering of C and H

(a) ^{13}C n.m.r.

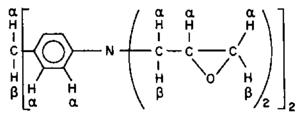
Carbons	C1	C2	C3	C4	C5	C6	C7	C8
Chemical shift (ppm) TGDDM	45.31 45.43	50.52 50.61	52.54 52.69	146.71	113.38 113.30	128.85	129.88	39.81
Carbons	CI	CII	CIII	CIV				
Chemical shift (ppm) DDS	154.90	113.74	128.82	129.82				

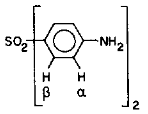

TGDDM


DDS

(b) ^{1}H n.m.r.

Protons	$H_\alpha(C1)$	$H_\beta(C1)$	$H_\alpha(C2)$	$H_\alpha(C3)$	$H_\beta(C3)$	$H_\alpha(C5)$	$H_\alpha(C6)$	$H_{\alpha\beta}(C8)$
Chemical shift (ppm) (and coupling constants)	2.54	2.71–2.74	3.12	3.41–3.36	3.72–3.69	6.82	7.05	3.74
TGDDM	$J[gem\ H_{\alpha-\beta}(C1)] = -5.1$ Hz		$J[H_\alpha(C1)–H_\alpha(C2)] = 4.0$ Hz		$J[H_\alpha(C2)–H_\alpha(C3)] = 3.2$ Hz		$J[gem\ H_{\alpha-\beta}(C3)] = -15.1$ Hz	
			$J[H_\beta(C1)–H_\alpha(C2)] = 2.6$ Hz		$J[H_\alpha(C2)–H_\beta(C3)] = 5.1$ Hz			
Protons	NH_2	$H_\alpha(CII)$	$H_\beta(CIII)$					
Chemical shift (ppm) DDS	5.38	6.65	7.48					


TGDDM


DDS

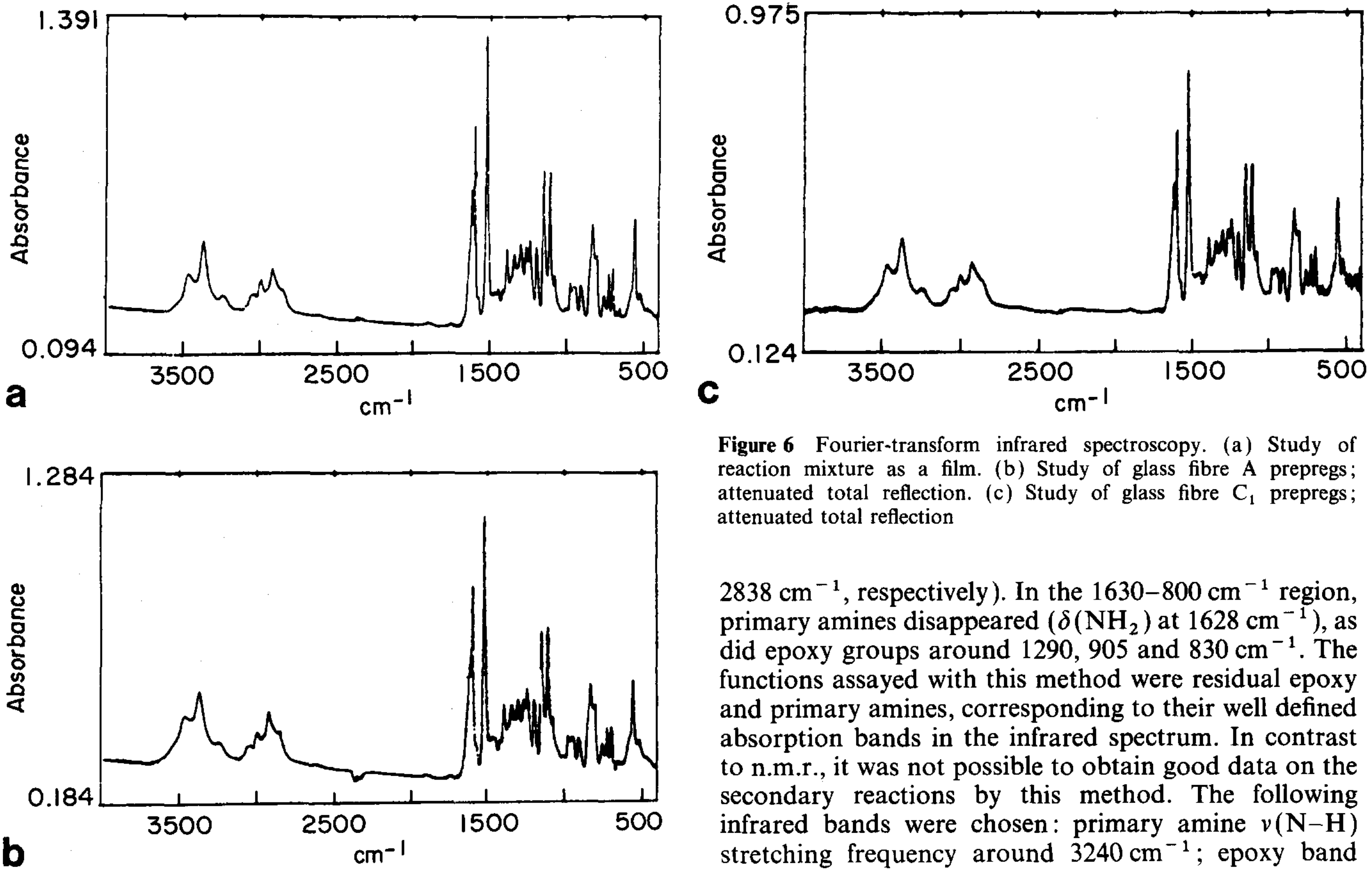


Figure 6 Fourier-transform infrared spectroscopy. (a) Study of reaction mixture as a film. (b) Study of glass fibre A prepregs; attenuated total reflection. (c) Study of glass fibre C_1 prepregs; attenuated total reflection

2838 cm^{-1}, respectively). In the 1630–800 cm^{-1} region, primary amines disappeared ($\delta(NH_2)$ at 1628 cm^{-1}), as did epoxy groups around 1290, 905 and 830 cm^{-1}. The functions assayed with this method were residual epoxy and primary amines, corresponding to their well defined absorption bands in the infrared spectrum. In contrast to n.m.r., it was not possible to obtain good data on the secondary reactions by this method. The following infrared bands were chosen: primary amine $\nu(N–H)$ stretching frequency around 3240 cm^{-1}; epoxy band

ν(C=O) stretching frequency around 902–910 cm^{-1}; and a reference band for standardizing the quantity of product and changes in the spectrum during the temperature rise, ν(C=C) bending frequency of the phenyl group around 1510 cm^{-1}. The quantification study could be done only after deconvolution of the spectra and enabled the bands to be followed in the course of the heat cycle.

The progress of the reaction was calculated with the following equations (where S = area):

$$\varepsilon_{\text{epoxy}}(t) = \frac{S_{\text{abs, epoxy}}(t)}{S_{\text{abs, reference}}(t)} \qquad (1)$$

$$\varepsilon_{\text{primary amine}}(t) = \frac{S_{\text{abs, primary amine}}(t)}{S_{\text{abs, reference}}(t)} \qquad (2)$$

The values thus determined are independent of the quantity of product in the sample and are proportional to the relative concentration of the NH_2 or epoxy function in relation to the unchanging reference moiety ($S_{\text{abs,ref}}\nu$(C=C) benzene ring at 1510 cm^{-1}). In order to compare the results obtained in the presence of reinforcing fibres to those obtained with the pure matrix, it was necessary to determine the values of $S_{\text{epoxy}}(t = 0)$ and $S_{NH_2}(t = 0)$. Based on the h.p.l.c. analysis (presented above) of epoxy level, these values were corrected by applying a coefficient characteristic of the progress of the reaction of the prepregs. The following were thus defined:

$$\text{epoxy consumed } (\%) = \frac{S_{\text{epoxy}}(t = 0) - S_{\text{epoxy}}(t)}{S_{\text{epoxy}}(t = 0)} \times 100 \qquad (3)$$

$$\text{amine consumed } (\%) = \frac{S_{NH_2}(t = 0) - S_{NH_2}(t)}{S_{NH_2}(t = 0)} \times 100 \qquad (4)$$

Calvet microcalorimetry. A sample of prepregs weighing about 1 g was placed in the cell of a fully automatic Calvet isothermal calorimeter. Thermal effects were followed for 8–10 h in the temperature range of 100–180°C. Reaction progress was calculated by:

$$\xi = k\frac{\sum \Delta H}{QN_e}$$

where k = calorimeter constant, ΔH = heat released, Q = total heat of reaction per epoxy group, i.e. 90 kJ/epoxy group for this prepolymer, and N_e = number of

Table 4 FTi.r. frequencies in the spectra of the different prepregs and attributions. (a) Frequencies of the tetraepoxy prepolymer TGDDM. (b) Frequencies of 4,4′-diaminodiphenylsulphone (DDS). (c) Common frequencies of prepolymer TGDDM and DDS

(a) TGDDM

Frequency (cm^{-1})	Attribution
3054	$\nu_{as}(CH_2{-}CH)$
2995*	$\nu(CH_2\underset{\diagdown\;O\;\diagup}{CH{-}CH_2})$
2950	$\nu_{as}(CH_2)$
2840	$\nu_s(CH_2)$
1480 1440 1410	$\delta(CH_2)$
1260*	ν_s (cyclic epoxide)
908*	ν_{as}
830*	ν_a
750	$\delta(CH_2)$ (rock)

(b) DDS

Frequency (cm^{-1})	Attribution
3470* 3380*	$\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ (in plane)
1625*	$\delta(NH_2)$ (in plane)
1105	$\nu_s(O_2)$
720*	$\delta(NH_2)$ (out of plane)
695	ν(C–S)

(c) Common

Frequency (cm^{-1})	Attribution
3190 3055 3030	ν(C=C arom)
1612 1567 1517 1465	Cyclic ϕ TGDDM
1593 1501 1435	Cyclic ϕ DDS
1380	ν(C(arom)–N) TGDDM
1280	ν(C(arom)–N) DDS
1230	ν(C(arom)–N) TGDDM
1190 1180 1070 1005	δ(C–H) (in plane) *para* substitution, DDS and TGDDM
825	δ(CH) (out of plane) DDS
800	δ(CH) (out of plane) TGDDM

*Change during polymerization

Table 5 D.s.c. heats of reaction

Sample	$T^{\circ}_{\max}$ (°C)	ΔH (J g^{-1}) prepregs	ΔH (J g^{-1}) resin	ΔH (kJ/mol epoxy)
TGDDM–DDS (pure matrix)			718	91.96
Glass fibre A	260.6	272.2	651	83.82
Glass fibre B_1	259.9	275.5	620	79.36
Glass fibre B_2	259.8	273.2	622	79.61
Glass fibre B_3	259.8	285.5	648	82.94
Glass fibre B_4	259.5	283.2	645	82.56
Carbon fibre C_1	259.1	334.8	683	87.42
Carbon fibre C_2	260.2	335.5	685	87.68
Carbon fibre C_4	258.4	256.4	708	90.62
Carbon fibre C_5	261.5	235.5	671	65.88
	Average = 600 J g^{-1} ≃ 84.38 kJ/mol epoxy			

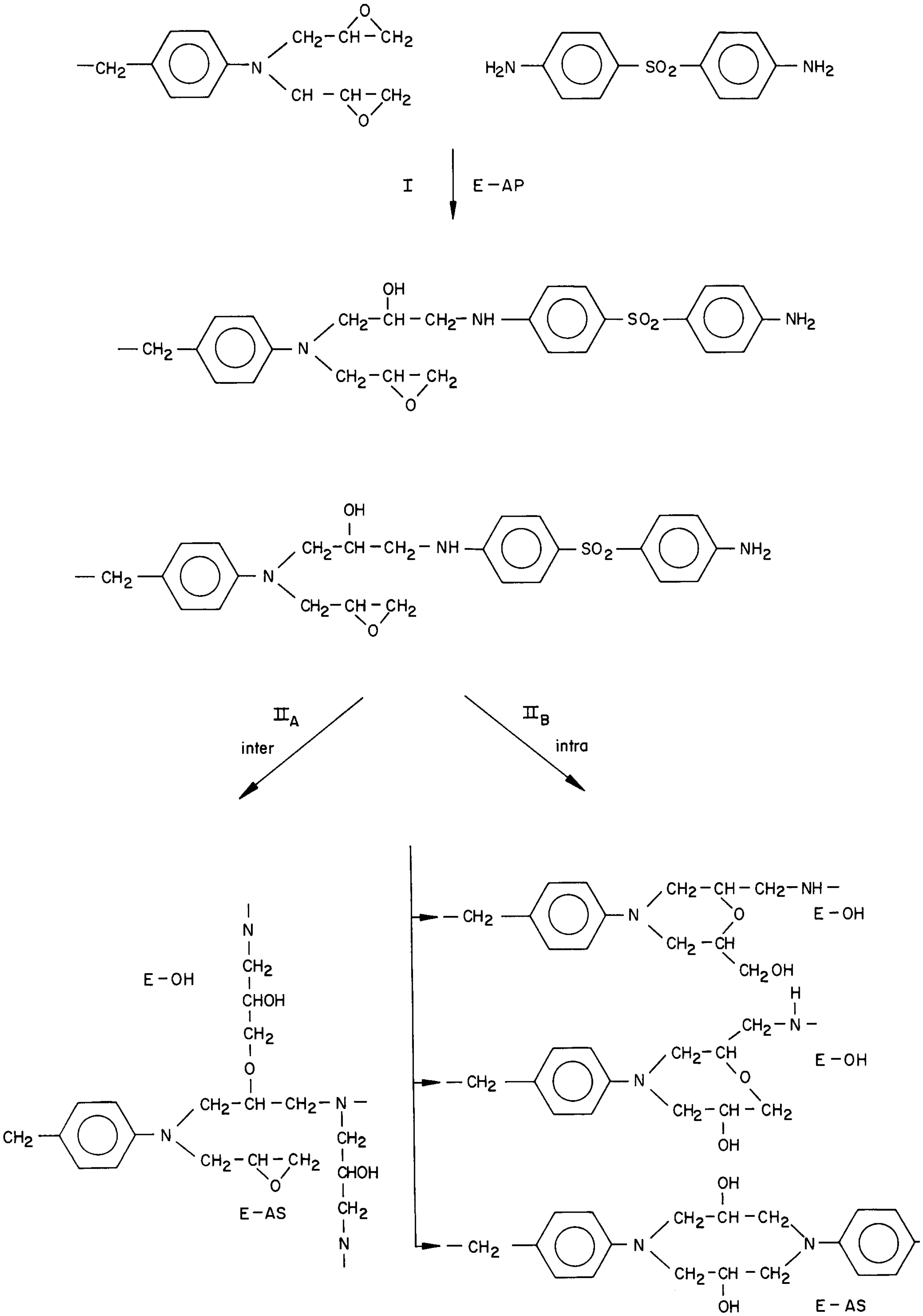


Figure 7 Reaction mechanisms of the TGDDM–DDS system in the molten state

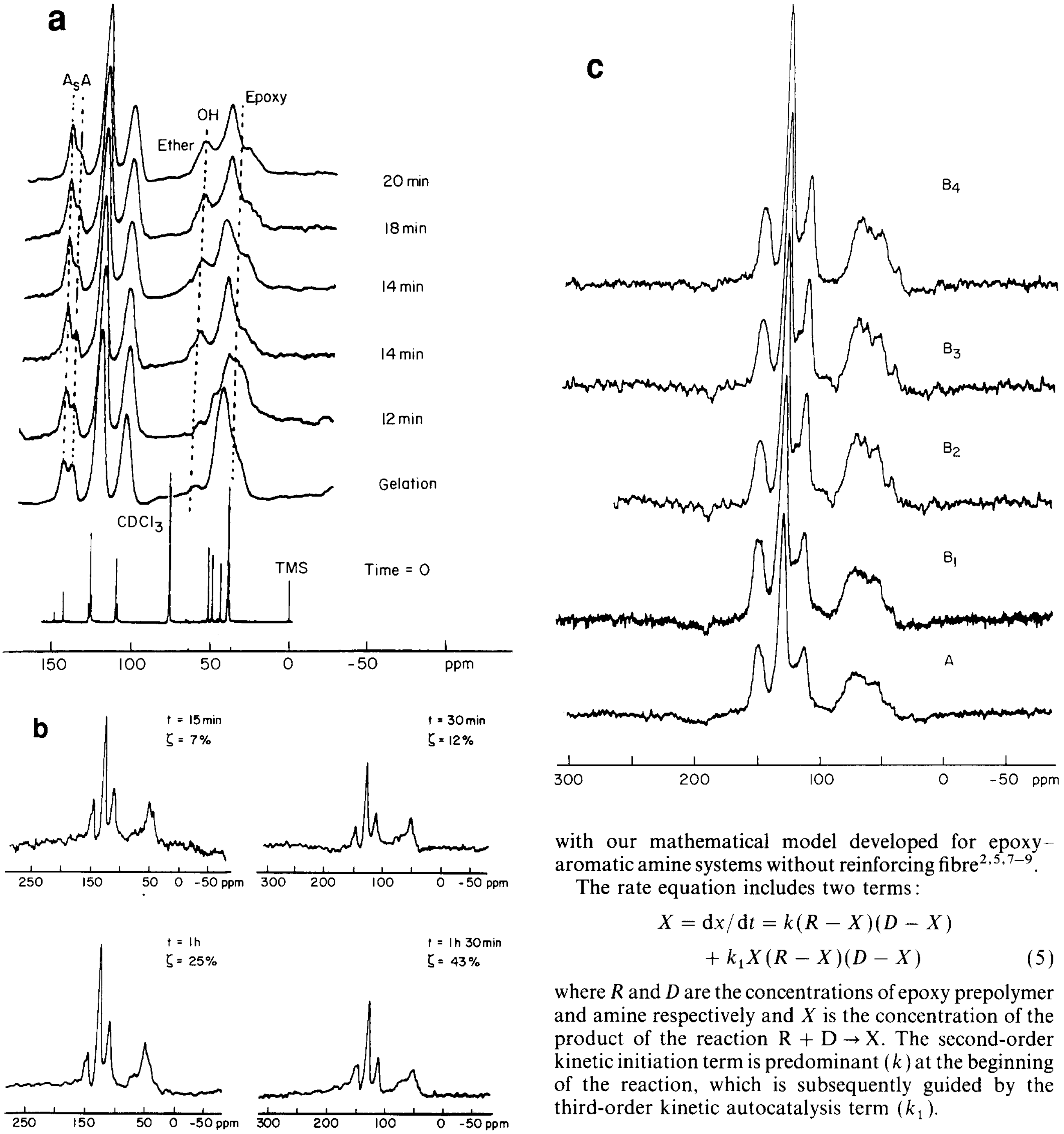


Figure 8 Solid-state ^{13}C CPMAS nuclear magnetic resonance. (a) Kinetics of the pure matrix, 150°C. (b) Kinetics of glass fibre B_1 prepregs, 150°C. (c) Different prepregs at the end of heat cycle: 150°C, 5 h

epoxy groups in the sample. *Figure 10* is an example of the heating diagram and curve of the progress of the reaction in the case of glass fibre B_2.

CONCLUSIONS

Comparison of techniques: kinetic model

The results obtained for fibre B_2 using the three methods are shown in *Figure 11*, with very good agreement between the results. These kinetic curves were obtained with different methods and could be processed with our mathematical model developed for epoxy–aromatic amine systems without reinforcing fibre[2,5,7–9].

The rate equation includes two terms:

$$X = \mathrm{d}x/\mathrm{d}t = k(R - X)(D - X) + k_1X(R - X)(D - X) \qquad (5)$$

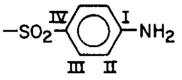
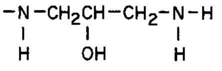
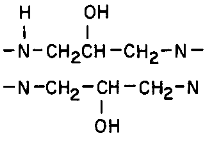
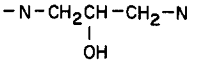
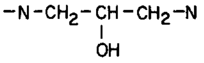
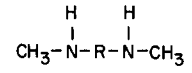
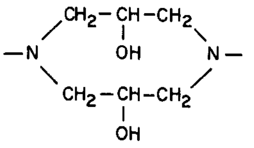
where R and D are the concentrations of epoxy prepolymer and amine respectively and X is the concentration of the product of the reaction $R + D \rightarrow X$. The second-order kinetic initiation term is predominant (k) at the beginning of the reaction, which is subsequently guided by the third-order kinetic autocatalysis term (k_1).

Effect of the reinforcement

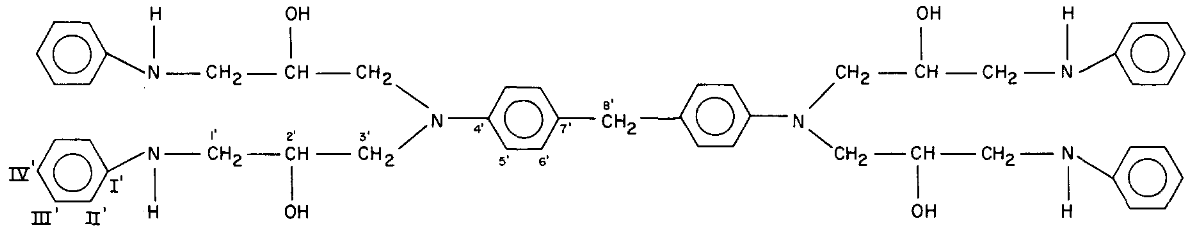
Examination of the values of the rate constants k and k_1 (*Table 7*) shows that the presence of glass or carbon fibres decreases the autocatalysis term by a considerable extent, whereas the initiation term was close to that of the pure matrix. It follows that the two rates at the onset of the reaction diverge as the reaction progresses, slowed by the presence of the reinforcing fibre. Kinetics are thus systematically slower in the presence of fibres (*Figure 12*).

There are two possible explanations for this. The fibres lead to a better dispersion of the heat of reaction and thus reduce its autocatalytic nature. In favour of this possibility is the observation that carbon fibres, good conductors of heat, generally reduce the reaction rate more than glass fibres, which are poor conductors. Alternatively, a trapping effect by the fibres could reduce the mobility of the system, decreasing the encounter

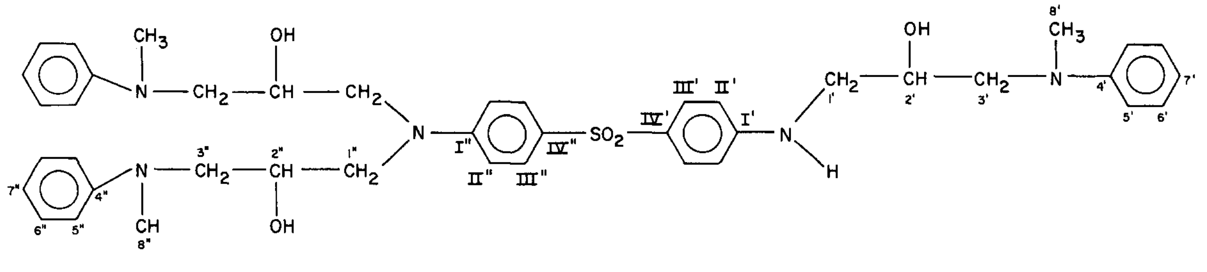
Table 6 Solid-state ^{13}C n.m.r. (CPMAS) shifts of the different models simulating the reaction mechanisms shown in *Figure* 7. See footnote for structures and numbering of C

Compounds	Characteristic fragments	Chemical shifts[a] (ppm)											
		1	2	3	4	5	6	7	8	I	II	III	IV
DDS										150.9 148.6	113.9 115.7	128.3	128.7
A TGDDM	 $-\underset{H}{N}-CH_2\underset{OH}{CH}-CH_2-\underset{H}{N}-H$	49.75	67.98	56.90 58.78	150.20	113.41	129.61	117.1	38.82				
B DDS	 $-\overset{H}{N}-CH_2\overset{OH}{CH}-CH_2-N-$ $-N-CH_2-\underset{OH}{CH}-CH_2-N$	48.22	69.78	57.85	150.92	114.61	129.49	117.65	39.75	152.74	112.92	129.67	129.67
C TGDDM	 $-N-CH_2\underset{OH}{CH}-CH_2-N$	57.37	67.30	57.37	146.48 146.52	112.50 113.47	129.57 129.55	116.36 116.23	38.70	149.78	113.47	129.57	116.36
D DDS	 $-N-CH_2-\underset{OH}{CH}-CH_2-N$	58.21	69.14	58.21	150.92	114.62	129.40			152.74	112.92	129.67	129.67
E DDS	 $CH_3-\overset{H}{N}-R-\overset{H}{N}-CH_3$								29.15	155.28 155.65	107.93 112.4	126.87 128.89	114.33 114.72
F		61.75	62.84	61.75	145.60	115.50	130.50	124.70	20.00	147.70	111.00	130.50	116.10

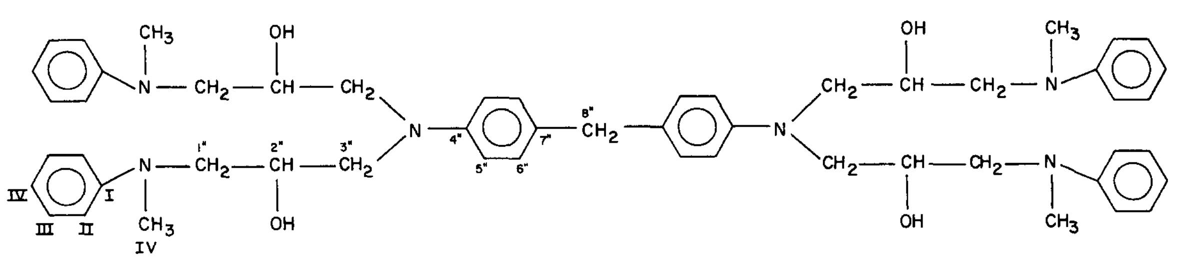
[a] Reference polyoxymethylene 80 ppm



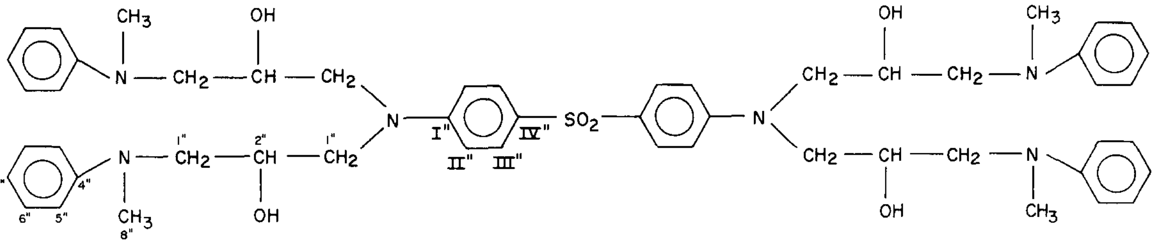
A



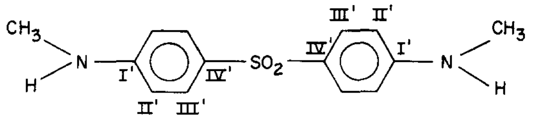
B



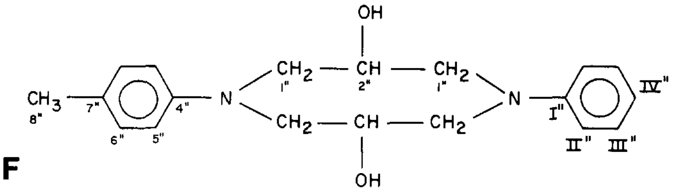
C



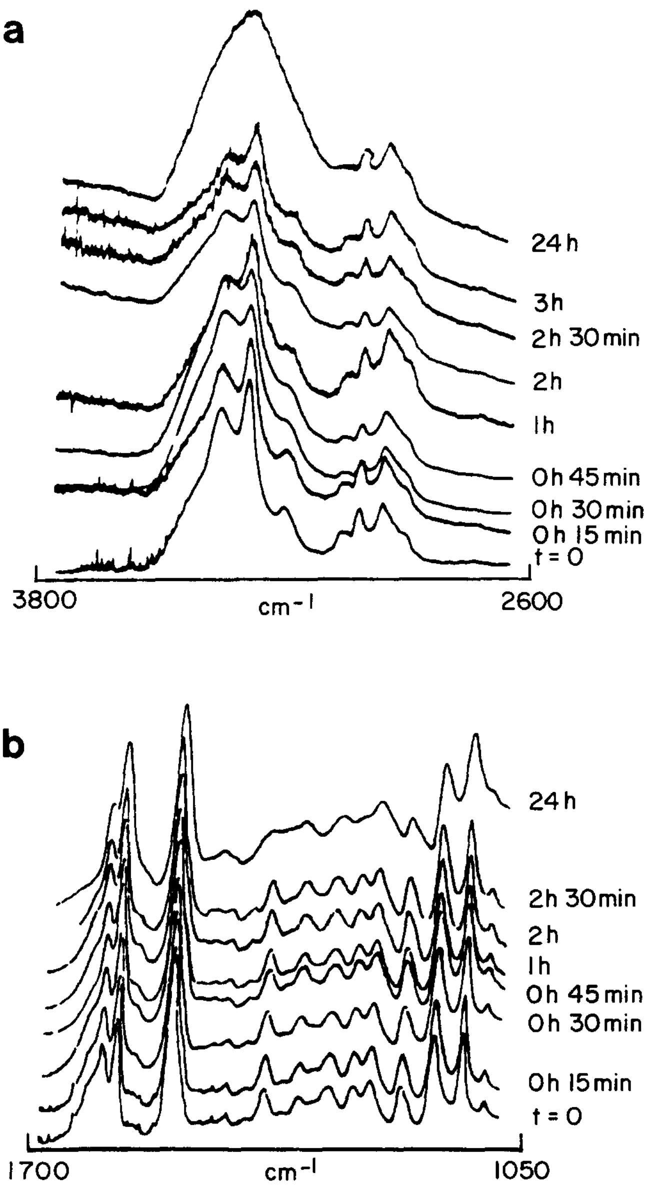
D



E



F



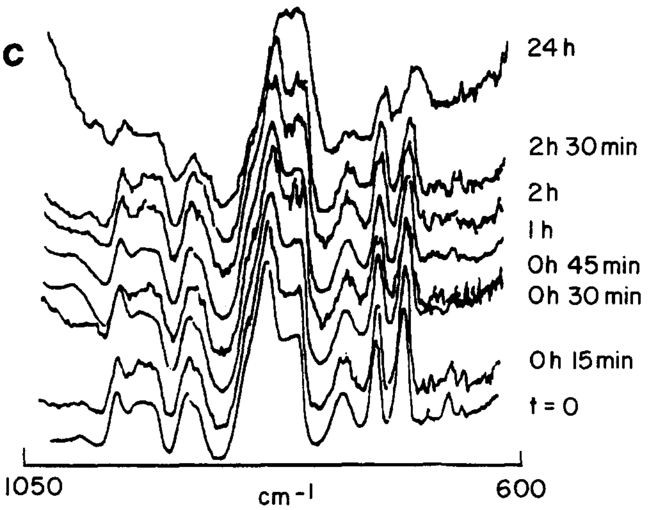


Figure 9 Fourier-transform infrared spectroscopy. Kinetics of prepregs, C_1, 150°C

probability between reactive species, proportional to the increase in viscosity of the medium. Comparison of the kinetics of samples C_2 and C_4 shows that a fabric decreases reactivity more than a unidirectional sheet, since reactive diffusion is hindered by the presence of heterogeneous components.

Effect of surface treatment

Glass fibres. Samples A, B_1 and B_3 were equivalent and the least reactive ($dx/dt = 0.14$ epoxy/h at 150°C). Thus, a textile-plastic coating (fibre A), no coating (fibre B_1) or silanizing (epoxy silane-chlorinated silane; fibre B_3) led to no change in system chemistry (*Table* 7). Silanizing (epoxy silane type; fibre B_4) resulted in a slight increase in maximum rate to 0.19 epoxy/h at 150°C. Silanizing treatment with chromium methacrylate salt, on the other hand, led to a substantial increase in the reactivity of the prepregs ($dx/dt = 0.23$ epoxy/h) (fibre

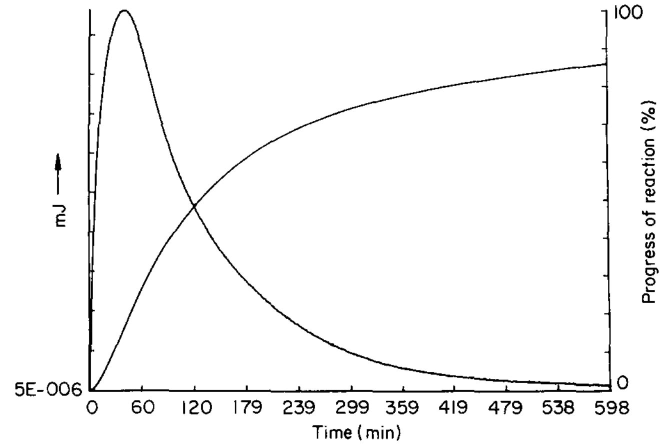


Figure 10 Typical Calvet microcalorimetry heat diagram. Prepregs B_1, 150°C

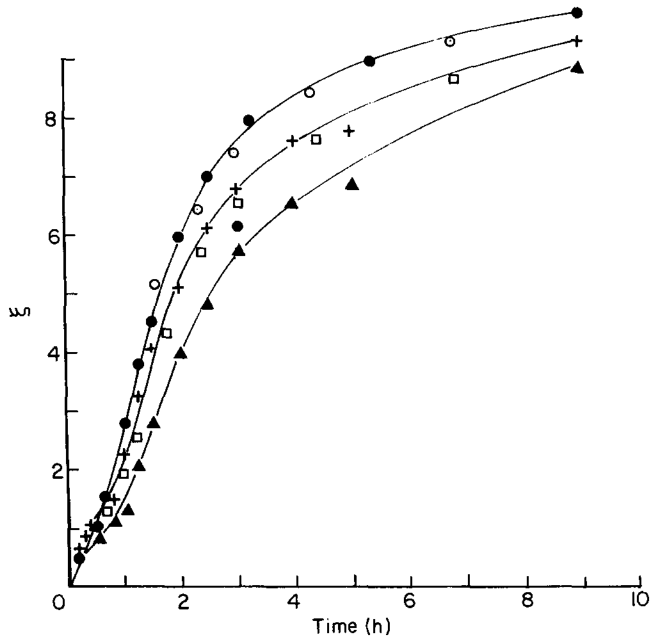


Figure 11 Kinetics in isothermal conditions. Comparison of results obtained with the different methods. Glass fibre B_2, 150°C. Symbols: ○, ●, pure matrix (n.m.r. and FTi.r.); ▲, carbon fibre prepregs (FTi.r.); +, □, glass fibre prepregs (FTi.r. and n.m.r.)

B_2). In addition, it is to be noted that the autocatalysis term was particularly sensitive to this treatment.

Carbon fibres. The order of reactivity of carbon fibre prepregs is shown in *Figure 13* to be:

$$\text{uncoated (fibre } C_1) < \text{coating (fibre } C_2) < \text{coating (fibre } C_4) < \text{coating (fibre } C_5)$$

Coating thus plays a role in the reactivity of prepregs. It is possible that these products, principally epoxy–(bisphenol A diglycidyl ether type) prepolymer plus more or less heavy unsaturated polyester, accelerated the reaction. O-epoxy groups are more reactive than N-epoxy groups of the prepolymer TGDDM[6–8].

The difference between coatings (fibre C_2) and (fibre C_4) (where only the per cent coating varies and not the nature) is insufficient to explain the higher reactivity of sample C_4 over C_2. This is most likely due to the difference in the prepregs (fabric and unidirectional sheet) and the more accentuated trapping effect for a fabric (fibre C_2) than for a filament (fibre C_4). This is substantiated by the very different adsorption properties we found in previous work involving the study and characterization of carbon fibre surfaces[18] between a fabric and a coated filament.

Table 7 Values of rate constants at 150°C

Sample	Rate constants	
	k (epoxy/h) initiation	k_1 (epoxy/h) autocatalysis
Pure matrix TGDDM-DDS	0.106	2.410
Glass fibre A	0.124	0.025
Glass fibre B_1	0.124	0.025
Glass fibre B_2	0.190	0.615
Glass fibre B_3	0.124	0.025
Glass fibre B_4	0.178	0.075
Carbon fibre C_1	0.127	0.188
Carbon fibre C_2	0.186	0.160
Carbon fibre C_4	0.100	0.947
Carbon fibre C_5	0.195	0.213

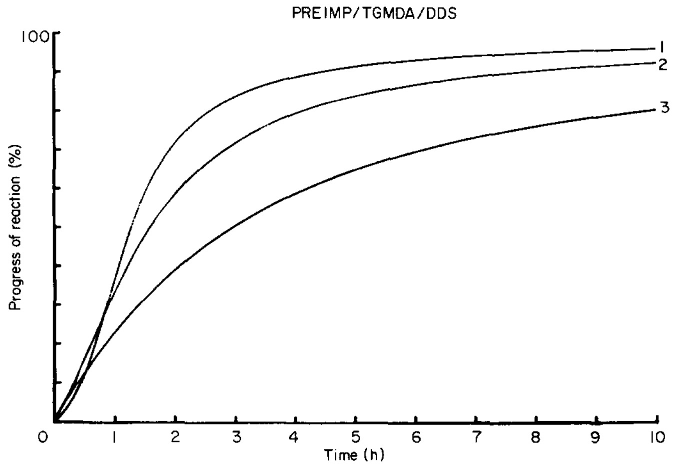


Figure 12 Kinetics in isothermal conditions. Effect of the reinforcer, 150°C. Curves: 1, pure matrix; 2, glass fibre (B_2); 3, carbon fibre (C_1)

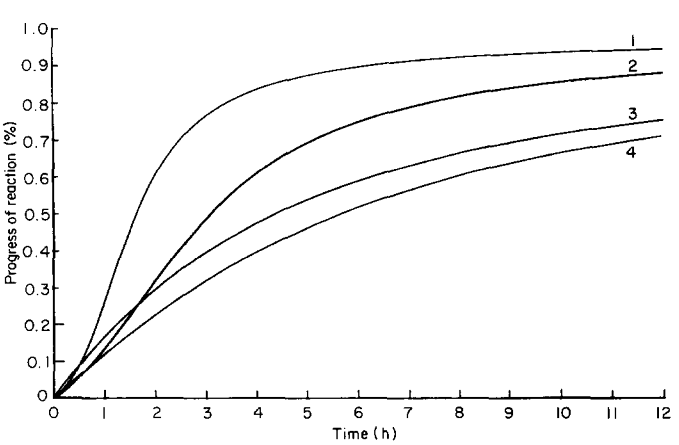


Figure 13 Kinetics in isothermal conditions (progress of the reaction), 150°C. Effects of treatments of carbon fibres: 1, pure matrix; 2, film C_3; 3, film C_2; 4, film C_1

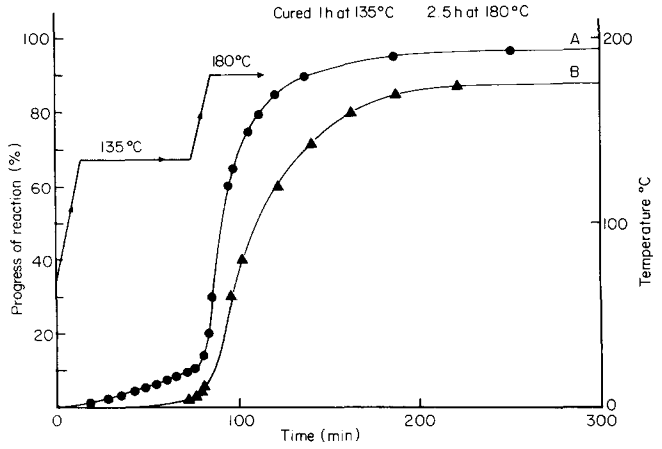


Figure 14 Kinetics followed with temperature programming of a curing cycle: A, pure resin; B, carbon fibre prepreg C_4

Effect of treatment and verification with heat cycles

The conditions chosen were close to the heat cycle used in industrial production: heating rate of 5°C min^{-1}, stationary for 1 h at 135°C, heating at 5°C min^{-1}, stationary for 2.5 h at 180°C (*Figure 14* is an example for fibre C_4 and the pure matrix). It follows that at the beginning of the second part of the cycle and application of pressure in the mould, the matrix has progressed to about 18% (corresponding to the gel point[7]), whereas the prepreg has progressed only to 5–10% (depending on treatment), thus still in a very fluid state, requiring the heat cycle to be adapted to each system.

In conclusion, this work has furnished two important pieces of information, which can be generalized to other types of prepregs. The presence of reinforcing agents, either glass or carbon fibre, does not change the reaction mechanisms or the network structure. We found the same proportion (within experimental errors inherent in each analytical method used) of 'classical' and 'secondary' reactions in the prepregs and in the matrix without fibre for the system we studied. On the contrary, the type of fibre reinforcement, the different treatments undergone and their formulation led to notable differences in the reaction rate, particularly at low temperatures.

Since industrial heating cycles always include a low-temperature plateau for these systems, the heat cycle should thus be adapted to each type of fibre. In particular, the length of the low-temperature stationary phase (generally 135°C) should be increased so that the second phase (crosslinking) starts at the same level of progress of of reaction.

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