The Beta Relaxation in Epoxy Resin-Based Networks

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Synopsis

The dynamic properties of epoxy–amine networks have been studied using a torsion pendulum, and the effect of replacement of resin by monoglycidyl ethers on the beta relaxation has been determined. It is shown that the loss peak is not sensitive to glyceryl units derived from the monofunctional diluents. From the effect of mixtures of aliphatic and aromatic-based epoxy resins on the relaxation and from the loss properties of systems with varying ratio of resin to curing agent and catalytically cured systems, it is suggested that the loss peak has at least two basic components. One is related to the presence of glyceryl units derived from polyfunctional glycidyl compounds, while the other may be related to the presence of diphenylpropane units in the resin.

INTRODUCTION

The beta relaxation in epoxy resin networks is defined here as that relaxation observed using dynamic methods near −50°C at 1 cps in conventional epoxy resins cured with amines. This relaxation was first observed by Kaelble[1] and has been reported in a wide range of resin systems.[2–4] It is generally assumed that the loss peak is caused by a relaxation of the glyceryl units with the structure

$$\underset{\displaystyle \overset{\textstyle OH}{|}}{-O-CH_2-CH-CH_2-}$$
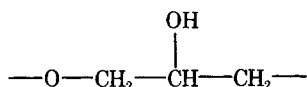
Variation of the structure of the resin[2,3] or curing agent[4] does not appear to affect the loss peak greatly. During cure the peak increases in height and shifts to a higher temperature,[5–8] which suggests that its occurrence is associated with a product of the polymerization reaction.

This assignment is also suggested by a study of the effect of variation of the ratio of curing agent to resin. A shortage of amine causes a decrease in peak height and shift to lower temperature,[5–8] whereas excess curing agent has little effect.[7,8] It has been suggested that the maximum value of the loss in the beta region may be dependent on the concentration of glyceryl units[9,10] and possibly on the functionality of the resin–curing agent system.[10]

The present study was to investigate the relationships between loss tangent and component concentration and functionality.

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0021-8995/79/0023-3433$01.00

EXPERIMENTAL

The epoxy resin used in this study was commercial Araldite 6004 supplied as an unmodified resin by Ciba Geigy (Australia) Ltd. Subsequent detailed analysis by nuclear magnetic resonance spectroscopy and high-pressure liquid chromatography showed that it contained 6 wt. % p-tert-butylphenyl glycidyl ether in addition to about 10% of the higher molecular weight materials normally found in commercial epoxy resins. Its epoxide equivalent was 5.28 mol/kg, whereas pure diglycidyl ether of 2,2-bis(4'-hydroxyphenyl)propane (DDGE) has a calculated epoxide equivalent of 5.88 mol/kg. It will be shown below that not all glycidyl entities react during cure to give equivalent glyceryl units. In order to estimate the proportion of functional and nonfunctional glyceryl units in the commercial resin, some pure DDGE was prepared by repeated solvent–nonsolvent crystallization of commercial resin.[11] This material was a white crystalline solid of mp 43–44°C. The dynamic properties of samples prepared using this resin and stoichometric quantities of several curing agents could not be distinguished from those of samples prepared using the commercial resin and the same quantities of curing agent. The impurities in the commercial resin were therefore considered to be of negligible concentration; and for the semiquantitative analysis below, the resin was assumed to be pure. This results in the presence of a slight excess of curing agent (about 10%) in all systems tested.

The sources and properties of the glycidyl components used are shown in Table I. Epoxide contents were measured by the method of Jay.[12] Chlorine content of the Araldite 6004 was found by elemental analysis to be 0.21 wt. %. Araldite DY022 was found to have an epoxide equivalent of 7.7 mol/kg, whereas the theoretical value for butanediol diglycidyl ether was 9.90 mol/kg. The commercial material was therefore redistilled under vacuum (bp 146–150°C/4 Torr).

The sample of 2-(4'-methoxyphenyl)-2,4'-(2,3-epoxypropoxyphenyl)propane (MGE) was prepared by partially methylating 2,2-bis(4'-hydroxyphenyl)propane (1 mole) with dimethyl sulfate (1 mole) in the presence of sodium hydroxide (2 moles), purifying the product by recrystallization of the sodium salt from water to give, on acidification, the monomethoxy derivative and forming the glycidyl derivative by reaction with excess epichlorhydrin under alkaline conditions. The product was liquid.

TABLE I
Glycidyl Compounds

Compound	Source	Abbrev.	Epoxide content, mol/kg	
			Found	Calcd
Diglycidyl ether of 2,2-bis(4'-hydroxyphenyl)propane (Araldite 6004)	Ciba-Geigy	DDGE	5.28	5.88
Diglycidyl ether of 1,4-butanediol (Araldite DY 022)	Ciba-Geigy (see experimental section)	BDGE	9.76	9.90
Butyl glycidyl ether	Shell Chemical (Australia)	BGE	7.15	7.69
Phenyl glycidyl ether (laboratory grade)	Koch–Light Laboratories	PGE	6.66	6.67
2-(4'-Methoxyphenyl)-2-[4'-(2,3-epoxypropoxy)phenyl]propane	See experimental section	MGE	2.82	2.82

Amines used were laboratory-grade materials obtained from Koch Light Laboratories Ltd. and were used without further purification.

Samples were prepared by preheating the resin to 60°C and adding the required amount of diluent. The appropriate weight of amine (premelted where necessary) was added and the mixture cast in copper molds lined with PTFE tubing to form cylindrical rods about 150 mm long and 5 mm in diameter.

The cure schedule used was 20 hr at 60°C followed by 200 min at 150°C. Samples cured with *sym*-di-N-methyl derivatives of diaminoethane, 1,3-diaminopropane, and 1,6-diaminohexane were not postcured because of formation of excessive voids in the thermoplastic products.

Dynamic mechanical properties were determined using an inverted, free-oscillation torsion pendulum supplied by Clanor Instruments, Melbourne. The accuracy of this instrument has been described.[13] The frequency of oscillation was adjusted to remain within the range 0.8–1.2 Hz. The temperature range studied was from −150°C to the glass transition region, which has been described earlier.[14]

Figure 1 shows the beta relaxation for a series of samples of DDGE cured with 1,3-diaminopropane modified by the partial replacement of the resin by PGE. Table II gives maximum values of the loss tangent and the temperatures of the maximum loss tangent for a series of typical systems. From values for peak constants for samples of the same composition, it is estimated that reproducibility is ±0.003 for the maximum loss tangent and ±2°C for the peak temperature. Table III shows the chemical composition of some typical systems.

The systems examined were: (i) DDGE modified with 0, 5, 10, 20 and 30 wt. % PGE cured with diaminoethane, 1,3-diaminopropane, 1,6-diaminohexane, and 1,12-diaminododecane and diethylenetriamine; and selected blends of DDGE and PGE cured with N-methyl and *sym*-N,N'-dimethyl derivatives of the first three amines; (ii) DDGE modified with BGE and MGE cured with 1,3-diaminopropane; (iii) DDGE modified with BDGE cured with 1,3-diaminopropane; (iv) DDGE cured with diaminoethane, 1,3-diaminopropane, 1,6-diaminohexane, and 1,12-diaminododecane and diethylenetriamine in 50%, 75%, 90%, 110%, 150%, and 200% of the stoichiometric amount; (v) DDGE cured with 1,3-diaminopropane in the 50%, 75%, and 90% of the stoichiometric ratios with diethylamine added to react with excess expoxide; (vi) DDGE cured with a range of concentrations of diethylamine or boron triflouride–monoethylamine complex (BF$_3$–MEA).

DISCUSSION

Significance of Maximum Value of Loss Tangent

In this study the maximum value of the loss tangent (D_m) has been used as a quantitative measure of the intensity of the relaxation. It could be measured conveniently, and the error and reporducibility were known. It will be proposed that the beta relaxation is composed of two components: one dependent on the presence of the glyceryl units that are derived from multifunctional glycidyl compounds, and the other on the presence of diphenylpropane units.

Comparison of the values of D_m for systems containing various diluents shows that there is a wide variation in D_m while the total glyceryl content varies very
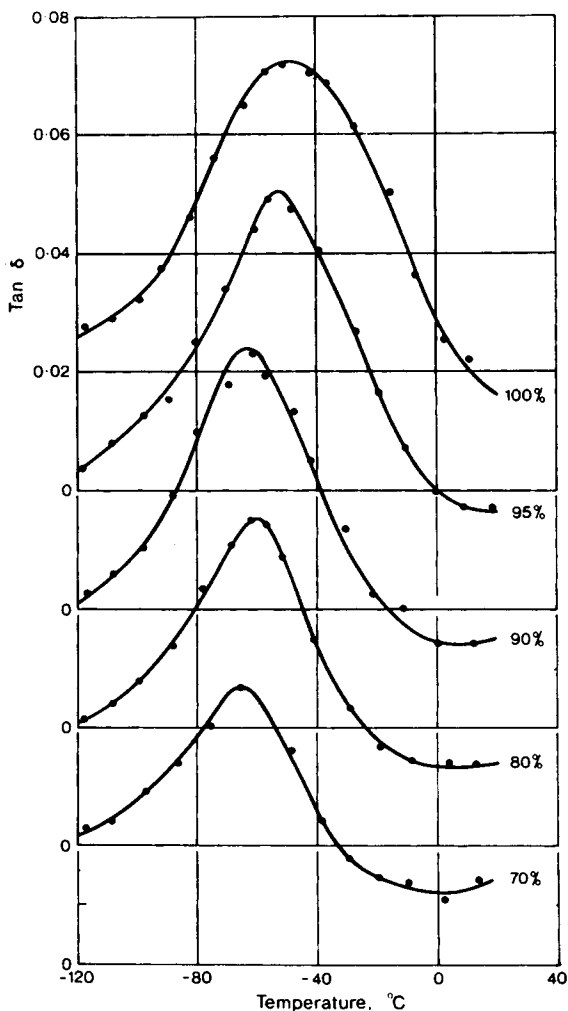
Fig. 1. Series of loss spectra for DDGE modified with PGE cured with 1,3-diaminopropane. Graphs are identified by the percentage by weight of resin in the DDGE/PGE mixture. To avoid confusion, successive curves have been shifted 0.02 units downward, as the diluent level is increased.

little. For example, replacement of 30% of the resin by PGE for systems cured with 1,3-diaminopropane increases the glyceryl concentration by less than 4%, while the height of the loss maximum decreases by more than 30% (systems 5 and 8, Tables II and III). The glyceryl group derived from the diluent does not have a large effect on the relaxation.

The concentration of the glyceryl groups formed from diglycidyl molecules may be calculated from the mixing ratio assuming 100% reaction. Infrared evidence[9] suggests that this cure schedule results in high degrees of conversion of the reactants for stoichiometric systems, and the slight excess of amine will ensure that all gycidyl groups will have reacted.

Analysis by differential scanning calorimetry (DSC using a DuPont 900 instrument) does not reveal any residual exotherm in specimens cured using this cycle. The calculated concentration of glycidyl molecules will be termed the

TABLE II
Typical Constants for the Beta Relaxation: Systems Based on DDGE

System no.	Amine[a]	Diluent	Maximum loss tangent				Temperature of maximum loss, °C			
			0[b]	10	20	30	0	10	20	30
1–4	C2	PGE	0.0685	0.0675	0.0535	0.0505	–50	–55	–63	–64
5–6	C3	PGE	0.0685	0.063	0.0555	0.047	–50	–61	–59	–63
9–12		MGE	0.0685	0.0665	0.061	0.051	—	–56	–62	–63
13–16		BGE	0.0685	0.065	0.0535	0.0425	—	–60	–70	–74
17–20	C3 Me	PGE	0.0725	0.062	0.048	0.0415	–55	–60	–63	–66
21, 8	C3 Me II		0.065	—	—	—	–57	—	—	—
22–25	C6	PGE	0.077	0.068	0.062	0.049	–48	–54	–62	–64
26–28	C12	PGE	0.0785	0.0705	—	0.056	–55	–61	—	–66
29–32	DET	PGE	0.0695	0.0625	0.0565	0.049	–47	–52	–58	–64

[a] Amines defined by letter C followed by the number of carbons in the polymethylene chain; for example, C6 = 1,6-diaminohexane. Substitution is either mono-N-methyl, abbreviated Me, or sym-dimethyl, abbreviated Me II. DET = diethylenetriamine.
[b] Diluent concentrations % (w/w) based on resin component excluding amine.

TABLE III
Some Typical Compositions of DDGE-Based Systems

System no.	DDGE, % (w/w)	Diluent	Diluent, % (w/w)	Amine	Amine, % (w/w)	Composition Total glyceryl content, mol/kg	Active glyceryl content, mol/kg	Crosslink density,[a] mol/kg
1	91.9	—	—	C2	8.1	5.41	5.41	1.35
5	90.2	—	—	C3	9.8	5.30	5.30	1.35
8	62.9	PGE	27.0	C3	10.1	5.49	3.70	0.24
12	63.9	MGE	27.4	C3	8.7	5.58	3.76	0.36
16	62.6	BGE	26.8	C3	10.6	5.47	3.68	0.20
21	76.9	—	—	C3 Me II	23.1	4.52	4.52	0
22	85.5	—	—	C6	14.5	5.03	5.03	1.26
26	77.3	—	—	C12	22.7	4.55	4.55	1.14
28	50.1	PGE	21.5	C12	28.4	4.38	2.95	0.23
29	89.2	—	—	DET	10.8	5.24	5.24	1.57

[a] Calculated from the equation

$$X_C = \frac{(W_R/M_R) - (W_A/M_A)}{W_R + W_A + W_D}$$

where X_C = crosslink density; W_A, W_R, W_D = weight of amine, resin and diluent, respectively; M_A, M_R = molecular weight of amine and resin, respectively (compare ref. 14).

active glyceryl concentration and is given in mol/kg. Figure 2 shows D_m as a function of the active glyceryl concentration for some systems. These plots can be reasonably described as linear and passing through the origin. If this description is correct, the ratio of D_m to the active glyceryl concentration will be
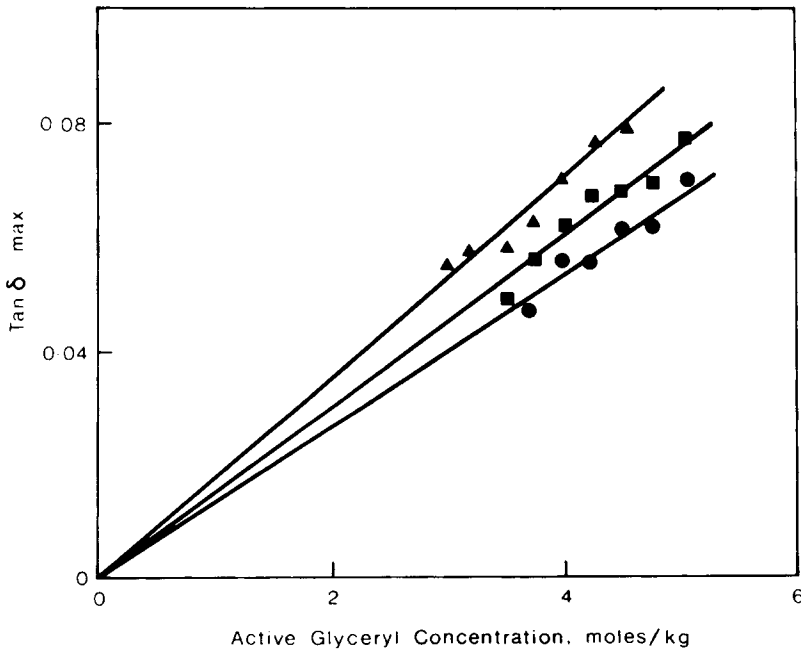

Fig. 2. Plots of the loss tangent maxima (D_m) as function of active glyceryl concentration: (▲) DDGE–PGE–C12; (■) DDGE–PGE–C6; (●) DDGE–PGE–C3.

a constant. Table IV shows values for this ratio for some systems studied at constant stoichiometry.

As the ratio appears insensitive to the amount of monofunctional diluent present, values averaged over all diluent levels tested are shown in Table V. It appears that the ratio is also independent of the degree of methylation of the amine and is specific to the structure of the resin and curing agent used.

Effect of Variation of Stoichiometry

The effect of variation of stoichiometry can best be explained by assuming that the relaxation contains a contribution from the diphenylpropane nucleus. The magnitude of this contribution is independent of the degree of cure of the resin, whereas if insufficient amine is added the contribution from active glyceryl groups is decreased.

For systems in which the stoichiometry is varied, the active glyceryl concentration may be calculated from the proportion of the deficient component in the

TABLE IV
Ratio of Loss Tangent Maxima to Active Glyceryl Content for Systems with Constant Stoichiometry

Amine	Ratio at indicated diluent concentration[a]			
	0	10	20	30
C3	0.0131	0.0132	0.0131	0.0127
C3 Me	0.0145	0.0129	0.0120	0.0117
C3[b]	0.0131	0.0137	0.0127	0.0116
C3[c]	0.0131	0.0139	0.0142	0.0136
C6	0.0153	0.0151	0.0155	0.0140
C12	0.0172	0.0177	0.0168	0.0190
DET	0.0132	0.0133	0.0135	0.0134

[a] Diluent level in % (w/w) in resin mix.
[b] Diluent BGE.
[c] Diluent MGE.

TABLE V
Ratios of Loss Tangent Maxima to Active Glyceryl Units Averaged Over All Diluent Levels

| Amine	Diluent	Ratio	n[a]
C2	PGE	0.0135	7
C2/C2 Me[b]	PGE	0.0137	7
C2 Me	PGE	0.0134	7
C2 Me/Me II[b]	PGE	0.0135	4
C3	BGE	0.0134	7
C3	MGE	0.0139	7
C3	PGE	0.0138	7
C3/C3 Me[b]	PGE	0.0139	7
C3 Me	PGE	0.0142	7
C3 Me/Me II[b]	PGE	0.0145	4
C3 Me II	—	0.0144	1
DET	PGE	0.0137	7
C6	PGE	0.0155	7
C12	PGE	0.0178	7

[a] Number of levels of diluent tested.
[b] Equimolar blends of amines.

mixture if it is assumed that the reaction between glycidyl groups and amines goes to completion and no interfering side reactions occur. Table VI shows the ratio of the D_m to the active glyceryl content so calculated. The ratio appears to be constant for systems based on diaminoethane and for systems based on 1,3-diaminopropane, 1,6-diaminohexane, and 1,12-diaminododecane and diethylenetriamine when overstoichiometric levels of amine are used. Below these levels the calculated ratio increases as the deviation from the stoichiometric amounts increases.

Side Reactions Possible During Cure

One explanation for the above result could be that, for systems with less than stoichiometric levels of amine, the active glyceryl content is much higher than calculated. A possible side reaction giving rise to substituted glyceryl groups is etherification[15,16]:

$$\overset{O}{R—CH—CH_2} + \overset{H \quad R}{O—CH—CH_2R} \longrightarrow \overset{OH \qquad\qquad R}{R—CH—CH_2—O—CH—CH_2R}$$
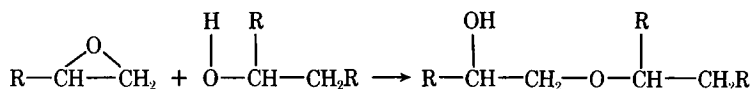
The source of hydroxyl groups for this reaction could be previously formed glyceryl units. This reaction does not occur under the present conditions, as is shown by the following evidence.

In order to explain the magnitude of the variation observed, it would be necessary for practically all excess epoxy groups to react into the system by this mechanism to give active glyceryl units (neglecting any influence of substitution on the hydroxy group on the mechanical activity). However, Newey[16] has shown that this reaction cannot occur to a significant extent under the normal cure conditions. He formed an adduct by reacting one mole diaminoethane with four moles phenyl glycidyl ether. A mixture of epoxy resin (91% w/w) and this purified, crystalline adduct (9% w/w) was heated at 100°C for 24 hr after which no significant increase in viscosity was observed.

To extend this report to the present conditions, similar adducts were prepared using diaminoethane, 1,3-diaminopropane, and 1,6-diaminohexane. The adducts (23% w/w) were mixed without purification with Araldite 6004 (77% w/w) and heated at 150°C for 8 hr. No increase in viscosity was observed. Infrared spectroscopy of the mixtures showed no significant reduction in the intensity

TABLE VI
Ratio of Loss Tangent Maxima to Apparent Glyceryl Content for Nonstoichiometric Systems

Amine level, % stoich[a]	Amine used			
	C2	C3	C6	C12
50	0.0137	0.0217	0.0228	0.0252
75	0.0138	0.0165	0.0187	0.0199
90	0.0144	0.0152	0.0166	0.0173
100	0.0127	0.0132	0.0155	0.0178
110	0.0128	0.0136	0.0152	0.0174
125	0.0134	0.0136	0.0161	0.0165
150	0.0131	0.0135	0.0166	0.0180
200	0.0117	0.0136	0.0166	0.0209

[a] Amine level expressed as a percentage required by the stoichiometric ratio.

of the absorption band due to the epoxide group near 910 cm^{-1}. It is concluded, therefore, that the etherification reaction is not catalyzed by any of the products of the epoxide–amine reaction and cannot be postulated to contribute to the cure of systems containing less than stoichiomentric amounts of amine.

The same conclusion is reached from a consideration of the effect of monofunctional, secondary amines in systems containing a deficiency of polyfunctional amine. For some systems containing lower than the stoichiometric ratios of 1,3-diaminopropane, the deficiency was made up by addition of the calculated quantity of diethylamine. The ratios of D_m of glyceryl content are shown in Table VII. It can be seen that there is no significant effect of the diethylamine on loss properties even though the reactivity of the secondary amine could be expected to at least greatly reduce the amount of etherification occurring. This suggests that the excess glycidyl groups in the understoichiometric systems are not being incorporated into the functional network by side reactions.

Relaxations in the Diphenylpropane Nucleus

The increased height of the loss peak for systems with low amine content may be due to a relaxation of another portion of the molecule. In all systems based on amines at or over the stoichiometric level, the concentration of glyceryl units is calculated from the polyfunctional resin content. At low amine levels the proportion of resin present increases relative to the amine. If another relaxation occurs in the resin component, it would be included in the calculation of glyceryl concentration as the resin content of the system. It has been suggested[17,18] that polymers containing paraphenylene linkages show a relaxation near −100°C. Such a relaxation could explain the characteristics of the beta loss peak in the systems presently examined, and it is shown in the Appendix that this is consistent with empirical relationships between the magnitude of the loss peak and the concentration of relaxing species.

CONCLUSIONS

The beta relaxation near −50°C at 1 Hz in epoxy–amine networks has been described for systems in which resin, curing agent, and stoichiometry are varied. It is shown that the maximum value of the loss tangent in this region can be

TABLE VII
Effect of Diethylamine on Loss Properties of Nonstoichiometric Systems Cured with
1,3-Diaminopropane

C3 level, % (w/w)	DEA level, % (w/w)	Epoxide reacted with C3, % stoich[a]	D_m	D_m/C_g[b]
5.1	0	50	0.06	0.0217
4.3	16.9	100	0.0485	0.0216
7.6	0	75	0.0675	0.0165
6.9	9.0	100	0.061	0.0166
8.9	0	90	0.0735	0.0152
8.6	3.7	100	0.070	0.0152

[a] Calculated percentage of epoxide reacted with C3.
[b] C_g = glyceryl content.

consistently explained in terms of contributions from relaxations of glyceryl units derived from polyfunctional glycidyl units and from relaxations of diphenylpropane units. Although an empirical relationship between the loss tangent maximum and concentration of species is sufficient to describe the present results, there is insufficient evidence to allow useful conclusions to be drawn from the form of this relationship. If any meaningful relationship does exist it must await a full numerical analysis based on an acceptable relaxation model.

Appendix

Empirical Analysis of Relationships Between Peak Heights and Constitution

For this analysis it is assumed that D_m can be expressed as the sum of the products of the relaxing species concentration and a constant characteristic of that group. D_m is assumed to be given by the equation:

$$D_m = \alpha C_g + \beta C_a \tag{1}$$

Where α and β are constants, C_g is the concentration of active glyceryl units in mol/kg, and C_a is the concentration of diphenylpropane units in mol/kg. It is assumed that each resin molecule that reacts fully gives rise to two active glyceryl units and one active diphenylpropane unit. Insufficient evidence is available from the present study to decide whether the active component is the phenylene unit or the diphenylpropane unit.

For all systems in which the amine is in stoichiometric or higher levels,

$$C_g = C_a/2 \tag{2}$$

and for these systems the ratio of height to active glyceryl concentration will be given by

$$D_m/C_g = \alpha + \beta/2 \tag{3}$$

An estimate of the value of the constant β can be obtained from systems cured catalytically using the complex of boron trifluoride and monoethylamine (curing agent BF$_3$–MEA) or by the use of diethylamine[15,16] as the chemistry of the catalyzed homopolymerization precludes the formation of significant proportions of active glyceryl units. Those glyceryl units formed initially react with glycidyl entities through the hydroxyl as shown above. Any unreacted glyceryl unit must therefore be a chain end and inactive.

Table VIII shows values for the height and temperature of the loss peak maximum and the ratio of D_m to concentration of resin species. The ratio appears to be independent of catalyst structure and concentration, provided sufficient catalyst is present to give full cure of the system. The cure schedule for the BF$_3$–MEA-based systems was 4 hr at 120°C followed by 4 hr at 150°C. DEA-based

TABLE VIII
Beta Peak for Catalytically Cured Systems

Curing agent	Curing agent, % (w/w)	D_m	T_{max}, °C	$D_m/C_a{}^c$
BF$_3$–MEA[a]	2.0	0.0365	−92	0.0127
	3.4	0.060	−80	0.0211
	4.8	0.059	−80	0.0211
DEA[b]	4.0	0.0405	−88	0.0143
	9.7	0.0525	−79	0.0198
	17.6	0.053	−80	0.0219

[a] Boron trifluoride complex with monethylamine.
[b] Diethylamine.
[c] C_a = concentration of resin species.

TABLE IX
Calculated Values of Constants α and β

	C2	C3		C6	C12	DET
	Table VI[a]	Table VI[a]	Table XI[b]	Table VI[a]	Table VI[a]	Table VI[a]
α	0.0030	0.0032	0.0046	0.0050	0.0178	0.0137
β	0.021	0.021	0.018	0.021	0.021	0.021

[a] Calculated using results in Table VI and IX.
[b] Calculated using results in Table XI.

TABLE X
Calculated and Observed Loss Tangent Maxima for Systems with Varying Stoichiometry

Amine level, % stoich[a]	C2		C3		C6		C12	
	Calcd	Obs	Calcd	Obs	Calcd	Obs	Calcd	Obs
50	0.067	0.0385	0.067	0.060	0.070	0.0615	0.072	0.0785
75	0.070	0.057	0.070	0.0675	0.074	0.073	0.077	0.077
90	0.072	0.0705	0.072	0.0735	0.076	0.076	0.079	0.0795
100	0.076	0.0685	0.076	0.074	0.081	0.077	0.084	0.079
110	0.075	0.0685	0.075	0.072	0.080	0.076	0.082	0.078
125	0.074	0.071	0.074	0.071	0.078	0.078	0.079	0.071
150	0.073	0.068	0.072	0.0685	0.075	0.078	0.075	0.074
200	0.070	0.0585	0.065	0.062	0.070	0.073	0.068	0.078

[a] Amine level expressed as a percentage of that required by the stoichiometric ratio.

TABLE XI
Loss Properties of Systems Based on Blends of DDGE and BDGE Cured with
1,3-Diaminopropane

BDGE in resin blend, % (w/w)	D_m	T_{max}, °C
0	0.074	−50
20	0.074	−50
70	0.076	−52
90	(0.079)	−62
100	(0.081)	−60

systems were cured as for the other aliphatic amine systems. A mean value of 0.021 is taken as an estimate of the constant β.

The value of the constant α can be obtained from the average value of the ratio of peak height to active glyceryl concentration by the use of eq. (3). Table IX shows the calculated values of α for the curing agents studied.

These values of α and β may be used to estimate D_m for systems with less amine present than required by stoichiometry. These estimates are shown in Table X.

An independent estimate of the constants α and β can be obtained by consideration of the heights for the beta peak as the epoxy resin component is replaced by 1,4-butanediol diglycidyl ether. The aliphatic resin alone, when cured with 1,3-diaminopropane, has a glass transition temperature near -10°C and the beta peak appears as a shoulder on the alpha peak near -60°C. In order to reduce the problem of overlapping peaks, a series of blends of Araldite 6004 and 1,4-butanediol diglycidyl ether were cured with 1,3-diaminopropane. The results are shown in Table XI. Values of D_m in brackets are not fully resolved from the alpha peak. As the aliphatic resin does not contribute to the diphenylpropane concentration, the ratio of glyceryl to diphenylpropane units varies and the values of α and β may be obtained and are included in Table IX. As there is reasonable agreement between values calculated by the different techniques, it is concluded that the results are consistent with the hypothesis of two overlapping relaxations.

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