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Epoxy resins based on the 1,2,3,4-tetrahydroquinoxaline and the 2,3,4,5-tetrahydro-1H-1,5-benzodiazepine ring systems

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Abstract

The synthesis and characterisation of novel polyfunctional *N*-glycidyl epoxies are reported. *N*,*N*′-Bis(3-chloro-2-hydroxypropyl)-1,2,3,4-tetrahydroquinoxaline underwent condensation with formaldehyde at the 6- and 7-positions to provide a mixture of the 6,6′-methylene and 6,6′/7,7′-dimethylene condensation products and oligomers, which were readily converted to the corresponding epoxy compounds. The product composition depended on the molar ratio of formaldehyde employed in the expected way. Enriched ^{13}C n.m.r. spectra indicated that condensation was not completely exclusive to the 6 and 7 positions, and this was confirmed by employing *N*,*N*′-bis(3-chloro-2-hydroxypropyl)-1,2,3,4-tetrahydro-6-methylquinoxaline in the condensation reaction. The effect of some other substituents and a more limited exercise with the 2,3,4,5-tetrahydro-1H-1,5-benzodiazepine ring are also described. Mixed coupled systems were prepared by condensing *N*,*N*′-bis(3-chloro-2-hydroxypropyl)-1,2,3,4-tetrahydroquinoxaline in the presence of *N*,*N*-bis(3-chloro-2-hydroxypropyl)-3-chloroaniline and *N*,*N*-bis(3-chloro-2-hydroxypropyl)-3,5-dichloroaniline, and simple physical blends were prepared by mixing 6,6′-methylene[*N*,*N*′-(2,3-epoxypropyl)-1,2,3,4-tetrahydroquinoxaline] with the corresponding dichloro and tetrachloro derivatives of bis[*N*,*N*-bis(2,3-epoxypropyl)-4-aminophenyl]methane. The glass transition temperatures and water absorptions of castings prepared from the diamine-cured epoxies are given. The effect of hygrothermal and oxidative aging on the interlaminar shear strength of the most promising systems as the matrix component in unidirectional carbon fibre reinforced composites showed no significant improvement over current high performance composites. © 1999 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Epoxies are favoured matrix materials because of good mechanical properties, low shrinkage on cure with no loss of volatiles, good adhesive properties, and excellent processing properties. Bis[*N*,*N*-bis(2,3-epoxypropyl)-4-aminophenyl]methane (TGDDM) is the most widely used high performance epoxy for carbon fibre reinforced composites in aerospace primary structural applications. It is usually cured with 4,4′-diaminodiphenyl-sulphone (DDS). The main problem with such systems is the well-established effect of water in depressing the glass transition temperature (T_g) of the cured systems, which can be as much as 20°C or more for each 1% of water absorbed [1]. For some years we have been interested in providing improved systems of this type particularly since there is evidence, based on the oxidative ageing of thin castings at elevated temperatures, that amine-cured *O*-glycidyl epoxies [2,3] suffer much larger falls in T_g than amine-cured *N*-glycidyl epoxies [4]. Indeed, in the course of our research [5], we have used dynamic mechanical thermal analysis (DMTA) to monitor the effects of air-ageing on T_g for a number of systems of both types as thin castings (0.050 cm thick), and this difference in behaviour seems to hold generally. An extreme case was provided by a DDS-cured tris[4-(2,3-epoxypropoxyphenyl)]methane, the T_g of which decreased from 315°C to about 200°C after air-aging for 30 days at 150°C or 8 months at 110°C, whereas that of DDS-cured TGDDM remained essentially the same at about 250°C.

We considered that the matrix performance might be improved by either preparing *N*-glycidyl systems having a similar T_g to that of TGDDM-based systems but with a lower water absorbtion, or systems having a higher T_g and a similar water absorption. A combination of a higher T_g and a lower water absorption would of course be highly desirable. Some years ago we reported [6] the preparation of some TGDDM derivatives containing halogen substituents and some properties of castings obtained by a diamine cure. The best thermosets showed significant improvements in

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water absorption with little sacrifice in T_g. This paper describes some of our investigations into the preparation of novel *N*-glycidyl epoxies designed with the objective of providing thermosets of higher T_g than those based on TGDDM.

2. Experimental

2.1. Instrumentation

For liquid chromatography, a Waters ALC/GPC 244 Chromatograph was used with ultraviolet detection at 280 nm recorded with a Spectra Physics SP4100 computing integrator. In the h.p.l.c. mode it was equipped with a 25 × 0.46 cm Zorbax SB-C18 column. Gradient elution was effected with water/THF using a flow rate of 2 ml $\min^{-1}$. For g.p.c., a 60 cm PL gel 3μ mixed E column was used. The eluent was dichloromethane containing 5% methanol at a flow rate of 1 ml $\min^{-1}$.

^{13}C.n.m.r. spectra were measured on approximately 20%(w/v) solutions in $CDCl_3$ at 75.459 MHz for ^{13}C (300.13 MHz for ^{1}H) at ambient temperature (approximately 22°C) on a Bruker MSL-300 superconducting multinuclear n.m.r. spectrometer.

T_gs were determined from the loss peaks obtained using a Polymer Laboratories DMTA operating at 10 Hz with a heating rate of 4°C $\min^{-1}$. Specimens were 0.5 mm thick for resins and 2.0 mm thick for composites. Water absorptions of 0.50 mm thick castings were monitored gravimetrically for 4 weeks at 70°C and a relative humidity of 83% (saturated aqueous sodium carbonate) using a Sartorius 4503 micro balance. Quoted saturation levels refer to values at the intercept of the extrapolated initial slope and the very low gradient slope which followed the point of nominal ‘Fickian’ saturation [7].

Cured castings were prepared by mixing the epoxy and curing agent at 130°C, degassing the resultant solutions (140°C at about 0.05 torr) and pouring them into moulds consisting of two glass plates separated by tailored Teflon/glass weave shims. The plates had been pre-treated with a mould release agent (Vydax 550, DuPont) at 220°C and wiped free of loose agent. As far as epoxy blends were concerned, homogeneous mixtures of equimolar amounts of the two epoxies (obtained by stirring warmed mixtures) were prepared before the addition of curing agent. The castings were initially cured for 5 h at 150°C in an air-circulating oven. Unidirectional carbon fibre bars (12 × 2.0 × ≈ 100 mm) containing about 70% w/w fibre were prepared by a reported procedure [8] using a compression mould. The specimens were removed from the moulds for subsequent post cures (3 h at 180°C, 2 h at 200°C and in some instances a further 1 h at 220°C) under nitrogen for the resin castings and under vacuum for the carbon-reinforced bars. Interlaminar shear strengths (ILSS) of composite specimens (14 × 12.5 × 2.0 mm) were measured using a three point short-beam test [9] in an Instron tensile test machine equipped with an integral oven.

3. Materials

Acrylic acid, 37% aqueous formaldehyde, 40% aqueous glyoxal, epichlorohydrin, 3-chloroaniline, 3,5-dichloroaniline, 2,3-dimethylquinoxaline, quinoxaline, and sodium bis(2-methoxy)dihydroaluminate (‘Redal’ reagent) were from Aldrich Chemicals, 20% aqueous formaldehyde-^{13}C (99% enriched) from C/D/N Isotopes, 4,4′-diaminodiphenylsulphone (HT976) from Ciba Polymers, 2,2-bis(4-amino-3,5 dimethyl)propane (Epon HPT1062) from Shell Research and tris[4-(2,3-epoxypropoxyphenyl)]methane (resin XD7342) from the Dow Chemical Company. These were used as supplied. 1,2-Diaminobenzene and 3,4-diaminotoluene (Aldrich Chemicals) were purified by sublimation.

Literature procedures were used to prepare 1,2,3,4-tetrahydroquinoxaline as white plates, m.p. 98–98.5°C (lit. [10] m.p. 98.5–99°C), 1,2,3,4-tetrahydro-2,3-dimethylquinoxaline as a mixture of isomers [11], 1,2,3,4-tetrahydro-6-methylquinoxaline (from 3,4-diaminotoluene and aqueous glyoxal) as a pale cream powder, m.p. 108–110°C (lit. [10] m.p. 104.5–105.5°C), and 1,3,4,5-tetrahydro-2H-1,5-benzodiazepin-2-one as white needles, m.p. 143°C (lit. [12] m.p. 140.5–141.5°C).

3.1. 2,3,4,5-tetrahydro-1H-1,5-benzodiazepine

In a flame-dried apparatus and under nitrogen, sodium bis(2-methoxy)dihydroaluminate (20 ml ‘Redal’ reagent, 70% solution in toluene), was added over 1 h to a stirred solution of 1,3,4,5-tetrahydro-2H-1,5-benzodiazepin-2-one (4.0 g, 0.025 mol) in toluene (40 ml) at 95°C. H.p.l.c. showed complete consumption of amide. The mixture was cooled and toluene (20 ml) was added to reduce the viscosity. Water (20 ml) was then carefully added and the organic layer, after filtration and removal of solvent by rotary evaporation, gave a brown waxy solid (100%). Recrystallisation from benzene gave 2,3,4,5-tetrahydro-1H-1,5-benzodiazepine as tan-coloured crystals, m.p 103–103.5°C (lit. [13] m.p. 99–101°C).

3.2. 6,6′-Methylenebis[bis(N,N′-2,3-epoxypropyl)-1,2,3,4-tetrahydroquinoxaline] and oligomers (MGTHQ)

1,2,3,4-Tetrahydroquinoxaline (13.4 g, 0.10 mol), epichlorohydrin (37.0 g, 0.40 mol) and acetic acid (0.27 ml, 0.0045 mol) in benzene (30 ml) were stirred under nitrogen at 60°C. As shown by h.p.l.c., the reaction was complete after about 3 h. Solvent and excess of reagents were removed by rotary evaporation, finally at 70°C (2 mmHg). The residue was dissolved under nitrogen in a solution of conc. HCl (15 g) in water (30 ml), 37% aqueous formaldehyde (5.7 g, 0.070 mol) added, and the mixture stirred at 60°C for 3 h. After cooling, the solution was

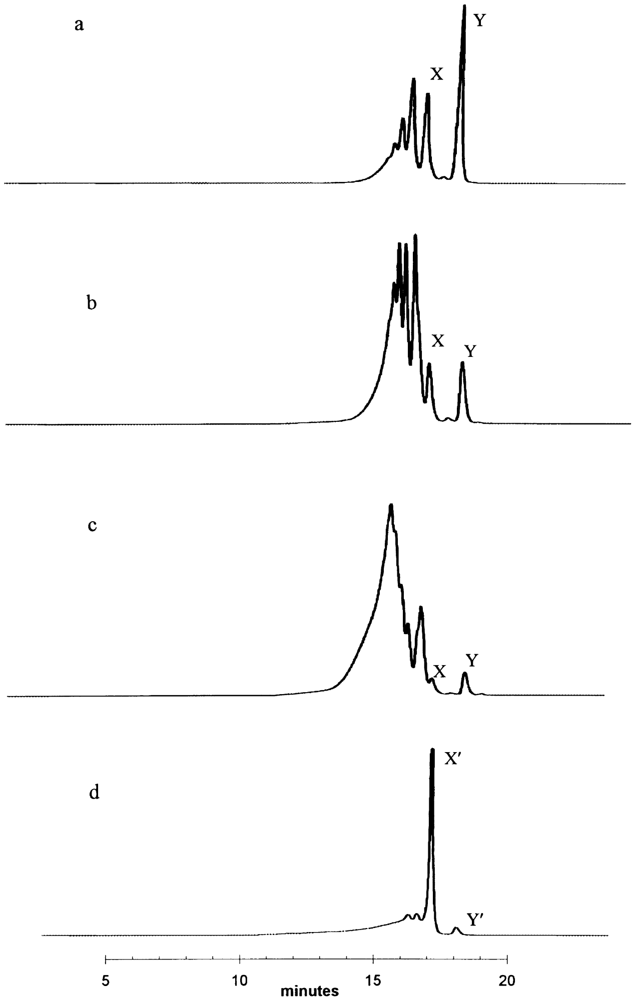


Fig. 1. G.p.c. traces of (a) MGTHQ80, (b) MGTHQ120, (c) MGTHQ160 and (d) MGTHMQ.

neutralised with 10% aqueous sodium hydroxide solution. The aqueous layer was decanted and the organic layer afforded, after removal of volatiles by rotary evaporation (finally at 70°C and 2 mmHg), a friable solid. This was finely powdered and treated under nitrogen with powdered sodium hydroxide (10.8 g, 0.27 mol) and 2-butanone (120 ml), and the resulting slurry vigorously stirred at 60°C for 2 h. The mixture was allowed to cool and settle, and filtered. The filtrate, after removal of solvent by rotary evaporation (finally at 70°C and 2 mmHg), gave an amber-coloured resinous product. This was purified by precipitation from dichloromethane with diethyl ether and dried at 70°C and 2 mmHg to give a solid product MGTHQ140 (typically 75% yield).

Similar reactions were carried out employing different molar proportions of formaldehyde (0.40, 0.60, and 0.80 mol) to 1,2,3,4-tetrahydroquinoxaline (1 mol) to give products assigned as MGTHQ80, MGTHQ120 and MGTHQ160. These three reactions were exactly repeated on a small scale (about 0.01 mol with respect to 1,2,3,4-tetrahydroquinoxaline) using ^{13}C-formaldehyde.

G.p.c. traces are shown in Fig. 1a–c and n.m.r. spectra in Fig. 2b and Fig. 3a–d.

3.3. 7,7′-Methylenebis[bis(N,N′-2,3-epoxypropyl)-1,2,3,4-tetrahydro-6-methylquinoxaline] and oligomers (MGTHMQ)

The general procedure was as described for MGTHQ. 1,2,3,4-Tetrahydro-6-methylquinoxaline (1.48 g, 0.010 mol), epichlorohydrin (3.7 g, 0.040 mol), and acetic acid (0.027 ml, 0.00045 mol) in benzene (3.0 ml) at 60°C for 3 h afforded the N,N'-bis(chlorohydrin). After removal of volatiles, the residue was dissolved in conc. HCl (1.5 g) in water (3 ml) and stirred with 37% aqueous formaldehyde (0.49 g, 0.006 mol) at 60°C for 2 h. After cooling and neutralisation with 10% aqueous sodium hydroxide, the organic layer yielded a friable solid. Treatment with powdered sodium hydroxide (1.0 g, 0.025 mol) in 2-butanone (12 ml) for 2 h at 60°C afforded the title product MGTHMQ (typically 75% yield) as an amber-coloured resin.

This reaction was exactly repeated using formaldehyde containing 40% of 99% enriched ^{13}C formaldehyde.

The g.p.c. trace is shown in Fig. 1d and n.m.r. spectra in Fig. 2a and Fig. 3e.

3.4. 6,6′-Phenylmethylenebis[bis(N,N′-2,3-epoxypropyl)-1,2,3,4-tetrahydroquinoxaline] and oligomers (PMGTHQ)

The general procedure was as described for MGTHQ. 1,2,3,4-Tetrahydroquinoxaline (1.34 g, 0.010 mol), epichlorohydrin (3.7 g, 0.040 mol) and acetic acid (0.027 ml, 0.00045 mol) in benzene at 60°C afforded the N,N'-bis(chlorohydrin). After removal of volatiles, a solution of the residue in conc. HCl (1.5 g) and water (3 ml) was stirred with benzaldehyde (0.64 g, 0.006 mol) at 90°C for 4 h during which time some phase separation occurred. After cooling and neutralisation with 10% aqueous sodium hydroxide, the organic layer yielded a friable solid. Treatment with powdered sodium hydroxide (1.0 g, 0.025 mol) in 2-butanone (12 ml) at 60°C for 3 h afforded the title product PMGTHQ, obtained as a tacky solid after purification by precipitation from dichloromethane with diethyl ether.

3.5. 6,6′-Methylenebis[bis(N,N′-2,3-epoxypropyl)-1,2,3,4-tetrahydro-2,3-dimethylquinoxaline] (MGTHDMQ)

The general procedure was as described for MGTHQ. 1,2,3,4-Tetrahydro-2,3-dimethyl-quinoxaline (1.62 g, 0.010 mol), epichlorohydrin (3.7 g, 0.040 mol) and acetic acid (0.10 ml, 0.0017 mol) in benzene (3 ml) 60°C for 4 h afforded the bis(N,N'-chlorohydrin). After removal of volatiles, the residue in conc. HCl (1.5 g) and water (3 ml) was stirred with 37% aqueous formaldehyde (0.57 g, 0.007 mol) at 50°C for 4 h. After cooling and neutralisation with 10% aqueous sodium hydroxide, the organic layer yielded a

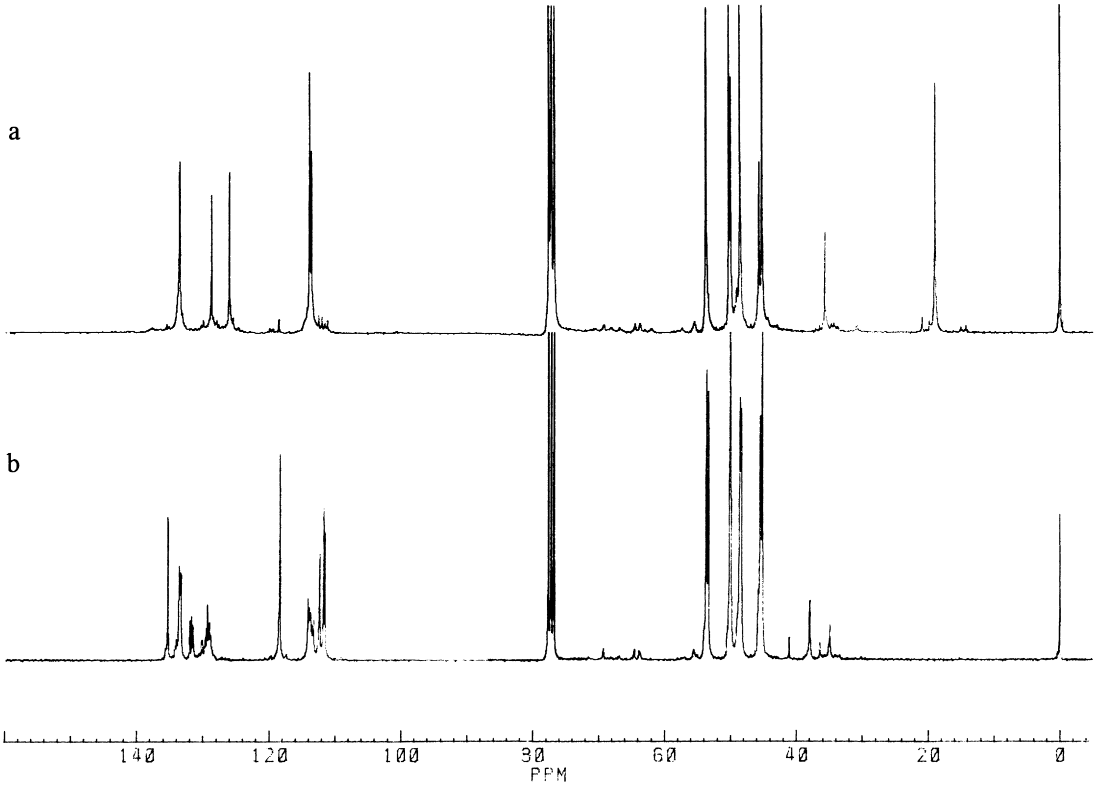


Fig. 2. ^{13}C n.m.r. spectra of (a) MGTHMQ and (b) MGTHQ120.

friable solid. Treatment with powdered sodium hydroxide (1.0 g, 0.025 mol) in 2-butanone (12 ml) at 60°C for 1 h afforded the title product MGTHDMQ as a solid after purification by precipitation from dichloromethane with diethyl ether.

3.6. *7,7′-Methylenebis[bis(N,N′-2,3-epoxypropyl)-2,3,4,5-tetrahydro-1H-1,5-benzodiazepine] and oligomers (MGTHBD)*

The general procedure was as used to prepare MGTHQ. 2,3,4,5-Tetrahydro-1H-1,5-benzodiazepine (1.48 g, 0.010 mol), epichlorohydrin (3.7 g, 0.040 mol) and acetic acid (0.027 ml, 0.00045 mol) in benzene (3 ml) at 60°C for 3 h afforded the bis(*N,N′*-chlorohydrin). After removal of volatiles, a solution of the residue in conc. HCl (3.0 g) and water (3 ml) was stirred with 37% aqueous formaldehyde (0.57 g, 0.007 mol) at 90°C for 10 h. After cooling and neutralisation with 10% aqueous sodium hydroxide, the organic layer yielded a friable solid. Treatment with powdered sodium hydroxide (1.0 g, 0.025 mol) in 2-butanone (12 ml) at 60°C for 2 h afforded the title product (MGTHBD) as a solid after purification by precipitation from dichloromethane with diethyl ether.

3.7. *Co-condensation of N,N′-bis(3-chloro-2-hydroxypropyl)-1,2,3,4-tetrahydro-quinoxaline and N,N-bis(3-chloro-2hydroxyepoxypropyl)-3-chloroaniline and conversion to epoxy product (MGTHQ-DCTGDDM)*

The general procedure was as used to prepare MGTHQ. 1,2,3,4-Tetrahydroquinoxaline (13.4 g, 0.10 mol), epichlorohydrin (37 g, 0.40 mol) and acetic acid (0.27 ml) at 60°C for 3 h afforded the bis(*N,N′*chlorohydrin). Likewise 3-chloroaniline (12.8 g, 0.10 mol) was converted to its bis(chlorohydrin) by treatment with epichlorohydrin (37 g, 0.40 mol) and acetic acid (5.0 ml) at 80°C for 4.5 h. After removal of volatiles, a mixture of the bis(chlorohydrins) (0.050 mol of each) was dissolved in conc. HCl (15.5 g) and water (30 ml) and stirred with 37% aqueous formaldehyde (4.9 g, 0.60 mol) at 75°C 3 h. After cooling and neutralisation with 10% aqueous sodium hydroxide, the dried organic layer yielded a friable solid. Treatment with powdered sodium hydroxide (10.8 g, 0.27 mol) in 2-butanone (120 ml) at 55°C for 40 min afforded the title product (MGTHQ-DCTGDDM), as an amber-coloured, highly viscous product (typically 80% yield) after purification by precipitation from dichloromethane with diethyl ether.

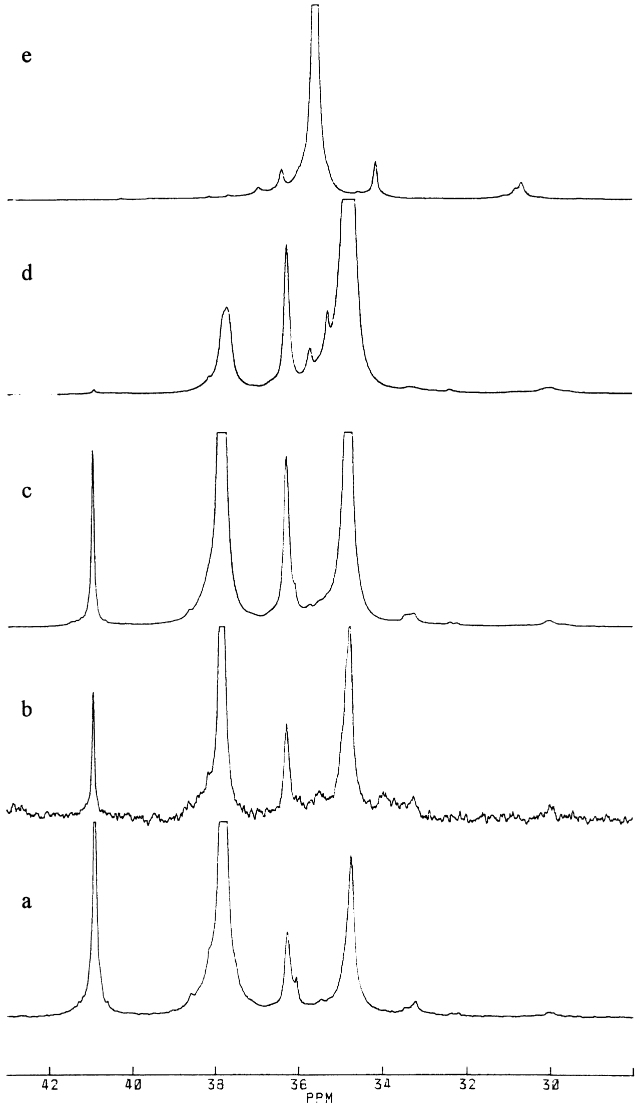


Fig. 3. Enriched ^{13}C n.m.r. spectra in the 25–43 p.p.m. region of (a) MGTHQ80, (c) MGTHQ120, (d) MGTHQ160 and (e) MGTHMQ with, for comparison (b) ^{13}C n.m.r. spectrum for MGTHQ120.

3.8. Co-condensation of N,N′-bis(3-chloro-2-hydroxypropyl)-1,2,3,4-tetrahydro-quinoxaline and N,N-bis(3-chloro-2-hydroxypropyl)-3,5-dichloroaniline and conversion to epoxy product (MGTHQ-TCTGDDM)

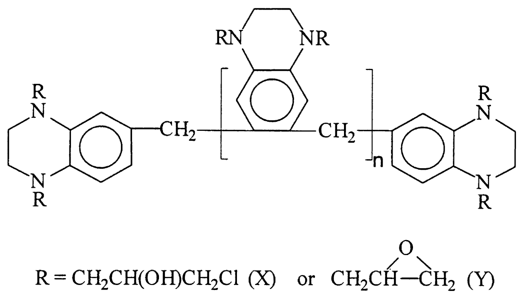
The general procedure was as used to prepare MGTHQ. 1,2,3,4-Tetrahydroquinoxaline (13.4 g, 0.10 mol), epichlorohydrin (37 g, 0.40 mol) and acetic acid (0.27 ml) at 50°C afforded the bis(*N*,*N*-dichlorohydrin). In a similar manner 3,5-dichloroaniline (16.2 g, 0.10 mol) was converted to its bis(chlorohydrin) by treatment with epichlorohydrin (37 g, 0.40 mol) and acetic acid (5.0 ml) at 80°C for 13 h. After removal of volatiles, a mixture of the bis(chlorohydrins) (0.050 mol of each) was dissolved in conc. HCl (15.5 g) in water (30 ml) and dioxane (20 ml), and stirred with 37% aqueous formaldehyde (4.9 g, 0.60 mol) at 80°C for 4.5 h. After cooling and neutralisation with 10% aqueous sodium hydroxide, the organic layer yielded a friable solid. Treatment with powdered sodium hydroxide (10.8 g, 0.27 mol) in 2-butanone (120 ml) at 55°C for 40 min gave the title product (MGTHQ-TCTGDDM) as a highly viscous product (typically 80% yield) after purification by precipitation from dichloromethane with diethyl ether.

4. Results and discussion

An inherent problem in the cure of TGDDM with aromatic diamines is that the nominal tetrafunctionality of the system is reduced because of competing intramolecular cyclisation reactions between *N*,*N*-diglycidyl and primary amine groups. In this respect, we recently reported [14,15] a detailed investigation into the formation of morpholine, perhydro-1,4-oxazepine, perhydro-1,5-diazecine and tetrahydroquinoline rings employing model compounds. We considered that tetrafunctional epoxy systems designed so as to be incapable of such intramolecular cyclisation reactions would provide higher network densities and thus correspondingly higher T_gs. It was considered that the condensation of the *N*,*N*′-diglycidyl derivatives of the 1,2,3,4-tetrahydroquinoxaline or 2,3,4,5-tetrahydro-1H-1,5-benzodiazepine rings with formaldehyde would provide a route to such tetrafunctional systems.

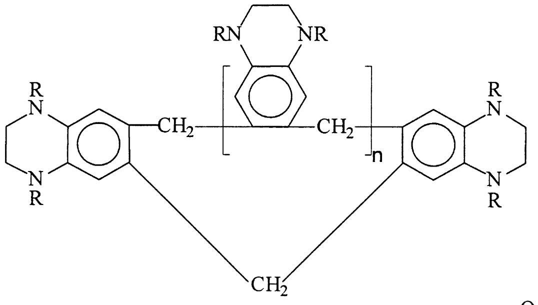
4.1. Preparation and structure of epoxies

The same synthetic approach was used as that to prepare some halogen-substituted derivatives of TGDDM [6] in that the powerful activating influence of the dialkylamino group in an aromatic ring on its acid-catalysed condensation with formaldehyde at the *para-* position was exploited. However, two such activated *para-* positions are present in these heterocyclic systems which, theoretically allow the ready formation of oligomers. Thus the condensation of the *N*,*N*′-bischlorhydrin derivative of 1,2,3,4-tetrahydroquinoxaline with formaldehyde could produce a mixture of the simple tetrachlorohydrin (**Ia**), oligomers (**IIa**) and (**IIIa**) and higher oligomers, as well as intramolecular cyclisation products such as (**IVa**). It was considered that steric factors might inhibit the formation of oligomers. The chlorohydrin products obtained were readily dehydrochlorinated to give the corresponding epoxide products (**Ib**–**IVb**). The epoxide mixtures produced were designated as MGTHQ80, MGTHQ120, MGTHQ140, and MGTHQ160 according to the molar proportion of formaldehyde used. (A value of 100 refers to that required for a stoichiometric reaction to produce solely (**Ia**).) Viscosity increased in the expected manner from the mobile MGTHQ80 to the highly viscous MGTHQ140, but MGTHQ160 was a solid. The g.p.c. traces for MGTHQ80, MGTHQ120, and MGTHQ160 are shown in Fig. 1a–c.

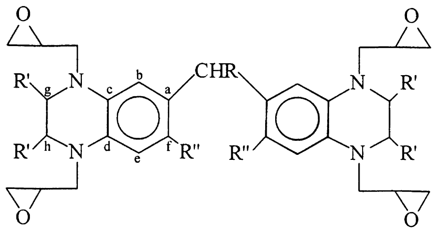


R = $CH_2CH(OH)CH_2Cl$ (X) or $CH_2\overset{O}{CH-CH_2}$ (Y)

Ia	n=0, R=X	Ib	n=0, R=Y
IIa	n=1, R=X	IIb	n=1, R=Y
IIIa	n=2, R=X	IIIb	n=2, R=Y



(IVa) R = $CH_2CH(OH)CH_2Cl$ (IVb) R = $CH_2\overset{O}{CH\cdot CH_2}$



(V) R, R' = H, R'' = CH_3 (VI) R,R'' = Cl

(VII) R,R''=H, R'=CH_3 (VIII) R,R''=H, R'=Cl

(IX) R = C_6H_5, R',R'' = H

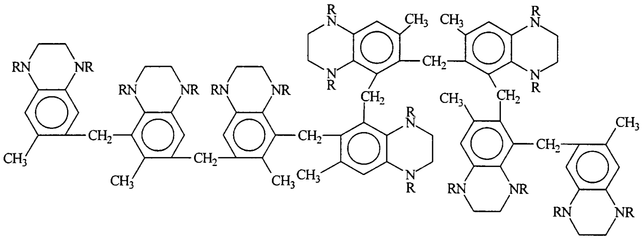
As expected, the proportion of oligomeric product was reduced and that of (**Ib**) (peak *X*) increased by decreasing the molar ratio of formaldehyde, yet the proportion of oligomer was still considerable, even with a deficiency of formaldehyde as in the production of MGTHQ80. Peak *Y* is attributed to *N*,*N*′-bis(2,3-epoxypropyl)-1,2,3,4-tetrahydroquinoxaline. The problem of oligomer formation was not completely overcome by blocking one of the *para*- positions with a methyl substituent. Thus, 1,2,3,4-tetrahydro-6-methylquinoxaline, afforded product (MGTHMQ) which was shown by g.p.c. (Fig. 1d) to contain (**V**) (peak *X*′), a trace of *N*,*N*′-bis(2,3-epoxypropyl)-1,2,3,4-tetrahydro-6-methylquinoxaline (peak *Y*′), and a small proportion of oligomer. It was not possible to make the analogous chlorine substituted derivative (**VI**) because all attempts to prepare the precursor, 6-chloro-1,2,3,4-tetrahydroquinoxaline, by reduction of 6-chloroquinoxaline failed.

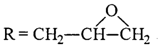
The ^{13}C n.m.r. spectra were consistent with the assigned structures and are shown in Figs. 2 and 3. As expected MGTHMQ (Fig. 2a) shows the simplest spectrum with the dominant peaks fully in agreement with structure (**V**). Thus, the aromatic carbons a and f occurred at 128.7 and 126.0 ppm, b and e occurred at 113.5 and 113.8 ppm, while c and d can just be resolved at 133.5 and 133.4 ppm. The ring *N*-methylene carbons (g) and (h) occurred at 48.6 ppm, the exocyclic *N*-methylene carbons at 53.7 ppm, the *O*-methylene and *N*-methine carbons (each as two peaks) at 45.2,45.7 and 50.0,50.2 ppm, the bridging-methylene carbons at 35.7 ppm, and the methyl carbon at 19.0 ppm. For comparison a spectrum of MGTHQ120 with its analogous features is shown in Fig. 2b. The complexity of the MGTHQ products was best reflected in the absorptions for the bridging methylene carbons which were confirmed by using 99% enriched formaldehyde-^{13}C to effect condensation. The enriched spectra for MGTHQ80, MGTHQ120 and MGTHQ160 in the aliphatic region are shown in Fig. 3a, c and d together with the non-enriched spectrum for MGTHQ120 in Fig. 3b. The enriched spectrum for MGTHMQ is shown in Fig. 3e. MGTHQ80 and MGTHQ120 showed four dominant peaks at 34.9, 36.5, 38.0 and 41.1 ppm whereas THQ160 showed the first three as dominant peaks but only a very minor 41.1 ppm peak. As expected, MGTHMQ showed only one strong peak, at 35.7 ppm, with very minor peaks at 30.8, 34.3 and 36.5 ppm. Peak interpretation follows from the *ortho*-substituent effect [16], and practically from the shift for MGTHMQ and the effect of formaldehyde concentration on the composition of the product as reflected by the relative peak intensities. Thus the 41.1 ppm peak which is essentially absent in MGTHQ160, is assigned to the methylene group in (**Ib**), and the 38.0 ppm peak to those which are influenced by a single adjacent *ortho*-methylene bridge, that is the methylene groups in (**IIb**) and also the terminal bridging methylene groups in (**IIIb**) and higher oligomers. The 35.0 ppm peak is attributed to in-chain methylene bridging groups present in (**IIIb**) and higher oligomers, each of which is influenced by two adjacent *ortho*-methylene groups (one in each attached ring), a similar situation to the bridging methylene group in (**V**) with its shift of 35.5 ppm. There remains the assignment of the 36.5 ppm peak. As mentioned earlier, g.p.c showed the presence of a small amount of oligomeric product in MGTHMQ. This implies that some condensation reaction occurs at the less activated 5- and 8-positions of the 1,2,3,4-tetrahydro-6-methylquinoxaline ring. The enhancement of very weak peaks at 30.8, 34.3, and 36.5 ppm (Fig. 3e) supports this and, taking the *ortho*- substituent effect into account, indicates the presence of bridging methylenes influenced by two, three or four adjacent *ortho*- substituents as in the hypothetical oligomer (***X***). The enriched spectra of the MGTHQ products

Table 1
Saturated water absorptions, *w* (gram H_2O/100 gram dry resin), and glass transition temperatures, T_g (°C) of cured resin systems. Values in parentheses refer to separately cured specimens

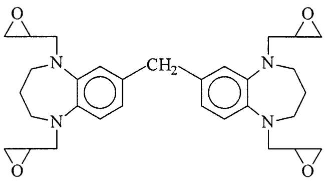
Epoxy resin	Cured with DDS		Cured with HPT1062	
	w	T_g	*w*	T_g
MGTHQ80	4.7	260		
MGTHQ120	5.8	295		
MGTHQ140	5.9	304	3.4	305
MGTHQ160	5.9	313		
MGTHMQ120	5.3	257		
PMGTHQ	4.5	270(272)		
MGTHDMQ/DCTGDDM blend	3.7	272(273)		
MGTHBD	–	261		
MGTHQ–DCTGDDM	4.2	290(291)	2.8	276
MGTHQ–TCTGDDM	4.7	295		
MGTHQ140/DCTGDDM blend	4.1	283	2.6	272
MGTHQ140/TCTGDDM blend	4.1	275		
MGTHQ140/DBTGDDM blend	4.0	278		
MGTHQ140/TGDDM blend	5.3	279	2.9	267
TGDDM	3.8	268	2.4	252

(Fig. 3a, c and d) show analogous features which indicate that some reaction at the 5- and 8-ring positions of the 1,2,3,4-tetrahydroquinoxaline ring has also occurred to produce a very small proportion of branched sites at which the bridging methylene carbons are subject to similar structural influences. Returning to the 36.5 ppm peak, it will be noted that it is much more intense than these additional peaks and is even quite marked in MGTHQ80. Thus the product responsible for the peak is fairly readily formed even in the presence of a deficiency of formaldehyde. For these reasons the peak is attributed to the methylene bridging carbons in the fused ring compound **IVb**(n = 0), a result of 6-membered ring formation involving activated *para*-carbon positions in the intramolecular condensation of **Ib** with formaldehyde.



(X)


$R = CH_2{-}\overset{O}{CH{-}CH_2}$



(XI)

We have reported [7] that *ortho*/*ortho* dimethyl substitution in an amine cured *N*,*N*-diglycidylaniline system provided lower water absorption. With the same objective, 1,2,3,4-tetrahydro-2,3-dimethylquinoxaline was employed in the reaction sequence to provide MGTHDMQ, a mixture of (**VII**) and oligomers. Attempts to form the chlorine-substituted analogous system (**VIII**) failed because attempts to reduce the 2,3-dichloroquinoxaline precursor were unsuccessful.

Benzaldehyde was successfully employed instead of formaldehyde to provide PMGTHQ, a mixture of (**IX**) and oligomers. However, no condensation could be effected with fluorenone.

A 6/7-fused ring system was examined to a limited extent by employing 2,3,4,5-tetrahydro-1H-1,5-benzodiazepine instead of 1,2,3,4-tetrahydro-quinoxaline. This gave MGTHBD, a mixture of (**XI**) and oligomers.

4.2. Evaluation of epoxy resins

Initial screening of these novel epoxies was based on the T_g and water absorption of thin castings prepared by curing them with one of two diamine curing agents. A staged cure in the absence of air at the successively higher temperatures of 150°C, 180°C, 200°C was used, with a final post cure 220°C. Higher cure temperatures for extended periods led to enhanced darkening of samples. T_gs were determined by DMTA, and water absorptions, at 70°C with the relative humidity at 83%, by monitoring weight gain well beyond the nominal saturation level. All were cured with DDS, and a selection were also cured with 2,2-bis(4-amino-3,5-dimethyl)propane (HPT1062), formulated [17] for bestowing low water absorption. The systems examined (epoxy and

Table 2
Effect of hygrothermal and oxidative ageing on selected matrices in unidirectional carbon fibre reinforced composites

Matrix system	Before ageing			Hygrothermally aged[a]			Air-aged[b]		
	Dry T_g (°C)	Dry ILSS (MPA)		Water absorbed (wt/wt%)	Wet ILSS (MPA)		T_g (°C)	ILSS (MPA)	
		120°C	150°C		120°C	150°C		120°C	150°C
MGTHQ140/DCTGDDM HPT1062	248	71	61	0.96	48	39	–	–	–
MY720 HPT1062	234	72	60	0.87	55	44	238	77	69
MGTHQ140 DDS	294	–	72	2.36	–	41	288	–	76
MGTHQ–DCTGDDM DDS	291	82	76	1.68	51	43	291	87	80
MGTHQ–TCTGDDM DDS	287	82	75	1.62	54	46	291	86	82
MY720 DDS	263	89	80	1.37	54	44	270	89	78
XD7342 DDS	329	71	67	1.30	41	36	328 (215)	71	66

[a] 150 days at 70°C and relative humidity of 83%.
[b] 80 days in an air-circulating oven at 150°C.

curing agent), and the T_gs and water absorptions of their cured castings, are listed in Table 1.

4.3. Epoxy resins cured with DDS

For the MGTHQ systems, the T_g decreased as the proportion of the simple condensation product (**Ib**) increased, and ranged from about 313°C for MGTHQ160 to 260°C for MGTHQ80, a value close to that (257°C) for cured MGTHMQ, which was essentially pure (**V**), and about 10°C lower than that for cured TGDDM. It would thus appear that the objective of increasing cross-link density by the elimination of intramolecular cyclisation reactions during cure was more than compensated by the adverse effect of the tetrahydroquinoxaline ring in effectively increasing the distance between cross-links by a $-CH_2-CH_2-N$-unit. It would also appear that any enhanced chain stiffening effect due to the tetrahydroquinoxaline ring and the extended fused ring system of (**IVb**)($n = 0$) was likewise overcome. As might be expected, incorporation of oligomeric structures into the network provided an additional increase in the cross-link density and thus the T_g. Water absorption increased with increasing T_g from 4.7% for MGTHQ80 and 5.3% for MGMTHQ to 5.9% for MGTHQ160, behaviour which we have observed with other structurally related systems [7]. It will be noted that although MGTHQ140 and MGTHQ160 had a T_g about 40°C higher than cured TGDDM, this was only achieved at the expense of a much higher water absorption (5.9% compared with 3.8% for cured TGDDM). Other structural changes such as replacing the bridging methylene with phenylmethylene (PMGTHQ) or the tetrahydroquinoxaline ring with a 6/7 fused 2,3,4,5-tetrahydro-1H-1,5-benzodiazepine ring (MGTHBD) only provided T_gs and water absorptions similar to the TGDDM-based system. (The high viscosity of the MGTHBD resin resulted in voids in the cured sample making it unsuitable for water absorption measurements.) The tetrahydroquinoxaline epoxy which contained a methyl substituent adjacent to each nitrogen atom (MGTHDMQ) was too viscous to be processed into a casting and was thus blended with a chlorine-containing TGDDM epoxy. The water absorption and T_g were much the same as for TGDDM.

Because of the beneficial effect of halogen-substitution in reducing water absorption, cross-coupled product was prepared by employing an equimolar mixture of N,N'-bis(3-chloro-2-hydroxypropyl)-1,2,3,4-tetrahydroquinoxaline and N,N'-bis(3-chloro-2-hydroxypropyl)-3-chloroaniline in the condensation reaction with formaldehyde. The epoxy product (MGTHQ-DCTGDDM) was, of course, highly complicated because of the simultaneous formation of self-condensed products. This cured epoxy system provided the best balance of properties with a T_g over 20°C higher and a water absorption only 0.4% higher than the values for cured TGDDM. The analogous cross-coupled product, MGTHQ-TCTGDDM was prepared by employing N,N'-bis(3-chloro-2-hydroxypropyl)-3,5-dichloroaniline instead of N,N'-bis(3-chloro-2-hydroxypropyl)-3-chloroaniline. Although this resulted in a further 5°C improvement in T_g, water absorption was also slightly higher. These cross-coupled epoxies were superior to the corresponding simple physical blends (1:1 molar ratio), MGTHQ/DCTGDDM and MGTHQ/TCTGDDM, which had similar water absorptions but T_gs some 10–20°C lower. Replacement of DCTGDDM by the analogous bromo derivative DBTGDDM in a physical blend with MGTHQ provided essentially the same T_g and water absorption values.

4.4. Epoxy resins cured with HPT1062

In all cases, as can be seen in Table 1, water absorption was reduced compared with the corresponding DDS-cured systems, but this was usually accompanied with a marked fall in T_g.

4.5. Evaluation of selected epoxies in unidirectional carbon fibre composites

As a result of screening the cured resins, the most promising systems were evaluated as the matrix component in unidirectional carbon fibre reinforced bars. Composite bars allow the determination of the interlaminar shear strength (ILSS), a matrix dominated property, and an excellent indicator of resin performance. ILSS was determined at 120°C, the temperature currently expected of epoxies, and at 150°C, the target temperature. The bars were subjected to hygrothermal ageing at 70°C with the relative humidity at 83% for 150 days, and oxidative ageing in air at 120 and 150°C for 80 days. The results obtained for the systems tested, together with comparative data [18] for composite bars from MY720 cured with DDS and with HPT1062 and XD7342 cured with DDS as the matrix materials, are listed in Table 2. Insufficient samples were produced to allow the study of MGTHQ140/DDS at 120°C and of MGTHQ140/DCTGDDM/HPT1062 after air ageing.

It will be noted that MGTHQ140 cured with HPT1062 had a similar water absorption to DDS-cured MY720 but a T_g about 30°C higher and so good composite properties were expected. Unfortunately, the viscosity of the mixture of MGTHQ140 and HPT1062 was too high to allow composite bars to be processed, and thus the epoxy was blended with the chloroepoxy resin DCTGDDM. The dry ILSS at 120 and 150°C was similar to that with MY720 cured with this hardener as matrix, but its performance on wet ageing was not so good.

The most promising system to emerge from the screening programme was the cross-coupled resin obtained from MGTHQ and TCTGDDM cured with DDS. Although initially inferior to the MY720 system, it was marginally better at the higher test temperature after hygrothermal ageing and oxidative ageing. Thus its initial ILSS was about 10% lower at 120°C but less so at 150°C, presumably because of its higher T_g. After hygrothermal and air ageing, the ILSS data at 120°C for both systems was very similar, but at 150°C that of the MGTHQ–TCTGDDM system was marginally better. It will be noted, in fact, that the ILSS values of the air aged materials are higher than the initial values suggesting that some additional cure during the ageing process. However, no further increase in T_g had been observed after an extended post cure. The MGTHQ–DCTGDDM system provided very similar ageing data to the MY720 system, but like the MGTHQ–TCTGDDM system, showed a marginal increase in ILSS after oxidative ageing. On balance, the performance of these mixed systems is probably not significantly better than that of the MY720 system. Comparison of the MGTHQ–TCTGDDM and MGTHQ–DCTGDDM results with those of the XD7342 system showed the former's superiority throughout despite the higher T_g of the latter.

As far as the effect of air-ageing at 150°C on T_g is concerned, the N-glycidyl systems, as expected from data on thin castings, suffered little effect.

5. Conclusions

Novel epoxy resins of high functionality containing 1,2,3,4-tetrahydroquinoxaline rings can be readily synthesised. Thus, the reaction of *N*,*N*′-bis(3-chloro-2-hydroxypropyl)-1,2,3,4-tetrahydroquinoxaline with formaldehyde occurred at the highly reactive 6- and 7-positions to give the simple condensation product as well as oligomers which were easily converted to the corresponding epoxy products. As expected, the oligomeric content increased as the proportion of formaldehyde employed was increased. Some minor reaction at the 5- and 8-positions was inferred since the blocking of one of the reactive sites with a methyl substituent did not completely prevent oligomer formation. This was confirmed by product structure analysis as provided by the chemical shifts of the bridging methylene ^{13}C n.m.r. peaks (confirmed by using 99% enriched formaldehyde-^{13}C in the condensation reactions) which were markedly sensitive to structural environment and readily assigned.

The evaluation of these epoxies when cured with 4,4′-diaminodiphenylsulphone showed that the objective of increasing the glass transition temperature by the prevention of intramolecular cyclisation reactions which reduce epoxy functionality was not realised, probably because of a lengthening of the network chains introduced by the 1,2,3,4-tetrahydroquinoxaline ring. However, increased oligomeric content (i.e., functionality) did lead to an increase in glass transition temperature with the highest values exceeding 300°C but with an associated increase in water absorption. To this extent the system offered no particular advantage over commercial systems based on bis[*N*,*N*′-bis(2,3-epoxypropyl)-4-aminophenyl]methane. Replacement of the diamine with 2,2-bis(4-amino-3,5-dimethyl)propane decreased water absorption but usually at the expense of a lower glass transition temperature and with added processing problems. Structural variations to the 1,2,3,4-tetrahydroquinoxaline system, such as introducing methyl substituents into the 2- and 3-positions or employing phenylmethylene as the bridging link, provided no additional benefit.

Mixed coupled systems could also be prepared by condensing *N*,*N*′-bis(3-chloro-2-hydroxypropyl)-1,2,3,4-

tetrahydroquinoxaline in the presence of N,N'-bis(3-chloro-2-hydroxypropyl)-3-chloroaniline or N,N'-bis(3-chloro-2-hydroxypropyl)-3,5-dichloroaniline chosen for reducing water absorption. Of all of the systems screened, these provided the best combination of properties with glass transition temperatures 20–25°C higher and water absorption only about 0.4–0.9% higher than for the corresponding bis[N,N'-bis(2,3-epoxypropyl)-4-aminophenyl]methane system. In comparison, simple blends of the corresponding epoxies led to no improvement. The improvement provided by these two mixed systems was not reflected by any significant corresponding improvement when the resin systems were evaluated in unidirectional carbon fibre composites either hygrothermally at 70°C or in air at 150°C.

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References

[1] Wright WW. Composite Polymers 1989;2:275.
[2] Merryl GT, Meeks AC. J Appl Pol Sci 1972;16:3389.
[3] Bellenger V, Verdu J, Francillette J, Horau P. Polymer Commun 1986;27:279.
[4] Thoseby MR, Dobinson B, Bull CH. British Polym J 1986;18:286.
[5] Johncock P, Tudgey GF. Unpublished results.
[6] Johncock P, Tudgey GF, Br Polym J 1983;15:14 and Johncock P. US Patent, 1982.
[7] Johncock P, Tudgey GF. Br Polym J 1986;18:292.
[8] Tudgey GF. Advanced Composite Letters 1993;2:215.
[9] Curtis PT. RAE Technical Report 88012, 1988.
[10] Cavagnol JC, Wiselogle FY. J Am Chem Soc 1947;69:795.
[11] Gibson CS. J Chem Soc 1927;343.
[12] Bachman GB, Heisey LV. J Am Chem Soc 1985;1949:71.
[13] Davoll J. J Chem Soc 1960;54:308.
[14] Johncock P, Tudgey GF, Cunliffe AV, Morrell RK. Polymer 1991;32:323.
[15] Johncock P, Cunliffe AV. Polymer 1992;33:2392.
[16] Stothers JB. Carbon-13 NMR spectroscopy. New York: Academic Press, 1972:112.
[17] Bauer RS, Filippov AG, Schaudt LM, Breitigem WV. 32nd International SAMPE Symposium and Exhibition, 6–9 April 1987:1104.
[18] Tudgey GF. Institute of Materials 3rd International Conference on Deformation and Fracture of Composites, University of Surrey, UK, 27–29 March 1995:433.