

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

V. Bellenger, W. Dhaoui and J. Verdu*

ENSAM 151 Bd de l'Hôpital, 75640 Paris, Cedex 13, France

and J. Galy, Y. G. Won and J. P. Pascault

INSA 20 Bd Einstein, 69621 Villeurbanne Cedex France

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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 approach⁷ 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 epoxies¹⁻⁵. The methods of prediction can be purely empirical or derived from various theoretical approaches⁶⁻¹⁰. 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^{6,7}.

It was recently shown⁵ 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 equation⁷:

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

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^{5,11,12} 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 DGEBD-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 DGEBA₁-DDM and DGEBD-DDM systems, a Perkin-Elmer DSC 2 apparatus was used at a 20 K min⁻¹ scanning rate, on 5 mg samples. For DGEBA₀/IPD/TMCA systems, a Mettler TA 3000 apparatus was used at a 10 K min⁻¹ 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

* To whom correspondence should be addressed

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

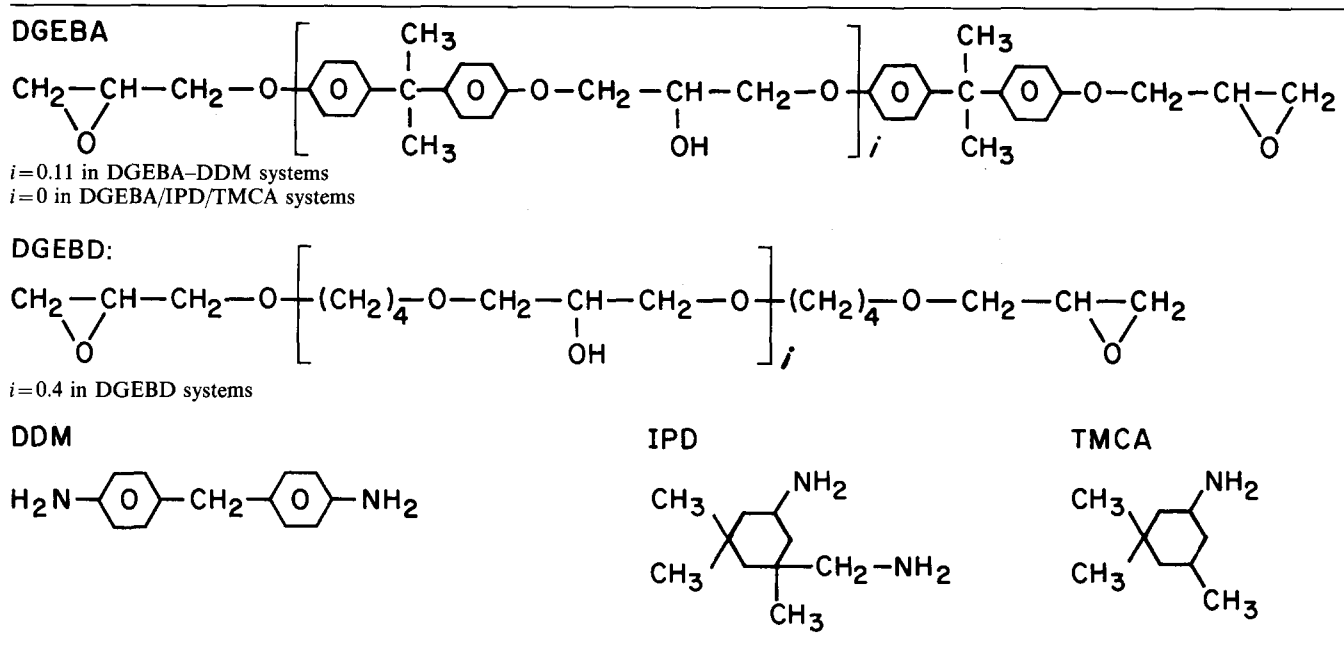


Table 2 Cure conditions of the systems under study

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 ⁻¹)	F (g M ⁻¹)	M_{NH}/T_{gNH} (g M ⁻¹)(K ⁻¹)	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	27.81	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

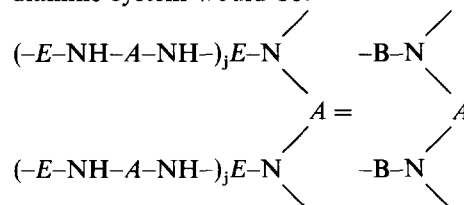
^a Calculated using $M_{NH}/T_{gNH}=0.02 \text{ g M}^{-1} \text{ K}^{-1}$

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

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