Dynamic mechanical behaviour and its dependence on preparation method of structural epoxide resin

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Dynamic mechanical measurements over the frequency range 10^{-4}–1 Hz and temperature range 100–470 K have been made on an epoxy resin made with the diglycidyl ether of bisphenol A (DGEBA) and 4,4′-diaminodiphenylmethane (DDM) under two conditions: (i) by mechanical mixing without a solvent, and (ii) by mixing their solutions in methyl ethyl ketone. Both epoxies have three relaxations, named γ, β and α in order of increasing temperature. The effect of preparation of the epoxy from the solvent is (i) reduction of both the temperature and the strength of the γ- and α-processes, (ii) decrease in the temperature and increase in the strength of the β-process, and (iii) a two-fold reduction in the rubber modulus of the epoxy. It is shown quantitatively that the decrease in the temperature of the α-peak and of the rubber modulus are due to a lower number of crosslinks in the solvent-prepared epoxy. The strength and the temperature of the peaks change in systematic manner with the thermal history of the samples. The characteristics of the γ- and β-processes are completely recovered on reversible thermal cycling, but those of the α-process are not. Thus physical ageing also plays a role in the dynamic mechanical behaviour of the epoxy resin. The effect of ageing differs from that of thermal degradation. The G', G'' or $\tan\phi$ data could not be reduced to a master curve by a horizontal displacement alone even when the change in G_U/G_R with temperature is taken into account. It is shown that a more discernible criterion for the validity of the time–temperature superposition is an analysis of the $\tan\phi$ spectrum rather than of the G' and G'' spectra. The fixed-frequency measurements of the dynamic mechanical properties give a lower temperature for a given rate of the α-process than do the isothermal measurements of the spectrum.

(Keywords: dynamic mechanical; epoxide resin; solvent effect; curing effect)

INTRODUCTION

The viscoelastic behaviour of epoxy resins must be considered for their load-bearing applications. This behaviour depends upon the thermal history of a polymer[1], and it is generally assumed that the morphology of a thermoplastic polymer remains unchanged with time at all temperatures far below T_g. But at temperatures near T_g, the magnitude of both the thermodynamic and kinetic properties changes, largely because the polymer chains tend to approach an equilibrium conformation of lower energy[1-3]. While such changes are generally known to occur for almost all types of thermoplastics (solidified by cooling the melt), time-dependent changes in physical properties have been observed in highly crosslinked thermosets[4,5] (obtained by curing a mixture of two liquid components). Epoxy and polyester resins undergo a structural rearrangement at ambient temperatures, which is usually substantially below their T_g, significant enough to cause a change in their mechanical properties[4,5]. This paper reports a study of such changes in an epoxy resin prepared by mixing the diglycidyl ether of bisphenol A (DGEBA) and diaminodiphenylmethane (DDM) in stoichiometric ratio of 2:1. Choy and Plazek[6] have recently studied the various physical properties during the curing of this epoxy resin, and Babayevski and Gillham[7] have studied the dynamic mechanical behaviour of the epoxy-braid composite during the curing process.

An epoxy resin or thermoset plastic can also be prepared by mixing the liquid components in a solvent and evaporating the solvent, which is followed by curing. Since the geometry and the extent of the crosslinked network of thermoset plastics is likely to depend upon the molecular distribution of the liquid components in a solvent and on the solvent–solute interactions, it is likely that the physical properties of a thermoset prepared without a solvent would differ from those of one prepared with a solvent. We further report a dynamic mechanical study of the epoxy resin prepared by mixing DGEBA and DDM in methyl ethyl ketone and the effect of thermal history on its properties. Such a study is also technologically important as the composites of thermoset plastics are usually prepared from a solvent medium.

Most measurements of dynamic mechanical spectra of polymers are made at a frequency of 1 Hz. This study is also significant in that it reports on the behaviour of an epoxy polymer at significantly lower frequencies and temperatures, where time–temperature superposition of the properties can be reliably tested.

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EXPERIMENTAL

The instrument used to measure the real and imaginary components of the shear modulus and the loss tangent has been described in earlier papers[8]. In this assembly, one end of the specimen was secured and the other end was connected to a magnet which oscillated in a magnetic field of desired frequency. The assembly was counterbalanced so that the specimen was under a very slight tension. Several measurements on samples cut to a dimension of ~6 x 50 x 1 mm were repeated for both the frequency and temperature variation and the results agreed within 1%. Measurements were made at 2 K intervals and the temperature of the sample was maintained constant within ~0.2 K, thus ensuring that the errors arising from temperature variation were minimal. The relative amplitude of deformation was less than 10^{-4}.

The epoxy specimens were prepared for us by the Laboratoire des Materiaux Macromoleculaire, CNRS ERA 745, INSA, 69261 Villeurbanne, France, from 78 parts by weight of purified diglycidyl ether of bisphenol A and 22 parts of 4,4'-diaminodiphenylmethane, which corresponds to a molar ratio of 2:1. Both components were separately heated to 363 K, until the DDM was completely melted, then mechanically mixed for 15 min. The blended liquid was poured into a cylindrical aluminium container of ~1 cm diameter. The standard curing procedure was as follows: for 5 h at ~363 K followed by 3 h at ~443 K and finally cooled at a rate much greater than $0.2\,\mathrm{K\,s^{-1}}$ (at ~400 K) to room temperature by removing it from the oven. This epoxy is referred to here as epoxy N.

The second epoxy sample was prepared by first dissolving DDM in methyl ethyl ketone in amount of 1 g DDM per millilitre of methyl ethyl ketone at room temperature. The solution was mechanically mixed with DGEBA at ~353 K for 15 min to provide a 2:1 molar ratio of DGEBA to DDM. Methyl ethyl ketone was evaporated from the solution by pumping at 358 K for 50 min. The epoxy was then cured for 4 h at ~363 K followed by 3 h at 443 K and cooled to room temperature at a rate much greater than $0.2\,\mathrm{K\,s^{-1}}$ (at ~400 K) by removing it from the oven. This epoxy is referred to as epoxy S.

RESULTS

Mechanically mixed epoxy resin (epoxy N)

The mechanical loss tangent tan ϕ ($=G''/G'$) of the epoxy resin measured at 1 Hz is plotted against temperature in *Figure 1*. It shows three relaxation regions: two as peaks below T_g, at ~223 K of height 4.5×10^{-2} and at ~326 K of height 1.8×10^{-2}, and one as a peak above T_g, at ~453 K of height 0.9. In order of increasing temperature, these three peaks are referred to as γ, β and α respectively, and are indicated in *Figure 1*. The temperature of the α-peak is the same as observed for the epoxy-braid by Babayevski and Gillham[7], but those of the γ- and β-peaks are much higher and the relative height of the γ-peak much lower than theirs. These discrepancies can be due to several factors, namely (i) the effect of braids on the epoxy network, (ii) the relatively large strain used in the torsional braid analysis and (iii) the effect of coating on the braid. It is difficult to ascertain whether the difference between our results and theirs is due to one or all of these factors.

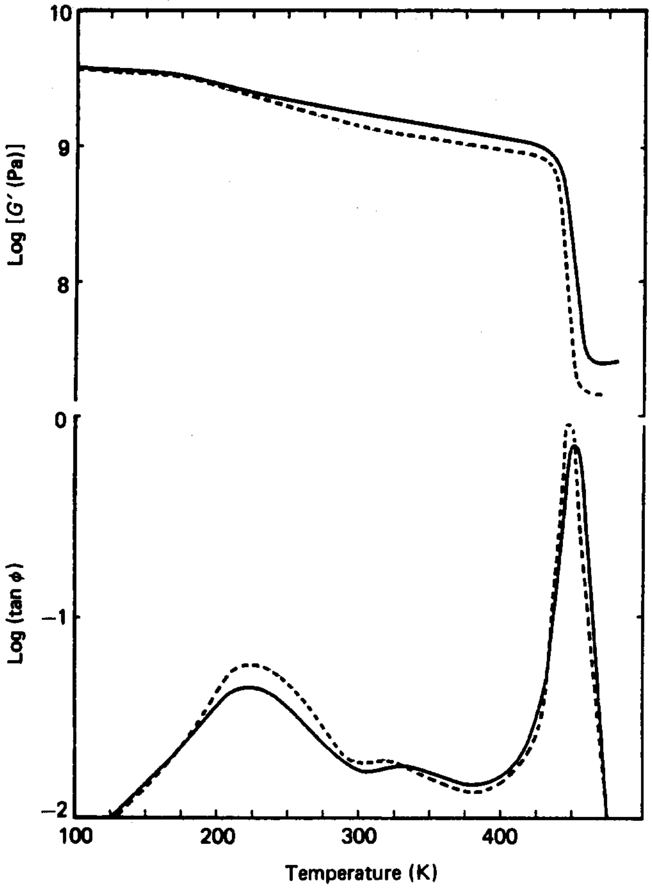

Figure 1 Plots of G' and tan ϕ against temperature of epoxy resin N measured at 1 Hz. The epoxy was obtained by mechanically mixing the pure components. Sample cured for 5 h at 363 K and 3 h at 443 K (———); same sample heated to 480 K for a long enough period to cause thermal degradation and cooled to 100 K (-----); see text for details

In order to determine the effect of degradation of the epoxy on its dynamic mechanical properties, another sample from the same stock was further cured at temperatures above 480 K for a time long enough to undergo a slight change of colour. The sample was cooled at a rate of $0.2\,\mathrm{K\,s^{-1}}$ to 100 K and measurements repeated. The tan ϕ of the thermally degraded sample is also plotted against temperature in *Figure 1*. The sample still showed three relaxation regions but with some changes. The γ-peak increased in height from 4.5×10^{-2} to 5.5×10^{-2}, with no change in its temperature. The height of the β-peak increased from 1.8×10^{-2} to 1.9×10^{-2}, and its temperature decreased by ~20°C. The height of the α-peak also increased from 0.9 to 1, and its temperature decreased by ~7°C. The thermal degradation also increased the ratio of unrelaxed to relaxed modulus by ~50%.

The real component of modulus, G', measured at 1 Hz is also plotted against temperature in *Figure 1*. G' decreased slowly at temperatures near 100 K followed by a relatively rapid decrease at the temperatures where γ- and β-peaks appeared and nearly two orders of magnitude decrease at the temperature of the α-relaxation peak. In all samples, which were not thermally degraded, the modulus increased with further increase in the temperature. This increase was 25% more than expected from the increase of the temperature alone and, therefore, was caused by the stiffening of the epoxy resin, which suggests an additional cure of the sample on heating above 443 K.

Epoxy resin from mixing in methyl ethyl ketone (epoxy S)

A bar cut from the freshly cured sample under vacuum at 443 K for 3 h, was cooled at a rate much greater than 0.2 K s^{-1} to 100 K and measured from 100 to 460 K while being heated at the rate of 1.7×10^{-2} K s^{-1}. Its G' and $\tan \phi$ are plotted against temperature in *Figure 2*. The three relaxation processes are more clearly resolved in epoxy S in *Figure 2* than in epoxy N in *Figure 1*. These are also referred to as γ, β- and α-relaxation processes in order of their appearance with increasing temperature. The temperatures for the γ, β- and α-relaxation peaks are: 205, 308 and 420 K respectively, with heights 4.5×10^{-2}, 3.0×10^{-2} and 0.82, respectively.

In order to study the history dependence of its dynamic mechanical behaviour, a new bar of epoxy S from the original stock, which had now remained at ~298 K for two weeks, was cut, cooled to 100 K and its G' and $\tan \phi$ were measured up to 263 K. Plot A in *Figure 3* shows the results. The sample was kept at 263 K for 15 min and then subsequently cooled to 100 K at a rate of 0.2 K s^{-1} and measured from 100 to 353 K while being heated at 1.7×10^{-2} K s^{-1}. These results are shown in plot B in *Figure 3*. The sample was then kept at 353 K for 15 min, cooled to 100 K and measured from 100 to 450 K. These results are shown in plot C in *Figure 3*. The sample was then kept at 450 K for 15 min, cooled to 100 K and measured from 100 to 450 K. These results are shown in plot D. In the last treatment, the sample was kept at ~443 K for 26 h in vacuum, cooled to 100 K at a rate greater than 0.2 K s^{-1} and measured up to ~460 K. These results are shown in plot E in *Figure 3*. Thus plot E refers to the sample which had undergone a maximum period of cure at various temperatures, but was cooled at a rate much greater than 0.2 K s^{-1} from 450 to 100 K.

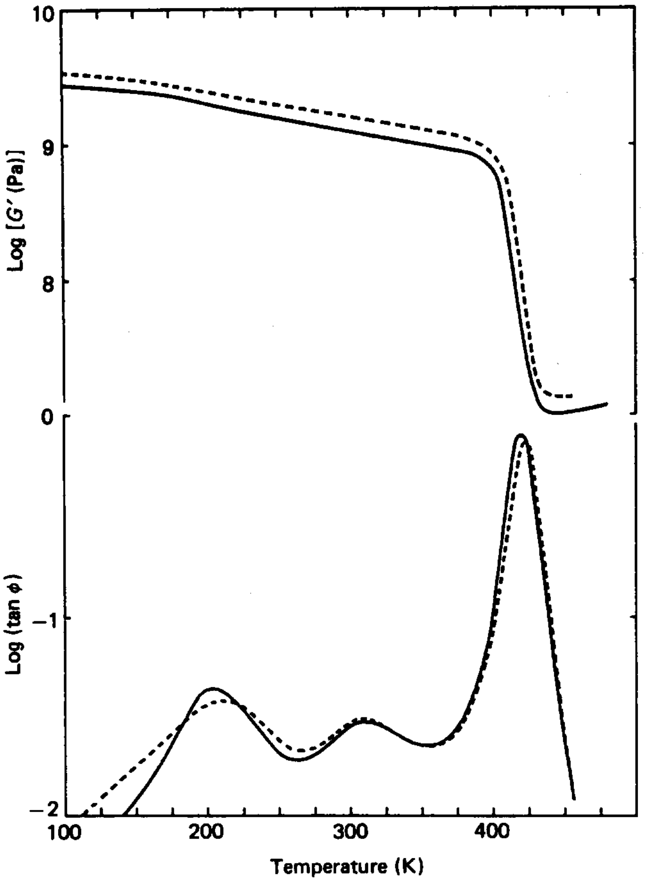

Figure 2 Plots of G' and $\tan \phi$ against temperature of epoxy resin S measured at 1 Hz. The epoxy was obtained by mixing the components in methyl ethyl ketone as solvent. Sample cured for 3 h at 443 K and heated at the rate of 1.7×10^{-2} K s^{-1} (———); the sample after the thermal treatments of A, B and C given in *Figure 3* (-----); see text for details

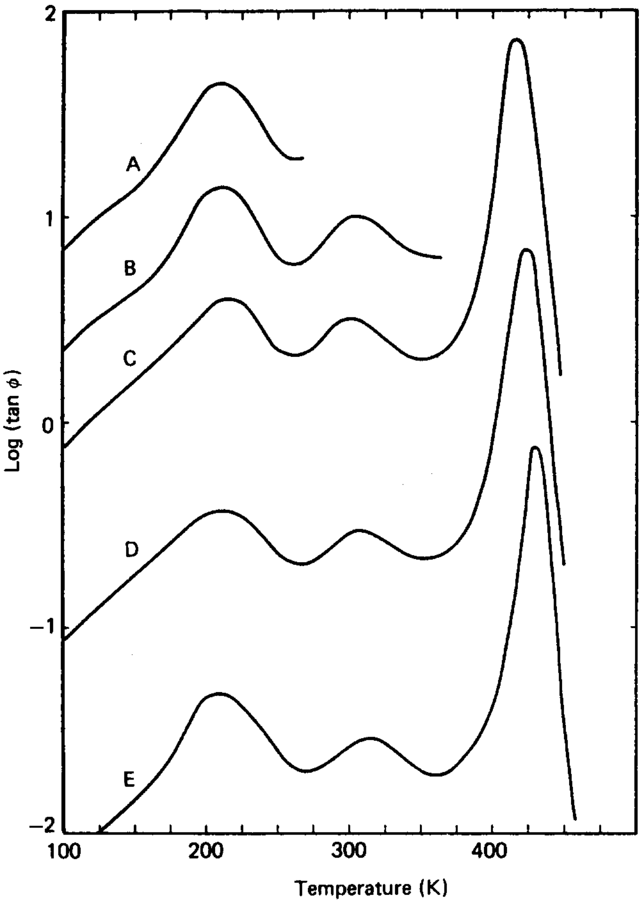

Figure 3 Plots of $\tan \phi$ against temperature of epoxy resin S cured for 3 h in vacuum at 443 K and measured at 1 Hz. Curve A, the as-cured sample measured during heating to 263 K; B, the same sample cooled to 100 K and measured up to 353 K; C, cooled to 100 K and measured up to 450 K; D, cooled to 100 K and measured up to 450 K; and E, kept at 443 K for 26 h, cooled at a rate much greater than 0.2 K s^{-1} to 100 K and measured. The heating rate during all measurements was 1.7×10^{-2} K s^{-1}. Plot E is to scale. Plots D, C and A are progressively shifted upwards by one decade. Plot B is shifted upwards by 2.5 decades of $\tan \phi$

The temperatures of the three peaks after various thermal treatments were as follows: The γ-peak appeared at 210 K in plot A, with a height of 4.6×10^{-2} and remained unchanged in both the temperature and height in plot B. It then appeared at 216 K with a height of 4.2×10^{-2} in plot C and then at 213 K with a height of 3.8×10^{-2} in plot D and finally at 210 K with a height of 4.9×10^{-2} in plot E. The β-peak at 308 K with a height of 3.2×10^{-2} in plot B appeared at 303 K with a height of 3.3×10^{-2} in plot C, at 308 K with a height of 3.0×10^{-2} in plot D and finally at 310 K with a height of 2.9×10^{-2} in plot E. The α-peak at 417 K a height of 0.8 or plot C appeared at 423 K of height 0.74 in plot D and finally at 430 K of height 0.81 in plot E.

The minimum at 1.9×10^{-2} between the γ- and β-peaks at 263 K in plot A appeared at 258 K and 1.8×10^{-2} in plot B and at 2.1×10^{-2} in plot C and then at 263 K in plots D and E with a minimum at 2.0×10^{-2} in both. The minimum at 2.1×10^{-2} between the β- and α-peaks at 353 K in plot B remain unchanged in plots C, D and E. The heights of the γ- and α-peaks decreased during and after each thermal treatment from A to D. This was significantly greater than the experimental scatter ($\sim 2\%$). Since plot E was obtained after additional curing and rapid quenching of epoxy S from 450 K, this plot is similar to that shown by the full curve in *Figure 2*, in that it resembles the G' and $\tan\phi$ isochrones of epoxy S studied prior to any thermal treatment.

In order to compare the relaxation characteristics of epoxy S before and after the thermal treatments of *Figure 3*, a plot of G' and $\tan\phi$ of a sample subjected to the thermal cycles of A, B and C is given in *Figure 2*. This plot is the same as plot D in *Figure 3*. Evidently, both the heights and the temperatures of the γ- and α-relaxation peaks changed in thermal treatment of the epoxy S.

The G' and $\tan\phi$ of epoxy N and epoxy S measured at 1 Hz are plotted against temperature in *Figure 4*. Data on the two epoxy samples with similar thermal histories are shown so that a useful comparison of their mechanical behaviour could be made. In comparison with epoxy S, the γ-peak amplitude of epoxy N is higher, the β-peak lower and the α-peak slightly higher. All the three peaks in epoxy N appear at a higher temperature than in epoxy S. The glassy modulus of epoxy N is slightly higher at all temperatures below T_g, but the rubbery modulus above T_g is nearly twice as high as that of epoxy S.

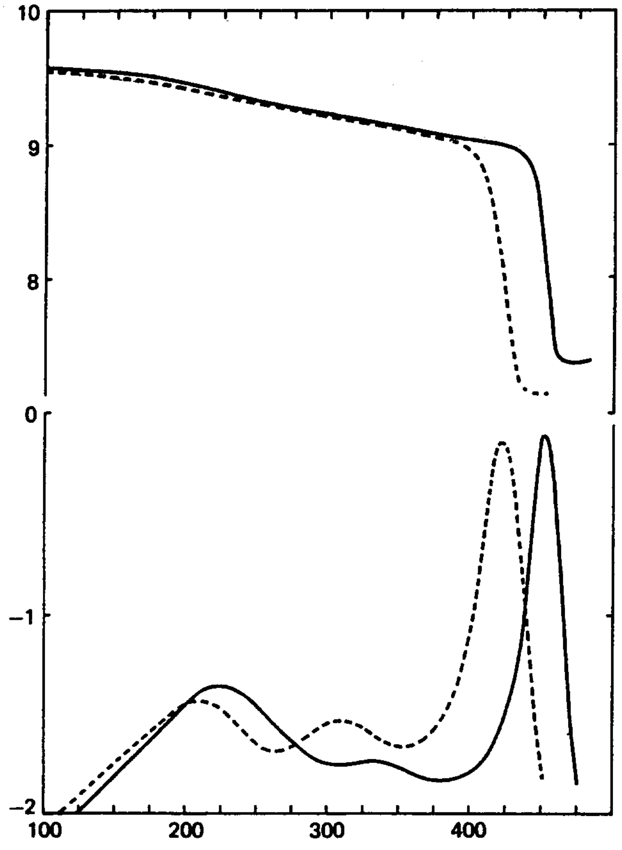

Figure 4 Plots of G' and $\tan\phi$ of epoxy resins. Epoxy N obtained by mechanical mixing, cured at ~ 353 K and further cured by heating to ~ 450 K at the rate of 1.7×10^{-2} K s^{-1} (———); the sample obtained by mixing in methyl ethyl ketone, curing at ~ 353 K in vacuum and then cured at different temperatures during the thermal cycling in *Figure 3* (– – –); see text for details

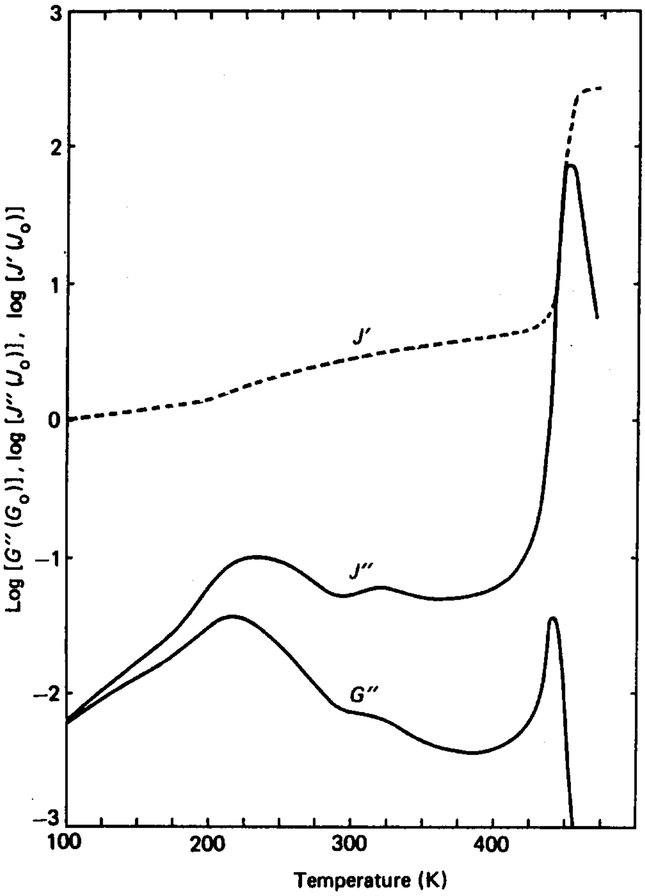

Figure 5 Plots of G'', J' and J'' of epoxy N measured at 1 Hz against temperatures. The corresponding plot of G' and $\tan\phi$ is shown by full curve in *Figure 1*. $G_0 = J_0^{-1} = 6$ GPa

DISCUSSION

The relaxation regions

Three relaxation processes occur in the epoxy resin, as typical dynamic mechanical isochrones for $\tan\phi$ and G' shown in *Figures 1* to *4* indicate. The lowest-temperature process whose peak at the frequency of 1 Hz appears in the range 203–213 K has been denoted as the γ-process. The temperature of this relaxation is remarkably similar to the temperature of the β-peak of 223 K in TGDDM–DDS measured at a frequency of 11 Hz by Keenan *et al.*[9] This relaxation was attributed primarily to localized motions of the polymeric chain. The β-relaxation, whose peak appears at 310–325 K in *Figures 1* to *4*, is denoted in other epoxy resins as ω-transition and its peak in the various epoxies is centred at a much higher temperature (e.g. ~ 373 K at 11 Hz in TGDDM–DDS but is not observed in DGEBA cured with acid anhydrides)[10]. This relaxation has been attributed to the unreacted molecular segments and/or inhomogeneities in the sample arising from dissimilar crosslinking resins[9,10]. The α-relaxation observed at 420–460 K in *Figures 1–4* is undoubtedly due to the long-range motions of the polymeric network, which become rapid at $T > T_g$, and is attributed to the glass transition of the material.

It is noteworthy that the temperature of these relaxation processes differs depending on the dynamic mechanical property under consideration, as is evident in *Figure 5*. Specifically, the position of the peaks in a temperature plane measured at 1 Hz depends upon the particular quantity, $\tan\phi$, G'' or J'', being plotted, and the choice of these parameters thus affects the estimates of the activation energies of the underlying processes. Therefore, the effect is important when the mechanism of relaxation is to be understood in terms of the polymer morphology. The temperature at which the peaks appear in measurements at a fixed frequency (isochronal) also differs significantly from the temperature at which the peaks appear in measurement made by varying the frequency[11], due to the temperature-sensitive strengths of ΔG and ΔJ. This choice of isochronal or isothermal data also affects the estimates of the activation energy of the underlying process. Since no conclusive explanations in terms of specific groups or segmental motions for these relaxations seem to have been offered for epoxy resins, we ignore here the effect of the choice of the dynamic mechanical parameters or of the method of measurement on the activation energies of the relaxation.

In view of the fact that relaxations similar to those observed in the epoxy also occur in a variety of polymers[12] and ionic glasses[13], and in the dielectric relaxation of rigid molecular glasses[14], it would seem that the existence of the γ- and β-relaxations indicate merely two types of local regions of mobility in the epoxy matrix, each region with its characteristic activation energy corresponding to its intermolecular environment. In this sense the γ-relaxation (β-transition in Keenan *et al.*'s[9] terminology) may indicate motion in those regions where polymer chains are relatively loosely packed and β-relaxation (ω-transition in Keenan *et al.*'s[9] terminology) motions in those regions where loose packing is caused by unreacted molecular segments and/or by substantially lower crosslinking densities.

Effect of thermal degradation of epoxy N

The two plots in *Figure 1* show that both the characteristics of the three relaxation processes and the modulus of the epoxy resin are significantly altered when the epoxy is thermally degraded. It means that the sample had undergone an irreversible change due to the cure at high temperature when the sample was kept at ~460 K, prior to measuring again from 100 to 480 K. A thermoset network is assumed to be fully cured when its glass transition occurs at a temperature above which no further reaction takes place. When so, the cured thermoset achieves its optimum mechanical properties. Since the glass transition temperature of the epoxy resin was not measured, we regard that the decrease in the temperature of the α-relaxation peak measured at 1 Hz as in *Figure 1* indicates a decrease in the glass transition temperature. Since thermal degradation decreases T_g of an epoxy[15], this implies that only the process of thermal degradation of the polymer thermoset occurred at high temperatures and contributed to the changes in its dynamic mechanical behaviour. This degradation introduced no new relaxation peaks but a change in the colour of the epoxy was detected.

The glass transition temperature, as indicated by the position of the α-peak, is decreased by ~7 K in *Figure 1* and the separation between the γ- and β-peaks is decreased by ~20 K. The slight increase in the height of the β-peak is due to greater overlap and, therefore, greater contribution to $\tan \phi$ from the γ-process. The height of the γ-peak is increased by ~20%. If the β-peak was due to the unreacted molecular segments of the components in the resin, thermal degradation is expected to raise its height. This has not been observed. The increase in the height of the γ-peak on degradation is attributable to the resulting increase in the number of local regions of lower density where motion of the polymer network is still possible. Thermal degradation also increased the ratio G_U/G_R, as is expected when the crosslink density is decreased due to either oxidation or bond rupture.

The increase in the height of the γ-peak and its lesser separation from both the β- and the α-peaks suggests an increase in the toughness of the epoxy resin and increased dissipation of mechanical energy into heat during the use of the degraded epoxy resin.

Time-dependent changes of epoxy S

A comparison of the data for epoxy S in *Figures 2* and *3* shows that ageing of the sample at ~298 K for two weeks increases the temperature or slows the rate of γ-relaxation without a significant change in the height of its peak. Further heat treatments at higher temperatures seen in *Figure 3* (A to D) increase the temperature of the γ-relaxation and decrease its peak height. The temperature of the β-peak as well as its height remain unchanged on ageing the sample at 298 K. The temperature and height of the α-peak in *Figure 2* remains unchanged in *Figure 3* (plot C), on the thermal treatments described in *Figure 3*. Further treatment raised the temperature to 423 K and reduced its height, as in plot D of *Figure 3*.

Evidently, the dynamic mechanical properties of epoxy S changed with time at all temperatures with the result that the strength of all relaxation processes became less when the sample was kept at temperatures above 298 K, but the temperature of the various peaks changed in different ways such that the separation between the β- and α-peaks increased. The increase in the temperature of the α-peak may indicate an increase in T_g as a result of further curing during the thermal treatments. But there are two further factors that may be partly responsible for such changes, though their relative importance is difficult to ascertain. One is the degree of frozen-in stresses in the sample which may make the sample appear stiffer to additional small stresses applied during the dynamic mechanical testing and thus shift the positions of both the γ- and β-peaks, and the second is the possibility of further chemical reactions at temperatures well below T_g, but only in localized regions of the rigid matrix where segmental or molecular orientation and/or diffusion persists. This would also lead to local curing or densification of the network in such regions. The latter possibility has not so far been considered in the sub-T_g cure of the epoxy resins.

The net effect of further curing can be seen in *Figure 2* where a plot of G' and $\tan \phi$ of epoxy S without a thermal treatment and after the treatments indicated by plots A, B and C of *Figure 3* are given. The height of the γ-peak is reduced by ~15% and its temperature increased by 5 K. The height of the α-peak is also decreased by 10% and its temperature increased by 5 K. Neither the height nor the temperature of the β-peak is affected by further curing. The latter indicates that the β-peak is not likely to be due to the unreacted components, as curing would reduce the amount of such components, and consequently the height of the β-peak would be reduced. In view of the fact that the α-peak, and therefore T_g, is significantly increased with time–temperature history of epoxy S, we suggest that the decrease in the height of the γ-peak is in part due to more complete network formation and the consequent reduction of the size of the local regions of molecular or segmental motions, and in part due to the densification that occurs during the physical ageing, or structural relaxation to a denser state, of a glassy polymer. Since plot E in *Figure 3* has the same temperature and magnitude of the γ-peak as the new sample of the epoxy in *Figure 2*, it seems that thermal cycling followed by rapid quenching may restore the rate and strength of the γ-peak despite the fact that the α-peak after this treatment appeared at a higher temperature. Thus the change in the γ-peak on thermal treatment may be largely due to physical ageing of the epoxy, rather than to its further curing during the thermal cycling.

Differences between epoxy N and epoxy S

One of the purposes of this study was to determine whether the cured epoxy prepared from mixing in a solvent had mechanical characteristics different from that prepared without a solvent. As seen in *Figure 4*, the differences are remarkable. The γ- and α-peaks in epoxy S are lower in both height and temperature and the β-peak higher in height but lower in temperature than the corresponding peaks in epoxy N. The observed decrease in G' at T_g of epoxy S is nearly twice that of epoxy N. Since the glassy modulus (at ~ 100 K) of epoxy S and epoxy N are nearly the same, this means that the rubber modulus is reduced by a factor of 2 when the epoxy is prepared from methyl ethyl ketone as solvent. This seems to be a remarkable effect of the method of preparation of the epoxy resin and, therefore, the possbiliity that the epoxy S may contain a residual amount of solvent which has acted as a plasticizer (as suggested by the decrease in the temperature by 30 K of the α-relaxation peak in *Figure 4*) was investigated by observing the infra-red spectrum of epoxy S. It showed less than 0.1% of methyl ethyl ketone, which could not be completely removed by pumping at 470 K. This treatment did not alter the dynamic mechanical behaviour of epoxy S. It also seems unlikely that the presence of less than 0.1% methyl ethyl ketone could decrease the position of the α-peak, or T_g by 30 K. The decreased rubbery modulus suggests a more loose network in epoxy S than in epoxy N and this may be partly responsible for the much greater strength of the β-process in it than in epoxy N. Since the fracture toughness of a polymer is related to the strength of β- and other sub-T_g relaxation processes, it follows that epoxy S would be tougher than epoxy N at ambient temperatures.

The effect of solvent on the crosslink density

The value of G_R of epoxy S is nearly half of that of epoxy N, assuming that the glassy moduli of the two epoxies at 100 K are nearly the same. The low value of G_R of epoxy S cannot be entirely explained by the presence of the solvent which could act as a plasticizer, for the amount needed to cause such a low value, estimated from results of entangled polymer chains in solutions[16], is greater than 10% and, for a crosslinked polymer, the amount of solvent needed should also be more than 10%. Our infra-red spectra of epoxy S showed less than 0.1% solvent residue. Therefore, the low value of the rubber modulus, G_R, is due to a lower crosslink density in the network of epoxy S than in that of epoxy N. Since $G_R \approx \rho RT/M_e$, where ρ is the density and M_e is the molecular weight between fixed entanglements or crosslinks, the decrease in G_R to nearly 0.56 times the value of epoxy N is due to a decrease in ρ/M_e by the same amount and since the change in ρ is relatively small, it follows that M_e of epoxy S is about 1.8 times as high as that of epoxy N. Alternatively, the crosslink density in epoxy N is about 1.8 times as high as that in epoxy S.

The analysis given above can be made quantitative and then compared with the experimental T_g values of epoxy S and epoxy N. For this, we follow the Gibbs–DiMarzio theory[17] of configurational entropy for glass transition in polymers. According to this theory[18], addition of crosslinks to uncrosslinked polymer increases the value of T_2, the second-order thermodynamic transition temperature at which the time-dependent configurational entropy becomes zero. Since the ratio, T_g/T_2 remains unaltered on crosslinking, or both T_g and T_2 increase in the same proportion, the relation given by DiMarzio[18] can be written as:

$$[T_g(x)-T_g(0)]/T_g(0)=Ax(1-Ax) \qquad (1)$$

where $T_g(x)$ refers to the T_g of the polymer with x number of crosslinks per gram and $T_g(0)$ with no crosslinks, $A=KM/\gamma$ where K is a constant[18] with a value of $(1.3\pm0.1)\times10^{-23}$, M is the mer molecular weight and γ is the number of flexible bonds per mer. $T_g(0)$ is equal to the glass transition temperature of the polymer, before crosslinking occurs, and would be in the same ratio to the temperature $T_\alpha(0)$, the temperature of the α-relaxation peak measured at 1 Hz of uncrosslinked polymer, as $T_g(x)$ is to the temperature $T_\alpha(x)$ of the corresponding peak of the cured polymer. Thus, $T_g(x)$ and $T_g(0)$ in equation (1) can be replaced by $T_\alpha(x)$ and $T_\alpha(0)$. $T_\alpha(0)$ for the epoxy of our study is 383 K[7]. By substituting the experimental value of $T_\alpha(x)=423$ K for epoxy S, the calculated value of $M/\gamma=45$ and $K=1.3\times10^{-23}$, we obtain $x=1.6\times10^{20}\,\mathrm{g}^{-1}$ for epoxy S. From the experimental value of $T_\alpha(x)=453$ K, we obtain $x=2.6\times10^{20}\,\mathrm{g}^{-1}$ for epoxy N. These values seem of a reasonable magnitude and show that the number of crosslinks per gram is decreased by a factor of 2 when the epoxy was prepared from the solvent.

An alternative test of our interpretation can be made by calculating the difference between the values of T_α of epoxy S and epoxy N by using equation (1) and substituting the value of 0.56 for the ratio of x in epoxy S to x in epoxy N. This gives a value of 30 K for the difference in T_g values. The value agrees surprisingly well with the experimental values of 30 K seen in *Figure 4*. Evidently the lower values of both T_g and G_R of epoxy S in comparison with those of epoxy N are due to a decreased number of crosslinks in epoxy S, and within the approximations of the configurational entropy theory, the decrease in G_R can be quantitatively related to the decrease in T_g of the epoxy.

In molecular terms, it means that the presence of methyl ethyl ketone as solvent decreases the probability of complete chemical bonding of DDM to DGEBA, or, alternatively, increases the probability of bonding between the DGEBA molecules. The latter needs to be further investigated by n.m.r. methods. Incomplete bonding between DDM and DGEBA would probably create more loosely packed regions in the glassy matrix of the epoxy and, therefore, both the γ- and β-relaxation peaks in epoxy S should be higher than in epoxy N. This too is seen in *Figure 4*. We, therefore, conclude that the dynamic mechanical behaviour of epoxy S is consistent with our interpretation that the use of solvent in the preparation decreases the number of crosslinks in the epoxy.

The time–temperature superposition

The dynamic mechanical spectrum and creep curves of polymers measured over a limited frequency, or time, range at different temperature are superimposed to obtain a single master curve, assuming that neither the height nor the slope of the spectrum is temperature-dependent. McCrum and Pogany[19] have ascertained the relative merits of the various methods of time–temperature superpositions using the creep data of an epoxy resin. They concluded that unless allowance is made for the temperature dependence of both the unrelaxed and relaxed compliances, a satisfactory master curve cannot be obtained by such superposition. In a recent paper[20] we also concluded that near T_g, the G' and G'' plots of polystyrene, although seemingly superimposable, are not superimposable when the loss factor is plotted instead. The use of tan ϕ heightens the effect. As seen in *Figure 6*, neither the G' nor the G'' plots of epoxy N are satisfactorily superimposible by a horizontal shift of the isotherms. Though on an intrinsically less sensitive logarithmic scale, the discrepancy from the time–temperature superposition may appear insignificant at first sight, it becomes remarkable when tan ϕ is plotted on a linear scale against frequency as in *Figure 7*. Clearly, the height of the tan ϕ peak increases with increasing temperature and its halfwidth decreases.

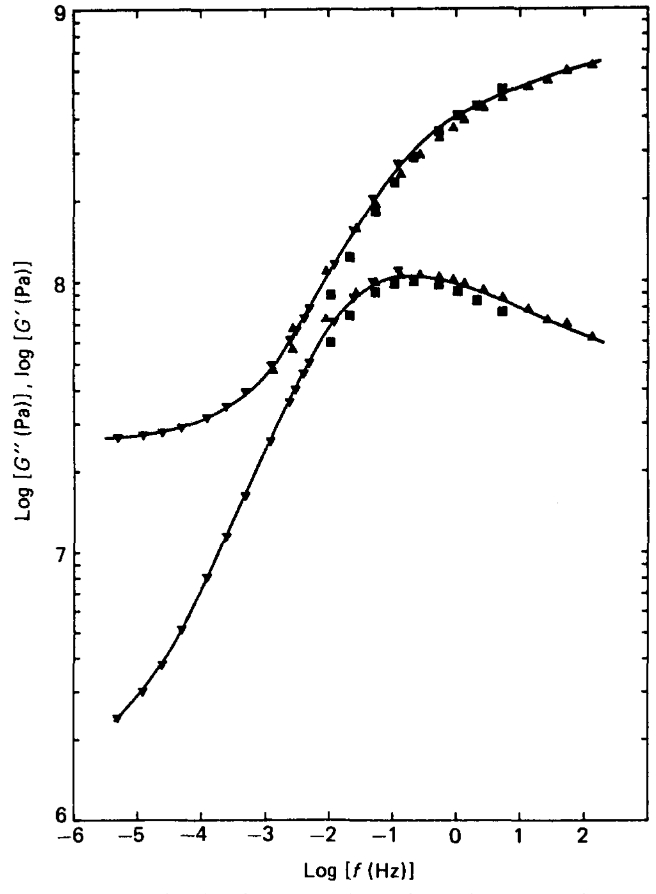

Figure 6 Plots showing the superposition of G' and G'' values of epoxy N obtained by mechanical mixing of the two components, curing at $\sim$298 K and heating to $\sim$460 K at the rate of 1.7×10^{-2} K s^{-1}. The shift factors in log f are 270 at 451 K (▲), 1 at 456 K (■) and 0.025 at 460 K (▼)

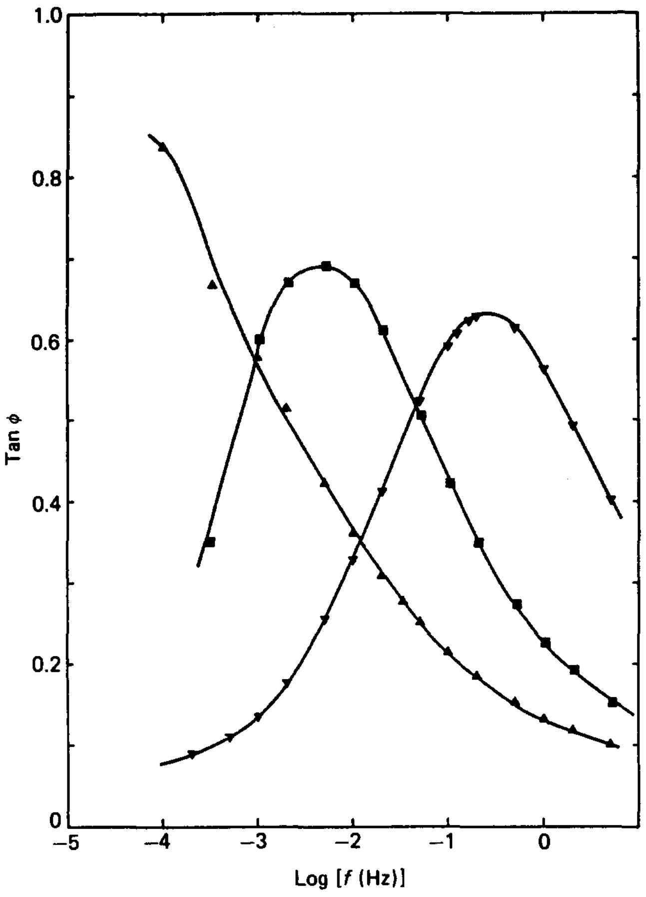

Figure 7 Plots of tan ϕ ($=G''/G'$) against frequency of the sample described in *Figure 6* at 451 K (▲), 456 K (■) and 460 (▼)

The principal importance of the time–temperature superposition is the demonstration that the relaxation times of individual polymer segments have the same temperature dependence, and superposition can be accomplished if the change in the magnitudes of G_U and G_R with temperature is corrected for. For simplicity, $\tan\phi \approx (G_U/G_R)^{1/2}/2$ for the dynamic mechanical behaviour of a single relaxation process. If G_U and G_R remain unchanged with temperature, the value of $\tan\phi_{max}$ would also remain unchanged and only its position on the frequency axis would change. For most polymers, the ratio G_U/G_R does vary with temperature and any deviation from the time–temperature superposition noted in *Figures 6* and *7* may partly be due to this variation. The change in $\tan\phi_{max}$ due to a change of G_U/G_R can be determined as follows: G_U is known to increase with decrease in temperature[21] by $\sim$0.01% K^{-1}, and G_R to decrease with decrease in temperature[22] by $\sim$0.3% K^{-1}; thus the combined variation in G_U and G_R would increase $\tan\phi_{max}$ by less than 0.2% K^{-1} when the temperature is decreased. The observed increase of tan ϕ by $\sim$4% K^{-1} from *Figure 7* is clearly much higher than that expected from the above temperature dependences of G_U and G_R. Therefore, we conclude that the predominant effect of decreasing the temperature of the epoxy is the change in the temperature dependence of relaxation times of correlated motions of chain segments and/or a decrease in the segmental correlation length involving regions of crosslinking in the epoxy (resin), and that this vitiates the time–temperature superposition.

Isochronal and isothermal measurements

The frequency and temperature of the peak determined from the isochronal measurement of *Figures 1–4* differ substantially from the frequency of the peak determined from the isothermal spectrum of *Figure 7*. For the α-process, the peak at 1 Hz frequency appears at 453 K for the cured sample in *Figure 1*. The $\tan \phi$ vs. frequency spectra of *Figure 7* show that the α-peak at 1 Hz would be at a temperature higher than 460 K. Evidently, for the same relaxation rate, the isochrones give a lower temperature than the isothermal spectrum. From a model calculation in an earlier paper[23], we showed that if the height of the loss peaks increased with increasing temperature, as is found in many dielectric studies of the sub-T_g relaxations[10], the isochrones give a higher temperature than the isothermal spectra. But if the height of the loss peaks decreased with increasing temperature, as is the case for the α-process in epoxy N in *Figure 7*, the isochrones give a lower temperature than the isotherms, as is observed here. Though part of the change in $\tan \phi$ could have occurred due to further curing of the epoxy during the isothermal measurements, this change would be small. We, therefore, suggest that the difference between the temperature of the peaks of the isochrones and isothermal spectrum can be used as an indication of whether or not the height of the loss peak would change if the isothermal spectrum were also measured.

The γ-relaxation in epoxy S

The γ-relaxation of epoxy S was further studied at different frequencies. The isochrones of $\tan \phi$ at three frequencies are shown in *Figure 8*. While their temperature increased with the frequency, their height remained nearly constant. The rate–temperature plots could be fitted to an Arrhenius equation with an activation energy of 54 kJ mol^{-1} and a pre-exponential factor of 4 THz.

CONCLUSIONS

DGEBA–DDM epoxy resin prepared by mixing pure components has three relaxation processes, of which the lowest-temperature and highest-temperature processes are affected on physical ageing and/or further curing.

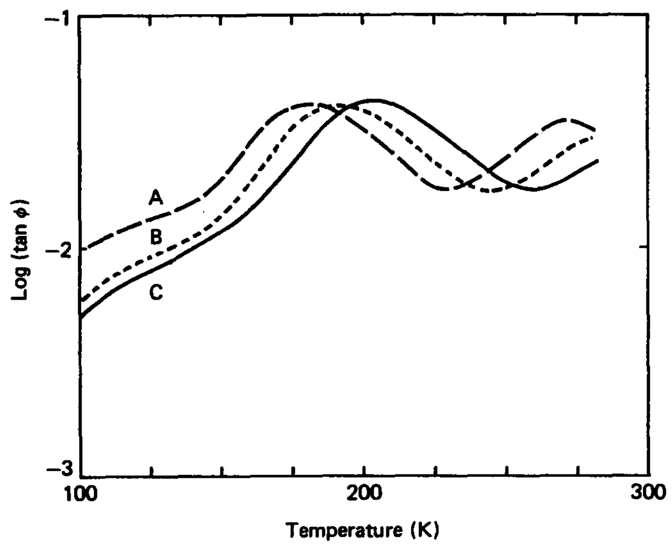

Figure 8 Plots of $\tan \phi$ in the γ-relaxation region of the epoxy S obtained by mixing the components in methyl ethyl ketone and curing at ~353 K in vacuum for 4 h, measured at 0.01 Hz (curve A), 0.1 Hz (curve B) and 1.0 Hz (curve C)

The epoxy prepared by mixing the components dissolved in methyl ethyl ketone also has three relaxation processes. The procedure reduces the strength of the processes observed at the lowest temperature and the highest temperature, and increases the strength of the intermediate-temperature process. It also lowers the glass transition temperature and the value of rubber modulus of the epoxy. The temperature of the γ- and the α-process decreases but that of β-process increases.

A quantitative analysis shows that both the decrease in T_g and in the rubber modulus of the epoxy prepared by using the solvent is due to a lower crosslink density in it. The number of crosslinks per gram in the epoxy prepared with the solvent is half as many as in the epoxy prepared without a solvent.

The time–temperature superposition of neither the G' nor G'' nor $\tan \phi$ spectra can be used satisfactorily to obtain the master curves. It is suggested that the superposition of the $\tan \phi$ spectrum provides a more discerning test for the applicability of the time–temperature superposition than the G' or G'' spectrum.

Isochronal or fixed-frequency measurements give a lower temperature for a given rate of the α-process than the isothermal measurement of the spectra. This is due to the rapid decrease in the height of the relaxation peak with increasing temperature.

The lowest-temperature relaxation has the characteristics of the sub-T_g relaxation observed in a variety of glasses. Its magnitude is decreased on physical ageing.

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