Journal of Thermal Analysis, Vol. 48 (1997) 297-307

GLASS TRANSITIONS IN CROSSLINKED EPOXY NETWORKS

Kinetic aspects

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(Received April 10, 1995; in revised form January 20, 1996)

Abstract

Epoxy resins of DGEBA type were thermally cured with diaminodiphenylmethane as crosslinking agent, and then analysed by Differential Scanning calorimetry (DSC) at various heating rates in order to determine the glass transition temperature T_g of the final networks. First it was shown that during cycling T_g is shifted towards higher values up to a maximum or T_{g_∞}. Such a change is attributed to an increasing extent of cure which develops during the thermal analysis, and also to relaxation processes thermally activated inside the polymeric matrix. Then the dependence of T_{g_∞} on the heating rate q imposed by the DSC apparatus was presented for q changing from 0.1 to 10°C min^{-1}. At heating rates exceeding 3°C min^{-1} only the classical temperature T_g was detected, but at smaller q values, an additional endothermic transition was revealed, located at higher temperature and linked to a physical aging-like phenomenon, which takes place at low heating rates. The plot of T_{g_∞} against log$q$ is divided into two quasi-linear parts on each side of q=3°C min^{-1}. In conclusions, an equation was given to describe the T_{g_∞} *vs.* log$q$ function.

Keywords: DSC analysis, epoxy resins, heating rate, glass transition

Introduction

Thermosetting prepolymers including epoxy resins of DGEBA type and tetrafunctional amines as crosslinking agents are currently used when cured as organic matrices for composite materials [1]. They are also considered as model systems for general studies on the kinetics of curing and the thermal characterization of three dimensional polymeric networks. Nevertheless, in spite of the great number of research groups working in the epoxy field, the actual knowledge of the ep-

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0368–4466/97/ $ 5.00

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oxy materials is not yet complete, since significant results are still being published in the area. However, the glass transition temperature T_g of an epoxy network is always considered as a main experimental parameter which is correlated with the extent of crosslinking, that is to say that T_g varies with the degree of cure. Particularly, a mathematical formula has been proposed [2] for the calculation of the extent of conversion of a thermosetting resin from its T_g value and the corresponding T_{g_∞}, or infinite value, of the same sample crosslinked at maximum through post-curing inside an oven at high temperature. But the experimental determination of T_g and T_{g_∞} still produces problems, because their values depend on the heating rate of the samples imposed by Differential Scanning Calorimetry (or DSC) commonly used for such measurements, the resolution of the thermal curves and the performance of the DSC equipment used. On the other hand, and especially in the case of crosslinked epoxy resin/curing amino agent systems, the variations of T_g due to long time thermal postcuring are not fully understood, because the chemistry of such systems is not yet well known. For instance, it is now admitted [3] that the extent of conversion of the stepgrowth polymerization reaction remains well below 100% in spite of efficient postcuring, that it is to say that a significant number of amino and epoxy groups are still unreacted. The contribution of van der Waals bonding between polar groups carried by the segments of the networks has also to be taken into consideration because it contributes to the hindrance of mobility of the polymeric segments and interferes in that way with the glass transition.

In the present paper a general study of the determination of T_g in crosslinked stoichiometric mixtures of DGEBA epoxy resin and DiaminoDiphentylMethane or DDM by DSC analysis, is reported with a view to better interpreting the glass transition in the epoxy networks and to optimizing their thermal characterization.

Experimental

The DSC equipment used was of SETARAM type, Model 111-B. The thermal analysis performed consists in the measurement of heat flow $Ø$ between an oven at programmed variable temperature T and aluminium pans containing polymeric samples to be tested. The rate of heating is $q = \mathrm{d}T/\mathrm{d}t$, where t is time. The curves $Ø = Ø(T)$ are continuously recorded; then the various inflexion points of the corresponding curves, which are linked to the transitions occurring in the polymers, are located in temperature on the basis of maxima or minima of the derivatives $Ø'(T) = \mathrm{d}Ø/\mathrm{d}T$. In the present case, this function is replaced by the derivatives $Ø'(t) = \mathrm{d}Ø/\mathrm{d}t$ which is justified since $\mathrm{d}Ø(t)/\mathrm{d}t = \mathrm{d}Ø(T)/\mathrm{d}T\,\mathrm{d}T/\mathrm{d}t = \mathrm{d}Ø/\mathrm{d}Tq$, with q constant. The true technical quality of such a DSC equipment is the possibility of analysing much larger amounts of sample (50–160 mg) than with other commercialized equipments, which provides facilities for a more accurate detection of transitions. Of course, for a given type of material, the suitable region of sample mass to be characterized has to be previously determined.

The condensation index of the DGEBA resin used (DER 332 from DOW CHEMICAL) in $n=0.06$. The curing agent is DDM from FLUKA (Ref: 32950).

First, DDM in fused state at 120°C is poured into the resin preheated at 60°C, in stoichiometric epoxide/amino proton ratio; then the mixture is mechanically stirred, degassed under vacuum and divided into portions of 20 g which are stored in cylindrical pyrex glass pill-boxes. Finally the samples are placed inside an oven (pulsed air) at 120°C for thermal curing during 24 h. Small pieces of the epoxy networks are taken for the DSC measurements.

Results and discussion

Figure 1 presents the curves $Ø=Ø(T)$ $Ø'(t)=dØ/dt$ recorded at $q=5°C\ min^{-1}$ for a sample (103.05 mg) of a DGEBA-DDM mixture cured at 120°C. The observed endothermal transition is the classical glass transition, given by the inflexion point of the thermal curve (Curve 1) and located in temperature at the minimum of $Ø'(t)=dØ/dt$. The corresponding T value is $T_{g_d}=185.0°C$. When the method of the asymptotes is used, one obtains $T_{g_a}=185.1°C$. The difference between T_{g_d} and T_{g_a} is not significant because of the linearity of the extreme segments of the $Ø$ curve which yields accurate data for T_{g_a}: when there is no linearity, the only possibility is to use the derivatives, which leads to T_{g_d}. Two other characteristic temperatures are also accessible: $T_1=168.1°C$ and $T_2=178.2°C$; T_2 is the onset value.

A postcuring can occur during DSC analysis, as it is shown in Fig. 2 which presents a series of curves recorded at $q=5°C\ min^{-1}$ for the same initial sample of crosslinked material. When the number of successive DSC runs increases, the $Ø$ curves are shifted towards higher T values; here, the corresponding T_{g_a} rises from

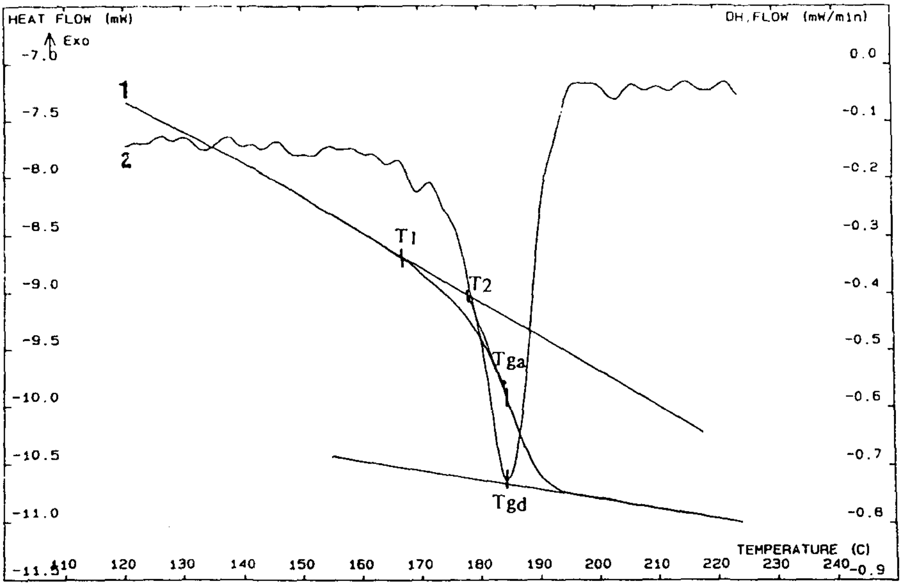

Fig. 1 DSC analysis of the epoxy network (103.05 mg) at $q=5°C\ min^{-1}$ (1): $Ø=Ø(T)$ (HEAT FLOW); (2): $Ø'=dØ/dt$ (DH. FLOW)

its initial level $T_{g_d}=168.4°C$ to a final value $T_{g_d}=185.0°C$ or $T_{g_{d\infty}}$. Such a variation of T_{g_d} has to be mainly attributed to postcuring which works at each DSC test and increases the extent of conversion of the polycondensation reaction. The change is especially pronounced between the first and the second thermal curve ($\Delta T_{g_d}=13.6°C$). However, no exothermal signal linked to the progress of the step-growth polymerization is observed because the process, hindered by the high viscosity of the polymeric medium, is distributed over large time or temperature domains, and it is opposed to the endothermal signal, linked to the phenomenon of glass transition. But relaxation processes in organic networks also contribute to the shifting of T_{g_d}, since a sample stabilized at $q=5°C\ min^{-1}$, and maintained at 20°C for a day for instance, has to be stabilized again, the starting T_{g_d} value being only one or two degrees lower than the preceding $T_{g_{b\infty}}$; on the other hand, the stabilization is now achieved only after two or three successive DSC runs. The interpretation of the relaxations involved cannot be provided at this time.

All the previous results observed at $q=5°C\ min^{-1}$ are reproducible provided that the T_{g_d} values and the shape of the thermal curves are not dependent on the weight of the samples to be analyzed, that it is to say that no thermal lag has to be taken into consideration. Figure 3 shows the dependence of $T_{g_{d\infty}}$ on the mass of sample to be analysed at $q=5°C\ min^{-1}$. $T_{g_{d\infty}}$ is practically constant as long as the mass of sample is chosen within the interval 50–160 mg, which is the working range of mass for the DSC equipment. Moreover, the corresponding thermal curves are similar in shape.

After this preliminary validation of the determination of T_{g_d} at $q=5°C\ min^{-1}$, the dependence of $T_{g_{d\infty}}$ on q was studied. Indeed, this study appears useful, since

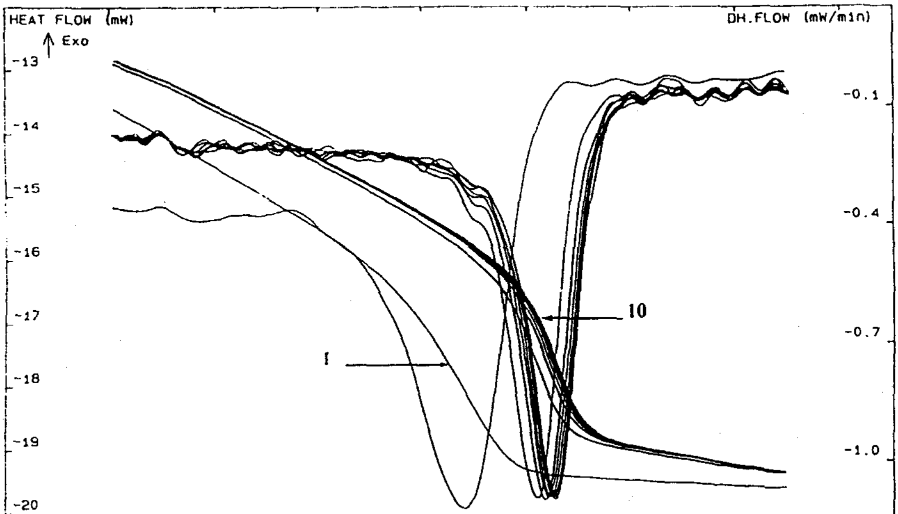

Fig. 2 Stabilization of the epoxy network at $q=5°C\ min^{-1}$ through successive DSC runs

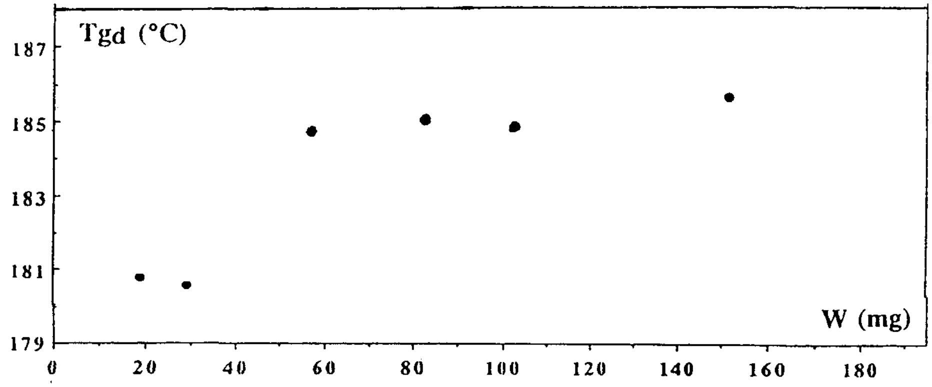

Fig. 3 Dependence of $T_{g_{d\infty}}$ on the mass of sample of epoxy network

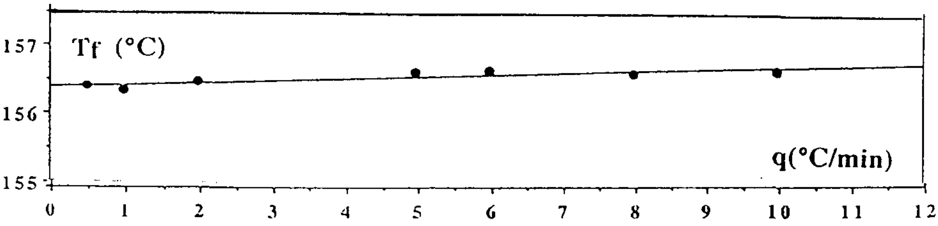

Fig. 4 Dependence of the onset temperature of fusion T_f of Indium on the heating rate (extrapolated value: 156.39°C)

most of the T_g measurements through DSC are currently carried out at two q values, 10 or 20°C min^{-1}, which are far from the quasi-static heating of the samples. On the other hand, one should also consider the problem of thermal lag when q varies. However, this can be alleviated as the onset temperature of fusion (T_f=156.4°C) of a sample (64.78 mg) of indium does not change much when q changes from 0.5 to 10°C min^{-1}, (Fig. 4). In addition, the shape of the respective thermal curves remains constant. Consequently, any thermal lag related to changes in q need not be taken into account. The extrapolation of these results to the case of the glass transition T_{g_d} of amorphous epoxy networks is allowed provided that the heating rate remains below 10°C min^{-1}, and the mass of the polymeric samples is between 50 and 160 mg.

After these statements, the dependence of T_{g_d} on q for the epoxy resins was investigated. Figure 5 shows various curves recorded at different q values, from 1 to 10°C min^{-1}, from a sample of crosslinked material (m=73.20 mg) pre-stabilized at q=5°C min^{-1}, expressing the variations of the normalized thermal flux $Ø(T)/q$, given in 60 mJ/°C. As long as q is higher than 3°C min^{-1}, a single endothermal transition of glassy type (T_{g_d}) is exhibited, whereas at lower heating rates a new endothermal transition is observed, located in temperature beyond T_{g_d} on the basis of the position of the minimum of the corresponding peak, or T_{peak}, when $Ø'(t)=0$ (Fig. 6). The positions of all charactheristic temperatures are presented in Fig. 6

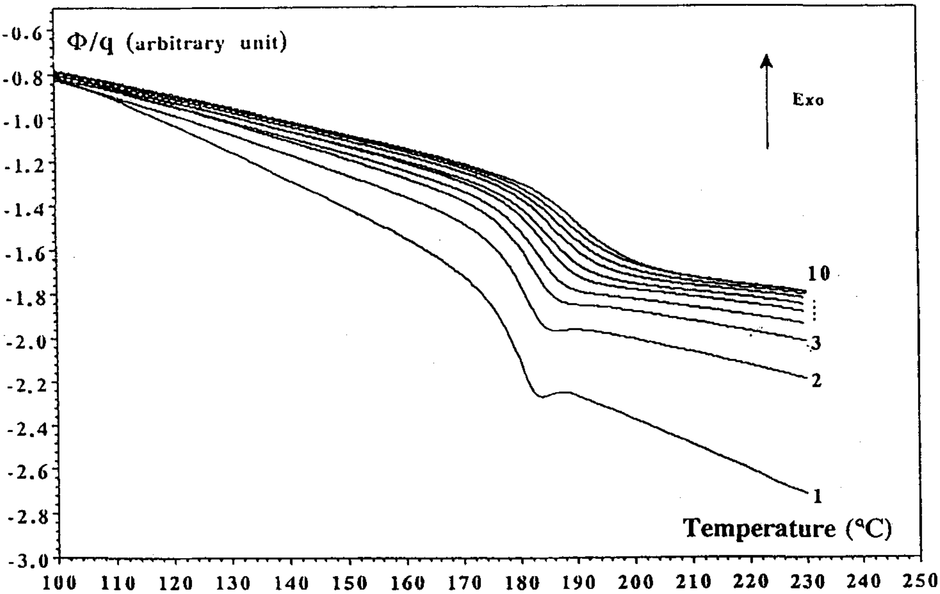

Fig. 5 Change of the normalized thermal flux $Ø/q$ with T for a given sample

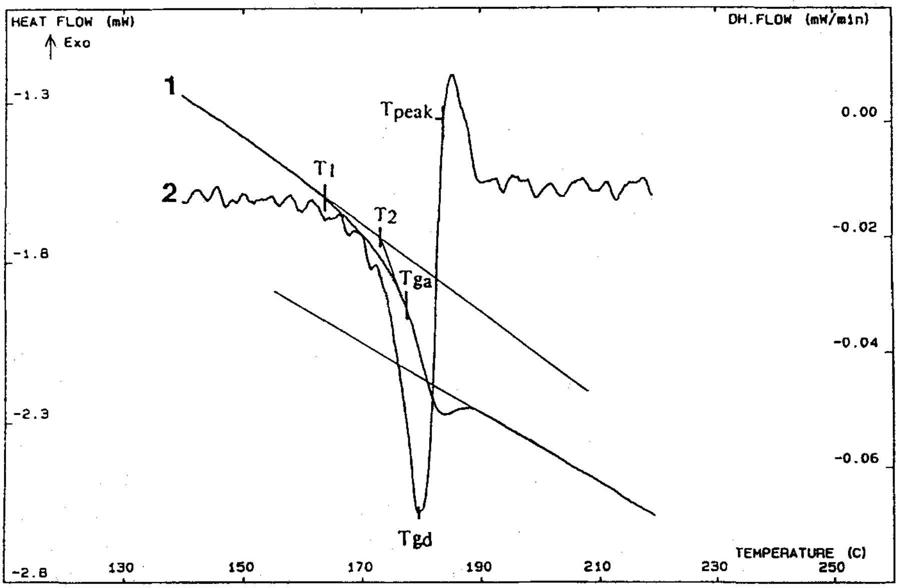

Fig. 6 DSC analysis at $q=1°C\ min^{-1}$ of a sample of epoxy network

for the experiment (m=73.20 mg) at q=1°C min^{-1} with T_1=163.9°C, T_2=172.6°C, T_{g_a}=176.8°C, T_{g_d}=179.4°C and T_{peak}=183.4°C. In addition to the possible existence of a second transition at temperatures higher than T_{g_d}, Fig. 5 shows that the curves are always confused in the glassy state, and that, on the contrary, they are more and more separated in the rubbery state, beyond T_{g_d}, the lowest rates leading to the highest flux or heat capacities. This variation is undoubtedly connected with the q values, since the flux at 230°C after the various heating procedures is identical for all q values, that is to say that the final physical state is not dependent on q.

The assignation of the high temperature transition (T_{peak}) requires careful discussion. It can be obviously assumed that it is not due to any thermal lag connected with too high heating rates or too large amounts of polymeric matter, since all precautionary measures have been taken before DSC testing. An interpretation is possible if one considers that at low heating rates the sample of polymeric matter spends a relatively long time at sub-T_g temperatures, which would induce a phenomenon of the physical aging type, also encountered in the case of linear atactic polystyrene [4] and crosslinked epoxy resins [5], and which develops well before T_g, and is displayed through a transition, classically detected beyond T_g and attributed to an enthalpic relaxation. Without any anticipation on the assignation of the high temperature transition, one can determine the associated enthalpy ΔH_f from the area under the peak limited by the Ø curve in this region and the straight line extrapolated from the final linear Ø segment, the peak temperature T_{peak} and the onset temperature T_{onset} determined from the tangent at the inflexion point in the Ø curve between T_{g_d} and T_{peak}. The results are listed in Table 1. All values of ΔH_f are compatible with those calculated for the sub-T_g annealing of polystyrene determined by DSC analysis at q=5°C min^{-1}. Such a result supports the attribution of the high temperature transition in the epoxy network to physical aging. Moreover, as expected, ΔH_f is the higher the lower the heating rate. The temperatures T_{peak} and T_{onset} vary with q as T_{g_d}, that it to say in the same sense as q.

Table 1 Dependence of the thermodynamic parameters of the high temperature transition on the heating rate q

q/°C min^{-1}	T_{gd}/°C	ΔH_f/J g^{-1}	T_{peak}/°C	T_{onset}/°C
1	179.4	0.361	183.4	180.9
2	180.8	0.191	186.1	183.6
3	181.7	0.114	188.4	186.9

A systematic study of the dependence of T_{g_d} on q has also been carried out, using the same sample per q value. Of course, each sample was pre-stabilized at q=5°C min^{-1} before a DSC analysis at given q, and its T_{g_d} determined at 5°C after this analysis. The invariability of T_g at 5°C min^{-1} indicates the preservation of the chemical structure of the network in spite of the thermal stress. Figure 7 shows the variation of T_{g_d} with the heating rate when q decreases from 10 to 0.1°C min^{-1}.

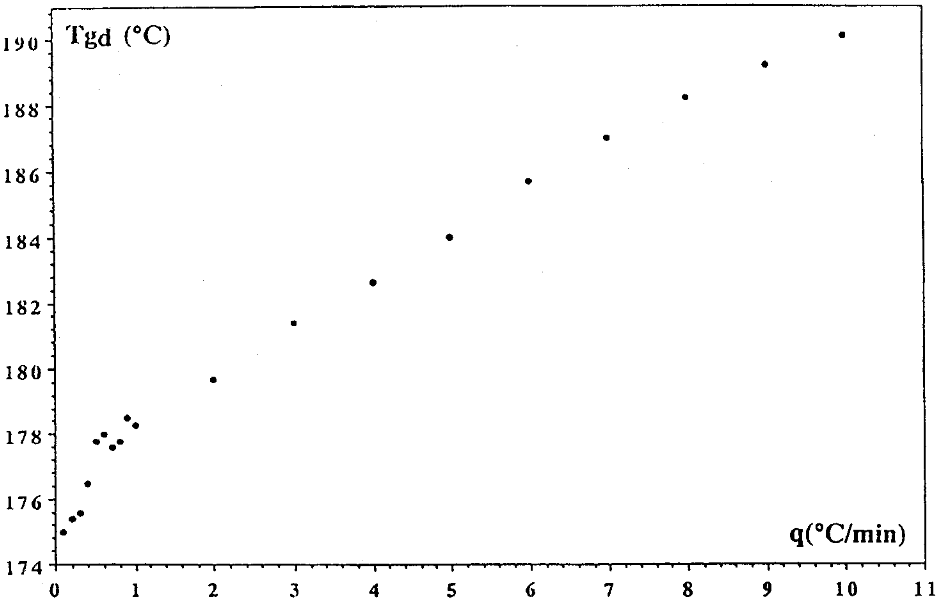

Fig. 7 Dependence of the glass transition temperature on q for a series of samples of epoxy network

T_{g_d} continuously goes down when q is decreased. A semi-logarithmic representation, T_{g_d} $\log q$, clears the situation (Fig. 8); the curve is divided into two linear parts intersecting at q=3.14°C min^{-1}. Beyond this critical q value a single transition or glass transition is detected, whereas for smaller heating rates another transition or high temperature transition appears. The variations of T_{g_d} in °C with $\log q$ are given by the following mathematical formulas, where q is expressed in °C min^{-1}:

$$\text{Part 1 (left)}\quad T_{g_{d\infty}} = 178.41 + 3.9319 \log q$$

$$\text{Part 2 (right)}\quad T_{g_{d\infty}} = 170.78 + 19.2640 \log q$$

By combining these equations, a general algebric expression can be provided

$$T_{g_{d\infty}} = T_{g_{do}} + \Delta\alpha\ [\log q - \log q_0]$$

$$\text{or } T_{g_{d\infty}} = T_{g_{do}} + \Delta\alpha\ [\log q/q_0]$$

with $\Delta\alpha$=15.3321°C, $\log q_0$=4976, q_0=3.1452°C min^{-1} and $T_{g_{do}}$=180.37°C.

The lowest T_{g_d} value which was detected by dynamic DSC is 175.0°C for q= 0.1°C min^{-1}. An approach of T_{g_d} at q=0°C min^{-1} (quasi-static heating) is carried out through the determination C_p^{d} (J g^{-1} K^{-1}) at variable temperature using the step heating method with $\Delta T=5°C$ and $q=1°C\ min^{-1}$ (Fig. 9). The position in temperature of the inflexion point gives a glass transition temperature: $T_g=174.0°C$, a value very close to that determined at $q=0.1°C\ min^{-1}$. This result is a proof that the measurements of T_{g_d} at low heating rate are not subject to thermal lag.

The activation energy of the glass transition ($T_{g_{d\infty}}$) can be determined using the equation introduced by H. Kissinger [6].

$$Ea=-k\frac{dLn(q/T^2_{g_{d\infty}})}{d(1/T_{g_{d\infty}})}$$

(k: Boltzmann constant)
provided there is linear relationship between $Ln(qT^2_{g_{d\infty}})$ and $1/T_{g_{d\infty}}$. The values of the activation energy are found, depending on whether q is higher or lower than $q_o=3.14°C\ min^{-1}$:

$$q<q_o\ E_{a1}=14.3\ eV/mol$$

$$q>q_o\ E_{a2}=3.7\ eV/mol$$

The difference between these two energies is certainly connected with the fact that a single transition of glassy type is observed if q is higher than $3.14°C\ min^{-1}$, when the glass transition is detected before the endothermal transition of the physical aging type occurs, which is not yet fully understood.

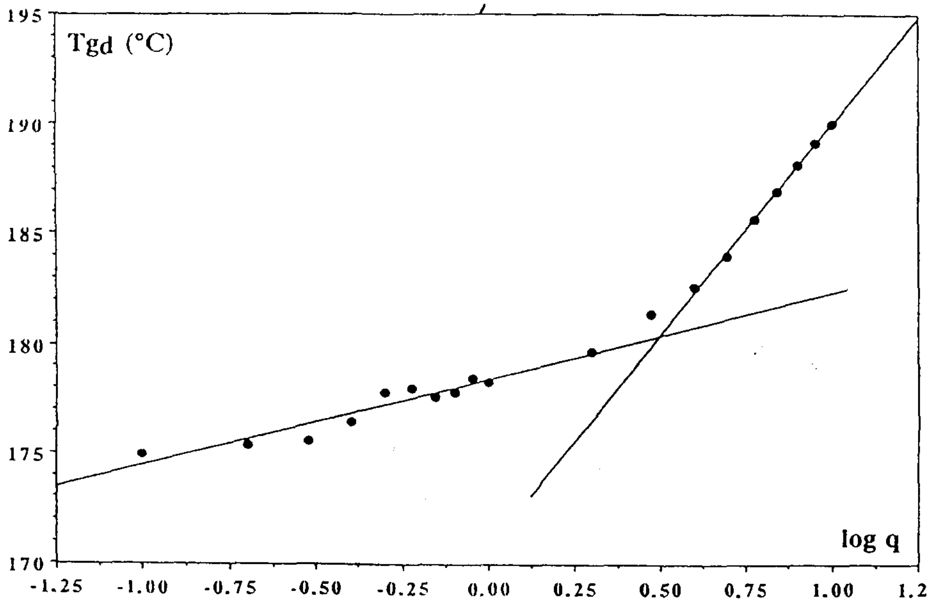

Fig. 8 Dependence of the glass transition temperature $T_{g_{d\infty}}$ of a series of samples of epoxy network on $\log q$

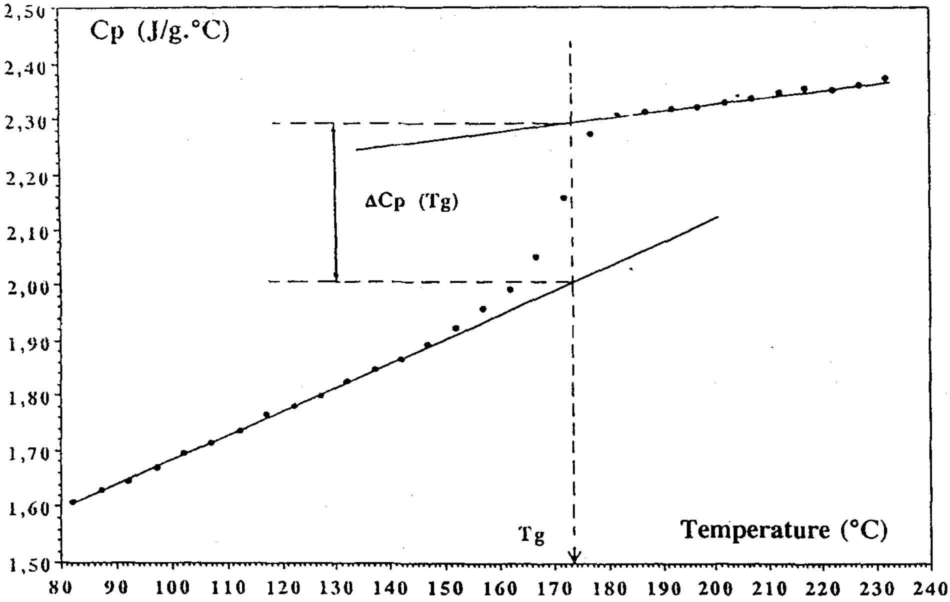

Fig. 9 Determination of $T_{g\infty}$ by the step heating method ($\Delta T=5°C$; $q=1°C$ min^{-1})

Conclusion

The present work on the glass transition in epoxy networks, where DSC analysis is used to study the thermal behaviour of such cosslinked materials, directs attention to several points:

- More than two successive DSC analyses between 20 and 230°C at given heating rate q are necessary to stabilize the glass transition temperature at Tg_{∞} or infinite value which is higher than the intermediate values; this shift has to be attributed to postcuring in the oven of the DSC apparatus and to relaxation phenomena inside the networks which depend on the heating rate.
- The glass transition temperature T_g depends on q and varies in the same sense as the heating rate ($T_g=189.5°C$ at $q=10°C$ min^{-1} and 179.4°C at $q=1°C$ min^{-1}); the dependence of T_g on log$q$ is linear on both sides of the q value of 3.14°C min^{-1}.
- At low heating rates ($q<3.14°C$ min^{-1}) an additional endothermal transition has to be taken into account, resulting from a physical aging, below T_g which becomes more pronounced as q is decreased.
- The thermal flux in the final rubbery state is also strongly dependent on the heating rate, its value increasing as q decreases; in other words, it is connected with relaxation processes inside the crosslinked polymeric materials.

The Tg values denoted by Tg_d, were determined from the DSC curves by means of the derivatives. The data thus determined are more precise than those provided by other DSC apparatus since we analyzed larger samples. This is the reason why the results obtained in this study are different from those previously described in the literature. On the other hand, most of the interpretations proposed cannot be extended too far because of insufficient knowledge available on the chemistry of epoxy resins and on the processes of relaxation inside glassy-amorphous crosslinked networks.

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