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Enthalpy relaxation of non-stoichiometric epoxy-amine resins

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Abstract

The effect of stoichiometry on the enthalpy relaxation of polyethertriamine-cured bisphenol-A-diglycidyl ether epoxies has been investigated by differential scanning calorimetry (DSC). As was expected, the glass transition temperature T_g decreases in the non-stoichiometric epoxies. The enthalpy loss determined by ageing experiments at $T_g - 20$ K, for times between 1 and 3000 h, allows the calculation of the rate of relaxation per decade (β_H) and the non-linearity parameter (x). These parameters have been determined for the stoichiometric resin and also for the non-stoichiometric resin with ratios (r) of amine/epoxy of 0.8 and 1.5. The other key parameters, namely the apparent activation energy (Δh^*) and the non-exponentiality parameter (β), have been determined from intrinsic cycles in which the sample is heated at 10 K min^{-1} following cooling at different rates. Results show that β_H and x increase and Δh^* decreases in the non-stoichiometric resins, with no significant change of the non-exponentiality parameter β. These results have been interpreted in terms of the changes of the network structure introduced by the non-stoichiometric ratios.

The Adam–Gibbs (AG) theory has also been applied to the enthalpy relaxation of all these systems, from which it is found that the configurational entropy at T_g increases in the non-stoichiometric systems, particularly for $r = 1.5$. By considering that the minimum number of configurations needed for cooperative relaxation (W^*) is constant for all systems, it is also shown that a decrease of the lower limit of cooperatively rearranging regions (z^*) is observed in the non-stoichiometric resins, again particularly for the resin $r = 1.5$. Values of T_2, the second-order transition temperature at which the configurational entropy reduces to zero, are derived from the measured values of the non-linearity parameter x, and found to be anomalously low. It is argued that this results from an inadequate extension of the AG theory to the non-equilibrium glassy state, and a recently proposed alternative approach is used to rationalise the observation in terms of processes at the glass transition that favour the freezing-in of either holes or high energy bond conformations.

Keywords: Enthalpy relaxation; Ageing; Non-stoichiometric epoxies

1. Introduction

Since the pioneering work of Ophir et al. [1] in 1978, structural (enthalpy) relaxation of epoxy resins has been widely studied by differential scanning calorimetry (DSC) [2–6]. More recently, enthalpy relaxation of fully [7,8] and partially cured [9] epoxy-anhydride networks, and fully cured epoxy-amine [10,11] networks has been analysed. The effect of additives has also been studied as the addition of a reactive diluent in an epoxy-anhydride resin [12] or a copolymer in an epoxy-amine resin [13]. However, all these systems have been cured in stoichiometric proportions, and, until now, no studies of the enthalpy relaxation in non-stoichiometric resins, with an excess of amine or epoxy, have been reported.

In epoxy-amine resins, the stoichiometric ratio is defined as $r = |A|/|E|$, where $|A|$ and $|E|$ are, respectively, the number of gram-equivalents (equiv.) of amine and epoxy monomers. Hence, $r < 1$ implies an excess of epoxy, $r > 1$ implies an excess of amine, and $r = 1$ determines the stoichiometric formulation. In the present paper, the effect of the stoichiometry on the enthalpy relaxation of a diepoxide-triamine network is studied. The reason for undertaking this work is to continue our attempts to relate the parameters of enthalpy relaxation, to be discussed below, to the chemical structure of the glassy system. The variation of the stoichiometric ratio provides a new and different way of modifying the network without modification of the chemical nature of the polymer chains or cross-links. In order to meet this objective, three different formulations have been used: one

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was prepared at the stoichiometric formulation ($r = 1$), and the other two were with an excess of amine ($r = 1.5$) and an excess of epoxy ($r = 0.8$).

As described elsewhere [14], the kinetics of structural relaxation exhibits both non-linear and non-exponential behaviour. The formalism to analyse the non-linearity is based on the dependence of the relaxation time on temperature and structure, which is often described by the so-called Tool–Narayanaswamy–Moynihan equation [15–17]:

$$\tau = \tau_0 \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right], \tag{1}$$

where T_f is the fictive temperature, which characterises the structure of the glass, x the non-linearity parameter, which defines the relative contributions of temperature and structure to the relaxation time, and Δh^* is the apparent activation energy. On the other hand, the non-exponentiality is a consequence of the distribution of relaxation times which may be introduced by means of the Kohlrausch–Williams–Watts (KWW) response function $\phi(t)$ [18]:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \tag{2}$$

where β is the non-exponentiality parameter, inversely related to the width of the distribution of relaxation times.

From an experimental point of view, the parameter x may be determined from ageing experiments, in which the sample is submitted to different intervals of ageing at a temperature below its glass transition. The other two parameters, β and Δh^*, may be determined from intrinsic cycles in which the sample is heated at 10 K $\min^{-1}$ following cooling at different rates. This experimental methodology has been applied previously to other epoxy resins [8,9,11–13] in order to obtain the three key parameters x, β and Δh^*. The main objective of this work is to study the effect of the stoichiometry ($r = 0.8$, 1 and 1.5) on the enthalpy relaxation of a diepoxide-triamine, as determined by these three key parameters. Besides providing information about the fundamental relationship between chemical structure and relaxation kinetics, the interest of this study lies also in the consequences of an inadequate formulation on the durability of an epoxy resin when it is used as a technical material for engineering applications.

2. Experimental

2.1. Materials

The epoxy resin was a commercial product based on diglycidyl ether of bisphenol-A (DGEBA) (Araldite F) with an epoxy equivalent of 188.8 g/equiv., cured by a polyethertriamine (Jeffamine T403) with an equivalent weight of 81 g/equiv. Fig. 1 shows the chemical structure of these reactives. The three different epoxy-amine networks were prepared at the stoichiometric ratios $r = 0.8$, 1 and 1.5, which correspond to compositions per 100 epoxy (Araldite F) parts per weight of 34.3, 42.9 and 64.4 amine (Jeffamine T403) parts, respectively. The samples were cured at 60°C for 3 h followed by a postcure at 180°C for 2 h for the stoichiometric ratios 1 and 0.8, and at 150°C for 2 h for $r = 1.5$. The glass transition temperature (T_g) has been measured in all systems as the mid-point of the change of C_p in a DSC scan obtained by heating at 10 K $\min^{-1}$ immediately after cooling from a temperature $T_0 = T_g + 20$ K at 20 K $\min^{-1}$.

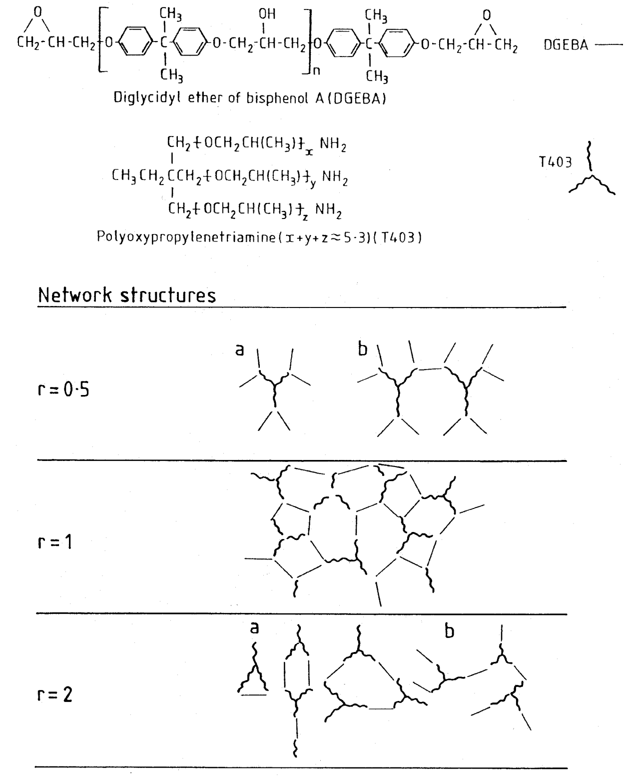

Fig. 1. Chemical structure of the epoxy resin and the hardener, and the possible network structures of the cured resins for different stoichiometric ratios r (after Morgan et al. Table 1 in Ref. [19], with permission).

2.2. Thermal analysis

The calorimetric measurements were performed using a Mettler TA4000 DSC30 and a Mettler DSC821e. Two different kind of calorimetric experiments were performed: annealing experiments and intrinsic cycles.

For the annealing experiment the sample is heated until about 20 K above the glass transition temperature, and then is cooled at a rate of 20 K $\min^{-1}$ to the annealing temperature, T_a ($T_a = T_g - 20$ K), where the sample is held for different periods of time between 0.5 h and several months (three months for $r = 1$, two months for $r = 0.8$ and five

Table 1
Glass transition temperature and annealing temperature

r	T_g (°C)	T_a (°C)
1	87.5	67.0
1.5	57.0	37.0
0.8	63.0	43.0

months for $r = 1.5$). After this period of annealing, the samples are cooled again at 20 K min^{-1} to about $T_a - 30$ K and then they are heated to $T_g + 20$ K at 10 K min^{-1} to obtain a DSC scan of the aged sample. The cycle is repeated without the annealing period in order to obtain a DSC scan of the unaged sample. The enthalpy loss is determined from the difference between the DSC scans of the aged and unaged samples while the peak temperature, T_p, is found from the maximum of the endotherm which appears in the DSC scan of the aged sample. These experiments allow a determination of the relaxation rate per decade, β_H, and of the non-linearity parameter, x. Table 1 summarises the characteristic temperatures of the thermal treatments used for each system.

Intrinsic cycles are obtained by cooling the samples from T_0 at different cooling rates (from -40 to -0.5 K min^{-1}) and immediately reheating at a constant rate of 10 K min^{-1}. These experiments allow a determination of the apparent activation energy, $\Delta h^*/R$, and an estimate of the non-exponentiality parameter, β.

3. Results and discussion

3.1. Glass transition temperature

Results for the glass transition temperature measured in these epoxy systems at different stoichiometric ratios are plotted in Fig. 2, which includes data for resins with $r = 0.6$, 1.2 and 1.4 for which the glass transition temperatures were measured in our laboratory in earlier work. The highest value of T_g, 87.5°C, is exhibited by the stoichiometric resin. This result agrees with the values quoted by Morgan et al. [19] in the same epoxy-amine resin and the same trend is observed by other authors in different epoxy resins [20–23]. In this resin, for $r = 1$, all amine hydrogens react with all epoxide groups, giving a network of interconnected rings. These rings consist of two or three epoxidic chains, which have reacted with the corresponding amine groups (for a detailed structure of these rings see Table 1 of Ref. [19], which has in part been reproduced in Fig. 1 of the present paper). On the other hand, in the resin prepared with an excess of epoxy, $r = 0.8$, all the NH_2 groups (called primary amines) and the NH groups (called secondary amines) react with 80% of the epoxy groups of the DGEBA molecules. Therefore, 20% of the epoxy groups do not react, giving a network with some bulky groups situated at the end of the epoxidic chain. This increase in the number of terminal groups of the chains gives rise to an increase of the free volume and, consequently, the glass transition of the resin decreases [24]. The unreacted epoxy groups may also exist as DGEBA molecules, which also contribute to an increase of the free volume, giving the same effect on the glass transition.

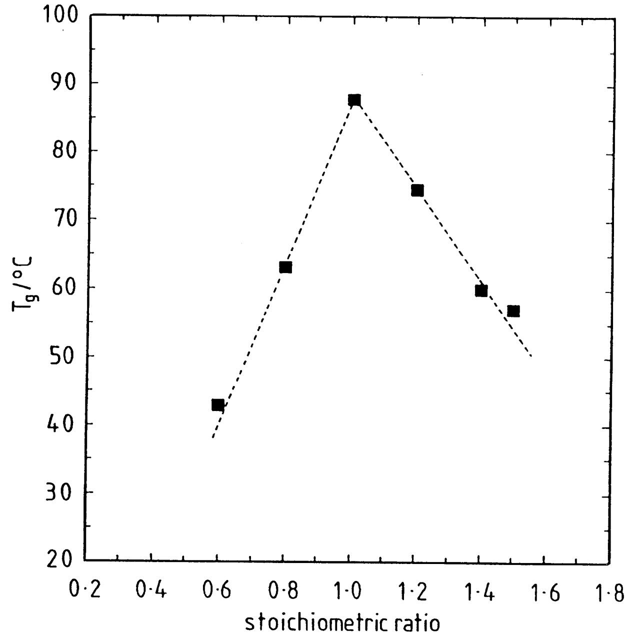

Fig. 2. Glass transition temperature versus stoichiometric ratio. The lines are to guide the eye.

In the resin prepared with an excess of amine, $r = 1.5$, all the epoxy groups react with all the primary amine groups and one third of the secondary amine groups. This means that two thirds of the NH groups do not react. According to Morgan et al. [19], under these conditions the epoxy tends to give branched structures, and occasionally may give rings consisting of the partially reacted triamine molecules and the epoxidic chain. These structures likewise contribute to an increase of the free volume of the system and, as a consequence, show a lower glass transition than the stoichiometric formulation. It must be taken into account that the network structures discussed in this section are based not only on the chemical structure of the DGEBA and the Jeffamine T403, but also on the following assumptions: (a) that the cross-linking reaction only results from the addition reaction of the epoxy and the amine, and (b) that the primary amine reacts prior to the secondary amine, due to the faster reaction rate of the former groups. Moreover, the structure of Jeffamine T403 has a methyl group in the position adjacent to the amine, which results in steric hindrance and slows the reaction of the secondary amine.

In Fig. 2, it can be seen that the glass transition temperature increases more sharply for formulations with an excess of epoxy ($r < 1$) than in formulations with an excess of amine ($r > 1$). This result seems to indicate that the presence of unreacted epoxy groups produces a greater effect on the increase of the free volume than does the

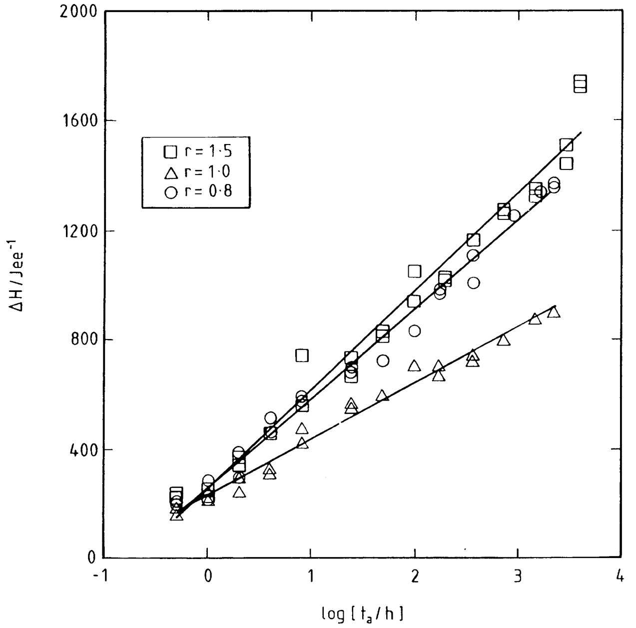

Fig. 3. Dependence of enthalpy loss during annealing at $T_g - 20$ K on logarithm of annealing time for the three stoichiometric ratios. The symbols for the three stoichiometric ratios are indicated in the inset. Full lines are linear fits to the experimental data.

presence of branched chains or rings with unreacted amine groups. This effect gives a faster decrease of the glass transition temperature per unit of stoichiometric ratio.

3.2. Annealing experiments. Non-linearity parameter

The annealing experiments performed over a wide interval of annealing times allow the determination of the enthalpy loss, ΔH, and the value of the peak temperature, T_p, from the DSC curves for each aged sample together with the reference scan. Figs. 3 and 4 show, respectively, the dependence of the enthalpy loss and of the peak temperature on the logarithm of the annealing time, t_a, at $T_a = T_g - 20$ K. The values of enthalpy loss have been calculated in J per epoxy equivalent (J ee^{-1}), as is usual in the reporting of thermodynamic properties for non-stoichiometric resins. Fig. 3 shows the best linear fits to the experimental points, from which the slopes give a measure of the relaxation rate per decade, β_H, at the selected annealing temperature.

The peak temperature increases linearly with log (annealing time), as is shown in Fig. 4. For samples with $r = 1$ and $r = 0.8$, a good linear correlation is found from 4 to about 2000 h, and for $r = 1.5$ the linear correlation is found from 2 to 3900 h. The restriction in the lower values of t_a can be understood by reference to Fig. 4, where a clear departure from a linear dependence is shown. Such behaviour is known to occur at short annealing times where the endothermic peak has a different significance [25–27]. This different behaviour has also been shown in other epoxy systems [8,9,11,12].

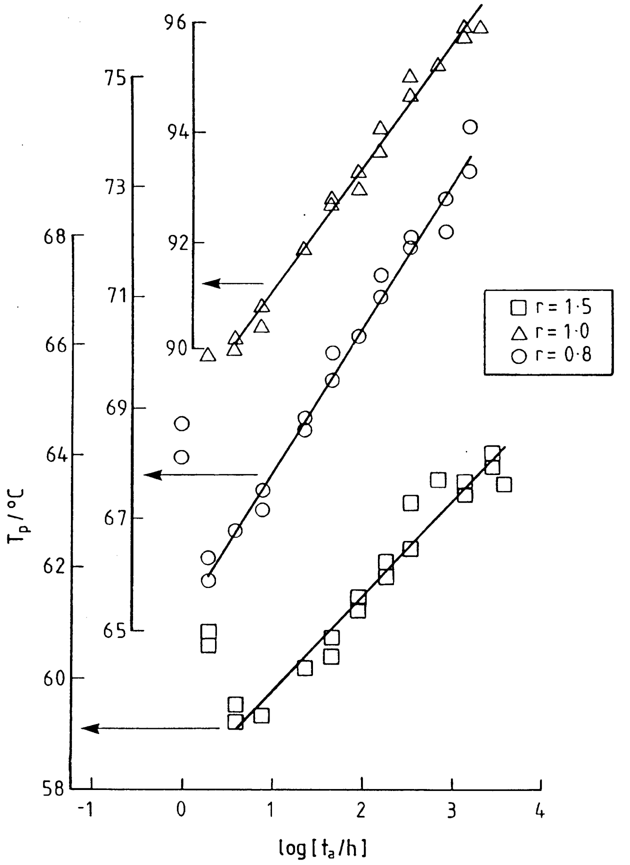

Fig. 4. Dependence of peak temperature during annealing at $T_g - 20$ K on logarithm of annealing time for the three stoichiometric ratios. The symbols for the three stoichiometric ratios are the same as in Fig. 3, and are indicated in the inset. Full lines are linear fits to the experimental data for times greater than or equal to 2 h.

Results corresponding to these annealing experiments for all the resins analysed are presented in Table 2 together with the values for the increment in heat capacity, ΔC_p, at the glass transition. It is observed that β_H increases significantly in the non-stoichiometric systems, from 204 J ee^{-1} K for $r = 1$ to 360 J ee^{-1} K for $r = 1.5$ and to 325 J ee^{-1}K for $r = 0.8$. According to the different structures discussed further below, stoichiometric samples form a network of interconnected rings with practically no unreacted groups, and hence with the highest cross-link density. This network structure inhibits the chain motions, and the relaxation process is thus slower than in the non-stoichiometric resins with a lower cross-link density. On the other hand, the higher relaxation rate β_H observed for $r = 1.5$ with respect to that for the resin with $r = 0.8$ may be a consequence of the branched structure in the resin with $r = 1.5$. This structure allows chain segments to move more easily than the unreacted bulky epoxy groups of the resin with $r = 0.8$.

In this paper, we use the peak-shift method [26,27] to calculate the non-linearity parameter x. When the peak temperature is analysed as a function of the enthalpy loss

Table 2
Values of the heat capacity increment (ΔC_p), relaxation rate per decade (β_H), non-linearity parameter (x), reduced apparent activation energy ($\Delta h^*/R$) and non-exponentiality parameter (β) for the three systems

r	ΔC_p (J ee^{-1} K)	β_H (J ee^{-1} K p.d.)	r^a	dT_p/dlog t_a (K p.d.)	r^b	x	$\Delta h^*/R$ (kK)	β
1	108±6	204±6	0.990	2.24±0.06	0.994	0.40±0.02	116±7	$0.3 < \beta < 0.4$
1.5	164±3	360±11	0.987	1.70±0.09	0.971	0.50±0.02	89±4	$0.3 < \beta < 0.4$
0.8	104±3	325±7	0.994	2.60±0.07	0.993	0.49±0.03	85±4	$0.3 < \beta < 0.4$

[a] Correlation coefficient of the linear fit of the enthalpy loss against log (annealing time).

[b] Correlation coefficient of the linear fit of the peak temperature against log (annealing time).

at T_a, the following dimensionless peak shift is obtained:

$$\hat{s}(\bar{D}) = \Delta C_p \left[\frac{\partial T_p}{\partial \Delta H} \right]_{q_1, q_2, T_a}, \tag{3}$$

where q_1 and q_2 are the cooling and heating rates, respectively, which are maintained constant in these annealing experiments, as also is the annealing temperature T_a. It has been shown theoretically [25,26] that this peak shift is a strong function of the non-linearity parameter x

$$\hat{s}(\bar{D}) = F(x), \tag{4}$$

where $F(x)$ is a dimensionless function essentially independent of the distribution of relaxation times and which has been calculated theoretically to give a master curve [26]. This method has been applied successfully to determine the parameter x in other epoxy resins [8,9,11–13] as well as other glassforming systems.

The values of x obtained by the peak-shift method for the three different epoxy formulations are shown in Table 2. The value of x for $r = 1$ is 0.4 ± 0.02 and for $r = 1.5$ and $r = 0.8$ is 0.50 ± 0.02 and 0.49 ± 0.03, respectively. Taking into account that $x = 0$ implies a pure structural dependence for the relaxation time, and $x = 1$ implies a pure temperature dependence, these results indicate that there is a greater contribution of the structure to the relaxation time for the stoichiometric resin than for the non-stoichiometric resins. Moreover, since the non-linearity increases as x decreases, this means that the degree of non-linearity is higher in the stoichiometric formulation. The modification of the stoichiometry of the resin introduces important changes in the physical structure of the network, and these results show that the non-linearity parameter decreases for the network formed with all the chemical groups reacted, without branching and with no unreacted epoxy groups. From this observation, one may conclude that the x parameter depends on the physical structure of the network.

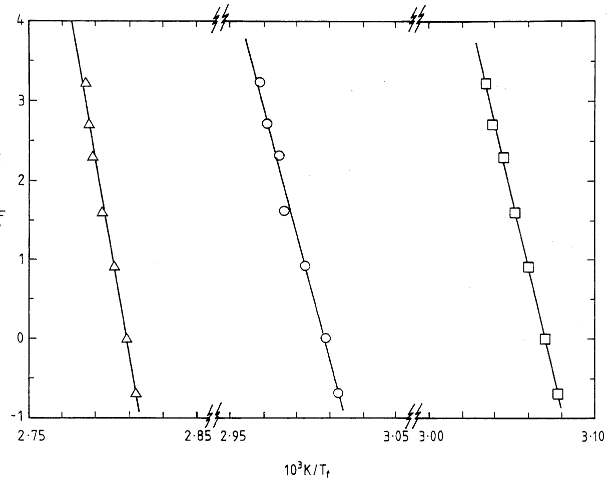

Fig. 5. Plot of logarithm of the cooling rate versus reciprocal fictive temperature for the three stoichiometric ratios.

3.3. Intrinsic cycles. Apparent activation energy

The experiments involving cooling at different rates and immediately reheating at a constant rate allow the evaluation of the apparent activation energy, Δh^*, from the dependence of the fictive temperature, T_f, on the cooling rate, q_1, in such intrinsic cycles. The appropiate equation proposed by Moynihan et al. [17]

$$\frac{\Delta h^*}{R} = -\left[\frac{\partial \ln|q_1|}{\partial (1/T_f)} \right]_{\Delta H = 0}, \tag{5}$$

where the condition $\Delta H = 0$ implies the need for intrinsic cycles. Fig. 5 shows the dependence of ln $|q_1|$ on $1/T_f$ for all the systems studied, from which the slopes give the values of the apparent activation energy which are listed in Table 2. The value of $\Delta h^*/R$ is very similar for the two non-stoichiometric resins (89 ± 4 kK for $r = 1.5$ and 85 ± 4 kK for $r = 0.8$) and is about 30% greater for the stoichiometric resins (116 ± 7 kK). The decrease in $\Delta h^*/R$ for the non-stoichiometric samples is compatible with the corresponding increase in the relaxation rate, β_H.

The value of the apparent activation energy for the ratio $r = 1$ is in good agreement with values found for other fully cured epoxy resins in stoichiometric conditions: 124 kK for a DGEBA–ethylenediamine [11], 112 kK for a DGEBA-Jeffamine D230 [11] and 120 kK for a DGEBA-anhydride [8]. This large value for the activation energy is related to a relaxation process which involves a large number of chain segments. The lower values of $\Delta h^*/R$ in the off-stoichiometry resins involves a smaller number of chain segments in the relaxation process.

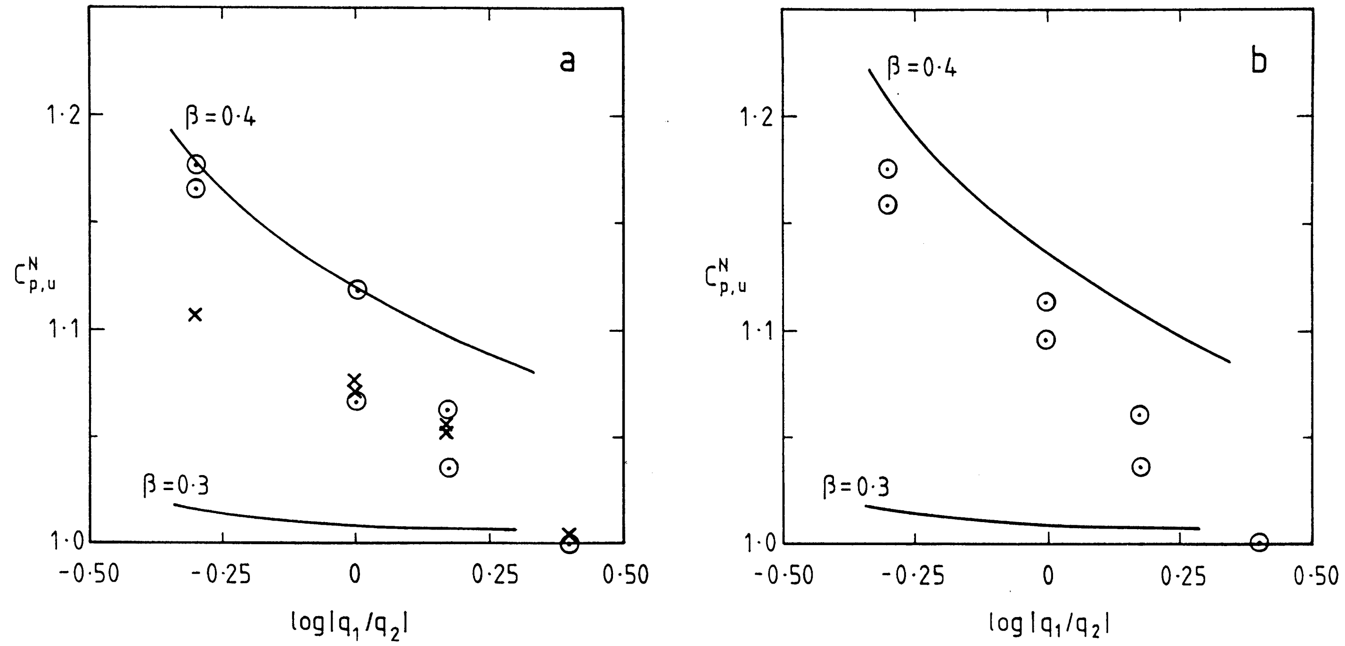

Fig. 6. Normalized upper peak height ($C^{N}_{p,u}$) versus ratio of cooling rate to heating rate for the resin systems: (a) $r = 1.5$, open circles; $r = 0.8$, crosses; $x = 0.5$; (b) $r = 1.0$, $x = 0.4$. Full lines represent theoretical variation for values of β indicated.

3.4. Estimation of the non-exponentiality parameter

An upper peak can be observed in intrinsic cycles for which the cooling rate is greater than the heating rate [28]. The dependence of this upper peak on the experimental variables is different from that found in the peak obtained from annealing experiments (main peak). One characteristic of the upper peak is its greater sensitivity to the non-exponentiality parameter than to the non-linearity parameter, since the glass is not very far from equilibrium at the endothermic peak if it has not previously been annealed. From these intrinsic cycles a normalised upper height $C^{N}_{p,u}$ can be defined

$$C^{N}_{p,u} = \frac{C_{p,u} - C_{p,g}}{C_{p,l} - C_{p,g}}, \tag{6}$$

where $C_{p,u}$ is the value of C_p at the upper peak temperature T_u, and $C_{p,l}$ and $C_{p,g}$ are the values of C_p corresponding to the equilibrium liquid and the glassy states, respectively, extrapolated to T_u.

In Fig. 6a the dependence of $C^{N}_{p,u}$ on the ratio of the cooling and heating rates $|q_1/q_2|$ for the non-stoichiometric systems is shown and is compared with the theoretical values of $C^{N}_{p,u}$ corresponding to the KWW function [18] for two different values of β (0.3 and 0.4) and for $x = 0.5$. This value of x was chosen as it corresponds very closely to that obtained for both of the off-stoichiometry resins. On the other hand, the same KWW function and the same values of β were combined with a value of $x = 0.4$ to provide the theoretical dependence for the stoichiometric resin with $r = 1$, which are compared with the experimental data in Fig. 6b. These results give an estimation of β between 0.3 and 0.4 for all the systems studied, with no significant differences of β between the three resins.

3.5. Correlation of x, β and Δh^*

Hodge has reported correlations between x, β and Δh^* in polymeric glasses [29–31], and it is common to observe a decrease of Δh^* as x increases. In good agreement with this correlation, the value of $\Delta h^*/R$ decreases as x increases, in parallel with departure from stoichiometry in the three resins analysed in the present work, as can be observed clearly in Fig. 7. In this figure, other results obtained for cross-linked polymer systems by the same methodology [8,9,11–13] are also represented. The majority of these epoxies, with the exception of the fully and partially cured epoxy-anhydride system discussed elsewhere [8,9], show this same trend, with all the data situated within a band between two straight lines, which has no significance other than to guide the reader's eye. As has been discussed previously in another paper [11], there is in general a good correlation of Δh^* with x, but it should not be considered a universal correlation, and has not yet received any satisfactory theoretical justification.

A linear correlation between β and x has also been described by Hodge [30,31], but a considerable dispersion is often observed. In our epoxies, when the formulation changes from $r = 1$ to either of the non-stoichiometric resins, it is not possible to discern any significant differences in the estimated of β with the increase of the parameter x.

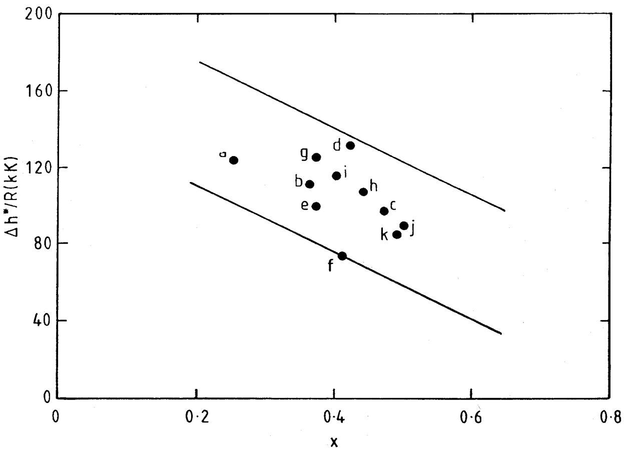

Fig. 7. Correlation of the reduced apparent activation energy with the non-linearity parameter for various epoxy systems. The letter close to each point indicates the particular epoxy system: (a) epoxy DGEBA cured with ethylenediamine [11]; (b) DGEBA cured with Jeffamine D-230 [11]; (c) DGEBA cured with Jeffamine D-400 [11]; (d) DGEBA cured with methyltetrahydrophthalic anhydride (fully cured) [8]; (e) as for (d), but with a reactive diluent [12]; (f) as for (d), but partially cured (70%) [9]; (g) DGEBA cured with an aromatic aminic hardener [13]; (h) as for (g), but with a carboxy terminated butadiene acrylonitrile copolymer [13]; (i) DGEBA cured with Jeffamine T-403 with a stoichiometric ratio $r = 1$ (this work); (j) as for (i), but $r = 1.5$ (this work); (k) as for (i), but $r = 0.8$ (this work). The faint parallel lines are drawn to guide the eye.

However, in other epoxy systems [11] an agreement with the usual trend of β increasing with x was found.

3.6. Non-linear Adam–Gibbs formulation

Originally, the Adam–Gibbs (AG) theory [32] was introduced to study the temperature dependence of the relaxation time in equilibrium, in the so-called cooperative relaxation processes of glass-forming liquids. The central assumption of the AG theory is that relaxation involves the cooperative rearrangement of some molecular entities, namely main chain molecular segments in the case of linear polymers. Using the same terminology as in the original paper of AG, such rearrangements occur in cooperatively rearranging regions (CRR) consisting of z molecular segments, for which the activation energy may be written as $E = z\Delta\mu$, where $\Delta\mu$ is the elementary activation energy hindering the cooperative rearrangement of each segment. There is only the minimum value of z, denoted as z^*, which contributes significantly to the relaxation time. This lower limit z^* of the CRR is determined by a critical number of configurations available to the subsystem, and hence by the critical configurational entropy, s_c^*, of the CRR and by the macroscopic molar configurational entropy of the system, $S_c(T)$

$$\frac{z^*(T)}{s_c^*} = \frac{N_A}{S_c(T)}, \tag{7}$$

where N_A is Avogadro's number. $S_c(T)$ is the macroscopic configurational entropy and s_c^* is the configurational entropy of the smallest number of particles capable of rearranging.

The configurational entropy $S_c(T)$ is defined by the difference between the entropy of the liquid (undercooled) and the entropy of the 'crystal' [32], and can be calculated as

$$S_c(T) = \int_{T_2}^{T} \frac{\Delta C_p}{T}\, dT, \tag{8}$$

where T_2 is the temperature at which $S_c(T_2) = 0$. This temperature is the so-called Kauzmann temperature, but in the application of the AG theory to the glass transition is considered as an adjustable parameter. The relaxation time in equilibrium takes the following form:

$$\tau(T) = A \exp\left(\frac{N_A s_c^* \Delta\mu}{kTS_c(T)}\right), \tag{9}$$

where k is Boltzmann's constant. This equation shows that T_2 is the temperature where the relaxation time becomes infinite in equilibrium.

The AG theory was extended to the non-equilibrium glassy state by Scherer [33] and Hodge [34] with the assumption that the configurational entropy of the glass is a function only of the fictive temperature, hence written as $S_c(T_f)$. It follows from this assumption that the equation for the relaxation time in the glassy state is a function of both T and T_f, often referred to as the non-linear AG equation:

$$\tau(T, T_f) = A \exp\left[\frac{N_A s_c^* \Delta\mu}{kTS_c(T_f)}\right]. \tag{10}$$

3.6.1. Analysis assuming hyperbolic form for ΔC_p

As was pointed out by Hodge [34], to solve the integral equation (Eq. (8)) for $S_c(T)$ two possibilities for ΔC_p have commonly been considered: $\Delta C_p = CT_2/T$ and $\Delta C_p =$ constant. Both lead to mathematically different expressions for τ but to quantitatively similar values. Considering the first expression for ΔC_p, in which C is the value of ΔC_p at T_2, the following equation for the relaxation time is obtained:

$$\tau(T, T_f) = A \exp\left[\frac{B}{T[1 - (T_2/T_f)]}\right], \tag{11}$$

where

$$B = \frac{N_A s_c^* \Delta\mu}{kC}. \tag{12}$$

Comparing the TNM equation (Eq. (1)) and the non-linear AG expression for the dependence of τ on T in equilibrium and at constant fictive temperature, the parameters from the two models may be related [34]

$$x \approx 1 - \frac{T_2}{T_f}, \tag{13}$$

$$\frac{\Delta h^*}{R} \approx \frac{B}{x^2}. \tag{14}$$

Table 3
Values of Adam–Gibbs parameters and related quantities for the three analysed systems, assuming a hyperbolic variation for $\Delta C_p = CT_2/T$

r	C (J ee^{-1} K)	T_2 (K)	T_g/T_2	B (kK)	$T_g - T_2$ (K)	$S_c(T_g)$ (J ee^{-1} K)	$N_A s_c^* \Delta\mu/k$. J ee^{-1}	z^* (T_g) $\Delta\mu/k$ (kK)
1	180	216.3	1.67	18.6	144.2	72.0	3341	46.4
1.5	328	165.0	2.00	22.3	165.0	164.0	7298	44.5
0.8	204	171.4	1.96	20.4	164.6	99.9	4162	41.6

Hence it is possible to evaluate the non-linear AG parameters, B and T_2, from the TNM parameters determined experimentally and given in Table 2; the results are presented in Table 3. Assuming the hyperbolic dependence for ΔC_p, it can be seen that B increases and T_2 decreases as the resins depart from the stoichiometric ratio $r = 1$, in the direction of either increasing or decreasing r. Following equation [13], the increase in T_2 corresponds to the decrease in x (see Table 2) as r approaches unity from either of the non-stoichiometric resins. However, in common with observations made in a previous paper [11], a closer examination of the absolute values of T_2 in Table 3 shows that this temperature is much further below T_g than would normally be anticipated for polymers. In fact, $T_g - T_2$ in Table 3 takes values between 144 and 165 K, whereas the 'universal' value derived from the WLF equation is 51.6 K [35]. The attainment of these anomalously low T_2 values has also been noted for other polymeric systems [11,36], and a recent reappraisal of the non-linear AG formalism [37] suggests, in fact, that this problem arises from the way in which the non-linearity has, until now, usually been introduced through $S_c(T_f)$. This possibility will be examined in more detail further below.

Despite the apparently anomalous values of T_2, we can continue the analysis of the other quantities of the current non-linear AG theory. The quantity $N_A s_c^* \Delta\mu/k$, which is equivalent to the product BC, is calculated and given in Table 3, and it is found to increase significantly as r departs from unity, both to $r = 0.8$ and to $r = 1.5$. The values of $S_c(T_g)$ and $z^*(T_g)\Delta\mu/k$ are also shown in Table 3: the former increases significantly in both of the non-stoichiometric formulations, whereas the latter, which is equal to $x\Delta h^*/R$ and represents the activation energy at constant fictive temperature, decreases by only about 10% as the ratio r decreases from 1 to 0.8, and by rather less for $r = 1.5$. In other networks with different chemical structures [11], changes of about 20% were observed.

3.6.2. Analysis assuming constant ΔC_p

In the same way as the analysis above has been made, one can consider $\Delta C_p = C' =$ constant and obtain the following equations:

$$\frac{x}{1-x} \approx \ln\left(\frac{T_f}{T_2}\right), \tag{15}$$

$$B' \approx \frac{x^2}{(1-x)} \frac{\Delta h^*}{R}. \tag{16}$$

A similar analysis using the foregoing procedure has been performed, and the results are given in Table 4. It can be seen that the AG related quantities $N_A s_c^* \Delta\mu/k$, $S_c(T_g)$ and $z^*(T_g)\Delta\mu/k$ are independent of the choice of temperature dependence for ΔC_p, as can be shown easily from the above equations [$N_A s_c^* \Delta\mu/k = (x^2/(1-x))(\Delta h^*/R)\Delta C_p$; $S_c(T_g) = (x/(1-x))\Delta C_p$; $z^* T_g \Delta\mu/k = x\Delta h^*/R$], while the quantities B (or B'), C (or C') and T_2 differ significantly. The values of T_2 assuming $\Delta C_p =$ constant are lower than those obtained assuming a hyperbolic variation of ΔC_p, so the problem presented before is even more pronounced when ΔC_p is constant.

3.6.3. Analysis assuming 'universal' value for $T_g - T_2$

An alternative approach is to assume the 'universal' WLF relation $T_g - T_2 = 51.6$ K in order to determine T_2, and then to use the relationship between B and T_2

$$B = \frac{\Delta h^*}{R}\left(1 - \frac{T_2}{T_g}\right)^2 \tag{17}$$

derived by combining Eqs. (13) and (14), in order to calculate B for each resin assuming the hyperbolic variation of ΔC_p. The quantities $N_A s_c^* \Delta\mu/k$, $S_c(T_g)$ and $z^*(T_g)\Delta\mu/k$ are then easily calculated, and are presented in Table 5. The equivalent results assuming $\Delta C_p =$ constant are shown in Table 6 using the following equation:

$$B' = \frac{\Delta h^*}{R}\left[\frac{\ln(T_g/T_2)}{1 + (1/\ln(T_g/T_2))}\right] \tag{18}$$

derived by combining Eqs. (15) and (16).

Table 4
Values of Adam–Gibbs parameters and related quantities for the three analysed systems, assuming $\Delta C_p = C' =$ constant

r	C' (J ee^{-1} K)	T_2 (K)	T_g/T_2	B' (kK)	$T_g - T_2$ (K)	$S_c(T_g)$ (J ee^{-1} K)	$N_A s_c^* \Delta\mu/k$ (J ee^{-1})	z^* (T_g) $\Delta\mu/k$ (kK)
1	108	185.1	1.95	30.9	175.4	72.0	3341	46.4
1.5	164	121.4	2.72	44.5	208.6	164.0	7298	44.5
0.8	104	128.6	2.61	40.0	207.4	99.9	4162	41.6

Table 5
Values of Adam–Gibbs parameters and related quantities for the three analysed systems, assuming $T_2 = T_g - 51.6$ K and a hyperbolic variation for $\Delta C_p = CT_2/T$

r	C (J ee^{-1} K)	T_2 (K)	T_g/T_2	B (kK)	$T_g - T_2$ (K)	$S_c(T_g)$ (J ee^{-1} K)	$N_A s_c^* \Delta\mu/k$ (J ee^{-1})	$z^*(T_g)\ \Delta\mu/k$ (kK)
1	126	308.9	1.17	2.38	51.6	18.0	299.5	16.6
1.5	194	278.4	1.19	2.18	51.6	30.4	423.0	13.9
0.8	123	284.4	1.18	2.00	51.6	18.9	246.3	13.0

Table 6
Values of Adam–Gibbs parameters and related quantities for the three analysed systems, assuming $T_2 = T_g - 51.6$ K and $\Delta C_p = C' =$ constant

r	C' (J ee^{-1} K)	T_2 (K)	T_g/T_2	B' (kK)	$T_g - T_2$ (K)	$S_c(T_g)$ (J ee^{-1} K)	$N_A s_c^* \Delta\mu/k$ (J ee^{-1})	$z^*(T_g)\ \Delta\mu/k$ (kK)
1	108.0	308.9	1.17	2.40	51.6	16.7	258.9	15.5
1.5	164.0	278.4	1.19	2.20	51.6	27.9	360.7	12.9
0.8	104.0	284.4	1.18	2.03	51.6	17.3	210.6	12.1

In this case, the parameters B and B' are essentially equal for the different assumptions about ΔC_p, but are now decreased in the non-stoichiometric resins relative to that with $r = 1$, whereas the opposite (an increase) was observed in Tables 3 and 4. Similarly, whereas in Tables 3 and 4 the AG related quantities $S_c(T_g)$, $N_A s_c^* \Delta\mu/k$ and $z^*(T_g)\Delta\mu/k$ were all independent of the assumption about ΔC_p, in Tables 5 and 6 there is a small variation in their values. Nevertheless the trend with changing stoichiometry remains the same between Tables 5 and 6, and is interestingly different from that observed in Tables 3 and 4 with respect to the quantity $N_A s_c^* \Delta\mu/k$. This is best seen by reference to Figs. 8 and 9, where each of these AG quantities, denoted in general by Q, is represented as a value normalised to that obtained for $r = 1$ and is plotted as a function of the stoichiometric ratio r. For example, in all cases the off-stoichiometry resins always show a relative increase in $S_c(T_g)$ and a relative decrease in $z^*(T_g)\Delta\mu/k$ (refer to Fig. 8); it is only the magnitude of the change which depends on whether the anomalously low values of T_2 are accepted (Tables 3 and 4) or the 'universal' WLF value is used (Tables 5 and 6). We may

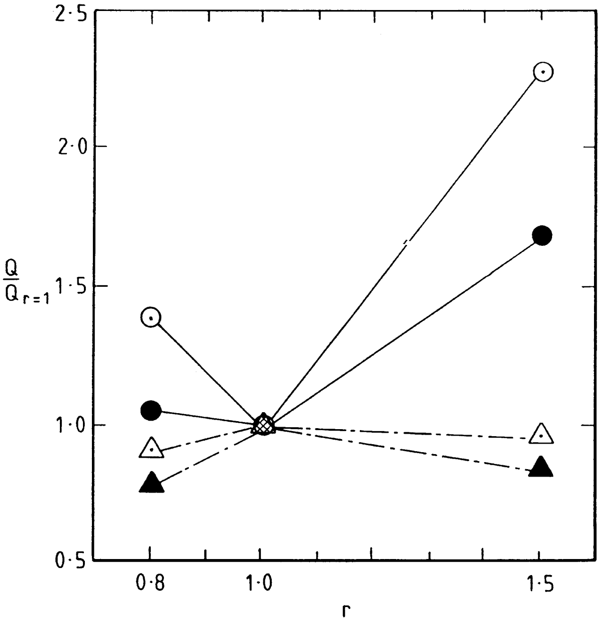

Fig. 8. Variation of the AG quantities Q, normalised to their values for $r = 1$, as a function of the stoichiometric ratio r. Open symbols refer to data from Tables 3 and 4, filled symbols to data from Tables 5 and 6 (these latter having been averaged); circles and full lines for $Q = S_c(T_g)$, triangles and dash–dotted lines for $Q = z^*(T_g)\Delta\mu/k$.

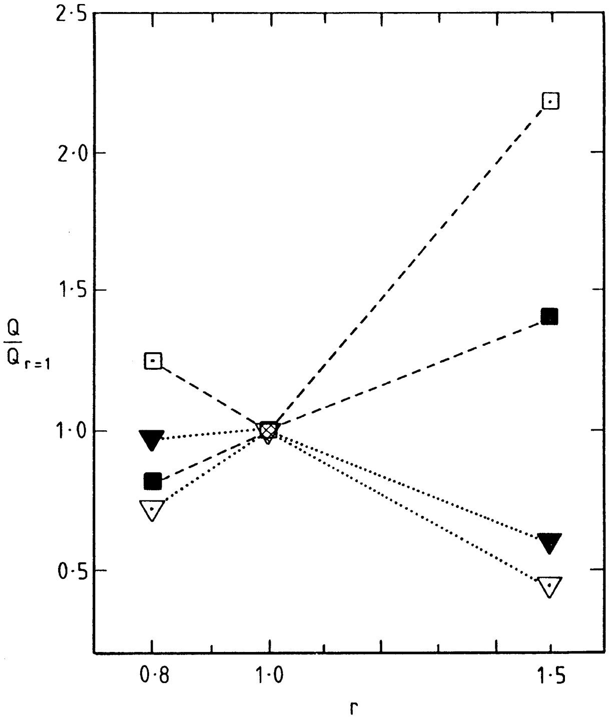

Fig. 9. Variation of the AG quantities Q, normalised to their values for $r = 1$, as a function of the stoichiometric ratio r. Open symbols refer to data from Tables 3 and 4, filled symbols to data from Tables 5 and 6 (these latter having been averaged); squares and dashed lines for $Q = N_A s_c^* \Delta\mu/k$, inverted triangles and dotted lines for $Q = z^*(T_g)/N_A s_c^*$.

therefore conclude that these trends with the stoichiometric ratio are real, as they are independent of the assumption made in the analysis. On the other hand, the quantity $N_A s_c^* \Delta\mu/k$ shows a relative increase for $r = 1.5$ for both analysis methods (refer to Fig. 9) but opposite effects for $r = 0.8$. As a consequence, it is difficult to draw any conclusions about this latter AG related quantity. These trends are discussed in more detail in the following section.

3.7. Evaluation of AG related quantities

Of the three AG related quantities discussed here, it is perhaps $S_c(T_g)$ which can most easily be interpreted in respect of the effect of the stoichiometry. In the first place, we note that the relative magnitudes of all the AG related quantities, and in particular of $S_c(T_g)$, are reduced when the temperature T_2 is constrained at its 'universal' WLF value. In our recent reappraisal of the application of the AG equation to the non-equilibrium glassy state [37], we reasoned that the explanation for T_2 being anomalously low in the usual AG analysis was that the assumption that the configurational entropy in the glassy state is a function only of the fictive temperature introduces excessive non-linearity into the analysis. This can easily be seen by examining the values of T_g/T_2 in Tables 5 and 6, which are smaller than the corresponding values in Tables 3 and 4. If we take these values from Tables 5 and 6 and use the normal AG relationship between x and T_2, given as Eq. (13) for Table 5 and Eq. (15) for Table 6, we obtain values of x between 0.14 and 0.16. These are extremely low values, and since small values of x indicate highly non-linear behaviour this clearly suggests that the usual AG expression, Eq. (10), for the non-equilibrium glassy state introduces excessive non-linearity.

This argument rationalises the observed reduction in the relative magnitudes of $S_c(T_g)$ shown in Fig. 8 (circles); the relative magnitudes of all the AG related quantities in Tables 3 and 4 are too large, because their evaluation through the use of Eqs. (13) and (15), respectively, introduced too much non-linearity. In particular with respect to $S_c(T_g)$, the excessive non-linearity leads directly to overestimates of the configurational entropy at T_g. If we take, therefore, the values from Tables 5 and 6 (though the same trends are also observed from Tables 3 and 4), indicated as filled circles in Fig. 8, it is evident that a departure from the stoichiometric ratio $r = 1$ causes a significant increase in the configurational entropy at T_g for $r = 1.5$ whereas for $r = 0.8$ the value of Q remains rather close to unity. While an increase of configurational entropy with respect to $r = 1$ would be anticipated intuitively for both $r = 0.8$ and $r = 1.5$, it is interesting to observe that the relative change in configurational entropy for these two off-stoichiometric resins shows the opposite behaviour to that of T_g, shown in Fig. 2, for which the greater change was observed for $r = 0.8$. If free volume is the explanation for the changes in T_g, then the implication is that configurational entropy and free volume do not follow a simple correlation, a conclusion that has been reached on several other occasions (e.g. see discussion in Ref. [38]). Evidently the branching and occasional ring structures associated with the excess of amine ($r = 1.5$) create greater configurational possibilities than do the unreacted bulky epoxy groups situated at the end of the epoxidic chain in the case of the excess of epoxy ($r = 0.8$), even though the latter appears to be dominant in the production of free volume. Again, this seems to be intuitively reasonable.

It is appropiate now to turn to aspects related to the CRR, namely s_c^* and $z^*(T_g)$. Unfortunately, it is not possible to evaluate these independently, since they appear always in a product with $\Delta\mu$, the fundamental energy barrier, which itself is likely to be a function of the stoichiometric ratio and corresponding network structure. Under these circumstances, a possible approach is to determine the quantity $z^*(T_g)/N_A s_c^*$ from the ratio of the values in the last two columns of Tables 3–6. The results are shown as the inverted triangles in Fig. 9.

Now, the configurational entropy of the smallest rearranging chain segment, s_c^*, may be estimated from

$$s_c^* = k \ln W^*, \tag{19}$$

where W^* is the minimum number of configurations needed for the cooperative rearrangement. It has been argued by Hodge [30,31] that W^* may be approximated as 2^3, albeit with considerable uncertainty, for linear polymers, which are geometrically constrained. In the present resin systems we are concerned with even more constrained network structures, and hence might anticipate W^* to be even greater. In our earlier work on the effect of cross-link length on enthalpy relaxation in fully cured stoichiometric epoxy-diamine resins [11], we considered both $W^* = 2^3$ and $W^* = 2^4$ as possibilities, and although the resulting magnitudes of the relevant AG related quantities was obviously influenced by this choice, it was shown that the trend with cross-link length was always the same.

Proceeding, therefore, on the assumption that W^*, and hence s_c^*, is practically the same for all three resin systems, it follows that the quantity Q indicated by the inverted triangles in Fig. 9 represents the dependence of $z^*(T_g)$ on the stoichiometric ratio. Interestingly, we see that it is the stoichiometric system with $r = 1$ for which $z^*(T_g)$ is highest, and that it reduces for each of the non-stoichiometric systems, albeit very slightly, if at all, for the filled symbol at $r = 0.8$. This means that the lower limit for the size of the CRR, and hence the number of molecular entities that are involved in the relaxation process, is greater in the stoichiometric system. This appears to be perfectly reasonable, given that its network structure is more compact, whereas the non-stoichiometric systems have a more open structure with correspondingly less requirement for cooperativity in the relaxation.

In fact, if the assumption of a 'universal' WLF value for T_2 is made (filled symbols in Fig. 9), the reduction in $z^*(T_g)$ is significantly greater for the resin with excess amine than it is for that with excess epoxy. Indeed, the latter has a value very close to unity, in parallel with the corresponding value of $S_c(T_g)$ in Fig. 8. This confirms our interpretation that the excess epoxy has little effect on the configurational rearrangements, but contributes to the relaxation through its influence on the free volume.

These arguments also permit us to examine the relative values of the fundamental energy barrier, $\Delta\mu$, to the cooperative rearrangements. Since we have assumed that s_c^* is practically the same for all three resin systems, it follows that the quantity Q identified by the squares in Fig. 9 is directly proportional to $\Delta\mu$. Considering again the results obtained assuming the 'universal' WLF values for T_2 (filled symbols), since these correspond to the most intuitively reasonable interpretation, it can be seen that, relative to the value for $r = 1$, $\Delta\mu$ decreases for $r = 0.8$, whereas it increases for $r = 1.5$. This should be compared with the experimentally measured reduced apparent activation energies, $\Delta h^*/R$, which are listed in Table 2 and show a different trend: $\Delta h^*/R$ decreases for both of the non-stoichiometric resins relative to the value for $r = 1$.

In interpreting this result, it must be remembered that $\Delta\mu$ and Δh^* represent different energies. The former is the fundamental barrier to molecular rearrangement within the CRR, whereas the latter is an overall activation energy resulting from the convolution of this fundamental activation energy barrier with the need for a cooperative rearrangement of a number of molecular segments, this number being determined by z^*. It was shown above that, for $r = 0.8$, z^* was almost equal to the value for $r = 1$ (filled inverted triangles in Fig. 9), while $\Delta\mu$ decreases (filled square in Fig. 9). Thus, for $r = 0.8$ compared with $r = 1$, while the cooperativity remains almost constant the fundamental energy barrier decreases, resulting in an observed decrease in the apparent activation energy Δh^*.

On the other hand, for $r = 1.5$ compared with $r = 1$ we see a decrease in the cooperativity (z^*, filled inverted triangles in Fig. 9) whereas the fundamental energy barrier increases (filled squares in Fig. 9). The overall effect will depend on the relative influence of each of these contributions. Since the apparent activation energy Δh^* decreases on going for $r = 1$ to 1.5, it appears that it is the effect of the cooperativity (z^*) which dominates.

3.8. New approach to configurational entropy in the glassy state

It is abundantly clear from the above discussion that the absolute magnitudes of the various AG related quantities Q depend on whether they are taken from Tables 3 and 4 or from Tables 5 and 6. We have argued that the latter values are more reasonable, and most of our interpretations have been developed accordingly. Our argument is based upon a recent reappraisal of the usual non-equilibrium AG expression [37] in which it is proposed that the configurational entropy in the glassy state is not a function only of the fictive temperature, $S_c(T_f)$, but it is a function of both thermodynamic and fictive temperatures, $S_c(T, T_f)$, with a partitioning parameter x_s determining their relative contributions

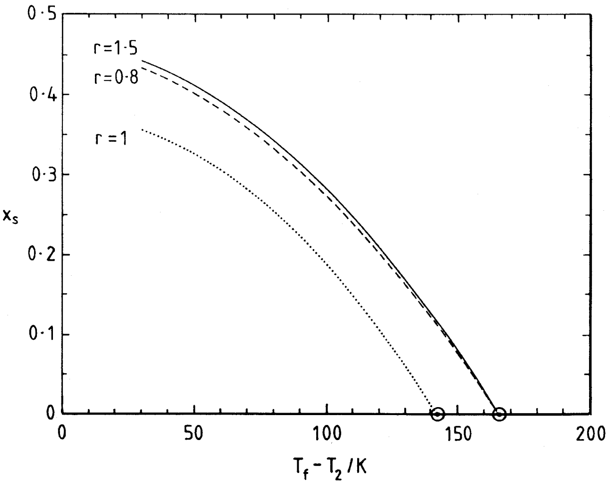

Fig. 10. Plot of entropic non-linearity parameter x_s as a function of the temperature difference $T_f - T_2$ for the three resin systems, calculated using Eq. (21), and assuming $T_f = T_g$.

$$S_c(T, T_f) = x_s S_c(T) + (1 - x_s) S_c(T_f), \tag{20}$$

The parameter x_s ($0 \leq x_s \leq 1$) is referred to as an entropic non-linearity parameter. Clearly, when $x_s = 0$ Eq. (20) reduces to the conventional AG dependence for the configurational entropy in the glassy state, whereas for $x_s = 1$ there is no fictive temperature dependence, and the system remains in equilibrium. It is possible to derive some interrelationships between the various parameters, one of which can be written as

$$1 - x_s \approx (1 - x)\frac{T_f}{T_2} \tag{21}$$

when the relaxation process is occurring at an annealing temperature T_a sufficiently close to T_f that the departure from equilibrium is not excessive. For simplicity we consider this to be the case here. The usual AG relationship between x and T_2, Eq. (13), can thus be seen as a special case of Eq. (21) when $x_s = 0$, the lower limit of x_s. When $x_s > 0$, Eq. (21) implies that T_2 increases as x_s increases, and hence reasonable values of T_2 will result from certain values for the entropic non-linearity parameter. Furthermore, by considering the original statistical mechanical quasi-lattice theory of Gibbs and DiMarzio, GD [39], it is possible to relate x_s to molecular aspects of physical significance: values of x_s tending towards zero imply preferential freezing-in of high energy bond conformations, whereas values tending towards unity imply preferential freezing-in of holes (a more detailed discussion about these aspects may be found in Ref. [37]).

Eq. (21) can be used to examine the possible values of x_s that may arise when a range of T_2 values is considered, together with the measured values of T_f and x (in Tables 1 and 2, respectively). This is shown in Fig. 10, where x_s is plotted as a function of $T_f - T_2$ for the three resin systems. The points plotted for $x_s = 0$ correspond to the $T_f - T_2$ values obtained by means of Eq. (13) and listed in Table 3, since for simplicity we are considering here only the hyperbolic dependence for ΔC_p. The first conclusion to be drawn from this figure is that, for all the resin systems, the very high values of $T_f - T_2$, of the order of 150 K, found in Table 3 for $x_s = 0$, are significantly reduced for reasonable values of x_s, and can yield the 'universal' WLF value of $T_g - T_2$ for x_s between 0.3 and 0.4. Second, we note that for a constant value of $T_f - T_2$ for all the resins, the stoichiometric resin has a value of x_s significantly smaller than for the off-stoichiometry resins. This implies that for the stoichiometric resin it is the high-energy bonds that are preferentially frozen-in at T_g, while for the off-stoichiometry resin it is the freezing-in of holes which dominates. This is qualitatively in agreement with the interpretation discussed above whereby the off-stoichiometry resins have a higher free volume as a result of the structural implications of the excess epoxy and amine.

It might appear that the close proximity of the off-stoichiometry resins in Fig. 10 implies very similar values of x_s, and hence very similar freezing-in processes. This in turn could be somewhat contradictory with the argument that the excess epoxy and excess amine have different structural effects, as is clearly shown by the asymmetry of Figs. 8 and 9 with respect to $r = 0.8$ and $r = 1.5$. However, it must be remembered that it is not necessary, indeed it is even unlikely, that $T_f - T_2$ be the same for all resins; what one would expect is that $T_f - T_2$ should lie between, say, 40 and 100 K, which covers the range usually associated with most polymers [35]. Thus the choice of T_2 has an influence on the value of x_s, and the present work offers no independent means of evaluating T_2. Nevertheless, it is possible to rationalise our earlier arguments, namely that the freezing-in of holes (free volume) is more dominant in the resin with excess epoxy ($r = 0.8$) than in that with excess amine ($r = 1.5$), by associating a smaller value of $T_f - T_2$ with the former. For example, from Fig. 10, the combination of $T_f - T_2 = 50$ K and $x_s = 0.4$ for the resin with $r = 0.8$ and the combination of $T_f - T_2 = 75$ K with $x_s = 0.35$ for the resin with $r = 1.5$ would be in qualitative agreement with all our earlier arguments. We believe that this kind of approach can provide significant insight into the glass transition behaviour, but the discussion above shows that an independent evaluation of T_2 is essential.

4. Conclusions

Epoxy resins with either stoichiometric ($r = 1$) or non-stoichiometric formulations ($r = 0.8$, excess of epoxy; $r = 1.5$, excess of amine) of amine to epoxy have been studied with respect to their enthalpy relaxation behaviour. The non-linearity parameter x has been evaluated from ageing experiments of up to 3000 h at 20 K below the glass transition temperature (T_g), while the apparent activation energy Δh^* and non-exponentiality parameter have been evaluated from intrinsic cycles. There is an increase in x and a decrease in Δh^* in both of the non-stoichiometric resins relative to that with $r = 1$, from which it is concluded that x is sensitive to the network structure while the reduction in Δh^* indicates that a smaller number of chain segments is involved in the relaxation process for the off-stoichiometry resins.

When the usual AG theory is applied, it is found that the configurational entropy at T_g increases in the off-stoichiometry resins, indicative of their less tightly cross-linked network structure. If it is further assumed that W^*, the minimum number of configurations needed for a cooperative rearrangement, is the same for each resin, it can be concluded that z^*, the lower limit of the size of the cooperatively rearranging region, is larger for the stoichiometric resin than it is for either of the off-stoichiometry systems. Again this is compatible with the tighter network structure of the former.

This usual AG approach, however, leads to unreasonably low values for T_2, the second order thermodynamic transition at which the configurational entropy reduces to zero. This can be resolved by adopting a new approach to applying the AG equation in the glassy state, which involves both a thermodynamic temperature and fictive temperature dependence of the configurational entropy, with a parameter x_s, the entropic non-linear parameter, defining their relative contributions. In this way, the results can be interpreted with reasonable values for T_2 for each of the resins and with x_s values between 0.3 and 0.4. It is tentatively concluded that there is a lower value of x_s for the stoichiometric resin than for either of the other resins, suggesting that in the former it is the freezing-in of high energy bond conformations which predominates at the glass transformation, whereas in the latter it is the freezing-in of holes, or free volume, which predominates. This interpretation correlates well with the measurements of both T_g and configurational entropy at T_g, and is in agreement with perceived ideas about the different kinds of network modification caused by stoichiometric ratios both less than (excess epoxy) and greater than (excess amine) unity.

Acknowledgements

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