

Characterization and behaviour of epoxy-based diaminodiphenylsulphone networks

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(Received 24 April 1985; revised 27 November 1986; accepted 4 December 1986)

We have analysed the polycondensation of the system based on diglycidyl ether of bisphenol A (DGEBA) crosslinked with 4,4'-diaminodiphenylsulphone (DDS) in the absence of or presence of a catalyst, benzyldimethylamine or BF_3 complex. Chemical data obtained with Fourier transform infra-red spectroscopy (FTi.r.) and solid state ^{13}C n.m.r. with CP MAS have enabled the various chemical species in the network to be qualitatively detected and quantitatively assayed. The molecular results related to reaction mechanisms, obtained as a function of the per cent catalyst present, were correlated with thermal (T_g), dielectric (β relaxation) and moisture absorption data.

(Keywords: polyepoxy; diaminodiphenylsulphone; etherification; transition; moisture absorption)

INTRODUCTION

In recent years epoxy resins have been extensively studied as matrix materials for composite structures as well as adhesives for aerospace applications. Numerous systems are based on an epoxy crosslinked with an aromatic amine, 4,4'-diaminodiphenylsulphone (DDS). Their properties depend on their network structure and morphology. The variation of T_g and water absorption with molecular parameters has been the subject of numerous experiments.

In a recent publication¹, we observed the cure behaviour of different epoxy systems by differential scanning calorimetry (d.s.c.). For different diamines, including DDS, we concluded that, without a catalytic agent only the amino hydrogens react with oxirane through an autocatalytic mechanism without side reactions. However, when we introduced a catalytic agent, especially with DDS hardener, the mechanism was quite different and side reactions were evident. The activation energy E_a of the reaction increased from 63 to 90 kJ mol⁻¹ and the temperature T_g of the network decreased by more than 70°C.

The aim of this work is to relate the variations of the temperature T_g and the water absorption of DGEBA-DDS networks to their structures. Chemical analysis is limited due to the insolubility and infusibility of the system, so that we used Fourier transform infra-red spectroscopy (FTi.r.) and solid state ^{13}C n.m.r. spectroscopy with cross-polarization and magic angle spinning (CP MAS). A few publications² have discussed the latter technique for analytical analysis of epoxy networks.

EXPERIMENTAL

Materials

A stoichiometric mixture of the diglycidyl ether of bisphenol A, DGEBA, $n=0$, (DER 332) and 4,4'-diaminodiphenylsulphone (DDS; Fluka) was prepared without or with a catalytic agent. Two catalysts were used: benzyldimethylamine (BDMA, Fluka) and a monoethylamine complex of boron trifluoride (BF_3 , Fluka). The preparation of models for the n.m.r. analysis has been described previously³.

In all experiments, the amine was added after the epoxy had been heated to 130°C. The mixture was stirred until the amine dissolved in the epoxy prepolymer (less than 5 min) and was then quenched at 80°C and degassed (≈ 1 torr) at this temperature for one hour. The catalytic agent was introduced just before the system was poured into a cold Teflon mould, placed in a heated oven and cured with a number of different processings (Table 1).

After curing, specimens were allowed to cool slowly to room temperature out of the oven, inside the Teflon moulds and were then placed in a dessicator.

Polyepoxy films (1 or 0.1 mm thick) were prepared as described.

Materials characterization

A DSC Mettler TA 3000 was used for all the T_g measurements, $q=10$ K/min.

Infra-red analyses were performed using a Nicolet MX1 Fourier transform infra-red spectrometer. Absorbance spectra were obtained with KBr pellets containing the finely ground materials.

Table 1 Different characteristics of the formulation: T_g , glass transition temperature; ΔC_p , heat capacity change at T_g ; and C_{pl} , heat capacity of the liquid state

DGEDA	DDS	Catalytic agent	T_g ($^{\circ}\text{C}$)	C_{pl} (J/g K)	ΔC_p (J/g K)
100 g	36 g	NO ^a	190	2.1	0.2
		BDMA 0.5 phr ^a	150	1.5	0.2
		BDMA 1 phr ^a	115	1.3	0.2
		BF ₃ -MEA 1 % ^b	170	—	—

^a Curing process: 1 h from room temperature to 190°C, 2 h at 205°C and 1 h post-cured at 220°C^b 2 h at 120°C and 2 h at 185°C

¹³C n.m.r. (solid and liquid) spectra were obtained with a Brücker WM 250 spectrometer operating in square low demodulation and equipped with a Brücker Aspect 2000 (DISNMRP PROGRAM) calculator and a solid CP MAS accessory.

Conditions for obtaining liquid state ¹³C spectra were the following: pulse angle 45° (14 μ s), 100 scans. The digital resolution was 0.925 Hz/point, corresponding to a spectrum length of 15 000 Hz and a memory capacity of 32 K. Chemical shifts were based on TMS (internal reference). For the recording of solid CP MAS spectra, a contact time of 1 μ s, a delay of 10 s between the sequences and a rotation of 5.3 kHz were used. An average of 1000 contacts was necessary.

Dielectric measurements

Dielectric measurements were carried out on samples metallized with aluminium to improve contact with the cell electrodes. Dielectric measurements were taken using an Apple II computer connected to a 4274-A multifrequency LCR Meter (Hewlett-Packard).

Samples were studied at frequencies from 10² to 10⁵ Hz and at temperatures from -100°C to +140°C.

Swelling

A dry film sample (≈ 1 mm thick) was immersed in distilled water at different temperatures. After a certain time period, the sample was removed from the water, dried on the surface, and the weight gain M_t was determined. The same sample was then placed back in the bath for a second time period, and weight was again determined. All weighing procedures were done in less than 10 s.

The average per cent weight gain of three specimens was plotted vs. time^{1/2}.

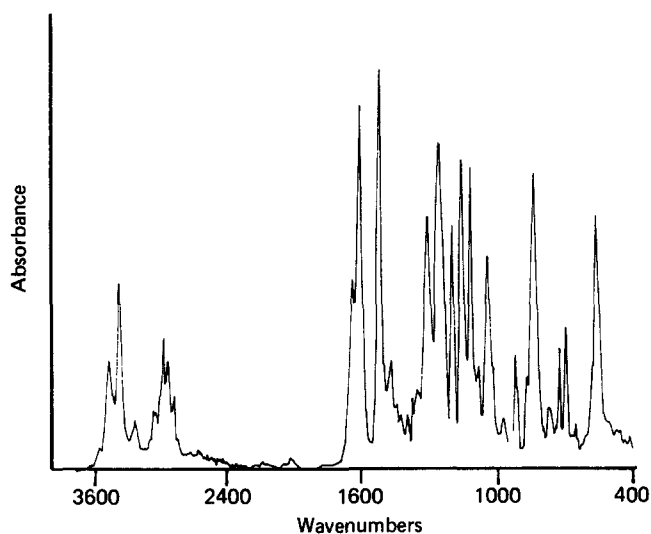
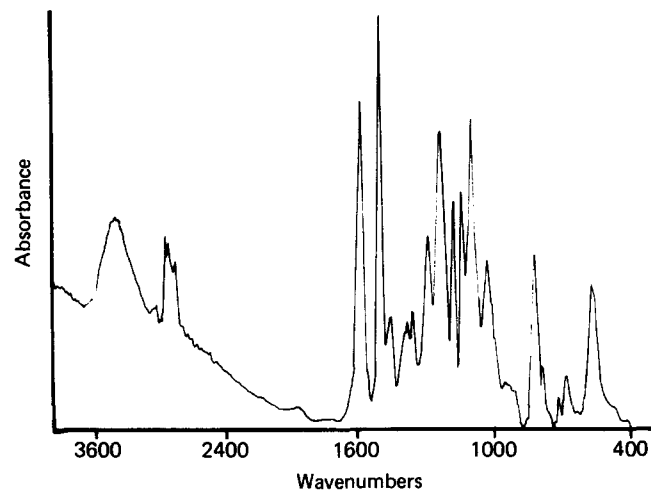
After 2000 h of exposure, the samples were dried in a vacuum oven at 50°C for two weeks. Their weights came to within 0.03 % of the initial weights.

RESULTS

Table 1 indicates the different T_g values and ΔC_p values at T_g measured for polyepoxy films. Without a catalytic agent, T_g is very high, but the temperature decreases when a catalytic agent is introduced in the formulation. The decrease is greater with BDMA than with the BF₃ complex.

FTi.r. results

Some spectra are given in Figures 1–3. Without the catalyst, the product of the DGEBA + DDS reaction gave a spectrum (Figure 2) which contained no NH₂ bands when the oxirane band (915 cm⁻¹) had disappeared quasi-completely. With 1 phr BDMA, the spectrum (Figure 3)

**Figure 1** FTi.r. spectrum of initial DGEBA-DDS mixture**Figure 2** FTi.r. spectrum of DGEBA-DDS network cured without catalyst

revealed the presence of NH₂: ν at 3480 and 3360 cm⁻¹ superposed on the OH band, less strong than in Figure 2 and δ at 1630 cm⁻¹ as a shoulder. These bands belong to NH₂ and not to NH because there are two scissoring bands and because the δ band of NH does not appear at 1630 cm⁻¹. It is clear that all the NH₂ has not reacted. In the spectrum in Figure 3 (DGEBA + DDS + 1 phr BDMA) the 1143 and 1105 cm⁻¹ bands (which normally belong to SO₂ of DDS alone) have been augmented considerably in comparison with the spectrum in Figure 2 (this augmentation is clear on the difference spectrum, not given here) and is very probably due to the superposition of ether bands (C–O–C) which are in this region¹³.

Taking 1180 cm^{-1} band as ref. 13, an estimation based on the ratio of absorbances A_{1630}/A_{1180} in the product and in the initial mixture gives a measure of residual NH_2 . The value is reported in Table 4.

Other manifestations less important in the $1300\text{--}1400\text{ cm}^{-1}$ region suggested that there is more tertiary

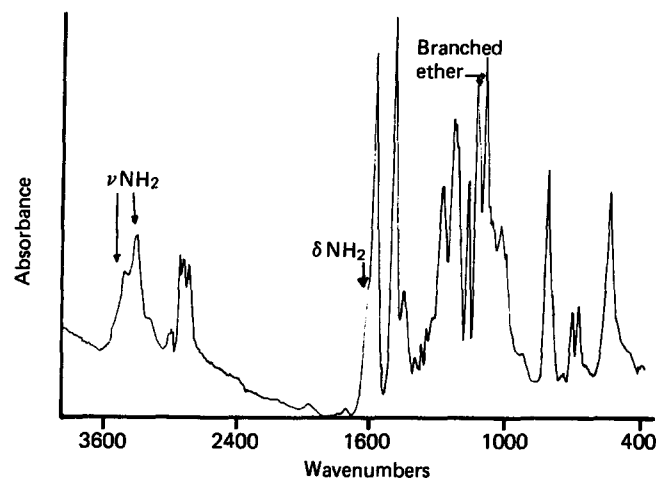


Figure 3 FTIR spectrum of DGEBA-DDS network cured with 1 phr BDMA

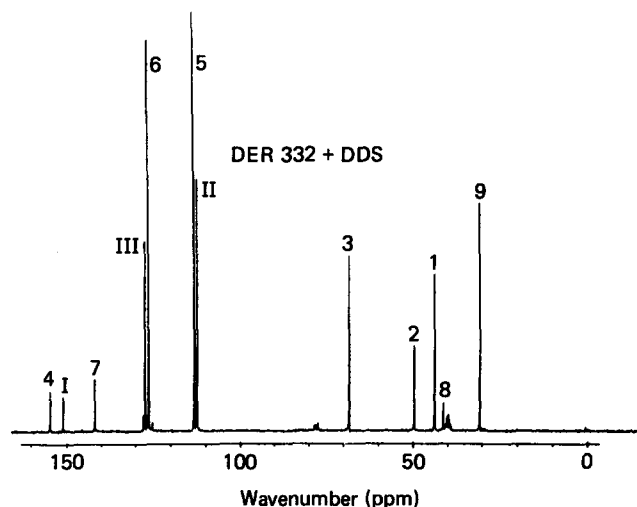


Figure 4 ^{13}C n.m.r. high resolution spectrum in liquid state (62.89 MHz): DGEBA-DDS system $t=0$; solvent CDCl_3 -DMSO; ref. TMS

C-N (1360 cm^{-1}) with 0% BDMA and more CH_2O (1420 cm^{-1}) with 1 phr BDMA.

NUCLEAR MAGNETIC RESONANCE

Attribution of bands in the initial mixture

Figure 4 (Table 2) shows the spectrum of the mixture at $t(\text{time})=0$. Two regions are interesting in the course of the polycondensation reaction, namely that between 40 and 80 ppm (oxirane ring carbons) and that between 140 and 160 ppm (aromatic ring carbons).

The signals from C_8 and C_9 , and from C_5 and C_6 are invariant in these two regions. In high resolution solid state ^{13}C n.m.r. with CP MAS, peaks II and 5, III and 6, and I and 4 are not separated. Thus, only C_8 and C_9 are internal probes in all the spectra. For all the samples examined, we verified that we were in conditions of quantitative assays.

Attribution of bands in the polycondensed mixture

In high resolution solid state ^{13}C n.m.r. with CP MAS, resolution is lower than in solution as a result of band width and coupling constants (J-C-N (50 Hz)) present in the solid state (see the spectrum in Figure 5 which involves carbons I and 1, see also Figure 6).

Based on the chemical shifts listed in Table 3, which are characteristic of the different functional groups obtained during polycondensation³, it can be seen that certain chemical species can be assayed:

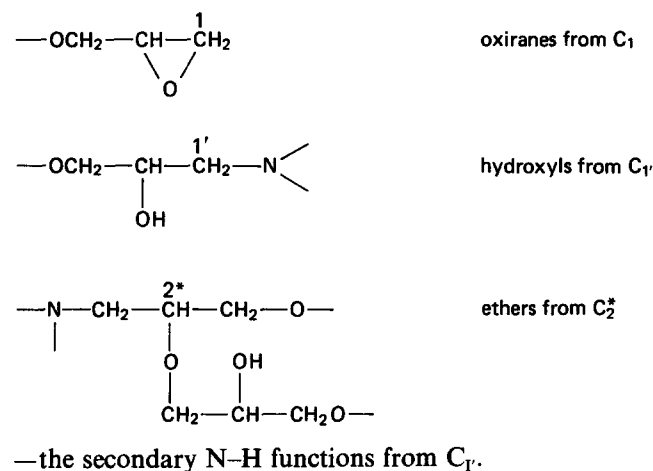


Table 2 ^{13}C chemical shifts ($r_{\text{H}}=0$) in solution (solvent CDCl_3); ref. TMS

Compounds	Carbons—chemical shifts (ppm)									
	1	2	3	4	5	6	7	8	9	
	44.6	50.2	68.9	156.4	114.1	127.7	143.6	41.7	31.9	
	I	II	III	IV						
	151.9	113.7	128.8	129.5						
	1	2	3	4	5	6	7	8	9	10
	46.7	68.9	70.1	158.6	111.6	129.4	122.2	139.7	115.6	21.5
	I	II	III	IV						
	148.3	113.4	129.3	118.0						

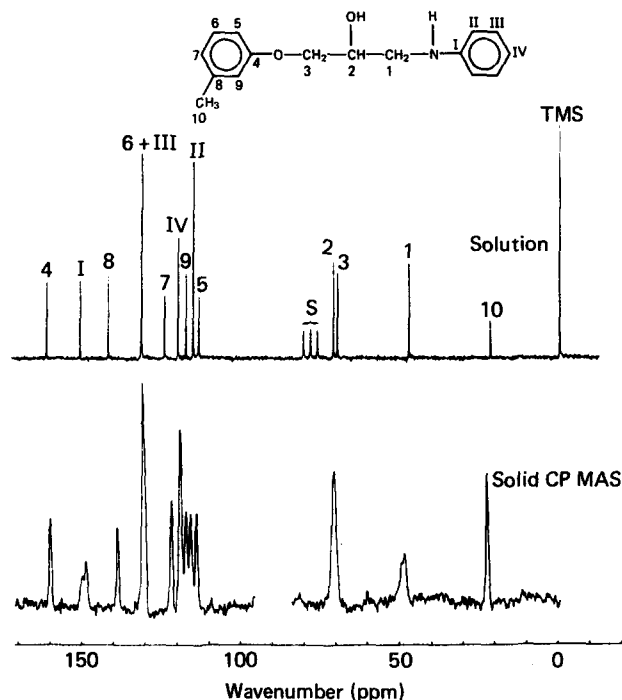


Figure 5 ^{13}C n.m.r. high resolution spectra (62.89 MHz) in liquid state (solvent CDCl_3) and solid state (CP MAS) of a model compound

In contrast to infra-red absorption spectroscopy it is not possible to assay primary amino hydrogens since peak I (Table 3, $\text{—C—CH}_2\text{—}$, 152 ppm) and peak 4

(Table 2, —C—O— , 156 ppm) are not clearly

separated. Nevertheless, taking into account the FTi.r. results it seems possible to separate peak I and peak I'

(Table 3, —C—N—R , 150 ppm) to give an

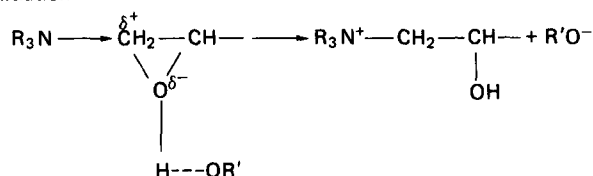
approximation of the per cent of residual secondary amino hydrogens (note that tertiary amine gives a peak

—C—N—R at 152 ppm).

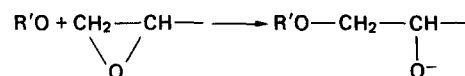
The introduction of BDMA or BF_3 complex in an epoxy formulation releases an ionic polymerization process which disturbs the stoichiometry of the polycondensation. The overall mechanism has been proposed²:

(a) ionic polymerization, for example with tertiary amines:

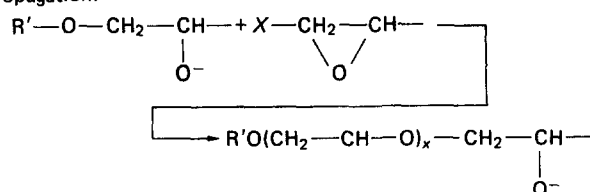
1 – Initiation:



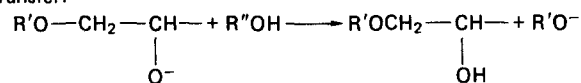
2



3 – Propagation:

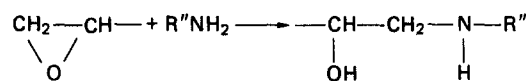


4 – Transfer:



(b) and polycondensation:

5



6

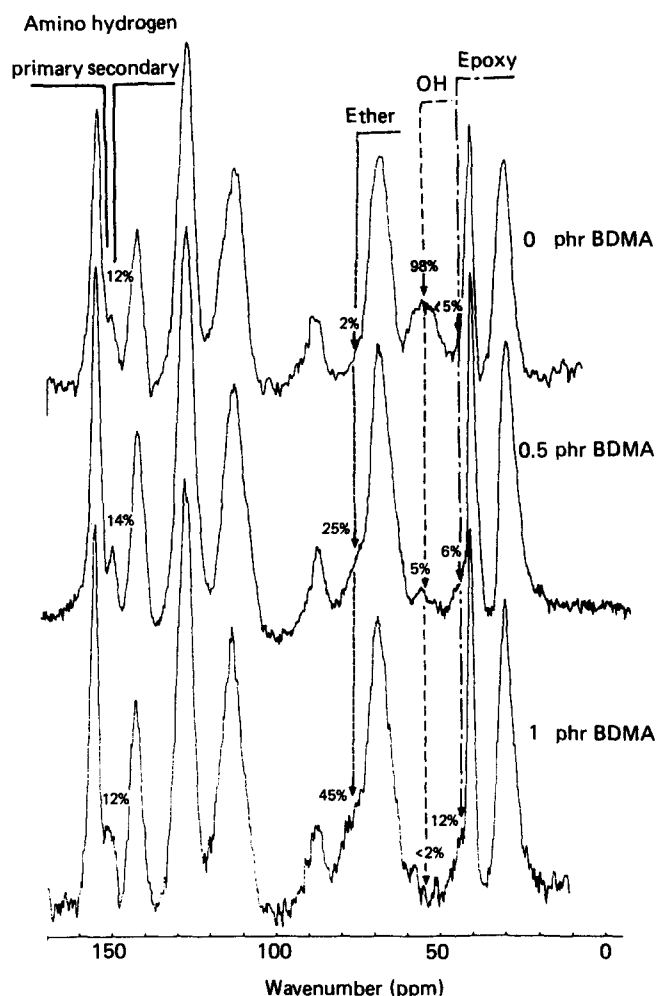
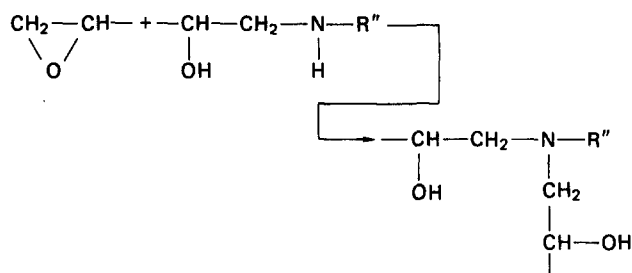
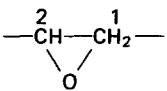
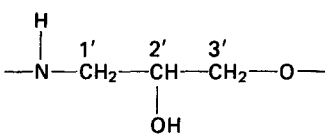
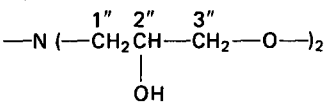
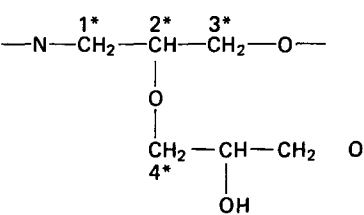
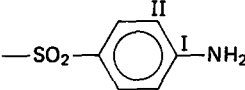
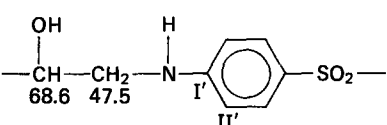




Figure 6 ^{13}C n.m.r. high resolution spectra (62.89 MHz) in solid state (CP MAS): DGEBA-DDS system

Table 3 ^{13}C chemical shifts of the model compounds

Model compound	Chemical shifts (ppm)			
	1 44.6	2 50.2		
	1' 47.5	2' 68.6	3' 71.1	
	1'' 52.4 53.4	2'' 67.9 68.0	3'' 71.1	
	1* 63.6	2* 76.5	3* 71.4	4* 70.0
	I 151.9	II 113.7		
	I' 150.0	II' 111.0		

Reactions 1 to 4 occur at low temperature, around 100°C , reactions 5 and 6 with DDS curing agent at high temperature². For DGEBA+DDS formulations with a stoichiometric ratio $r=1.0$ we should look for the following groups when BDMA or BF_3 complex is added:

- the emergence of an ether linkage $(-\text{CH}_2-\text{CH}-\text{O}-)$

- the disappearance of hydroxyls $(-\text{CH}_2-\text{CH}-\text{CH}_2-)$

- and the presence of residual amino hydrogen groups.

The results are summarized in Table 4. The percentage of residual functions is expressed with reference to 100 initial epoxy, primary amino hydrogen and secondary amino hydrogen functions. On the other hand, the percentage of hydroxyl or ether linkages formed is based on 100 initial epoxy functions. Without a catalytic agent, we have less than 5% residual epoxy groups, 12% residual secondary amino hydrogens and we form essentially hydroxyl groups. With the BF_3 complex, and especially with BDMA, we can see a decrease of hydroxyl groups and an increase of ether linkages. Residual epoxy and secondary amino hydrogens are fairly constant but a large excess of primary amino hydrogens appears with 1% BF_3 or 1 phr BDMA.

The temperature T_g vs. per cent ether linkages is linear (Figure 7). The decrease in T_g can be explained by the higher flexibility of ether linkages. Compared with DDS+1 phr BDMA, the polyepoxy prepared with DDS+1% BF_3 complex contains a low per cent of ether linkages, and the decrease in the temperature T_g can be explained in this case by epoxy or amine dangling groups.

Observation of β relaxation

In the pure epoxy system, two relaxations have been identified: a high temperature α process usually associated with the glass transition process T_g and a lower temperature β process associated first with the relaxation of the glycidyl units $-\text{OCH}_2-\text{CH}-\text{CH}_2-$ and secondly

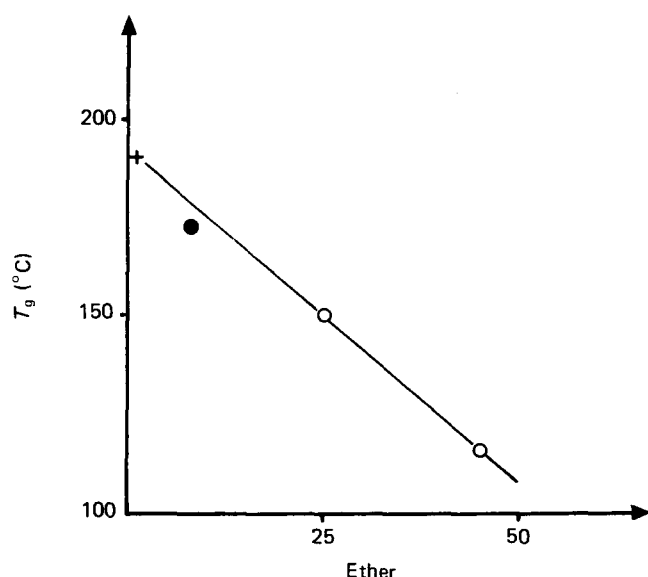


at lower temperature with the relaxation of the diphenylpropane units. This assignment is supported by the observed variations in the amplitude of the relaxation with change in the ratio of curing agent to prepolymer, while no variations being observed with different curing agents⁴⁻⁷.

We obtained the β relaxation by dielectric measurements and the results are plotted for three different polyepoxies in Figure 8. The temperature of the maximum of $\text{tg}\delta$ and its amplitude decrease when the percentage of BDMA catalytic agent increases, or when the percentage of hydroxyl groups decreases. This confirms the assignment of the β relaxation to glycidyl

Table 4 Schedule of the ^{13}C n.m.r. and FTi.r. analyses. E: epoxy function; A: amino hydrogen groups

Catalytic agent	% E ^a	Residual		Formed	
		% A ^a (secondary)	% A ^b (primary)	% OH ^a	% ether ^a
NO	< 5	12	≈ 0	98	2
0.5 phr BDMA	6	14	≈ 0	5	25
1.0 phr BDMA	12	12	20	< 2	45
1% BF ₃ -MEA	12	10	18	72	8

^a ^{13}C n.m.r. analysis^b FTi.r. analysis**Figure 7** Relation between the T_g measured by d.s.c. and the ether function obtained from n.m.r. measurements: +, without catalytic agent; O, with BDMA; ●, with BF₃-MEA

plus diphenylpropane units⁷ and is in good agreement with the results in Table 4.

SWELLING RESULTS

The diffusion of penetrant molecules into polymers depends on two factors, the availability of appropriate molecular size holes in the polymer network and the attraction forces between the penetrant molecules and the polymer. The presence of holes is determined by the polymer structure and morphology reflected in its crosslink density and molecular chain stiffness, and the ability to pack closely in the glass state.

The first factor affecting diffusion processes is essentially a geometrical one, how much free volume is available with the polymer for occupation by penetrant molecules such as water^{8,9}.

The second factor concerns the chemical nature of the penetrants *versus* that of the polymer. This factor determines the penetrant-polymer affinity and, in general, the more 'polar' the polymer, the larger is the amount of water absorbed. It is well known that the relatively high water absorption capacity of epoxy networks results from the presence of

—CH₂—CH—CH₂—N< β amino
|
OH
hydroxyl groups attracting polar water molecules¹⁰.

The percentage weight gain M_t is plotted *versus* time^{1/2} for three polyepoxies in Figure 9. The equilibrium moisture level M_∞ and diffusivity D of the films at 68°C can be obtained directly from Figure 9. The diffusivity is obtained from the initial slope: (l =thickness of the sample).

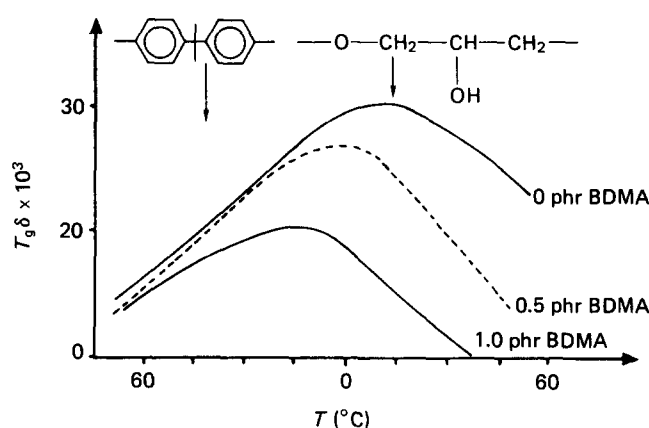
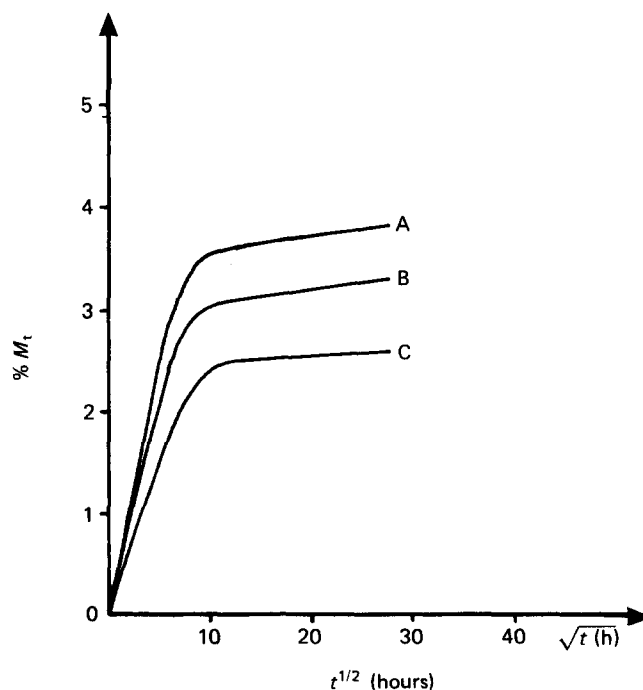
$$D = \pi \left(\frac{1}{4M_\infty} \right)^2 \frac{(M_2 - M_1)^2}{t_2 - t_1}$$

It is evident that both moisture content and diffusivity decrease with increasing catalytic amounts of BDMA.

These results can be explained both by decreasing the free volume fraction or decreasing the quantity of polar sites, when the percentage of BDMA increases.

The excess of free volume $\delta = \frac{V - V_\infty}{V_\infty}$ can be shown by

the equation¹¹: $\delta = \Delta\alpha(T_g - T)$ with $\Delta\alpha = \frac{\alpha_1 - \alpha_g}{V_\infty}$ (thermal expansion coefficient change at T_g) or by $\delta = \Delta C_p(T_g - T)$ with $\Delta C_p = C_{p1} - C_{pg}$ (heat capacity change at T_g). If we consider $\Delta\alpha$ or ΔC_p as constant (Table 1), δ is proportional to T_g and the excess of free volume δ decreases with T_g .

**Figure 8** Influence of catalytic agent BDMA on the β relaxation observed by dielectric measurements (4 kHz)**Figure 9** Swelling in water at 68°C for the three polyepoxies: (A) without BDMA; (B) 0.5 phr; (C) 1.0 phr

On the other hand, the decrease of T_g is due to the formation of ether linkages instead of tertiary β -amino hydroxyl groups $\text{—CH}_2\text{—CH—CH}_2\text{—N}\begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix}$. So the two



terms, excess of free volume and number of polar sites, are related to T_g and it is difficult to conclude on the predominant effect of one term on swelling behaviour.

For the partially cured DGEBA–DDS system, Gillham¹² observed similar results, a higher equilibrium moisture content and higher diffusivity with increasing cure of the polyepoxy network.

CONCLUSION

Using FTi.r. spectroscopy and solid state ^{13}C n.m.r. with CP MAS, we have analysed the chemical structures of the polycondensed DGEBA–DDS system while varying the catalyst concentration between 0 and 1 %, or 1 phr. Up to now the data are quantitative only on the final networks. Quantitative results during the course of the reaction will be obtained and the determination of the rates of reaction will be the subject of a subsequent publication.

Chemical analysis on the final networks showed (i) that in the absence of the catalyst, only normal amine–oxirane reactions occur; (ii) that in the presence of the catalyst, secondary oxirane–hydroxyl reactions appear, predominating in relation to the hydroxyl groups.

These data were confirmed by dielectric measurements. The maximum temperature of $\text{tg}\delta$ characteristic of the

glycidyl fragment, and its amplitude decreased with increasing catalyst concentration.

These molecular results (assay of residual and formed functions) were compared to thermal properties (variation of glass transition temperatures T_g), and to moisture absorption. We were thus able to show that the presence of ether linkages (percentage increasing with increased catalyst concentration) led to a decrease of the T_g and water absorption values. These results are explained by the higher flexibility of the ether linkages, the decrease of number of polar sites and/or of free volume fractions when the catalyst concentration increases.

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