Linear viscoelastic properties of epoxy resin polymers in dilatation and shear in the glass transition region:
2. Measurement of the glass transition temperature

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Measurements of the 20 second creep compliances in dilatation and shear, over a range of temperature spanning the glass transition region, have been made for six epoxy resin polymers. The linear thermal expansion behaviour has been determined in the same temperature range. Shear and dilatational compliances, and the linear thermal expansion properties may all be measured on the same specimen. Values of the glass transition temperature derived from 20 sec shear and bulk compliance data agree well with values obtained from thermal expansion data. When T_g was derived from creep data obtained at longer creep times (in part 1 of this paper), it was found that T_g in dilatation exceeds T_g in shear. It was shown that this is consistent with the difference in activation energies in dilatation and shear obtained in part 1 of this paper. An example is given of how systematic errors of the order of 1°C in temperature measurement may lead to maxima or minima when Poisson's ratio is calculated from measured values of shear and tensile compliances.

INTRODUCTION

The glass transition in polymers is a phenomenon which manifests itself in many ways. One of its most important characteristics is the step in the thermal expansion coefficient as a function of temperature, but similar transitions are observed in specific heat, and many other physical properties of the material (for example shear modulus, dielectric constant and tensile strength). Below the glass transition temperature, T_g, the polymer is in a glassy state, and large-scale motion of the main backbone chain is impossible. The ability of the polymer to deform in response to applied stresses is therefore rather restricted. Above T_g the main backbone chains possess much greater freedom of motion, and large-scale motion is possible. The polymer is now in the rubbery state and response to applied stress is much more pronounced. There are several competing theories which attempt to explain the glass transition phenomenon but perhaps the most widely accepted explanation is that based on free volume[1–4].

The glass transition is a rate-dependent phenomenon, and its situation on the temperature scale depends on the time scale of observation. In most polymers the transition spans at least 20°C, and various procedures have been used for the determination of a value for T_g. The most common method used is the construction shown in *Figure 1*. T_g may also be measured from curves of B, J or D (the bulk, shear and tensile compliances respectively) against temperature and a construction to do this is given in *Figure 4 (Part I)*. These two constructions are the ones used in this paper.

When the glass transition is studied by observation of different physical properties it is expected that the transition region should be the same in each case, provided that the time scale of the different experiments is the same. Very few attempts have been made to compare the values of T_g by observation of different physical properties, and most of the available data have been obtained from mechanical property measurements. However, from these data it would appear that the T_g measured in different deformation modes is not necessarily the same.

Kono[5,6] studied the elastic constants M^* and G^* at ultrasonic frequencies of several polymers as a function of temperature. K^*, the complex bulk modulus, is found from the complex longitudinal wave modulus, M^*, and complex shear modulus, G^* by

$$K^* = M^* - \frac{4}{3} G^*$$

Each modulus may be written as the sum of the real and the imaginary parts (e.g. $K^* = K' + iK''$), where the real part is the storage modulus and the imaginary part is the loss modulus. The materials used were a series of methacrylate polymers (which have bulky side groups) and a set of polymers

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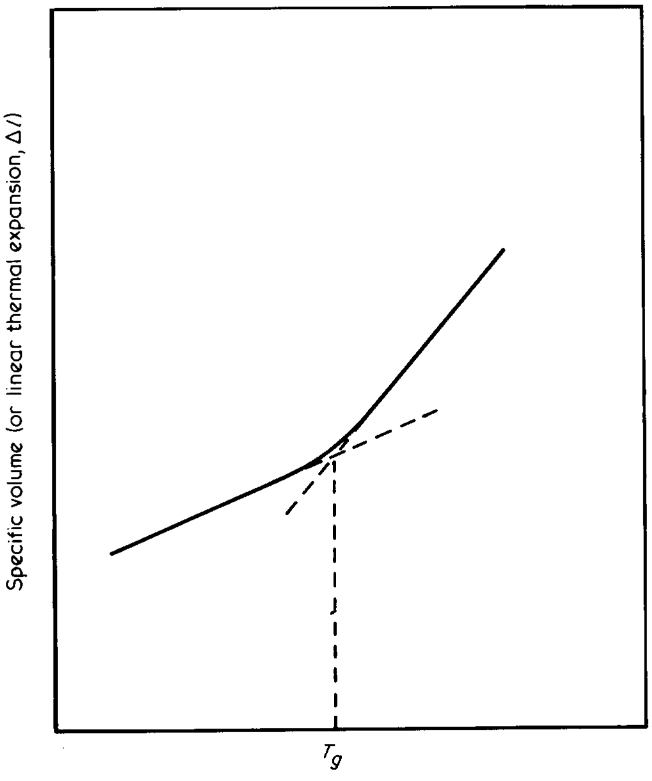

Figure 1 Measurement of T_g from thermal expansion data

(PVC, vulcanized rubber and polytrifluoromonochloroethylene) with no side groups, and Kono found that the temperature of the maximum in K'' was greater than that for G'' for the methacrylate series. The difference between the two T_g values increased as the length of the side chain increased. Kono also found that the activation energy (as measured by shift with frequency of the maxima in the imaginary modulus plots) in bulk was greater than that in shear, and concluded that the two relaxations may be caused by different molecular mechanisms.

Waterman[7] used ultrasonic techniques to measure the complex shear and longitudinal wave moduli of some polyethylenes, and bulk moduli data were calculated from M^* and G^*. In this work the main interest was in the γ transition, which is a secondary transition occurring at temperatures below the main glass transition. Differences of up to 20°C were noted between transition temperatures in bulk and shear with the bulk transition usually occurring at the lower temperature.

Perhaps one of the most complete studies is that of Koppelman[8–10] who measured the complex shear, Young's (E*) and longitudinal wave moduli of plasticised and unplasticised PVC, and polymethylmethacrylate (PMMA) as functions of frequency over a wide temperature range. For both polymers the transition in E^* and G^* occurred at different frequencies, the shear transition occurring at the lower frequency. This observation is consistent with having $T_{gE} < T_{gG}$ (where the subscript indicates the deformation mode) in the case of isochronous measurements. Koppelman also noticed that if the real part of the complex Poisson's ratio ν' as a function of frequency was calculated from E^* and G^*, it went through a minimum in the transition region, and this effect is closely connected with the occurrence of a difference in transition temperatures in different modes.

This latter effect has also been seen by Heydemann[11] in his work on plasticised PVC and PMMA. E^*, G^* and K^* were measured as functions of temperature in the transition region at 1 KHz and from the results ν' was calculated. If ν' was calculated from E^* and G^* (ν'_{EG}) then a minimum was observed in the transition region, but when calculated from E^* and K^* (ν'_{EK}) a monotonic increase from about 0.35 in the glassy region to 0.45 in the rubbery region was observed. However Heydemann found that if a longer period was allowed for the specimen to come to equilibrium at each temperature the minimum in ν_{EG}' was no longer apparent.

A similar result was noticed by Lewis and Tobin[12] who studied the complex shear and Young's moduli of polypropylene, nylon-6,6 and PMMA. ν' was calculated from E^* and G^* and in all three cases a minimum was observed in the transition region.

A theoretical contribution to the subject has been made by Freundenthal and Henry[14,15] who used various models of viscoelastic behaviour to calculate the dependence of Poisson's ratio on time for a tensile creep experiment. The models used for the shear behaviour were the Kelvin body, the Maxwell body, the standard anelastic body, and the Burgers or four parameter body, and for each case the Poisson's ratio was calculated assuming the volume response to be purely elastic. This is a rather unrealistic simplification, and as an improvement they considered the cases where the volume response is given by the standard anelastic body, and the shear response is given by (a) the standard anelastic body, (b) the Maxwell body. The result was calculated for

$$\tau_K = 5\tau_G \text{ and } \tau_K = \frac{1}{5}\tau_G$$

in each case, where τ_K is the bulk relaxation time; τ_G is the shear relaxation time.

When $\tau_K = 1/5\ \tau_G$ the Poisson's ratio goes through a minimum with time for case (a) and (b), whereas when $\tau_K = 5\tau_G$ the Poisson's ratio shows a maximum with time for case (a), and a monotonic increase with time for case (b). A further assumption made in the analysis is that $G/K = 3/8$, where K and G are the spring constants in bulk and shear, and for the standard anelastic body the values of the two spring constants are assumed to be equal. The above approach has limitations in that it assumes linear response in shear and bulk, and uses only single relaxation time models.

Part I of the present paper discussed the time temperature superposition of an epoxy resin polymer in dilatation and shear. The aim of the work presented in part II of this paper was to investigate the possibility of T_g differences in different deformation modes, in a series of epoxy resin-based polymers. For each material all the measurements could be made on a single specimen.

EXPERIMENTAL

In Kono's work on methacrylates, polymers with bulky side groups were found to display the largest temperatures difference between bulk and shear relaxations. The temperature difference was thought to originate from the steric hindrance introduced by the bulky side groups. One of the aims of this study was to see if differences in bulk and shear relaxations occurred in epoxy resins, and the approach adopted was to use one epoxy resin, and to use various curing agents to introduce different amounts of steric hindrance to molecular motion. The curing agents used were all acid anhydrides. The epoxy resin used was diglycidyl ether of bis-

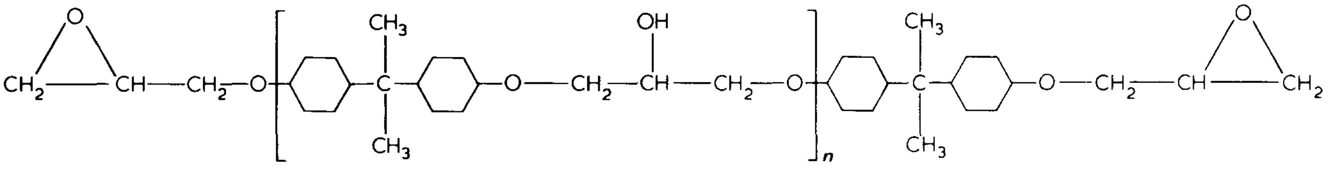

Figure 2 Chemical formula of diglycidyl ether of bisphenol A

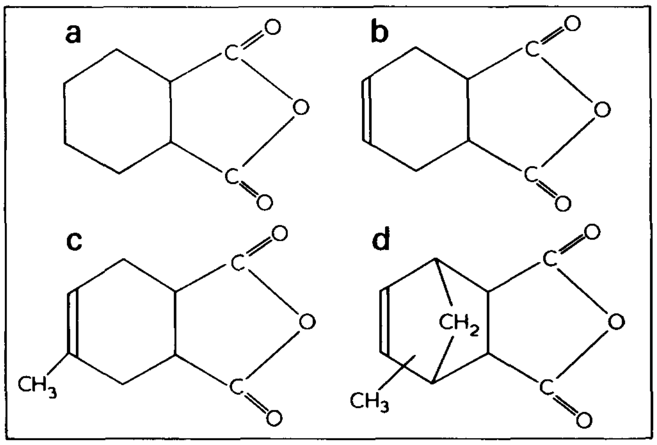

Figure 3 Chemical formulae of the anhydride hardeners
(a) Hexahydrophthalic anhyride (HHPA)
(b) Tetrahydrophthalic anhydride (THPA)
(c) Methyltetrahydrophthalic anhydride (MTHPA)
(d) Nadic Methyl Anhydride (NMA)

Table 1 A list of chemical names, suppliers and supplier's code names for the materials used in this work

Chemical Name and abbreviation	Supplier	Supplier's code name
Triethylamine (TEA)	BDH	
Nadic methyl anhydride (NMA)	CIBA-Geigy	HY 906
Hexahydrophthalic anhydride HHPA)	CIBA-Geigy	HT 907
Tetrahydrophthalic anhydride THPA)	Shell	Epikure RXE-11
Methyltetrahydrophthalic anhydride (MTHPA)	CIBA-Geigy	HY 917
Diglycidyl ether of bisphenol A (DGEBA)	CIBA-Geigy	MY 750

Table 2 Details of the ratios of components used in the different resin systems

Resin System	Material	Mass (arbitrary units)
A	DGEBA	100
	NMA	100
	TEA	2
B	DGEBA	100
	HHPA	85
	TEA	2
C	DGEBA	100
	THPA	85
	TEA	2
D	DGEBA	100
	MTHPA	92
	TEA	2
E	DGEBA	100
	NMA	85
	TEA	1.85
F	DGEBA	100
	HHPA	100
	TEA	2

phenol A (DGEBA) (CIBA-Geigy resin, MY 750), and a diagram is given in *Figure 2*. The portion of the molecule in square brackets is a repeating unit, and a typical value of n for this resin is 0.2, so that each molecule has two reactive epoxy end groups, and one molecule in five has an OH group available for reaction. Chemical formulae of the hardeners are given in *Figure 3*, and the chemical names, suppliers and suppliers code names are given in *Table 1*. With each resin formulation a small quantity of triethylamine was added as an accelerator. Details of the proportions used in each resin formulation are given in *Table 2*. In each case the proportions of the components have been chosen to give the approximate stoichiometric ratio. The method of specimen preparation has been described in part I of this paper, and in more detail by Crowson[16]. In each case the cure cycle was 16 h at 100°C, followed by 1 h at 150°C, and 0.5 h at 200°C.

Using the methods described in Part I of this paper the temperature dependence of the bulk and shear compliances $B(t,T)$ and $J(t,T)$ were determined over the temperature range from 20° to 200°C, which includes the glass transition for all the materials studied here. In all cases the creep time was 20 sec. The testing procedure adopted was to anneal the specimen at 180°C (which is about 40°C above T_g as measured for a 20 sec creep test for most of these materials), and allow to cool to 20°C before commencing testing. It was difficult to exert much control over the quench, but by switching off the heater at 180°C and allowing an hour before testing it was possible to ensure that the specimens had had very similar thermal and stress histories when the experiment started. Measurements were then taken at 10°C intervals except in the transition region where intervals of 5°C were used, and at each temperature the specimen was allowed 30 min to come to equilibrium before the load was applied. This period is ample for the specimen to come to thermal equilibrium, but may not be sufficient for volume equilibrium to be achieved. Above T_g volume equilibrium is reached very rapidly (within a few seconds of the achievement of thermal equilibrium), but the time required to reach volume equilibrium increases drastically as temperature decreases below T_g and may be several years for polymers in their glassy state. The problem of the approach to volume equilibrium, and the large effect this has on mechanical properties has been studied by Struik[17,18] and is more difficult to resolve for creep experiments which last for long periods. In the experiments described here the change of volume which occurs during testing, due to the approach to equilibrium of the specimen, is very small because the test period is very short (20 sec) compared with the period of

Table 3 T_g values obtained from compliance and thermal expansion data for the different resin systems

Material	T_g in °C From shear compliance data	 From bulk compliance data	 From thermal expansion data
Resin system A	139	144	139
Resin system B	125	–	121
Resin system C	123	125	–
Resin system D	125	125	124
Resin system E	156	160	152
Resin system F	119	120	118

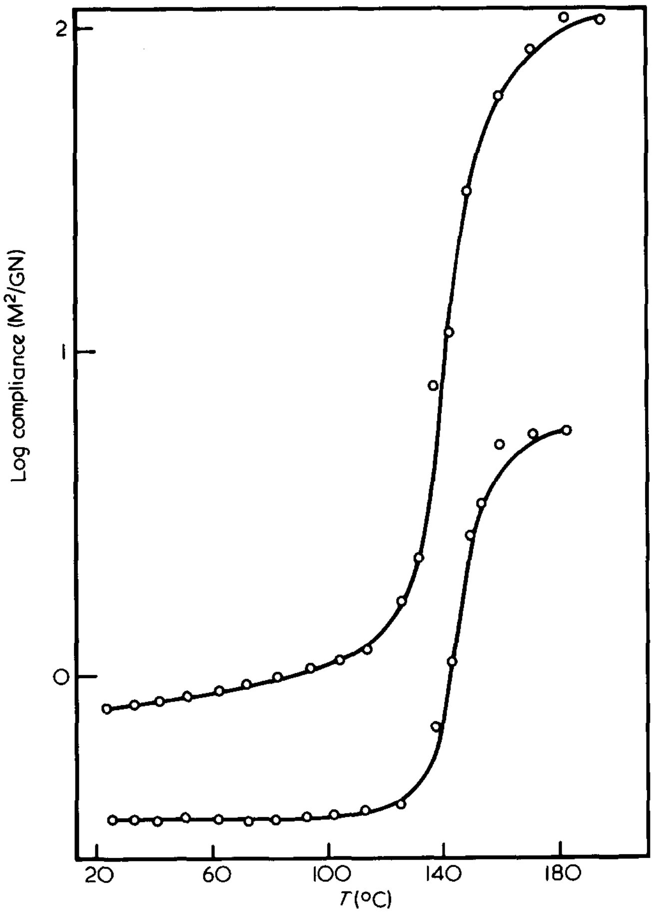

Figure 4 Bulk and shear compliance versus temperature for resin system A (upper curve shear, lower curve bulk)

equilibration (30 min). Thus in these experiments the specimen will be in equilibrium at high temperatures, and will be far from equilibrium at low temperatures, and so the T_g valued measured will depend on the heating rate used. Comparisons may only be drawn between data obtained for the same heating rate and at the same frequency.

Measurements of compliances were made only for ascending temperature. This had the advantage that any unrecovered strain at the end of one creep experiment is allowed to recover very rapidly when the temperature is increased for the next measurement. If measurements were made for descending temperatures, any unrecovered strain would be 'frozen' in, and would continue to recover whilst the specimen was being tested at the lower temperature.

In addition to the compliance measurements described above, the linear thermal expansion behaviour of each of the materials was studied. The specimen was clamped at the top end, and the displacement of the lower end of the specimen was measured using the displacement measuring system described in Part I[19] of this paper. Temperature was varied using the coil-wound heater, also described in Part I of this paper[19]. The procedure adopted was to change temperature in steps of 10°C, allowing 10 min between each reading. Readings were taken both for ascending and descending temperatures. The T_g values were obtained for the mechanical measurements, and the thermal measurements by the constructions given in *Figures 1* and *Part I, Figure 4.*

RESULTS AND DISCUSSION

The main results are given in *Table 3*, where the T_g values obtained from bulk and shear compliance and from thermal expansion measurements are tabulated. *Figure 4* shows the temperature dependence of bulk and shear compliance for resin system A, and the thermal expansion versus temperature is plotted in *Figure 5* for resin system A. Individual graphs for the other materials tested are omitted here, but the essential results are tabulated in *Table 3*. An examination of these figures reveals several interesting features. The behaviour of each of the polymers may be separated into three regions; the glassy region where B is fairly constant, with a value of about

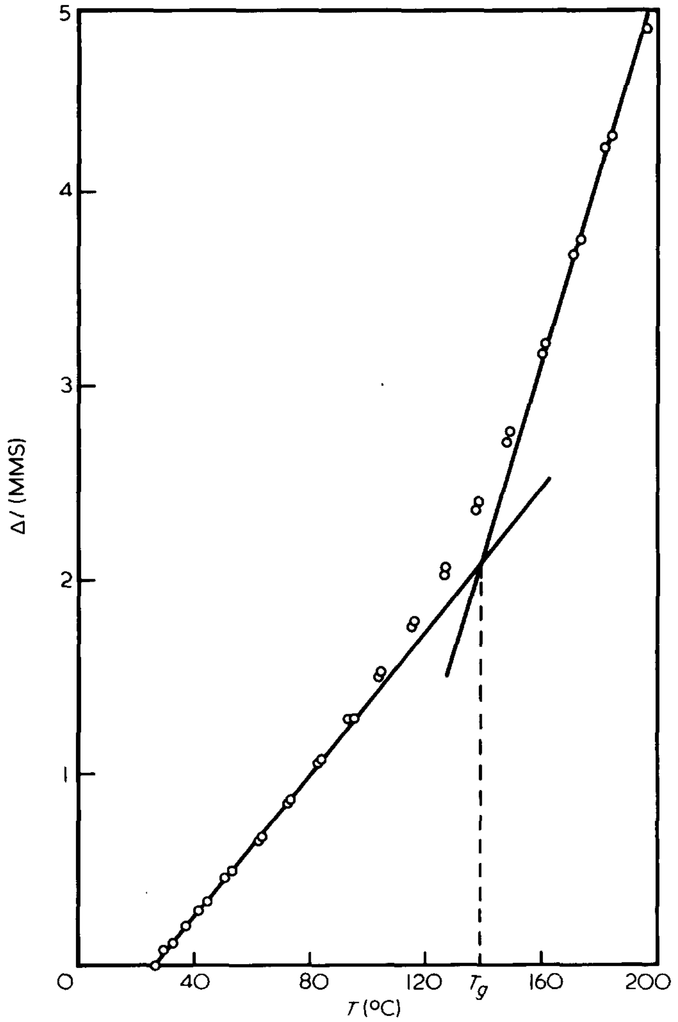

Figure 5 Linear expansion versus temperature for resin system A. (l_0 = 285.6 mm)

0.35 m^2/GN, and J increases slowly with temperature from about 0.8 to 1.2 m^2/GN in 100°C; the transition region where both B and J rise rapidly; and the rubbery region where both compliances are again fairly constant. In the present study there is insufficient data above T_g to say much about the behaviour in the rubbery region.

For the shear relaxation $J_r/J_g \sim 1000$ (J_r = rubbery shear compliance, J_g = glassy shear compliance) which is typical for a crosslinked polymer. In bulk the compliance increases by a factor of about fifteen (i.e. $B_r/B_g \sim 25$, where B_r = rubbery bulk compliance, B_g = glassy bulk compliance), which is comparable with Theocaris' semiempirical analysis[20], where a bulk compliance change of about tenfold is obtained. This is rather larger than that seen in the few existing studies of the behaviour of bulk-compliance in the glass transition region.

McKinney *et al.*[21,22] have given what is probably the most complete study of the bulk viscoelastic behaviour and observe a difference in bulk compliance of a factor of two between glassy and rubbery regions, and this value is typical of that seen by other authors. For example Heydemann and Guicking[23] and Warfield[24], have seen relaxations in bulk compliance of about a factor of 2.

It seems very likely that the reason for these differences lies in the magnitude of the pressure used to determine B. In the few studies which have been made of the bulk compliance as a function of temperature over the transition region at different pressures it emerges that B_r/B_g decreases as P increases. (Heydemann and Guicking[23]; Hellwege Knappe and Lehman[25]; McKinney and Belcher[22]). In the present study the volume strain was kept below 0.01%, and in Theocaris' work[20] data for bulk deformation were derived from measurements at low strain of the tensile creep compliance and stress relaxation modulus. In the studies quoted above[23,24] volume strains were in excess of 2%. It thus seems likely that the large B_r/B_g ratio observed here is due to the extremely low volume strains used in this method. In the work by McKinney *et al.*[21,22] a small sinusoidally varying pressure was used. In this case the volume strain was small, and the reason for the small relaxation in bulk compliance is unclear. From *Table 3* a difference in T_g of the different materials is apparent. Glass transition temperatures obtained by the procedures illustrated in *Figures 1* and *Part I, Figure 4* are accurate to about ±2°C for the present study, and it is interesting that for the specimens polymerized using HHPA, THPA and MTHPA as hardener the T_g values are all very close to 125°C. Only the specimens cured with NMA show T_g values greater than this (between 139 and 160°C depending on ratio of components). This is probably a reflection of the stereochemistry of the hardener molecules used: HHPA, MTHPA and THPA are all similar, and consist of phthalic anhydride with different substitutions on the cyclohexyl ring, (see *Figure 3*). The NMA molecule differs in that it contains a bulky bridge and it would seem that this makes it more difficult for the resultant polymer to move freely, and larger amounts of energy are required to allow these structural units to move, hence the high value of T_g. Another observation which may be drawn from *Table 2* is that the T_g values in bulk and shear differ by less than 5°C, which is of the same order as experimental error. This difference in T_g values is thus not thought to be significant.

As was mentioned in the introduction, there is a considerable amount of work in the literature which argues the case for the existence of T_g differences in different deformation modes, and the consequent peculiarities in the behaviour of Poisson's ratio. Of these studies, most deduce the minimum in Poisson's ratio from measurement of E and G. It is of some interest to consider the errors involved in calculation of ν from measurements of E, G and K. The three equations used to find ν from E, G and K are

$$\nu_{KG} = \frac{3K - 2G}{6K + 2G} \qquad (1)$$

$$\nu_{EG} = \frac{E}{2G} - 1 \qquad (2)$$

$$\nu_{KE} = \frac{1}{2}\left(1 - \frac{E}{3K}\right) \qquad (3)$$

These equations were originally derived for purely elastic materials. Since here we are dealing with viscoelastic materials we follow common practice and merely insert the appropriate complex moduli or creep functions depending on whether the data are derived from dynamic or transient tests. The three equations above are only valid for isotropic materials. Because of the way the terms combine, the errors in the three cases are very different. If we choose values of E, K and G typical of a glassy polymer ($K = E = 3$ GN/m^2, $G = 1.1$ GN/m^2), and assume that each modulus contains a 10% error we find that ν_{KG} contains a 20% error, ν_{EG} has an 80% error, and ν_{KE} a 10% error. Similarly if values are chosen typical of the rubbery state ($K = 200$ MN/m^2, $G = 10$ MN/m^2, $E = 30$ MN/m^2, the errors are 15% in ν_{KG}, 60% in ν_{EG}, and 1% in ν_{KE}.

In the glass transition region the chances of error in ν are larger because the contribution of an error in temperature measurement to the error in compliance is much greater. In the glassy and rubbery regions the compliance (D, J, or B) varies only slowly with temperature, but in the transition region compliance can increase by a factor of 10 in 20°C, (see for example *Figure 4*). Thus a 5°C error in temperature measurement could lead to an error in compliance of up to 100% (or an error of 1°C is likely to contribute a 15% error to compliance). Bulk compliance varies rather less in the transition region than either shear or tensile compliance, and for this reason it is preferable to use B as one of the compliances to derive ν. However, one should still be very critical of values of ν derived from other viscoelastic functions in the transition region. An illustration of the magnitude of the errors created in ν merely by an error in temperature measurement is shown in *Figure 6*. We use the relation

$$\nu_{DJ}(T) = 2\frac{J(T)}{D(T)} - 1 \qquad (4)$$

in order to calculate $\nu(T)$ from the compliance versus temperature data presented in *Figure 4*. This equation is analogous to equation (2) for the elastic case, and serves to define the creep Poisson's ratio. The $B(T)$ and $J(T)$ data have been smoothed, in that the values used here were read off from a curve drawn through the actual data points. From these data $D(T)$ values were calculated using the relation

$$D(T) = \frac{3B(T) + J(T)}{9B(T)J(T)} \qquad (5)$$

ν_{DJ} values were then calculated, and this gives curve (A) of

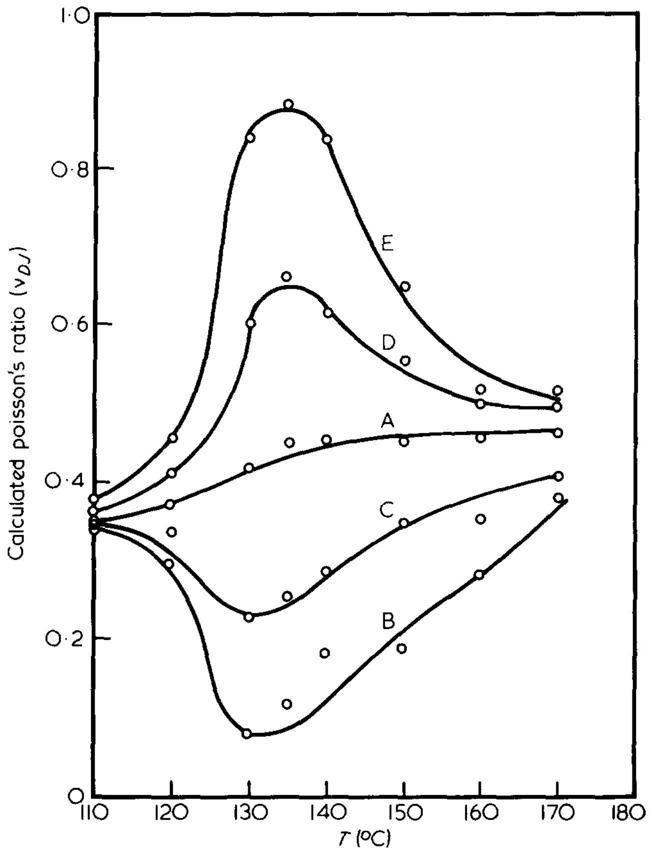

Figure 6 Calculated Poisson's ratio, ν_{DJ}, versus temperature. A, $\nu_{D(T)}$, J(T); B, $\nu_{D(T)}$, J(T-2); C, $\nu_{D(T)}$, J(T-1); D, $\nu_{D(T)}$, J(T + 1); E, $\nu_{D(T)}$, J(T + 2)

Figure 6. In order to show the effect of an error in temperature measurement several sets of $J(T + x)$,data were read off from *Figure 4*. Here $J(T + x)$ is the value of J which would be obtained if the temperature of measurement was $T + x$ instead of T, (i.e., temperature measurement was $-x°$ (in error). Sets of $J(T + x)$ data were obtained for four values of x; −2, −1, +1 and +2 C. Each set of $J(T + x)$ data was used together with the $D(T)$ data to calculate a set of values of $\nu_{DJ(T)}$. Thus curve (B) consists of a set of values of Poisson's ratio calculated from $D(T)$ and $J(T - 2)$, $[\nu_{DJ(T-2)}]$; curve (C) represents $\nu_{DJ(T-1)}$; and curve (D) is $\nu_{DJ(T+1)}$; and curve (E) is $\nu_{DJ}(T+2)$;

An inspection of *Figure 6* reveals that if ν_{DJ} is calculated from the original $D(T)$ and $J(T)$ data, one obtains the usual monotonic increase of ν_{DJ} from a value of about 0.35 at the glassy end of the transition region to about 0.46 at the rubbery end of the transition region [curve (A)]. However if there were a systematic error of 2°C in the temperature measuring equipment in the shear measurements, then the shear transition would appear to occur at a higher temperature than the transition in tensile compliance, and curve (B) which shows a sharp minimum in the transition region, would be obtained for the Poisson's ratio. If the error in temperature measurement was only 1°C then curve (C) would be obtained, which shows a much smaller minimum, and if the error in temperature measurement was −1°C the shear transition would now occur at a lower temperature than the tensile compliance transition, and the calculated ν_{DJ} would show a maximum in the transition region [curve (D)]. Similarly for −2°C error curve (E) is obtained, which shows a larger maximum. Both curve (E) and curve (D) have their maxima at values of ν in excess of 0.5.

In view of the serious effect which slight errors in temperature measurement or compliance measurement may have on the Poisson's ratio derived from D and J it is prudent to be very critical of values of ν calculated in this way, especially in the glass transition region. Values of ν calculated from J and B, or better from D and B show much less variation from curve (A) when temperature errors are artificially introduced into the readings. It seems likely that Heydemann's results[11] may be in error in this way, because he observed a minimum in ν calculated from shear and tensile measurements which disappeared when ν was calculated from measurements in bulk and shear. Keppelman[8–10], Philipoff and Brodnyan[13] and Lewis and Tobin's[12] results are probably in error for the same reason. However, although it seems as if there is no strong evidence for the existence of a minimum in Poisson's ratio, there is still the evidence of Kono[5,6,26], and Waterman[7] for the existence of T_g differences in different deformation modes. In Kono's work[5,6,26] $T_{g_K} > T_{g_G}$, which would lead to a maximum in ν if the T_g difference was large enough, whereas Waterman[7] found larger transition temperatures in shear for the most part which would lead to a Poisson's ratio minimum. Although no confirmation of the existence of T_g differences has been found in the creep experiments represented in *Table 3* and *Figures 4* and *5* some evidence is available from the longer creep time data presented in Part 1 of this paper[19]. From this work it appears that in the rubbery region the bulk activation energy ΔH_K = 210 Kcal/mole, whereas the shear activation energy ΔH_G = 160 Kcal/mole. In the glassy region ΔH_G = 60 Kcal/mole. The activation energy for bulk deformation below T_g was not determined. If the bulk and shear activation energies are different at all temperatures and times we may show that regions must exist where the glass transition temperatures in bulk and shear differ. (see Appendix). Consequently we should expect differences in bulk and shear transition temperatures in the creep data obtained in part 1 of this paper. This is confirmed in *Table 4*, which shows the T_g values obtained in bulk and shear for the isochronous plots shown in *Figures 4* and *14* of part 1 of this paper. This material is resin system *E*. An examination of *Table 4* reveals that $T_{gK} \sim T_{gK}$ for creep time of between 2 and 10 sec, but for longer creep times it appears that $T_{gK} > T_{gG}$. From the present study it is not possible to be emphatic on this point and further experiments in bulk at longer creep times would be very useful. However, the evidence suggests that at long creep times the bulk relaxation occurs at a higher temperature than the shear

Table 4 T_g values in bulk and shear for different creep times (From Crowson and Arridge[19])

log t (secs)	T_{gG} (K)	T_{gK} (K)	ΔT_g (K) ($T_{gK} - T_{gK}$)
0			
0.25	435	436	1
0.5	433	434	1
0.75	430.8	432.3	1.5
1.0	429.2	431.6	2.4
1.25	427.4	430.7	3.3
1.5	426.0	430.1	4.1
1.75	424.8	429.7	4.9
2.0	423.3	429	5.7
2.25	422.1		
2.5	421.0		
2.75	420.4		
3.0	419.6		
3.25	417.8		

relaxation, and the above analysis shows that this is consistent with the difference in bulk and shear activation energies found in Part 1 of this paper[19].

CONCLUSIONS

The temperature dependence of the bulk and shear compliances of a series of anhydride-cured epoxy resins has been determined over a range spanning the glass transition region for a creep time of 20 sec and the linear thermal expansion behaviour has also been determined in this range. The following conclusions have been drawn.

1. The glass transition temperatures as measured in bulk, shear and expansion all agree within 5°C under the testing conditions used in this chapter.
2. The HHPA, THPA, MTHPA – cured specimens all have T_g's of about 120 to 125°C, whereas the T_g of the NMA – cured material is considerably higher (140 to 160°C depending on cure). The probable reason is that the HHPA, THPA and MTHPA molecules are all similar and fairly flat molecules but NMA has a methyl bridge across the molecule and consequently is bulkier. This may well mean that the NMA–cured specimen requires more energy for the bulky NMA molecules to be able to move freely.
3. A relaxation of about one hundred fold in J and fifteen fold in B was observed. The bulk relaxation is larger than is commonly seen, and the reason is thought to be that the measurements here are for lower strains than is usual.
4. Poisson's ratio derived from E and G measurements is subject to very large errors especially in the glass transition region. It is preferable to calculate ν from K and E measurements. Minima or maxima observed in ν_{EG} may stem from errors in temperature measurement of E and/or G.
5. There is some evidence in the literature for T_g differences in G and K^{5-7}. Part I of this paper[19] indicates that the activation energies in bulk and shear may be different for one of the materials used in this chapter. A small T_g difference is noticed at long creep times in the data of part I[19]. Further work is required at longer creep periods in bulk to check this finding.

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APPENDIX

We assume here that the relaxation behaviour may be described by the Arrhenius equation at all times and temperatures, both in dilatation and in shear, and that $\Delta H_G < \Delta H_K$ for all temperatures (as seems to be the case in the rubbery region[19]).

The Arrhenius equation may be written

$$\left.\begin{aligned}\tau_K &= \tau_{\infty K}\exp\left(\frac{\Delta H_K}{RT}\right)\\ \tau_G &= \tau_{\infty G}\exp\left(\frac{\Delta H_G}{RT}\right)\end{aligned}\right\} \qquad (1A)$$

where the subscript K denotes bulk deformation and the subscript G denotes shear deformations.

Thus τ_K and τ_G are relaxation times at T

$\tau_{\infty K}$ and $\tau_{\infty G}$ are relaxation times at $T = \infty$

R is the universal gas constant

Now let T_c be a temperature for which the bulk and shear transitions occur at the same creep time.

We aim to show that at any other creep time t', the bulk and shear transitions will occur at different temperatures.

A schematic representation is given in *Figure 7*. By the time-temperature superposition principle the point P_1 (which is the transition point) on the shear compliance curve at T_c shifts on to the point P_1' when the temperature is changed from T_c to T_{gG}. The shift factor, $\log a_T$ is given by

$$\log a_T = \log\left(\frac{t'}{t_c}\right) = \frac{\Delta H_G}{2.303R}\left(\frac{1}{T_{gG}} - \frac{1}{T_c}\right)$$

Similarly in bulk deformation P_2 shifts on to point P_2' and we obtain (2A)

$$\log a_T = \log\left(\frac{t'}{t_c}\right) = \frac{\Delta H_K}{2.303R}\left(\frac{1}{T_{gK}} - \frac{1}{T_c}\right)$$

hence

$$\left.\begin{aligned}T_c - T_{gG} &= \frac{\log(t'/t_c)\,2.303R\,T_{gG}T_c}{\Delta H_G}\\ T_c - T_{gK} &= \frac{\log(t'/t_c)\,2.303R\,T_{gK}T_c}{\Delta H_K}\end{aligned}\right\} \qquad (3A)$$

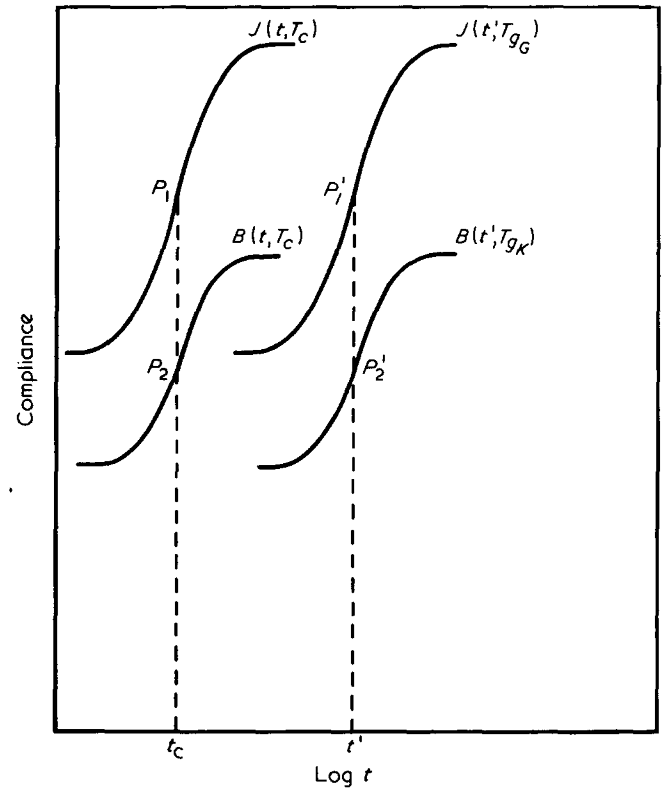

Figure 7 Schematic diagram of the dependence of bulk and shear compliances on temperature and creep time

Dividing by T_{gG} and T_{gK} respectively we obtain

$$\left.\begin{aligned} \frac{T_c}{T_{gG}} - 1 &= \frac{\log(t'/t_c)\, 2.303 R\, T_c}{\Delta H_G} \\ \frac{T_c}{T_{gK}} - 1 &= \frac{\log(t'/t_c)\, 2.303 R T_c}{\Delta H_K} \end{aligned}\right\} \tag{4A}$$

hence

$$\left.\begin{aligned} T_{gG} &= \frac{T_c}{\dfrac{\log(t'/t_c)\, 2.303 R\, T_c + 1}{\Delta H_G}} \\ T_{gK} &= \frac{T_c}{\dfrac{\log(t'/t_c)\, 2.303 R\, T_c + 1}{\Delta H_K}} \end{aligned}\right\} \tag{5A}$$

$$T_{g_K} - T_{gK} =$$

$$T_c \left[\frac{1}{\dfrac{\log(t'/t_c)\, 2.303\, R T_c + 1}{\Delta H_G}} - \frac{1}{\dfrac{\log(t'/t_c)\, 2.303\, R\, T_c + 1}{\Delta H_K}} \right]$$

and using equation (4A) we obtain

$$T_{gG} - T_{gK} =$$

$$T_c \left[\frac{\left\{ \dfrac{\log(t'/t_c)\, 2.303\, R\, T_c + 1}{\Delta H_K} \right\} - \left\{ \dfrac{\log(t'/t_c)\, 2.3\text{-}3 R\, T_c + 1}{\Delta H_G} \right\}}{\dfrac{T_c}{T_{gG}} \times \dfrac{T_c}{T_{gK}}} \right]$$

$$= \log(t/t_c)\, 2.303\, R\, T_{gG}\, T_{gK}\, (1/\Delta H_K - 1/\Delta H_G)$$

$$= \frac{2.303\, R\, T_{gG}\, T_{gK}}{\Delta H_K\, \Delta H_G} \log(t'/t_c)\, (\Delta H_G - \Delta H_K). \tag{6A}$$

From equation (6A) we see that 2.303 $R\, T_{gG} T_{gK} / \Delta H_G \Delta H_K$ is positive.

For the material under consideration $\Delta H_G - \Delta H_K$ is negative,

Thus for $t' > t_c$ we obtain $T_{gK} > T_{gG}$

and for $t' < t_c$ we obtain $T_{gK} < T_{gG}$

Thus for a material for which the bulk activation energy exceeds the activation energy in shear, one should expect to find a region at long creep times where the bulk transition temperature T_{gK} exceeds the shear transition temperature T_{gK}, and similarly at short creep times $T_{gG} > T_{gK}$, (provided that the response of the material in bulk and shear may be described by the Arrhenius equation over the range of temperatures and times of interest).