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Ageing

Influence of Physical Ageing on the α Dielectric Relaxation of Poly(Methyl Acrylaie)

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Summary

In this work are examined changes of the α relaxation spectrum of PMA during the structural relaxation process which follows a quenching from a temperature T_0 above T_g to another T_1 below T_g, which is mantained constant. It is found that the relaxation times spectrum is shifted towards longer times as the ageing time increases. At the same time, its form becomes more and more wide, approaching the form of the relaxation times spectrum calculated at temperatures above T_g from alternative dielectric measurements. A parameter measuring the shift of the spectrum, $a(t_a)$, is defined and its dependence on ageing time and annealig temperature is studied. The effective relaxation time of the structural relaxation process is calculated from $a(t_a)$ and it is found dependent on the temperature of annealing as well as on the value of $a(t_a)$itself.

Introduction

The study of the glassy state of amorpous polymers includes necessarily consideration of the kinetics of the process of structural relaxation. The most adequate variables for this study are specific volume and enthalpy. Nevertheless, the kind of molecular rearrangement motion that provokes structural relaxation is the same as that which produces viscoelastic or dielectric α relaxation in amorphous polymers, that is, conformational movements of more or less long parts of the chain backbone (SAITO et.al.,1963; FERRY, 1970; ROBERTSON, 1981). Thus, the changes undergone by the spectrum of the dielectric α relaxation (plot of ϵ'', imaginary part of the complex dielectric permitivity, versus frequency of the applied field) during the process of structural relaxation may provide information about the way such process affects the mobility of the chain backbone in the glassy state.

At temperatures above the glass transition temperature, T_g, the tests which are employed to determine the spectrum of dielectric relaxation are performed starting from a state of thermodynamical equilibrium, be they alternative tests, measuring the complex dielectric permitivity, or transient tests, measuring the permitivity in time. These tests amount to remove the system from equilibrium by means of an electric field and to study the velocity of the system tending to a new state of equilibrium, In the following, the experimental results are expresed always in terms of $\epsilon''(f)$; when the tests are transient, transformation methods will be employed to calculate $\epsilon''(f)$ from $\epsilon(t)$.

The dielectric spectrum of relaxation is displaced towards lower frequencies (equivalent to longer relaxation times) the lower is the temperature. In fact, at temperatures below T_g the maximum corresponding to the α relaxation is at frequencies so low that only the portion to the right of the maximum, i.e. for the higher frequencies of the spectrum, can be experimentally determined. The range of frequencies of this terminal region is that which corresponds to the transient tests (10^{-4}-10^{-2} hz.).

The study of the changes in the dielectric relaxation spectrum during the process of structural relaxation is accomplished by means of succesive transient tests (measurement of the polarization and depolarization current in a sample after the sudden switch on or off respectively of an electric field) at a constant temperature below T_g after a quenching from a temperature above T_g. Following STRUIK (1978), we call the time ellapsed since the quenching the ageing time.

These tests are wholly analogous to those performed by Struik in creep. The results are transformed to values of $\epsilon''(f)$ allowing thus a comparison with the alternative tests at temperatures above T_g.

The study concerns poly (methyl acrylate) (PMA) because it shows a single secondary relaxation at a temperature sufficiently low to neglect its overlap with the α relaxation.

Experimental

With 0.05% AZBN as initiator the methylacrylate monomer (fron Merk) was block polymerized at 60°C during 12 hours, with a final treatment 80°C for 4 hours. After polymerization the sample was vacuum dried at 70°C until its weight remained constant in order to remove low molecular weight substances.

The sample which was employed had a thickness of 1.25 mm. Its T_g was of 8°C as measured in a differential scanning calorimeter Mettler 3000 with a rate of increase of temperature of 10°C/min.

The alternative tests were performed in a capacitor bridge General Radio 1620 A with a cell provided with guard ring. The measurements of depolarization current were performed on a electrometer HP 4329 A; the applied field was of 500 V/mm and the polarization time of 90 min (6 times greater than the measuring time of the depolarization current). The values of ϵ'' as function of the frequency between 10^{-4} an 5×10^{-2} hz were calculated from those of $i(t)$ by means of the method of HAMON (1952).

The thermal treatments were performed by sudden immersion of the measuring cell (at an initial temperature of approximately 18°C) in liquid nitrogen until its temperature became a little below than that chosen for the test. Afterwards the temperature was stabilized in a thermostating bath, with a precission of ± 0.2°C. The first measurement always took place 2 hours after the quenching, and the ageing time was counted starting from the instant of quenching.

Results.

Tests at four different annealing temperatures below T_g have been performed. The values found for $\epsilon''(f)$ corresponding to different ageing times are shown on figure 1. The spectrum of the α relaxation is shifted towards lower frequencies (that is, towards longer relaxation times) with increasing of ageing time. This signifies that the dielectric relaxation times become greater with decreasing free volume, but, in opposition to the viscoelastic results of STRUIK (1978), it seems that the decrease in free volume doesn't affect in the same way all relaxation times, i.e., the shape of relaxation spectrum is not conserved with increasing ageing time: it is not possible to superpose the $\epsilon''(f)$ curves corresponding to different ageing times by means of horizontal shifts.

In order to clarily this point one can compare the shape of these curves with that of a master curve $\epsilon''(f)$ obtained by superposition of the different relaxation spectra at temperatures above T_g, that is, with the shape of the equilibrium relaxation spectrum. The influence of the relaxation on the terminal zone of the β relaxation was disconted in order to draw this curve. The component of ϵ'' due to the β relaxation is very small at temperatures below T_g, but increases at higher temperatures when the α and β relaxations approach each ofter. The β relaxation can be characterized by means of the model of FUOSS and KIRKWOOD (1941)

$$\epsilon'' = \epsilon''_m \frac{(f/f_m)^m}{1 + (f/f_m)^{2m}}$$

and the parameters resulting are (GOMEZ, 1983)

$$m = 0.0437 + 0.00073\ T$$
$$\epsilon''_m = 0.102 + 9.09\times10^{-4}\ T$$
$$\log f_m = 13.51 - 1700/T$$

Thus the time-temperature superposition principle is satisfactoriusly fulfilled by the α relaxation, with only small vertical displacements needed to correct the change in the intensity of the relaxation with temperature. This master curve is represented superposed on the isotherm corresponding to 9.0°C in figure 2.

The slopes of the curves obtained during the structural relaxation suggest that close after quenching the dielectric relaxation times distribution is narrow, and becomes broader as the ageing time increases, tending to the equilibrium distribution. A possible explanation of this fact can be the larger distance between neighbour chains immediatly after the quenching. Thus, the intermolecular contribution to the potential enengy acting on the segments of the backbone chain is smaller. This intermolecular contribution is the principal responsible of the width of the relaxation times spectrum, because it is dependent on the neigh-

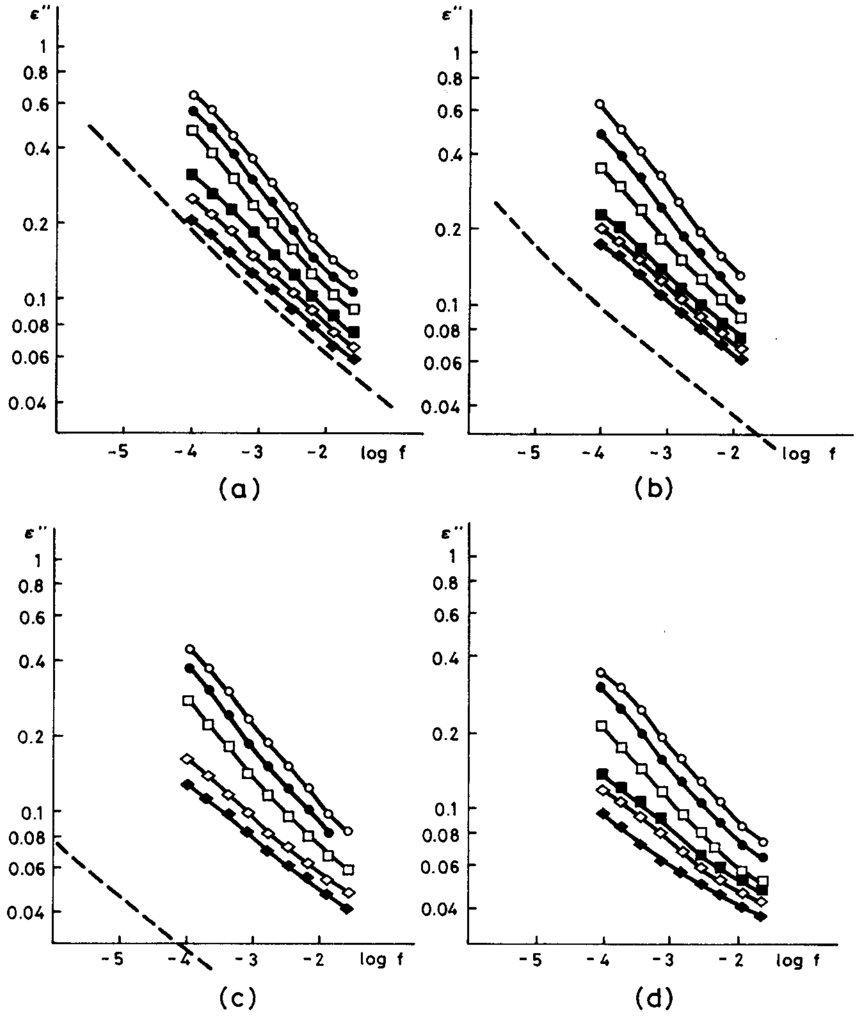

Fig.1. Relaxation spectrum measured at different annealing temperatures T after a quenching from a temperature above T_g at different ageing times. a) T = 5.8°C, ○ 2.25 hours, ● 4.25 h., □ 8.25 h., ■ 24.5 h., ◇ 48 h., ◆ 168.5 h. b) T = 3.4°C, ○ 2.3 h., ● 4.5 h., □ 9.2 h., ■ 26.7 h., ◇ 32.5 h., ◆ 48.8 h. c) T = 0.6°C, ○ 2.5 h., ● 4.5 h., □ 9.2 h., ■ 25.5 h., ◇ 49.3 h. d) T = -1.2°C, ○ 2.5 h., ● 4.5 h., □ 8.25 h., ■ 24.8 h., ◇ 31.2 h., ◆ 72.8 h. The equilibrium spectrum is dashed drawn. See text.

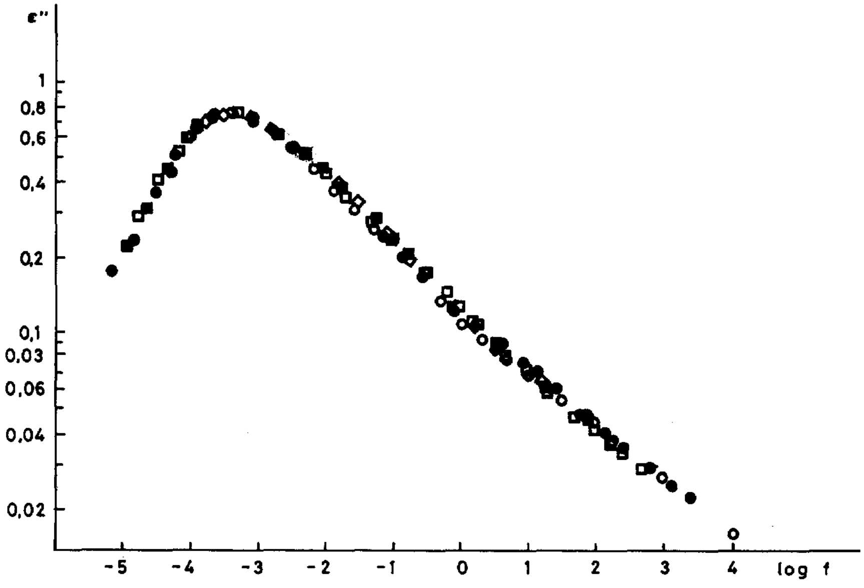

Fig. 2. Master curve of the α relaxation obtained by superposition on the curve corresponding to 9.0°C. See text. (GOMEZ 1983)
○ 9.0°C, ● 11.6°C, □ 14.6°C, ■ 17.3°C, ◇ 21.0°C.

bourhood of each group. Thus, the relaxation times spectrum is narrower a little after the quenching, and becomes more and more wide when the ageing time increases, diminishing the free volume and the distance between neighbouring chains.

Phenomenologically, the structural relaxation process can be characterized by means of the position of the spectrum of the α relaxation along the frequency axis, in the same way as specific volume or enthalpy are employed to characterize the process. As it is not possible to superpose the curves for different ageing times in order to employ, as STRUIK (1978) does, the shift factor as a measure of the position of the spectrum, we have prefered to calculate this position through the logarithm of the frequency at which ϵ'' attains a fixed value ϵ''_1, log $a(T,t_a)$,being T the temperature of annealing and t_a the ageing time. Log a depends slightly on the choice of ϵ''_1. The values of ϵ''_1 chosen for the different ageing temperatures are given in table 1.

Table 1

Temperature of annealing (°C)	5.8	3.4	0.6	-1.2
ϵ'_1	0.2	0.15	0.1	0.1
$a(T,\infty)$	-4.1	-4.72	-6.4	-8.48

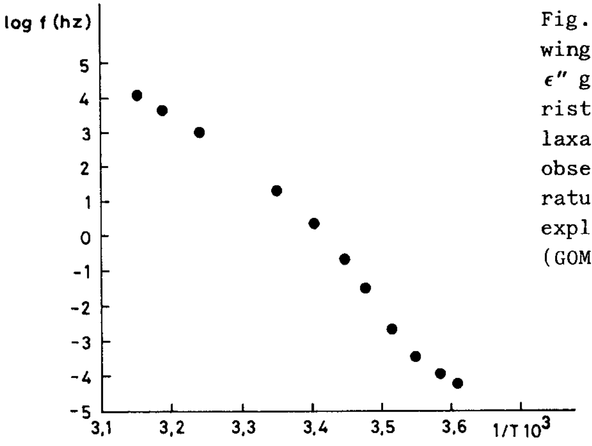

Fig.3. Arrhenius diagram showing the frequency at which ϵ'' goes through the characteristic maximum of the α relaxation. The singularity observed at the lowest temperatures (below T_g) has been explained in another work (GOMEZ and DIAZ, 1985)

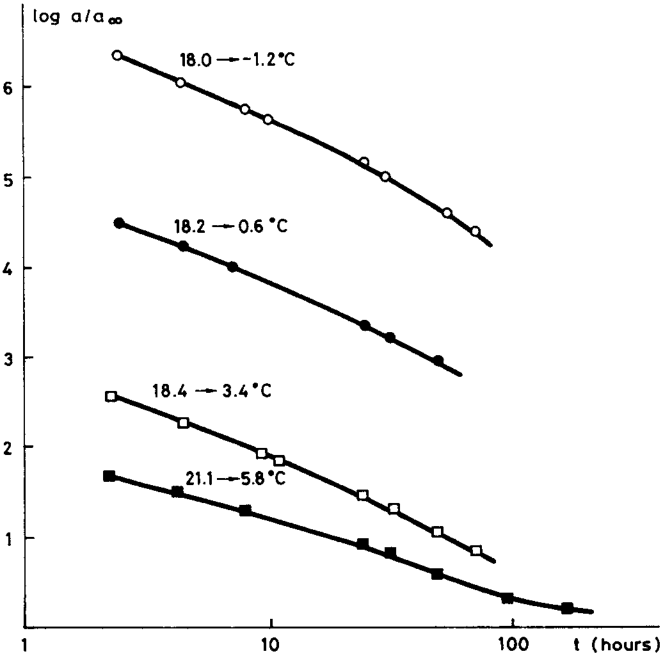

Fig.4. Values of $a(T,t_a)$ measured after temperature jumps $T_0 \rightarrow T_1$ ○ 18.0 → -1.2°C, ● 18.2 → 0.6°C, □ 18.4 → 3.4°C, ■ 21.1 → 5.8°C, (DIAZ and GOMEZ, 1985)(by kind permission of Elsevier Applied Science Publishers Ltd.)

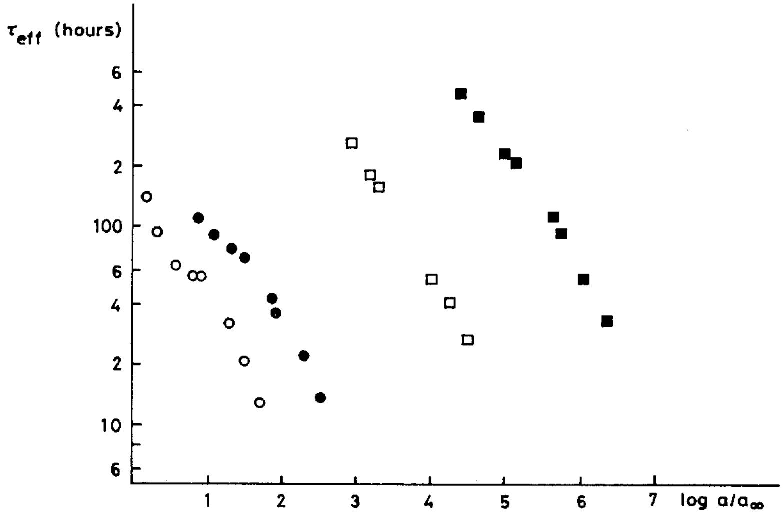

Fig.5. Effective relaxation times of structural relaxation process as a function of departure from equilibrium, at different annealing temperatures: ○ 5.8 °C, ● 3.4°C, □ 0.6°C, ■ -1.2°C.

One of the conclusions of the study of structural relaxation (KOVACS et.al.,1979; MOYNIHAN et.al.,1976; ADACHI and KOTAKA, 1982) is the imposibility of describing the process by means of a model with a single relaxation time, as it is clear through the appearence of the memory effect. Nevertheless, in tests such as those performed here, with a single temperature jump, it is useful to define an effective relaxation time through

$$\frac{d \log a(T,t_a)}{d t} = - \frac{\log(a(T,t_a)/a(T,\infty))}{\tau_{eff}}$$

where the effective relaxation time depends on temperature and on the departure from equilibrium, that is, on the ratio $\log (a(T,t_a)/a(T, \infty))$. As the form of the equilibrium dielectric relaxation spectrum was taken the master curve of figure 2, and its position for every temperature below T_g was fixed by determining log f at which ϵ'' goes through the maximum by extrapolation of the values of log f_m obtained at temperatures above T_g (fig.3), these values were fitted into the equation:

$$\log f_m = 10.604 - \frac{431.11}{T + 20}$$

The equilibrium spectrum has been dashed-drawn in figure 1. Log $a(T, \infty)$ was measured in this way. Values of lof $a(T,\infty)$ are given in table 1. In the case of the curve corresponding to 5.8°C very close to T_g, we prefered to calculate log $a(5.8, \infty)$ extrapolating the values of

$\log a(5.8, t_a)$ to very long times, so that the error in extrapolation is smaller.

Figure 4 represents the values of $\log(a(T,t_a)/a(T,\infty))$ as a function of the ageing time for each of the four annealing temperatures employed.

Figure 5 shows the effective relaxation times calculated following equation 2; there appears the dependence on temperature and on $\log(a(T,t_a)/a(T,\infty))$, i.e., on the departure from equilibrium. It is found that the effective relaxation times can be fitted into an equation of the type:

$$\tau_{eff} = A(T)\exp(-B/\log(a(T,t_a)/a(T,\infty)))$$

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