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Investigation of physical ageing in polymethylmethacrylate using positron annihilation, dielectric relaxation and dynamic mechanical thermal analysis

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The physical ageing of polymethylmethacrylate is investigated using a combination of positron annihilation, dielectric relaxation and dynamic mechanical thermal analysis. Correlations are observed between the three types of observation; however, no simple theory can be seen to fit all of the data. The dielectric data indicates that 'thermorheologically simplicity' is probably not a valid assumption for this system. The data also suggest that the free volume distribution probably changes during ageing; however, it was not probably to quantify these changes from the current positron annihilation study. Comparison of the experimental data from these various techniques clearly indicates that processes occurring at a molecular level are complex and not simply the result of one single type of conformational rearrangement and have an apparent activation energy comparable to that of the glass–rubber transition. © 1997 Elsevier Science Ltd.

(Keywords: physical ageing; positron annihilation; dielectric relaxation)

INTRODUCTION

Physical ageing is a spontaneous, thermally reversible change that occurs in glassy materials and has been studied for over 30 years[1]. A number of phenomenological theories have been proposed to describe the time-dependent changes observed in the physical properties of polymers and associated with physical ageing[1,2]. Many of these theories are based on free volume as the rate controlling factor. The glass transition process (T_g) is ascribed to long-range conformational change of the polymer backbone and is sensitive to free volume. Cooling through T_g produces a non-equilibrium thermodynamic conformational distribution which slowly attempts to reach an equilibrium value appropriate to the annealing temperature. The changes which occur in the conformational distribution and related physical properties are attributed to physical ageing. Below T_β, the highest secondary transition which is usually insensitive to volume effects, physical ageing ceases[1,2]. The activation energy for T_β is usually between 30 and 50 kJ mol^{-1} and rises to between 200 and 300S kJ mol^{-1} for T_g[3]. The former are localized conformational changes requiring motion about only one or two bonds whereas the glass transition is a more cooperative motion involving between 8 and 20 bonds moving collectively. The precise number of bonds involved depends to the model used to interpret the dynamic data and the nature of the probe used to sense the motion. The density, yield stress and elastic modulus of the polymer increase; impact strength, fracture energy, ultimate elongation decrease; creep and stress relaxation rates decrease.

In order to understand physical ageing it is therefore desirable to be able to probe the free volume of the amorphous system as it changes due to physical ageing. Positron annihilation spectroscopy (PAS) has been used to explore the void structure in molecular systems and free volume in amorphous materials[2,3]. Polymethylmethacrylate, being a polar polymer, exhibits a dielectric relaxation spectrum (DES) and allows characterization of the effects of changes in the local environment on the motion of the dipole. For this reason PMMA was selected for the present study. Longer range cooperative molecular motions dominate mechanical properties both in the viscous and solid state and can be characterized by dynamic mechanical thermal analysis (DMTA). Combination of data from PAS, DES and DMTA provides information on the changes in the free volume and its effects on short- and long-range molecular motions in the system undergoing ageing. The aim of this study being to probe at a molecular level the changes which occur within a system undergoing physical ageing.

Doolittle[4] and Williams–Landell–Ferry (WLF)[5] have derived equations describing phenomenologically the effects of free volume (V_f) on a range of physical parameters. These theories were developed to describe the behaviour of systems above their T_g and are not necessarily appropriate for interpretation of effects below T_g. Any model of physical ageing below T_g must be able to predict that a slower cooling rate results in a lower T_g and that the precise value depends upon whether the sample is heated or cooled. The structural or volume relaxation rate also depends on the direction and magnitude of the quenching process through T_g. For symmetric behaviour to be observed, contraction and expansion isotherms would be mirror images of each other, which is not usually the case.

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Structural relaxation processes, with mean lifetime τ, are observed to be non-exponential and are represented by a continuous distribution or a stretched exponential terms[6]. A single value of the distribution parameter is not usually sufficient to describe all the data[7,8], implying that the relaxation processes contains different types of molecular motion. In a volume relaxation process, faster motions will allow elements of the chain to come close to or reach equilibrium during the quenching procedure. The slower molecular motions will, however, still be in the non equilibrium state and are frozen-in at T_g. The fast motions allow these elements of the chain to reach equilibrium and have a T_g that is equivalent to T_1, the equilibration temperature. The observed T_g is therefore a function of the thermal history of the sample. Thermorheologically simplicity (TRS) is often assumed and implies that the molecular relaxation process has the same form at different temperatures[9]. Whether or not this is correct is one of the issues addressed in this paper.

Kovacs[10] has described the isobaric volume recovery using free volume and enthalpy approaches[11]. Although any single parameter model will have limitations, the free volume theory has been useful in quantitatively describing non-equilibrium behaviour[1,12,13] in a number of systems. Struik[1] showed that all free volume models[4–6,14,15] have limitations. If free volume[14,15] is distributed over various hole sizes, there will be a corresponding distribution of molecular environments and relaxation times leading to a pseudo-linear theory. Only hole sizes above a critical size will contribute to mobility. This proposal is intuitively correct, but needs to be assessed experimentally.

Tool[16] generated a non-equilibrium theory based on a viscoelastic hydrostatic stress relaxation model which has been extended by Narayanaswamy[9]. Since non-linearity arises from the time dependence of τ, linearity can be restored by using a reduced time which allows for non-linearity. An alternative relaxation model based on changes in the distribution parameter has been developed by Scherer[17,18].

In this paper comparison of data from various techniques will be used to test certain of the assumptions in the above models and may throw light on the molecular nature of physical ageing.

EXPERIMENTAL

Materials

ICI (Diakon), commercial atactic PMMA, has a weight average molar mass (M_w) of 136 000, a T_g of 105°C and was annealed at 120°C. It is recognized that tacticity could have an effect on the physical ageing; however, pure tactic forms were not available in sufficient quantity to allow them to be injection moulded. Dog bones (120 × 10 × 3.25 mm), square plaques (60 × 60 × 3.25 mm) and creep bars (15 × 20 × 3.25 mm) were compression moulded for this study. Isothermal ageing was performed on samples previously equilibrated at a defined annealing temperature followed by rapid quenching to room temperature, ~298K and reheating to the ageing temperature T_e.

Dielectric relaxation spectroscopy (DRS)

Isothermal and isochronus ageing studies were carried out over a frequency range between 10^{-2} and 6.5×10^5 Hz at 10°C temperature intervals between 30 and 120°C, using a computer-controlled frequency response analyser Schlumberger 1250[19]. The temperature was controlled using an Oxford Instruments cryostat (DN1704). A compression moulded 15 × 15 × 0.95 mm sample of PMMA was annealed and quenched and placed between the electrodes.

Dynamic mechanical analysis

A Rheometrics dynamic mechanical thermal analyser (DMTA) used in a single cantilever arrangement with a 12 N power head and injection moulded 'creep' bars were used. A clamping torque of 30 N and a double lock–nut system secured with 'Loctite' adhesive was used to ensure that the clamps did not slip with time for the isothermal experiments. Both E' and $\tan\delta$ were measured as a function of temperature at a frequency of 1 Hz over the temperature range −145 to +150°C and a heating rate of 2°C min^{-1} for the isochronal experiments.

Positron annihilation lifetime spectroscopy (PALS)

A fast–fast PALS system using cylindrical (40 mm diameter × 15 mm thick) BaF_2 scintillators [20] arranged at 90° to each other to avoid pulse pile-up problems. A count rate of 150–300 cps was achieved with a ^{22}Na source and a instrument resolution of 220–240 ps FWHM for a 50 μCi source. Benzophenone and ^{60}Co were used to determine the resolution and source correction. The spectrum was analysed using POSITRONFIT[21] which describes the spectrum as a convolution of the instrument resolution function and a finite number (n) of negative exponentials:

$$y(t) = R(t)^* \left(N_t \sum_{i=1}^{n} \alpha_i \lambda_i e^{-\lambda_i t} + B \right) \qquad (1)$$

where $y(t)$ is the experimental data, $R(t)$ is the instrument resolution function, N_t is the normalized total count, B is the background, λ_i is the inverse of the ith lifetime component (τ_i), and ($\alpha_i\lambda_i$) is its intensity. A 'fixed analysis' is used in this paper and assumes τ_1 is fixed at 0.125 ns (p-Ps), τ_2 at 0.400 ns or 0.360 ns (free e$^-$) and the ratio of I_3/I_1 at 3:1. Isochronous experiments involved the samples being aged for various times at a defined temperature before being thermally scanned. Isothermal experiments involved the sample being measured continuously as a function of ageing time at a particular temperature. The latter require the dedication of the equipment for these studies over the entire period of the ageing experiment. The sample measured was constructed by inserting the source, ^{22}Na deposited on Kaptan foil, between two plaques of the PMMA, each 15 × 15 × 2 mm. Calibration using a dummy source sample 'sandwich', indicated that thermal equilibration takes 8 min. PALS were collected at 10°C intervals from 30 to 100°C. Data collection time was 60 min at each temperature corresponding to 500–600 k counts and both 'fixed' and 'free' analysis were carried out on the PALS spectra.

Recently, with the development of the computer program CONTIN[22–24], it has been possible to resolve positron lifetime spectra into continuous lifetime distributions. Comparison of the results obtained from the analysis using POSITRONFIT and CONTIN indicated that spectra containing 10^6 counts or greater are required to justify the use of the CONTIN analysis. Spectra containing a smaller number of counts did not allow differentiation between the analysis and therefore the analysis reported in this paper is based on POSITRONFIT. Increasing the data collection time to achieve the required level of counts decreases the precision with which the ageing time is defined and consequently increases the uncertainty in the distribution parameter. The compromise which has been adopted is therefore to collect 500–660 k counts and use POSITRONFIT and compare the results of fixed and free analysis of a test of the consistency of the analysis. In practice the comparison was good in most cases and improved as the T_g was approached.

RESULTS AND DISCUSSION

Positron annihilation data

Li and Boyce[25] have shown that the o-P_{sI} is influenced by the irradiation time and source strength, as well as effects due to physical ageing. It was found that electrical grounding of the source and material reduced the rate of decrease in o-P_{sI} due to the build-up of an electric field in the material[26–28]. Li and Boyce[25] found that in PMMA the charging effects were minimal, confirming the study by Brandt and Wilkenfelds[26] who indicating that o-Ps formation is not affected by the presence of an electric field. In this study samples were annealed for 30 min at the temperatures given in *Table 1* using a fan-assisted oven before ageing was performed. Quenching was achieved by immersing the annealed samples directly into water at room temperature for around 1 min. The effects of electrical grounding were explored and found in this case to have little or no effect on the intensity or lifetime in confirmation of the observations of Brandt and Wilkenfelds[26].

Isothermal ageing of poly(methyl methacrylate)

In order to establish the extent to which ageing can influence the void size, the 'equilibrium' liquid line was measured by studying the o-Ps lifetime τ_3 *versus* temperature between 30 and 150°C (*Figure 1*). Isothermal measurements were carried out to reduce any errors associated with inconsistencies in the thermal history inherent in an isochronus experiment (*Table 2*). A variety of different models have been proposed to fit lifetime data. Hill *et al.*[29,30] have used structural relaxation functions to describe o-Ps behaviour at or below T_g[15]. The models which were used in this study include log, single exponential, double additive exponential and the Narayanaswamy model[9]:

$$\text{Logarithmic regression } \tau_3 = a \times \log(t) + b \qquad (2)$$

$$\text{Single exponential } \tau_3 = a \times \exp^{(-t/\tau)} + b \qquad (3)$$

$$\text{Double additive exponential } \tau_3 = a \times \exp^{(-t/\tau)} + b \times \exp^{(-t/\tau)} + c \qquad (4)$$

$$\text{Narayanaswamy } \tau_3 = \exp^{(-t/\tau)^{\beta}} \qquad (5)$$

All mathematical fitting was carried out using the computer package Fig-P (V6.0). Fitting of the lifetime variation with time was limited to logarithmic (*Figure 2*) and simple single

Table 1 Annealing temperatures used in this study

Material	Ageing temperature (°C)	Ageing time (h) 0	4	8	16	32	64
PMMA	30	✓	✓	✓	✓	✓	✓
PMMA	50	✓		✓	✓	✓	✓
PMMA	80	✓		✓	✓	✓	✓

Table 2 Isothermal ageing experiments for PMMA

Material	Ageing temperatures (°C) 30	70	80	90	100	110	120
PMMA	✓	✓	✓	✓	✓	✓	✓

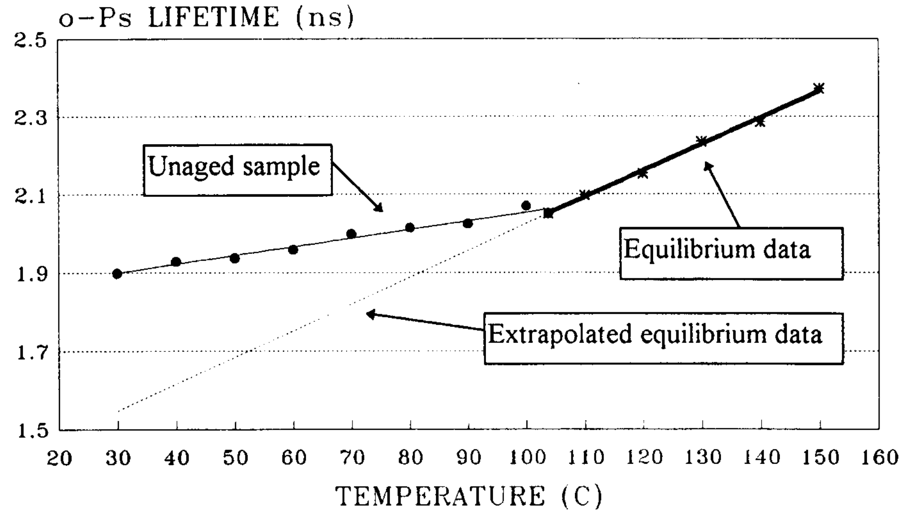

Figure 1 Plot of τ_3 *versus* temperature data for PMMA, including extrapolation of equilibrium 'liquid' line below T_g

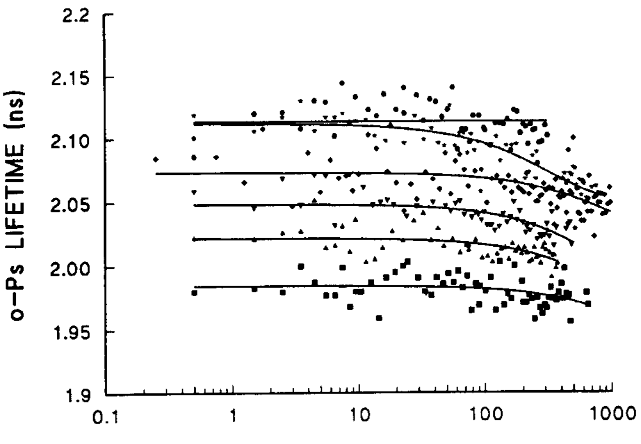

Figure 2 Exponential fits to isothermal τ_3 data for PMMA over the temperature range 70–120°C. The 120°C data is fit with the equation of a straight line. Data is in order of increasing temperature from the bottom of the plot upwards: (■) 70°C; (△) 80°C; (▽) 90°C; (◆) 100°C; (★) 110°C; (•) 120°C

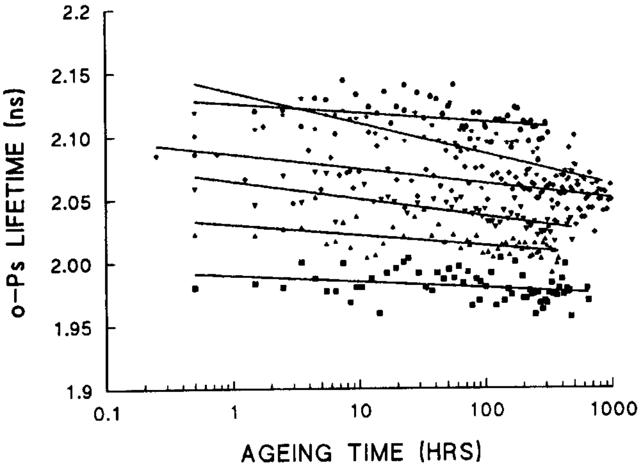

Figure 3 Logarithmic fits to isothermal τ_3 data for PMMA over the temperature range 70–120°C. Data is in order of increasing temperature from the bottom of the plot upwards: (■) 70°C; (△) 80°C; (▽) 90°C; (◆) 100°C; (★) 110°C; (●) 120°C

exponentials fits (*Figure 3*). The experimental scatter in the data made the use of more sophisticated models invalid. The scatter is a reflection of a combination of factors involving long-term instrument stability, temperature stability of the sample ~ ± 0.1K and charging effects. The fitting parameters are presented in *Table 3*. The variation of the lifetime analysis may be investigated as a function of the ageing temperature and an Arrhenius-like behaviour is observed (*Figure 4*). The slope of the curve yields an activation energy for the volume relaxation of $84 \pm 6\,\mathrm{kJ\,mol^{-1}}$, close to that observed for the T_g process as measured by other techniques[31]. The 'rate' of ageing is measured as the slope of the log curve (*Figure 5*), is remarkably similar in shape to Struik's[1] ageing rate *versus* temperature plot derived from mechanical small-strain creep experiments. Struick defines the ageing rate as $\mu = \mathrm{d}(\log\tau)/\mathrm{d}(\log t)$, making this parameter a dimensionless quantity; the plots used in this paper contain an implicit normalization factor and hence parallel the approach used previously, although clearly are not intrinsically related. This similarity implies a correlation between the free volume V_f measured by positron annihilation and that determining mechanical measurements, but does not necessarily define the connectivity at a molecular level. Only if the form of the free volume function influencing the creep relaxation is identical to that measured with positron annihilation will a one-to-one relationship be expected. Assuming that the o-Ps annihilation intensity I_3 is unaffected by charging effects in PMMA, then the product $\tau_3 \times I_3$ may be used to represent V_f as a function of temperature[30] (*Figure 6*). Since no $I_3(t = \infty)$ data is available it was not possible to fit the data to any of the specific relaxation models. Data for 110°C does not fit the overall pattern of increasing $\tau_3 \times I_3$ product, this is due to lower than expected values of I_3. It has been observed previously that motion of the side chain of PMMA can lead to an anomalous reduction in the value of I_3 as a consequence of its rotation into the cavity within the o-Ps lifetime[32–35]. It is probable that if the intensity were to be corrected for the effects of internal cavity relaxation then a more appropriate form for the temperature dependence would emerge. Such a correction was not attempted because of the possible additional effects of the charge mobility changes on the intensity.

Dielectric relaxation data

Dielectric permittivity and loss data were measured over the temperature range 30–120°C for unaged PMMA (*Figure 7*). A direct comparison between the aged and unaged data is shown in *Figure 8* ageing at 90°C. The peak at high frequency in the dielectric loss at 10^3–10^5 Hz has been attributed to rotation of the $-COOCH_3$ side group in PMMA[33,31]. The feature at lower frequency is the tail of the T_g process which occurs at approximately 10^{-5} Hz at this temperature. Ageing leads to a narrowing of the β-relaxation process and reduction in the lower frequency amplitude, which is consistent with both a change in the distribution of relaxations and an increase in the effective T_g. The dielectric data indicates that thermodynamic simplicity is an oversimplification since the changes in intensity occur to different extents across the total spectrum.

Table 3 Summary of fitting parameters for isothermal τ_3 ageing data over temperature range 70–120°C

	Single exponential fit			
Ageing temperature (°C)	τ_3 ($t = \infty$) (ns) (fixed)	τ_3 (h) (relaxation time constant)	$\Delta\tau_3$ (ns) (extent of ageing)	Log fit 'Rate' $\mathrm{d}\tau_3/\mathrm{dlog}t$ (gradient)
70	1.820	6339	0.165	−0.0050
80	1.888	2478	0.131	−0.0085
90	1.956	1240	0.092	−0.0140
100	2.024	610	0.049	−0.0117
110	2.050	324	0.062	−0.0242
120	—	—	—	−0.0074

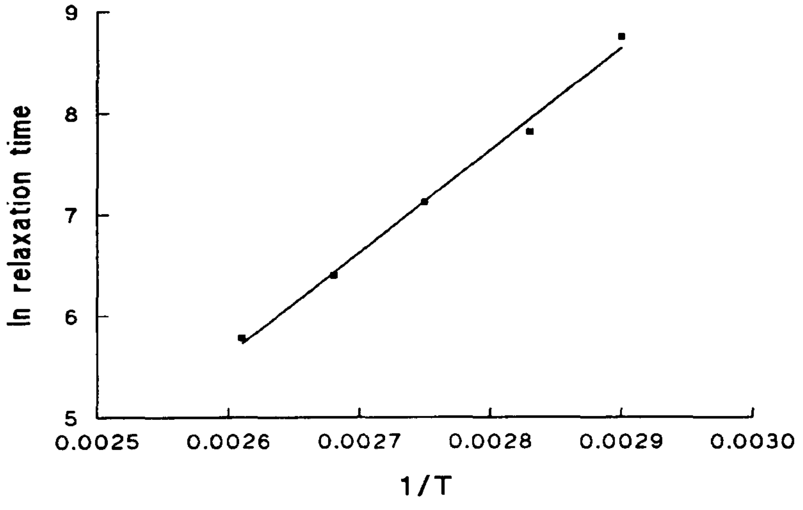

Figure 4 Arrhenius plot of lnτ *versus* $1/T$ for PMMA over the temperature range 70–110°C

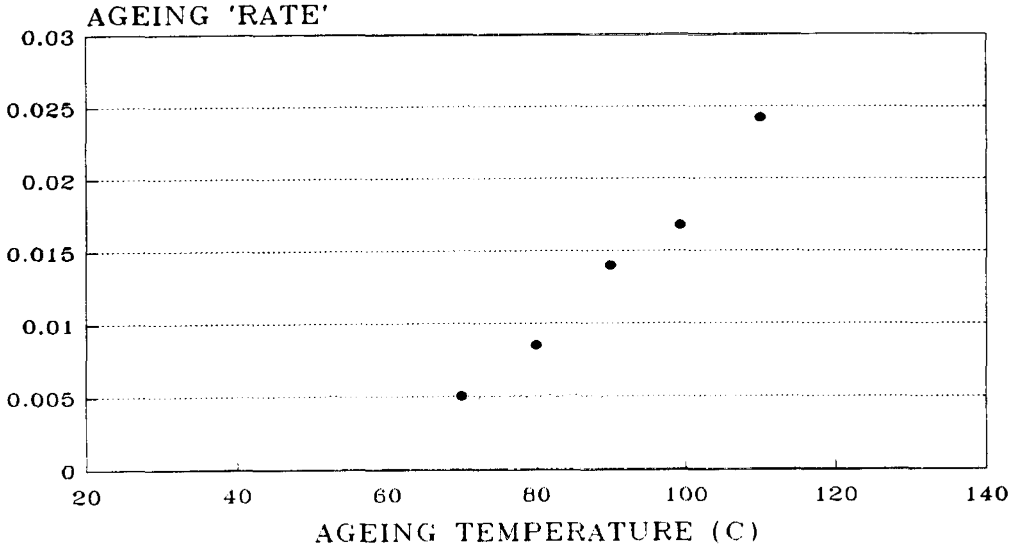

Figure 5 Ageing 'rate' *versus* temperature for PMMA over the temperature range 70-120°C

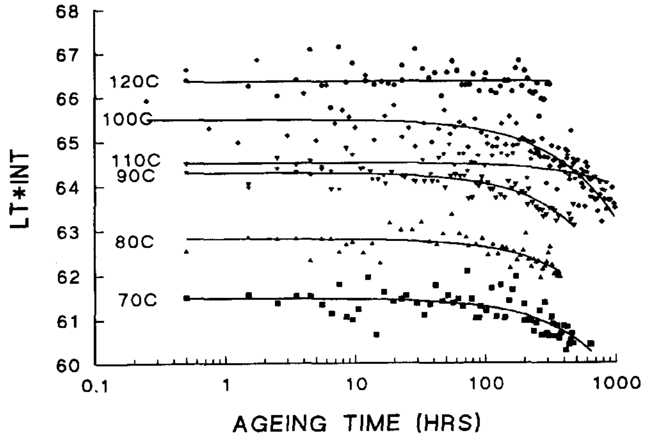

Figure 6 Product of $\tau_3 \times I_3$ *versus* ageing time for PMMA over the temperature range 70–120°C. Fitted curves are simple single exponentials: (■) 70°C; (△) 80°C; (▽) 90°C; (♦) 100°C; (★) 110°C; (●) 120°C

The dielectric data for this sample is in agreement with previously published isothermal data[31].

Mechanical relaxation data

A single isochronus ageing experiment was carried out to illustrate the effect of ageing on both the dynamic modulus and tan δ as a function of temperature. An unaged sample was equilibrated for 100 h at 90°C in an air-circulating oven (*Figure 9*). The onset of T_g, observed as a drop in E', occurs at a slightly higher temperature in the aged as compared to the unaged material. The tan δ plots show two peaks: at around 40°C a β-relaxation and at 120°C an α-relaxation. In PMMA there is a large degree of overlap of these processes, the β-process being especially broad and usually associated with rotational isomerism of the pendant ester grouping. These results show that the largest change in tan δ occurs when samples are aged over the temperature range between the two main relaxation processes and is consistent with the earlier observations of Struik[1,32].

Isothermal ageing experiments

Both E' and tan δ data were collected as a function of the isothermal ageing time over the temperature range

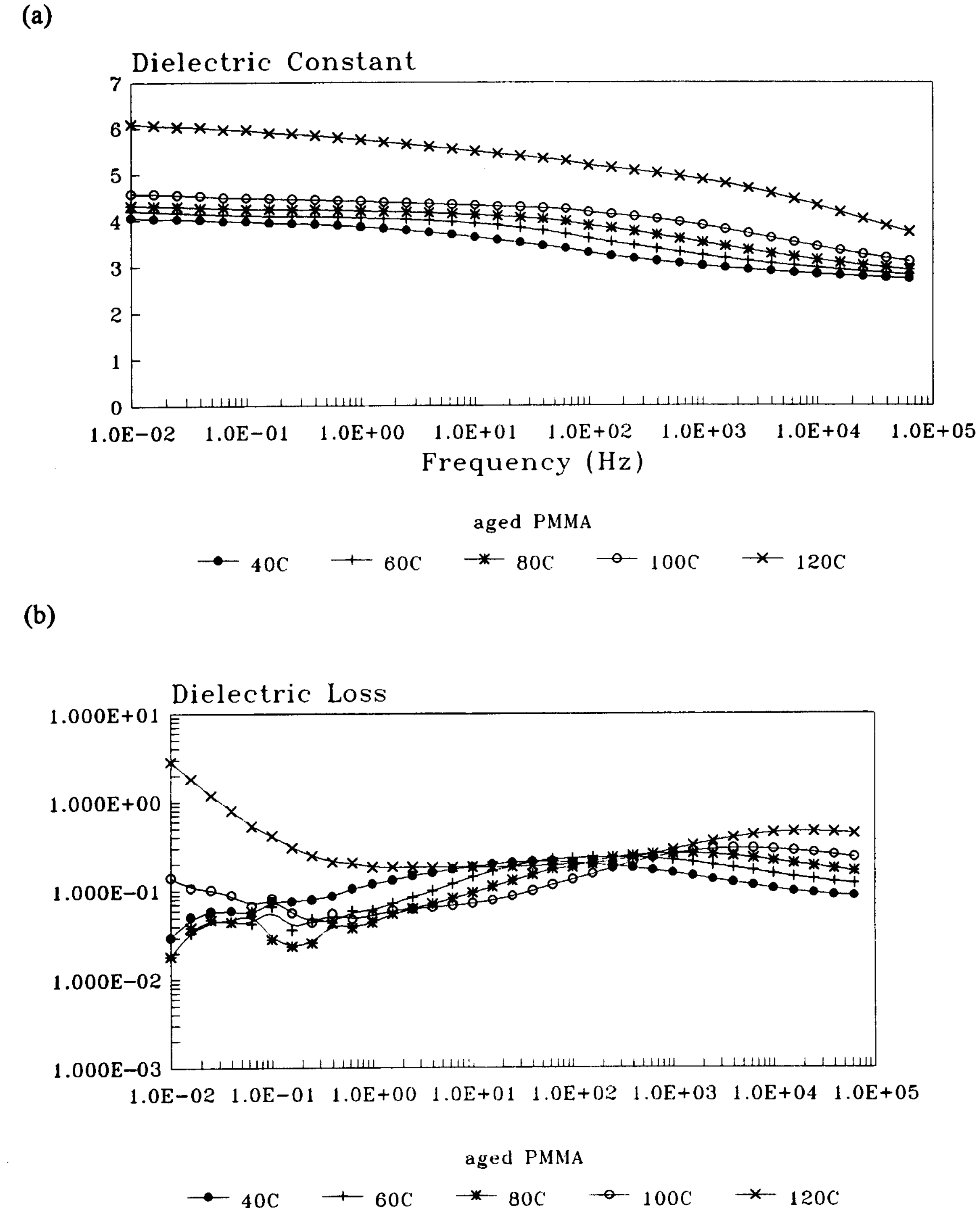

Figure 7 Frequency dependence of ϵ' (a) and ϵ'' (b) for aged PMMA over the temperature range 40–120°C

70–100°C at 10°C intervals with a precision of ± 0.1°C at a frequency of 1 Hz. The sample heat-up time to the ageing temperature after quenching was ~5 min, whilst the oven reached this temperature in 2 min, a delay in sample equilibration being observed due to the low thermal conductivity of PPMA. Data was collected at 15 min intervals for periods of up to 200 h depending on the ageing temperature. Since tan δ is the ratio E''/E' it does not vary with sample dimensions and is therefore insensitive to changes in geometry during the experiment. Isothermal tan δ data for PMMA over the temperature range 70–120°C were measured (*Figure 10*).

Below 110°C tan δ varies approximately linearly with log time over the time range measured consistent with the results of Venditti and Gillham[35]. Above 110°C a rapid decrease in tan δ followed by a stable value indicating equilibration occurs very quickly. Data for ageing over the temperature range 70–100°C was fit with both double-exponential and logarithmic functions. The single-exponential fit to the data was inappropriate at lower temperatures. The double-exponential data does not follow the expected pattern shown by both PALS and dielectric data, of increasing relaxation time for the relaxation process with decreasing temperature. Attempts were made to mathematically fit the data using a variety of fitting procedures (*Table 4*). Where no result is given, unreliable

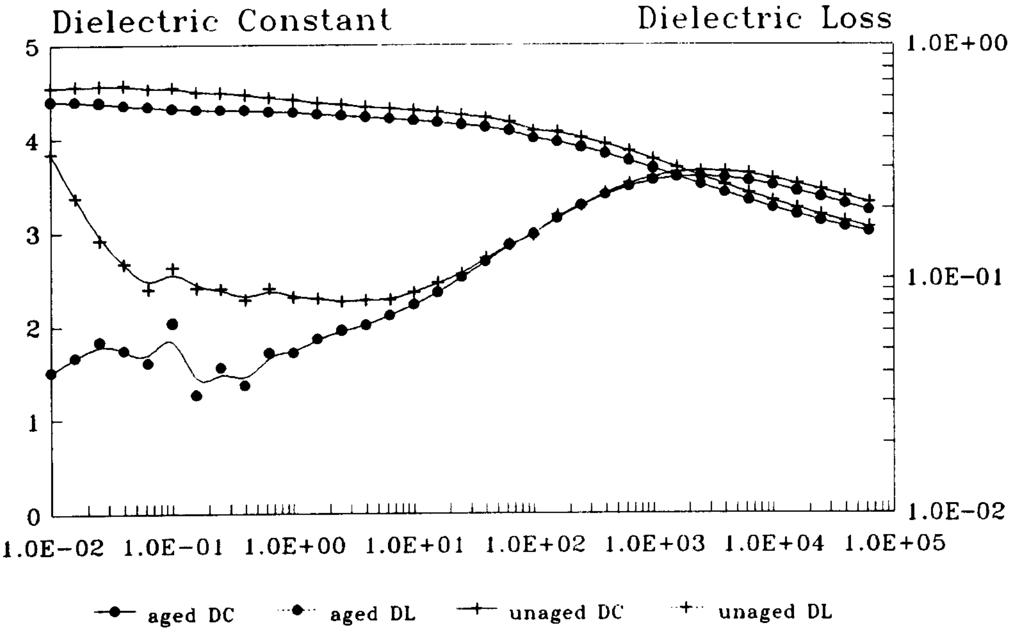

Figure 8 Frequency dependence of ϵ' and ϵ'' for aged/unaged PMMA at 90°C

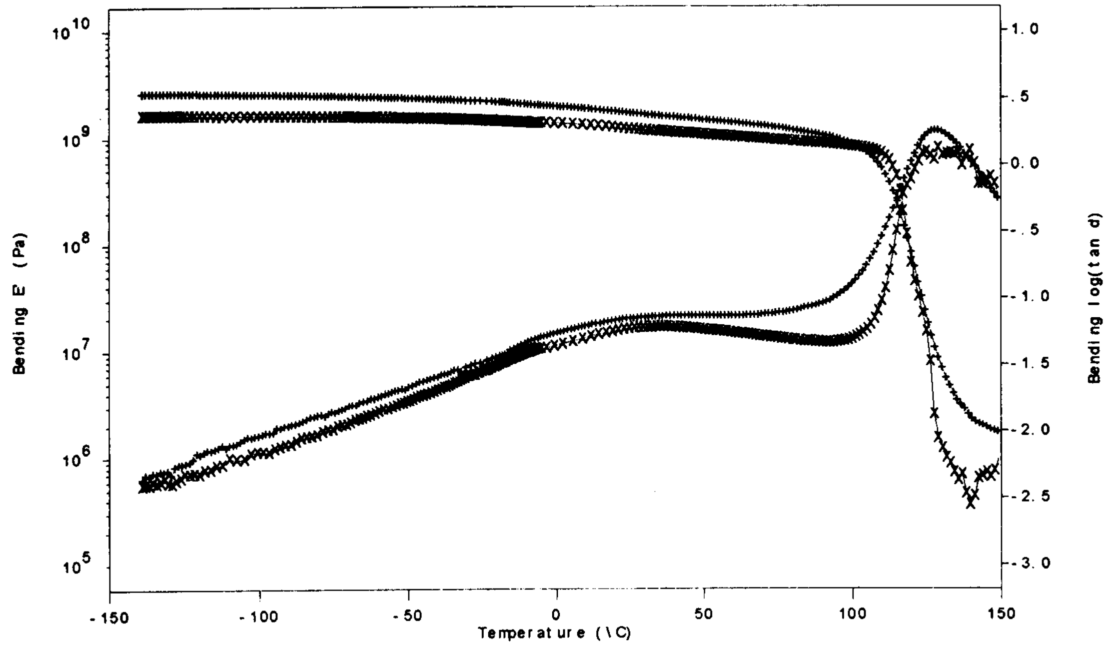

Figure 9 Dynamic mechanical spectra showing both E' and tanδ of unaged (+) and aged (×) PMMA over the temperature range − 145 to + 150°C at 1 Hz frequency

Table 4 Fitting parameters for mechanical data

Ageing temperature (°C)	1-exponential fit τ (h)	2-exponential fit τ_1 (h)	τ_2 (h)	Log fit (gradient)
70	NRS	1.4	40	−0.00528
80	NRS	1.1	30	−0.00767
90	NRS	0.8	62	−0.00841
100	NRS	1.5	33	−0.0276
110	2.3	NRS	NRS	−0.0654
120	0.6	NRS	NRS	NRS

fits obtained due to large deviations between experiment and theory were obtained and no result is given. Both double exponential and logarithmic fits exhibited gross deviations from actual data, but usually at different temperatures. This behaviour is indicative of the variation in character of the processes occurring as the temperature is changed. In the case of 110°C data the fitting parameter for the log fit given in *Table 4* is for ageing times of up to a few hours and

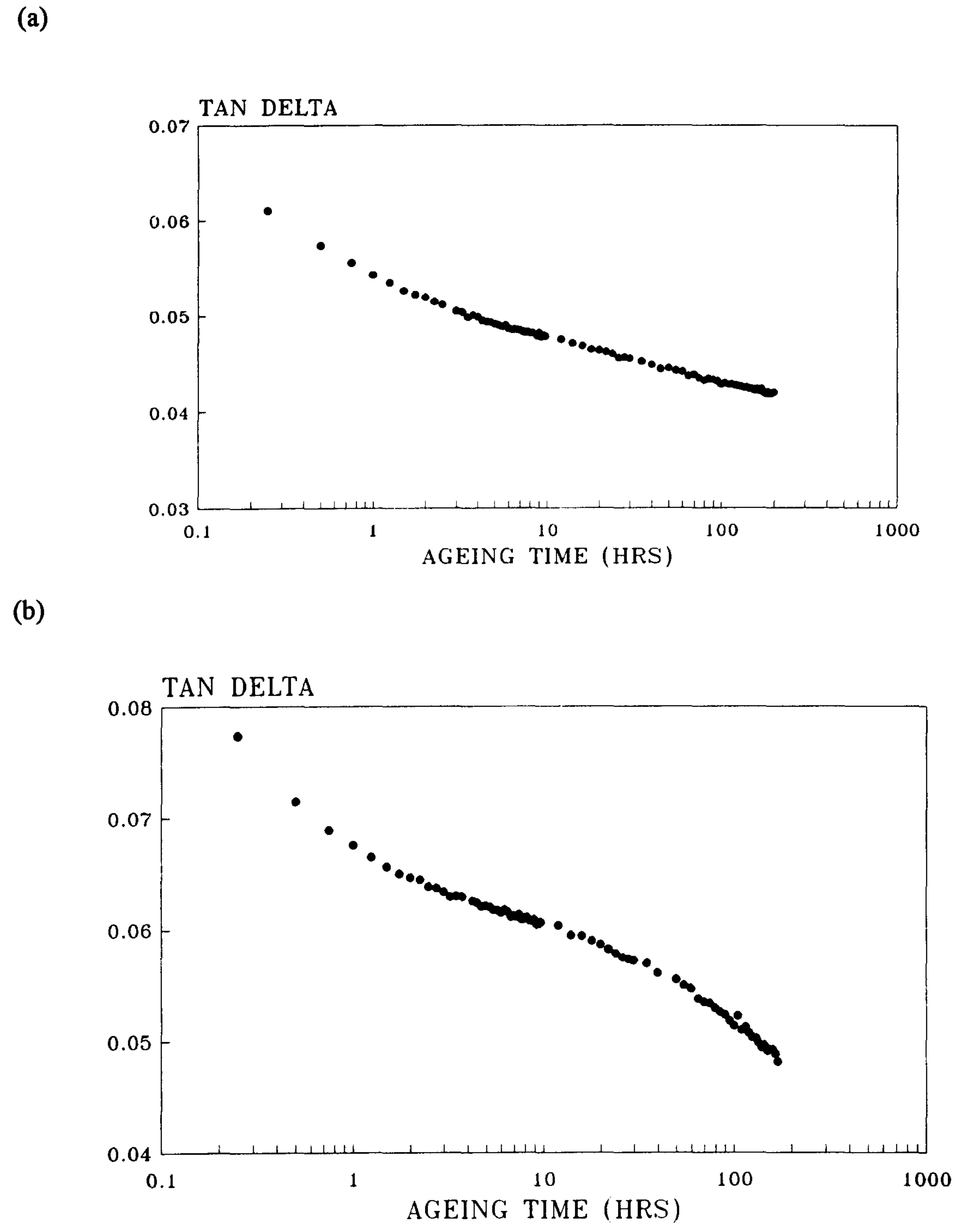

Figure 10 Isothermal tanδ data for PMMA aged at 70°C (a) and at 90°C (b)

corresponds to the region over which tan δ varies linearly with log time. Beyond this time scale the ageing 'rate' decreases rapidly to zero. This approach was taken to allow calculation of the ageing 'rate' for 110°C data to allow comparison with both PALS and DRS ageing 'rate' data. The single-exponential form for the relaxation function suggests that only one relaxation process is taking place over the time scale of the measurement. Guerdoux *et al.*[36] carried out DMA experiments on PMMA as a function of ageing over a wide time range and observed horizontal shifts to superimpose materials of different ageing histories was not completely effective, and their results are similar to those reported here.

The double-exponential fits to data for ageing experiments over the temperature range 70–100°C are presented in *Figure 11*. Although the double-exponential relaxation function appears to fit the data over an extended time range, it cannot be concluded that the relaxation function is a double-exponential. This implies that the relaxation process is composed of more than one component and infers a dual molecular origin for the process. It is, however, important to note that in this system close to the T_g, the single exponential fit is adequate for the system implying a 'simplification' of the system in this region. The 'rate' of ageing is measured as the slope of the log fits (*Figure 11*) and the temperature dependence (*Figure 12*), is remarkably similar to Struik's[1] ageing rate plots derived from mechanical relaxation (small-strain creep). Good

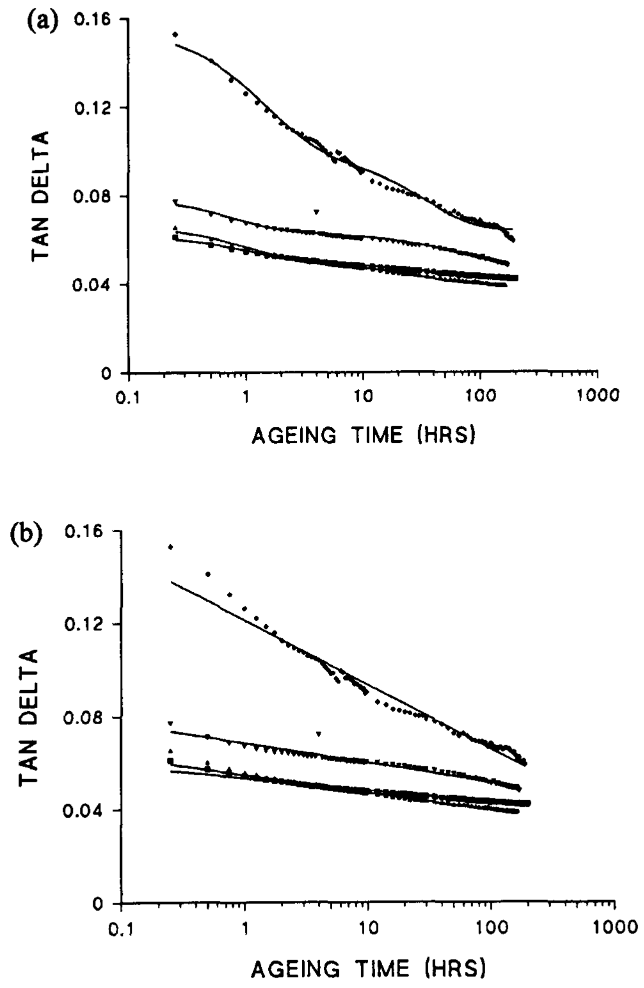

Figure 11 Double-exponential (a) and logarithmic (b) fits to tanδ data for PMMA aged 70–100°C. Fitting parameters for these fits are shown in Table 4. (■) 70°C; (△) 80°C; (▽) 90°C; (◆) 100°C

correlation is also observed with the ageing rate behaviour measured on the same material using PALS (*Figure 13*).

In summary, it can be said that none of the various forms of relaxation function used to fit tan δ ageing data are completely satisfactory. The double-exponential fit appears to represent data well over the whole time range pictorially, but analysis of relaxation parameters for this type of function do not follow any discernible pattern. Single-exponential fits were possible for ageing close to T_g, suggesting that as this temperature is reached the relaxation function is composed of only one major component, rather than the two suggested by the double-exponential fits at lower temperatures. The logarithmic fits, while not providing any parameter which can be directly related to any physical process, can nonetheless provide a useful measure of the ageing 'rate' for comparison purposes.

DISCUSSION

The lack of a universal model describing physical ageing has led to a number of assumptions being made about the molecular nature of the processes occurring during physical ageing. This study has shown that none of the various forms of relaxation function used to fit tan δ ageing data are completely satisfactory. At a molecular level TRS does not appear to be appropriate and implies that the simple theories which use relaxation time shifts to model physical ageing are unlikely to be correct.

In order to correlate the changes in free volume measured by PALS with variation in both microscopic and macroscopic mobility, DRS and DMA measurements were made with time. An empirical parameter, with no direct physical significance, was determined by a simple summation of the dielectric loss over the whole frequency range measured which covers the relaxation region between T_g and T_β. This parameter, denoted the sum of dielectric loss (SDL), allowed quantification of observed changes in ϵ'' spectra and occurs in the frequency range between the α- and β-transitions. No value corresponding to infinite ageing time was available for this parameter, since equilibrium spectra at the respective ageing temperatures were not available and models which incorporated a fitting parameter for this factor gave poor fits. This is especially true at the low end of the temperature range, where only a small part of the relaxation spectra, far from equilibrium, is observed. Such models include single and double as well as stretched-exponential fits and the Narayanaswamy model could not be used.

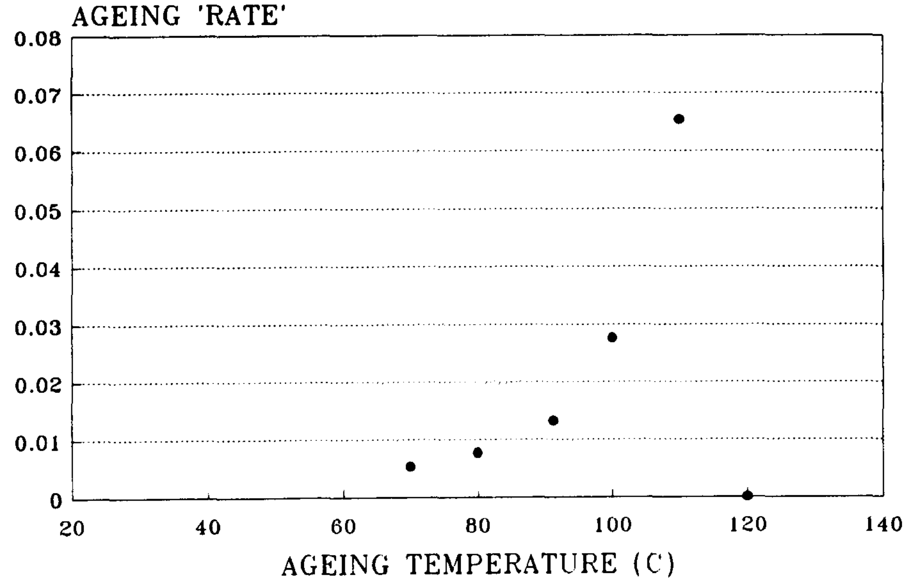

Figure 12 Ageing 'rate' *versus* temperature for PMMA over the temperature range 70–120°C. The 'rate' was calculated as the slopes of log fits to tanδ data

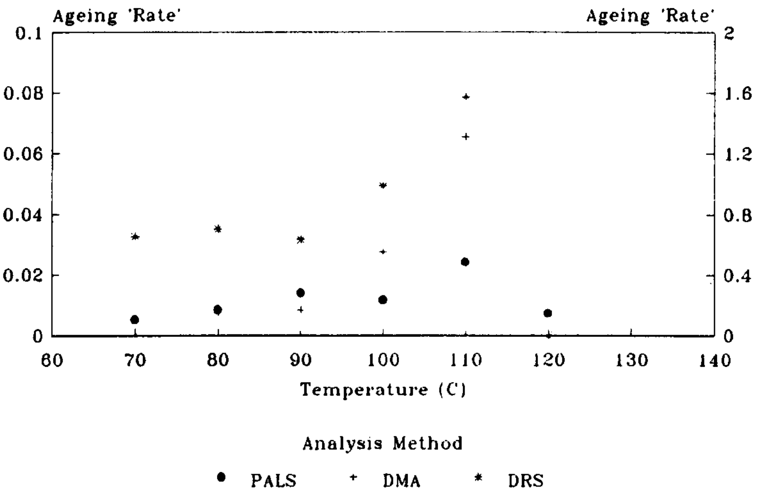

Figure 13 Ageing 'rates' determined by DRS, PALS and DMA experiments as a function of temperature

Despite the failure to analyse in more detail the structural relaxation behaviour determined using the three-measurement techniques, correlation between results is still possible. The most useful comparison is between the ageing 'rates' calculated for each temperature (*Figures 5, 8, and 12*). In each case 'rates' are low and relatively constant at temperatures below T_g and increase to a maximum at around T_g, before decreasing to zero above T_g where equilibrium prevails. More detailed analysis of the correlation of ageing data (*Figure 14*) show an excellent approximately linear correlation between all data.

Despite the diversity of probes used to measure physical ageing in this study, in each case the same underlying fundamental property change is being assessed and a direct relationship between microscopic properties (both volume and molecular mobility) and macroscopic mechanical properties has been demonstrated. Curro *et al.*[37,38] have studied the change in density fluctuation with temperature and annealing time for PMMA[39] and compared it with specific volume data. On isothermal ageing, the behaviour is not identical. While the volume data varies approximately linearly with ageing time over a wide range below T_g, the density fluctuation is seen to change with ageing time only in the transition region. On isothermal annealing, the change with time in the specific volume is observable both in the transition region and glass transition. The kinetics of volume change is fairly distinct from that below T_g, the latter being described by a linear function of log *t*. Such a relationship exists in enthalpy[40], creep[1] and dynamic mechanical measurements[35] for short time measurement, but may not be followed in the longer time. The techniques used in this study are more sensitive to the short time changes and we must not imply that changes in the form of the time dependent behaviour do not occur at longer times. In contrast, the density fluctuation shows no observable change outside the transition region, even on prolonged annealing. It has been suggested that this difference in the behaviour may be explained by considering that the density fluctuation depends on the longer time end of the overall relaxation spectrum and hence will give different kinetic behaviour from other properties[41].

Positron annihilation data on PMMA[42,43] has been interpreted in terms of free volume. Hasan *et al.*[43] investigated the yield and post-yield behaviour of PMMA and found that an inelastic stress affected the V_f through an increased yields of o-Ps$_T$. For some time it has been believed that the V_f in a polymer is composed of a dynamic distribution of hole sizes[15,16]. For each hole size o-Ps will annihilate in a particular characteristic time, the mathematical form of which is a decaying exponential, the decay constant describing this exponential is known as the lifetime (o-Ps$_T$). For a distribution of hole sizes there will exist many decaying exponentials, each with a different characteristic lifetime. The composite of these many exponentials can itself be approximated to an exponential, and it is the decay constant that is used to represent the mean lifetime, and therefore mean hole size.

CONCLUSIONS

Comparison of data from the three techniques allows the following conclusions to be drawn:

- that there exist a correlation between the 'free volume' as measured by PAS and the changes which occur in the DRS and DMTA;
- that TRS is probably an oversimplification and that the process of physical ageing is associated with a redistribution and not just a shift of relaxation processes;
- the relaxation distribution does change as the T_g is approached and simplification of the process occurs in the case of PMMA;
- the 'free volume' distribution probably changes during ageing, although the precision of the experimental data precluded its determination in this study. It is clear that further work is required before a complete understanding of the processes occurring will be obtained.

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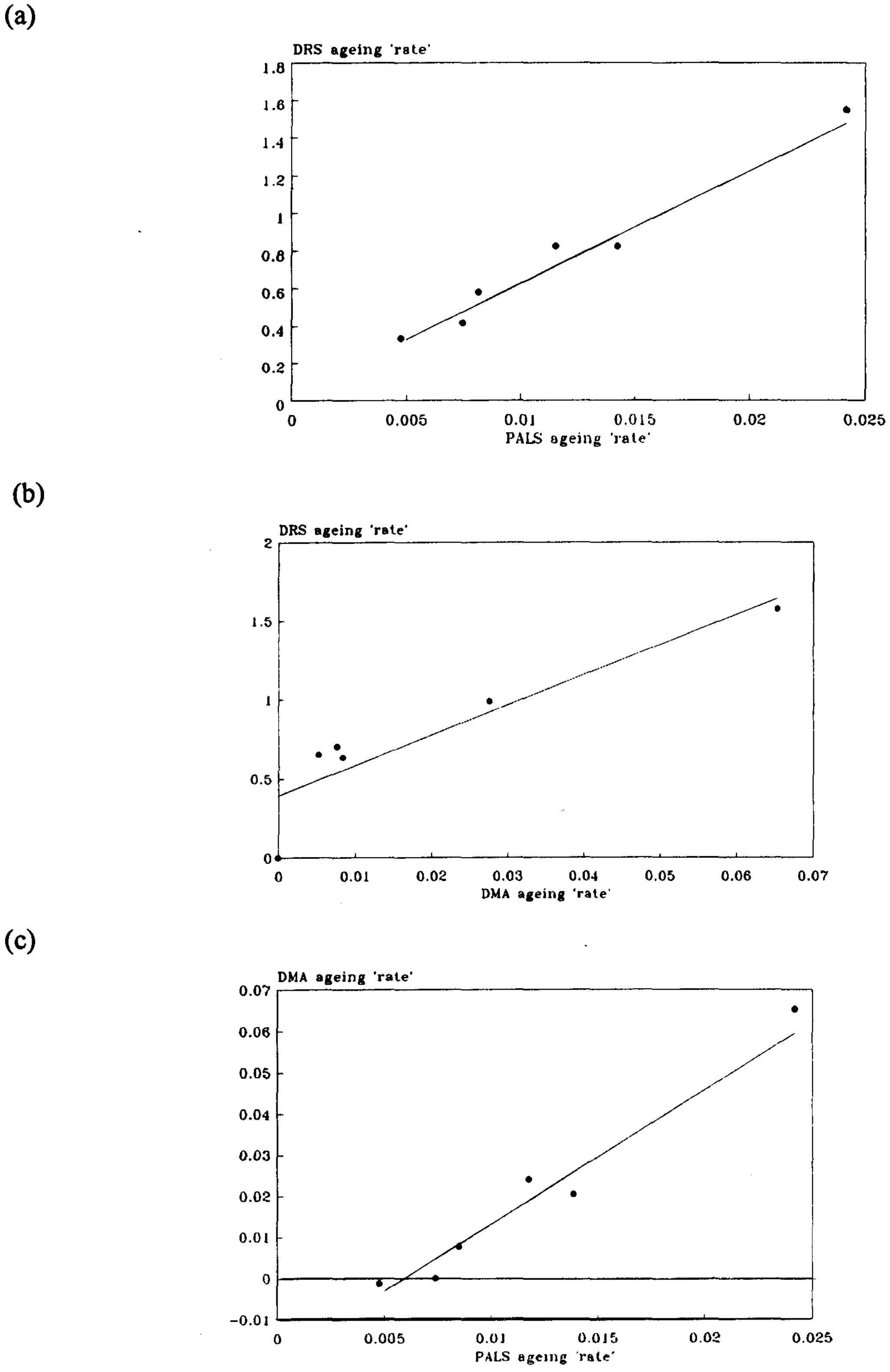

Figure 14 Correlation between ageing 'rates' from DRS, PALS and DMA experiments

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