Mechanical and viscoelastic properties of epoxy networks cured with aromatic diamines

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The mechanical and viscoelastic properties of epoxy networks based on the diglycidyl ether of bisphenol A epoxy prepolymer cured with various aromatic diamines, viz. 4,4′- and 3,3′-diaminodiphenylsulphone, 4,4′-diaminodiphenylmethane, bis(4-(4-aminophenoxy)phenyl)sulphone and (4-(aminophenoxy)phenyl)-propane, were studied. General characteristics, like density, crosslink density, flexibility, packing density and molecular weight between crosslinks, were determined and related to the structure of the curing agent. Dynamic mechanical spectra were used to study both the α and β relaxations. Tensile tests were used to determine the Young's moduli in the glassy state, and compression tests were used to determine the yield stress. Impact tests and linear elastic fracture mechanics allowed us to determine R_s and K_{Ic}.

(Keywords: epoxy; amine; network; viscoelasticity; mechanical properties)

INTRODUCTION

Epoxy copolymers are a major generic class of polymeric materials used by the aerospace and leisure industries in the form of matrices for composite materials or as structural adhesives.

However, the main disadvantage of these materials is their brittleness, which is due to their highly crosslinked structure. A lot of studies have been conducted in order to improve the toughness. Generally, a reactive liquid rubber was incorporated as a dispersed phase in a rigid epoxy matrix[1–4]. But, depending on the kinetics of the reaction, the phase separation, which is a competitive mechanism, was not always complete. Therefore, part of the rubber was dissolved in the matrix, and unacceptable decreases of both modulus and glass transition temperature T_g were observed[4]. Another possible way of toughening epoxy networks is to act on the structure of the epoxy prepolymer[5–9] or of the diamine comonomer[10–12].

The aim of this work is to evaluate the effects of curing agent structure on the mechanical and viscoelastic properties of various epoxy–amine networks.

In order to maintain a high value of T_g, five aromatic diamines differing in backbone stiffness were chosen. Two of them, 2,2-bis(4,4′-(aminophenoxy)phenyl)propane (BAPP) and 4-bis(4-aminophenoxy)phenyl)sulphone (BAPS), have been studied previously by Delvigs[11]. These diamines contain three flexibilizing groups. The three other curing agents are 4,4′- and 3,3′-diaminodiphenylsulphone (4,4′-DDS and 3,3′-DDS) and diaminodiphenylmethane (DDM), which each have only one flexibilizing group. The introduction of an oxygen link between the two phenyl groups in BAPP and BAPS creates an additional rotational degree and a longer distance between crosslink points.

The influence of the structure of the curing agent on the cure kinetics has been presented in a previous publication[12]; the relative reactivities of the diamines were as follows: 4,4′-DDS < 3,3′-DDS < BAPS < BAPP < DDM.

According to Delvigs[11] the incorporation of flexibilized diamines into epoxy networks is expected to improve fracture toughness and impact strength.

EXPERIMENTAL

Sample preparation

The formulations used in this study are based on the diglycidyl ether of bisphenol A (DGEBA) prepolymer, Dow DER 332, cured with various aromatic diamines as comonomers: 4,4′- and 3,3′-diaminodiphenylsulphone, 4,4′-diaminodiphenylmethane, bis(4-(4-aminophenoxy)-phenyl)sulphone and 2,2′-bis((4-aminophenoxy)phenyl)-propane. The formulae, suppliers, molecular weights and melting points of the various products are listed in *Table 1*. These products are used as received. The curing agents are not soluble at room temperature in the epoxy prepolymer, and therefore the stoichiometric mixture of DGEBA/diamine is heated to 135°C (or 80°C for the DGEBA/DDM mixture) and degassed under mechanical stirring until a clear solution is obtained. In all cases, the reaction between the epoxy and amine functions begins during the heating but at various extents depending on the nature of the curing agent. The curing cycles are shown in *Table 2*. The conversion of epoxy functions was measured by size exclusion chromatography (s.e.c.)[12] and was found equal to 4%, 5%, 15%, 2% and 50% for the

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Table 1 Structure and characteristics of the various monomers

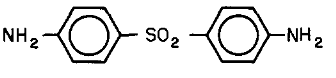
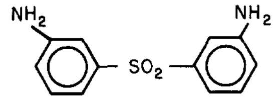
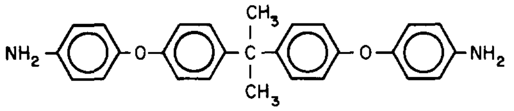
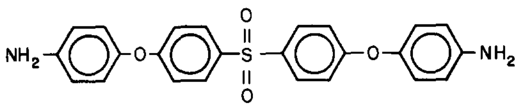
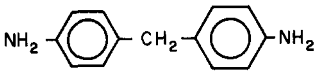
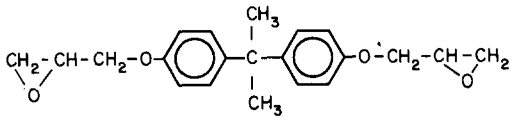
Monomers	Formula	Supplier	Molecular weight (g mol^{-1})	Melting temperature (°C)
4,4′-Diaminodiphenylsulphone (4,4′-DDS)		Fluka	248	175
3,3′-Diaminodiphenylsulphone (3,3′-DDS)		Fluka	248	164
2,2′-Bis(4-(4-aminophenoxy)phenyl)propane (BAPP)		Mallinkrodt	410	126
Bis(4-(4-aminophenoxyl)phenyl)sulphone (BAPS)		Mallinkrodt	432	193
4,4′-Diaminodiphenylmethane (DDM)		Fluka	198	88
Diglycidyl ether of bisphenol A (DGEBA)		Dow Chemical	340	47

Table 2 Curing cycles used to prepare samples (* without dissolving the diamine)

Network	Curing cycle
DGEBA/4,4′-DDS	2 h 180°C ± 2 h 230°C
DGEBA/3,3′-DDS	2 h 180°C ± 1 h 210°C
DGEBA/BAPP	2 h 180°C ± 1 h 200°C
DGEBA/BAPS*	1 h 140°C ± 2 h 180°C ± 1 h 200°C
DGEBA/DDM	3 h 110°C ± 3 h 190°C

4,4′-DDS/DGEBA, 3,3′-DDS/DGEBA, DDM/DGEBA, BAPP/DGEBA and BAPS/DGEBA mixtures respectively. The homogeneous reaction mixture was then poured into a mould (150 × 150 × 4 mm^3), except for the formulation based on BAPS curing agent. In this case, a heterogeneous mixture of BAPS/DGEBA was used because the extent of reaction during the dissolution of the BAPS at 135°C is too high to allow the casting. A rotating mould is used to avoid the settling of the BAPS powder.

Differential scanning calorimetry

D.s.c. analyses were run with a Mettler TA 3000 apparatus, at a heating rate of 10°C min^{-1} under an argon atmosphere. The glass transition temperature T_g is taken at the beginning of the change in heat capacity (onset value).

Determination of the packing density

The packing density is given by:

$$\rho^* = \rho(V_W/M) \qquad (1)$$

where ρ is the density, M is the molecular weight of a constitutional repeat unit (CRU) and V_W is the Van der Waals volume of the latter. V_W is obtained by summation of the molar group contributions given by Bondi[13]. The CRU chosen, which is representative of the network structure, is based on two molecules of DGEBA and one of diamine[14].

Densities are determined using Archimedes' method.

Dynamic mechanical measurements

The β relaxation is studied using a Polymer Laboratories Dynamic Mechanical Thermal Analyser (PL-DMTA) in double cantilever bending mode, between −100 and 30°C, at a heating rate of 2°C min^{-1} in a frequency range from 3.3×10^{-2} to 30 Hz. The apparent activation energy $E_{a\beta}$ of the β relaxation was determined using an Arrhenius law on the maxima of the β peak (T_β):

$$\log \nu = E_{a\beta}/RT_\beta + \text{constant} \qquad (2)$$

The α transition and the rubbery state were studied using a Rheometrics Dynamic Analyser (RDA 700), from 100 to 300°C at a heating rate of 2°C min^{-1} and at a frequency of 3 Hz. The strain was applied by torsion. From the value of the rubbery modulus, the molecular weight between crosslinks M_c was calculated using the simplified form of the equation of rubber elasticity (front factor $\phi = 1$):

$$M_c = 3\rho RT/E'_c \qquad (3)$$

where ρ = density of the network at T and E'_c = Young's modulus at T.

M_c can also be calculated theoretically with the equation:

$$M_c = (m_a + 2m_e)/3 \qquad (4)$$

where m_a and m_e are the molecular weights of the diamine and diepoxide, respectively.

Table 3 Characteristics of the different networks

Network	T_g (°C)	ρ (g cm^{-3})	ρ^*	$M_{c,th}$ (g mol^{-1})	[OH] (10^{-3} mol g^{-1})	[DPP] (10^{-3} mol g^{-1})
DGEBA/4,4′-DDS	218	1.233	0.673	312	4.32	2.20
DGEBA/3,3′-DDS	171	1.237	0.675	312	4.32	2.20
DGEBA/BAPP	169	1.186	0.661	367	3.69	5.51
DGEBA/BAPS	183	1.233	0.665	374	3.62	1.84
DGEBA/DDM	178	1.183	0.669	296	4.45	2.29

T_g = glass transition temperature
ρ = density
ρ^* = packing density
$M_{c,th}$ = theoretical molecular weight between crosslinks
[OH] = theoretical concentration of hydroxyl groups
[DDP] = theoretical concentration of diphenyl propane groups

Mechanical tests

Tensile tests were performed on a DY25 Adamel–Lhomargy machine at room temperature at a strain rate of $\dot{\varepsilon} = 8.3 \times 10^{-4}\ \mathrm{s}^{-1}$. Test specimens were milled to the ISO 60 standard (NF 51034). Elongation measurements were taken using an Adamel–Lhomargy EX10 extensometer. The Young's modulus E was computed from the linear part of the curve; elongation and stress at break were also recorded.

Compression tests were made using the same testing machine, at a strain rate of $\dot{\varepsilon} = 7.6\ \mathrm{s}^{-1}$. Cylindrical rods ($\phi = 9.7$ mm, $h = 22$ mm) were deformed in a compression rig between steel plates. The yield stress σ_y and the yield strain ε_y were determined.

Impact tests were done on unnotched specimens using a Charpy-type impact pendulum[15,16] with a speed of $3\ \mathrm{m\,s}^{-1}$. A piezoelectric transducer recorded the load–time curve through a computer and allowed the determination of the surface resilience (or fracture impact energy) R_s. The estimated frequency of the impact is between 200 Hz and 1 kHz.

For linear elastic fracture mechanics (LEFM), single-edge-notched specimens (thickness = 6 mm, width $w = 12$ mm) were used in three-point bending mode (span length = 48 mm). Cracks of various lengths a were machined with a saw and the crack tip was achieved with a razor blade.

Fracture toughness K_{Ic} was determined using the formula:

$$K_{Ic} = \sigma_c(\pi a)^{1/2} f(a/w) \qquad (5)$$

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

$$G_{Ic} = (K_{Ic}^2/E)(1 - \nu^2) \qquad (6)$$

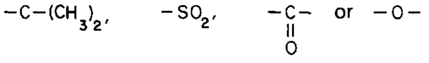
where ν is Poisson's ratio and E is Young's modulus.

RESULTS AND DISCUSSION

The glass transition temperatures T_g obtained by d.s.c. after complete cure, the densities ρ, the packing densities ρ^* and the theoretical molecular weight between crosslinks M_c are presented in *Table 3*. Values of the theoretical concentration of hydroxy groups (created by the reaction of the epoxy function with the amine function) and values of the concentration of diphenylpropane units (DDP, coming from the bisphenol A segment) are also reported in *Table 3*.

The network based on 4,4′-DDS exhibits the highest glass transition temperature, and, in the case of 3,3′-DDS, the isomerization in the *meta* position induces a decrease in T_g. The network based on DDM has a glass transition temperature near that of the DGEBA/3,3′-DDS system. The effect of the flexibilizing diamine BAPP and BAPS is a decrease in T_g, due to the presence of the –O– bridge. The SO_2 has the opposite effect: it increases the value of T_g.

Van Hoorn[17] has studied various aromatic linear polymers, where the ring substituents are hydrogen, methyl or chlorine and the bisphenol bridge groups are



$$-C-(CH_3)_2, \quad -SO_2, \quad -\underset{\underset{O}{\|}}{C}- \ \text{or} \ -O-$$

The results indicate that to a large extent the –OH and –SO_2 interaction by hydrogen bonding causes the high value of T_g observed for the sulphone-based polymers.

The densities of the networks based on sulphone diamine (3,3′-DDS, 4,4′-DDS and BAPS) are higher than for the other systems, due to the higher atomic weight of S.

It is well known[13] that the packing densities of epoxy–amine networks are higher than the average of linear polymers. The packing density seems to increase with the crosslink density and to be the link to the cohesive energy.

For the networks under study, the lowest values of the packing densities are observed for the flexibilized systems, DGEBA/BAPP and DGEBA/BAPS, while the highest values are observed for the networks based on DDS. But the method used to calculate the packing density does not take into account the effect of the substitution of the diamine DDS on the phenyl ring.

In our cases, the molecules having the highest concentration of phenyl groups (BAPP and BAPS) are also the most flexible because of the flexibilizing effect of the –O– group.

So, in this series of networks there is no simple relation between the packing density and the crosslink density.

Dynamic mechanical measurements

A typical plot of the storage modulus E' and tan δ, measured at 3 Hz, as a function of temperature, is shown in *Figure 1* for the DGEBA/3,3′-DDS network. Three relaxations are observed:

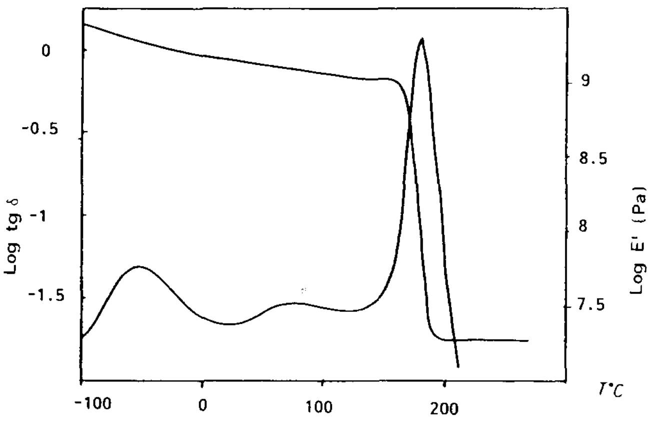


Figure 1 Dynamic mechanical properties of the DGEBA/3,3'-DDS network, measured at 3 Hz

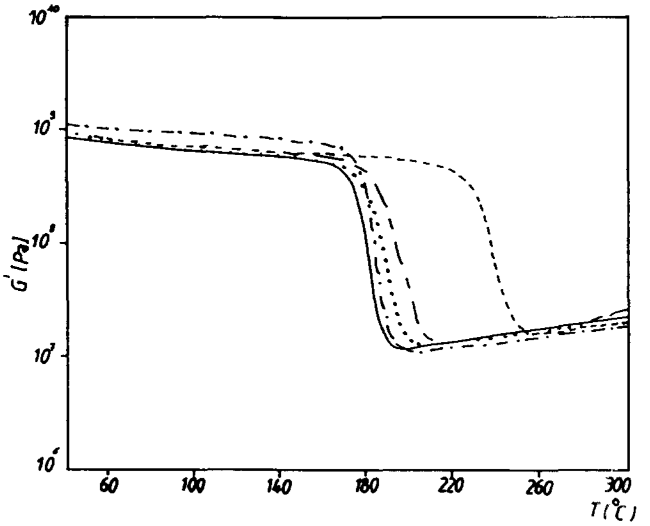


Figure 2 Modulus as a function of temperature at 3 Hz (Rheometrics) for: (----) DGEBA/4,4'-DDS; (-·-·-) DGEBA/3,3'-DDS; (———) DGEBA/BAPP; (——) DGEBA/BAPS; (·····) DGEBA/DDM

(i) a main transition, α, in the high-temperature region, is associated with the glass transition;

(ii) a secondary relaxation, β, below 0°C; and

(iii) an intermediate relaxation, ω, between 0 and 100°C.

In this work, only the α and β relaxations are characterized for the various networks.

Glass transition region

The α transition. The dynamic mechanical spectra for the high-temperature region are shown in *Figures 2* and *3* for the five networks.

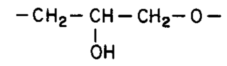
Table 4 gives the values of the mechanical relaxation T_m determined at the maximum of the loss peak, the intensity at this maximum and the value of the rubbery modulus at $T_{m+30°C}$.

The differences between the shapes of the α peaks are due to the structure of the hardener: the isomerization in the *meta* position for the 3,3'-DDS compared to 4,4'-DDS leads to a decrease in T_m and an increase in tan δ_{max}. The same effect is noticed when the central group $-SO_2$ (in BAPS) is replaced by $-C-(CH_3)_2$ (in BAPP).

The molecular weights between crosslinks calculated by the rubber elasticity theory (*Table 4*) are close to the theoretical values (*Table 3*), except for 3,3'-DDS and DDM, for which some differences are noticed.

The β relaxation. The assignment of the β relaxation to molecular segment motion depends on the chemical structure of the compounds[18–21].

For epoxy–diamine networks, most authors[22–28] associate the β relaxation (between −80 and −40°C) with the sum of the motions of diphenylpropane groups and glyceryl units:



$$-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-O-$$

The spectra are presented in *Figure 4* for the five networks and their characteristics (T_m = temperature of tan δ_{max}, S_β = area under the tan δ curve) are reported in *Table 5*.

The highest intensity of the β relaxation is observed for the network cured with BAPP. This system shows a different behaviour compared to the others. At a low frequency, the β peak exhibits a different shape than at high frequency (*Figure 5*): two maxima are observed. The relaxation occurring at the lowest temperature (T_m = −70°C at ν = 0.1 Hz) is linked to the higher amount of

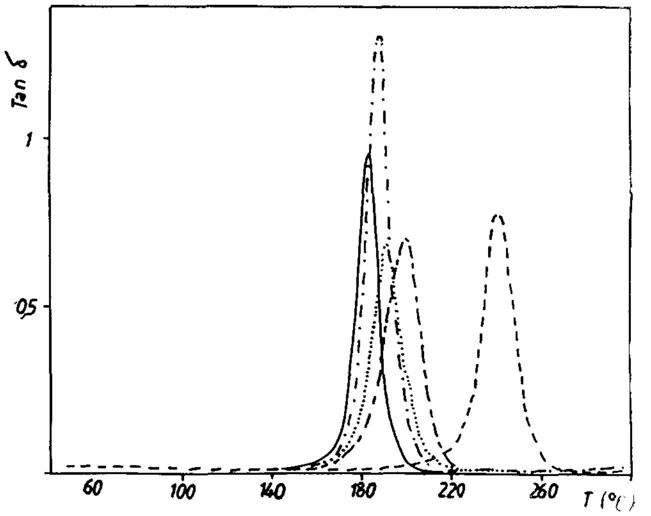


Figure 3 Tan δ as a function of temperature at 3 Hz (PLDM-TA) for: (----) DGEBA/4,4'-DDS; (-·-·-) DGEBA/3,3'-DDS; (———) DGEBA/BAPP; (——) DGEBA/BAPS; (·····) DGEBA/DDM

Table 4 Characteristics of the α relaxation (Rheometrics at 3 Hz)

Networks	T_m (°C)	tan δ	G'_r (MPa)	$M_{c,exp}$ (g mol^{-1})
DGEBA/4,4'-DDS	240	0.78	17.2	324
DGEBA/3,3'-DDS	187	1.29	12.3	410
DGEBA/BAPP	183	0.95	12.7	378
DGEBA/BAPS	199	0.70	13.9	370
DGEBA/DDM	184	0.7	13	364

T_m = temperature at the maximum
tan δ = amplitude of the loss peak at its maximum
G' = modulus
$M_{c,exp}$ = value of the molecular weight between crosslinks calculated using equation (3)

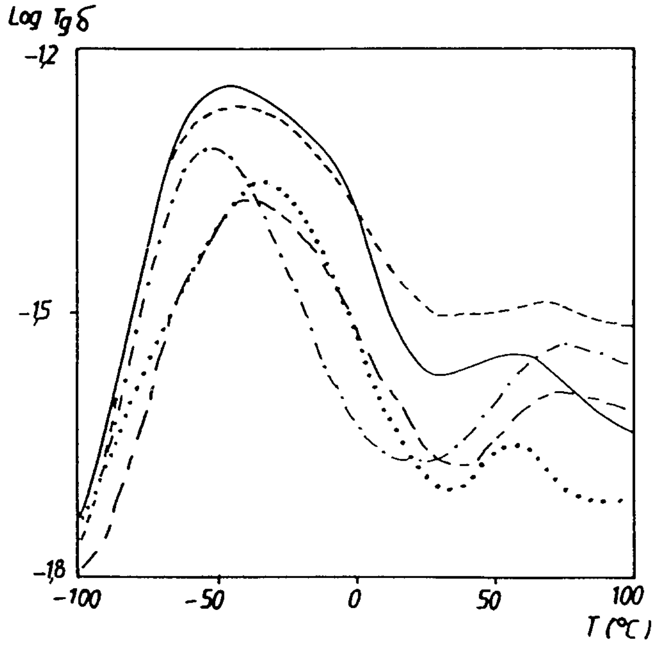


Figure 4 β Relaxation for the various networks measured at 3 Hz: (– – –) DGEBA/4,4′-DDS; (–·–·–) DGEBA/3,3′-DDS; (———) DGEBA/BAPP; (———) DGEBA/BAPS; (·····) DGEBA/DDM

Table 5 Characteristics of the β relaxation (PL-DMTA) at 3 Hz

Network	T_m (°C)	S_β	E_a (kJ mol^{-1})
DGEBA/4,4′-DDS	−44	54.1	86
DGEBA/3,3′-DDS	−53	43.2	74
DGEBA/BAPP	−47	58.4	77
DGEBA/BAPS	−39	47.7	78
DGEBA/DDM	−35	47.3	81

T_m = temperature at the maximum
S_β = area under the β peak
E_a = activation energy

diphenylpropane units present in this network. When the measurement frequency is increased, these two maxima are overlapped, which is responsible for the high intensity observed.

The networks based on 3,3′-DDS or 4,4′-DDS have the same theoretical concentration of hydroxy ether and diphenylpropane groups, but their β relaxations are different. The β relaxation of the DGEBA/4,4′-DDS network is very similar to the relaxation of the DGEBA/BAPP network, while the relaxation of the DGEBA/3,3′-DDS network is narrower: the shape is very different on the high-temperature side. In this case, the area under the curve S_β is lower than for the other networks. This effect is probably due to the *meta* position of the amine function on the aromatic ring.

The networks cured with BAPS or DDS show a very similar β relaxation, but this relaxation occurs at a higher temperature and has a lower intensity than the β relaxation of the DGEBA/BAPP network. The substitution of the $-SO_2$ group in BAPS by a $-C-(CH_3)_2$ group in BAPP causes the flexibility of the molecule[11].

The apparent activation energy $E_{a\beta}$ of the β relaxation is related to the experimental molecular weight between crosslink points. On *Figure 6*, we observe that $E_{a\beta}$ is a decreasing monotonic function of M_c, as seen previously by Arridge *et al.*[29] and Charlesworth[30]. These authors have concluded that, when M_c increases, the release of steric restrictions due to the crosslinks lowers the apparent activation energy.

Mechanical properties

The results related to tensile and compressive tests are reported in *Table 6*.

During the tensile tests, the epoxy networks under study broke with no yielding. The network based on 3,3′-DDS has a high modulus as compared to the network cured with 4,4′-DDS, while their T_g values show an opposite trend. A similar result has been reported by Lewis *et al.*[31].

In *Figure 7* it can be observed that a high modulus is related to a low peak area of the β relaxation. This behaviour was observed by Won *et al.*[32] on a series of networks based on DGEBA, isophorone diamine (IPD) curing agent and trimethylcyclohexylamine (TMCA) chain extender. These authors show that the tensile moduli at room temperature decrease when the crosslink density (or T_g) increase but the moduli before the β relaxation are identical. The peak area of the β relaxation was found to decrease when the crosslink density

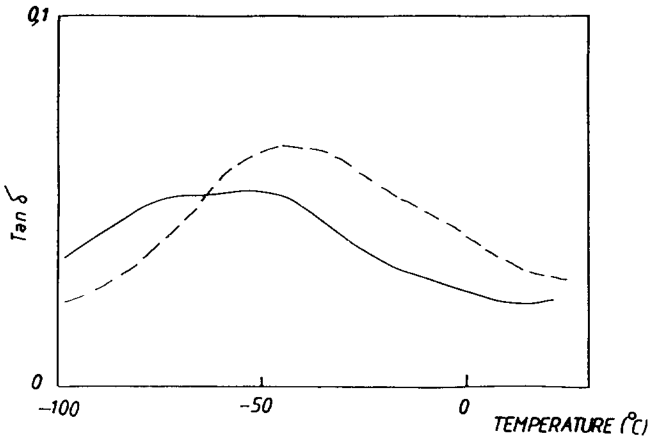


Figure 5 β Relaxation for the DGEBA/BAPP network: (———) at 0.1 Hz; (– – –) at 10 Hz

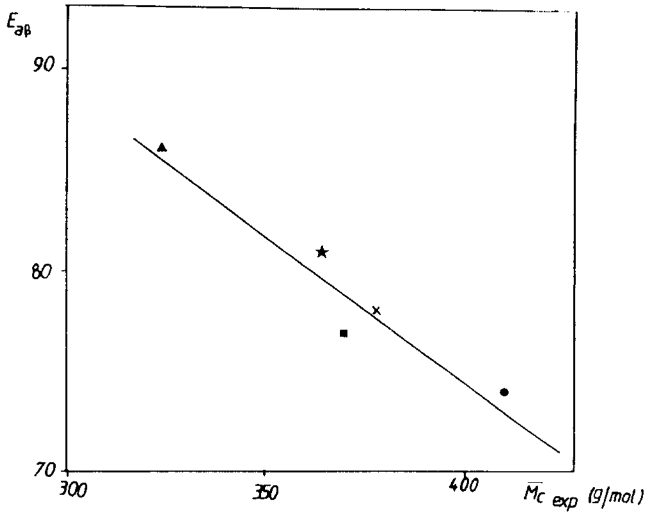


Figure 6 Variation of $E_{a\beta}$ as a function of the experimental molecular weight M_c for: (▲) DGEBA/4,4′-DDS; (●) DGEBA/3,3′-DDS; (×) DGEBA/BAPP; (■) DGEBA/BAPS; (★) DGEBA/DDM

Table 6 Mechanical characterization

Networks	E (10^9 Pa)	σ_r (10^6 Pa)	ε_r	σ_y (10^6 Pa)	ε_y
DGEBA/4,4′-DDS	2.79 ± 0.03	61 ± 3	0.034 ± 0.003	141 ± 3	0.14 ± 0.02
DGEBA/3,3′-DDS	3.25 ± 0.05	83 ± 7	0.040 ± 0.008	145.3 ± 0.3	0.103 ± 0.006
DGEBA/BAPP	2.45 ± 0.08	66 ± 1	0.044 ± 0.008	104.1 ± 0.7	0.110 ± 0.006
DGEBA/BAPS	2.45 ± 0.05	23 ± 10	0.010 ± 0.006	110 ± 4	0.091 ± 0.006
DGEBA/DDM	2.13 ± 0.05	54	0.03 ± 0.005	–	–

E = Young's modulus
σ_r, ε_r = stress, strain at break
σ_y, ε_y = stress, strain at the yield point

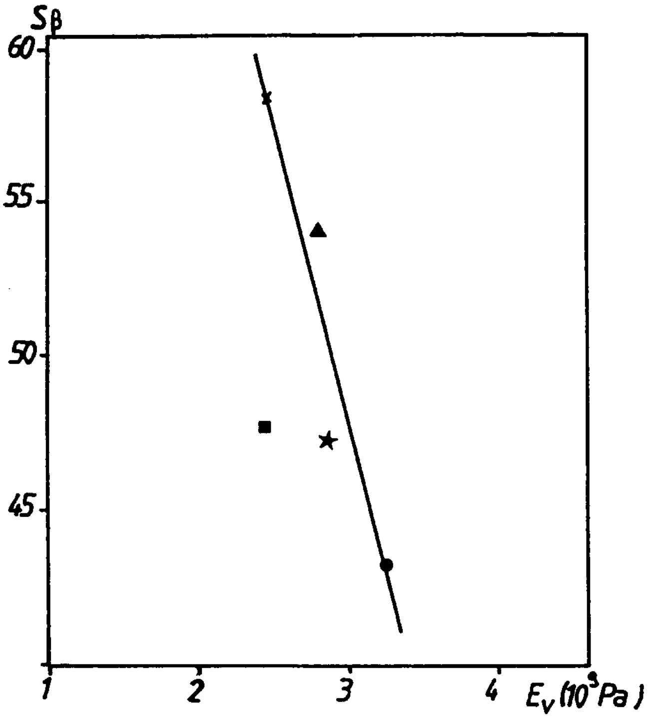


Figure 7 Area of the β relaxation as a function of Young's modulus

decreases. This is a typical case of internal antiplasticization, which is defined by an increase of the Young's modulus, and at the same time a decrease in the glass transition temperature and in the amplitude of the β relaxation.

The network based on 3,3′-DDS shows a similar behaviour.

The characteristics at the yield point (particularly the yield stress) are higher for the networks based on the two DDS systems than those generally found for epoxy–diamine networks[33,34]. The *meta* isomerization of the DDS and the change of the central group (propane or sulphone) do not seem to have an influence on the yield stress.

Kinloch and Williams[34] have defined the value of 100 MPa as a critical value between unstable and stable crack growth. Yield stresses σ_y for the networks based on BAPP and BAPS are near this value.

The results concerning the fracture toughness are reported in *Table 7*.The values obtained for the networks cured with 3,3′-DDS or 4,4′-DDS are close to the values generally observed for high-T_g epoxy–amine networks. The network based on the flexibilized diamine BAPP exhibits very high values of R_s (surface resilience) and of K_{Ic}. The sample based on DDM has a very similar behaviour to the Charpy impact test (high value of R_s) but the value of K_{Ic} is lower.

Table 7 Toughness properties

Networks	R_s (kJ m^{-2})	K_{Ic} (MPa m)	G_{Ic} (kJ m^{-2})
DGEBA/4,4′-DDS	13 ± 2	0.62	0.14
DGEBA/3,3′-DDS	16 ± 4	0.67	0.12
DGEBA/BAPP	20 ± 5	1.73	1.09
DGEBA/BAPS	12 ± 8	–	–
DGEBA/DDM	22 ± 8	1.16	0.56

R_s = surface resilience

The fracture toughness of a material depends on its ability to absorb or dissipate energy, which requires chain mobility. Therefore, the impact resistance seems to increase when the flexibility is increased. BAPS is more flexible than 4,4′-DDS due to the ether bridge, but it shows a poor impact behaviour. This is related to processing difficulties, which produce defects.

It has been observed experimentally that high impact resistance at room temperature can be correlated with secondary transitions in glassy polymers[35–38]. An impact stress pulse corresponds to a high-frequency measurement (in our case, Charpy impact tester, $v \approx 1$ kHz), which has the effect of raising the secondary relaxation to a higher temperature.

Using the Arrhenius expression, the maximum temperatures of the β relaxation peaks at the impact frequency were calculated to be −8°C, −14°C, −13°C, −10°C and −23°C for the networks cured with 4,4′-DDS, 3,3′-DDS, BAPP, BAPS and DDM respectively.

In each case, the networks were studied above the temperature of the β relaxation during the impact test at room temperature.

CONCLUSIONS

We have studied various epoxy–amine networks cured with aromatic hardeners differing by their chemical structure and flexibility.

The glass transition temperature is directly related to the structure of the diamine: isomerization in the *meta* position, replacement of the central sulphone group by $-CH_2-$ or propane group, and adjunction of an ether linkage between aromatic groups lead to a lower T_g.

The molecular weights between crosslinks calculated using the rubber modulus were close to the theoretical value. The apparent activation energy of the β relaxation and the area of the loss peak decrease when M_c increases.

The Young's modulus E is also linked to the amplitude of the β relaxation: a high value of E is associated with a low amplitude of the β peak.

The networks based on BAPP and DDM exhibit excellent fracture toughness properties as compared to classical epoxy–amine networks.

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