# Epoxy networks based on dicyandiamide: effect of the cure cycle on viscoelastic and mechanical properties

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Benzyldimethylamine-catalysed epoxy networks based on dicyandiamide hardener were prepared using various cure schedules. It was shown using $^{13}C$ nuclear magnetic resonance and Fourier-transform infra-red spectroscopies that the chemical reactions are temperature-dependent. At low cure temperature the formation of ether linkages was favoured, thus increasing the crosslink density. Consequently, the glass transition temperature of the networks increases with decrease of the cure temperature. The viscoelastic spectra exhibited both $\alpha$ and $\beta$ relaxations. The amplitude of the $\alpha$ peak increased with increasing cure temperature. Also the rubbery modulus allowed us to calculate $\bar{M}_c$. The Young's moduli in the glassy state did not depend on the cure schedule. The ability to deform plastically determined both via $K$ parameter and yield stress increases on decreasing the crosslink density, as shown with the high cure temperature. Linear elastic fracture mechanics allowed us to determine $K_{Ic}$ and $G_{Ic}$. Both of the fracture parameters increased with decreasing crosslink density. The improvement in the retardation of crack propagation is probably due to a crack blunting mechanism associated with the ability of the material to deform plastically.

**(Keywords: epoxy–amine networks; dicyandiamide; glass transition; dynamic mechanical behaviour; mechanical properties)**

## INTRODUCTION

The curing mechanism of dicyandiamide and epoxy prepolymer is well known[1–7]. However, only a very small part of the literature relates to the viscoelastic and mechanical behaviour as a function of cure cycle for such cured epoxy networks[7,8].

Nevertheless, dicyandiamide (DDA or Dicy) is a widely used hardener in many industrial epoxy systems and especially in epoxy-resin prepregs and structural adhesives. Various authors have shown that, in benzyldimethylamine (BDMA)-catalysed diglycidyl ether of bisphenol A (DGEBA)–DDA systems, the curing process is a competition between the condensation reaction (addition of amine to epoxy) and the etherification reaction (reaction between epoxy groups and hydroxyls proceeding from the initial DGEBA prepolymer and/or from the addition reaction) (*Figure 1*). These reaction mechanisms are greatly dependent on cure temperature[7,8]: at low temperature (100°C) of pre-curing or curing, epoxy homopolymerization (scheme 2 in *Figure 1*) is favoured and the reaction mechanism of the DDA itself is modified. A large part of the reacted species contain both nitrile and imine groups. The epoxy homopolymerization induces changes in the network microstructure and leads to effective crosslinks with higher functionality. In addition, dicyandiamide, which is a crystalline solid at room temperature (m.p. 208°C), is relatively insoluble in epoxy resins. It was found[7,9,10] that, for unfilled and filled epoxy networks, high amounts of residual unreacted DDA ($<30\%$) remained in samples pre-cured at 100°C even when, with a pre-cure at 160°C, all of the DDA is fully dissolved and reacted. The homopolymerization in BDMA-catalysed DGEBA–DDA systems is important since the maximum glass transition temperature ($T_g$) is obtained with an amine-to-epoxy ratio (a/e) $= 0.6$[5–7]. It was shown that, independently of the cure conditions and the nature of the catalyst, the maximum $T_g$ for this network is obtained with this stoichiometric ratio (0.6), as opposed to the common epoxy–amine system (a/e $= 1$ in this case). The etherification reaction balances the lack of DDA. Increases in modulus in the rubbery state and $T_g$ values are generally found when a pre-cure at 100°C is employed, which can be explained by the copolymer effect (reactions and homopolymerization involving nitrile groups), additional crosslinks (etherification) and change in functionality of the crosslinks[5,7,8]. Also, macroscopic crosslinks could be introduced by the DDA particles.

This paper details the effects of the cure cycle, especially the pre-cure temperature ($T_p$), on the viscoelastic and mechanical properties of BDMA-accelerated DGEBA–DDA networks. This study is necessary for understanding the nature of the matrix in DGEBA–DDA/glass bead composites[11]. With such an exothermic thermosetting matrix, during curing the temperature in the mould is not the same for unfilled and filled systems[12]. Therefore, the aim of this work is to elucidate the influence of cure on mechanical properties, specifically plastic deformation and fracture properties, and to try to establish relationships between modifications of chemical mechanisms and final properties of the material.

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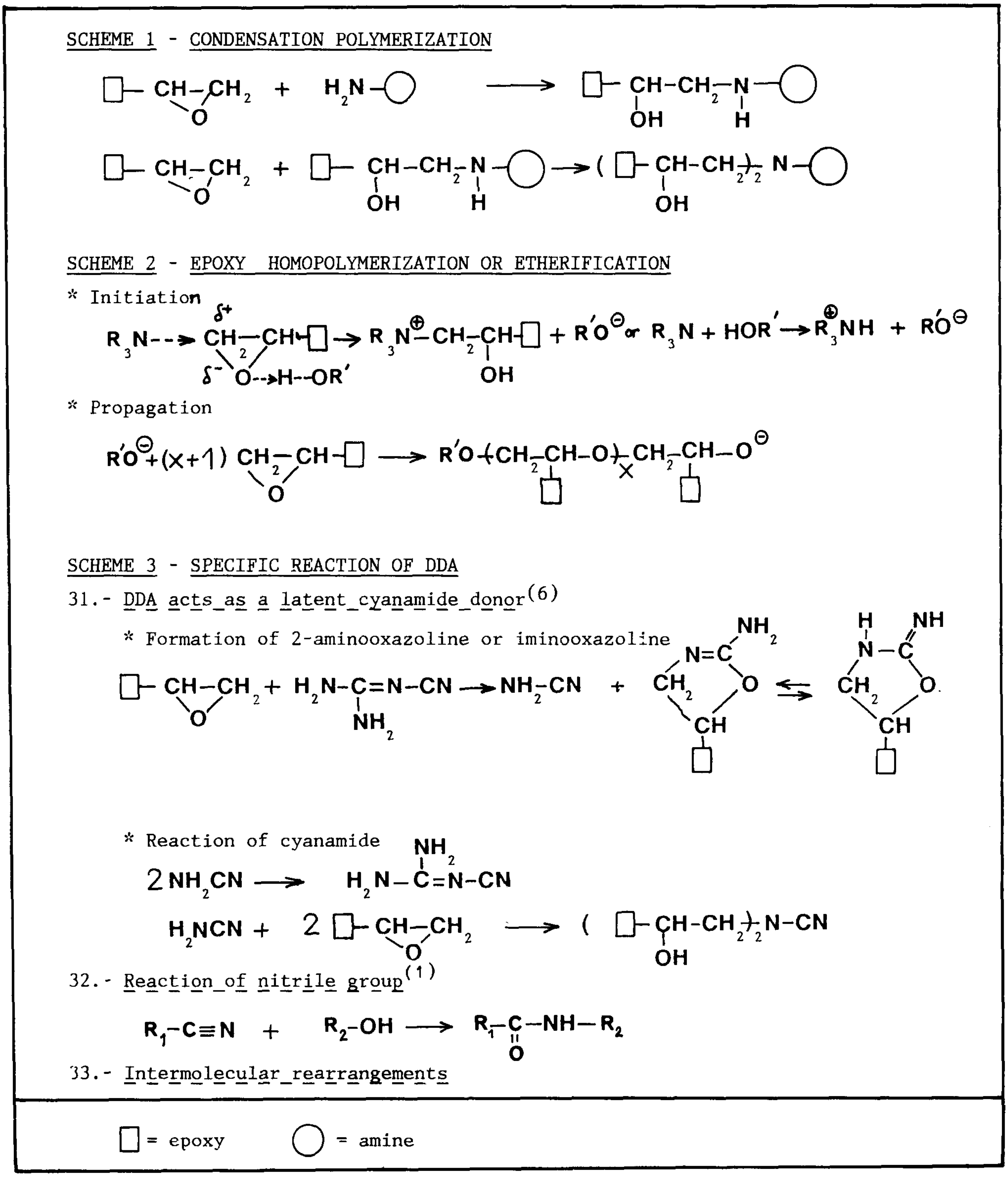


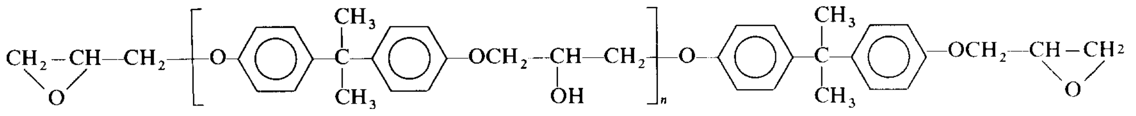
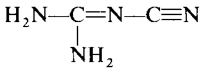
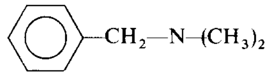
**Figure 1** Main reaction pathways for epoxy systems based on DDA as the hardener

## EXPERIMENTAL

### *Materials*

The chemical formulae of the epoxy prepolymer diglycidyl ether of bisphenol A (DGEBA), the hardener dicyandiamide (DDA) and the catalyst benzyldimethylamine (BDMA) used are depicted in *Table 1*. The DDA used is previously mixed with DGEBA ($\bar{n}=0.15$) by the manufacturer in a ratio of 50:50 by weight. This reagent is a white crystalline solid insoluble in liquid epoxy prepolymer at room temperature[13,14]. It is necessary to use it in the form of a fine powder perfectly dispersed in the DGEBA. In our case, the particle size was about 4 μm. The influence of DDA particle size on cure chemistry and mechanical and viscoelastic properties has been previously described in the literature[2,3,15]. These materials were mixed by mechanical stirring under vacuum at 60°C for 1 h. The mixture was then cured in a polytetrafluoroethylene (PTFE)-coated mould with three different cure schedules (denoted 100/180, 110/180 and 120/180—see *Table 2*). The dimensions of the mould are $180 \times 180 \times 6\,\mathrm{mm}^3$. Because of the nature of DDA, it

**Table 1** Chemical products used in the synthesis of epoxy networks

| Name | Chemical formula | Supplier, tradename |
|---|---|---|
| DGEBA | <br>$\bar{n}=0.15$; $\bar{M}_n=380$<br>Epoxy prepolymer | Bakelite 0164 |
| DDA |  $H_2N{-}C(NH_2){=}N{-}C{\equiv}N$<br>Cyanoguanidine or dicyandiamide | Bakelite<br>VE 2560 |
| BDMA | <br>Catalyst or initiator | Aldrich |

was necessary to rotate the mould during the first stages of the cure cycle to prevent the DDA from precipitating.

### *Characterization of the epoxy networks*

*Chemical and physical characterization.* The epoxy networks prepared with different cure schedules were studied by Fourier-transform infra-red (*FT*i.r.) spectroscopy and solid-state $^{13}C$ nuclear magnetic resonance (n.m.r.) (cross-polarization, magic angle spinning (CP-MAS)). Infra-red analyses were performed using a Nicolet MX1 *FT*i.r. spectrometer with KBr pellets containing the finely ground materials.

$^{13}C$ n.m.r. spectroscopy was used on the same finely ground specimens from plates with a Brucker WM 250 spectrometer at 62.89 MHz in solid state (CP-MAS). The operating conditions[16] enabled us to obtain quantitative data.

Glass transition temperatures ($T_g$) were determined by differential scanning calorimetry (d.s.c.) using a Mettler TA3000 calorimeter with a heating rate of $10°C\,min^{-1}$. Linear expansion coefficients in the glassy and rubbery states ($\alpha_g$ and $\alpha_r$ respectively) were measured using a Mettler thermomechanical analyser (t.m.a.) with a heating rate of $10°C\,min^{-1}$.

*Dynamic mechanical measurements.* Dynamic mechanical spectra for the three networks were performed with a Rheometrics RDA 700 apparatus (torsion mode) at 10 Hz. Storage shear modulus ($G'$) and loss factor ($\tan\delta$) were recorded during a temperature ramp from $-150°C$ to $+250°C$ with a heating rate of $1°C\,min^{-1}$.

Apparent activation energies ($E^{\ddagger}_{a\beta}$) of the $\beta$ relaxation were determined using an Arrhenius law on the maxima of the $\beta$ peak ($T_\beta$):

$$\log \nu = -\frac{E^{\ddagger}_{a\beta}}{RT_\beta} + \text{constant}$$

For this determination, measurements were performed on a Dynamic Mechanical Thermal Analyser (d.m.t.a.) from Polymer Laboratories in a frequency range from $3.3\times10^{-2}$ to 30 Hz during a frequency–temperature sweep.

*Mechanical tests.* Young's moduli ($E$) were obtained from a tensile test at room temperature on an Adamel–Lhomargy (DY25) machine. Strain measurements were performed with an EX10 extensometer at a strain rate of $3.3\times10^{-4}\,s^{-1}$. Compression tests at a strain rate of $8.3\times10^{-4}\,s^{-1}$ were made using the same tensile testing machine on parallelepipedic specimens ($20\times10\times6\,mm^3$) to determine the yield stress ($\sigma_y$).

The measurements of the non-elastic work-hardening rate $K$ were made in the pre-yield stage during the compression tests at a constant rate ($\dot{\varepsilon}=2\times10^{-4}\,s^{-1}$) (Instron machine on cylindrical specimens 9.2 mm long, with 5 mm diameter). This method has already been described in previous papers[17–19]. In brief, from a metallurgical point of view, $K$ is related to the nucleation rate of defects per unit stress. Thus, $K$ is a measure of the resistance of the material to develop plastic strain.

For linear elastic fracture mechanics (LEFM), single-edge notched (SEN) specimens (thickness about 6 mm and width $w$ about 12 mm) were used in three-point bending mode (span-to-length = 48 mm). Cracks of various length ($a$) were machined with a saw; and the crack tip was achieved with a razor blade at a temperature above $T_g$. The radius of the tip was about 5 μm. Fracture toughness, $K_{Ic}$, was calculated using the formula:

$$K_{Ic} = \sigma_c(\pi a)^{1/2} f(a/w)$$

where $\sigma_c$ is the critical stress for crack propagation and $f(a/w)$ a form factor previously described[20]. The fracture energy $G_{Ic}$ in plane strain conditions is defined as:

$$G_{Ic} = (K_{Ic}^2/E)(1-\nu^2)$$

where $\nu$ is Poisson's ratio and $E$ is Young's modulus. Poisson's ratio $\nu$ was measured during tensile tests using two 90° crossed deformation gauges.

*Fractography.* The fracture surface of the broken SEN specimens were observed by scanning electron microscopy (SEM) using a Jeol 840 A microscope operating at 15 kV. The surfaces were sputter-coated with a thin layer of gold before observation.

## RESULTS AND DISCUSSION

### *Cure schedules, glass transition temperature and structures of the epoxy networks*

As shown in *Figure 2*, during the cure this epoxy system exhibits a large exothermicity. The temperature in the mould passes through a maximum, after about 20 min, that is far beyond the temperature range of the oven (*Figure 2*).

*Table 2* lists the maximum temperatures ($T_M$) recorded in the mould as a function of the cure schedule. $T_M$ decreases rapidly with the temperature of the first part of the cure cycle (with the same geometry and characteristics of the PTFE-coated mould). Only for the cure cycle denoted 120/180 did the temperature in the middle of the mould surpass the melt temperature of DDA (204°C). In the three cases, the plates were transparent, so it was possible to see that there was no evidence of undissolved DDA.

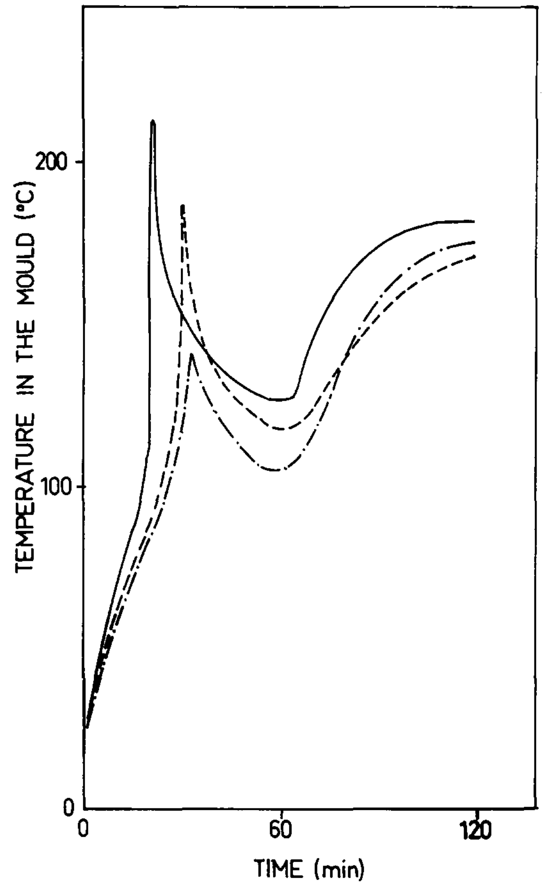


**Figure 2** Temperature recording in the middle of the mould during curing of BDMA-catalysed DGEBA–DDA systems (a/e = 0.6) with different cure schedules: —·—·—, 100/180; ---, 110/180; ——, 120/180

The glass transition temperatures ($T_g$) determined by d.s.c. temperature scans are also reported in *Table 2*. During a second scan on the same sample, no exothermic reaction peak after the glass transition was observed. Therefore, for these three systems no residual reaction occurs and the crosslinking reaction was complete. This is confirmed by the fact that no shift in $T_g$ at the higher temperatures was noted. The network denoted 100/180 (cured 1 h at 100°C and 1 h at 180°C) exhibited the highest glass transition temperature. There was no significant difference in $T_g$ between the two networks prepared at the higher cure temperatures.

These $T_g$ results agree with a previous study[7] on the same BDMA-catalysed epoxy–DDA system. In this study by Lin, plates ($150 \times 150 \times 4\,\text{mm}^3$) were prepared with the same system and with a stoichiometric ratio equal to 0.6. A similar decrease of $T_g$ on increasing cure temperature was observed as in our study (*Table 2*). In addition, it is necessary to note that, with these larger mould dimensions, a cure of 1 h at 160°C followed by 1 h at 180°C is impossible because of the high temperature in the mould inducing oxidation of the specimen ($T_M > 300$°C).

In contrast to Schneider[4], who assumed that the reaction mechanism does not vary with temperature (in the range 100–160°C with a Monuron-catalysed system), Lin *et al.*[7] expected a variation of reaction mechanism with cure temperature in the same range as for BDMA-catalysed systems. By following the reaction during curing by *FT*i.r., they observed that, in networks pre-cured at a lower temperature, a greater amount of ether linkages were present. In fact, in this system there is competition between the two different pathways: addition and etherification mechanisms (*Figure 1*)[1–7]. The etherification, in effect, leads to crosslinks in addition to the crosslinking occurring from the epoxy–amine reaction.

The $^{13}$C n.m.r. (CP-MAS) spectra in the 0–200 ppm region of the three final networks are shown in *Figure 3*. Sabra *et al.*[16] attributed the signals of different carbons to the epoxy-based diaminodiphenylsulphone networks.

For the 100/180 network, the surface area of the peak from 58 to 81 ppm increases by 15%; this phenomenon could be attributed to the emergence of ether linkages. The *FT*i.r. spectra of the final networks do not exhibit large differences in the ether range (1120 cm$^{-1}$) because of the superposition with other bands. Another interesting point is the increase of the peak located at 156–157 ppm for the network pre-cured at 120°C: the surface area increased by 8%. This increase could be attributed to the superposition of a peak associated with a carbonyl

**Table 2** Maximum temperature ($T_M$) recorded in the mould and glass transition temperature ($T_g$) of the epoxy networks processed with different cure schedules (a/e = 0.6)

| Cure schedule | Reference | Dimensions of mould (mm) | $T_M$ (°C) | $T_g$[a] (°C) |
|---|---|---|---|---|
| 1 h at 100°C/1 h at 180°C | 100/180 | 180 × 180 × 6 | 141 | 147(154) |
| 1 h at 110°C/1 h at 180°C | 110/180 | 180 × 180 × 6 | 186 | 142(148) |
| 1 h at 120°C/1 h at 180°C | 120/180 | 180 × 180 × 6 | 212 | 139(145) |
| 3 h at 100°C/1 h at 180°C | 7 | 170 × 150 × 4 | 120 | 128(146) |
| 1 h at 160°C/1 h at 180°C | 7 | 170 × 150 × 4 | 205 | 127(134) |

[a] Values in parentheses correspond to $T_g$ kept at the inflection point on d.s.c. records

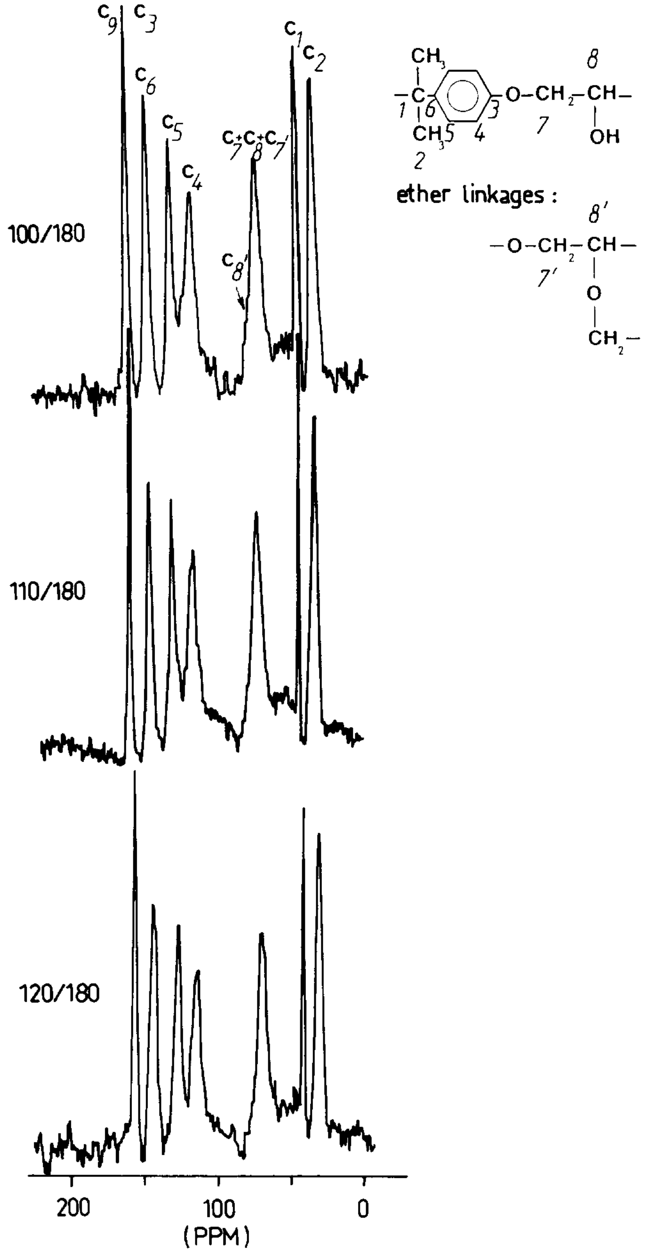
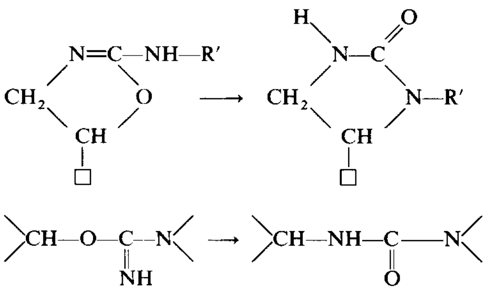


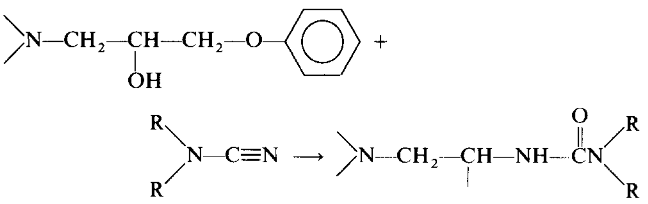
**Figure 3** $^{13}C$ n.m.r. high-resolution spectra (62.89 MHz) in the solid state for the three DGEBA–DDA matrices

carbon (C9). Indeed, Zahir[6] proposed that, for a higher cure temperature, intra- or intermolecular rearrangements are possible from 2-aminooxazoline or iminooxazoline and that nitrile groups react with hydroxyl groups (see below).

Intramolecular:



Intermolecular:



This hypothesis along with the n.m.r. observations are confirmed by the increase of the 1740 cm$^{-1}$ band associated with carbonyl–urea groups[1] on the *FT*i.r. spectrum of the 120/180 network (*Figure 4*).

All of these observations show that the reaction pathway of dicyandiamide with the epoxy prepolymer DGEBA varies with curing temperature. Etherification is favoured at low temperatures, explaining the increase in glass transition temperature for the network 100/180 ($\Delta T_g = 7°C$). Etherification reactions create additional crosslinks in addition to epoxy–amine crosslinks, thus increasing the functionality of crosslinks. The critical pre-curing temperature was found to be 100°C for BDMA-catalysed DGEBA–DDA systems[7]. This influence of the pre-cure temperature on the chemistry is not erased by a post-cure treatment at 180°C, as is the case with other epoxy–amine systems.

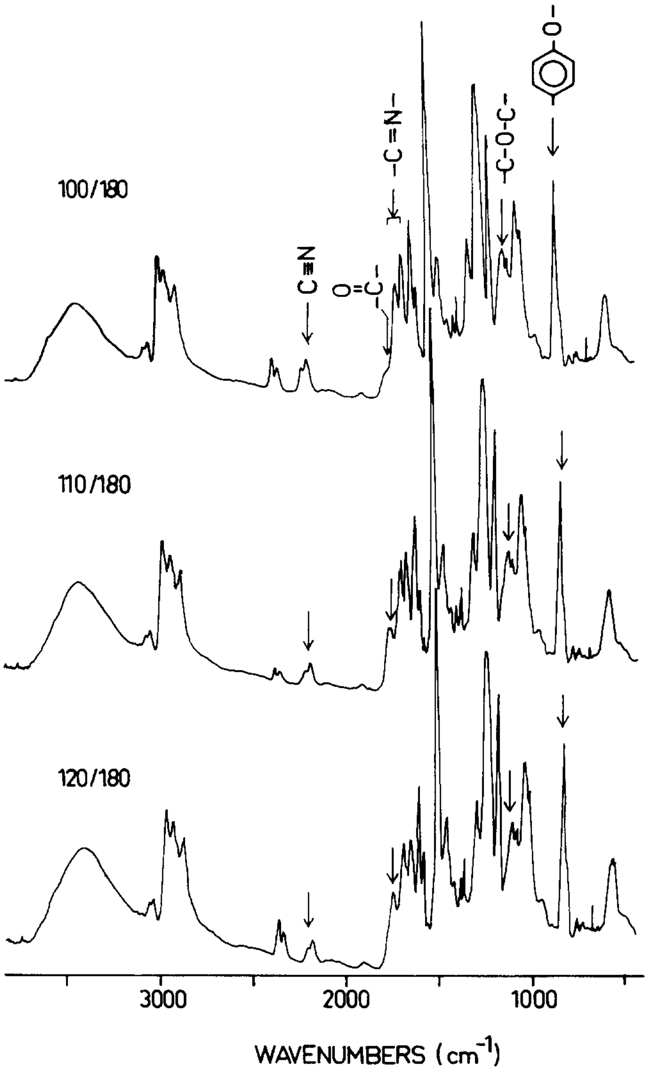


**Figure 4** *FT*i.r. spectra of DGEBA–DDA networks cured with the three different schedules

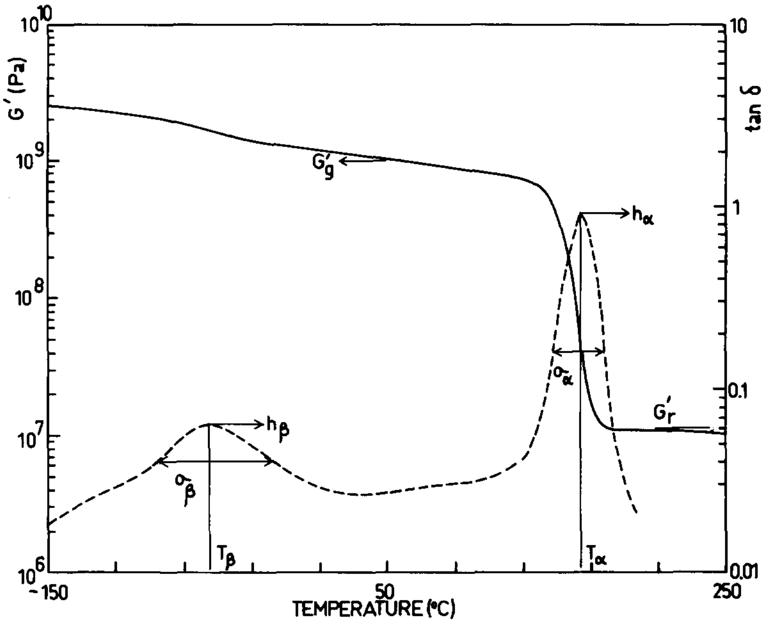


**Figure 5** Dynamic mechanical spectrum (storage modulus $G'$ and loss factor tan $\delta$ vs. temperature at 10 Hz) for the 100/180 DGEBA–DDA network (cured 1 h at 100°C and 1 h at 180°C)

**Table 3** Dynamic mechanical behaviour above room temperature ($\alpha$ transition) for the three DGEBA–DDA networks prepared using different cure schedules. Also given are thermal expansion coefficients (in the glassy ($\alpha_g$) and rubbery ($\alpha_r$) states determined by t.m.a.)

| Epoxy network | $G'_v$ [a] (GPa) | $G'_r$ [b] (MPa) | $T_\alpha$ [c] (°C) | $h_\alpha$ [c] | $\bar{M}_c$ (g mol$^{-1}$) | $\alpha_g$ ($10^{-6}$ K$^{-1}$) | $\alpha_r$ ($10^{-6}$ K$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 100/180 | 1.02 | 10.7 | 165 | 0.89 | 420 | 61 | 193 |
| 110/180 | 1.01 | 8.4 | 164 | 0.97 | 530 | 65 | 213 |
| 120/180 | 0.95 | 7.2 | 157 | 1.01 | 640 | 70 | 237 |

[a] At 50°C
[b] At 200°C ($\simeq T_\alpha + 40$°C)
[c] At 10 Hz

### *Viscoelastic properties of the polyepoxy networks*

*Figure 5* shows a typical dynamic mechanical spectrum of a DGEBA–DDA network. Storage shear modulus ($G'$) and loss factor (tan $\delta$) are recorded *versus* temperature at a frequency of 10 Hz. The tan $\delta$ vs. temperature curve passes through a maximum ($\alpha$ peak) near 165°C. This main mechanical relaxation is associated with the glass transition. In the same temperature range, $G'$ decreases by two orders of magnitude and the modulus $G_r$ in the rubbery state could be determined. At lower temperatures, a secondary transition ($\beta$ peak) is displayed (near $-50$°C). This relaxation is generally associated with motions of diphenylpropane units and hydroxy ether groups[21–24]. The various data determined from these spectra are summarized in *Table 3*.

The position of the tan $\delta$ peak vs. temperature of pre-curing confirms the d.s.c. data. Higher $T_\alpha$, thus higher glass transition temperatures, were obtained for the cure schedule 100/180. An increase of $G'_r$, the rubbery modulus at $T_g + 40$°C, was also observed when the pre-cure temperature ($T_p$) decreases (*Figure 6a*). This observation confirms that additional crosslinking points are created via the etherification reaction for 100/180 network as predicted by the n.m.r. data.

The molecular weight between crosslinks, $\bar{M}_c$, could be obtained by the following relation for crosslinked rubbers[25]:

$$G'_r = \frac{\bar{r}_i^2}{\bar{r}_f^2}\frac{\rho RT}{\bar{M}_c}\left(1 - \frac{2\bar{M}_c}{\bar{M}_n}\right)$$

where $\bar{r}_i^2/\bar{r}_f^2$ is the ratio of the mean-square end-to-end distance of the polymer chain and in a randomly coiled chain, which was assumed to be equal to 1, $\rho$ is the polymer density, $R$ is the universal gas constant and $T$ is the absolute temperature. The correction factor, $(1 - 2\bar{M}_c/\bar{M}_n)$, where $\bar{M}_n$ is the chain-backbone molecular weight, is negligible in our case because it could be assumed that chain ends are not active. Thus, $G'_r$ measured in the rubbery plateau at a temperature 40°C above $T_g$ is related to $\bar{M}_c$ by the relation[26]:

$$G'_r = \rho RT/\bar{M}_c$$

This very simple relation assumes that all the chains and crosslinking junctions are equivalent in terms of functionality and flexibility. This is not really true in our case. Indeed, Lin[7] demonstrates that etherification induces a higher functionality of crosslinks in these systems.

Nevertheless, with this calculation it is possible to compare relatively the three BDMA-catalysed DGEBA–DDA networks. In our case, $\bar{M}_c$ decreases with decreasing $T_p$, showing that etherification creates additional crosslinks. The higher degree of crosslinking leads to a higher

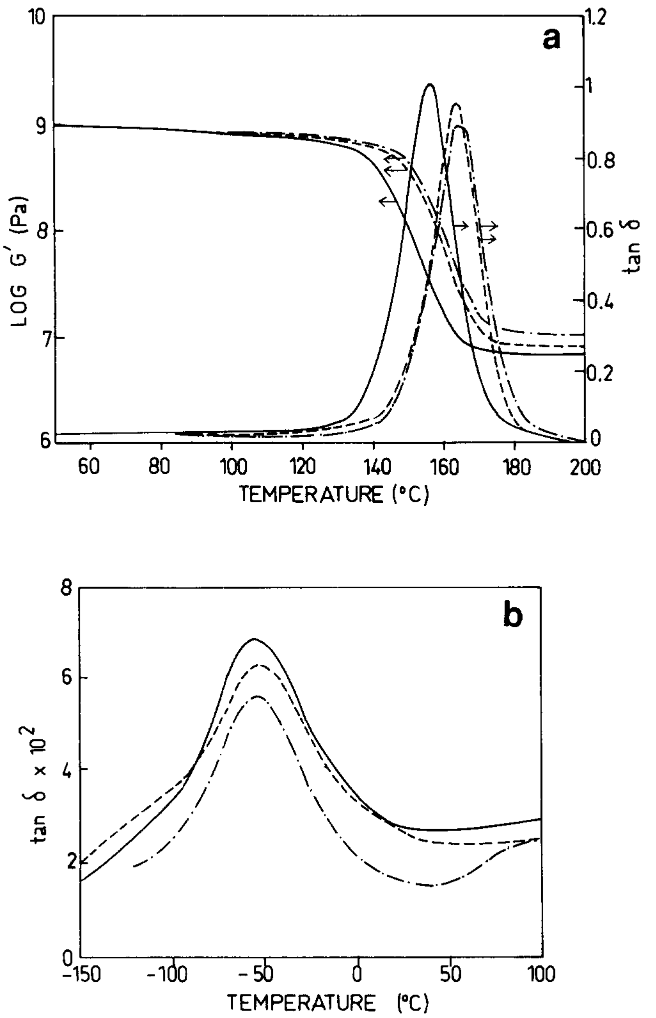


**Figure 6** Dynamic mechanical spectra ($G'$ and tan $\delta$ vs. temperature) in (a) $\alpha$ and (b) $\beta$ regions for the different DGEBA–DDA epoxy networks (at 10 Hz)

glass transition temperature for the lower pre-cure temperature (100°C). The amplitude of the $\alpha$ peak ($h_\alpha$) (*Table 2* and *Figure 6a*) also shows a higher mobility of the macromolecular chains for the network pre-cured at 120°C, as has been observed previously[12].

The thermal expansion data below and above $T_g$ are given in *Table 3* for the three samples; $\alpha_g$ and $\alpha_r$ decrease with increasing $T_p$. Therefore, below and above $T_g$, the coefficients are the lowest for the most crosslinked network (100/180). The $\alpha_r$ and $\alpha_g$ values confirm the higher crosslink density induced by etherification.

The data obtained on relaxations (*Figure 6b*) for the samples cured with the three schedules are listed in *Table 4*. There are no large differences between the temperatures at the maximum tan $\delta$ ($T_\beta$), values of apparent activation energies $E^{\ddagger}_{a\beta}$, or values for $\sigma_\beta$ for the three networks. On the other hand, the amplitude of the $\beta$ peak ($h_\beta$) increases with increasing temperature of pre-curing. In the literature, motions of hydroxy ether segments of the main chain are responsible for the $\beta$ loss peak in epoxy networks, and an increase in the number of these groups can shift the peak to higher temperature. No clear relationship has been established between free volume and $\beta$ transition. Therefore, it is generally assumed that the number of hydroxy ether groups is the principal factor determining this transition. In our case, from the values of $h_\beta$ and the shape of the three $\beta$ peaks, it seems that changes occur in the number and mobility of the hydroxy ethers for the three networks. For the 100/180 cure, hydroxy ether groups are also probably fewer, confirming the hypothesis of the etherification reaction in the case of the low pre-cure temperature. Our results for the $\beta$ amplitude are in agreement with Sabra's data on DGEBA–diphenylsulphone networks[16]. In this work, the $\beta$ relaxation was studied by dielectric measurements and the $\beta$ dependence on etherification is clearly displayed. The fact that, contrary to Sabra's work, $T_\beta$ does not shift with increasing etherification at lower temperatures can be explained by the small variation of ether amount in our case. Between the 120/180 and 100/180 networks, the variation displayed by n.m.r. analysis is only about 15% even though Sabra observed 45% of additional ethers. The second point is that there is a difference in the frequency used for the measurements (over two orders of magnitude of frequency: 4 kHz and 10 Hz in our case) and in the nature of the epoxy–amine system.

The apparent activation energies were nearly the same for the three samples cured at different temperatures, which is in agreement with other studies[27].

### *Mechanical properties of the networks*

The cure schedules had no effect on the elastic properties, such as Young's modulus ($E$) of the DGEBA–DDA epoxy networks (*Table 5*). In all cases, $E$ was equal to 2.9 GPa, in agreement with other studies[28], showing that Young's modulus in the glassy state is mainly dependent on the interactions between the chains or on free volume rather than on the degree of crosslinking. Significant differences are only displayed with the plastic behaviour.

In fact, the non-elastic work-hardening rate $K$ measured during the compression tests at a constant strain rate decreased with increasing pre-cure temperature. In previous studies, it was shown that $K$, defined from a metallurgical point of view, varies as the inverse of the nucleation rate of defects in the pre-yield stage and is sensitive to any change in the chemical mesostructure of the glassy polymer. Thus $K$ is a reliable probe for characterizing the evolution of the polymer[18,29]. In the case of the BDMA-catalysed DGEBA–DDA networks,

**Table 4** The $\beta$ relaxation characteristics as function of curing schedules of DGEBA–DDA networks

| Epoxy networks | $T_\beta$[a] (°C) | $h_\beta$[a] ($\times 10^{-2}$) | $\sigma_\beta$[a] (°C) | $E^{\ddagger}_{a\beta}$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| 100/180 | −54 | 5.4 | 59 | 67 |
| 110/180 | −53 | 6.3 | 64 | 65 |
| 120/180 | −55 | 6.8 | 58 | 70 |

[a] At 10 Hz

**Table 5** Elastic, pre-yielding and yielding properties of the DGEBA–DDA epoxy networks

| Network (curing) | $E$ (GPa) | $V_0$ (Å$^3$) | $K$ (MPa) | $\sigma_y$ (MPa) | $e_y$ (%) |
|---|---|---|---|---|---|
| 100/180 | 2.9 | 1199 | 2348 | 114 | 11.4 |
| 110/180 | 2.9 | 1278 | 1770 | 112 | 10.5 |
| 120/180 | 2.9 | 1512 | 1557 | 108 | 9.3 |

the $K$ value indicates that pre-curing at a low temperature tends to decrease the ability of the network to deform non-elastically. Thus $K$ seems to be directly related to the molecular weight between crosslinks $\bar{M}_c$ and consequently to the degree of crosslinking. This result of the decrease of aptitude to plastic deformation with increasing crosslinking is in agreement with studies on other thermosetting systems[18,30,31]. Specifically, with polyaminobismaleimide resins[18], it has been found that the yield stress $\sigma_y$ does not vary noticeably with degree of crosslinking; however, the non-elastic work-hardening rate $K$ is greatly affected by crosslinking. For the present systems, the yield stress ($\sigma_y$) determined during a compression test is slightly dependent on the pre-cure temperature and therefore on degree of crosslinking. The network 120/180 showed the lowest $\sigma_y$ and $e_y$ (strain at the yield point), but values are of the same order within the accuracy of the measurements.

These variations only confirm the previous observations on $K$ values in the pre-yielding stage. In the same way, the apparent activation volume[17] involved in the plastic deformation ($V_0$) indicates that a higher crosslinking density induces a lower $V_0$, thus decreasing the ability to deform plastically.

Using linear elastic fracture mechanics (LEFM), the critical values of $K_{Ic}$ (stress intensity factor) and $G_{Ic}$ (strain energy release rate) are determined (*Table 6*). The $K_{Ic}$ and $G_{Ic}$ values were strongly dependent on cure schedule. For the 100/180 network, $G_{Ic}$ is 50% lower than for the 120/180 network, indicating that the degree of crosslinking affects the fracture behaviour. The observations of the fracture surfaces of specimens (*Figure 7*) are in a good agreement with the previous values of $G_{Ic}$. The fracture surface of the 120/180 network is rougher with more secondary cracks (*Figure 7c*) than the surface of the 100/180 specimen (*Figure 7a*). Therefore, the fracture energy $G_{Ic}$ is higher for the 120/180 network due to the creation of additional fracture surfaces of the microcracks. Some authors[32–34] have tried to establish relationships between fracture energy and molecular weight between crosslinks, $\bar{M}_c$. A linear relation between $G_{Ic}$ and $\bar{M}_c^{\frac{1}{2}}$ is generally observed for series of the same structure. In *Figure 8*, $G_{Ic}$ is plotted *versus* $\bar{M}_c^{\frac{1}{2}}$ as determined using dynamic mechanical measurements and rubber elasticity theory (*Table 4*). The relatively good correlation obtained indicates that the deformation process involved is related to that observed in rubbery materials. The free volume may increase in the crack tip region due to a dilational stress field and locally $T_g$ may be lowered. Then the material is 'rubber-like' deformed, leading to a dependence between fracture energy and crosslink density. Usually improvement of epoxy network is related to the ability for shear yielding to occur[35] and thus crazing is not displayed. Yamini and Young[36] have

**Table 6** Fracture properties (critical stress intensity factor $K_{Ic}$ and critical strain energy release rate $G_{Ic}$) of the DGEBA–DDA epoxy networks

| Network (curing) | $K_{Ic}$ (MPa m$^{1/2}$) | $G_{Ic}$ (kJ m$^{-2}$) |
|---|---|---|
| 100/180 | 1.3 | 0.49 |
| 110/180 | 1.4 | 0.60 |
| 120/180 | 1.6 | 0.75 |

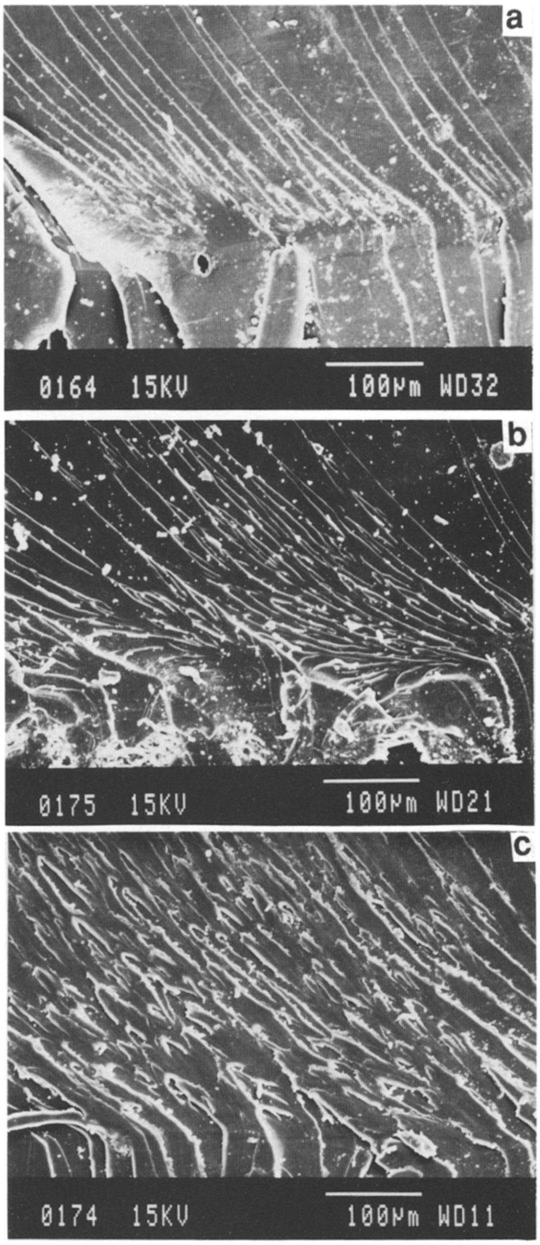


**Figure 7** Fracture surfaces of SEN specimens for the different DGEBA–DDA networks as observed by SEM: (a) 100/180; (b) 110/180; (c) 120/180

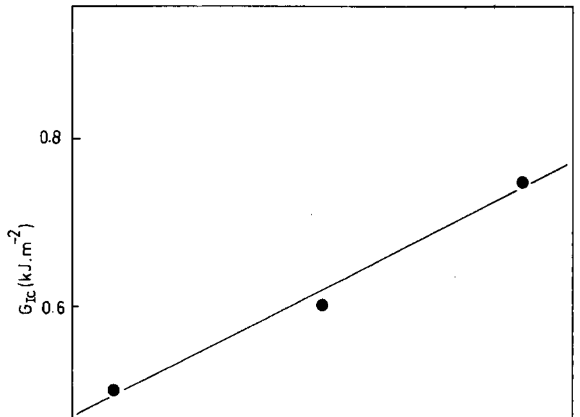


**Figure 8** Fracture energy $G_{Ic}$ (measured at room temperature) *versus* $\bar{M}_c^{\frac{1}{2}}$ for DGEBA–DDA networks

shown with epoxy–amine systems that $K_{Ic}$ increases with decreasing yield stress $\sigma_y$. This effect can be explained by the existence of a crack blunting mechanism, which occurs at the crack tip. This phenomenon is favoured when the material has the ability to deform plastically.

As a whole the mechanical property data on the DGEBA–DDA networks show that the final properties of the epoxy materials are, in this case, greatly dependent on the chemistry involved. Many studies have been done in order to understand this relationship with chemical structure of epoxy networks by changing the molecular weight between crosslinks. Different methods have been investigated using different cure schedules, blending epoxy prepolymers[34] or changing the stoichiometric ratio[35]. However, it seems that there is no molecular-weight distribution effect[34]. In our case, the relationship between fracture behaviour and structural properties was not affected by the LEFM measurements made at different temperatures between room temperature and the glass transition temperature.

## CONCLUSIONS

In this work, we have shown that the chemical pathways of the reaction between DDA and the epoxy prepolymer DGEBA catalysed by BDMA is strongly dependent on the cure schedule. As shown previously, 100°C is demonstrated to be the 'critical' pre-cure temperature at which etherification reactions occur. This etherification induces additional crosslinks, which change the final properties of the cured systems. Mechanical properties, especially plastic behaviour and fracture toughness, were shown to be greatly dependent on crosslink density. The fracture energy $G_{Ic}$ is proportional to $\bar{M}_c^{\frac{1}{2}}$ ($\bar{M}_c$ is the molecular weight between crosslinks determined experimentally). This study showed that networks of the same general structure can be modified by modifications of the chemical reactions, thus inducing changes in the final macroscopic properties.

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