# The relaxation spectrum and physical ageing of polyetherimide

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*(Received 11 June 1990; revised 18 July 1990; accepted 17 August 1990)*

The development of physical ageing in polyetherimide with time and at various temperatures up to 30 K below the glass transition temperature, $T_g$, has been studied using differential scanning calorimetry (d.s.c.). The value of the exotherm which developed on heating an aged specimen through $T_g$ with time was used to analyse the kinetics of the process and so determine the time for the glass to reach equilibrium. The $T_g$ was determined calorimetrically for glasses prepared at different cooling rates from 0.32 to 160 K min$^{-1}$ and an activation energy for glass formation was found to be $1150 \pm 150$ kJ mol$^{-1}$. This compares with that of physical ageing of $1470 \pm 300$ kJ mol$^{-1}$. In this analysis the specific heat of polyetherimide (PEI) has been measured over a temperature range either side of $T_g$ and the change in heat capacity, $\Delta C_p(T_g)$, determined as 210 J kg$^{-1}$ K$^{-1}$. Dynamic mechanical and dielectric studies have also been carried out in order to determine the effect of physical ageing on the relaxation spectra of PEI, and the monomeric friction coefficient was also calculated. Tan $\delta$ and the flexural modulus have been measured over a range of frequencies and temperature. A composite curve incorporating the measured values of $T_g$ by various techniques including dynamic mechanical and dielectric thermal analyses, d.s.c. and physical ageing covering a relaxation timescale of 20 decades highlights the kinetic nature of the glass transition and clearly associates physical ageing with the glass forming process.

**(Keywords: physical ageing; Ultem; polyetherimide; dynamic mechanical thermal analysis; dielectric thermal analysis; d.s.c.)**

## INTRODUCTION

Polyetherimide, PEI, is a 'high performance engineering thermoplastic material' displaying high heat resistance, high strength, high modulus, high glass transition temperature, $T_g$, good electrical properties and remains stable over a wide range of temperatures and frequencies. It also has good processibility[1]. It is amorphous and if unmodified is transparent exhibiting inherent flame resistance and low smoke evolution. It is thus a convenient material for the study of structure–property relationships and in particular their dependence on thermal history. It exhibits strong relaxations, associated with the glass transition, which makes it important in comparing dynamical mechanical and dielectric spectra.

This paper considers the development of physical ageing in PEI as measured by differential scanning calorimetry (d.s.c.) and changes in its relaxation spectrum as measured by dynamic mechanical and dielectric behaviour.

## EXPERIMENTAL

A commercial grade of PEI, Ultem 1000, was used as supplied by General Electric Company Ltd. It had a number average molecular weight of $\sim 2 \times 10^4$. The moulding pellets were dried at 150°C for 4 h prior to compression moulding at 380°C into sheets ($150 \times 150 \times 1$ mm). The sheets were quenched into ice/water. This quenched glass was taken as a standard material against which all changes due to further thermal treatment were measured.

Rectangular specimens ($35 \times 15 \times 1$ mm) and circular discs (35 mm diameter) were cut directly from the sheets for analysis using dynamic mechanical and dielectric thermal analysers as manufactured by Polymer Laboratories Ltd. Each analyser was controlled by an IBM PS2 model 30 microprocessor, and their use has been described previously[2]. The frequency range used was 0.01–200 Hz for dynamic mechanical thermal analysis (d.m.t.a.) and 0.020–$10^5$ kHz for dielectric thermal analysis (d.e.t.a). Both instruments were used in a multi-frequency temperature scan mode from $-150$ to 350°C at heating rates between 0.5°C min$^{-1}$ and 20°C min$^{-1}$ as well as in an isothermal mode.

Circular specimens (3 mm) were used for thermal analysis, using a Perkin Elmer differential scanning calorimeter (DSC model 2C) interfaced to a BBC Master microprocessor, as described elsewhere[3]. The temperature read-out of the calorimeter was calibrated from the melting points of pure indium, tin and lead, and the thermal response from the enthalpy of fusion of indium. Correction was made for thermal lag by correcting for thermal mass of the specimen. Glass transition temperatures were measured as outlined by Richardson and Savill[3] and the extent of physical ageing as described elsewhere[4].

## RESULTS

### *The glass transition and physical ageing*

A d.s.c. trace, of relative heat flow against temperature, for a sample of PEI taken directly from the quenched moulded sheets is shown in *Figure 1*. Only a glass transition at $\sim 220$°C is apparent, and the $T_g$ was

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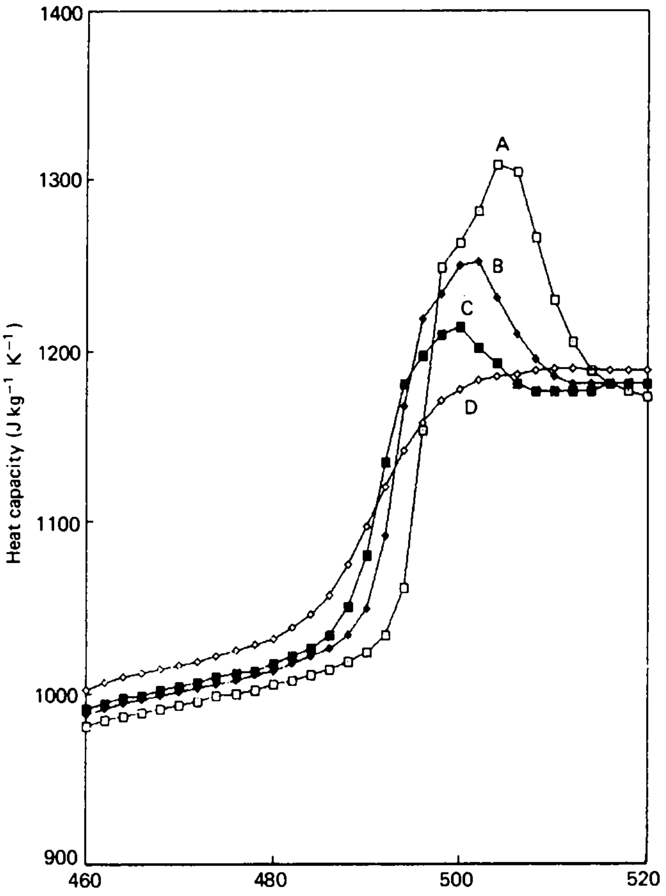

**Figure 1** Change in specific heat of PEI with temperature and the effect of ageing. A, 40 h; B, 4 h; C, 1 h; D, quenched

**Table 1** Specific heats of PEI

| Temperature (K) | $C_p$ (glass) (J kg$^{-1}$ K$^{-1}$) ($\pm$10) | Temperature (K) | $C_p$ (liquid) (J kg$^{-1}$ K$^{-1}$) ($\pm$10) |
|---|---|---|---|
| 448 | 1475 | 512 | 1907 |
| 450 | 1477 | 514 | 1917 |
| 452 | 1478 | 516 | 1927 |
| 454 | 1495 | 518 | 1933 |
| 456 | 1507 | 520 | 1930 |
| 458 | 1514 | 522 | 1926 |
| 460 | 1516 | 524 | 1938 |
| 462 | 1511 | 526 | 1952 |
| 464 | 1522 | 528 | 1957 |
| 466 | 1534 | 530 | 1964 |
| 468 | 1544 | 532 | 1963 |
| 470 | 1548 | 534 | 1977 |
| 472 | 1550 | 536 | 1989 |
| 474 | 1563 | 538 | 1994 |
| 476 | 1575 | 540 | 2008 |
| 478 | 1581 | - | - |
| 480 | 1582 | - | - |
| 480–512 | Glass transition region | | |

evaluated by the procedure adopted by Richardson and Savill[3]. The $T_g$ of the quenched glass was found to be 214.6 ± 0.5°C, with correction being made for sample size.

On heating the sample for periods of time at temperatures below $T_g$, the transition moved to higher temperatures and was accompanied by an endothermic peak (*Figure 1*). These changes are consistent with the development of physical ageing[4] by which the glass slowly relaxes towards the extrapolated properties of the liquid. The difference between the areas under the specific heat–temperature plots of the quenched and aged glasses between two fixed temperatures well above and below the transition is a measure of physical ageing, $\Delta H_t$ at time $t$. At constant temperature the extent of physical ageing developed progressively with the logarithm of time, and following previous studies[4], the maximum change in enthalpy, $\Delta H_{max}$, was evaluated as

$$\Delta H_{max} = \Delta C_p \, \Delta T \qquad (1)$$

where $\Delta C_p$ is the change in the heat capacity of the quenched glass and the liquid at $(T_g + T_a)/2$, and $\Delta T = T_g - T_a$ where $T_a$ is the ageing temperature.

The specific heat of PEI was measured over a wide range of temperature (*Table 1*) and from this $\Delta C_p(T_g)$ was determined to be 210 J kg$^{-1}$ K$^{-1}$ (*Table 2*).

The fractional extent of physical ageing was measured as $\Delta H_t/\Delta H_{max}$, and the extent towards equilibrium $(1 - \Delta H_t/\Delta H_{max})$ decreased logarithmically with time, $t$, at each temperature studied (*Figure 2*) in agreement with

**Table 2** Variation of $\Delta C_p$ with ageing temperature, $T_a$

| | | | | | |
|---|---|---|---|---|---|
| $T_a$ (K) ($\pm$0.5) | 482.5 | 476.0 | 470.0 | 463.5 | 457.0 |
| $\Delta T$ (K) ($\pm$1.0) | 6.0 | 12.5 | 18.5 | 25.0 | 31.5 |
| $\Delta C_p$ (J kg$^{-1}$ K$^{-1}$) | 211 | 213 | 214 | 215 | 216 |
| $\Delta H_{max}$ (J kg$^{-1}$) | 1240 | 2650 | 4010 | 5390 | 6770 |

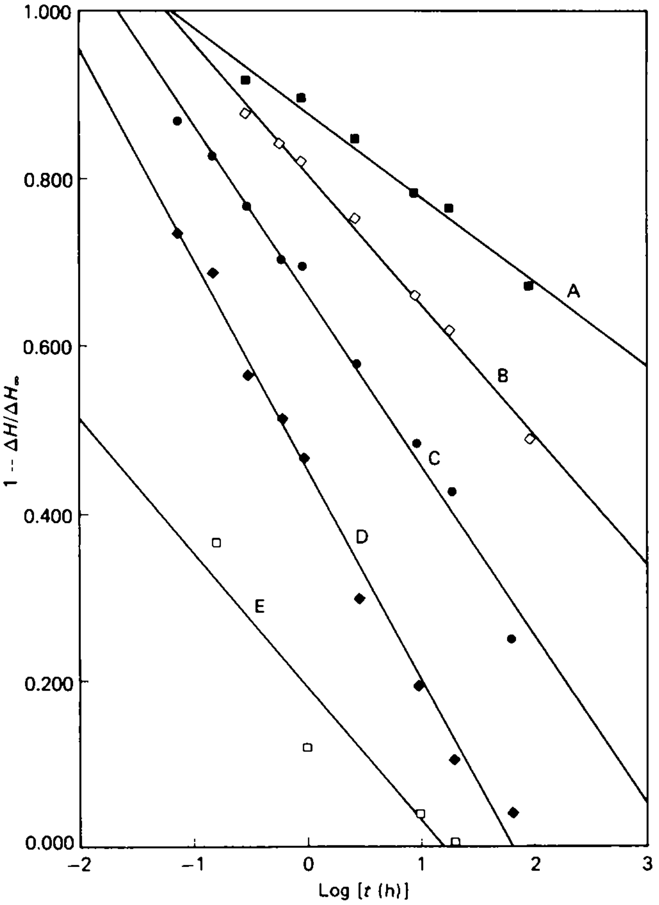

**Figure 2** Extent of physical ageing developing logarithmically with time. A, 457.1 K; B, 463.4 K; C, 469.7 K; D, 476 K; E, 482.4 K

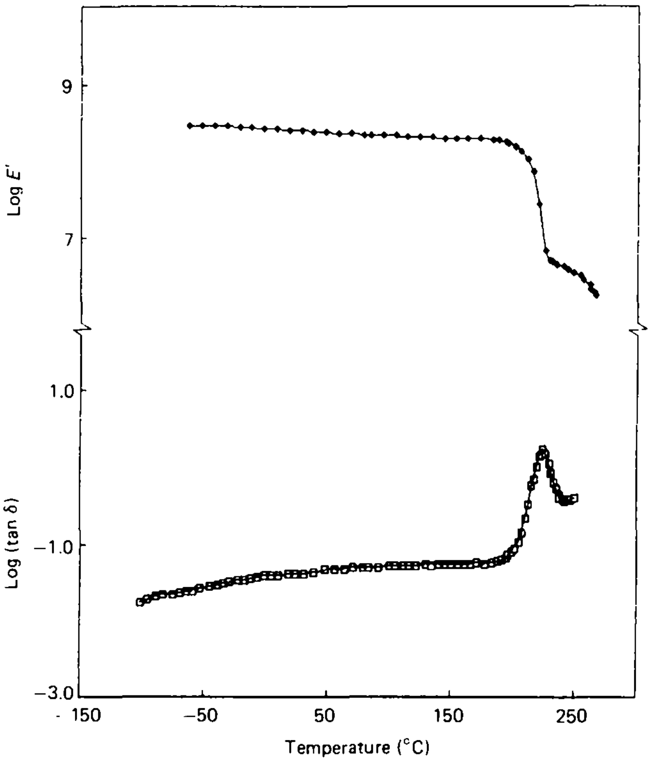

**Figure 3** D.m.t.a. scan of PEI at 1 Hz. Log tan $\delta$ and log $E'$ *versus* temperature

the derived relationship

$$(1-\Delta H_t/\Delta H_{max}) = A \ln (3/2)(t/\tau) \qquad (2)$$

where $A$ is a constant and $\tau$ the time to attain equilibrium.

From these plots $\tau$ was evaluated and varied with the degree of undercooling from the $T_g$, $\Delta T$. An activation energy of $1470 \pm 300$ kJ mol$^{-1}$ was obtained for the process of physical ageing from an Arrhenius plot of the logarithm of $\tau$ against reciprocal temperature.

The value of $T_g$ measured by d.s.c. also varied with the rate of cooling. Different glasses were produced by cooling through the transition region at cooling rates from 160 to 0.32°C min$^{-1}$ within the calorimeter. The $T_g$ shifted to lower values with slower rates of cooling, and an Arrhenius plot of the logarithm of the cooling rate against the reciprocal $T_g$ was linear with an activation energy of $1150 \pm 200$ kJ mol$^{-1}$, in line with the value obtained for physical ageing, measured at lower rates.

### *Dynamic mechanical and dielectric properties*

The variation of tan $\delta$ and dynamic flexural modulus, $E'$, of PEI at 1 Hz with temperature is shown in *Figure 3*. The tan $\delta$ plot shows only one primary dispersion peak which reflects segmental or micro-Brownian motion of molecular chains associated with the glass–rubber relaxation. The temperature corresponding with the maximum in tan $\delta$ occurs at 228°C at 1 Hz as measured by d.m.t.a. Similar studies by d.e.t.a. (*Figure 4*) show that this maximum has moved to 240°C consistent with the frequency dependence. The maximum in tan $\delta$ as measured by d.m.t.a. is 2.07, and only 0.10 by d.e.t.a.

There is little change in $E'$ from −100 to ~180°C and then there is a large drop of about two orders of magnitude, from ~0.1 GPa to ~1.5 MPa over 50°C. This is characteristic of the glass transition.

The values of the modulus, shown in *Figure 3*, are incorrect since no correction has been made for sample free length. The effective sample length between clamping bars is greater than that measured, and this leads to an underestimate of the geometric constant involved in the modulus calculation. An end correction procedure was adopted of measuring the effective modulus of a range of samples of different free lengths. The corrected modulus was measured from the slope of the plot of $l_m/(E'_m)^{1/3}$ where $l_m$ is the measured length, and $E'_m$ the measured flexural modulus. Significant corrections are involved in this procedure below the glass transition in that there is a change from 0.25 to 2.5 GPa at 50°C. The corrected flexural modulus at 25°C, 3.20 GPa, compares well with the literature value[1] of 3.31 GPa. A plot of corrected modulus against measured modulus is shown in *Figure 5* and only in the glass transition region were the corrected and uncorrected values of the modulus similar.

An Arrhenius plot of logarithm of the frequency against the reciprocal of the temperature corresponding to the maximum value of tan $\delta$, for both d.m.t.a. and d.e.t.a. was curved, and could be fitted with a second order polynomial

$$\ln f = 1.393 + 1.5 \times 10^6/T - 4 \times 10^8/T^2 \qquad (3)$$

and the apparent enthalpy, $\Delta H$, for the glass transition process which is temperature dependent, is

$$-\Delta H/R = 1.5 \times 10^6 - 8.0 \times 10^8/T \qquad (4)$$

For the frequency range 0.1–$10^5$ Hz the apparent activation energy varied between 330 kJ mol$^{-1}$ and 1250 kJ mol$^{-1}$.

### *The time–temperature superposition*

The temperature–frequency dependence of the dynamic properties in the region of the glass transition can

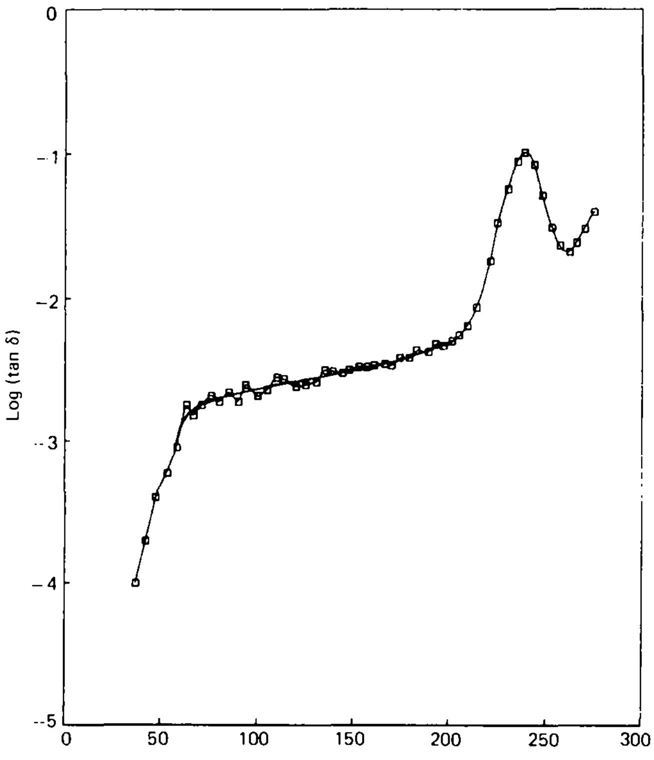

**Figure 4** D.e.t.a. scan of PEI at 1 kHz

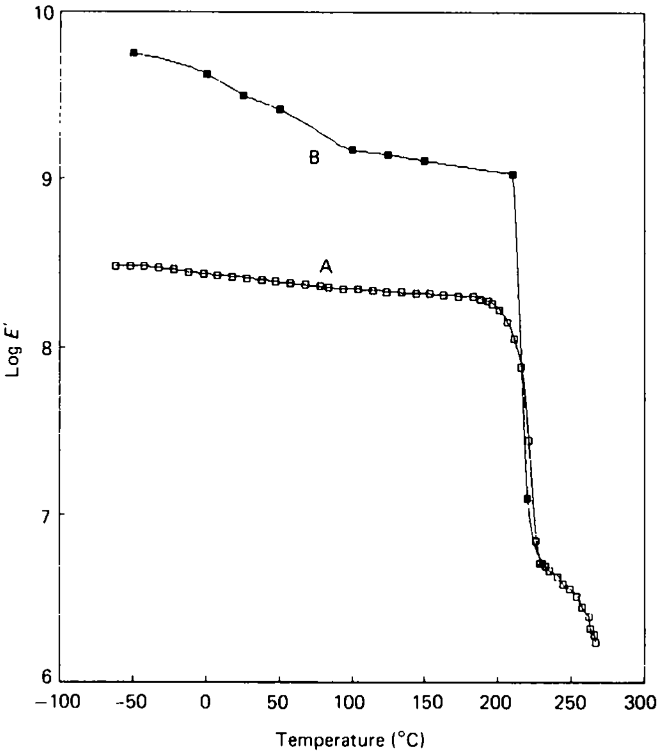

**Figure 5** Dynamic flexural modulus of PEI at 1 Hz. A, Experimental; B, adjusted for end corrections

be described by the Williams Landel Ferry, WLF, equation[5], i.e.

$$\log a_T = -C_1(T-T_0)/[C_2+(T-T_0)] \qquad (5)$$

where $a_T$ is the shift factor or degree of horizontal shift required to superimpose a given set of data onto a reference set at the chosen reference temperature, $T_0$ and $C_1$ and $C_2$ are constants. For many amorphous polymers $C_1$ and $C_2$ have the values of 17.4 and 51.6, respectively, when $T_g$ at 1 Hz is chosen as the reference temperature. The WLF equation is useful in practice in providing data over a wider frequency range than is experimentally available.

*Figure 6a* shows a series of isothermal flexural modulus curves measured for PEI at temperatures between 180°C and 220°C in the frequency range 0.1–30 Hz. A master curve of dynamic modulus against logarithm of the frequency was generated by shifting each curve horizontally on to the curve at the chosen reference temperature. The shift factor $\log a_T$ was noted in each case. Values of $C_1 = 6.7$ and $C_2 = 46.4$ were obtained from the slope and intercept of a linear plot of $(T-T_0)/\log a_T$ against $(T-T_0)$. Further values of $\log a_T$ were calculated from the WLF equation using these constants. This amounted to a smoothing of the initial estimated values and close agreement was found between the estimated and observed values of $\log a_T$ with the former being used in the calculation of the master curve. Using these values of $C_1$ and $C_2$ a master curve was also constructed from the isothermal modulus curves shown in *Figure 6b* obtained on a sample of PEI obtained after physical ageing at 196°C for 240 h. The flexural modulus master curves at the same reference temperature for aged and unaged

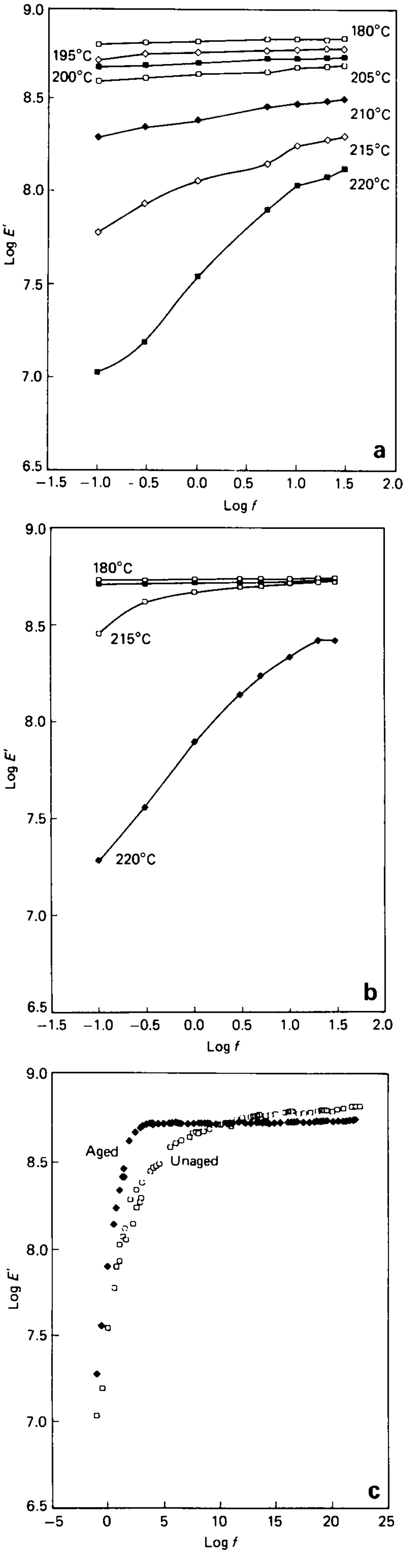

**Figure 6** Isothermal modulus curves for PEI. (a) Unaged glass, (b) aged at 196°C for 240 h, and (c) master curves for aged and unaged, $T_0 = 220$°C

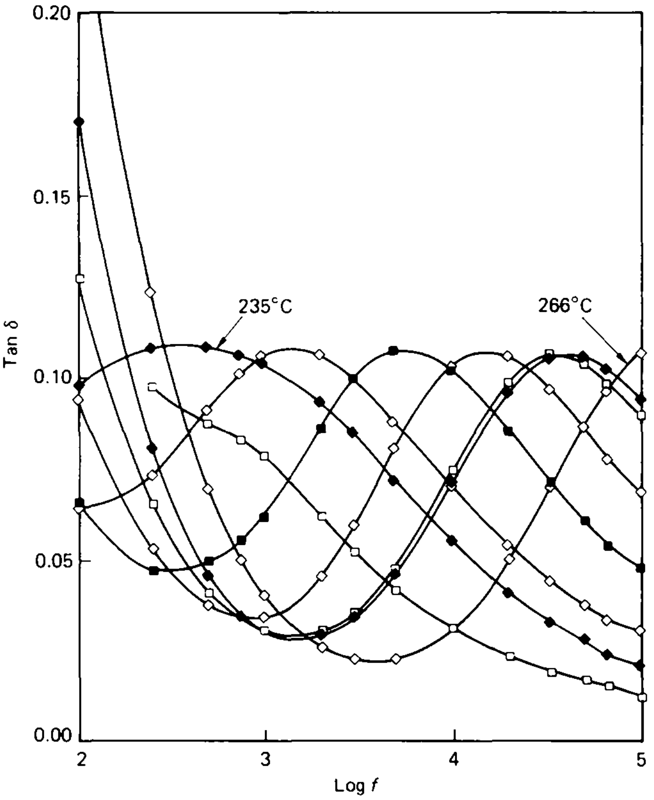

**Figure 7** Isothermal d.e.t.a. loss curves for unaged PEI

samples are shown in *Figure 6c*. They cannot be superimposed in the frequency range corresponding to temperatures below $T_g$. The shapes of the two curves are substantially different.

The modulus of the aged sample remains essentially constant with increasing frequency while that of the unaged sample increases and eventually exceeds that of the aged material. In the frequency region corresponding to the glass transition, the modulus of the aged material drops sharply until it merges with that of the unaged material at low frequency.

An alternative method was used to estimate $C_1$ and $C_2$ by writing the WLF equation as

$$\log a_T = \log(f_0/f) \qquad (6)$$

where $f_0$ is the chosen reference frequency. The temperature and frequency data analysed by this method incorporated both d.m.t.a. and d.e.t.a. results. The highest measuring frequency $10^5$ Hz was taken for $f_0$ and this corresponded with a $T_0$ of 259°C, corresponding with the maximum in tan $\delta$. Values for $C_1$ and $C_2$ were determined to be 6.3 and 94.9, respectively, from a WLF plot. These values were used to construct a tan $\delta$ master curve from the isothermal d.e.t.a. loss curves (*Figure 7*). The dielectric loss master curve is shown in *Figure 8*. The high frequency skew of the master curve is a characteristic feature of the amorphous polymers and is well accounted for by the Havriliak–Negami phenomenological equation for the complex dielectric constant[5].

### *The relaxation spectra*

In the frequency plane the behaviour of a system with a single relaxation time, $\tau$, is given by

$$E'(\omega) = E_r + (E_u - E_r)\omega^2\tau^2/(1+\omega^2\tau^2) \qquad (7)$$

and

$$E''(\omega) = E_r + (E_u - E_r)\omega\tau/(1+\omega^2\tau^2) \qquad (8)$$

where $E_u$ and $E_r$ are the unrelaxed and relaxed values of the modulus, respectively, and $\omega$ the angular frequency. These are analogous to the Debye equation[6] in dielectric theory. For the broad relaxation processes occurring in polymers the single relaxation time equations are replaced by summations over all possible relaxation times giving the integral expressions

$$E'(\omega) = E_r + \int_{-\infty}^{+\infty} H(\tau)\omega^2\tau^2/(1+\omega^2\tau^2)\,\mathrm{d}\ln(\tau) \qquad (9)$$

and

$$E''(\omega) = E_r + \int_{-\infty}^{+\infty} H(\tau)\omega\tau/(1+\omega^2\tau^2)\,\mathrm{d}\ln(\tau) \qquad (10)$$

where $H(\tau)$ is the relaxation spectrum.

Knowledge of the relaxation spectrum allows any viscoelastic function to be derived. However, because of the wide frequency range involved the full spectrum is difficult to determine in practice and approximate spectra can be obtained from data measured over a few decades by approximations, such as

$$H(\tau) = AG'\,\mathrm{d}\log G'/\mathrm{d}\log\omega\big|_{1/\omega=\tau} \qquad (11)$$

where $A$ is a function of the log $H(\tau)$ against log $\tau$ plot and is derived from first order approximations. The calculation of $H(\tau)$ is carried out in two stages according to the method of Ferry and Williams[6]. From the master curves (*Figure 6c*) the relaxation spectra for unaged and aged PEI were calculated and are shown in *Figure 9*.

Two of the three characteristic zones of the viscoelastic time scale are apparent in the relaxation spectra, the

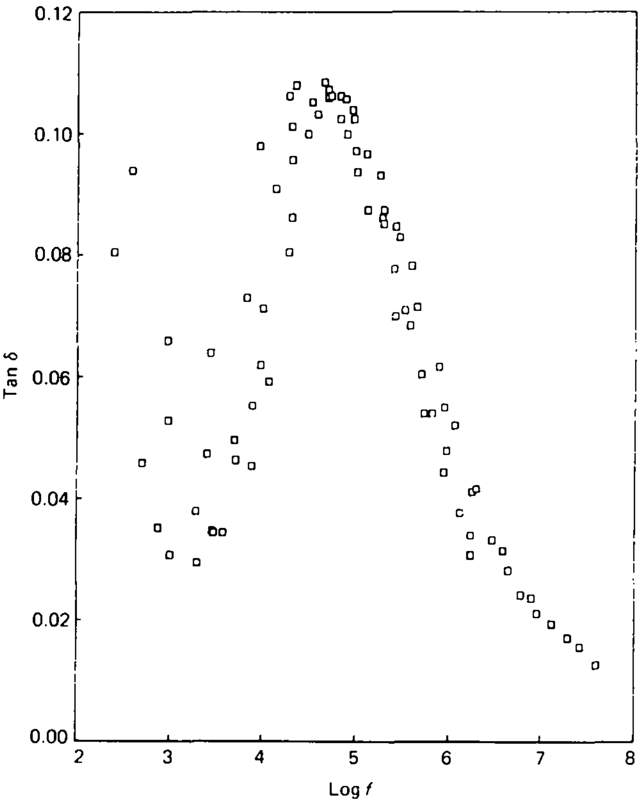

**Figure 8** D.e.t.a. loss master curves for unaged PEI, $T_0 = 259$°C

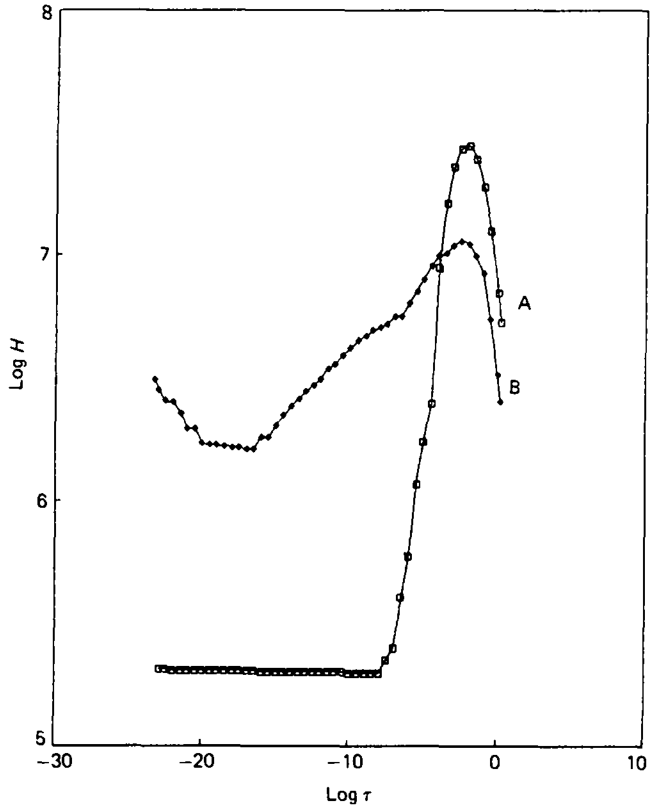

**Figure 9** Relaxation spectra for unaged (A) and aged (B) PEI, $T_0 = 220°C$

glassy zone to the left of the maximum and the transition zone in which log $H(\tau)$ changes steeply. The maxima are associated with the glass-rubber transition. The frequency range is not wide enough to incorporate much of the terminal zone, associated with the mobile liquid phase. The spectra can be shifted along the log time axis by altering $T_0$, and the frequency corresponding to $T_g$, but it is apparent that there is less difference between the spectra of the aged and quenched specimens. This portion of the spectra can be interpreted in terms of Rouse[7] and Zimm[8] models of molecular chain motion.

The changes observed in the spectra at low time scales reflect differences in the free volume and in particular the increased modes of motion within the quenched compared with the aged sample.

### *Monomeric friction coefficient*

This is a measure of the frictional resistance per monomeric unit encountered by a chain segment in translatory motion. It depends on the free volume, intermolecular forces and steric hindrance to rotation about the chain bonds. It can be calculated from dynamic mechanical measurements made in the glass-rubber region.

The monomeric friction coefficient, $\phi_0$, is given by rearranging the theoretical Rouse equation

$$H = (a\rho N_a / 2\pi M_0)(\phi_0 kT/6)^{1/2} \tau^{-1/2} \qquad (12)$$

to give

$$\log \phi_0 = 2 \log H + \log \tau + \log(6/kT) + 2 \log(2\pi M_0 / a\rho N_a) \qquad (13)$$

where $M_0$ is the monomer molecular mass, $a$ is the root mean square end to end length per square root of the number of monomer units and $\rho$ is the bulk density of the polymer.

In *Figure 9*, a region can be seen for the aged and unaged spectra of Ultem which conform to the required slope of $-\frac{1}{2}$. From the position of the tangents $\phi_0$ was calculated. A value of $a = 34.4 \times 10^{-8}$ cm was used, estimated from standard bond length data. The density, $\rho$, was taken to be 1.27 g cm$^{-3}$. At 220°C $\phi_0$ was $10^{4.6}$ for unaged and $10^{6.8}$ for aged Ultem.

## DISCUSSION

Each technique adopted, d.m.t.a., d.e.t.a. and d.s.c., incorporating both cooling rate data and the time to attain equilibrium on physical ageing, determines very different values for the $T_g$ of PEI. This highlights the kinetic nature of the transition from the very rapid response of the segments in dielectric studies to the extremely slow development of equilibrium on physical ageing, and the difficulty of quoting a value for the $T_g$ without stating the time scale of the measurement involved.

A composite curve of the dependence of $T_g$ on the relaxation time of the imposed frequency was drawn up for the d.e.t.a. and d.m.t.a. techniques (*Figure 10*). A similar dependence was observed for the cooling rate and physical ageing dependence of the glass transition but these were displaced relative to one another and to the d.m.t.a. and d.e.t.a. data. Since the $T_g$s measured by different techniques overlapped, a master curve could be drawn incorporating all the data from each procedure by shifting each set of data by an amount equivalent to the shift factor, $a$, of the WLF equation, i.e.

$$-\log a = \log f/f_0 \qquad (14)$$

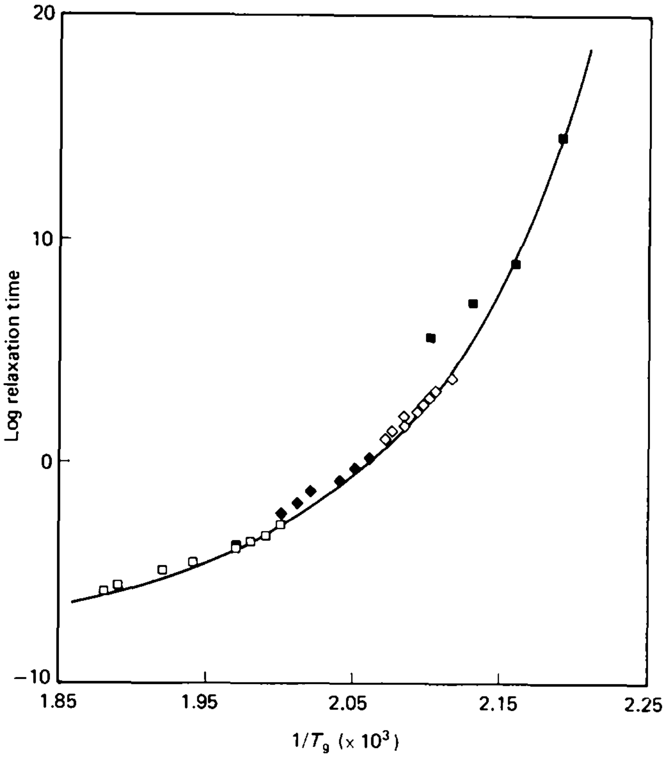

**Figure 10** Variation of reciprocal glass transition temperature with the logarithm of the relaxation time

where $f$ and $f_0$ refer to the imposed frequency at the same temperature.

*Figure 10* displays the master curve of the dependence of the reciprocal $T_g$ on the logarithm of the relaxation time covering about 20 decades. The glass forming process clearly does not follow an Arrhenius dependence and the enthalpy of the process is temperature dependent

$$\Delta H/R = 6.30 \times 10^4 - 9.60 \times 10^7/T_g \qquad (15)$$

The master curve also clearly indicates that physical ageing is an extension of the glass forming process, which occurs during normal cooling but is extended into very long times during the process of physical ageing.

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