

# Glass transition temperature predictions for non-stoichiometric epoxide-amine networks

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The glass transition temperature of various diepoxide-diamine binary or diepoxide/diamine/monoamine ternary systems containing an amine or an epoxide excess, was determined by d.s.c. after complete cure. The copolymer effect of various species such as secondary amines and chain ends, was deduced from Di Marzio's approach<sup>7</sup> to the crosslinking effect on  $T_g$  and the hypothesis of additivity of the group molar contributions  $M_i T_{gi}^{-1}$  of the difunctional groups. The results suggest that all tertiary nitrogens, even branching point ones, act as crosslink points. The chain end contribution depends on their structure but can be considered as constant in a given structural series, thus allowing good  $T_g$  predictions with only one adjustable parameter.

(Keywords: glass transition temperature; epoxide; amine)

## INTRODUCTION

There is a noticeable scientific and technological interest for the glass transition temperature ( $T_g$ ) prediction in the field of crosslinked epoxies<sup>1-5</sup>. The methods of prediction can be purely empirical or derived from various theoretical approaches<sup>6-10</sup>. The corresponding equations contain parameters which are generally difficult to determine with precision, for instance, the crosslink density, or which are poorly defined, for example the glass transition temperature  $T_{gL}$  of the 'equivalent linear polymer' containing all the difunctional units of the network<sup>6,7</sup>.

It was recently shown<sup>5</sup> that, at least for the aromatic backbone polymers and homologue series of epoxide/amine networks,  $T_{gL}$  values of reasonable physical validity can be determined from:

$$M_L T_{gL}^{-1} = \sum M_i T_{gi}^{-1}$$

where  $M_i$  and  $T_{gi}$  are the molar mass and the component value of the difunctional group  $i$ , respectively, and  $M_L = \sum M_i$  corresponds to the structural unit, representative of the network composition, chosen for the calculation. The crosslinking effect can be represented by the Di Marzio's equation<sup>7</sup>:

$$T_g = T_{gL} / (1 - KFn)$$

where  $K$  is a universal constant ( $K=2.91$  for trifunctional crosslinks),  $F$  is a flex parameter expressed in weight unit per mole of flexible bond, and  $n$  is the crosslink density expressed in moles per weight unit. This method gave good predictions for about 60 epoxide-amine networks, including ternary systems, of  $T_g$  ranging from 0 to 250°C<sup>5,11,12</sup> but was limited to stoichiometric completely cured systems.

The aim of the present paper is to try to apply this method to various non-stoichiometric systems whether or not they contain free chain ends.

## EXPERIMENTAL

### Materials

The designating code and structure of the diepoxides and amines under study are presented in Table 1. In the case of the diepoxides, the degree of polymerization was deduced from epoxide titrations according to the French standard AFNOR NFT 51522 (AFNOR, Tour Europe Cedex 7, 92080 Paris la Défense). The binary DGEBA-DDM and DGEBA-DDM systems were cured in the conditions summarized in Table 2. The ternary DGEBA/IPD/TMCA systems were cured in the d.s.c. cell. The reaction exotherm was recorded during the first run and  $T_g$  was measured during the second run in which no exotherm was observed.

### D.s.c. measurements

For DGEBA<sub>1</sub>-DDM and DGEBA-DDM systems, a Perkin-Elmer DSC 2 apparatus was used at a 20 K min<sup>-1</sup> scanning rate, on 5 mg samples. For DGEBA<sub>0</sub>/IPD/TMCA systems, a Mettler TA 3000 apparatus was used at a 10 K min<sup>-1</sup> scanning rate. In both cases  $T_g$  was taken at the inflexion point of the thermogram. In these conditions, no significant difference was found between the two experimental methods.

## RESULTS

The glass transition temperatures are reported in Tables 3-6. In all the cases under study, they vary with the amine/epoxide molar ratio ( $r$ ) and are maximum for the

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Table 1 Structure and designating code of the epoxides and amines under study

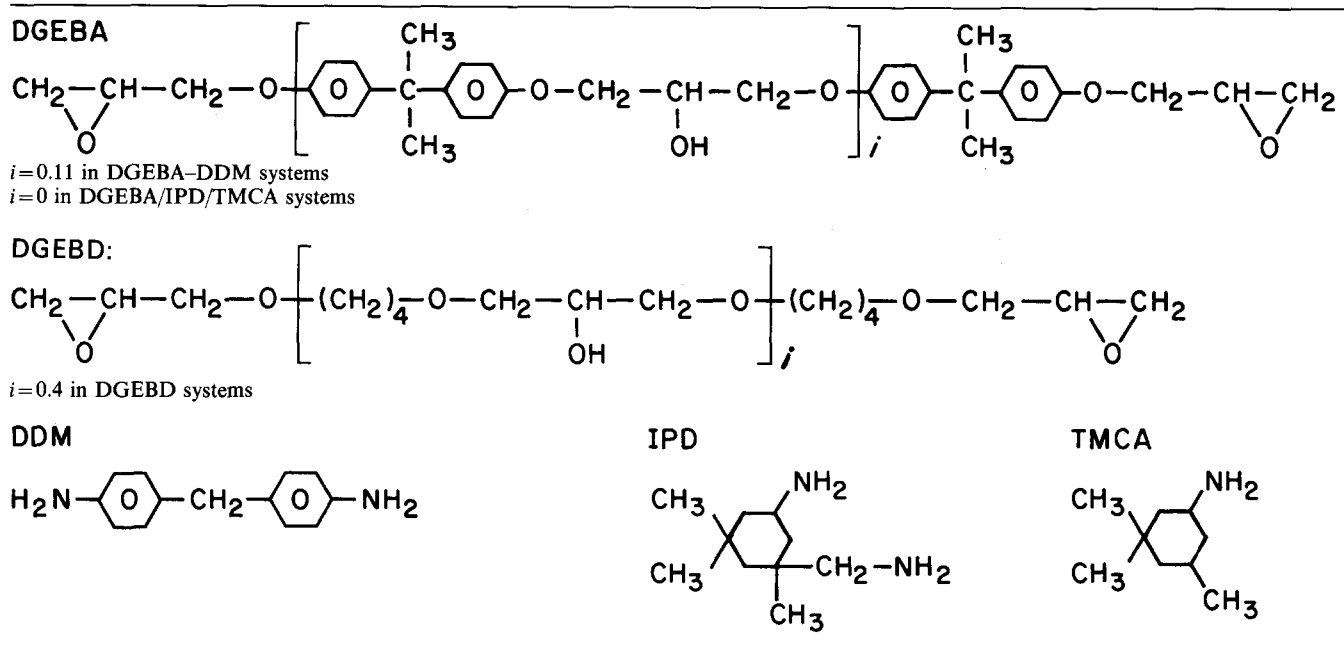


Table 2 Cure conditions of the systems under study

System	105°C	150°C under vacuum	180°C under vacuum
DGEBA-DDM	1 h	-	1.25 h
DGEBD-DDM	2.5 h	1 h	-

Table 3 Characteristics of the binary systems having an amine excess

System	$r$	$M$ (g M <sup>-1</sup> )	$F$ (g M <sup>-1</sup> )	$M_{NH}/T_{gNH}$ (g M <sup>-1</sup> )(K <sup>-1</sup> )	$T_{gL}$ (K)	$T_{gexp}$ (K)	$T_{gcalc}^a$ (K)
DGEBA-DDM	1.0	941	33.15	-	350	449	440
	1.2	1225	33.93	-0.143	354	443	422
	1.4	1700	34.63	≈ 0	358	411	406
	1.6	2648	35.25	≈ 0	362	399	392
	1.8	5494	35.81	0.002	365	387	378
DGEBD-DDM	1.0	719	24.37	-	267	334	333
	1.2	948	25.39	0.003	275	327	325
	1.4	1330	26.32	0.032	281	316	318
	1.6	2094	27.17	0.018	288	312	311
	1.8	4188	27.17	0.018	288	312	311
DGEBA-IPD	1.0	850	30.50	-	346	438	437
	1.2	1104	31.06	0.087	350	410	419
	1.4	1527	31.56	0.039	354	398	403

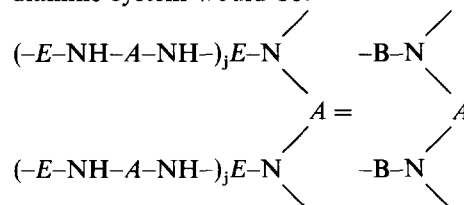
<sup>a</sup> Calculated using  $M_{NH}/T_{gNH}=0.02 \text{ g M}^{-1} \text{ K}^{-1}$

value  $r = 1$ . In the case of the ternary systems DGEBA/IPD/TMCA,  $T_g$  is an increasing function of the IPD molar fraction, e.g. of the crosslink density.

*Amine excess in binary systems*

It is well known that primary amines are more reactive than secondary ones. In this case, 'closed cell' networks (e.g. without free chain ends) would be created. Their average constitutional repeat unit (CRU) for a diepoxide-

diamine system would be:



where  $-E-$  is the reacted diepoxide structural unit and

**Table 4** Characteristics of the binary systems having an epoxide excess

System	$r$	$M$ (g M <sup>-1</sup> )	$n$ (M kg <sup>-1</sup> )	$F$ (g M <sup>-1</sup> )	$b$ (g M <sup>-1</sup> K <sup>-1</sup> )	$F$ (g M <sup>-1</sup> )	$b$ (g M <sup>-1</sup> K <sup>-1</sup> )	$n$ (M kg <sup>-1</sup> )	$F$ (g M <sup>-1</sup> )	$b$ (g <sup>3</sup> M <sup>-1</sup> K <sup>-1</sup> )	$T_{g,exp}$ (K)	$T_{g,calc}^a$ (K)
DGEBA-DDM	0.7	881	0.227	43.39	-0.085	33.15	-0.098	1.59	33.15	0.165	378	377
	0.8	901	0.888	37.70	-0.063	33.15	-0.103	1.78	33.15	0.171	397	397
	0.9	921	1.520	34.86	-0.120	33.15	-0.175	0.96	33.15	0.108	422	418
DGEBD-DDM	0.7	659	0.303	27.49	-0.300	24.37	-0.310	2.12	24.37	-0.097	321	320
	0.8	679	1.178	25.76	-0.300	24.37	-0.320	2.36	24.37	-0.090	324	324
	0.9	699	2.003	24.89	-0.320	24.37	-0.346	2.58	24.37	-0.100	329	328
Mode of calculation:		Method (a), equation (22)			Method (a), equation (21)			Method (b), equation (21)				

<sup>a</sup> Calculated using  $b=0.17$  g M<sup>-1</sup> K<sup>-1</sup> for DGEBA-DDM and  $-0.09$  g M<sup>-1</sup> K<sup>-1</sup> for DGEBD-DDM and method (b) equation (21)

**Table 5** Characteristics of the ternary systems IPD/TMCA/DGEBA which have an amine excess ( $r=1.2$ )

$f$	$x$	$y$	$M$ (g M <sup>-1</sup> )	$N$ (M kg <sup>-1</sup> )	$F$ (g M <sup>-1</sup> )	$T_{gl}$ (K)	$d$ (g M <sup>-1</sup> K <sup>-1</sup> )	$n$ (M kg <sup>-1</sup> )	$T_{gl}$ (K)	$d$ (g M <sup>-1</sup> K <sup>-1</sup> )	$T_{gl,calc}^a$ (K)	$T_{g,calc}^a$ (K)	$T_{g,exp}$ (K)
1.0	1.2	0	884	1.81	31.06	343	-	1.810	343	-	350	419	410
0.9	1.08	0.24	897	1.52	31.83	348	0.315	1.605	345	0.380	350	411	405
0.7	0.84	0.72	924	0.95	33.38	351	0.083	1.212	341	0.351	348	394	387
0.5	0.69	1.20	951	0.92	34.92	358	-0.036	0.841	342	0.231	346	378	374
0.3	0.36	1.68	978	0	-	370	-0.163	0.491	351	0.062	345	364	370
0.17	0.204	1.992	997	0	-	359	-0.013	0.273	348	0.099	344	355	359
Hypothesis (b) <sup>b</sup>			Hypothesis (a) <sup>b</sup>				Hypothesis (b) <sup>b</sup>						

<sup>a</sup> Calculated using hypothesis (b) and  $d=0.15$  g M<sup>-1</sup> K<sup>-1</sup>

<sup>b</sup> See text

**Table 6** Characteristics of the ternary systems IPD/TMCA/DGEBA having an epoxide excess ( $r=0.8$ )

$f$	$x$	$y$	$M$ (g M <sup>-1</sup> )	$n$ (M kg <sup>-1</sup> )	$F$ (g M <sup>-1</sup> )	$T_{gl}$ (K)	$b$ (g M <sup>-1</sup> K <sup>-1</sup> )	$n$ (M kg <sup>-1</sup> )	$F$ (g M <sup>-1</sup> )	$T_{gl}$ (K)	$b$ (g M <sup>-1</sup> K <sup>-1</sup> )	$T_{gl,calc}^a$ (K)	$T_{g,calc}^a$ (K)	$T_{g,exp}$ (K)
1.0	0.80	0.00	816	0.980	35.30	339	0.080	1.96	30.50	311	0.299	314	380	377
0.9	0.72	0.16	825	0.776	36.07	343	0.065	1.75	31.27	313	0.295	315	375	372
0.7	0.56	0.48	843	0.380	37.62	349	0.018	1.33	32.82	318	0.268	318	364	364
0.5	0.40	0.80	861	0.000	39.17	348	0.041	0.93	34.37	316	0.313	320	352	348
0.3	0.24	1.12	879	0.000	40.71	346	0.058	0.55	35.91	326	0.223	322	341	346
0.1	0.08	1.44	897	0.000	42.26	331	0.203	0.18	37.46	325	0.261	324	331	331
0.0	0.00	1.60	906	0.000	43.03	330	0.214	0.00	38.23	330	0.214	325	325	330
Hypothesis (b) <sup>b</sup>			(a) <sup>b</sup>				(b) <sup>b</sup>							

<sup>a</sup> Calculated using hypothesis (b) and  $b=0.27$  g M<sup>-1</sup> K<sup>-1</sup>

<sup>b</sup> See text

$A$  is the amine structural unit. If  $r$  is the amine/epoxide molar ratio, it can be written:

$$j = (r - 1) / (2 - r) \quad (1)$$

the molar weight is:

$$M = 2M_E + M_A + 28 + 2j(M_E + M_A + 2M_{NH}) \quad (2)$$

The CRU molar weight of the corresponding linear copolymer is:

$$M_L = M - 28 \quad (3)$$

The crosslink density is:

$$n = 2/M \quad (4)$$

The copolymer effect of the difunctional groups can be written:

$$M_L/T_{gL} = 2M/T_{gE} + M_A/T_{gA} + 2j(M_E/T_{gE} + M_A/T_{gA} + 2M_{NH}/T_{gNH}) \quad (5)$$

which leads to:

$$M_{NH}/T_{gNH} = 1/4j[M_L/T_{gL} - (2 + 2j)M_E/T_{gE} - (1 + 2j)M_A/T_{gA}] \quad (6)$$

The only unknown quantity, except  $M_{NH}/T_{gNH}$ , is  $T_{gl}$  which can be calculated with the Di Marzio's equation<sup>7</sup>:

$$T_{gl} = T_g(1 - KFn) \quad (7)$$

where  $K = 2.91$ , and

$$F = \frac{1}{3}(F_A + 2F_B) \quad (\text{ref. 5}) \quad (8)$$

where

$$F_A = M_A/\gamma_A \quad (9)$$

$$F_B = M_B/\gamma_B = M_E + j(M_A + M_E + 2M_{NH})/\gamma_E + j(\gamma_E + \gamma_A) \quad (10)$$

where  $\gamma_E$  and  $\gamma_A$  are the number of rotatable bonds in respectively the diepoxide and diamine structural units<sup>5</sup>.  $M_{NH}/T_{gNH}$  was determined in three systems: DGEBA-



can be written:

$$F = \frac{1}{3} \frac{(2F_E + F_C) + (F_E + F_A + F_C) + (2i-1)(2F_E + F_A)}{1 + 2i} \quad (18)$$

which can be rearranged into:

$$F = F_S + \frac{1}{3}(2F_C - F_E - F_A/(1 + 2i)) \quad (19)$$

where  $F_S = \frac{1}{3}(2F_E + F_A)$  corresponds to the stoichiometric system. The methods of determination of  $F_E$  and  $F_A$  have already been reported<sup>5,11,12</sup>. The case of  $F_C$  needs a short discussion:

$$F_C = M_C/\gamma_C \approx M_S/\gamma_C \quad (20)$$

where  $M_S$  is the molar weight of the stoichiometric CRU and  $\gamma_C$  is the number of flexible bonds. In principle, the motions in the branch  $E'$  contribute to entropy changes, thus:

$$\gamma_C = \gamma_A + \gamma_E + \gamma_{E'} \quad (21)$$

In this case, the first term in parenthesis in equation (19) would be practically equal to zero and  $F$  would be practically independent of the amine-epoxide molar ratio and equal to  $F_S$ . However, an earlier work<sup>12</sup>, it was found that good results can be obtained by considering that the rotatable bonds in branches are not to be taken into account. In this case:

$$\gamma_C = \gamma_A + \gamma_E \quad (22)$$

Here,  $2F_C > F_A + F_E$  and  $F$  increases when the amine/epoxide molar ratio decreases. To determine the number of crosslink mers  $N$ , two methods were used:

method (a):

$$N = 2r - 0.8 \quad (23a)$$

method (b):

$$N = 2r \quad (23b)$$

Both methods differ in that in (b) branching points are assimilated to crosslinks but in (a) they are not. All the data relative to the systems DGEBA-DDM and DGEBD-DDM are listed in Table 4.

Three values of  $b$  are given.  $b_1$ : method (a), equation (22);  $b_2$ : method (a), equation (21);  $b_3$ : method (b), equation (21).

It is interesting to note that method (a) leads to systematically negative  $b$  values. Indeed, equation (22), which overestimates the crosslinking effect, leads to slightly lower values of  $T_{gL}$  than equation (21) but the difference never exceeds 5000. Higher values are obtained with the method (b). Values become positive (0.1 to 0.2) for DGEBA-DDM, but they remain negative ( $\approx 0.08-0.09$ ) for DGEBD-DDM.

#### Amine excess in ternary systems

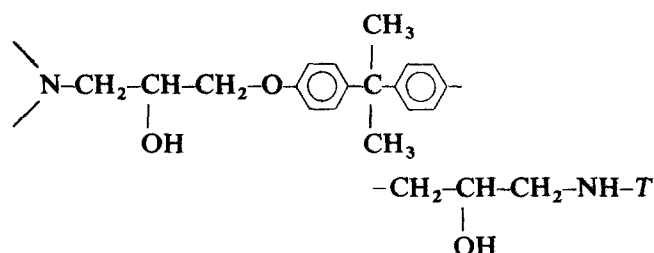
The stoichiometric DGEBA/IPD/TMCA ternary systems were previously studied, and their glass transition temperature accurately predicted by the method under study<sup>12</sup>. Here homologue systems with an amine excess ( $r = 1.2$ ) will be investigated. It is interesting to consider, in this case, the CRU based on two moles of DGEBA,  $x$  moles of IPD and  $y$  moles of TMCA. If  $f$  is the molar

fraction of IPD in the amine mixture, it can be written:

$$y = 1.2(2 - x) \quad (24)$$

$$x = 1.2f \quad (25)$$

The secondary amines are IH (IPD) and TH (TMCA). Indeed, because TMCA is a monoamine, TH is a chain end:



The number of chain ends per monomer unit TH can be estimated, assuming that IPD and TMCA have the same reactivity with DGEBA<sub>0</sub>:

$$\text{IH/TH} = 2x/y \quad (26)$$

Furthermore,

$$\text{IH} + \text{TH} = 0.8 \quad (27)$$

(amine excess for  $r = 1.2$ ).

The copolymer effect can be ascribed:

$$M_L/T_{gL} = 2M_E/T_{gE} + xM_I/T_{gI} + yM_T/T_{gT} + 0.8M_{NH}/T_{gNH} + zd \quad (28)$$

where  $M_E T_{gE}^{-1} = 1.02262$ ;  $M_I T_{gI}^{-1} = 0.33$ ;  $M_T T_{gT}^{-1} = 0.33$ ;  $M_{NH} T_{gNH}^{-1} = 0.02$ .  $z$  is the number of chain ends (TH), and  $d$  their contribution to  $M T_{g}^{-1}$ , including the chain end and branching effect. As before,  $T_{gI}$  can be obtained from  $T_g$  by Di Marzio's equation<sup>7</sup> and  $d$  must be determined by equation (28). The flux parameter can be estimated from the results obtained for the stoichiometric systems<sup>12</sup>:

$$F_{(r=1)} = 38.23 - 7.73f \quad (29)$$

It has been found previously that:

$$F_{(r=1.2)} - F_{(r=1)} = 0.56 \quad (30)$$

We hypothesize that the difference is conserved over the whole range of  $f$  values so finally:

$$F = 38.79 - 7.73f \quad (31)$$

To determine the crosslink density, two methods were used. In method (a) crosslink number = tertiary nitrogen number - chain end number:

$$N = 2x - 0.8 \quad (32)$$

In method (b) crosslink number = tertiary nitrogen number:

$$N = 2x - \text{TH} \quad (33)$$

The results are shown in Table 5. According to method (a) the term  $zd$  would be very low or negative for some systems, whereas it would be positive in all the cases for method (b). Relative uncertainties equal to 100% or higher can be expected if we consider the calculation method. The most accurate value is, in principle, obtained for the highest value of  $z$ , e.g. for the system ( $f = 0.17$ ).  $d = -0.19$  (method a) or  $d = 0.15$  (method b).

## Epoxide excess in ternary systems

Here the system under investigation is DGEBA/IPD/TMCA with  $r=0.8$ . By taking, as before, the CRU containing 2 moles of DGEBA,  $x$  moles of IPD and  $y$  moles of TMCA, it can be written that the number of chain ends (unreacted epoxides)  $z=4(1-r)=0.8$ ; and the copolymer effect:

$$M_L/T_{gL} = 2M_E/T_{gE} + xM_I/T_{gI} + yM_T/T_{gT} + 0.8b \quad (34)$$

the crosslink number:  $N=2x-0.8$  (method a) or  $N=2x$  (method b).

By assuming, as in the preceding part, that  $F$  varies linearly with the composition:

$$F = 43.03 - 7.73f \quad (35)$$

where  $f$  is the IPD/TMCA molar ratio. All these data and the experimental values of  $T_g$  lead to the results of Table 6.

In the case of the method (a),  $b$  varies with  $f$ . It is interesting to note that four samples ( $f=0.5$  to 0) are ungelled systems in which  $b$  is a decreasing function of the branching ratio. In the case of method (b), no clear propensity can be observed in variations of  $b$ . It can be assumed that  $b=0.3 \pm 0.1$ . Whatever the method of determination, the contribution of chain ends appears to be higher for epoxide excess than for amine excess (Table 5).

## DISCUSSION

In the easiest case of diamine excess, it will be possible to predict  $T_g$  accurately from the chemical composition, by considering the network as a 'closed cell' without chain ends. All the needed characteristics can be derived from the data on stoichiometric systems<sup>5,12</sup>, except for the contribution of the secondary amine  $M_{NH}T_{gNH}^{-1} \simeq 0.02$ .

The problem of the systems containing free chain ends is considerably more complicated because three new component values are involved: the own chain end effect, the branching effect, and the copolymer effect of end groups which can be appreciated by the comparison of amine and epoxide chain ends. The following observations can be made.

The most important fact is that generally, method (a) for the determination of the crosslink density leads to negative values of the chain end effect. It is noteworthy that in a reciprocal function such as  $MT_g^{-1}$ , a negative contribution indicates a crosslinking (or similar) effect. Thus, the chain ends would have an opposite effect in linear and tridimensional polymers, which seems difficult to justify. In fact, each chain end is associated with a branch so that at least two opposite effects can be considered:  $T_g$  increases due to the reduction of the number of available configurational states by the presence of a branch; and  $T_g$  decreases due to the free volume excess of the chain ends. The fact that  $d$  or  $b$  are negative, indicates only that the first effect predominates over the second in the cases under study. A simple approach to the first effect consists in considering the branching points as crosslinks (method b). To appreciate its physical validity, it is interesting to consider the data obtained

on linear polymers. For linear polymers:

$$M/T_g = M/T_{g\infty} + 2b \quad (36)$$

( $b$  = chain end contribution)

This gives for high  $M$  values, the Fox and Flory relation<sup>6</sup>:

$$T_g = T_{g\infty} - 2bT_{g\infty}^2/M$$

From the experimental results on DGEBA linear polymers<sup>5</sup>, it can be obtained:  $T_g = 365$  K;  $2bT_{g\infty}^2 = 6.6 \times 10^4$  K Mg<sup>-1</sup> and  $b = 0.25$  g M<sup>-1</sup> K<sup>-1</sup>. This latter value is of the same order as the ones obtained by method (b) in the networks under study ( $b = 0.1$  to  $0.4$  g M<sup>-1</sup> K<sup>-1</sup> for epoxide chain ends). Obviously,  $b$  depends on the nature of the diepoxide:  $b \simeq -0.1$  for DGEBA and  $\simeq 0.03$  for DGEBA, but further investigations would be needed to interpret these differences.

Noticeable differences are also found between amine and epoxide chain ends (see Tables 5 and 6):  $b$  (epoxide)  $>$   $d$  (amine). A possible explanation can be given by equation (18), if:  $M_F T_{gF}^{-1} > M_G T_{gG}^{-1}$ , e.g. if the replacement of an epoxide by an alcohol increases  $T_g$ . This seems to be reasonable considering the small<sup>11</sup> but non-negligible effect of hydrogen bonding by OH groups on  $T_g$ .

From a practical point of view, method (b) for crosslink counting is the most interesting one because it requires only one adjustable parameter ( $b$  or  $d$  stands for the chain end effect). Another advantage of the method is that  $F$  can be considered constant and can be determined in an ordinary case (for instance, the stoichiometric systems).  $T_g$  was calculated for all the systems under study by using:

$$M_{NH}/T_{gNH} = 0.02$$

$$b = -0.09 \text{ (DGEBA-IPD/TMCA)}; 0.17 \text{ (DGEBA-DDM)}; 0.27 \text{ (DGEBA/IPD/TMCA)}$$

$$d = 0.15 \text{ (DGEBA/IPD/TMCA, } r = 1.2).$$

The absolute error of the prediction is less than 10 K in all cases except one (DGEBA-DDM,  $r = 1.2$ ). The systematic underestimation of  $T_g$  in Table 4 could be linked to the uncertainty of the measurement of the polymerization degree of the diepoxide. The average relative error  $\Delta T_g/T_g$  is less than 1.2% for the 28 systems under study, which is largely within the experimental scatter.

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