ELSEVIER Thermochimica Acta 256 (1995) 123–135

thermochimica
acta

The thermal properties of polyether sulphone ☆

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Abstract

The thermal properties of poly(ether sulphone) (PES) have been measured as a function of physical aging. The development of enthalpic relaxation with time, at several temperatures up to 70 K below T_g, has been investigated using differential scanning calorimetry (DSC). The kinetics of the aging process were determined from the change in enthalpy of the glass with time. The T_g was determined for glasses prepared at different cooling rates from 0.32 to 160 K min^{-1} and the activation energy for glass formation was found to be 700 ± 100 kJ mol^{-1}. It was compared with those determined by dielectric thermal analysis (DETA), dynamic mechanical thermal analysis (DMTA), and physical aging. A composite curve incorporating the measured T_g values by various techniques covering a relaxation time scale of 20 decades has been constructed.

The heat capacity of PES has been measured over a temperature range, from which the change at T_g ($\Delta C_p(T_g)$) was found to be 180 J kg^{-1} K^{-1}.

Dielectric thermal analysis studies have also been carried out on aged specimens.

Keywords: DETA; DMTA; DSC; Enthalpic relaxation; Glass transition; Polyethersulphone

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1. Introduction

Poly(ether sulphone) (PES) is a high-performance engineering thermoplastic with a wide range of applications due to its good thermal stability for extended periods

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☆ Presented at the 14th Symposium on Thermal Analysis and Calorimetry, Oslo, Norway, 15–17 June 1994.

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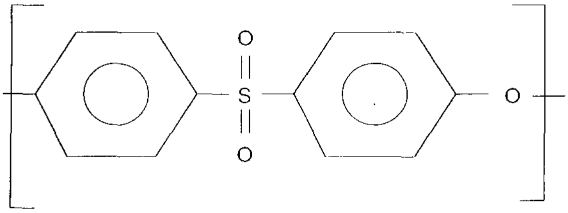
SSDI 0040-6031(94)02168-6



Scheme 1. The repeat unit of PES.

at high temperature, its fracture toughness, good water and steam resistance, and high glass transition temperature T_g. Its main competitors include not only other engineering thermoplastic materials such as poly(ether imide) but also ceramics and metals. Other characteristics such as good electrical properties and transparency, as well as ease of moulding, are also desirable. Its chemical repeat unit is shown in Scheme 1.

PES is generally used after melt processing as an amorphous glass, because it is unable to crystallize from the melt. Crystalline samples of PES can be produced from solution but bulk-processed PES products are amorphous.

Organic glasses are not in thermal equilibrium and their thermal history has a pronounced effect on the material properties. As a result of this non-equilibrium state, the glass approaches equilibrium over extended periods. The gradual change in properties towards those of the equilibrium glass is described as enthalpic relaxation and also physical aging. Physical aging only occurs below T_g and the process is accelerated as the temperature of the sample approaches T_g while the extent of it decreases. Heating through T_g reverses physical aging. This paper considers the process of enthalpic relaxation in PES as measured by DSC and the corresponding changes in mechanical and dielectric response as measured by DETA and DMTA, associated with physical aging.

2. Experimental

A commercial grade of PES, Radel A200 supplied by Amoco Chemical U.K., was used as received. Prior to moulding, the pellets were dried at 200°C for 4 h in vacuo and plaques ($150 \times 150 \times 1$ mm^3) were pressure moulded at 300°C. The sheets were quenched into ice/water. This quenched material was taken as a standard glass against which all changes in properties due to further thermal treatment were measured.

Circular discs (3 mm in diameter) were cut from the plaques and used for thermal analysis, using a Perkin-Elmer differential scanning calorimeter, DSC model 2C, interfaced to a BBC master microcomputer, as described elsewhere [1]. The temperature readout of the calorimeter was calibrated using the melting points of ultra-pure indium, tin and lead. The thermal response of the calorimeter was calibrated using the enthalpy of fusion of indium. An adjustment was made for thermal lag by correcting for the thermal mass of the specimen. Glass transition temperatures were measured using the procedures outlined by Richardson and Savill [2] and the extent of physical aging was measured as described elsewhere [3].

Dynamic mechanical and dielectric analyses were carried out using equipment manufactured by Polymer Laboratories Ltd. Each analyser was controlled by an IBM PS2 model 30 computer and their use has been described previously [4]. DMTA was used in the frequency range 1–200 Hz and DETA equipment was used in the range 0.020–100 kHz. Both instruments were used in the multi-frequency/temperature and isothermal modes.

3. Results and discussion

3.1. The glass transition and enthalpic relaxation

Quenched PES when heated from 350 to 500 K undergoes only one transition, the glass transitions at about 496 K, see Fig. 1. The value of T_g for the quenched glass was measured using Richardson and Savill's [2] procedure of equating the enthalpies of the glass and the liquid at T_g and was found to be 493 ± 1 K after correction for thermal lag. Repeating the procedure using glasses prepared with different cooling rates R_c in the DSC produced a range of values increasing with increased cooling rate (see below) and applying the Arrhenius equation for a thermally activated process, an overall activation energy of the glass formation process was found to be 700 ± 100 kJ mol^{-1}.

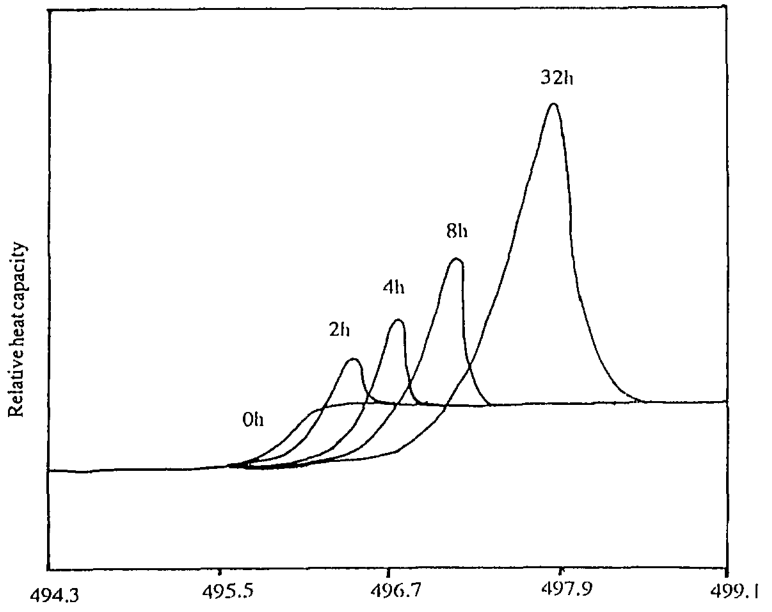


Fig. 1. The effect of aging at 480.5 K on the glass transition of PES by DSC at 10 K min^{-1}.

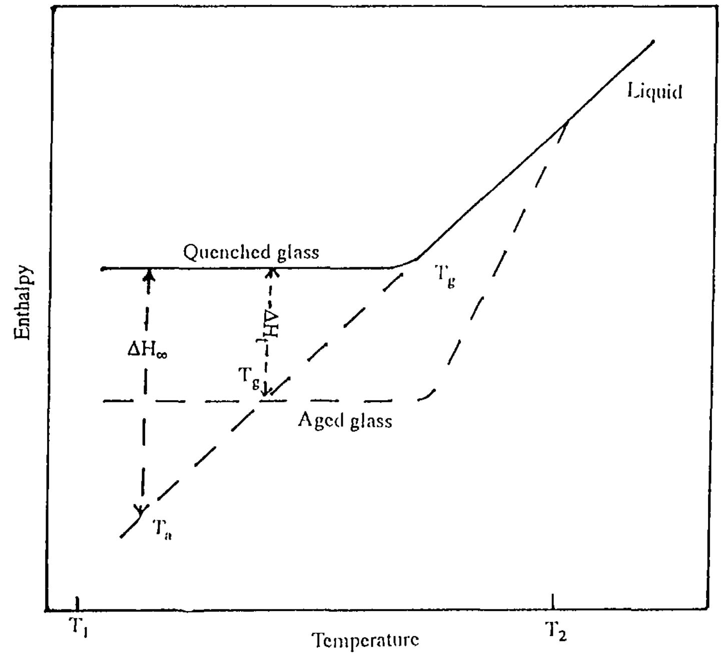


Fig. 2. Enthalpy changes at the glass–liquid transition accompanying isothermal aging at T_a.

Ice/water-quenched samples were relaxed by leaving for extended periods at aging temperatures T_a, below T_g. Enthalpic relaxation of the glass manifested itself by the progressive development of an endothermic peak on heating to the T_g, accompanied by an apparent shift in the T_g to higher temperatures, see Fig. 1. The apparent increase in the transition temperature is an artefact of the heating rate because the enthalpy of the aged glass is lower than that of the quenched, see Fig. 2. The difference between the areas under the specific heat–temperature plots obtained from the DSC for the quenched and aged glasses between two fixed temperatures is a measure of the development of enthalpic relaxation, and of the extent of the glass changing towards the extrapolated liquid enthalpy at T_a. At constant temperature, the endothermic peak developed progressively with time until a maximum value ΔH_∞ was reached and the extent of relaxation was analysed using the following relationships proposed by Cowie and Ferguson [5], following earlier work by Cook et al. [6], and Hodge [7] and Kovacs et al. [8].

The isothermal data can be expressed by

$$\Delta H(t_a) = \Delta H_\infty [1 - \phi(t_a)] \tag{1}$$

where ΔH_∞ represents the equilibrium enthalpy of relaxation at $t_a \to \infty$. The extent of relaxation $\phi(t_a)$ is conventionally related to the empirical Williams–Watts stretched exponential function for a multi-relaxation process [9], giving for the time dependence of enthalpic relaxation

$$\phi(t_a) = \exp[-(t_a/\tau)^\beta] \tag{2}$$

with τ an average relaxation time and β ($0 < \beta < 1$) a parameter which is a reciprocal measure of the breadth of the distribution of the relaxation–time spectra.

The enthalpic relaxation data were analysed in two ways; from a log ($\ln[\phi(t_a)]$) versus $\log(t)$ plot and a non-linear regression fit of the data. A plot of $\log[-\ln(1 - \Delta H/\Delta H_\infty)]$ versus $\log t_a$ was linear with a slope of β from which τ was calculated. A typical plot can be seen in Fig. 3. In this analysis, a value of ΔH_∞ ($= \Delta C_p(T_g)(T_g - T_a)$) was used, as defined in Fig. 2. The non-linear regression analysis did not require a value for ΔH_∞ because iteration of the ΔH versus time data yielded all three parameters, ΔH_∞, β, and τ. A typical non-linear fit of the data is shown in Fig. 3(b). The enthalpic relaxation parameters measured and calculated for PES are shown in Table 1. Analysis of the results using the iterative procedure produced β values of about 0.43, but varying between 0.30 and 0.46; β values obtained from double-log plots were similar but essentially constant within experimental error at low degrees of supercooling ΔT, but decreased at very high supercoolings. An overall master curve of $\phi(t_a)$ against $\ln(t/\tau)$ is shown in Fig. 3(c) from which an average β value could be determined as 0.43. This was consistent with β being essentially independent of the aging temperature.

The enthalpic relaxation was studied isothermally with supercoolings between 5 and 100 K. As previously noted [10], excess enthalpies due to physical aging were observed up to supercoolings of 60 K and no relaxation endotherms were observed above a degree of supercooling of 70 K. The DSC thermograph of the specimen aged for an extended period was identical to that of the quenched specimen.

The activation energy for enthalpic relaxation, obtained from an Arrhenius plot of $\log(\tau)$ versus reciprocal aging temperature, was 700 ± 100 kJ mol^{-1}.

From the maximum enthalpy changes implied in Fig. 2, the maximum extent of physical aging [3] $\Delta H_{\max}$ is related to the undercooling ΔT from the glass transition, i.e. $\Delta H_{\max} = \Delta C_p(T_g - T_a)$, where ΔC_p is the change in heat capacity between the liquid and glass at T_g. A plot of $\Delta H_{\max}$ determined experimentally and from the iterative fit of Eq. (2) is plotted against aging temperatures in Fig. 4. A linear fit was obtained up to ΔT values of 20 K with an intercept of 493 ± 1.0 K equivalent to the T_g of the quenched glass and slope of 180 J kg^{-1} K^{-1} for ΔC_p. Both values compare favourably with values of 493 K and 180 J kg^{-1} K^{-1} determined experimentally on the quenched glass.

3.2. Dynamic mechanical thermal analysis

The variation of $\tan\delta$ and the flexural modulus E' with temperature and frequency are conventionally used to identify transitions in polymers. PES undergoes an α-transition which reflects the onset of segmental motion in the polymer chains associated with the glass transition. The temperature corresponding to the maximum in $\tan\delta$ was taken to be the transition temperature at that frequency. Dynamic mechanical analysis exhibited a maximum in $\tan\delta$, see Fig. 5(a), and a

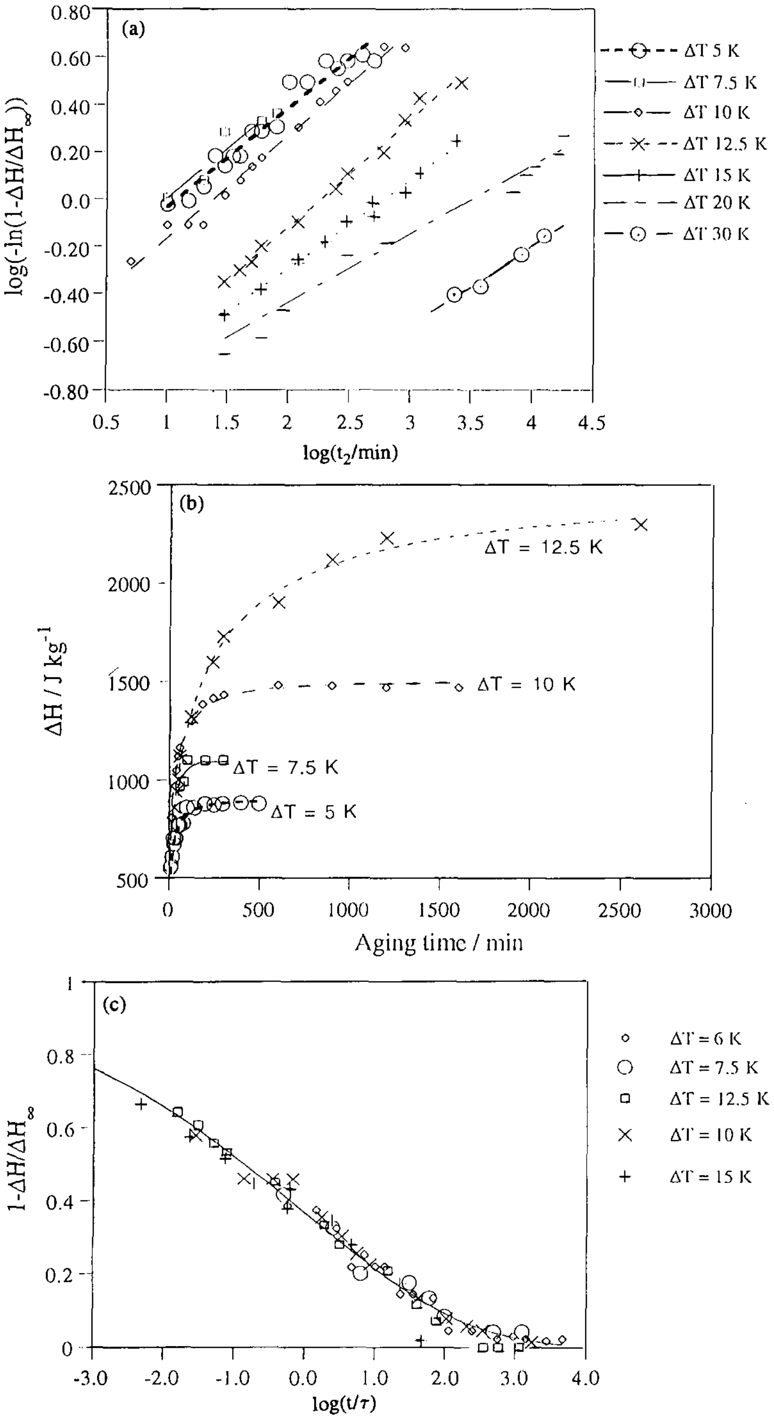

(a)
log(-ln(1-ΔH/ΔH∞))
0.80
0.60
0.40
0.20
0.0
-0.20
-0.40
-0.60
-0.80
0.5
1
1.5
2
2.5
3
3.5
4
4.5
log(t2/min)
ΔT 5 K
ΔT 7.5 K
ΔT 10 K
ΔT 12.5 K
ΔT 15 K
ΔT 20 K
ΔT 30 K
(b)
ΔH / J kg-1
2500
2000
1500
1000
500
0
500
1000
1500
2000
2500
3000
Aging time / min
ΔT = 12.5 K
ΔT = 10 K
ΔT = 7.5 K
ΔT = 5 K
(c)
1-ΔH/ΔH∞
1
0.8
0.6
0.4
0.2
0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
log(t/τ)
ΔT = 6 K
ΔT = 7.5 K
ΔT = 12.5 K
ΔT = 10 K
ΔT = 15 K

Table 1
Enthalpic relaxation kinetic data

Supercooling ΔT in K	β value	t in min	$\Delta H_{\max}$ in J kg^{-1}	$\Delta C_p \Delta T$ in J kg^{-1}
A. Non-linear iteration				
5.0	0.46	13	900	900
7.5	0.46	15	1100	1350
10.0	0.44	24	1500	1800
12.5	0.46	190	2400	2250
15.0	0.43	250	2400	2700
20.0	0.30	3350	3500	3600
B. Log–log plot				
5.0	0.44	13	900	900
7.5	0.42	14	1200	1350
10.0	0.45	24	1500	1800
12.5	0.45	180	2400	2250
15.0	0.37	600	2900	2700
20.0	0.29	3300	3800	3600
30.0	0.34	62400	5600	5400

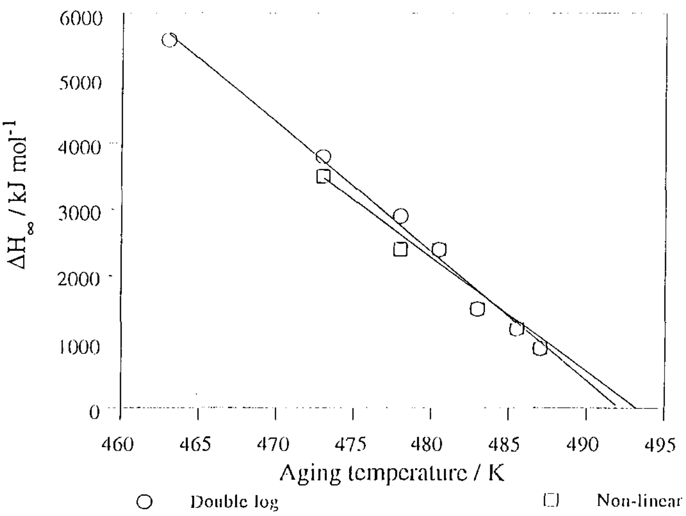


Fig. 4. The variation of the maximum enthalpy of aging with temperature.

rapid decrease in modulus E', see Fig. 5(b), corresponding to the α-transition. An Arrhenius plot of the logarithm of the frequency against the reciprocal of the temperature corresponding to the maximum of the tan δ was linear for both

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Fig. 3. (a) Log–log fit of the extent of aging with time. (b) The development of the endothermic process with aging time. (c) Reduced time plot for the aging of PES, assuming an average β value of 0.43.

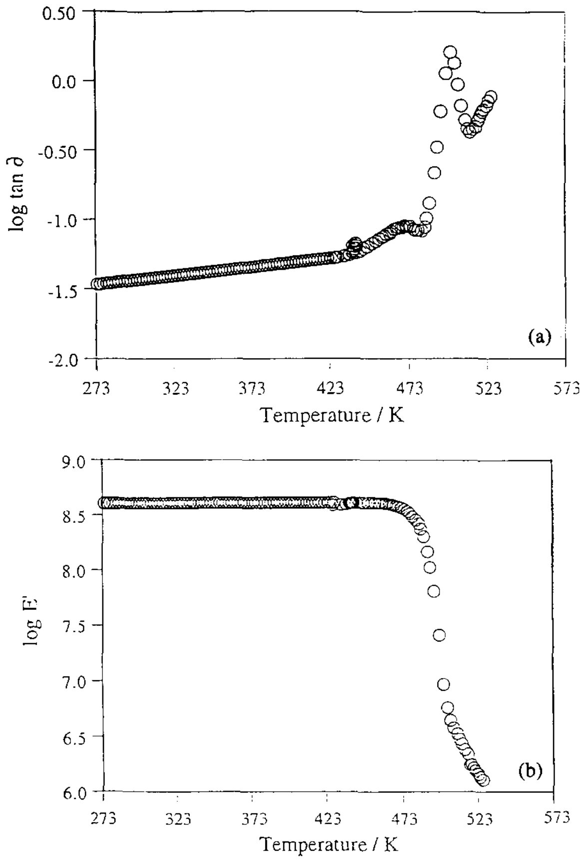

Fig. 5. (a) Variation of tan δ with temperature. (b) Variation of log E' with temperature for unaged PES at 1 Hz.

DMTA and DETA with activation energies of 600 ± 200 and 700 ± 200 kJ mol^{-1}, respectively.

A secondary β-transition with peak temperature between 238 and 275 K for 1 to 100 kHz was also observed. Its activation energy was found to be 18 ± 10 kJ mol^{-1} from this frequency shift in the transition temperature.

The investigation of the effect of enthalpic relaxation on the mechanical response of PES was carried out on samples with different thermal histories: quenched, aged, and slow cooled. There was a general increase in flexural modulus E' with increasing aging at each temperature and frequency but this was limited to 3 decades. Master curves were established using a standard temperature T_0 of 493 K from the Williams–Landel–Ferry equation

$$-\log(a) = C_1(T - T_0)/(C_2 + [T - T_0])$$

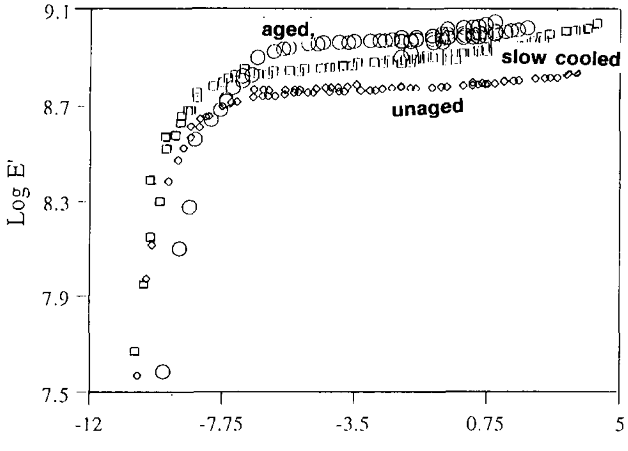

Fig. 6. Isothermal master curves for aged, unaged and slow cooled PES at 493 K.

with log(a) the horizontal shift factor required to superimpose the E' data with log(frequency), see Fig. 6. Values of $C_1 = 17.4$ and $C_2 = 51.6$ K were derived from the gradient and intercept of linear plots of $(T - T_0)/\log(a)$ against $(T - T_0)$. The master curves showed that the aged specimens were less temperature-dependent, see Fig. 6, than the quenched material, consistent with the general trend in DSC measurements that the transition moves to higher temperatures on aging.

3.3. Dielectric thermal analysis

The change in dielectric response of PES accompanying physical aging was investigated using DETA and analysed in terms of complex plane plots, more commonly called Cole–Cole plots. The frequency of measurement of the dielectric constants of many liquids and solids has a marked effect on the constants being measured. The dielectric constant has a static value at low temperature and a limiting value at high frequencies [11]. These two values are ε_0 and ε_∞ respectively. The region between these two values is the "absorption conductivity" [11]. This region is described in terms of a complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$. The frequency dependence of ε' and ε'' was first described by Debye [12]. Differences between ε_0 and ε_∞ were attributed to dipole polarization. The orientation of polar molecules in an alternating-current field is opposed by thermal agitation and molecular interactions. The molecular interactions are represented by a picture of viscous damping, and the molecules are considered as a set of spheres in a continuous viscous medium. The theoretical analysis leads to [12]

$$\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/(1 + \omega\tau_0) \tag{3}$$

where ω is 2π frequency and τ_0 is a relaxation time for the process.

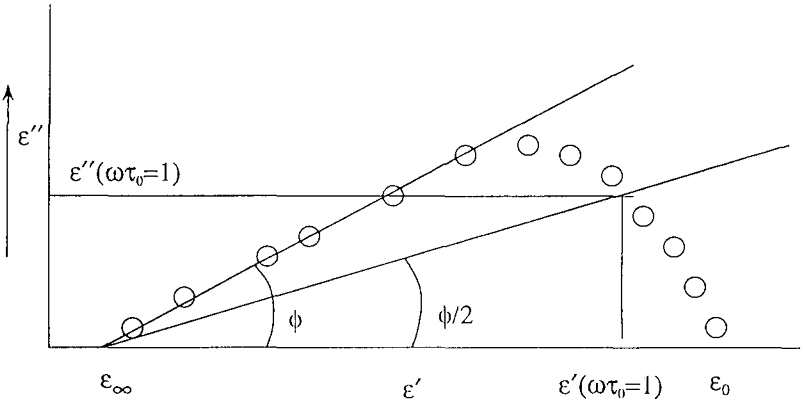

Fig. 7. An idealized complex plane Cole–Cole plot, defining parameters.

Work carried out by Cole and Cole [11] showed that the complex plane plot is a convenient way of representing complex dielectric data. Relaxations for polymers show broader dispersion curves with lower loss maxima, however, than those predicted by the Debye model. This has led to other models based on the Debye model that try to account for this behaviour. The first model was suggested by Cole and Cole [11] in that they represented the material behaviour with the semi-empirical equation

$$\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/[1 + (\omega\tau_0)^{1-\alpha}] \tag{4}$$

where α is a parameter that governs the breadth of the dielectric relaxation distribution and $0 < \alpha < 1$. This equation produces a complex plane plot with the centre of the semi-circle depressed below and abscissa. The lower the value for α, the narrower the range of relaxation times that are symmetrically distributed about the relaxation time τ_0.

It is often the case that complex plane plots are not a semi-circle but are skewed. In an attempt to fit this, Davidson and Cole [13] used the function

$$\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/(1 + \omega\tau_0)^\beta \tag{5}$$

where β is the skewness factor and $0 < \beta < 1$.

An empirical expression proposed by Havriliak and Negami [14] has been used to account for both variations from the Debye model, and combined corrections for Cole–Cole and Cole–Davidson leads to

$$\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/[1 + (\omega\tau_0)^{1-\alpha}]^\beta \tag{6}$$

where the α and β are the same as before, i.e. a measure of the breadth and skewness of the distribution.

Complex plane plots are a convenient way to represent dielectric data graphically. They facilitate the easy measurement of all the parameters in Eqs. (3)–(6). A generalized complex plane plot showing the parameters is shown in Fig. 7. Complex

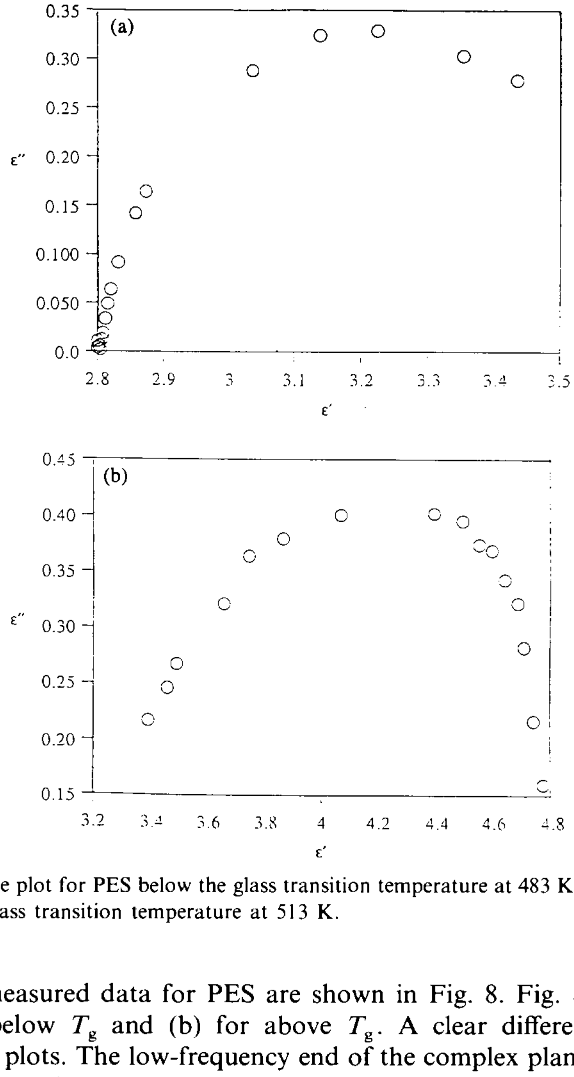

Fig. 8. (a) Cole–Cole plot for PES below the glass transition temperature at 483 K. (b) Cole–Cole plots of PES above the glass transition temperature at 513 K.

plane plots of measured data for PES are shown in Fig. 8. Fig. 8(a) is a plot for data obtained below T_g and (b) for above T_g. A clear difference can be seen between the two plots. The low-frequency end of the complex plane plot is not well defined below T_g and a more complete data set is available only if the sample is heated through T_g. The use of these plots to investigate physical aging limits the data collection to below T_g. Although the value of β and hence $(1-\alpha)\beta\pi/2$ can be measured from most data sets, there is not always sufficient data to apply the Havriliak and Negami [14] deconvolution procedure.

The results obtained are shown in Table 2. The β^* values quoted include both the skewness and breadth of the relaxation spectra, i.e. $(1-\alpha)\beta\pi/2$. From these results it can be seen that there is a general decrease in the β^* values with physical aging.

The larger the supercooling, the higher the β^* value. This is consistent with the narrowing of the spectra associated with the relaxation occurring in physical aging. The values of the β^* decreased dramatically at temperatures higher than T_g.

Table 2
β^* Value from complex plane analysis

Aging temperature in K	Supercooling ΔT in K	Average β^* value	Aging temperature in K	Supercooling ΔT in K	Aging β^* value
278.2	15.0	0.85	293.2	0	0.68
280.7	12.5	0.81	308.2	−15.0	0.62
283.2	15.0	0.79	313.2	−20.0	0.31
285.7	7.5	0.73	318.2	−25.0	0.18
288.2	5.0	0.79			

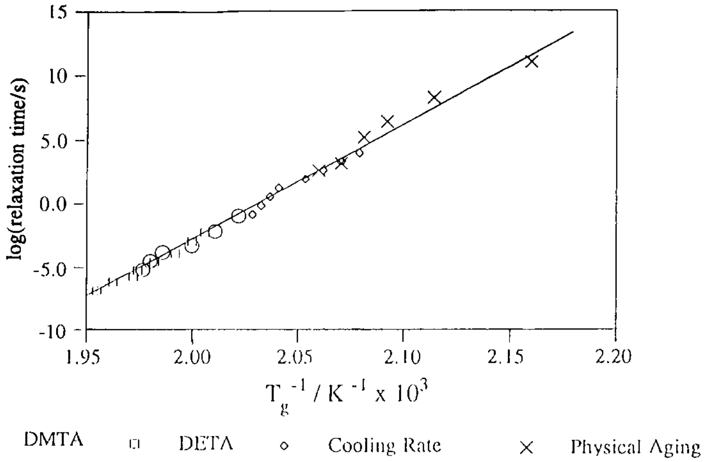

Fig. 9. Relaxation time master plot for PES, combining measured T_g values from DETA, DMTA, DSC cooling rates, and enthalpic relaxation data.

4. Conclusions

The enthalpic relaxation of PES is adequately described by the Cowie–Ferguson equation as the parameters derived, ΔH_{max}, ΔC_p, and T_g, compare favourably with those determined experimentally. As has been observed with all the polymer systems studied, enthalpic relaxation occurs in a narrow window of about 60 K below the glass transition temperature, and clearly this is reminiscent of the thermodynamic limit imposed on the glass transition, T_2, and Kauzmann's paradox [15] of the conformational entropy of the glass being less than that of the crystalline solid.

Using the Williams–Landel–Ferry equation as described above, the overall dependence of the glass transition temperature as determined by DETA, DMTA, the cooling rate of the DSC, and the relaxation time for physical aging were superimposed and the overall frequency dependence of the glass transition determined, see Fig. 9. This gives direct evidence that enthalpic relaxation as measured by DSC is a continuation of the glass-forming process and the kinetics of the alpha transition.

The β^* parameters as measured by DETA and the Williams–Watt stretched exponential are not directly comparable because the former is measured in the frequency field and the latter is a time domain function. Alvarez et al. [16] have recently considered this and have established a method for deriving related functions from the latter. The two values derived are not inconsistent with this approach.

Acknowledgements

A.A.M-A. is indebted to the SERC and ICI Ltd., Speciality Plastic Group of the award of a studentship during the tenure of this work.

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