Study of structural relaxation by dynamic-mechanical methods in poly(methyl methacrylate)

Ricardo Diaz-Calleja*, Amparo Ribes-Greus and Jose L. Gomez-Ribelles
Laboratory of Thermodynamic and Physical Chemistry, E.T.S.I.I.V., Universidad Politecnica de Valencia, Apartado 22012, 46071 Valencia, Spain
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A systematic study of the influence of ageing on the dynamic properties of amorphous poly(methyl methacrylate) (PPMA) has been made. During isothermal annealing a decrease in loss tangent and an increase in modulus with ageing time in a broad zone between 30 and 90°C have been observed. The ageing in the zone of the β peak has been investigated and an interpretation of the results is proposed on the basis of recent theories. The existence of the memory effect after two-jump experiments has been proved.

(Keywords: ageing; poly(methyl methacrylate); dynamic mechanical properties)

INTRODUCTION

Amorphous polymers as supercooled liquids are not in thermodynamic equilibrium below the glass transition (T_g). In fact, when this type of material is suddenly cooled from $T_1 > T_g$ to $T_2 < T_g$ a process of slow but progressive internal recovery is produced. At low mobility (high viscosity) the chain relaxes to thermodynamic equilibrium isothermally at T_2. This structural relaxation, which has been given the technical name of 'physical ageing'[1], was observed some years ago by Kovacs[2] as a decrease of specific volume, and more recently it has also been seen in specific enthalpy (and specific heat) curves by differential scanning calorimetry (d.s.c.)[3,4].

However, many other properties of the material can be affected by ageing. In recent years the effect of the thermal history on dynamic-mechanical[5,6] and dielectric[7,8] relaxation properties of solid amorphous polymers has been reported. Some of these results are controversial, as a consequence of the fact that the effect of ageing on dynamic relaxations in amorphous polymers has been insufficiently explored.

One of the general facts observed in dynamic tests on aged samples is an increase in modulus and a decrease in permittivity and loss tangent[5-8]. Moreover, these effects are mainly observed in the zone between T_g and the first of the secondary relaxations (β relaxation)[1] and have been associated with the mobility due to a residual free volume below T_g that allows structural recovery.

A first explanation could be that at T_β there is still a quantity of free volume, which disappears below this temperature, and which can be the cause of the motions in the main backbone giving structural recovery. This theory could be consistent for polymers in which the β relaxation is caused by a 'crankshaft' or 'kink' motion in the main chain, but if the motion causing the β relaxation is attributed to the lateral rotating groups (as for example in poly(methyl methacrylate), PMMA) it would seem a little fortuitous that T_β can also be the limit for a motion taking place in the main chain, as is commonly assumed.

These phenomena can also be viewed on the basis of recent theories[9,10] according to which the amorphous polymers can be considered as a close packing of monomers where density fluctuations produced by quenching or after compression moulding during manufacture are present, thus giving a non-randomly distributed free volume. During experimental and under the effect of mechanical stress the so-called 'sheared microdomains'[10] are activated around the defects of density. These defects would leave sufficient free volume to allow the initiation of internal motions of restricted parts of the macromolecular units associated with the β relaxation. At the same time, due to the overlapping effects of mechanical stress and temperature, the 'sheared microdomains' expand and this implies a correlation (or coupling) effect between the zone in which the shear movement is initiated and the neighbouring molecules that propagates the deformation. The effects propagate at longer distances in the polymeric chain to yield the glass transition temperature (at which cooperative motions of the main chain take place).

This picture allows us to consider the β relaxation as a precursor of the glass transition, but at the same time this relaxation retains a specific molecular origin as the rotation of the lateral carboxymethyl group in PMMA. In this context structural recovery would imply an annihilation of defective zones via a selective densification in these zones of the glass during ageing. The above mentioned correlation (or coupling) effects would be altered by ageing and due to it the β relaxation would also be altered, diminishing the damping. The more striking effects, however, would take place near (but below) T_g. Thus the effect of a decrease in loss tangent in the low temperature tail of the α relaxation (i.e. in the T_g zone) can also be the origin of the decrease in loss tangent in the β zone if both relaxations are a little overlapped (as is the case, for example, in polystyrene and to a lesser extent in poly(methyl methacrylate)).

These reasons, and the lack of detailed thermal

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*To whom correspondence should be addressed

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histories in the literature, seem to justify a systematic study of the influence of ageing on the dynamic properties of an amorphous polymer. We selected poly(methyl methacrylate) for the study described in this paper.

EXPERIMENTAL

The PMMA was prepared by radical bulk polymerization at 60°C for 14 h of a monomer (Merck), using 0.06% AZBN as initiator. The sample was annealed to finish the polymerization and then dried in a vacuum stove at constant weight.

Dynamic viscoelastic measurements were made with a dynamic mechanical thermal analyser (DMTA); the samples were prismatic bars of section $7 \times 4\,\mathrm{mm}^2$ and the flexure mode was employed. Three different types of experiments were done:

(1) In a first group of tests the sample was cooled suddenly in liquid N_2 from $T_g + 20$°C and then clamped in the DMTA. The temperature was then raised to the temperature selected as the ageing temperature. The time needed to attain thermal equilibrium was about 10 min. The temperature was maintained for different times in the DMTA for a maximum of 624 h. Then the sample was suddenly cooled in the apparatus to -70°C and the modulus and tan δ were measured from this temperature to about 150°C at a heating rate of 3°C min^{-1}. We also measured a quenched (non-aged) sample.

(2) Because the isochronal measurements are not in isoconfigurational condition, and to avoid experimental errors present in short-time ageing experiments of the type mentioned above (that arise from a complex thermal history consisting of ageing for a short time followed by quenching to -70°C and a later increase of the temperature at a heating rate of 3°C min^{-1} to 150°C), we designed a different type of experiment. The sample was clamped in the DMTA apparatus after quenching it in liquid N_2 from high temperature, and the temperature was then raised to the ageing temperature as rapidly as possible. Log E' and tan δ were measured as a function of the time elapsed from the quenching (ageing time). The longest experimental ageing time was about 50 h. The temperature was held within ± 0.5°C of the ageing temperature.

(3) To analyse the 'memory effect', two-jump experiments were carried out. The sample was cooled from above T_g to T_1, kept at this temperature for a period of time and then heated to T_2 ($T_2 > T_1$). Log E' and tan δ were measured as a function of the time elapsed since the temperature T_2 was reached.

Some comments on the use of liquid N_2 are pertinent. Struik[6] has rejected liquid N_2 for quenching for two reasons: first to obtain dry samples and second to avoid internal stresses caused by quenching from above T_g. However, the DMTA is prepared for measurements in a dry N_2 atmosphere to avoid moisture. Water can affect the dynamic-mechanical properties of PMMA after quenching if the head of DMTA is removed at sub-ambient temperature in order to reclamp the sample. The effect of the absorbed water can be observed in *Figure 1*, where measurements obtained with and without precautions to avoid moisture are compared. In the second case we obtain a new peak in the viscoelastic spectrum, revealing the presence of water. It is true that rapid quenching can be the origin of thermal stresses. On the other hand, use of the liquid N_2 allows a fast quenching. A slow cooling implies a greater departure from the typical jump in temperature required by the theory than if we use liquid N_2. Moreover, the first 10 min (until the stabilization of the temperature at the ageing value) lose their significance for the analysis of results. These effects can obscure the influence of ageing during a period in which ageing is very important in magnitude, and leads to erroneous conclusions in the zone in which ageing is less apparent. There is also an uncertainty in the assignment of the time origin (zero time) for the process. Due to the smaller changes at high frequency (see below), low temperature, this uncertainty is also less in these zones.

Thus we have a choice between two inconvenient situations: good quenching with possible internal stresses and bad quenching without internal stresses. To test the effect of the thermal stresses on the results we made repeated experiments of type 2 and obtained significant differences only for ageing times $\leqslant 10$ min (*Figure 2*).

Some comments on thermal lag between the temperature programmer and the temperature in the specimen are relevant. The configuration of the head of the DMTA apparatus, completely surrounded by the heating resistor, allows a rapid evolution to thermal equilibrium. In the sample, in the isothermal experiment, equilibrium is attained within about 10–20 min. For shorter times, results must be considered with concern. This is another reason why there is no reproducibility for times <20 min in *Figure 2* and why we do not interpolate the curves in *Figures 7, 8* and *10* for times <10 min. For memory experiments the thermal lag is

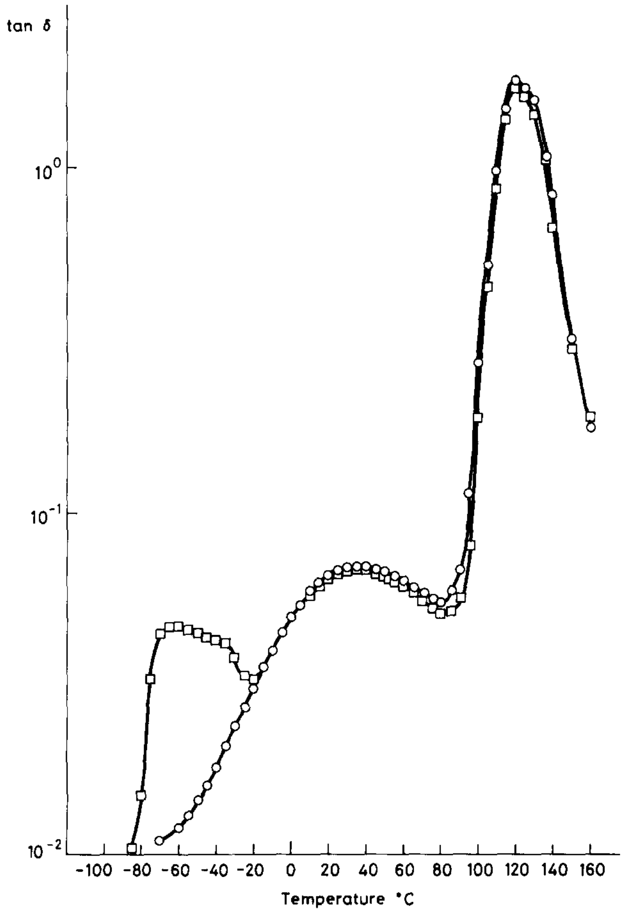

Figure 1 Loss tangent *versus* temperature after different ageing times at 76°C and 1 Hz: □, 70 h; ○, 22 h

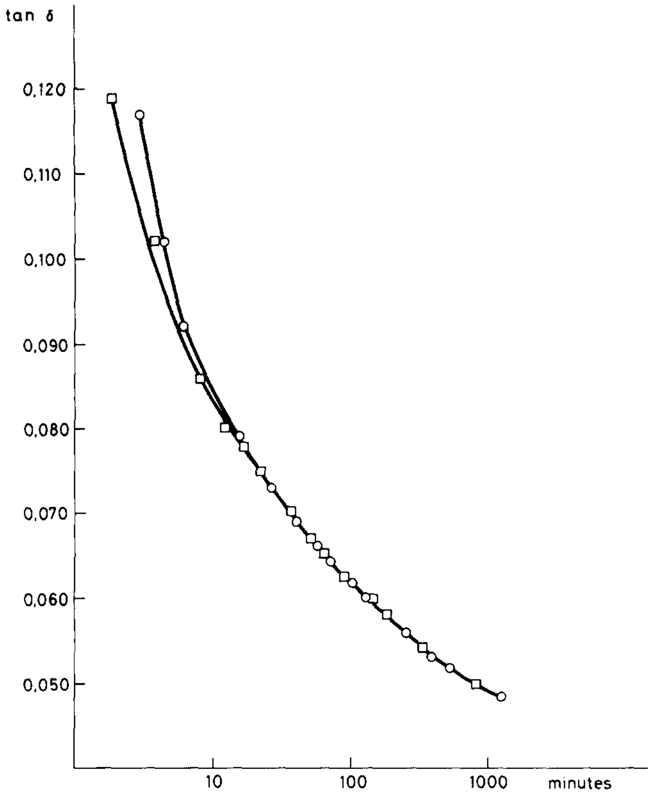

Figure 2 Loss tangent *versus* ageing time for ageing temperature 77°C and frequency 1 Hz. Symbols ○ and □ correspond to two sets of points obtained for the same type of experiment showing poor reproducibility below 10 min

less than for isothermal experiments and thus equilibrium can be attained in a typical range between 5 and 10 min.

RESULTS AND DISCUSSION

Modulus and loss tangent after different ageing times at 59.5±0.5°C obtained from experiments of type 1 are shown in *Figure 3*. The ageing temperature has been selected to be near that of the minimum between the α and β relaxations. In these curves a decrease of loss tangent with ageing time in a broad zone can be observed, the effect being greater between 30 and 90°C. At the same time, the α and β relaxations are clearly present. These results agree with expectations about the dynamic-mechanical behaviour in ageing of the amorphous polymers (see Reference 6 for example) and also with results obtained by two of us previously using dielectric techniques[8]. Due to the overlap of the two peaks, α and β, the effect of ageing on the relative position of the β peak at each frequency is not easy to see, especially for the short time ageing experiments, i.e. we cannot calculate the effect of ageing on the activation energy.

It seemed interesting to investigate ageing in the zone of the β peak. Ageing at 46°C for 22 h was induced in a sample in a typical experiment. This temperature corresponds to the high temperature side of the β relaxation, and the results can be seen in *Figure 4*, which reveals an interesting fact: a new peak can be observed superimposed on the β relaxation and immediately after the ageing temperature. We will try to explain this below.

Isothermal experiments (type 2) were made at different temperatures, revealing different kinetic behaviour with temperature (*Figure 5*). At temperatures $< T_\beta$ ageing is less pronounced than at intermediate temperatures between the α and β relaxations. *Figure 6* shows the effect of the frequency of the measurements on the kinetics of ageing. These curves predict greater ageing at lower frequencies than at higher ones. This result is equivalent to a more pronounced ageing at higher temperatures than at lower ones, as can be seen in *Figure 3*.

It is also interesting to examine the curves of the loss modulus or tangent resulting from an interpolation between different ageing times (*Figure 5*) and as a function of the temperature. Results are shown in

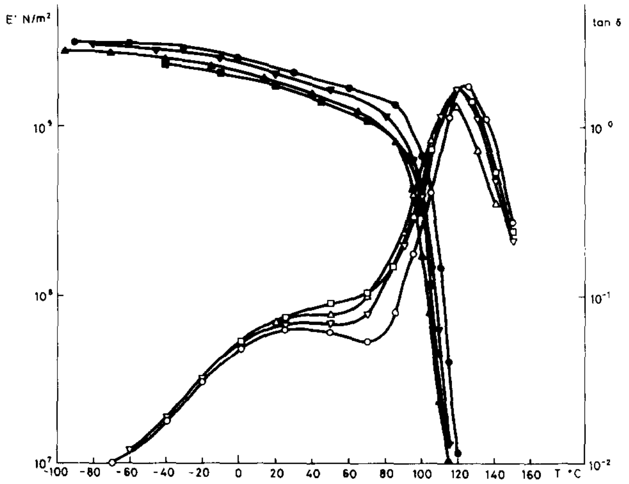

Figure 3 Loss tangent (filled symbols) and modulus (open symbols) *versus* temperature after different ageing times at 59.5°C and 1 Hz: □, ■, quenched sample; △, ▲, 1 h ageing; ▽, ▼, 17 h ageing; ○, ●, 624 h ageing

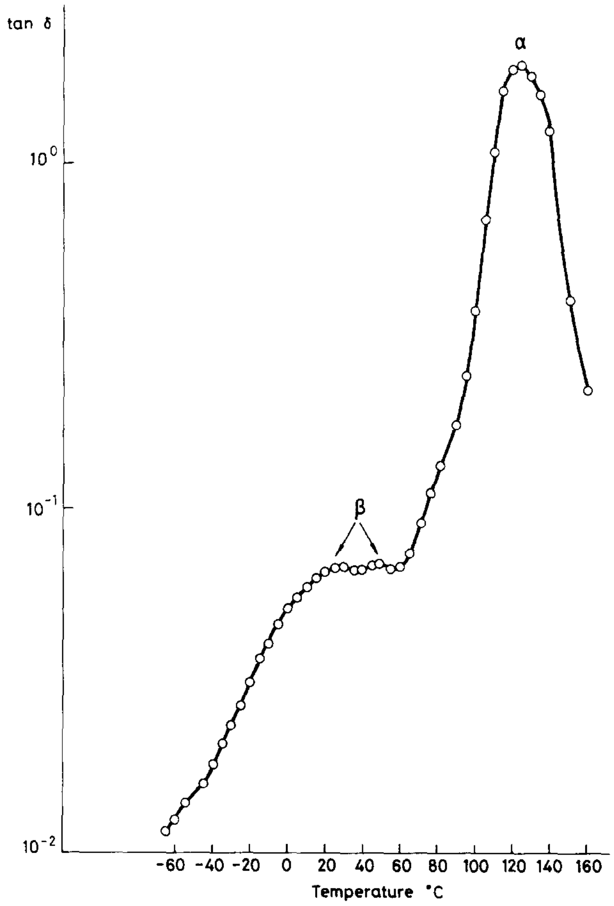

Figure 4 Loss tangent *versus* temperature after 22 h ageing at 46°C and 1 Hz

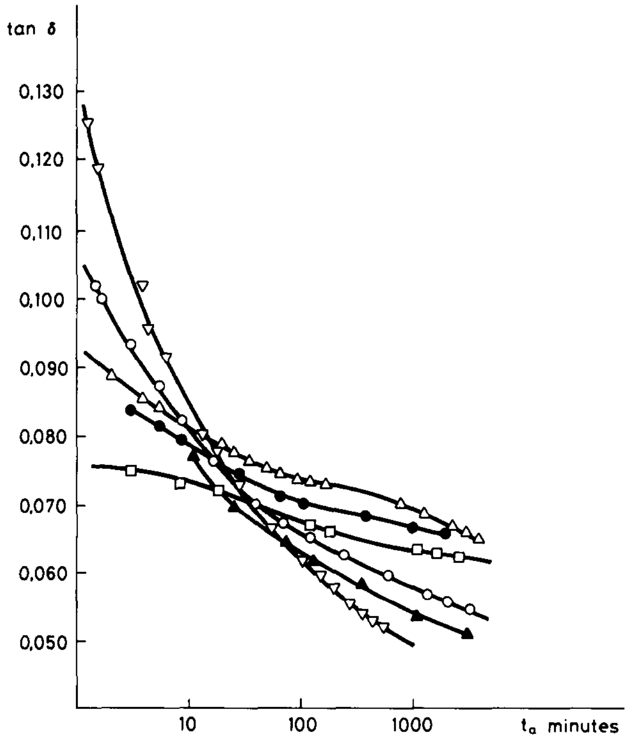

Figure 5 Loss tangent *versus* ageing time at 1 Hz and different ageing temperatures (°C): □, 28; ●, 37; △, 46; ○, 59.5; ▲, 68.5; ▽, 77

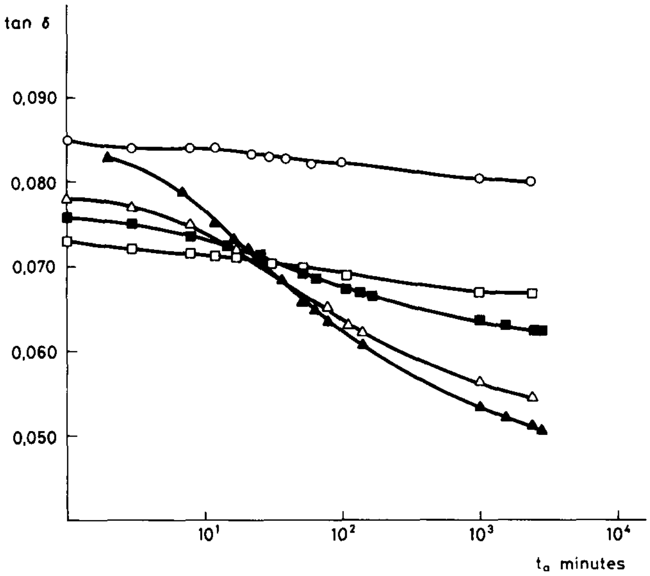

Figure 6 Loss tangent *versus* ageing time for ageing temperature 28°C and frequencies (Hz): ▲, 0.033; △, 0.1; ■, 1; □, 30; ○, 90

Figures 7 and *8*, where a decrease of the loss in the β zone and a still more pronounced decrease at higher temperatures can be observed. These results are consistent with those of *Figure 3*, in spite of the different thermal histories suffered by the samples during tests 1 and 2.

Finally, we have proved the existence of the memory effect after a two-jump experiment. The sample was quenched from T_g+20°C to 28°C and kept at this temperature for different intervals of time (7 and 45.5 h); afterwards the temperature was increased to 46°C and the loss tangent and the logarithm of the modulus were measured. *Figure 9* shows the effect of the temperature jump. A more pronounced peak appears at short times and at lower temperatures, making it clear that the sample 'remembers' at short ageing times the former thermal history, and this effect is more important since the former thermal history is longer. For comparison the ageing curve at 46°C is shown in *Figures 9* and *10*.

The memory effect proves the existence of at least two relaxation times (in general a distribution) in the recovery spectrum of relaxation times. A very simple explanation of this phenomenon has been given by Adachi and Kotaka[11] on the basis of only two (a short and a long) relaxation times.

The effect of the thermal history on secondary relaxations in glasses and amorphous polymers has been discussed before[6,9] but these authors advanced contradictory conclusions in many senses. Our conclusions are obviously restricted to PMMA. It is clear from our results that isothermal annealing decreases the loss tangent and increases the modulus (*Figure 3*). However, in contrast with conclusion (c) of Reference 6, new peaks can arise after ageing at temperatures between the β and α relaxations. The origin, however, depends on the

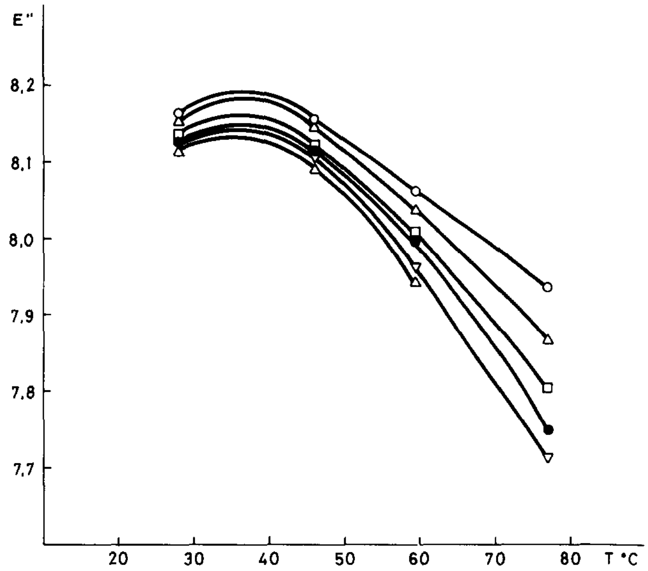

Figure 7 Loss modulus *versus* temperature resulting from an interpolation between different ageing times (min): ○, 10; △, 30; □, 100; ●, 300; ▽, 1000; ▲, 3000

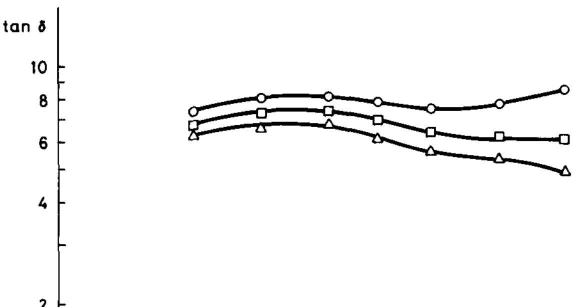

Figure 8 Loss tangent *versus* temperature resulting from an interpolation between different ageing times (min): ○, 10; □, 100; △, 1000

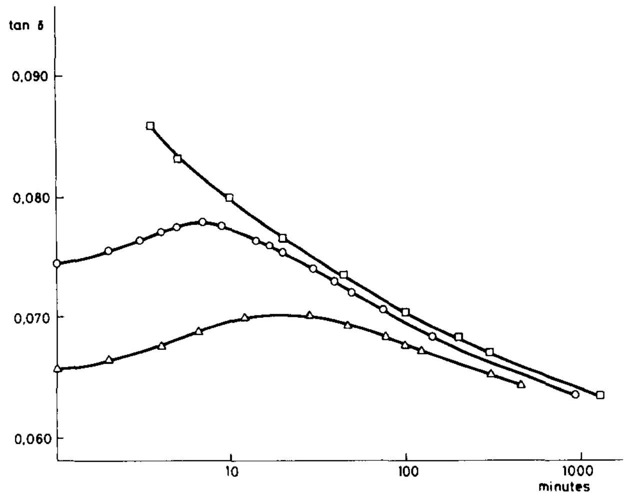

Figure 9 Loss tangent *versus* ageing time. □, Isothermal ageing curve at 46°C; ○, isothermal ageing curve with a temperature jump to 46°C after ageing at 28°C for 7 h; △, isothermal ageing curve with a temperature jump to 46°C after ageing at 28°C for 64 h

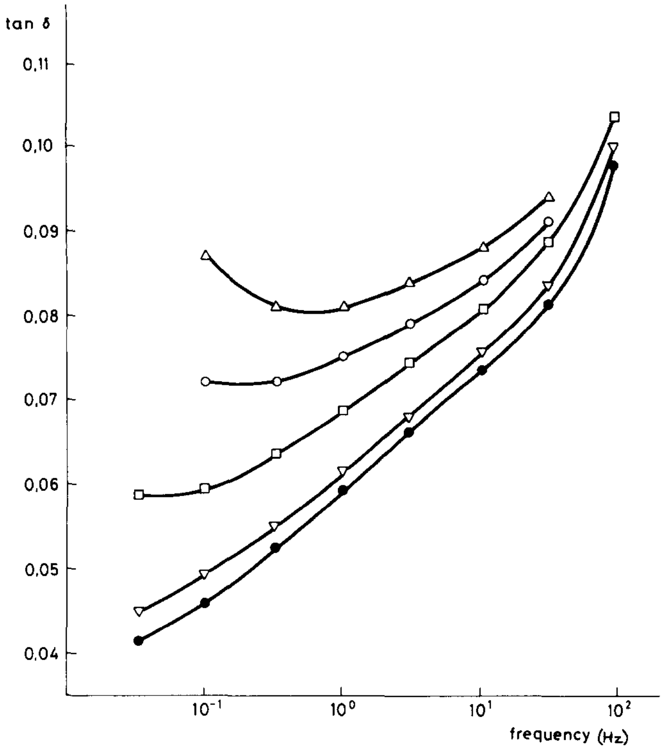

Figure 10 Loss tangent *versus* frequency at different ageing times (min): △, 10; ○, 25; □, 115; ▽, 1650; ●, 4200

polymer. We have observed a new peak in dielectric measurements in PVC[12,13]. We have interpreted[13] the new β′ peak in PVC, at about 40°C (1 Hz), as due to molecular motions inside the microdomains, detected in this polymer by d.s.c. by other authors[14] for PVC without plasticizer, which can increase on isothermal annealing. This phenomenon is not observed in PMMA, and we interpret the new peak in this polymer (*Figure 4*) as a consequence of the fact that the ageing produces a decrease of the loss tangent up to the ageing temperature but leaves the loss above this temperature unaltered, thus giving a spurious peak.

The influence of ageing on the β peak is more important at higher temperatures in isochronal experiments or low frequency isothermal curves. These results allow us to conclude that the decrease of the β peaks with ageing is due to the shift of the α relaxation towards lower frequencies (higher temperatures) with ageing.

However, as seen in *Figure 6*, for tests at 28°C (i.e. at temperatures below T_β), the loss decreases during ageing and we think that this fact requires further interpretation.

Secondary relaxations in polymers have been attributed to specific motions of the small parts or lateral groups of the structural unity. For PMMA the partial rotation of the carboxymethyl group has been widely proposed as the origin of the β relaxation (References 15 and 16 and references cited therein). This motion would be hindered by the α methyl group, thus being governed mainly by an intramolecular barrier. However, recent studies of molecular mechanics[17,18] have shown that, besides the previously mentioned intramolecular barrier, to attain the value of activation energy observed by different techniques it is necessary to introduce constraints in the main chain, bringing a supplementary component to the barrier. This second contribution clearly has an intermolecular origin and it can consist for example of constraints on the motion provoked by torsion angles in the chain backbone. This means that the main chain plays a significant role in the molecular origin of the β relaxation in PMMA. Densification via compression or ageing will thus modify the β relaxation.

To see the effect of densification on secondary loss peaks in a polymer specific experiments are needed. Recent dielectric studies on PMMA by Koppelmann[19] have proved that in constant volume (high pressure) experiments, the dielectric spectrum is shifted to low frequencies (high temperatures) also diminishing the height of the peak. Although compression has, macroscopically, the same effect as ageing, i.e. densification of the sample, from a kinetic point of view at the molecular level the effect of the compression is to decrease all the interatomic distances and to increase the barrier opposing the motion (more specifically, the intermolecular component of the barrier), leading also to a decrease of the height of the peak via a decrease of the population of groups that relax. On the contrary, ageing does not decrease the intermolecular distances overall but only in loosely packed zones, giving also a decrease in the population of molecules that are able to take part in the motion associated with the β relaxation.

According to our measurements (*Figures 7* and *8*), ageing diminishes the height but not the relative position of the β peak (decrease of the population of groups that relax but not of the barrier). Thus, besides a transition of the α peak to higher temperatures, the effect of ageing, at least in our case, can also be the mentioned decrease of the height of the peak.

If we accept that the free volume is the cause of ageing in the glassy state and that it is not randomly distributed but concentrated in the defective zones, as we mentioned in the Introduction, structural recovery would imply an annihilation of defective zones in the glass during ageing, i.e. a decrease in the population and size of the defective zones where molecular motion provoking the β peak can take place. This may explain the change in the intensity of the β relaxation during the ageing process without change in the apparent activation energy.

Our hypothesis allows us simultaneously to retain the original idea of the rotation of the carboxymethyl group as the origin of the β peak subjected to a barrier of an intra- and intermolecular origin and to explain the effect of ageing on this relaxation in terms of annihilation of defective zones where relaxation is produced.

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