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Study of model systems as a powerful tool for producing reliable structure—property relationships in epoxy networks***)

Summary — Series of epoxy-amine networks were designed to separate the effects on the properties of chain rigidity and of architectural characteristics, *i.e.*, cross-link density and extender type. Glass transition temperature (T_g) was shown to increase with the increasing cross-link density and rigidity of the epoxide and amine residues, but these effects were not completely decoupled. In addition, inspection of non-stoichiometric systems revealed the occurrence of peculiar effects in the presence of unreacted epoxide moieties. A general correlation between the values of the rubbery modulus and T_g has been proposed. As regards the sub-T_g β-transition, the onset of the process has been shown to occur at the same temperature irrespective of chain stiffness and cross-link density as a result of short-range cooperativity of the hydroxypropyl ether motions. As a consequence of practical interest, the higher cross-link densities lead to the lower Young moduli at room temperature.

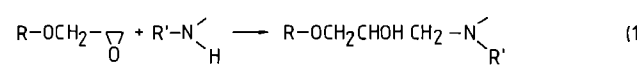
For years epoxy resins have been used in a wide range of industrial applications because of their versatile properties. Therefore, they have been studied extensively and amply reported and reviewed [1]. However, there still remains a need for relationships on the molecular level between their chemical structure and mechanical properties.

The aim of this paper is to report on some recent aspects of a long-term research program on epoxy-amine systems realized in this Laboratory [2]. Rather than with commercial formulations which are quite complex, this program deals with model networks especially designed to separate the influences of cross-link density and chain flexibility on properties.

First, the powerful tool is described, *viz.*, the design of networks exhibiting progressive changes in architecture and chemical structure. Then, emphasis is laid on the viscoelastic properties in the glass transition (T_g) and the rubbery regions and in the secondary relaxation (β-transition) region. The influence of the β-process on the Young modulus at room temperature, a property of practical importance, has also been investigated. Finally, some other studies on the model networks have been reviewed, which are to be reported in separate publications.

THE DESIGN OF MODEL NETWORKS

The chemistry of epoxy-amine resins is based on the well-known simple reaction of epoxide ring opening by the N-H functions of primary or secondary amines:



(1)

Thus, three-dimensional networks can be prepared by the reaction of diepoxides with primary diamines; when the chemicals are used in stoichiometric proportions the resulting networks are densely cross-linked. It is possible to control the network rigidity by choosing monomers with an appropriate molecular structure. Diglycidyl ethers of bisphenol-A (DGEBA), resorcinol (DGERO) and 1,4-butanediol (DGEBU) yield chains with respectively rigid, semirigid and flexible epoxide residues. Diaminodiphenylmethane (DDM) and hexamethylenediamine (HMDA) yield chains with respectively rigid

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and flexible amine residues. The repeat unit of a dense network and the chemical structure of the corresponding residues are given in Fig. 1. Thus, we are dealing with the networks of the type DGEBA-DDM, DGEBA-HMDA, DGERO-DDM, DGERO-HMDA, DGEBU-DDM or DGEBU-HMDA.

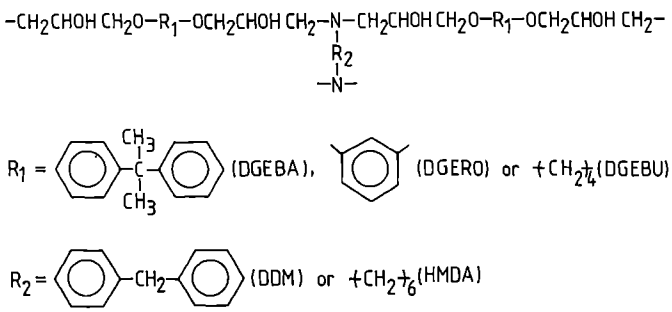

Fig. 1. Scheme of the repeat unit of the densely cross-linked networks

A crude manner to reduce the cross-link density is to limit the extent of the reaction by undercuring or by mixing the ingredients in nonstoichiometric ratios. In these cases, large amounts of unreacted epoxides (or amines) remain present in the form of pending groups. In a more refined way, the cross-link density can be decreased controllably in each series, with chain flexibility remaining unaffected, by using a mixture of amines as the cure agent, kept in stoichiometric proportions. The bending group extenders are incorporated into these loosely cross-linked networks when the amine added to the primary diamine is a primary monoamine [4-benzylaniline (BAN) mixed with diaminodiphenylmethane, and hexylamine (HA) mixed with hexamethylenediamine]. As an example, the repeat unit of the network diglycidyl ether of resorcinol—hexamethylenediamine/hexylamine (called DGERO—HMDA/HA) is given in Fig. 2a. The loosely cross-linked networks can also include main-chain extenders, provided the primary monoamine is replaced by a secondary diamine in the cure agent mixture [N,N'-dimethyldiaminodiphenylmethane (DMDDM) and N,N'-dimethylhexamethylenediamine (DMHMDA) instead of BAN and HA, respectively]. An example of this kind is the repeat unit of the diglycidyl ether of resorcinol—hexamethylenediamine/N,N'-dimethylhexamethylenediamine network (called DGERO—HMDA/DMHMDA) (Fig. 2b).

All the above networks can be regarded as „model systems" in the sense that each exhibits a well-defined architecture. Indeed, the side reaction of ether formation, which would result from the opening of the epoxide rings by the resulting alcohol functions, has never been detected with these systems at the sensitivity level of NMR [3]. Moreover, the extent of the epoxide-amine reactions is as complete as possible (around 0.9), owing to a post-cure stage applied for 24 hours at 30°C above the final T_g, which favors the diffusion-controlled reaction of most of the unreacted chemical functions [4].

EXPERIMENTAL

Materials

Chemicals

Diglycidyl ethers of bisphenol-A (DGEBA) and resorcinol (DGERO), purchased from Bakelite Co. (grade Rutapox 0162) and Lancaster, respectively, were used as received owing to their high purity and very low degree of polymerization. Diglycidyl ether of 1,4-butanediol (DGEBU) was purchased from Janssen Chimica and was fractionated under vacuum before use. The fraction used in this study had a boiling point of 70°C at 0.06 Torr.

Diaminodiphenylmethane (DDM) purchased from Janssen Chimica and hexamethylene (HMDA), hexylamine (HA) and N,N'-hexamethylenediamine (DMHMDA) purchased from Aldrich, each high-purity grade, were used as received. 4-Benzylaniline (BAN) and N,N'-dimethyldiaminodiphenylmethane (DMDDM) were synthesized in this Laboratory by Dr. B. Jasse and Mrs. F. Costa-Torro by the reported methods [2c] and their purity was checked by elemental analysis.

Network preparation

Diglycidyl ether of bisphenol-A (DGEBA) had been heated at 50°C and briefly degassed under vacuum before the amines were added. This step was omitted in the case of diglycidyl ethers of resorcinol and 1,4-buta-

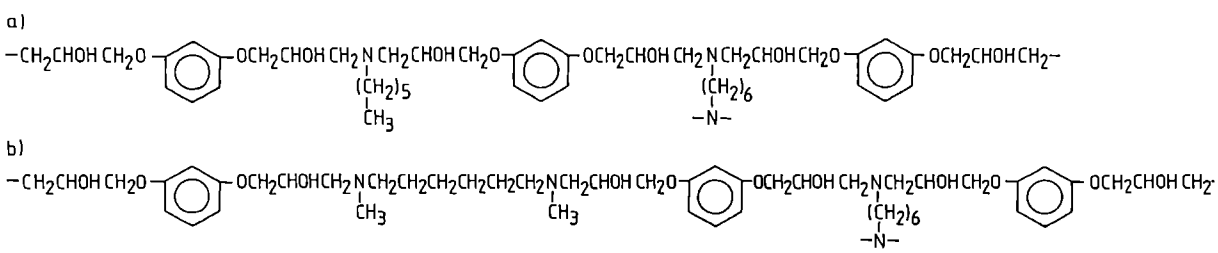

Fig. 2. Scheme of the repeat unit of the loosely cross-linked networks based on diglycidyl ether of resorcinol (DGERO) and hexamethylenediamine (HMDA): (a) with pending primary monoamine (HA) residue, (b) with main-chain secondary diamine (DMHMDA) residue

nediol (DGERO and DGEBU), which are liquid at room temperature. The amines were dissolved under nitrogen gas, aliphatic at 35°C and aromatic at 80°C. The typical cure cycle consisted of a few 2-hour steps at temperatures below the exotherm, followed by a 3-hour step at the exotherm and finally by a 24-hour post-cure at 30°C above T_g.

Network code

As anticipated before (*cf.* the Design of model networks), the samples are coded on the basis of the acronyms corresponding to the diepoxide and the amine(s). In the case of ternary mixtures, the additional figure represents the mole percentage of the total NH functions that come from the primary diamine. As an example, the code DGERO—HMDA/HA-40 refers to the network made of diglycidyl ether of resorcinol, hexamethylenediamine and hexylamine used in the stoichiometric proportions, with 40 mol% of the NH functions coming from the hexamethylenediamine molecules; this corresponds to the relative amounts of 5 mols DGERO, 1 mol HMDA and 3 mols HA. In the case of nonstoichiometric binary mixtures, the figure following the two acronyms represents the ratio r of the number of NH functions to the number of the epoxide rings. An example of this kind of networks is DGEBA-DDM-0.8, which corresponds to the relative amounts of 5 mols DGEBA and 2 mols DDM.

Theoretical cross-link density of the networks

The theoretical number of cross-link points per network mass unit, ζ_M, may easily be calculated provided the mole numbers and the molecular weights of the reactants are known. The following relation holds for the stoichiometric systems:

$$\zeta_M\,(\text{mol}\cdot\text{kg}^{-1}) = \frac{2000N_4}{N_4(M_4 + 2M_e) + N_2(M_2 + M_e)} \qquad (2)$$

where M_e, M_4 *and* M_2 *are the molecular weights of diepoxide, primary diamine and difunctional amine, respectively, and* N_4 *and* N_2 *are the mole numbers of primary diamine and difunctional amine, respectively.*

This relation is also valid in the special case of diepoxide—primary diamine binary mixtures with zero taken for N_2. For the binary systems which contain an excess of diepoxide ($r < 1$),

$$\zeta_M\,(\text{mol}\cdot\text{kg}^{-1}) = \frac{2000\,(3r - 2)}{rM_4 + 2M_e} \qquad (3)$$

and for those which contain an excess of primary diamine ($r > 1$):

$$\zeta_M\,(\text{mol}\cdot\text{kg}^{-1}) = \frac{2000\,(2 - r)}{rM_4 + 2M_e} \qquad (4)$$

Knowing ζ_M and the density ρ of the networks (reported elsewhere [2c, 5]), it is possible to calculate the so-called theoretical cross-link density, ζ_V (mol·dm^{-3}) = $\rho\zeta_M$. This quantity would coincide with the true cross-link density, if the actual extents of reaction were unity.

Viscoelastic measurements

Dynamic mechanical testing

Depending on the temperature range under consideration, two complementary set-ups of equipment were used:

(i) A servohydraulic testing machine MTS 831.10, operated in the tensile mode. A sinusoidal deformation (strain amplitude as small as 0.1%) was superimposed on the static deformation of about 0.1%. The frequency domain covered by the experiments ranged from 0.02 Hz to 80 Hz. For each sample, measurements were performed from -90°C to T_g +30°C. Sample size was 3 x 15 x 40 mm^3.

(ii) A Du Pont DMA 983 dynamic mechanical analyzer. This machine was used for measurements covering a temperature range of -150°C to 30°C and a frequency range of 0.1 Hz to 2 Hz. The strain applied was 0.15% in the flexural mode. Samples of about 2 x 10 x 40 mm^3 were used.

Systematically, temperature increments between two consecutive series of measurements were 4°C in the β-transition region and 2°C in the T_g and the rubbery plateau regions. Viscoelastic experiments performed in the tensile mode yielded directly the storage modulus E', the loss modulus E'' and the damping $\tan\delta = E''/E'$. The flexural data were transformed into E' and E'' by using a routine available on the DMA and taking a Poisson's ratio equal to 0.33 in the glassy state.

Data analysis

Conventionally [4, 6] the T_g of a sample was taken to be the temperature at which the loss modulus E'' goes through a maximum when the frequency is 1 Hz. Hereafter, it is called T_g(1 Hz). The rubbery modulus, E_r, which increases slightly with increasing temperature [7], was taken as the lowest value of E' at temperatures greater than T_g. This value is nearly independent of frequency, within the experimental uncertainty.

According to the frequency-temperature superposition principle [7], the different E' (or E'') *versus* frequency curves can be reduced to a unique master curve, provided appropriate shifts, log a_T, are made along the frequency scale. Vertical shifts accounting for changes in density over the temperature range under consideration were systematically neglected. With the temperature variation of log a_T in the T_g region described by the WLF equation [7]:

$$\log a_T = \frac{-C_1^g(T - T_g)}{C_2^g + T - T_g} \qquad (5)$$

the viscoelastic coefficients C_1^g and C_2^g at the reference temperature T_g can be easily extracted from the plot of $(T_g - T)/\log a_T$ *versus* $(T - T_g)$ [4, 6]. On the basis of the free

volume concept, C_1^g and C_2^g can be related to quantities on the molecular scale, namely, the fractional free volume available at T_g, f_g, and the expansion coefficient of the free volume above T_g, α_f [4, 6, 7]:

$$C_1^g = \frac{B}{2.3 f_g}, \quad C_2^g = \frac{f_g}{\alpha_f}, \quad \text{and hence} \quad C_1^g \cdot C_2^g = \frac{B}{2.3\,\alpha_f} \tag{6}$$

where *B is an empirical constant usually taken equal to unity.*

Master curves can also be built from the different curves E' (or E'') *versus* frequency obtained in the β-transition region [8]. In this case, the temperature dependence of log a_T obeys an Arrhenius-type equation of the form [7]:

$$\log a_T = \log \frac{f_o}{f} = \frac{E_a}{2.3R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \tag{7}$$

where *E_a is the activation energy, R the gas constant and T and T_o are the temperatures of the maximum of E'' at the frequencies f and f_o, respectively.*

Additional information can be derived by considering E_a as the free energy [9] and separating it into an enthalpic contribution $\Delta H^{\ddagger}$, and an entropic contribution $\Delta S^{\ddagger}$, according to the equation:

$$f = \frac{kT}{2ph} \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \tag{8}$$

where *h is the Planck constant.*

According to Starkweather [9], the cooperativity of segmental motions of the neighboring groups appears when $\Delta S^{\ddagger}$ is as large as about 100 $J \cdot K^{-1} \cdot mol^{-1}$.

RESULTS AND DISCUSSION

Viscoelastic characteristics in the glass transition region

Glass transition temperatures at 1 Hz

Stoichiometric networks

The values of T_g(1 Hz) relative to the stoichiometric networks are reported in Table 1, together with the theoretical cross-link densities. Change from densely cross-linked to more and more loosely cross-linked networks leads, as expected [11], to a progressive decrease of T_g. This effect can be accounted quantitatively in each series by plotting T_g(1 Hz) as a function of the theoretical cross-link density ζ_V (Fig. 3). One could wonder whether this quantity is suitable for this purpose. Ideally, the true cross-link density should be used, but its determination would imply the knowledge of the actual extent of reaction of all the systems. Yet, this time-consuming task was only performed on a few model systems of quite different architectures and it has been shown that the extent of reaction of the post-cured systems is independent, within the experimental error, of the nature of the reactants [20]. Therefore, ζ_V differs from the true cross-link density only by a roughly constant (and close to unity) multiplication factor. From the analysis of the linear plots of T_g(1 Hz) *vs* ζ_V, one can extract the values of the parameters T_{go} and p of a Fox-Loshaek type equation [12]:

$$T_g = T_{go} + p\zeta_V \tag{9}$$

where *temperatures are given in Kelvin and T_{go} represents the glass transition temperature of uncross-linked chains which would be prepared from binary mixtures of a diepoxide and a primary monoamine.*

The values of T_{go} and p relative to the different series of resins are given in Table 2.

The values of T_{go} are governed by the rigidity of the constitutive units of the chains, as can be illustrated by the „evolution cycles" sketched in Fig. 4. Two separate

Table 1. THEORETICAL CROSS-LINK DENSITIES AND T_g's OF THE STOICHIOMETRIC NETWORKS

Network	ζ_V mol/dm^3	T_g, °C	Reported T_g, °C
DGEBA—DDM	2.71	188	184 [2b]
DGEBA—DDM/BAN-75	1.94	146	—
DGEBA—DDM/BAN-40	0.97	115	—
DGEBA—DDM/BAN-20	0.47	101	—
DGEBA—DDM/BAN-5	0.11	86	—
DGEBA—DDM/DMDDM-40	0.98	113	112 [2b]
DGEBA—HMDA	2.92	121	118 [2b]
DGEBA—HMDA/HA-40	1.08	70	63.5 [2b]
DGEBA—HMDA/HA-5	0.58	56	—
DGEBA—HMDA/DMHMDA-40	1.00	60	42 [2b]
DGERO—DDM	3.95	144	123 [10]
DGERO—DDM/BAN-75	2.72	110	—
DGERO—DDM/BAN-40	1.33	85	—
DGERO—DDM/BAN-5	0.12	64	—
DGERO—DDM/DMDDM-40	1.23	81	—
DGERO—HMDA	4.42	84	79 [10]
DGERO—HMDA/HA-40	1.55	44	—
DGERO—HMDA/DMHMDA-40	1.42	30	—
DGEBU—DDM	3.95	75	76 [2b]
DGEBU—DDM/BAN-40	1.34	32	—
DGEBU—DDM/BAN-20	0.64	23	—
DGEBU—DDM/BAN-5	0.15	18	—
DGEBU—DDM/DMDDM-40	1.23	28	—
DGEBU—HMDA	4.37	-5	
DGEBU—HMDA/HA-5	0.16	-34	

Table 2. VALUES OF T_{go} AND p [Eq. (9)] FOR THE TERNARY SYSTEMS DIEPOXIDE—PRIMARY DIAMINE/PRIMARY MONOAMINE

Series	T_{go}, °C	T_{go}, K	p, K/(mol·dm^3)
DGEBA—DDM/BAN	81	354	39
DGEBA—HMDA/HA	47	320	25
DGERO—DDM/BAN	64	337	21
DGERO—HMDA/HA	22	295	14
DGEBU—DDM/BAN	13	286	16
DGEBU—HMDA/HA	-35	238	7

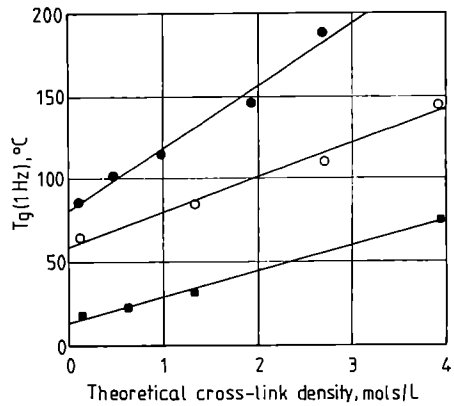

Fig. 3. T_g(1 Hz) versus theoretical cross-link density ζ_V for the different series of loosely cross-linked networks with pending groups: • — series DGEBA—DDM, ○ — series DGERO—DDM, ■ — series DGEBU—DDM

paths can be followed to move from a rigid epoxide—rigid amine system (*e.g.*, DGEBA—DDM) to a more flexible epoxide—more flexible amine system (*e.g.*, DGEBU—HMDA or DGERO—HMDA), depending on whether the first applied decrease in rigidity comes from the substitution of the epoxide or the amine moiety. Whatever the example under consideration, it appears clearly that the same epoxide substitution provokes roughly the same decrease, ΔT_{go}, of T_{go} along the two paths. The same conclusion holds for the amine substitution. In passing from the DGEBA—DDM to the DGEBU—HMDA, the major influence comes from the strong decrease in epoxide rigidity. In contrast, the influence of the decrease of amine rigidity prevails in the evolution from DGEBA—DDM to DGERO—HMDA, because the differences in rigidity of DGEBA and DGERO are rather small. These results can be interpreted on the molecular scale: the glass transition phenomenon is dominated by large-scale cooperative motions of the hydroxypropyl ether sequences (-O-CH_2-CHOH-CH_2-), which can be impeded, first by the rigidity of the epoxide residues and also by the limitation of mobility of the cross-link points close to aromatic amine residues. These ideas are consistent with the solid-state NMR observations of Eustache [2a].

Another important result consistent with earlier observations [13] is that the slope p increases markedly with the increasing rigidity: thus, the greater the rigidity, the greater the sensitivity of T_g to the cross-link density. Therefore, a fit of our data shows that Equation (9) can be rewritten in the form of a power law of T_{go}:

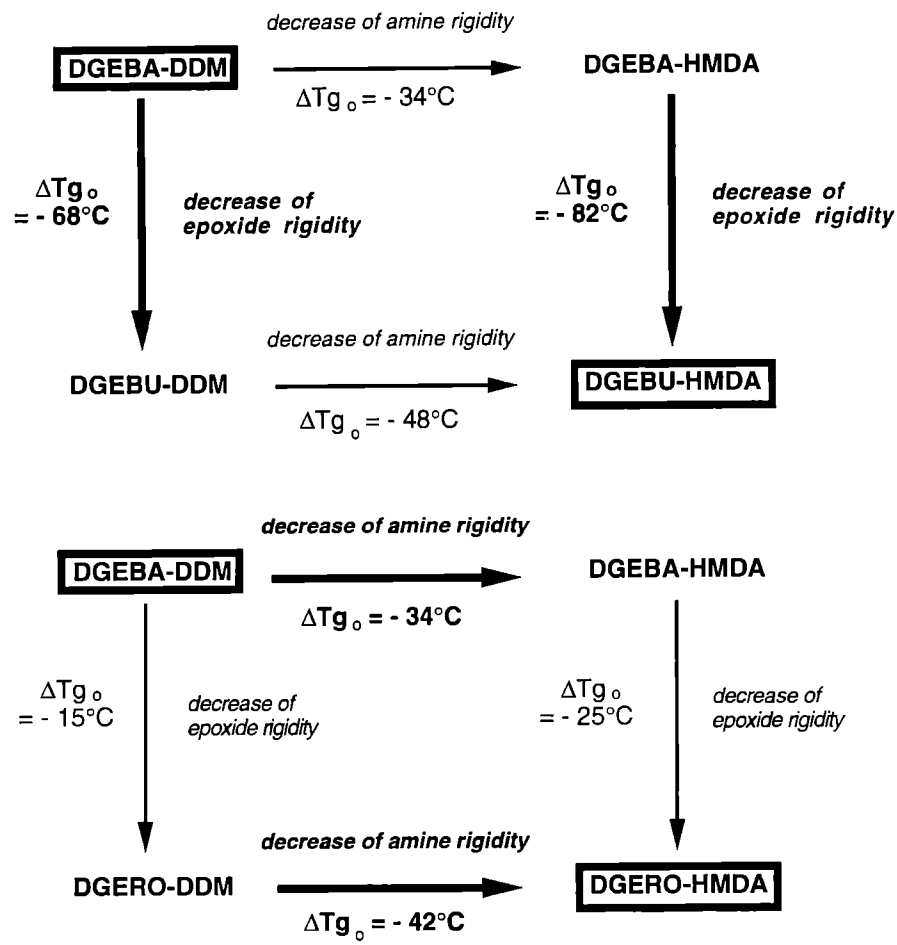

Fig. 4. Evolution cycles illustrating the relative influence of epoxide residue rigidity and amine residue rigidity on the value of T_{go}

Table 3. INFLUENCE OF THE NATURE OF THE CHAIN EXTENDER ON T_g IN TERNARY MIXTURES CONTAINING 40 mol% OF PRIMARY DIAMINE

Network	$T_{g'}$ °C pending extender	$T_{g'}$ °C main-chain extender	$\Delta T_{g'}$ °C
DGEBA—DDM/(BAN or DMDDM)-40	115	113	2
DGEBA—HMDA/(HA or DMHMDA)-40	85	81	4
DGERO—DDM/(BAN or DMDDM)-40	32	28	4
DGERO—HMDA/(HA or DMHMDA)-40	70	60	10
DGEBU—DDM/(BAN or DMDDM)-40	44	30	14

$$T_g = T_{go} + p'\zeta_V T_{go}^4 \quad (\text{with } p' = 2{\cdot}10^{-9}) \qquad (10)$$

This means also that the relationships established between the T_{go}-values and the epoxide and amine rigidities not only hold but are even enhanced as compared with the T_g(1 Hz) values at the same cross-link density.

All the above conclusions are also supported by the comparison of the T_g of the systems which differ from each other only by the type of the extender (Table 3). Pending and main-chain extender moieties have quite similar effects when they are rigid. In contrast, marked differences in T_g are observed when noticeable mobility can be introduced in the main chains by the aliphatic amine moieties.

Nonstoichiometric networks

The values of T_g(1 Hz) relative to nonstoichiometric networks of the DGEBA—DDM and DGEBU—DDM series are reported in Table 4, together with their theoretical cross-link densities. In accordance with the literature [14—16], the common representation of T_g *versus* stoichiometric ratio r (Fig. 5a) shows that T_g is maximum for $r = 1$ and drops more rapidly for $r < 1$ (excess of diepoxide) than for $r > 1$ (excess of primary diamine). However, one should realize that these trends have much to do with the relevant changes in cross-link density. Therefore, it is probably more instructive to plot T_g *versus* ζ_V (Fig. 5b).

Table 4. THEORETICAL CROSS-LINK DENSITIES AND T_g OF THE NONSTOICHIOMETRIC NETWORKS

Network	ζ_V, mol/dm^3	$T_{g'}$ °C
DGEBA—DDM-0.7	0.29	96
DGEBA—DDM-0.8	1.14	144
DGEBA—DDM-0.9	1.94	182
DGEBA—DDM	2.71	188
DGEBA—DDM-1.1	2.39	177
DGEBA—DDM-1.2	2.08	164
DGEBA—DDM-1.3	1.78	153
DGEBA—DDM-0.7	0.45	1
DGEBA—DDM-0.8	1.72	40
DGEBA—DDM-0.9	2.9	65
DGEBA—DDM	3.95	78
DGEBA—DDM-1.1	3.48	65
DGEBA—DDM-1.2	3.01	62
DGEBA—DDM-1.3	2.56	58

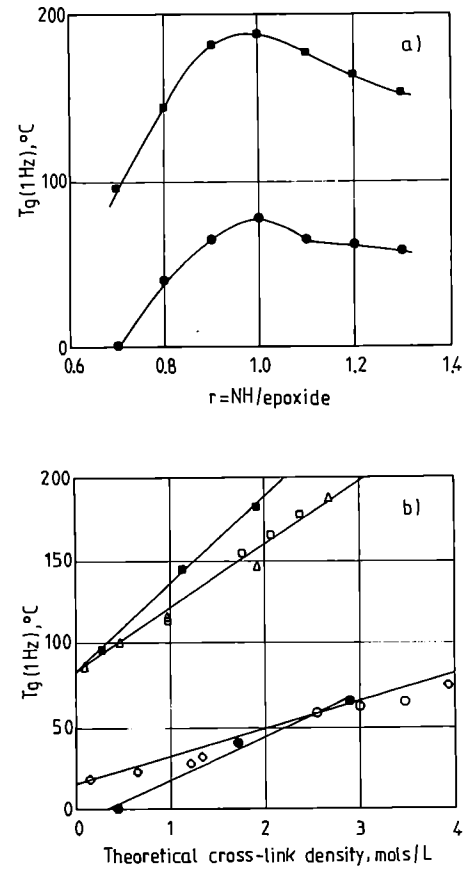

Fig. 5. Analysis of the T_g(1 Hz) of the nonstoichiometric networks. (a) T_g(1 Hz) versus stoichiometric ratio r: ■ — series DGEBA—DDM, ● — series DGEBU—DDM; (b) T_g(1 Hz) versus theoretical cross-link density ζ_V: ■ — series DGEBA—DDM r<1, □ — series DGEBA—DDM r>1, △ — DGEBA—DDM r=1, ● — series DGEBU—DDM r<1, ○ — series DGEBU—DDM r>1, ◇ — series DGEBU—DDM r=1

As expected, the T_g of the nonstoichiometric systems with an excess of amine lie on the same straight line as those of the ternary diepoxide—primary diamine/(primary monoamine or secondary diamine) networks. Indeed, they exhibit the same kind of pending or main-chain residues, as can be seen from a comparison of Fig. 6a with Figs. 2a and 2b. In contrast, the diepoxide-rich nonstoichiometric systems exhibit a particular T_g behavior, which is a function of diepoxide rigidity. This results from the presence of sequences of a new type (Fig. 6b). These sequences are more rigid when the diepoxide residue is DGEBA, and they lead to an increase in T_g at an identical cross-link density. In contrast, they are very flexible in the presence of DGEBU, leading to a decrease of T_g.

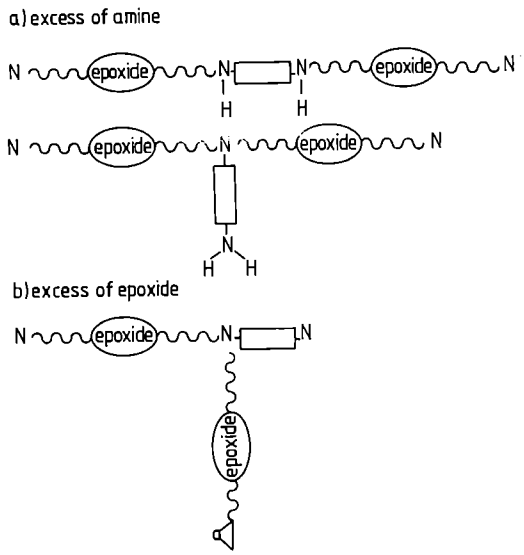

Fig. 6. Schematic drawing of the additional sequences present in nonstoichiometric networks: (a) excess of amine; (b) excess of epoxide

Viscoelastic coefficients C_1^g and C_2^g

The master curve methodology detailed in the experimental section was successfully applied to the analysis of the frequency dependence of the viscoelastic moduli E' and E'' and the values of C_1^g and C_2^g were computed for some selected networks (Table 5). It is recognized that the error bars on such calculations are quite large

Table 5. COMPUTED VISCOELASTIC CHARACTERISTICS OF SOME MODEL NETWORKS

Network	C_1^g	C_2^g, °C	$10^2 f_g/B$	$10^3 \cdot \alpha_f/B$
DGEBA—DDM	10.9	34.8	3.99	1.15
DGEBA—DDM/BAN-75	9.7	39.5	4.48	1.13
DGEBA—HMDA	11.0	41.5	3.95	0.95
DGEBA—HMDA/HA-40	9.9	34.5	4.39	1.27
DGERO—DDM	10.5	39	4.14	1.06
DGERO—DDM/BAN-75	10.3	33	4.22	1.28
DGERO—HMDA	11.6	47	3.75	0.80

(especially for C_2^g). However, Table 5 shows that significant differences exist on the fraction of free volume, f_g, which is available at T_g and on the free volume expansion coefficient, α_f, above T_g. Both quantities decrease when the network cross-link density is increased, in agreement with our previous findings [4]. Besides, Fig. 7 shows that reasonable semiquantitative relationships, independent of chain rigidity, correlate f_g and α_f with the theoretical cross-link density. Thus, the temperature—frequency relationships for the networks seem to be governed by cross-links only.

Rubbery modulus

The rubbery modulus data, E_r, taken (as indicated in the experimental section) from the viscoelastic measure-

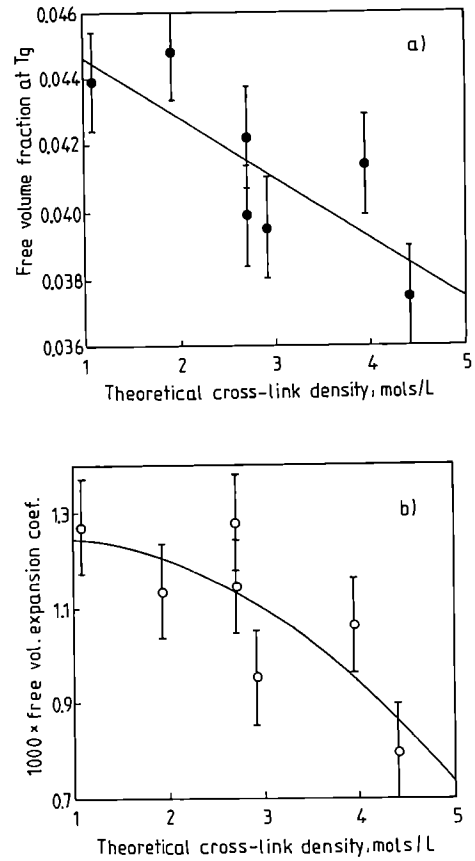

Fig. 7. Analysis of the free volume characteristics of the networks: (a) fraction of free volume available at T_g(1 Hz), f_g, versus theoretical cross-link density ζ_V; (b) free volume expansion coefficient above T_g versus theoretical cross-link density ζ_V

ments at temperatures well above T_g, are given in Table 6. In agreement with the pioneering study of LeMay [17] using diepoxide prepolymers of variable chain length, it is recognized that the behavior of the epoxy networks well above T_g is described by the well-known laws of rubber elasticity. Therefore, it is common in the literature to use the equation:

$$E_r = 3\Phi\rho RT/M_c \qquad (11)$$

where ρ *is the density, R the gas constant, and* M_c *the mean chain molecular weight between cross-links.*

The problem with Equation (11) is that M_c has no physical meaning on the molecular level as far as comparison of different chemical structures is concerned. For this reason, the front factor Φ may differ appreciably from unity and is shown to vary when network architecture is varied.

Inspection of the selected data of Table 6 reveals that the rubbery modulus decreases in any given series when the cross-link density is decreased. On a molecular scale, the rubbery modulus is governed by the number of chemical bonds able to rotate between two adjacent cross-link points: the larger the number of bonds, the lower the modulus. This theoretical prediction is well verified by the data of Table 6, provided, of course, we

Table 6. RUBBERY MODULI

Network	ζ_V, mol/dm^3	E_r, MPa
DGEBA—DDM	2.71	43.0
DGEBA—DDM/BAN-75	1.94	19.7
DGEBA—DDM/BAN-40	0.97	10.5
DGEBA—DDM/DMDDM-40	0.98	9.7
DGEBA—HMDA	2.92	27.5
DGEBA—HMDA/HA-40	1.08	8.9
DGEBA—HMDA/DMHMDA-40	1.00	6.0
DGERO—DDM	3.95	39.0
DGERO—DDM/BAN-75	2.72	12.3
DGERO—HMDA	4.42	18.6
DGEBU—DDM	3.95	18.5

compare the networks which present the same amine links and the same cross-link density. As an example, E_r is higher in the case of DGERO—DDM (2 bonds involving the epoxide among a total of 10 bonds) than in the case of DGEBU—DDM (5 bonds involving the epoxide among a total of 13 bonds). Similarly, E_r is higher for DGEBA—HMDA/HA-40 than for DGEBA—HMDA/DMHMDA-40 because the number of active bonds in the former extender moiety is lower (20 instead of 27, see Fig. 2). In the previous section, the flexibility of a chemical unit was also related implicitly to the number of its mobile bonds, thus a crude conclusion could be that E_r depends indirectly on chain flexibility. Since E_r varies as a function of both cross-link density and chain rigidity in the same direction as T_g does, it is not surprising that relationships hold between E_r and T_g (Fig. 8).

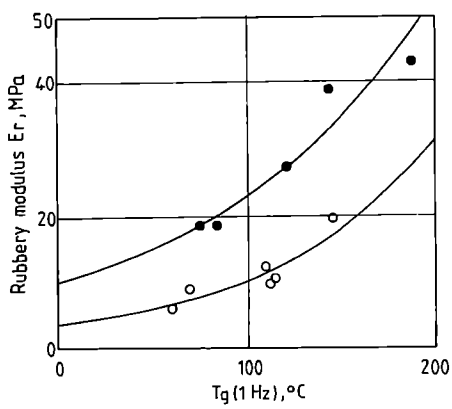

Fig. 8. Rubbery modulus E_r versus T_g(1 Hz) (full circles: densely cross-linked networks; open circles: loosely cross-linked networks)

Sub-T_g secondary transition β

Independently of their chemical structure, all the networks exhibit in the glassy state a secondary transition, called the β-transition, which has been attributed [18, 19] to motions involving the hydroxypropyl ether units. It is characterized by a maximum of E'' at 1 Hz in the temperature range of -80°C to -40°C. Some major features of this transition have been brought to light by Cukierman [8] on some of our model networks. They can be summarized as follows: (i) the onset of the β-process is shown to occur at the same temperature irrespective of chain flexibility and network cross-link density; (ii) both amplitude and temperature range of the relevant damping E'' increase with increasing cross-link density; and surprisingly (iii) the higher cross-link densities lead to the lower moduli. The reverse is observed at low temperatures and corresponds, as expected, to an increase in the modulus with the increasing cross-link density. The moduli E' observed at 25°C are simply interpreted as the consequence of the β-process: the broader and more intense the E'' damping peak, the greater the decrease of E'. Figure 9, taken from [8], illustrates this general behavior on the example of networks of the

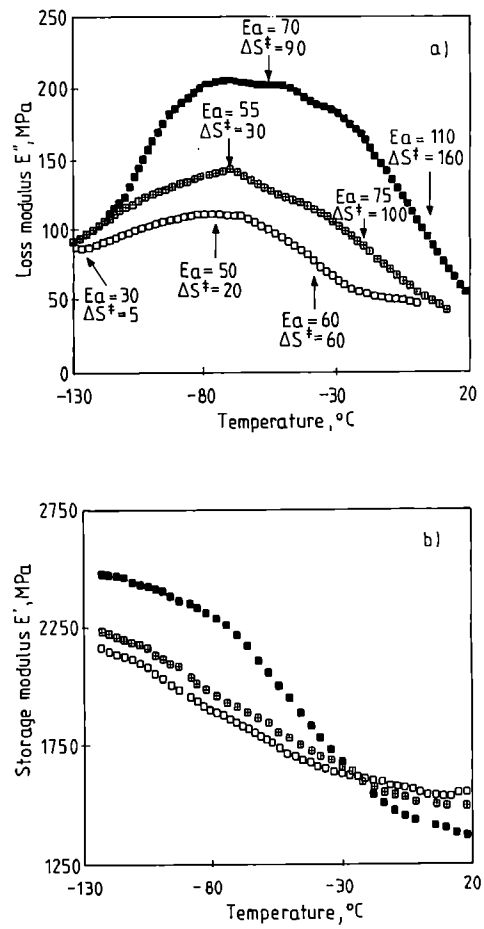

Fig. 9. Viscoelastic behavior of the networks in the β-transition region: ■ — DGEBA—HMDA, ⊠ — DGEBA—HMDA/HA-40, □ — DGEBA—HMDA/HA-5. (a) Loss moduli E'' at 1 Hz versus temperature (the quantities E_a and $\Delta S^{\ddagger}$ mean the approximate values of the activation energy (kJ·mol^{-1}) and of the activation entropy (J·mol^{-1}·K^{-1}), respectively, at the positions indicated by the arrows); (b) Storage moduli E' at 1 Hz versus temperature (the occurrence of a unique cross-over is probably fortuitous)

DGEBA—HMDA series. Its molecular interpretation is based on the idea that isolated hydroxypropyl ether movements occur at low temperatures, whereas short-range cooperative motions of the hydroxypropyl ether develop at higher temperatures. The higher the cross-link density in any given series, the greater the chance for cooperative motions to develop. In other words, the E'' damping peak would be a complex peak in which contributions of local and cooperative motions overlap. These conclusions are supported by the analysis of the activation energies E_a and entropies $\Delta S^{\ddagger}$ along the E'' peaks (see Fig. 9a). Three factors have a crucial influence on the occurrence of cooperative hydroxypropyl ether motions, namely: (1) the number of cross-links per volume unit, (2) the mobility of the cross-link points (which is a function of the nature of the primary diamine), and (3) the flexibility of the diepoxide residues. In this respect, comparison of the β damping peaks of the DGEBA—DDM, DGERO—DDM and DGEBA—DDM/BAN-75 systems is instructive. As shown in Fig. 10, the amplitude and the temperature range of the E''

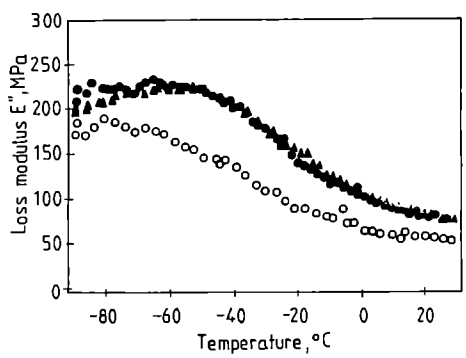

Fig. 10. Loss moduli E'' at 1 Hz versus temperature for the networks in the β-transition region: ▲ — DGEBA—DDM, ● — DGERO—DDM, ○ — DGEBA—DDM/BAN-75

damping peaks of DGEBA—DDM and DGERO—DDM in the β-transition region are quite similar in spite of substantial differences in cross-link density. In turn, matching of the cross-link densities (samples DGEBA-DDM and DGEBA—DDM/BAN-75) yields a more imposing peak in the case of the DGEBA—DDM. An explanation for these results can be found in the molecular structure of the diepoxides: the meta-phenylene unit of 2 is shorter than the bisphenol-A residue of 1; it would be also more rigid within this temperature range (in contrast to what is observed in the T_g region): indeed, the asymmetry of the epoxide linkages is supposed to limit the meta-phenylene rings to wagging motions whereas the aromatic rings of bisphenol-A yet undergo flips [20] about the C_2 axis and may bend relative to one another *via* the bridging isopropylidene groups.

Further studies on the model networks

First of all, more information on the nature of the segmental motions which occur below T_g were obtained by using high-resolution solid-state ^{13}C-NMR. Following the above-mentioned publications of Laupretre [2e, 19], much effort was made to combine information from dynamic mechanical analysis and NMR and to get a comprehensive view of the sub-T_g motions, especially in the case of networks of the DGEBA—HMDA/HA series [2d, 21]. All the conclusions on the existence of a „network effect" leading to the occurrence of cooperative β motions were nicely confirmed by this refined study. They were also corroborated by the data concerning the antiplasticization of the networks by appropriate small organic molecules [2d, 22]. The role of an antiplasticizer is related to its capability to hinder most of the hydroxypropyl ether cooperative β motions. Network moisture uptake has also been related to the β-transition processes [23]. It was shown that the water diffusion coefficient in model epoxy networks increases with increasing cross-link density and thus suggested that the hydroxypropyl ether movements act as carriers for water molecules.

At the same time, measurements were performed on the model networks in order to determine the influence of architecture on the densities and thermal expansion coefficients [2c, 5]. The use of Bondi's volume approach yielded network packing densities and, for the first time, evidence was given for a valuable relationship between the calculated packing density and the experimental hole volume, as sampled from positron annihilation lifetime spectroscopy measurements [24]. Finally, the generation of residual stresses was analyzed during the cooling down of glass-epoxy bilayers from temperatures above T_g [2c, 25]. The extent of the residual stresses mainly depends on the modulus and the thermal expansion coefficient of the network, and, as a direct consequence, on the cross-link density. Viscoelastic effects are shown to play a negligible role, except over a restricted range of temperatures close to T_g.

CONCLUSIONS

Two major conclusions can be drawn from this study. The first one has general implications. If unambiguous structure-property relationships are established here, it is because the model systems especially designed for this purpose have been used. These relationships are surely useful as guidelines for the formulation of new industrial systems, whereas direct study of commercial networks might fail, because of their complex formulations leading to inextricable competing effects. The second message deals especially with the molecular dynamics of the epoxy networks. It is worth noting that

the hydroxypropyl ether moieties play a major role. The molecular mobility associated with the glass transition involves their large-scale cooperative motions. The development of such motions depends mainly on the flexibility of the epoxide residues and also on the constraints imposed by the vicinity of the nitrogen cross-link points. In addition, both isolated and short-scale cooperative motions of the hydroxypropyl ethers govern the β relaxation process, which, in turn, affects many properties in the glassy state.

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