Internal stress in a cured epoxy resin system

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An epoxy resin system based on a diglycidyl ether of bisphenol-A type difunctional epoxy resin containing different amounts of a tetrafunctional curing agent, namely metaphenylene diamine, was used to prepare two types of specimen. First, an aluminium strip was coated with a thin layer of the epoxy–amine mixture and then subjected to two curing–cooling cycles. Second, bulk specimens were cast in the form of sheets which were cut into rectangles and their dynamic torsional spectra obtained from −100 to 180°C. In the resin-coated metal plate, the internal stress was measured by the bending beam technique and was found to be highest in samples with high glass transition temperatures (T_gs). This is apparently because the internal stress arises due to the difference in the thermal contraction coefficients between the resin and the metal and develops as the sample cools from the T_g to room temperature. The rate of stress relaxation in these samples is also high, apparently because they are the farthest from their equilibrium state and so have higher free volume and a more open structure. In the case of cast sheets, the internal stresses are again the highest in samples with high T_g but arise from non-uniform cooling. An intermediate relaxation peak, the α′ peak, observed in these samples has been shown to be related to the frozen-in internal stresses which relax on sub-T_g ageing due to free volume collapse.

(Keywords: epoxy resin; crosslink density; internal stress; thermal stress; free volume; glass transition temperature)

INTRODUCTION

It is known that when epoxy resin is cured, it can develop internal stresses. These stresses reduce adhesive strength and occasionally induce cracks in the casting materials. Thus it is useful to have an understanding of the origin of these stresses in cured epoxy resin. With this aim, the internal stress which develops in a diglycidyl ether of bisphenol-A based epoxy resin cured with different amounts of curing agent has been measured. The measurements were made on a resin-coated aluminium strip which was subjected to the following two curing cycles which involve high temperature curing followed by cooling to room temperature (RT): (1) 75°C for 2 h, followed by 125°C for 2 h (standard cure); and (2) the standard-cure sample post-cured for 6 h in nitrogen (post cure). The curvature acquired by the strip as it cools after curing provides a measure of the internal stress; in the present investigations it showed considerable time dependence due to stress relaxation. Some comments are also made on the origin of internal stress and its relaxation. In addition, dynamic torsional studies between −100°C and +180°C were conducted on cured, and cured and then sub-glass transition temperature (T_g)-aged bulk samples. It was observed that the intermediate relaxation, the α′ relaxation, occurring above RT, flattened with ageing and thus appeared to be related to the local motion of chains which were in a state of internal stress.

EXPERIMENTAL

Sample preparation

Materials used. The epoxy resin used was Araldite GY 250, which is based on diglycidyl ether of bisphenol-A and manufactured by Hindustan Ciba Geigy Ltd. It has an epoxy equivalent of 190 and molecular weight of 380. The curing agent used was a tetrafunctional aromatic diamine, metaphenylene diamine (mPDA), with a melting point of 69°C. The structures of the resin and curing agent have been given in an earlier publication[1].

Resin-coated aluminium strips. Thin, flat aluminium strips (90 mm long, 15 mm wide, 0.2 mm thick) were used as the base plate. A degassed resin–amine mixture containing 10, 14.5, 20 and 25 phr of mPDA was then applied as a thin coating on one side of the strip using a thin glass rod. The corresponding initial molar ratios of the reactive groups, P = [NH]/[E], for these four samples were 0.71, 1.0, 1.42 and 1.77, respectively. The coated strip was placed between two parallel metal plates with spacers to give a resin coating of 0.1 mm. A release agent was applied to the surface of the top metal plate which was in contact with the resin. The strips were then subjected to standard and post-cure cycles as described in the next section.

On completion of the cure cycle, the oven was switched off and the top metal plate was removed. The samples were then allowed to come to RT in the oven.

Casting of sheets. Cast sheets (2.5 mm thick) were prepared by first mixing 10, 14.5, 20 and 25 phr of molten mPDA and then curing the resin mixture between casting

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plates. The casting plate assembly consisted of a U-shaped poly(tetrafluoroethylene) spacer clamped between two polished steel plates using clamping metal strips. The following two curing cycles were used[1]: (1) Standard cure. The resin and the amine were taken in two different beakers and heated separately to 75°C. The resin and the molten amine were then mixed well and degassed in the oven for 7 min. The resin mixture was then poured in the space between the metal plates which had been preheated to 75°C. The casting plate assembly was then heated at 75°C for 2 h followed by 125°C for 2 h. The oven was then switched off and the sample was allowed to come to RT in the oven before being removed; (2) Post cure. The standard-cure sample was post-cured at 175°C for 6 h in a vacuum oven in the presence of nitrogen, after which the oven was switched off and the sample was allowed to come to RT in the oven. Rectangular samples were cut from these sheets for torsional studies.

Sub T_g *ageing of the samples.* Only the rectangular samples cut from the cast sheet containing a stoichiometric amount of curing agent (14.5 phr) were subjected to sub-T_g ageing treatment in an oven at 130°C for 10, 100, 1000 and 5000 min, respectively, in a nitrogen atmosphere. After the ageing treatment, the samples were allowed to come to RT in the oven at a cooling rate of 0.2°C min^{-1}.

Measurements

Glass transition temperature. The T_gs of the samples were obtained from the peak positions of the tan δ curves obtained using a torsion pendulum.

Macrodensity. The density values of the cured samples cut from cast sheets were determined in a carbon tetrachloride/n-heptane density gradient column (Davenport, UK) containing standard floats. Four small pieces of each sample were introduced to the column and allowed to settle for 24 h before readings were taken. In each case, at least two readings were taken. The average macrodensity could thus be estimated to the third decimal place.

Internal stress. In the resin-coated metal strip, internal stress is primarily generated during the cooling of the cured resin which is attached to a substrate with a different thermal expansion coefficient and is otherwise constrained from normal thermal contraction[2]. This results in a bending of the coated strip. The curvature of the strip (ρ_c) was measured using a spherometer with a least count of 0.01 mm and related to the internal stress, σ_i, by the expression[3]:

$$\sigma_i = \frac{E_1 h_1^3}{12 h_2} \times \frac{2}{\rho_c H} \times \left[1 + \frac{1}{3}\left(\frac{h_1^2}{H^2}\right)\right] \qquad (1)$$

where E_1 is the Young's modulus of the aluminium strip, h_1 and h_2 are the thicknesses of the aluminium plate and the epoxy coating, respectively, and $H = h_1 + h_2$. The initial bending in the middle of the strip could be as high as 5 mm which gradually reduced with time. The beam deflection could be measured accurately using this method.

In each case, measurements were made on at least four coated strips. The first measurement was made after cooling for 12 h in the oven. Further measurements were made on three subsequent days at 24 h intervals.

Dynamic torsional measurements. Dynamic torsional measurements were carried out on small rectangular specimens cut from the cast sheets using a free oscillating inverted torsion pendulum[4]. Damping curves were obtained in the temperature range −100 to +180°C, from which tan δ was estimated and the storage torsional modulus, G', was calculated using standard procedures laid down in ASTM D-2236.

RESULTS AND DISCUSSION

Glass transition temperature

The T_g values as obtained from tan δ peaks in torsion are presented in *Figure 1*. The T_g values show good correspondence with crosslink density; the higher the crosslink density, the higher the T_g. This has been discussed in greater detail in a previous publication[1].

Macrodensity

The density data are shown in *Figure 2*. The data show a trend opposite to that shown by the T_g data (*Figure*

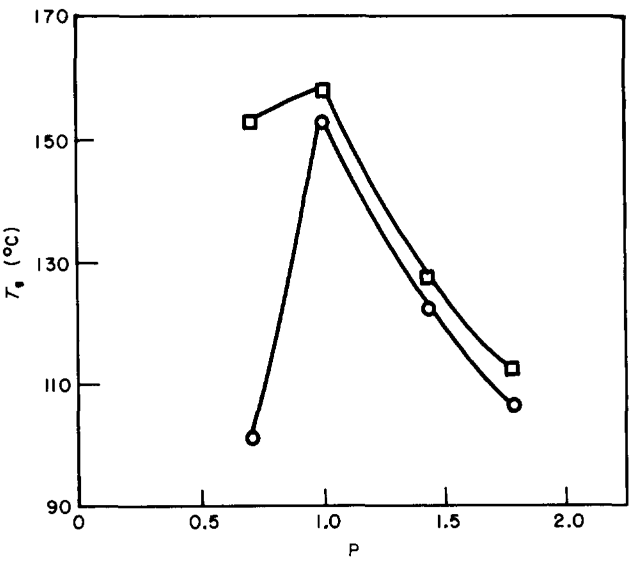

Figure 1 Glass transition temperatures as obtained from the tan δ peak in torsion, for standard-cure (○) and post-cure (□) samples

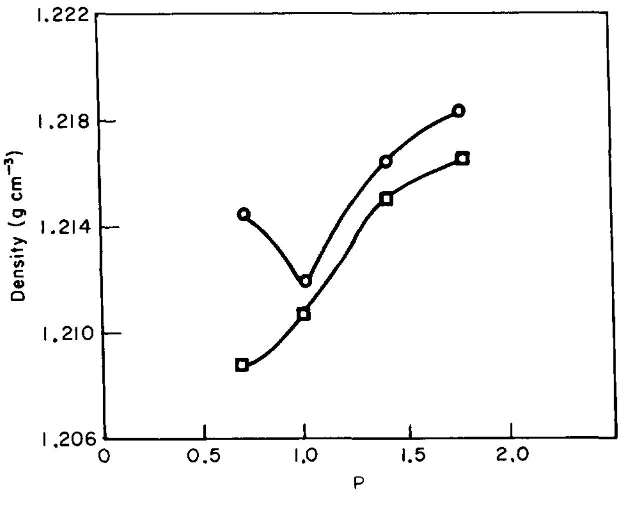

Figure 2 Room temperature density data obtained from a density gradient column. Symbols as in *Figure 1*

1); the most highly crosslinked samples now show the lowest density. This has been attributed to the trapping of relatively more free volume by samples having higher crosslink density[1].

Internal stress

Experimental data. The internal stress generated in the resin-coated metal strip is principally due to the difference in the expansion coefficients between the resin and the metal plate[2]. Provided that the resin adheres well to the aluminium plate, most of the volume shrinkage will be expected to occur as a decrease in thickness with only a minor lateral contraction. The epoxy–aluminium interface was examined on a scanning electron microscope and was found to be intact implying good adhesion between the resin and the substrate.

Another factor which may also contribute to the generation of internal stress in the laminate is the kinetic nature of the T_g[5,6]. This will be related mainly to the rate of cooling of the sample, from the T_g downwards; the higher the rate of cooling, the further the sample would be from its equilibrium state and the greater the internal stress.

The internal stress data for the standard- and post-cure samples are shown in *Figure 3* as a function of measurement time. The following points are noteworthy.

(1) *Standard-cure samples.* The highest internal stress is generated in the stoichiometric sample which has the highest T_g (*Figure 1*) and the highest crosslink density[1] amongst the standard-cure samples. The stress generated in the off-stoichiometric samples is relatively less.

The stress relaxation occurring in the standard-cure samples is not very significant over the period studied, namely 84 h.

(2) *Post-cure samples.* On post curing of the standard-cure samples, the internal stress shows a significant increase in the case of the 10 and 14.5 phr samples, which have the higher T_gs (*Figure 1*) and the higher crosslink densities[1] amongst the post cure samples. In other samples, there is relatively less increase of internal stress.

The stress relaxation in the 10 and 14.5 phr post-cure samples is very rapid. After 84 h the internal stress is slightly lower in all the post-cure samples compared to that in the corresponding standard-cure samples.

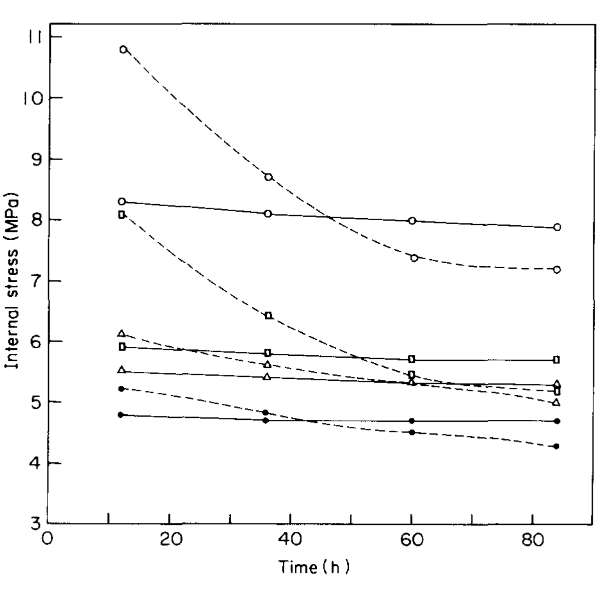

Figure 3 Internal stress data for standard-cure (——) and post-cure (–·–) samples: (□) 10.0; (○) 14.5; (△) 20.0; (●) 25.0 phr

The origin of internal stress. There has been considerable interest in understanding the origin and level of stresses that develop in cured epoxy resin systems, particularly in the coating systems as the coating is cured and cooled. These stresses can have different origins and the various terms used in the literature to describe them have been considered by White[7].

Shimbo *et al.*[8] have presented work on thin coatings of epoxy on aluminium strips which shows that above the T_g of the epoxy there are no stresses present because in the rubber-like state the relaxation processes alleviate any stresses that develop. Upon cooling to temperatures below the T_g, the stresses increase because in the glassy state epoxy contracts at a rate greater than that of aluminium. The calculated stress, $\sigma_{\text{calc.}}$, achieved at, say, RT where RT$\ll T_g$, can be obtained from[2]:

$$\sigma_{\text{calc.}} = \int_{\text{RT}}^{T_g} E_e(\beta_e - \beta_{al})\,\mathrm{d}T \qquad (2)$$

where E_e is the elastic modulus of the epoxy resin and β_e and β_{al} are the linear expansion coefficients of the epoxy resin and aluminium, respectively. The latter was taken to be $2.30 \times 10^{-5}\,\mathrm{K}^{-1}$.

The main assumption made in deriving this relationship is that the contraction of the resin in the glassy region is completely restricted and that it is totally converted to internal stress.

Ochi *et al.*[9] embedded a steel ring in the epoxy resin so that as the resin cured and cooled, the internal stresses, which developed because contraction of the resin was constrained by the metal ring, deformed the ring. From measuring this deformation the stress could be measured. When the measured internal stress was plotted against the internal stress calculated from equation (2), they found that the data fell on the line given by $\sigma_{\text{calc.}} = 3.8\sigma_{\text{obs}}$, where σ_{obs} was the experimentally measured internal stress. They concluded that all the shrinkage stress was not converted to internal stress. Paipetis[10] has also clearly established that shrinkage has no stress-producing effect except in a constrained system.

For the present epoxy resin system, both the thermal expansion data and the torsional modulus data were obtained only for the post-cure samples because, as shown elsewhere[11], in these samples, the curing is complete and, therefore, the sample chemistry does not undergo any change during measurement. The volumetric thermal expansion coefficient data have been published in an earlier publication[1] and the linear expansion coefficient was taken to be one-third of the volumetric coefficient. The torsional modulus data are shown in *Figure 4*. The value of E_e in equation (2) can be calculated from G' by using an assumed value of 0.33 for Poisson's ratio, which gives $E_e = 2.66G'$.

The values of internal stress for the post-cure samples calculated using equation (2) along with the measured values on the basis of equation (1) after 12 and 84 h of stress relaxation are shown in *Table 1*. There are two noteworthy observations. First, the calculated values are considerably higher than the measured values. And second, the measured stress values show clearly that there is considerable stress relaxation with time, particularly in the most highly crosslinked samples, as was also clear

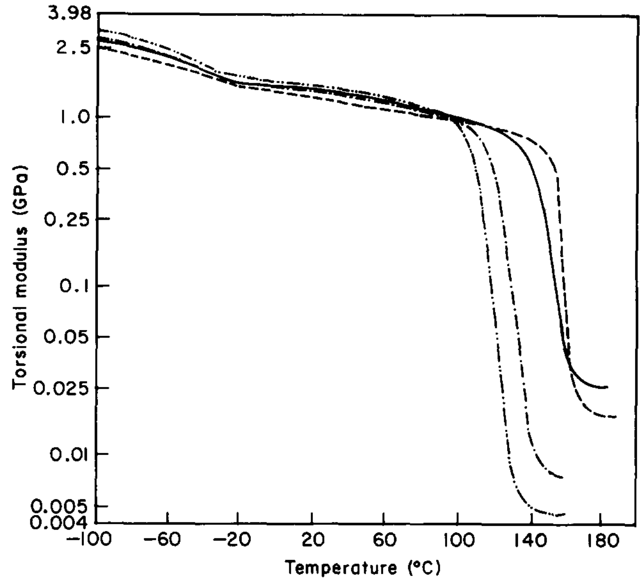

Figure 4 Torsional modulus data for the post-cure samples: (——) 10; (– –) 14.5; (–·) 20; (–··) 25 phr

Table 1 Internal stress in post-cure resin samples

Sample (phr)	Internal stress (MPa)		
		Measured^b	
	Calculated^a	12 h	84 h
10	18.12	8.2	5.2
14.5	15.86	10.8	7.2
20	11.95	6.1	5.0
25	10.40	5.2	4.4

^{a}From equation (2)
^{b}From equation (1)

from *Figure 3*. It needs to be emphasized that the first measurement was recorded 12 h after switching the oven off. A considerable amount of stress relaxation would already have occurred during this period. Considering this, the general trend predicted by equation (2) appears to be reasonably good, thus suggesting that the shrinkage in the glassy region seems to be directly converted to internal stress because the motion of network segments is restricted in this region. In the present investigation, the most highly crosslinked samples develop the highest internal stress though their elastic moduli are the lowest. Thus it would appear that the T_g plays a predominant role in determining the magnitude of internal stress; the higher the T_g, the higher the internal stress.

A mechanistic interpretation for the bending of the strip. The aluminium–epoxy laminate can be considered as a bimetallic strip[12] as shown in *Figure 5*. As it cools from above the T_g to RT the interaction between the two strips (which have been considered to be of equal thickness in the present discussion) produces a non-uniform force. As shown in *Figure 5*, the deformation of the common surface occurs in such a manner that the aluminium layer is compressed and the epoxy layer is extended. If the internal force is P, it gives rise to a direct load P at the centre of each section together with a bending moment M in each strip[13], as shown in *Figure 5*. For equilibrium of the cross-section:

$$M_A + M_E = Pt \tag{3}$$

where t is the thickness of each layer. The tensile force on the epoxy layer will tend to enhance molecular mobility and result in higher segmental motion in the epoxy layer.

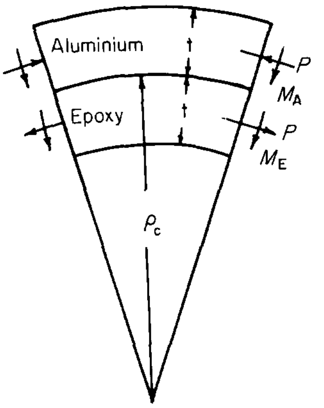

Figure 5 Forces arising from the interaction between the two layers of epoxy-coated aluminium

Structural factors affecting stress relaxation. The epoxy layer is non-linearly viscoelastic. With the passage of time, therefore, the stress measured is expected to relax. However, the overall equilibrium always holds in the entire specimen, i.e. the redistribution of stress in aluminium and epoxy occurs continuously.

The highest internal stress and stress relaxation rate are observed in samples with the highest crosslink density. A number of factors may be responsible for this. First, the higher the internal stress, the higher the viscoelasticity and greater the non-linearity. Second, it has been clearly demonstrated in an earlier publication[1] that samples with high crosslink density or high T_g have also the highest specific volume and free volume below the T_g and at RT they are the farthest from the equilibrium position. Also, they have the lowest density amongst the samples of different stoichiometries (*Figure 2*). The high free volume will allow greater molecular mobility. Finally, as shown in the previous section, the high internal stress in samples of high crosslink density will result in high tensile force on the epoxy layer. All these factors will be expected to enhance the relaxation rate.

Ochi *et al.* showed[9] that in a cured epoxy resin system the internal stress was ~6 MPa at RT and decreased to zero at the T_g. The RT value is reasonably close to the value of internal stress in the present investigation. However, significant stress relaxation is observed at RT in the present samples.

The α′ relaxation

In a previous publication[14], a broad, weak relaxation called the α′ peak in the same epoxy system was shown to occur during torsional measurements in the 50–100°C range, having an activation energy of ~210 kJ mol^{-1}. It was also seen that this relaxation was more prominent in the stoichiometric post-cure sample than in the standard-cure sample.

Small relaxation regions intermediate between the α and β relaxations have also been reported for polycarbonate[15] and atactic polystyrene[16]. These relaxations reduce in intensity or disappear on annealing and have therefore been attributed to the presence of non-equilibrium stresses frozen in these samples during preparation. Recently, after this work had been completed, we have seen the work of Sasuga and Udagawa who have observed[17] similar relaxation in several epoxy resins and have attributed it to internal stress.

The tan δ data in torsion for the stoichiometric post-cure sample before and after sub-T_g ageing are shown in *Figure 6*. The corresponding torsional modulus data are shown in *Figure 7*. It is interesting to note that the α′ peak becomes progressively flatter as the ageing time is increased. Also, the aged samples show high torsional modulus.

It is generally agreed that on sub-T_g ageing, non-equilibrium stresses can relax through free volume collapse[6]. The reduction in free volume consequently results in reduced segmental mobility. Thus the α′ peak appears to be related to free volume or to the frozen-in stress. It may be pointed out that in the torsion pendulum studies, the frequency is ~1 Hz. The stress relaxation has, on the other hand, been studied from 12 to 84 h. At longer times or lower frequencies, the transition may shift to lower temperatures and could be partially effective in introducing molecular mobility at RT also.

It must be emphasized that the origin of internal stress in the cast sheets, from which the torsional specimens have been machined, is different to that for the resin-coated plate. In the samples subjected to ageing, differential shrinkage is not relevant. Instead, the internal stress would primarily result from non-uniform cooling of the sheet[5,6,18]; the shell solidifying first, with the core shrinking next. The shell is thus under compressive stresses, while tensile stresses are induced inside. In addition, the non-equilibrium stresses can also be trapped due to the kinetic nature of the glass transition phenomenon[5,6].

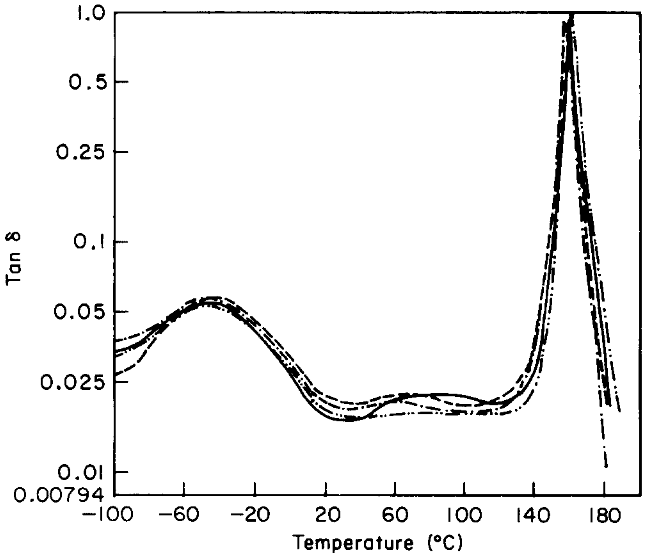

Figure 6 Tan δ curves for post-cure and sub-T_g aged samples: (——) 14.5 phr; (— —) 100 min; (—·) 1000 min; (—··) 5000 min

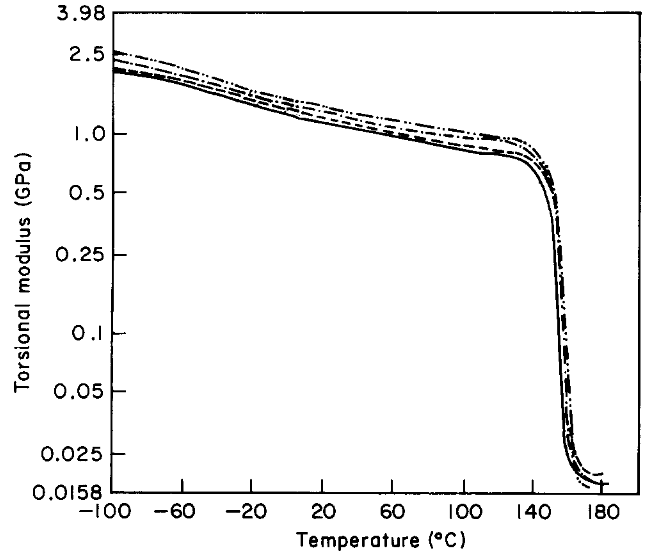

Figure 7 Torsional modulus data for post-cure and sub-T_g aged samples. Symbols as in *Figure 6*

CONCLUSIONS

The internal stress that develops as an aluminium strip coated with a thin layer of epoxy resin is cured and cooled has been measured at RT and shown to be high for samples having a high T_g. This is shown to be predominantly due to the difference in the thermal contraction coefficients between the resin and aluminium which results in the generation of these stresses from the T_g to RT due to the constraints to lateral shrinkage of the adhesive layer. The rate of stress relaxation is also high in the high T_g samples because they are the farthest from their equilibrium state and consequently show a greater degree of non-linear viscoelasticity.

In the case of cast sheets, internal stresses arise mainly due to non-uniform cooling. The α′ peak in the 50–100°C range in the dynamic torsional spectrum of the neat stoichiometric bulk sample cut from the cast sheet is relatively more pronounced. When this sample is subjected to sub-T_g ageing, the peak flattens. Thus the α′ peak in these samples could originate from the frozen-in internal stresses which relax on sub-T_g ageing due to free volume collapse.

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