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Structure-properties relationships for densely crosslinked epoxide–amine systems based on epoxide or amine mixtures

Part 1 *Glass transition temperature*

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Four series of samples based on epoxide mixtures crosslinked by aromatic diamines or single epoxides crosslinked by amine mixtures were studied by dynamic thermomechanical analysis, differential scanning calorimetry and heat deflection temperature measurements. The glass transition temperature (T_g) was found to increase with the crosslink density in each series, but was independent of the cohesive energy or hydrogen bonding densities. A previously established method of T_g prediction was shown to be applicable to these systems. In one series, (diglycidyl ether or bisphenol A/triglycidyl derivative of *p*-amino phenol/diamino diphenyl methane), a phase separation occurred during the sample preparation. The T_g–structure relationships were used to determine the phase composition.

1. Introduction

The structure-properties relationships for epoxide–amine thermosets have been widely studied for obvious reasons linked to their high technological interest in composite and adhesive areas, but also because it is possible in many cases to obtain relatively well-defined structures and networks of regular architecture [1]. It may be observed, however, that the attention of research workers was mainly focused on systems based on diepoxides, essentially of the diglycidyl ether of bisphenol A (DGEBA) type, whose crosslink density never exceeds 2.5 mol kg^{-1} as shown, for instance, by refs [1–5].

It is noticeable that more densely crosslinked systems (typically $n = 5$ to 7 mol kg^{-1}), for instance those based on the tetraglycidyl derivative of methylene dianiline (TGMDA) are nevertheless widely used. Although a relatively large amount of literature exists on these systems, it cannot yet lead to suitable structure-properties relationships, owing to the complexity and variability of starting epoxide composition [6], and the occurrence of many side reactions during crosslinking [7, 8], making the final network structure very difficult to establish accurately. Furthermore, practically no data is available for systems having crosslink densities in the 3 to 6 mol kg^{-1} range.

It seemed interesting to us to investigate this range by using "Copolymers" made of epoxide or amine mixtures. Four sample families will be studied. The first one is based on a mixture of practically pure monomers of diepoxide (DGEBA) and triepoxide (triglycidyl derivative of *p*-amino phenol: TGAP), crosslinked by diamino diphenyl methane (DDM). The second one is similar to the first one, except for the hardener which is a tetraethyl derivative of DDM (DDMe), all the ethyl groups being in ortho position relative to amine groups. In the third and fourth ones, a single epoxide was used (respectively TGAP and DGEBA), but the hardener was a mixture of DDM and aniline, this latter acting as chain extender, due to its difunctional character [9].

In all cases, epoxides and amines were in stoichiometric ratio. This first part is devoted to the study of the glass transition temperature T. A previously proposed approach [10], mainly based on the configurational entropy theory of di Marzio [11], will be used to predict T_g from the network structure.

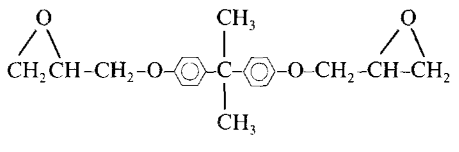
2. Experimental procedure

2.1. Materials

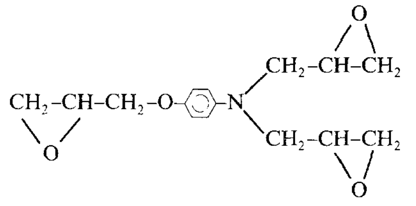
The epoxides and amines under study and their designating code are given in Table I. The epoxides DGEBA and TGAP are practically pure monomers as established by epoxide titration using a standard method (AFNOR T 51-522 French Standard). The amines displayed a single peak in gel permeation chromatography runs (microstyragel 1×50 nm, 2×10 nm columns, refractometric detection).

Four sample series were studied: A 0, A 25, A 50, A 80 and A 100: mixtures DGEBA/TGAP/DDM where the code indicates the weight percent of TGAP in the epoxide mixture. B 0, B 25, B 50, B 75 and B 100: mixtures of DGEBA/TGAP/DDMe with the same numerical code as in series A.C0, C 25, C 50, C 75: mixtures TGAP/DDM/aniline where the code indicates the weight percent of aniline in the epoxide mixture, (note that C0 = A 100). D 33, D 50 and D 67: mixtures DGEBA/DDM/aniline where the

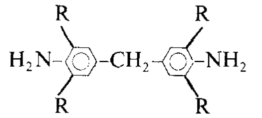
TABLE I Epoxides and amines under study



DGEBA

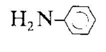


TGAP



R = H → DDM

R = -CH$_2$-CH$_3$ → DDMe



Aniline

numerical code indicates the molar fraction of aniline in the amine mixture.

In all cases, epoxides and amines were in stoichiometric ratio and the mixing and cure conditions were optimized in order to complete the crosslinking reaction. No residual cure exotherm was found in DSC scans. Some details on the cure thermal treatments are given in Table II.

2.2. Characterization

DSC measurements were made with a DUPONT 910 apparatus at 10 K min^{-1} for series A, B and C and with a PERKIN ELMER DSC 2 apparatus at 20 K min^{-1} for series D. T_g was taken at the inflection point of the thermogram.

HDT measurements were made according to ASTM D 648. The applied stress was 0.18 MPa. Dynamic mechanical thermal analysis was made with the DMTA apparatus of Polymer Laboratories at 0.33 Hz, the scanning rate being 3 K min^{-1}. The samples were tested in a flexural mode, on bars of 30 mm length and 3 mm thickness. The storage modulus and tan δ were simultaneously recorded, T_g (DMTA) was arbitrarily assimilated to the tan δ peak temperature.

2.3. Principles of T_g Calculation

The principles of T_g calculation were previously published [10] and will be only briefly recalled. We shall use the di Marzio equation [11]

$$T_g = \frac{T_{gl}}{1 - KFn} \qquad (1)$$

where K is a universal constant and n the crosslink density. T_{gl} is the glass transition temperature of a hypothetical linear copolymer containing all the difunctional units of the network. T_{gl} can be calculated using the following relation

$$\frac{M_l}{T_{gl}} = \Sigma \frac{M_i}{T_{gi}} \qquad (2)$$

Where $M_l = \Sigma M_i$, M_i and T_{gi} are respectively the molar mass and the "component value" of the difunctional group. The T_{gi} values for the groups under study are listed in Table III. They are valid for prediction of DSC data.

For a given crosslink mer linked to three linear segments A, B and C, F is given by:

$$F = \frac{1}{3}\left(\frac{m_A}{\gamma_A} + \frac{m_B}{\gamma_B} + \frac{m_C}{\gamma_C}\right) \qquad (3)$$

Where m is the molar mass of the segment which contains γ rotatable bonds in its skeleton.

When many types of crosslink mers coexist, it can be written

$$F = \frac{1}{\Sigma N_j} \Sigma N_j F_j \qquad (4)$$

Where N_j is the number of crosslink mers of type j in the "monomer unit".

3. Results

The results of the three methods of measurement will be reported below. They are generally in good agreement. As expected, T_g(DMTA) $\geqslant T_g$ (DSC) $\geqslant T_g$ (HDT), which results from the well-known influence of the time scale of experiment on T_g. The majority of the samples exhibit a single, relatively sharp and almost symmetric damping α peak in DMTA spectra. This indicates in principle that these systems are nearly homogeneous at the supermolecular level. In contrast, for all the samples based on DGEBA/TGAP/DDM mixtures, a splitting of the α peak, indicating a diphasic structure, can be observed.

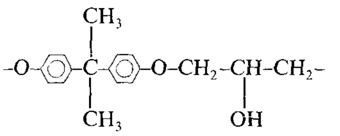
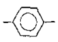
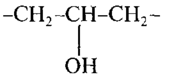
3.1. DGEBA/TGAP/DDMe systems

The DMTA traces of the samples B are presented in Fig. 1. As expected, the glass transition temperature increases with the TGAP concentration, e.g. with the crosslink density. In this case, the component value

TABLE II Processing conditions

Samples			Blending temperature of amine and epoxide	curing
DGEBA	TGAP	DDMe	120° C	3 hours at 180° C
TGAP	DDM	aniline	80° C	3 hours at 180° C
DGEBA	TGAP	DDM	70° C	3 hours at 180° C
DGEBA	DDM	aniline	80° C	1 hour at 80° C + 1 hour at 170° C + 3 hours at 190° C

TABLE III Component values used for T_{gl} calculations

Unit	MT_g^{-1} (g mol^{-1} K^{-1})	T_g (K)
	0.78000	364
$-O-$	0.06306	254
$-CH_2-$	0.06000	233
$-C(CH_3)_2-$	0.07586	554
	0.1677	453
 $-CH_2-CH(OH)-CH_2-$	0.24262	239

of the DDMe unit (ethyl substituted phenylenes) is not known, however, it can be determined using our method of T_g prediction. Indeed, the validity of this method could be questioned if the calculated "component value" would vary from one system to another.

The calculation can be made as follows. Let us consider a network structure unit, representative of the whole sample composition, containing the following groups

x can be determined from the weight fraction, t, of TGAP in the epoxide mixture

$$x = \frac{2040t}{27700 + 233t} \tag{5}$$

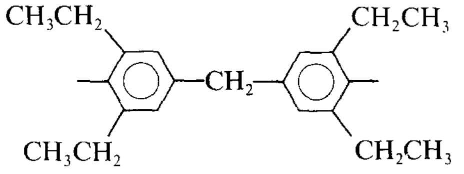
The "copolymer effect" of difunctional units can be written using Equation 2.

$$\frac{M_l}{T_{gl}} = \frac{3M_{A'}}{T_{gA'}} + \frac{12M_G}{T_{gG}} + \frac{6M_D}{T_{gD}} + x\left(\frac{M_T}{T_{gT}} - \frac{3}{2}\frac{M_D}{T_{gD}}\right) \tag{6}$$

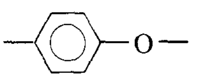
Where

$$\begin{aligned} M_l &= 3M_{A'} + 12M_G + 6M_D + x\left(M_T - \tfrac{3}{2}M_D\right) \\ &= 2886 - 247x \end{aligned} \tag{7}$$

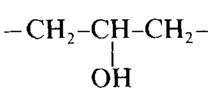
The only unknown quantities in Equation 2 are T_{gl} and $T_{gA'}$. T_{gl} can be determined using Equation 1 if F is known. To determine F, we must first determine the number of each type of crosslink polymer in the structural unit under study. This can be made as follows. Only four types of segments are to be taken into consideration in such networks: their designating code, structure and characteristics are given in Table IV.



A′, 3 moles

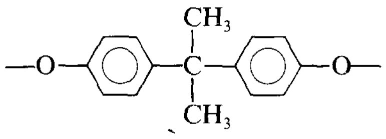


T, x moles

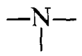


$-CH_2-CH(OH)-CH_2-$

G, 12 moles



D, $\frac{1}{2}(12 - 3x)$ moles



crosslinks, $(6 + x)$ moles

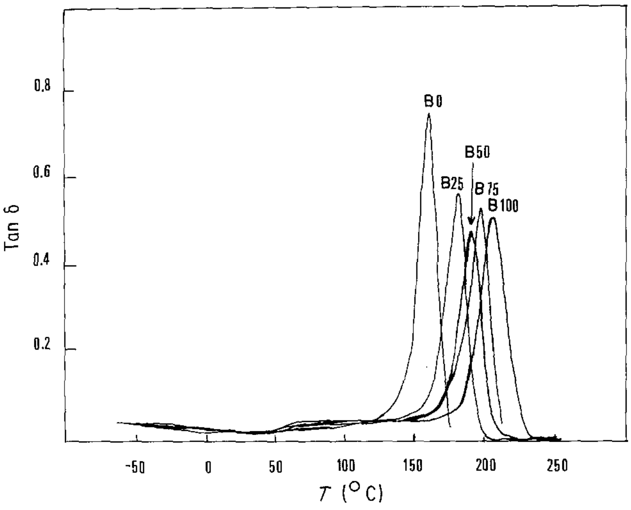


Figure 1 DMTA traces of series B: DGEBA/TGAP/DDMe.

They can be associated in seven types of crosslink mers: GGP, GGA′, GPA′, PPA′, EEA′, EGA′ and EPA′. To determine their number, we shall suppose that all the epoxide groups have an equal probability p to react. It can be thus written

$$p(\text{GGP}) = x \quad \text{(TGAP unit)} \tag{8}$$

$$\begin{aligned} p(\text{GGA}') &= p(\text{GPA}') \\ &\text{or, better, } p(\text{GPA}' + \text{PGA}') \\ &= 2p(\text{PPA}') \end{aligned} \tag{9}$$

$$p(\text{EEA}')/p(\text{EPA}') = (12 - 3x)/x \tag{10}$$

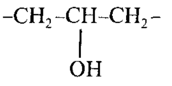
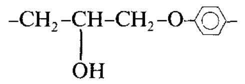
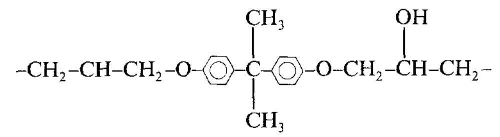
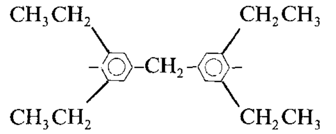
$$p(\text{EGA}') = 2p(\text{EPA}') \tag{11}$$

and

$$\Sigma p(\;) = 6 + x$$

$$\text{(overall number of crosslink polymers)} \tag{12}$$

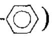
TABLE IV Segments of the networks of type B, molar mass, number of rotatable bonds in the skeleton and "flex parameter"

Code	Segment	m ($\mathrm{g\,mol^{-1}}$)	γ	$F = m/\gamma$ ($\mathrm{g\,mol^{-1}}$)
G	 $-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-$	58	4	14.50
P		150	6	25.00
E		342	12	28.50
A′		278	4	69.50

The resolution of the above system of equations leads to the data of Table V which allow the calculation of F for each system. Then, T_{gl} can be determined by Equation 1 and used for the calculation of $T_{\sigma A'}$ by Equation 6.

All the experimental and calculated data are summarized in Table VI. All the component values $T_{gA'}$ are practically equal. The variations of ±4% around the average value ($T_{gA'} = 300\,\mathrm{K}$), are largely within the experimental scatter and would not have a significant influence on an eventual prediction of T_g.

3.2. TGAP/DDM/aniline systems

The DMTA traces of series C are shown in Fig. 2. Here, also, T_g decreases sharply with the crosslink density. For T_g predictions, we lack, in this case, the component value of the aniline moiety (B = >N-) but, as precedingly, it can be determined using Equation 1. It is interesting to take in consideration, here, the following network structural unit: G (12 moles), T (4 moles), B (x moles), A ($3 - x/2$) moles, $-\underset{|}{N}-$ (only crosslink mers): ($10 - x$) moles. All the groups were previously defined except for (DDM) unit). x is given by the relation

$$x = \frac{594b}{9300 + 6b} \tag{13}$$

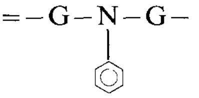
where b is the aniline weight fraction in the amine mixture. The copolymer effect (Equation 2) can be written:

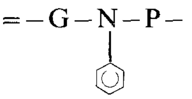
$$\frac{M_l}{T_{gl}} = \frac{4M_T}{T_{gT}} + \frac{12M_G}{T_{gG}} + \frac{3M_A}{T_{gA}} + x\left(\frac{M_B}{T_{gB}} - \frac{1}{2}\frac{M_A}{T_{gA}}\right) \tag{14}$$

where $M_l = 1562 + 8x$ and the unknown quantities are T_{gl} and T_{gB}.

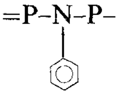
For the crosslinking effect, six different segments are to be considered.

G, P and A, ($F_A = 41.5\,\mathrm{g\,mol^{-1}}$) and

K=  ($F = 25.875\,\mathrm{g\,mol^{-1}}$)

L=  ($F = 29.90\,\mathrm{g\,mol^{-1}}$)

and

M=  ($F = 32.58\,\mathrm{g\,mol^{-1}}$)

In the case of TGAP-DDM (A 100), whose network architecture is in principle the same as for TGAP-

TABLE V Distribution of the various types of crosslink polymers in the series B and resulting F value

	B O	B 25	B 50	B 75	B 100
GGP	0	1.521	2.592	3.387	4.000
GGA′	0	0.2753	0.9566	1.7322	2.4000
GPA′	0	0.2753	0.9566	1.7322	2.4000
PPA′	0	0.1377	0.4783	0.8661	1.2000
EEA′	6	3.2919	1.2702	0.2585	0
EGA′	0	1.3465	1.5589	0.94056	0
EPA′	0	0.6732	0.7794	0.47028	0
F	42.17	35.74	32.105	29.905	28.578

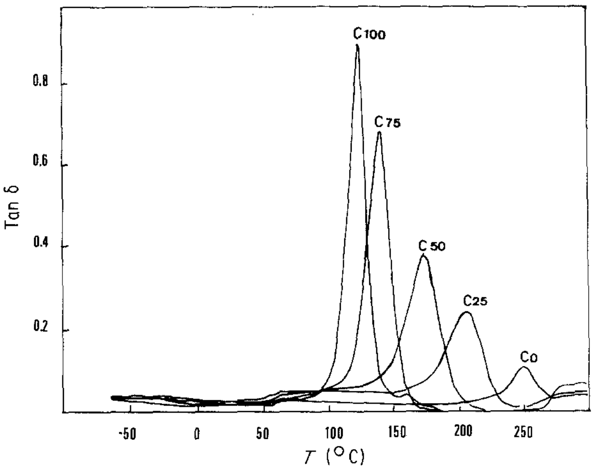


Figure 2 DMTA traces of series C: TGAP/DDM/aniline.

TABLE VI Characteristics of the samples of the series B based on DDMe (series B)

Sample	n (mol kg^{-1})	F (g mol^{-1})	T_g (DSC) (K)	T_g (DMTA) (K)	T_g (HDT) (K)	T_{gl} (calc) (K)	T_{gA} (calc) (K)
B 0	2.02	42.17	426	435	417	320	290
B 25	2.86	35.74	451	454	439	317	313
B 50	3.63	32.105	459	464	456	303	302
B 75	4.30	29.905	473	470	464	296	305
B 100	4.91	28.58	479	480	471	283	291

DDMe (B 100), F can be determined as previously shown, which leads to $F = 22.98\,\mathrm{g\,mol^{-1}}$.

In the case of TGAP-aniline (C 100), only six types of crosslink mers exist: KKL, KKM, KLL, KLM, LLL, and LLM. The same approach as in the preceding section leads to $F = 28.59$.

In the case of amine mixtures: C 25, C 50 and C 75, the situation is considerably more complicated because 21 types of crosslink polymers coexist. To simplify, we shall hypothesize that F is a linear function of the molar fraction of aniline containing segments f_b:

$$f_b = \frac{x}{15 - \frac{3x}{2}} \tag{15}$$

Thus

$$F = 22.98 + f(28.59 - 22.98) \tag{16}$$

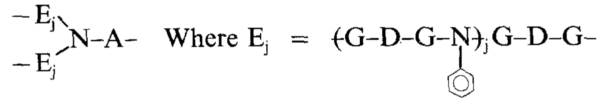
Then, we are able to determine T_{gl} using Equation 1 and T_{gB} using Equation 14. The results are summarized in Table VII, they will be commented upon in the following section and in the discussion part.

3.3. DGEBA/DDM/aniline system

For this series, only DSC measurements were made. We shall use the same approach as precedingly, the chosen structural unit containing in this case: 4 moles of G, 2 moles of D, x moles of B, $(1 - x/2)$ moles of A and $(2 - x)$ moles of crosslink mers. All the group designating codes were previously defined. The copolymer effect can be ascribed

$$\frac{M_l}{T_{gl}} = \frac{4M_G}{T_{gG}} + \frac{2M_D}{T_{gD}} + \frac{M_A}{T_{gA}} + x\left(\frac{M_B}{T_{gB}} - \frac{1}{2}\frac{M_A}{T_{gA}}\right) \tag{17}$$

For the crosslinking effect, it is interesting to write, here, the network structural unit as follows:



$$\begin{matrix}-\mathrm{E_j}\diagdown \\ \mathrm{N{-}A{-}} \\ -\mathrm{E_j}\diagup\end{matrix} \quad \text{Where } \mathrm{E_j} = \mathrm{(G{-}D{-}G{-}\underset{\substack{|\\ \bigcirc}}{N})_j G{-}D{-}G{-}}$$

Thus

$$F(E_j) = \frac{342(j + 1) + 91j}{12(j + 1)} \quad \text{and } j = \frac{x}{2 - x} \tag{18}$$

As in the preceding cases, T_{gl} can be determined by Equation 1 and then T_{gB} can be derived from Equation 17.

The results are given in Table VIII. Taking into account the fact that small errors on T_g have a great repercussion on T_{gB} values, it can be concluded that the results of series C and D are in acceptable agreement and that $M_B/T_{gB} \simeq 0.225$ which leads to $T_{gB} \simeq 400\,\mathrm{K}$.

We attempt a verification assuming that the properties of the >N-⌬ unit are very close to those of the >CH-⌬ one. In the case of polystyrene ($T_g \simeq 370\,\mathrm{K}$), we can write

$$\frac{M(\mathrm{PS})}{T_g(\mathrm{PS})} = \frac{M_{\mathrm{CH_2}}}{T_{g\mathrm{CH_2}}} + \frac{M_B}{T_{gB}} \tag{19}$$

Using the data of Table III ($M_{\mathrm{CH_2}}/T_{g\mathrm{CH_2}} = 0.06$) leads to $M_B/T_{gB} \simeq 0.221$ or $T_{gB} = 412\,\mathrm{K}$; e.g. practically the same value as precedingly determined.

Finally, the glass transition temperatures of the networks of series C and D were calculated using this latter value of T_{gB}. The results are given in Tables VII and VIII. They are in excellent agreement with experimental values since the error never exceeds 3.2% for all the aniline containing systems.

3.4. DGEBA/TGAP/DDM systems

The DMTA traces are presented in Fig. 3 for the materials of the series A. As previously quoted, a phase separation is clearly attested by the splitting of the α peak into two components in "copolymers" A25, A50 and A80. The corresponding glass transition temperatures T_{g1} and T_{g2}, ($T_{g1} < T_{g2}$) were estimated by a simple graphical deconvolution. It is noteworthy that, in all cases, T_{g1} and T_{g2} are higher than the glass transition temperature of the DGEBA–DDM homopolymer (AO) which indicates that both phases are densely crosslinked. This observation led us to calculate the glass transition temperature of the corresponding hypothetical homogeneous networks. The

TABLE VII Characteristics of the systems TGAP/DDM/aniline, (series C)

Sample	x	n (mol kg^{-1})	F (g mol^{-1})	T_g (DSC) (K)	T_g (DMTA) (K)	T_g (HDT) (K)	$M_B T_{gB}^{-1}$ (g mol^{-1} K^{-1})	T_g (calc) (K)
C 0	0	5.88	22.98	493	521	499	–	513
C 25	1.54	4.98	23.68	485	481	470	0.1482	473
C 50	3.094	4.10	24.26	440	449	440	0.2264	441
C 75	4.569	3.24	26.13	412	417	408	0.2257	414
C 100	6	2.40	28.59	378	396	391	0.2479	390

TABLE VIII Characteristics of the DGEBA/DDM/aniline systems, (series D)

Sample	x	n (mol kg^{-1})	F (g mol^{-1})	T_g (DSC) (K)	$M_B T_{gB}^{-1}$ ($\text{g mol}^{-1}\,\text{K}^{-1}$)	T_g (calc) (K)
D 0	0	2.28	32.83	441	–	445
D 33	0.66	1.53	34.50	401	0.3179	411
D 50	1.00	1.046	35.36	393	0.2036	390
D 67	1.34	0.762	36.22	382	0.2048	379

TABLE IX Calculated data for hypothetical DGEBA/TGAP/DDM homogeneous systems. Experimental value from DSC and HDT measurements. In the case of samples A25, A50 and A80 it was difficult to determine precisely T_g by DSC

Sample	x	n (mol kg^{-1})	F (g mol^{-1})	T_g (calc) (DSC) (K)	T_g (DSC)	T_g (exp) (HDT) (K)
A 0	0	2.28	32.83	445	441	443
A 25	1.521	3.30	28.30	463	–	466
A 50	2.592	4.23	25.59	478	–	472
A 80	3.522	5.25	23.70	497	–	486
A 100	4.000	5.88	22.98	513	493	499

TABLE X Experimental and calculated values of T_g (DMTA), weight fraction of TGAP in the epoxide mixture for phases 1 and 2, weight fractions of phases 1 and 2. Note values interpolated using Equation 19

Sample	T_{g1} (DMTA) (K)	T_{g2} (DMTA) (K)	T_g (DMTA) (calc) (K)	t_1 (%)	t_2 (%)	f_1 (%)	f_2 (%)
A 0	458	–	458	100	0	100	0
A 25	463	477	475^a	8	30	22	78
A 50	475	504	489^a	27	73	48	52
A 80	488	518	508^a	48	95	30	70
A 100	–	521	521	0	100	0	100

method is the same as for the series A, the only difference being in the replacement of the DDMe unit by the DDM one.

The results, expressed in terms of DSC data, are given in Table IX. It can be shown that T_g varies almost linearly with the TGAP weight fraction t. Indeed, DMTA data must display the same trends so that

$$T_g(\text{DMTA}) = 458 + 0.63t \qquad (20)$$

The experimental DMTA data, and the calculated values of T_g by Equation 20 are given in Table X. It can be observed that the glass transition temperature of the (hypothetical) homogeneous system is always intermediary between T_{g1} and T_{g2}. In such systems, where secondary crosslinking processes are negligible, T_g is maximum when amines and epoxides are in stoichiometric ratio and completely reacted. It is easy to demonstrate that if $T_{g2} > T_g$ (homogeneous), the phase 2 and, consequently the phase 1 are networks in which epoxides and amines are very close to the stoichiometric ratio and completely reacted. Any other combination would lead to $T_{g2} < T_g$ (homogeneous) and, in the great majority of the cases, to $T_{g1} < T_g$ (DGEBA-DDM), which was never observed.

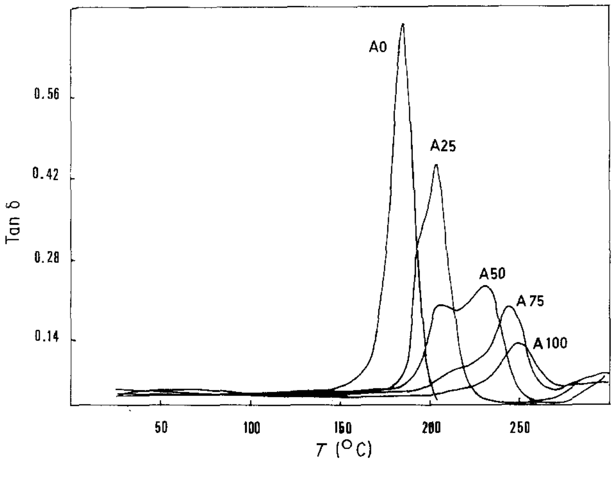


Figure 3 DMTA traces of series A: DGEBA/TGAP/DDM.

In these conditions, Equation 20 can be used to determine the weight fractions of TGAP t_1 and t_2 in both phases, and the phase weight fractions f_1 and f_2 can be calculated from t_1 and t_2. All the data relative to the diphasic character of the series A are given in Table X. It can be observed that, in all cases, $f_1 < f_2$, and that the phase separation is more equilibrated in the sample A 50 than in samples A 25 or A 80, which is clearly corroborated by an examination of peak amplitudes in Fig. 3.

4. Discussion

The above results call for the following comments.

(1) With systems B, C and D, it is confirmed that the glass transition temperature of epoxide-amine networks can be reasonably predicted with the proposed approach which gave already good results for about 40 "homopolymer" systems [10].

(2) In series C and D, where aniline replaces partially or totally DDM, acting as chain extender, the overall content in hydrogen bonding groups or, more generally in polar structures, remains almost constant or rather, increases slightly with the aniline concentration. Yet, T_g decreases considerably when the DDM concentration (e.g. the crosslink density)

decreases. This result indicates clearly that the cohesive energy plays, in these systems, an insignificant role compared to the crosslink density and the segment stiffness. This result invalidates, at least for epoxide–amine networks, the glass transition theories based on the cohesive energy concept [12, 13].

(3) For homologue systems, T_g(DDM) > T_g(DDMe), cannot be attributed to the difference in concentration of polar structures existing between these systems. Furthermore, the number of skeleton bonds between crosslinks are the same for both types of network, which invalidates the T_g – structure relationships based on this characteristic [14].

It seems more reasonable to suppose that the "copolymer effect" results from the additivity of free volume or entropy contributions of difunctional groups. As a matter of fact, Equation 2 is often considered as deriving more or less empirically from the free volume theory [15], and, in certain conditions, free volume (reciprocal) and entropy (logarithmic [16]) relations are mathematically equivalent [5]. The effect of crosslinking, in contrast, seems to derive exclusively from the entropy theory [11].

(4) With the copolymers of the series A, we dispose of interesting diphasic systems, whose structure and composition can be reasonably estimated, and which could be used as model systems in an eventual further study of the influence of morphology on the physical properties.

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