

Physical ageing of PMMA and polycarbonate in the region of secondary relaxation

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Physical ageing of two amorphous polymers (PMMA and polycarbonate) was studied by dielectric measurements in the range 80 Hz–10⁵ Hz and by thermally stimulated depolarization currents. It is shown that secondary relaxations do not age by simple shifting along the log time scale but rather through a reduction in relaxation magnitude.

INTRODUCTION

It is known that the properties of polymers that have been quenched through the glass transition change with time. This physical ageing is characterized, for instance, by a decrease in specific volume^{1,2}, of enthalpy³ as well as an increase in modulus⁴.

Various explanations for this phenomenon have been given. Struik has shown that creep curves of quenched amorphous polymers are nearly horizontally shifted towards longer times with increase in ageing time. From this, he concludes that the retardation spectrum is shifted without any modification during ageing. However, no quantitative relation between experimental findings and classical free volume theories could be found.

Various authors have observed that the superposition by a horizontal shift of creep or relaxation curves obtained at different ageing times is no longer possible when the complete time scale of measurement is carefully considered^{5,6}.

From thermally stimulated creep measurements⁶, it has been found that physical ageing has no influence on mechanisms with retardation times greater than the effective ageing time. Thus it seems necessary to consider a possible modification of the spectrum and, if so, the interpretation of physical ageing becomes extremely complicated.

In a subsequent paper⁷, we will show, in the case of two amorphous polymers, that it is possible to obtain master curves of the modulus $G(t)$, $G'(\omega)$ and $G''(\omega)$ with a set of three parameters, this set being the same for superposition of $G(t)$, $G'(\omega)$ as well as $G''(\omega)$ curves.

In this paper, a similar study of the effect of ageing on the permittivity is made on the same polymers.

EXPERIMENTAL

Samples

We have studied two amorphous polymers: polymethylmethacrylate (PMMA) and polycarbonate. PMMA was supplied by Altulor (commercial name: Altuglas). The samples were cut from large plates obtained by bulk polymerization. The extruded plates of polycarbonate were supplied by Röhm and Haas (commercial name: Tuffak).

All measurements were made on samples quenched, rather cooled, as quick as possible. We have employed the same procedure as Struik⁴. For instance, the time of measurement was always ten times less than the ageing time.

Dynamic permittivity measurements

The real and imaginary components of the dielectric constant were measured in the 80 Hz–100 k Hz frequency range by means of a General Radio 1616 Precision Capacitance Bridge, 1316 Oscillator and 1238 Detector. The sample was clamped between two planar circular electrodes (diameter 3.5 cm) of a specimen test capacitor Rohde and Schwarz, type KMS BN 57411. Departure from sample plane-parallelism was less than 0.01 mm and thus coating could be avoided.

Samples were cut from large plates of thicknesses in the range 2–3 mm. The sample's shapes were squares of 4 cm side length, as recommended by the constructor of the cell. The sample holder was placed in an oven in which the temperature was controlled to within 0.05 °C.

We measured the effect of external temperature variations on the capacitance readings and checked that it was negligible with respect to the capacitance changes due to ageing. Shielded cables were used to connect the cell to the three bridge terminals.

The real part ϵ' of the dielectric constant was determined from capacitance measurements

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$$\varepsilon' = \frac{C_m}{C_0} \quad (1)$$

C_m is the capacitance of the cell with sample, C_0 the capacitance of the cell with air between the electrodes. In both cases, the spacing (a) and diameter (d) of the electrode were the same.

An unavoidable fringe field disturbance due to the absence of a guard ring introduces a capacitance C_f . Furthermore, a residual capacitance C_r must also be accounted for in the measured value C'_m of the assembly. Thus, C_m and C'_m are related through:

$$C_m = C'_m - C_f - C_r \quad (2)$$

The same corrections apply for the empty capacitor:

$$C_0 = C'_0 - C_{f0} - C_r \quad (3)$$

C_f and C_{f0} are given by the constructor of the cell as a function of dielectric constant and spacing. To evaluate C_0 , we determined $(C'_0)_a$ for various values of spacing a . The values of $(C'_0)_a$ vs. $1/a$ fall on a straight line. For $1/a=0$, $(C'_0)_{a=0} = C_{f0} + C_r$; application of equation 3 and the corresponding value of C_{f0} given by the constructor gives C_0 for the desired electrode spacing. Finally,

$$\varepsilon' = \frac{C'_m - C'_0}{C_0} + A \quad (4)$$

where A varies from 0.91 to 0.95 in our experiments.

The imaginary part ε'' of the dielectric constant is obtained by measuring the equivalent parallel conductance $1/R$ of the cell

$$\varepsilon'' = \frac{1}{\omega C_0 R} \quad (5)$$

ω is the frequency in radians/s.

Thermally stimulated depolarization currents

The samples, diameter 2.6 cm, were metal coated by painting a colloidal silver suspension which dries quickly. They were then placed between two stainless steel electrodes of the same diameter in a nitrogen filled chamber. A d.c. voltage $V=2000$ V was applied at the polarizing temperature T_p during $t_p=15$ min. In all cases, T_p was equal to the temperature at which the samples were aged. The polymer was then quickly cooled to liquid nitrogen temperature. After removal of the field at this low temperature, the samples were warmed at a reasonably uniform heating rate and the current intensity was recorded. Dipole de-orientation produces a peak when current intensity I is recorded against temperature.

A Cary 31 CV vibrating-reed electrometer was used to measure the current. The thermocouple was set in one of the electrodes near the sample surface and connected to a two-pen recorder. Temperature and current were recorded simultaneously. It was not always practical to heat at an exactly constant heating rate throughout the entire temperature range. Our measurements were made at decreasing heating rates ($7^{\circ}\text{--}4^{\circ}\text{C min}^{-1}$) as temperature raised up to -100°C . Beyond this temperature, the heating rate was constant and equal to $4^{\circ}\text{C min}^{-1}$.

Mechanical measurements

A mechanical spectrometer (Rheometrics type RMS 7200) was used for mechanical measurements.

RESULTS AND DISCUSSIONS

Dielectric dynamic measurements

For the two polymers, the experiments were carried out at temperatures and frequencies which concern the region of secondary relaxations. In Figure 1 the effect of ageing on the dielectric properties of PMMA at 72°C are shown. For the sake of clarity, the experimental results are given at one frequency (1000 Hz) by plotting the change in capacity $(C'_m)^{t_v} - C'_m{}^{t_{v0}}$ and in conductance $\left(\frac{1}{R}\right)^{t_v} - \left(\frac{1}{R}\right)^{t_{v0}}$ vs. $\log t_v$. $C'_m{}^{t_v}$, $C'_m{}^{t_{v0}}$, $\left(\frac{1}{R}\right)^{t_v}$ and $\left(\frac{1}{R}\right)^{t_{v0}}$ are the measured values of C'_m and $\left(\frac{1}{R}\right)$ at ageing times t_v and $t_{v0}=7400$ min. Owing to the extreme precision of the measurements, it was possible, through the changing aspects of the curves, to see the effects of ageing on the dielectric properties. By mechanical measurements at -10°C and lower frequencies (region of secondary relaxations) we could only obtain an overall, but not a quantitative, view of the physical ageing.

In both our mechanical⁷ and dielectric data, it appears that a simple horizontal shift along the log frequency axis is not sufficient to obtain a master curve. To analyse our results, we apply the formalism used by McCrum *et al.*⁸ to account for their temperature induced changes of the complex modulus or compliance. The final expressions are given below for the dielectric case:

$$\varepsilon'(\omega)^{t_{v0}} = B_r + C_v \varepsilon'^{t_v}(\omega/a_r) \quad (6)$$

$$\varepsilon''(\omega)^{t_{v0}} = C_v \varepsilon''^{t_v}(\omega/a_r) \quad (7)$$

$$B_r = \frac{\varepsilon_u^{t_{v0}} \varepsilon_R^{t_{v0}} (c_r - d_v)}{c_v \varepsilon_u^{t_{v0}} - d_v \varepsilon_R^{t_{v0}}} \quad (8)$$

$$C_v = \frac{\varepsilon_u^{t_{v0}} - \varepsilon_R^{t_{v0}}}{c_v \varepsilon_u^{t_{v0}} - d_v \varepsilon_R^{t_{v0}}} \quad (9)$$

$$\varepsilon_u^{t_v} = c_v \varepsilon_u^{t_{v0}} \quad (10)$$

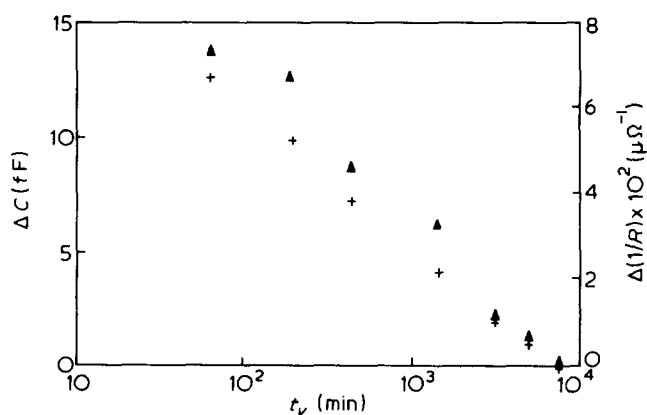


Figure 1 Change in capacitance ΔC (▲) and in conductance $\Delta(1/R)$ (x) with ageing time t_v for PMMA at 72°C , $f = 1000$ Hz. Log scale for t_v

Table 1 Ageing parameters for PMMA at 72°C

t_v (min)	65	197	445	1440	3145	4955	7400
B_v	4.36×10^{-2}	4.27×10^{-2}	3.09×10^{-2}	1.74×10^{-2}	8.30×10^{-3}	4.2×10^{-3}	0
C_v	0.984	0.984	0.988	0.993	0.997	0.9985	1
B_v/C_v	4.43×10^{-2}	4.34×10^{-2}	3.13×10^{-2}	1.75×10^{-2}	8.32×10^{-3}	4.21×10^{-3}	0
$B_v/1-C_v$	2.725	2.669	2.575	2.486	2.767	2.800	

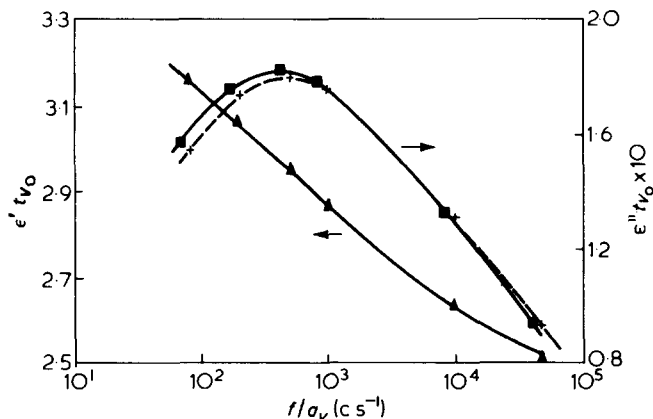


Figure 2 Master curves of the real and imaginary parts of the dielectric constant of PMMA at 72°C vs. frequency f . $t_{v0} = 7400$ min. Log scale for f [(\blacktriangle) ϵ' , ($+$) ϵ''] $\nu = 0$; [(\blacksquare) ϵ''] $\nu = 0.1$, $t_v = 1440$ min

$$\epsilon_R^{tv} = d_v \epsilon_R^{t_{v0}} \quad (11)$$

ϵ_u^{tv} and ϵ_R^{tv} are respectively the limiting high and low frequency dielectric constants of the secondary relaxation process for an ageing time t_v . t_{v0} is the reference ageing time (the greatest ageing time), $\log a_v$ is the horizontal shift factor between the curves giving $\epsilon'(\omega)$ vs. $\log \omega$ (or vs. $\log f$) for ageing times t_v and t_{v0} . This analysis involves a shift of the relaxation (or retardation) spectrum by $\log a_v$ and a change of magnitude of this spectrum by a factor b_v when the ageing time increases from t_v to t_{v0} ; in other words, the relaxation spectrum is assumed to change in magnitude but not in shape during ageing.

$$b_v = \frac{\epsilon_u^{tv} - \epsilon_R^{tv}}{\epsilon_u^{t_{v0}} - \epsilon_R^{t_{v0}}} = \frac{1}{C_v} \quad (12)$$

To determine the set of values (a_v , B_v and C_v) for each value of t_v we proceed as follows: First find the best polynomial function

$$\epsilon^{tv0}(\omega) = A_0 + A_1 \log \omega + A_2 \log^2 \omega + A_3 \log^3 \omega$$

corresponding to the experimental points, by a method which gives a good correlation factor. Then calculate the set of values $\epsilon^{tv}(\omega/a_v)$ for different values of

$$\nu = - \frac{d \log a_v}{d \log t_v}$$

Through a linear regression method on $\epsilon^{tv}(\omega/a_v)$ and $\epsilon^{tv0}(\omega)$, determine C_v and B_v for each ageing time and each value of a_v (in practice, for each t_v and each value of ν). Among the values (a_v , B_v and C_v), choose those which lead to a satisfactory master curve $\epsilon'(\omega)$. Finally, with these parameters, check that a good master curve is also

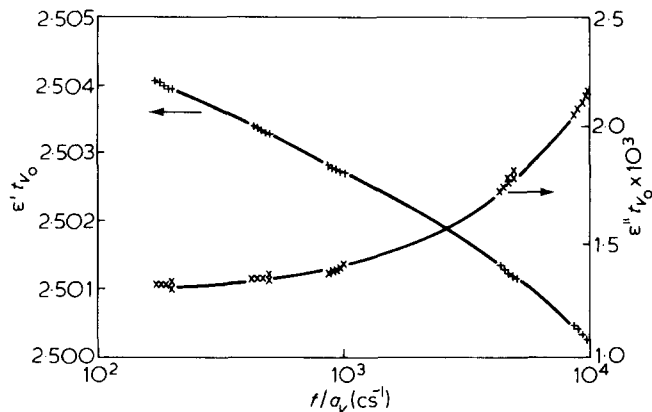


Figure 3 Master curves of the real and imaginary parts of the dielectric constant of polycarbonate at 30°C vs. frequency f . $t_{v0} = 1593$ min. Log scale for f ; $\nu = 0.04$. Increasing ageing times run from left to right ($+$) ϵ' ; (\times) ϵ''

obtained for $\epsilon''(\omega)$. This was always the case in our results, thereby showing the consistency of the method.

For PMMA at 72°C, we found that the value of a_v is unity which means that during the ageing process in the region of secondary relaxations there is no translation of the spectrum. From the determination of B_v and C_v (see Table 1), we obtained the variations of ϵ_v and ϵ_R with physical ageing. The master curves of ϵ' and ϵ'' for PMMA at 72°C are plotted in Figure 2. Because the shift factor is unity, the values of ϵ' and ϵ'' corresponding to different ageing times, for each frequency, coincide on the master curve. We have also plotted the results of ϵ'' for a shift factor $\nu = 0.1$ ($t_v = 1440$ min) to show the drastic effect of a small shift factor. Thus, we can safely conclude that our master curve obtained with the parameters given in Table 1 is unique.

The master curves for polycarbonate at 30°C are plotted on Figure 3 and the values of B_v and C_v are summarized in Table 2. To obtain these curves, we used the value $\nu = 0.04$. We have also made experiments with polycarbonate at 70°C, but it was impossible to determine the intensities of the vertical shifts because the curves $\epsilon'(\omega)$ and $\epsilon''(\omega)$ were nearly straight lines. However, there certainly was a great vertical shift because the values of ν were higher than unity. (In our results, the measured horizontal shift varied from 2.5 to 4).

From the results of Tables 1 and 2, we cannot obtain directly the values of c_v and d_v (Equations 10 and 11). However, the change of magnitude of the relaxation spectrum $H(\ln \tau)$ with ageing time is known:

$$H^{tv}(\ln \tau) = b_v H^{t_{v0}} \ln \left(\frac{\tau}{a_v} \right) \quad (13)$$

For the two polymers, $b_v = 1/C_v$ is always greater than unity. In the case of PMMA ($a_v = 1$), it means that the

Table 2 Ageing parameters for polycarbonate at 30°C

t_v (min)	64	143	388	988	1353	1593
B_v	0.483	0.347	0.199	6.07×10^{-2}	1.08×10^{-2}	0
C_v	0.808	0.862	0.922	0.976	0.996	1
B_v/C_v	0.598	0.403	0.216	6.22×10^{-2}	1.08×10^{-2}	0
$B_v/1-C_v$	2.516	2.514	2.551	2.529	2.700	

magnitude of the relaxation spectrum decreases when the physical ageing time increases. Consequently, it appears that the absolute value of the difference ($\epsilon_u - \epsilon_R$) decreases with ageing time increase.

So far, we do not know if the change of ($\epsilon_u - \epsilon_R$) with ageing time is due to: (i) changes of both limiting dielectric constants ϵ_u and ϵ_R or (ii) a change of only one of these constants. If we hypothesize that ϵ_u is invariant with time ageing, we can write:

$$\frac{B_v}{1-C_v} = \epsilon_u^{t_v} n n = CT \quad (14)$$

The same argument, applied to ϵ_R , would also lead to $B_v/1 - C_v = Ct$. The values calculated above for $B_v/1 - C_v$ vary with ageing time and thus we can conclude that both the high and the low frequency limits of the dielectric constants of secondary relaxations are affected by physical ageing.

By using expressions 8 and 9, we obtain

$$\frac{B_v}{C_v} = \frac{\epsilon_u^{t_v} \epsilon_R^{t_v}}{\epsilon_u^{t_v} - \epsilon_R^{t_v}} (c_r - d_r) \quad (15)$$

For PMMA, values of ϵ_u and ϵ_R are known from Ishida *et al.*⁹

Using their data, ($\epsilon_u \epsilon_R / (\epsilon_u - \epsilon_R) \simeq -7.5$), it is possible to determine the variation of the parameter ($c_r - d_r$) with ageing time. It can be seen that the variations of this parameter with ageing time are greater for polycarbonate.

Finally, from dynamic mechanical measurements for PMMA at -10°C , we find no shift of the secondary relaxation peak, in agreement with the dielectric results.

Thermally stimulated depolarization currents

By polarizing the sample at temperature T_p and subsequent quenching to T_q , the polarization at T_p is frozen in. The change in polarization while heating from T_q to T_p is proportional to the change in dielectric constant $\Delta\epsilon$ of all the processes which are active in the temperature range covered. It is also proportional to the area under the I vs. time curve:

$$\Delta P = \epsilon_0 \Delta\epsilon E = \int_{t_q}^{\infty} j dt$$

$j = \frac{I}{S}$, current density; S , sample surface;

ϵ_0 = permittivity of vacuum $\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$;

t_q = time at which thermo stimulated discharge (t.s.d.) is started;

E = polarizing field.

If the polarization time t_p is long enough to allow a complete setting in of the state of polarization at T_p , and if T_p and T_q are far from the temperature of peak maxima, $\Delta\epsilon$

is equal to the change in dielectric constant at frequencies above and below those at which the same processes have taken place in isothermal measurements at T_p . Thus, for one process, $\Delta\epsilon = \epsilon_R - \epsilon_u$. Since the equivalent frequency of t.s.d. is low ($10^{-3} - 10^{-4} \text{ Hz}$)¹⁰, the various peaks appear well-separated compared to those obtained through dielectric measurements made in the (usually higher) frequency domain.

The advantage of using t.s.d. for studying possible effects of physical ageing on secondary relaxation in polymers appears immediately:

(i) For overlapping processes, it is possible, through an appropriate choice of T_p , T_q and t_p to reveal only specific processes.

(ii) One can cover what would be the equivalent of many decades in the frequency domain of dielectric measurements in a short time interval. Furthermore, the time needed for the measurement hardly interferes with the ageing time as far as secondary transitions are involved since these processes will usually appear at extremely low temperatures. Once the ageing time is reached at T_p , the measurement involves a subsequent thermal cycle at much lower temperatures at which the ageing is slowed down. At higher temperatures, especially near T_g , this will no longer be true: the thermal history needed to produce the depolarization current will influence the ageing process.

(iii) The method is sensitive and the results are reproducible.

Unless otherwise stated, the samples were polarized at 20°C . On complete t.s.d. curves ($T_p > T_g$, T_g : glass transition temperature), this temperature is situated at a minimum, above the so-called β secondary relaxation and below the α relaxation located near T_g . Thus, at $T_p = 20^\circ\text{C}$, processes with relaxation times longer than t_p will not respond to the field. We have chosen $t_p = 15 \text{ min}$ in the following experiments. Under those conditions, the state of polarization of secondary relaxation is complete. Any change in the t.s.d. curves will be due to changes due to ageing.

When t.s.d. was performed on as-received samples, the curve in the region where secondary relaxations occur is complex, both for PMMA and for polycarbonate. For the latter, its shape is similar to that obtained by Vanderschueren¹¹ on amorphous polycarbonate rather than that reported by Aoki *et al.*^{12a,b} where two well separated maxima are seen. After vacuum drying for three days at 130°C for PMMA, 150°C for polycarbonate, the curves had simpler shapes: a peak located at -120°C was no longer apparent in the PMMA case, and only one, rather broad maximum is seen in polycarbonate.

Ageing was carried out on the dried samples by annealing for one hour at 140°C for PMMA, 150°C for polycarbonate, subsequent quenching to 20°C by dipping in water, drying the samples by wiping, and leaving them in a dry atmosphere.

The t.s.d. recordings were done from $T_q = -190^\circ\text{C}$ to a

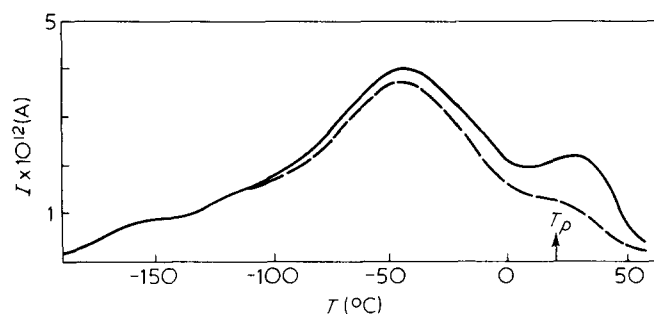


Figure 4 T.s.d. currents vs. temperature for PMMA, aged at 20°C $E = 6.6 \text{ kV cm}^{-1}$; $T_p = 20^\circ\text{C}$; — $t_v = 30 \text{ min}$; --- $t_v = 7 \text{ days}$

Table 3 I_M/SEb and $(\epsilon_R - \epsilon_U)$ values for PMMA at 20°C; $T_p = 20^\circ\text{C}$; $E = 6.6 \text{ KV cm}^{-1}$

$t_v \text{ (min)}$	30	210	1440	10080
$I_M/SEb \times 10^{14}$ (SI units)	15.2	14.6	14.1	14.2
$(\epsilon_R - \epsilon_U)T$	1.92	1.78	1.67	1.62
$(\epsilon_R - \epsilon_U)\beta$	1.79	1.70	1.61	1.57

temperature above $T_p = 20^\circ\text{C}$, that is, high enough to observe a drop in current to zero so as to achieve complete deorientation of all the dipoles which were oriented at T_p . Each t.s.d. experiment was done on a different sample; they all had the same thermal history, except for the ageing time t_v .

Figure 4 represents t.s.d. curves for two PMMA samples, $t_v = 30 \text{ min}$ and $t_v = 7 \text{ days}$. The heating rate was exactly the same in both experiments. Clearly, the area beneath the curve obtained after longer ageing is smaller. Intermediate ageing times were also investigated and the results are given in Table 3. The main peak located near -40°C (for a heating rate $b = 5^\circ\text{C min}^{-1}$) has been ascribed to the orientation of the polar side groups by local motion around the C-C bond¹⁰ (β relaxation). Since two shoulders appear on both sides of the β peak, we compare in the second row the maximum current I_M of the β peak. At a constant heating rate, I_M is proportional to the total polarization involved in a single Debye process. For a distributed process, this is still true, I_M being lowered by a factor which depends on the shape of the distribution, assuming a one-parameter distribution describes the process¹⁰. Since T_M at I_M is unchanged by physical ageing, we can assume that the shape of the distribution function of relaxation times of the β process is also unchanged; thus I_M is proportional to the change $(\epsilon_R - \epsilon_U)_\beta$.

Through dielectric relaxation, Johari and Goldstein found secondary relaxational processes in various glasses made of organic molecules or fused salt. In the 1-chloronaphtalene-pyridine glass mixture he found that the height of the corresponding peak decreases on slow cooling or annealing, but not its position¹⁴. The similarity in the relaxation behaviour of organic molecular glasses and polymers can thus be extended to physical ageing.

The low-temperature shoulder of the β peak must be ascribed to the γ relaxation observed in dynamic mechanical experiments¹³. The small peak located at about 30°C (called peak C) decreases when ageing increases. This has not been reported before. It could be an incompletely polarized α peak: to clarify this point, t.s.d. was performed on PMMA with $T_p = 44^\circ\text{C}$ or $T_p = 65^\circ\text{C}$, that is, by poling

at temperatures closer to T_g and thus closer to I_M of the α relaxation. In the resulting curves, peak C is still apparent next to the partially filled α peak which appears slightly above T_p . This is illustrated in Figure 5 for the case $T_p = 65^\circ\text{C}$, $t_p = 15 \text{ min}$, $t_v = 30 \text{ min}$ where two peaks are seen above 0°C . Thus peak C is clearly separated from an incompletely filled α peak.

The decrease of the area of peak C with ageing time must be related to the observations that:

(i) for the β relaxation, physical ageing affects only the high and low frequency limits of the dielectric constant without any modification of relaxation times, as shown above.

(ii) for relaxation times greater than those involved in the β relaxation there is a shift of relaxation times toward longer times⁴ when ageing proceeds. Therefore one can expect the state of polarization to be different for samples having different ageing times in the above experiments.

Peak C also appears in the t.s.d. curves of polycarbonate. This is illustrated on Figure 6 for $T_p = 20^\circ\text{C}$. It is located at the same temperature as in PMMA although the T_g of polycarbonate is 40°C higher. When the polycarbonate samples were poled at increasing temperatures in the range $20^\circ\text{--}40^\circ\text{C}$, the maximum of peak C also shifts to higher temperature without any systematic increase in height. Furthermore, by poling at 80°C the partially filled α peak, located at 90°C , is faint. This proves the lack of interference of peak C with the α relaxation in polycarbonate.

All the features observed in the case of PMMA are observed for polycarbonate: a decrease of the area under the curve in the region of β relaxation and the disappearance of peak C as ageing proceeds. In Figures 6 and 7 the t.s.d. currents are shown for three ageing times. Müller *et al.*¹⁵ have studied the influence of various treatments of polycarbonate on the dielectric relaxation. The comparison of the results of a quenched sample to an as-

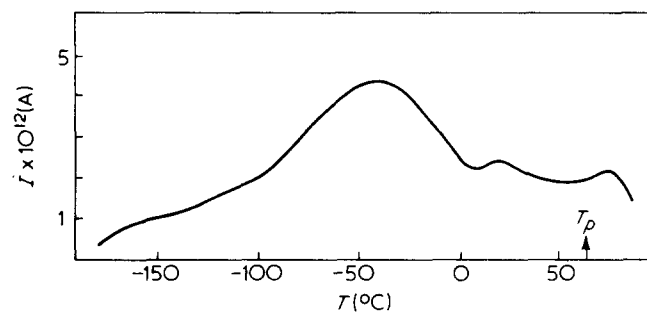


Figure 5 T.s.d. currents vs. temperature for PMMA aged at 65°C . $E = 6.6 \text{ kV cm}^{-1}$, $T_p = 65^\circ\text{C}$, $t_v = 30 \text{ min}$

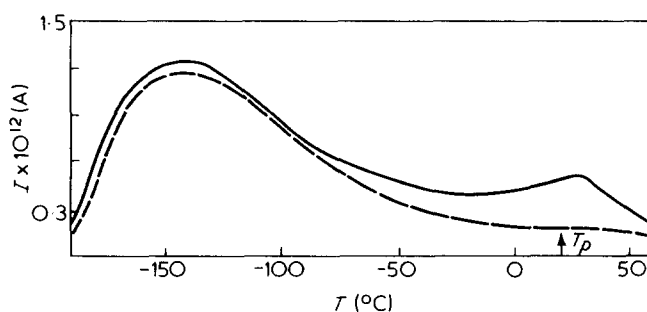


Figure 6 T.s.d. currents vs. temperature for polycarbonate aged at 20°C ; $E = 9.9 \text{ kV cm}^{-1}$; $T_p = 20^\circ\text{C}$; — $t_v = 30 \text{ min}$; --- $t_v = 7 \text{ days}$

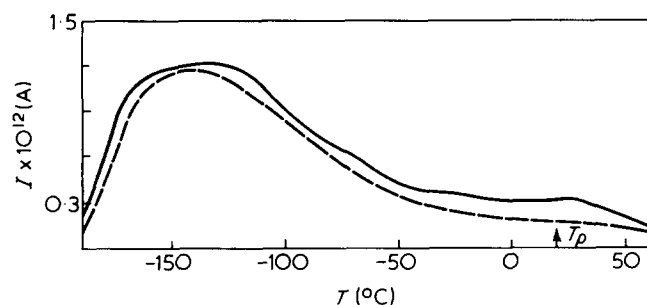


Figure 7 T.s.d. currents vs. temperature for polycarbonate aged at 20°C. See Figure 6; — $t_v = 24$ h; - - - $t_v = 7$ days

Table 4 $(\epsilon_R - \epsilon_u)T$ values for polycarbonate at 20°C; $T_p = 20^\circ\text{C}$, $E = 9.9$ kV cm $^{-1}$

t_v (min)	30	210	1440	10080
$(\epsilon_R - \epsilon_u)T$	0.260	0.239	0.227	0.209
$(\epsilon_R - \epsilon_u)\beta$	0.224	0.218	0.213	0.209

received sample led them to the same conclusions. Peak C observed above seems to correspond to the peak observed at 60°C in Müller's experiments at 1 kHz. It is also visible in Figure 1 in ref 12b and vanished after annealing for one week at 100°C.

The values of $\epsilon_R - \epsilon_u$ are given in Tables 3 and 4 respectively for PMMA and polycarbonate for ageing done at 20°C. $(\epsilon_R - \epsilon_u)_T$ is calculated from the area beneath the whole curve, whereas $(\epsilon_R - \epsilon_u)_\beta$ is $(\epsilon_R - \epsilon_u)_T$ minus the contribution of peak C. I_M/SEb values are given for PMMA in Table 3. They are not reported for polycarbonate since the maximum in the β region of this polymer is rather flat and the shape of the curve seems to change slightly with ageing time.

When PMMA is aged at 65°C, $T_p = 65^\circ\text{C}$, $I_M/SEb = 17.14 \times 10^{-14}$ and $(\epsilon_R - \epsilon_u)_\beta = 1.90$. An increase of the β absorption with increasing temperature was also found by Ishida *et al.*⁹. They developed a theory of the α and β dielectric absorption of polyalkylmethacrylates by using a site model. Through this model they related the magnitude of the two absorptions and explained the increase with temperature of the β absorption.

Thermostimulated mechanical relaxation

The effects of physical ageing on relaxation times greater than the effective ageing time have been investigated for polypropylene by Chai *et al.*⁶ using thermostimulated creep experiments. We have carried out thermally stimulated mechanical relaxation experiments on amorphous PMMA and obtained results similar to those reported by Chai *et al.* in the case of semi-crystalline polypropylene, e.g. no variation with ageing of the portion of the relaxation spectrum in which relaxation times greater than the effective ageing time are located.

It would be interesting to study ageing effects on relaxation times which are in the order of the ageing time. To this end, one must conceive a fairly complicated thermomechanical history which leads to a very tedious interpretation of the resulting experiments. It thus seems that the effects of ageing on the smaller relaxation times cannot easily be studied by a method based on thermostimulated processes.

Rather, isothermal depolarization curves would seem more suitable. The poling can be done above T_g (before ageing) if the whole spectrum of relaxation times is

wanted, or at the ageing temperature if one is only concerned with shorter relaxation times. Through an adequate choice of poling time one can still reduce the spectral region. Furthermore, conduction will not interfere. Isothermal charging and discharging current measurements for the study of basic aspects of physical ageing have been done by Van Turnhout *et al.*¹⁶ and Uchidoi *et al.*¹⁷; however these authors did not mention effects on secondary relaxations.

CONCLUSIONS

By investigating the dielectric properties of two amorphous polymers, PMMA and polycarbonate, it was shown that the limiting dielectric constants of secondary relaxation as well as its total increment change with ageing time once the polymers are quenched through the glass transition temperature. A peak which does not seem to be characteristic of a specific polymer is apparent in t.s.d. curves for short ageing time. Relaxation times longer than ageing time are not modified. It would be interesting to study more thoroughly the effect of ageing on shorter relaxation times.

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Note added to proof: Haddad, J. and Goldstein, M., in a publication we were not aware of (*J. Non-Cryst. Solids* 1978, **30**, 1) discuss the origin of the decrease in dielectric absorption with increasing fictive temperature observed in the β relaxation region of molecular glasses: it could be due to the decrease in strength of the β relaxation itself (observed in some systems) or to that of the background absorption whose origin is not well understood. Background loss may also be present in the above systems.

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