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Physical Ageing in Polymethylmethacrylate – A Dielectric Investigation

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Polymethylmethacrylate aged for various times at temperatures below the glass transition temperature, T_g , were studied using dielectric spectroscopy. The study uses dipole relaxation as a probe for the physical ageing process. Isothermal measurements indicate that the dominant changes occurring in the dielectric loss spectrum at temperatures between the T_g and the side chain (β) relaxation process are associated with changes in the dipole relaxation distribution and the ionic charge mobility. Differences between the spectra for aged and unaged samples are used to assess the nature of the changes occurring at a molecular level. The rate of change of dielectric loss was estimated as a function of the ageing temperature and the observed behaviour was found to be similar in form to that observed from creep and structural relaxation.

Keywords: Polymethylmethacrylate; Physical ageing; Dielectric spectroscopy

INTRODUCTION

Physical ageing is a spontaneous, thermally reversible process that occurs in glassy materials [1]. The yield stress, density and elastic modulus of the polymer increase; impact strength, fracture energy, ultimate elongation decrease; creep and stress relaxation rates decrease with ageing time at a particular temperature [2]. Any model of physical ageing must be able to predict that a slow cooling rate results in a

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lowering of T_g and the precise value depends upon how the sample is heated or cooled [1, 2]. The time dependence of the physical ageing process often does not exhibit a simple exponential behaviour and is usually represented by a continuous distribution of exponential terms or a single stretched exponential form [3, 4]. Free volume appears to be a rate controlling factor and many theories attempt to predict the behaviour in terms of a simple shift of the relaxation spectrum along the time/frequency axis and are referred to as having thermorheological simplicity (TRS). Some of the models proposed do, however, allow for changes in the frequency distribution but it is not clear how these are connected to the molecular processes occurring in the solid. Physical ageing ceases below the temperature – time – frequency locus for the side chain relaxation, which is usually the highest secondary transition temperature and is insensitive to pressure [1, 2] with an activation energy between 30 and 50 kJ/mol. In contrast, the T_g process has an apparent activation energy between 200 and 300 kJ/mole³ and is sensitive to application of pressure. In this study we attempt to examine the way in which the molecular mobility changes as a function of physical ageing time in a polar polymer, polymethylmethacrylate – PMMA. The dielectric properties of PMMA are well understood, and hence it is possible to interpret changes in the spectrum in terms of specific molecular processes associated with dipole reorientation and ionic conduction [5].

EXPERIMENTAL

Materials

Commercial polymethylmethacrylate, ICI (Diakon), having a weight average molar mass (M_w) of 136,000, a T_g of 105°C was used in this study. Compression moulded 15 × 15 × 0.95 mm samples of PMMA were annealed at 120°C and quenched to room temperature in an ice bath. Isothermal ageing was performed on samples previously equilibrated at a defined annealing temperature, followed by rapid quenching to room temperature and reheating to the ageing temperature T_e .

Dielectric Relaxation Spectroscopy (DRS)

Isothermal and isochronous ageing studies were carried out over a frequency range from 10^{-2} to 6.5×10^5 Hz at 10°C temperature intervals between 30 – 120°C , using a computer controlled frequency response analyser Schlumberger 1250 [6]. The temperature was controlled using an Oxford Instruments cryostat (DN1704). The thicknesses of the samples were determined using a digital micrometer and the mean value taken as the average of twenty measurements, was used to calculate the equivalent air capacitance of the sample.

RESULTS AND DISCUSSION

The experiments described in this paper can be divided into two sections; isochronous and isothermal experiments.

Isochronous Ageing

The isochronous experiments were performed in order to determine the temperature and frequency range over which isothermal ageing studies should be carried out. A sample was annealed at 120°C , quenched and dielectric data were obtained at 10°C intervals between 40 – 120°C , Figure 1. Samples were then cooled to room temperature by immersing in an ice bath before being aged in an air circulating oven for 115 hrs at 90°C and re-measured and found to be essentially identical with the original trace. The dielectric relaxation behaviour of PMMA has been studied extensively and the main dipole (α) relaxation processes assigned to reorientation co-operative motion of the backbone – T_g [7] and the lower temperature process to re-orientation of the side chain ester group. The β process is located at 100 Hz at 40°C and moves to 10^5 Hz at 120°C . The backbone relaxation will become active only above T_g and appears as an increase in the dielectric loss below 10^{-1} Hz as T_g is approached. At high temperatures and high frequencies, the T_g and side chain motions merge and become indistinguishable. In the temperature range of physical ageing used in this study they are well resolved. Comparison

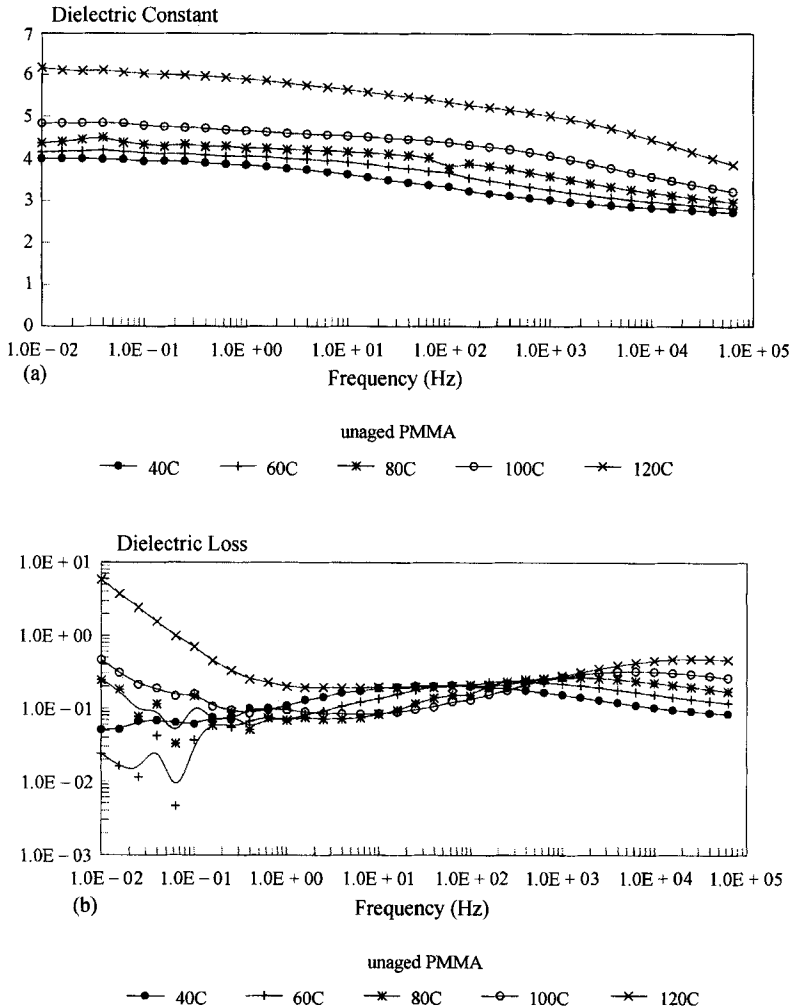


FIGURE 1 (a) Frequency dependence of ϵ' and (b) ϵ'' for unaged PMMA over the temperature range 40–120°C.

of plots from aged and unaged samples at 90°C, Figure 2, indicates that the T_g peak appears to have shifted to lower frequency and the T_β peak has moved to higher frequencies and increased slightly in magnitude with ageing. Extension of the dielectric measurements to lower frequency will increase the collection time substantially and did not allow a more detailed study of the T_g process. The frequency

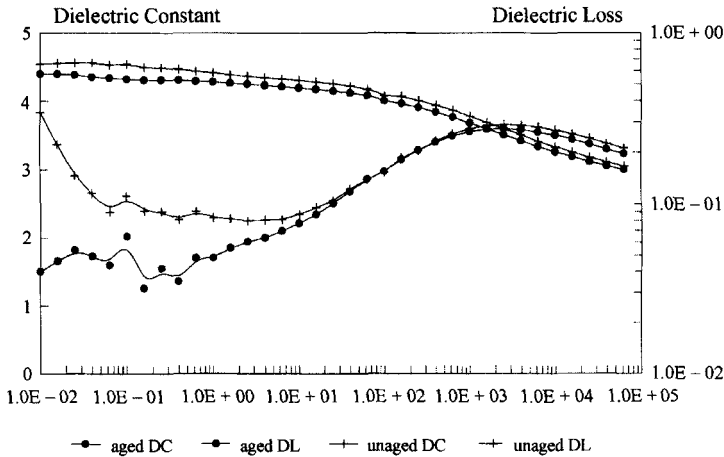


FIGURE 2 Frequency dependence of ϵ' and ϵ'' for aged/unaged PMMA at 90°C.

interval is therefore a compromise between increasing the precision and increasing the uncertainty of the measured rate of change. In the traces obtained above 110°C, Figure 1, the loss peak does not match exactly the profile of permittivity, indicating that there is a contribution arising from ionic conduction in the sample. No attempt has been made to generate dielectric loss curves by subtraction of a conductivity contribution due to the short range over which the $\sigma/2\pi$ frequency can be fitted accurately. Ageing of the sample will lead to an increasing of the value of the T_g and consequentially a decrease in the ionic mobility and hence dielectric loss at low frequency.

Isothermal Ageing

Measurements were performed over the temperature range 70–120°C as a function of ageing time. To avoid any problems with variation within materials, the same sample was used for each ageing experiment; the previous thermal history being erased prior to each experiment by annealing for 30 minutes at 130°C and quenching in water at room temperature. Over the period of contact with water, typically about 5 minutes, the absorption may be assumed to be negligible and not to have any significant effect on the results. There was no apparent difference between samples quenched in carbon dioxide

and water. The isothermal ageing temperature was reached in less than 1 minute, however to ensure true thermal equilibrium a further 9 minutes were allowed to elapse before measurements were started. The changes in dielectric loss with ageing time ϵ'' between 70 and 120°C were investigated, Figures 3 and 4. One example of the variation of ϵ' for ageing at 70°C is presented. Conventionally, dielectric

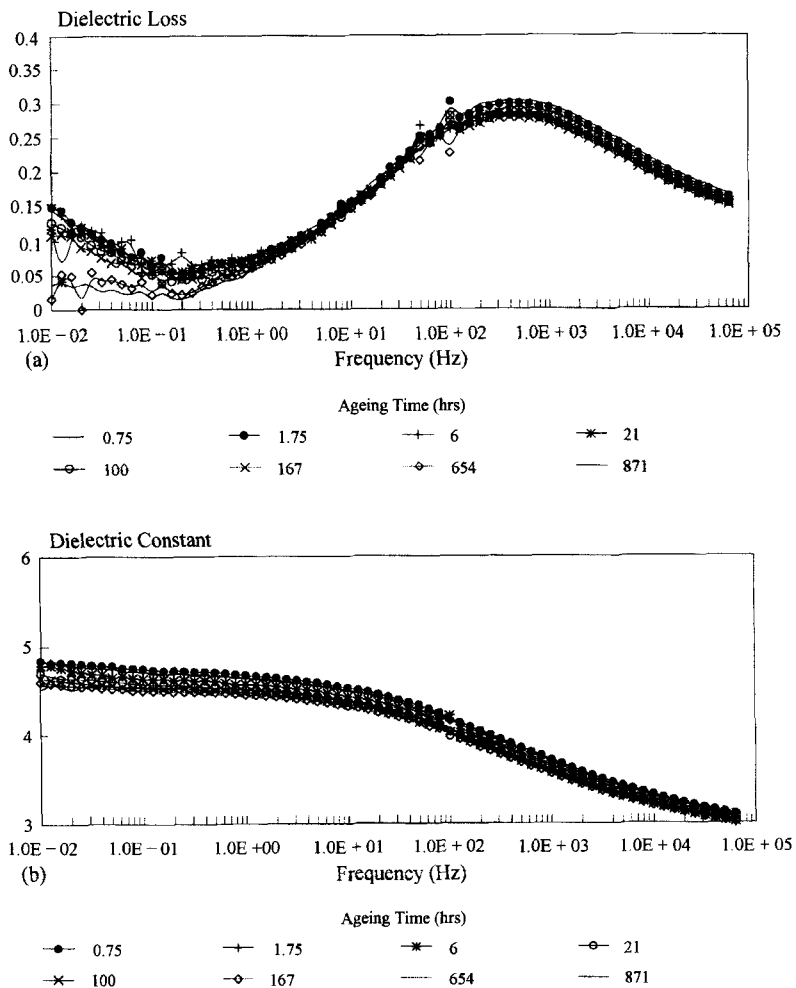


FIGURE 3 ϵ'' and ϵ' as a function of frequency for different ageing times at 70°C.

spectra are fitted to a semi-empirical relation which describes the 'distribution' of relaxation processes which exists. Since it is not possible to carry out observations within the same time – temperature – frequency range with the same degree of precision for both dielectric relaxation processes, an alternative approach will be adopted for

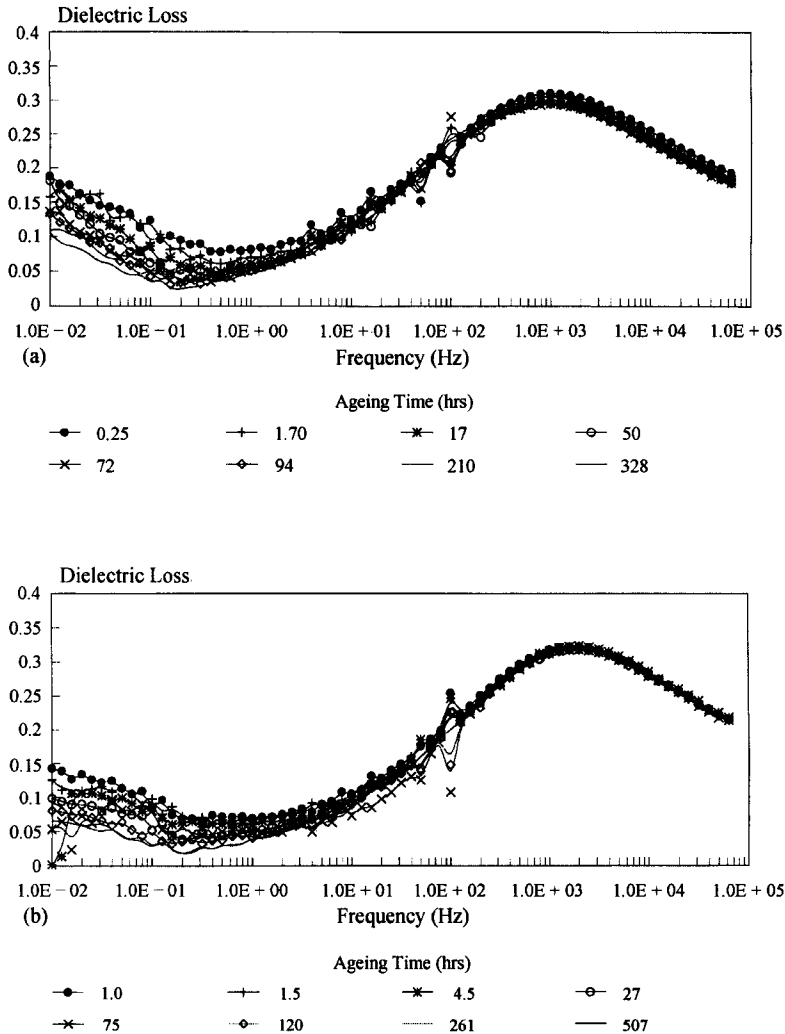


FIGURE 4 ϵ'' as a function of frequency for different ageing times (a) at 80°C, (b) at 90°C, (c) at 100°C, (d) at 110°C, (e) at 120°C.

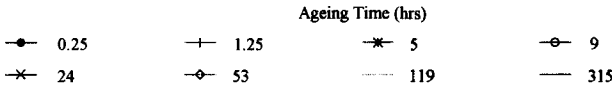
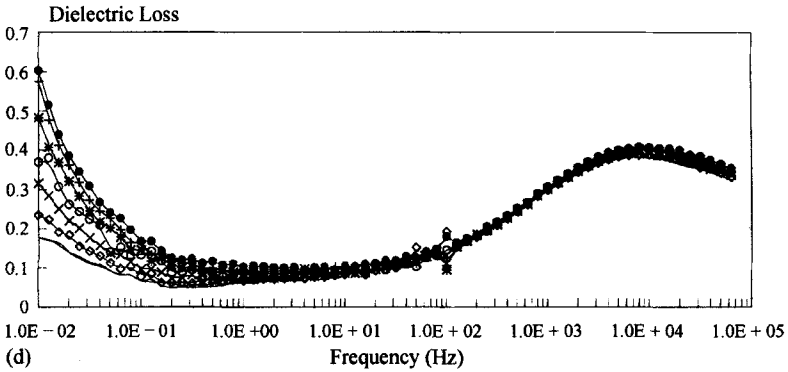
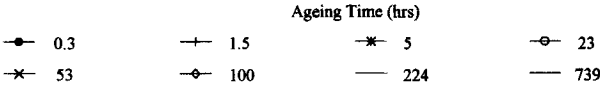
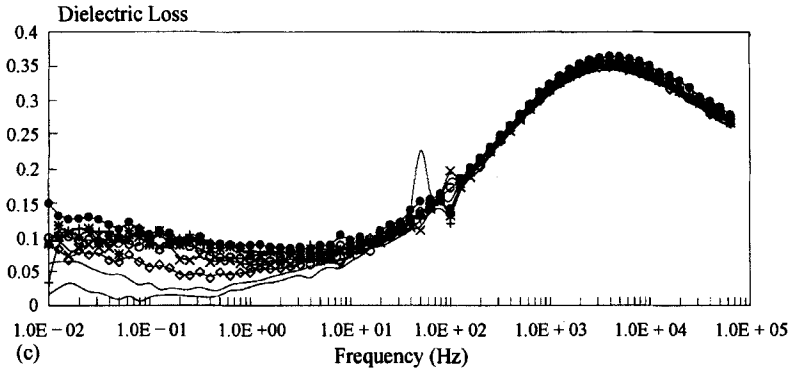


FIGURE 4 (Continued).

analysis of the data. It is also conventional to attempt to subtract the ionic conductivity from the dielectric loss data, however since this relatively arbitrary process will increase the uncertainty in the loss data without aiding the analysis, it is proposed to analyse the changes in the total dielectric loss data.

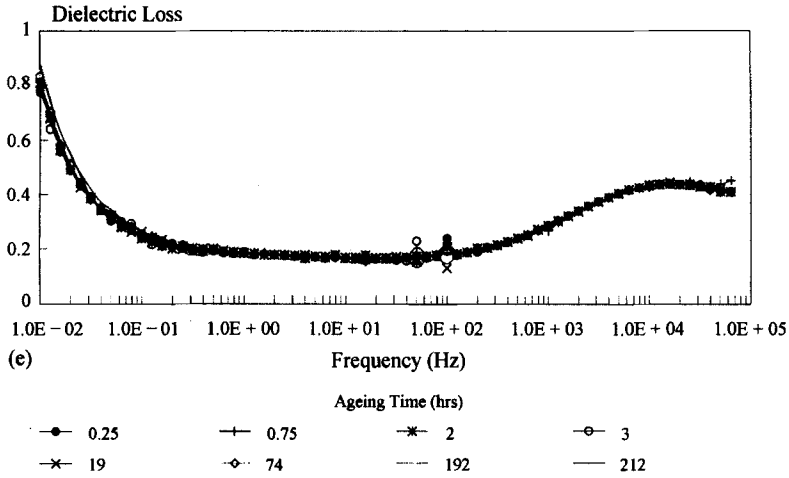


FIGURE 4 (Continued).

Analysis of Dielectric Loss Data

The 'difference spectra' defined by subtraction of the spectra for a freshly quenched and the aged sample were calculated for each ageing temperature, Figure 5. The difference spectra were then used to define the change in the dielectric relaxation distribution as a function of ageing time. As ageing proceeds so the β process becomes narrower and the co-operative transition is sharpened, consistent with an increase in the T_g , there is also the possibility of a suppression of the conductivity contribution as the density of the matrix increases. Several theories have been proposed to describe physical ageing and attempts have been made to fit the variation in terms of various functions:

$$\text{Logarithmic regression } I_3 = a \times \log(t) + b \quad (1)$$

$$\text{Single exponential } I_3 = a \times \exp(-t/\tau) + b \quad (2)$$

$$\text{Double additive exponential } I_3 = a \times \exp(-t/\tau_1) + b \times \exp(-t/\tau_2) + c \quad (3)$$

$$\text{Narayanaswamy [8] } I_3 = \exp(-t/\tau)^\beta \quad (4)$$

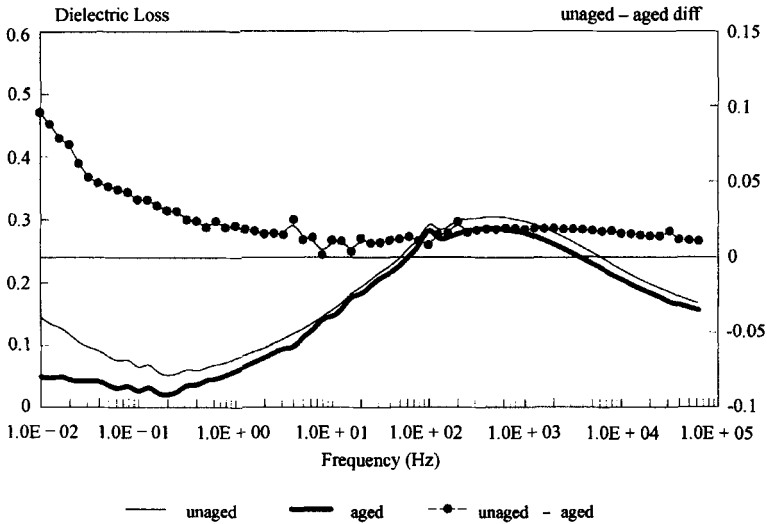


FIGURE 5 An example of ϵ'' data for material 'unaged', 'aged' and 'difference spectrum' (unaged-aged) at 70°C as a function of frequency.

where I_3 is the structural relaxation function which is changing at a rate defined by the relaxation time, where

$$I_3(t) = \frac{P_T(t) - P_T(\text{eq})}{P_{T_g} - P_T(\text{eq})} \quad (5)$$

where $P_T(t)$ is a physical property at some time of ageing t and temperature T , $P_T(\text{eq})$ is the equilibrium value of that property as t tends to infinity and P_{T_g} its value at T_g . In the current calculations the property used is the dielectric loss which is directly related to the dipole activity, provided there is negligible contribution from conductivity. This assumption is correct at temperatures below T_g but is probably questionable close to and above T_g . Since the dielectric permittivity is calculated from a knowledge of an equivalent air capacitance and ageing can alter the thickness of the sample, the dipole activity is estimated in terms of the dielectric loss which does not depend on the thickness. The frequency window for the experiments was determined by a combination of sampling time – which determines the lower frequency limit, and the response time of the instrument

which determines the upper limit. Ideally the frequency window should include completely both the α and β relaxation processes, but this is not practically possible. The limitations imposed are not considered to be serious, as the region examined includes the features that show marked changes on ageing, Figure 5. The sum of the dielectric loss (SDL), defined as the area below the plot of ϵ'' against $\log f$ is related to the relaxation strength $\Delta\epsilon''$ by

$$\int_{f_1}^{f_2} \epsilon'' d \log f = \Delta\epsilon\pi/2 \quad (6)$$

where f_1 and f_2 are respectively the upper and lower limits of the frequency interval used for the integration. Ideally the value of the lower frequency should be below any relaxation process being considered. In practice for the T_g process examined below its T_g this would require measurements down to a frequency of 10^{-5} Hz or lower. A frequency of 10^{-5} is accessible at Strathclyde, however it requires measurements to be conducted over a period of two days, which is long compared with the process being studied. The compromise which has been adopted is to assess the changes down to an arbitrary frequency of 10^{-3} Hz. The decrease in the SDL due to ageing is therefore equal to the decrease in relaxation strength $\delta\epsilon''$

$$\delta\epsilon'' = \Delta\epsilon_{\text{aged}} - \Delta\epsilon_{\text{unaged}} \quad (7)$$

Since the SDL is a direct measure of the effective dipole activity over the frequency range at the chosen test temperature, plots of the type shown in Figure 6 are useful in relating dipole activity to ageing time. All mathematical fitting was carried out using the computer package Fig-P (V6.0). The loss processes observed may be attributed to respectively at low frequency the T_g process and at higher frequency the β process. As indicated previously, no conductivity contribution is observed within the frequency – temperature range of these measurements at temperatures below T_g . The SDL for ageing temperatures 70–120°C does not exhibit a simple exponential dependence upon ageing time, and double-exponential, stretched-exponential or logarithmic models were also used to curve-fit these sets of data, Table I. However, the concept of a ‘rate’ of ageing determined as the gradient of \log fits to ageing data is commonly employed [1, 9–14].

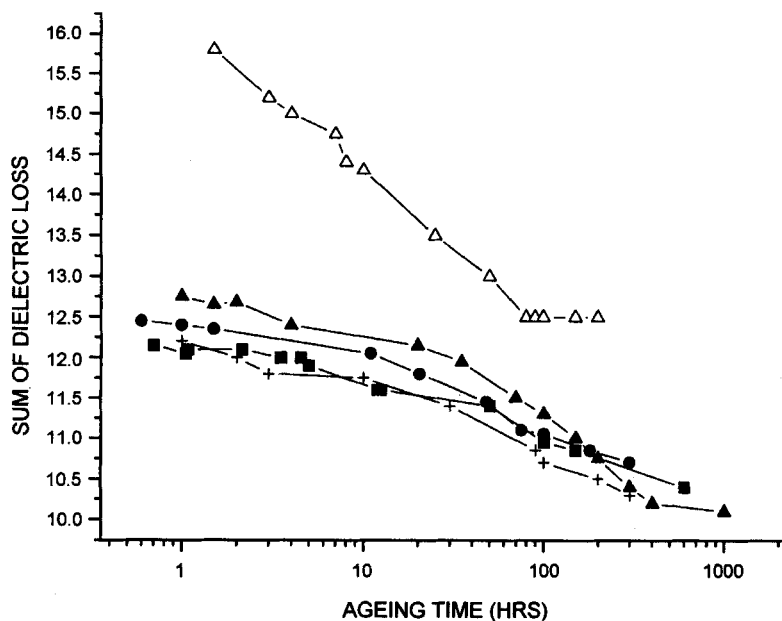


FIGURE 6 Sum of dielectric loss *versus* isothermal ageing time for PMMA at: 70°C (a), 80°C (b), 90°C (c), 100°C (d), 110°C (e), 120°C (f).

TABLE I Summary of fitting parameters for various fits to isothermal SDL data for PMMA over the temperature range 70–120°C

Ageing temp (°C)	Equation (2) 1-exp. Fit τ (hrs)	Equation (3) 2-exp. fit		Equation (1) log fit (gradient)
		τ_1 (hrs)	τ_2 (hrs)	
70	47	8.5	157	-0.633
80	57	0.2	56	-0.652
90	106	3.0	98	-0.702
100	145	1.5	181	-0.988
110	23	1.3	29	-1.572
120	—	—	—	0

No values are given for stretched-exponential fits (Eq. (4)), the solutions for which were very unstable. Also no values are given for exponential fits for ageing at 120°C since at this temperature SDL was independent of ageing above the T_g of the material. In the case of double-exponential models an improvement in the quality of the fit to this data is observed at short times, however there is a lack of a

defined pattern to the temperature variation for this fit which emerges. The pattern of behaviour obtained using logarithmic regression (Eq. (1)) of the rate increasing as T_g is approached and then apparently dropping to zero is remarkable similar to Struik's [1] ageing 'rate' *versus* temperature plot derived from small-strain creep experiments.

CONCLUSIONS

The dielectric behaviour observed when PMMA is aged is consistent with a reduction in the amplitude of dipole processes having a mixed characteristic and lying between the main T_g and β processes. The time dependence of the change is not easily modelled in terms of a simple relationship but shows close similarity with behaviour observed from analysis of physical ageing observed with creep or volume relaxation. The latter are not subject to the uncertainties of the complications arising from conductivity influencing the data. The fact that the data does not appear consistent with a simple shift of the relaxation distribution with time questions the validity of thermorheological simplicity. At temperatures close to the T_g there is possibly a contribution due to ionic mobility leading to a conductivity contribution to the dielectric loss and this may influence the analysis of the data in this region. Physical ageing is a complex process and clearly needs further fundamental study. However, the dielectric study indicates that the changes in dipole activity are consistent with a loss of processes that have a character intermediate between that of the α and β processes. The equilibrium state exhibits dipole activity in which the two processes are sharpened relative to the unaged material and the loss of activity is consistent with the T_g increasing on ageing as observed by other techniques. The main relaxations do not shift significantly on the temperature – frequency axes, there being a loss of dipole activity between the two processes.

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