Rejuvenation and annealing effects on the loss curve of polycarbonate: 2. Cooling and ageing dependence

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Loss curves at 1 Hz were measured for polycarbonate (PC) samples with various mechanical and thermal histories on heating from -50 to 140°C or on cycling within these limits. The α' peak, on the left side of the α peak, was found to shift to higher temperatures with decreasing θ values of the samples and even to disappear from the heating loss curve as predicted by the model presented in the first part of this series of papers[1]. The left side of the α peak is correctly predicted in all cases, but an additional peak, called α'', which was not predicted, appeared to the right of the β peak for samples cooled from temperatures $T_a \geqq T_g - 65$ K or for quenched samples. The α'' peak was found to vanish on ageing the samples at room temperature and to be erased by plastic deformation. A new definition of ageing and annealing phenomena is advanced using the concept of structural temperature. The α'' and α' peaks seem to be linked to ageing and annealing, respectively.

(Keywords: polycarbonate; annealing; ageing; structural temperature; loss curve)

INTRODUCTION

The first part of this series of papers[1] dealt with the α' peak appearing on the loss curve of polycarbonate (PC) obtained on heating rejuvenated samples up to T_g. The shape, the height and the position of this peak were investigated as a function of heating rate and frequency. First of all, the effect of annealing the rejuvenated samples, at constant temperature, for various times prior to annealing, was pointed out. A quantitative interpretation of the loss curve was given by means of a model supported by classical equations and the concept of structural temperature θ (refs 2–5). The annealing temperature values were restricted to 40 and 60°C. This was a deliberate choice because in such conditions, a well defined α' peak appears to the exclusion of other peaks between the β and α peaks. For clarity, such simple cases were treated first.

The model implies that the α' peak is shifted towards higher temperatures for samples with a low θ value prior to the damping test and that it may even disappear from the heating loss curve. To check this implication experimentally we have measured the heating loss curve of samples pre-annealed 2 h at 80°C, 100°C and 120°C. Concerning the left side of the α peak we found a good agreement between theoretical and experimental loss curves, but we were astonished to discover a new additional peak, denoted by α'', arising on the right side of the β peak.

Another implication of the model refers to the cyclic loss curves approaching T_g: the α' peak must not appear on the second run, i.e. the cooling loss curve of the cycle. Once again, theoretical and experimental cooling loss curves were found to agree. This demonstrated the ability of the model to take into account the left side of the α peak, but the experimental cooling loss curve exhibited an α'' peak which was not predicted.

Therefore, in addition to checking some implications of the model, the present paper is devoted to the conditions in which the α'' peak appears on, or disappears from, the loss curve of PC samples. One of the purposes is to show experimentally that the α'' peak is linked to cooling and ageing effects. This is in contrast to the α' peak which is related to annealing effects influencing the θ value of the sample. Results presented here reinforce the assumption expressed by one of us[6] that ageing and annealing appear to be distinct phenomena.

EXPERIMENTAL

Damping tests

Internal friction was measured as in the first part of this series[1]. The testing frequency was equal to 1 Hz throughout. Heating loss curves and cyclic loss curves were taken from -50 to 140°C. The heating and cooling rates were 60 K/h.

Samples

Details about the material and the samples used can be found in the first part of this series[1]. In addition to PC rejuvenated by cold rolling, we have investigated samples rejuvenated by ice quenching from 165°C and samples as received. Varied thermal histories were imposed prior to damping measurements. The rejuvenation conditions and the thermal histories for each sample are outlined in *Table 1* where the θ values acquired prior to the damping tests are also listed. These structural temperatures are denoted by θ_{ir} for the rejuvenated samples and by θ_a for the annealed ones. The figure in which the data are given is also noted.

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Table 1 Samples investigated

Code number	Rejuvenation conditions	Thermal history		θ_{ir} (K)	θ_a (K)	Figures
		Annealing conditions	Ageing time (20°C)			
1	cold rolled	2 h at 80°C	not aged		423.7	3
2	cold rolled	2 h at 100°C	not aged		417.4	3
3	cold rolled	2 h at 120°C	not aged		412.3	4
4	cold rolled	2 h at 120°C	3 weeks		412.3	4
5	as received	48 h at 100°C	not aged		412.8	5
6	as received	48 h at 100°C	6 years		412.8	5
7	cold rolled	2 h at 60°C	not aged		431 (run 1)	6
					413 (run 2)	6
8	quenched	not annealed	not aged	421		7
9	quenched	not annealed	6 years	421		7

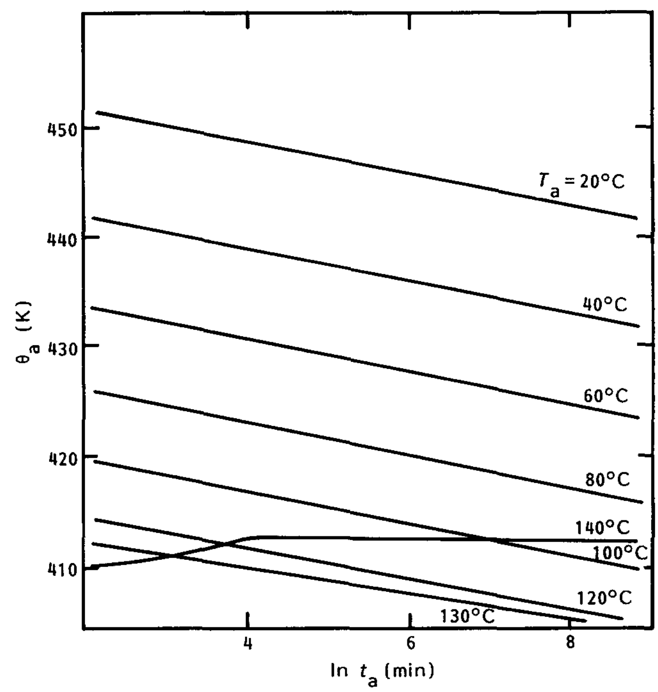

Figure 1 Plot of the calculated θ_a value as a function of $\ln t_a$ for a series of constant T_a; equation (1) is used throughout

Presentation of experimental results

The arrangement in which the loss curves are presented fulfils the following purposes:

To show that α' is shifted toward higher temperatures with decreasing θ_a values until it disappears from the heating loss curves;
To show that α' is not reversible;
To show that α'' vanishes for samples aged at room temperature;
To show that α'' is enhanced for samples quenched from temperatures above T_g.

All the curves are given in the same linear scales to allow comparison of the data.

Background level

The background level considered here is that related to the loss curves at 1 Hz in the first paper in this series[1], i.e. 5.14×10^{-3}. This value appears to be remarkably reproducible on all the curves provided loss peaks do not overlap. It is indicated as a dashed horizontal line on each loss curve.

SHIFT OF THE α' PEAK

The origin of the α' peak on a loss curve has been attributed to a decrease of the θ value during damping measurements obtained when the sample is heated[1]. If a sample is pre-annealed before the damping measurements, the model predicts that this peak is shifted toward higher temperatures with decreasing θ_a values. It is possible to determine the condition of the thermal treatment in such a way that the related θ_a value is too low to be affected by further heating during the measurements. In that case, α' disappears from the loss curve.

Let us recall the annealing equation given in the first paper in this series[1]:

$$d\theta = 10^{-95}(T_a - \theta)\exp(0.7\theta - (3.2 \times 10^4/T_a))\,dt_a \quad (1)$$

which by numerical integration provides the θ_a value as a function of the annealing time t_a at constant annealing temperature T_a. The plot of θ_a *versus* $\ln t_a$ is given in *Figure 1*. This type of theoretical graph was presented previously[5] but was related to numerical values of the parameters which were slightly different from those used in equation (1). Let θ_{ir} denote the θ value of a sample prior to the annealing treatment and θ_{a1} a given value of θ_a. Provided $\theta_{ir} > \theta_{a1}$ the graph of *Figure 1* holds and a sample annealed during t_{a1} at T_{a1} will acquire the θ_{a1} value which does not depend on θ_{ir} (except perhaps in the very beginning of the annealing treatment). When $\theta_{a1} > \theta_{ir}$, the related annealing treatment does not affect θ_{ir}, if one excludes the T_a range from 140 to 150°C, i.e. around T_g.

The variation of θ as a function of the current temperature T of the damping test, is given by:

$$d\theta = 6 \times 10^{-94}(T - \theta)\exp(0.7\theta - (3.2 \times 10^4/T))\,dT \quad (2)$$

for the heating rate of 60 K/h used here. By numerical integration from $\theta = \theta_a$ curves giving θ *versus* T may be obtained. Examples are presented in *Figure 2*. Cold rolled samples 1 and 2, pre-annealed 2 h at 80 and 100°C fulfil the condition for the α' peak to appear according to *Figure 2*. The related heating loss curves a and b are given in *Figure 3*. Clearly the α' peak is shifted to higher temperatures with decreasing θ_a and becomes barely perceptible on curve b related to $\theta_a = 417.4$ K, which seems to be lower limiting value for the occurrence of such a peak. Full lines on *Figure 3* are theoretical. They were calculated using the expression of the loss tangent

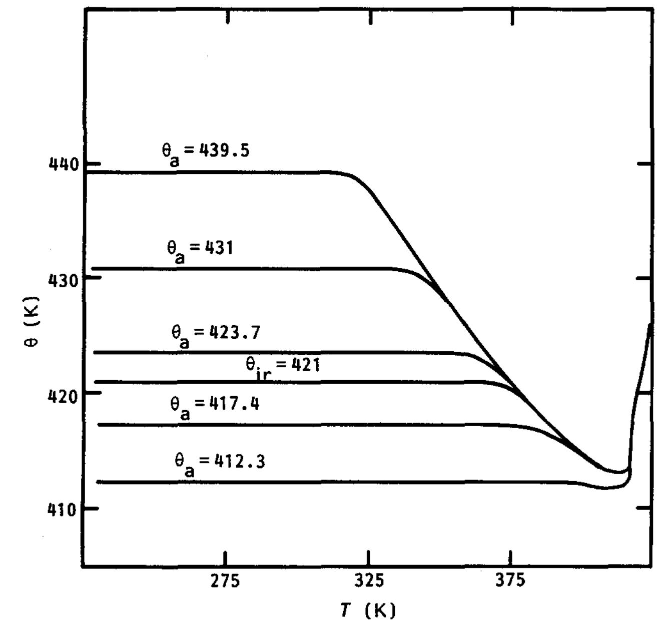

Figure 2 Plot of the calculated θ value as a function of the test temperature for samples having different thermal histories prior to the damping tests, including samples 1 to 4 and 7 to 9; equation (2) is used throughout

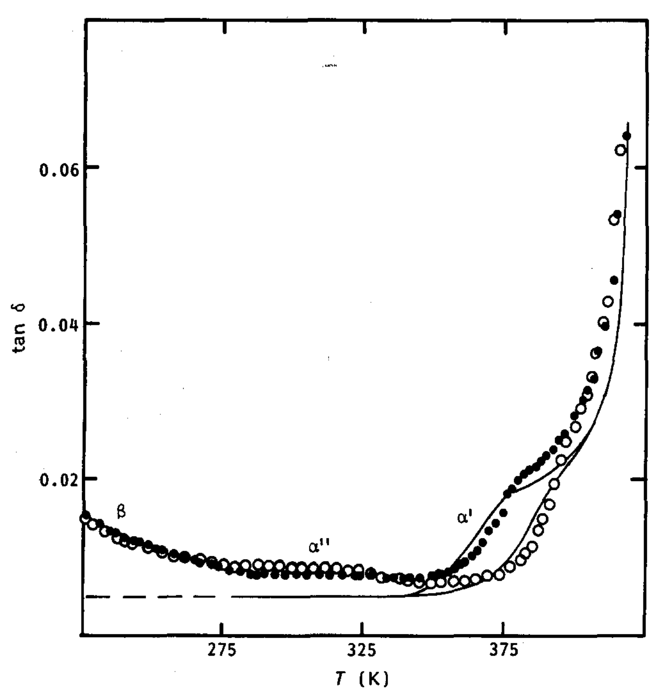

Figure 3 Loss curves related to samples 1 (●) and 2 (○) exhibiting both the α' and α'' peaks. Full lines represent the response of equation (3) associated with equation (1). The dashed line coincides with the background level

previously established[1]:

$$\tan\delta = 5.14\times10^{-3} + ((5.62/T)\times10^{4}) \times 10^{-115.2}\exp(0.83\theta-(3.8\times10^{4}/T))^{0.36} \quad (3)$$

and equation (2). These equations model the left side of the α peak, as in the first paper in this series[1]. The agreement with the data is satisfactory. At the left of the α' peak the data reveal another peak, called α'', which was not predicted by the model and not exhibited by the loss curves considered previously[1] where the tan δ value reached the background level between the β and α peaks. Coming back to *Figure 2*, it can be considered that samples characterized by a θ_a value between 413 and 411 K keep this value during the damping test. No noticeable θ decrease occurs and therefore no α' peak appears. Examples of heating loss curves related to samples 3 to 6 fulfilling this condition are given in *Figures 4* and *5* in which no α' peak can be discerned. Full lines on the graphs represent the response of equation (3), now associated with the following condition:

$$\theta = \theta_a = \text{constant} \quad (4)$$

with the θ_a value of the samples under consideration.

Let us point out that a pre-treatment leading to a low θ_a value on cold rolled samples completely recovers the rejuvenation effect produced by plastic deformation. Samples 3 and 4 (cold rolled) and samples 5 and 6 (as received), annealed under conditions leading to nearly equal θ_a values exhibit quite similar loss curves. In both cases, for curve a, damping measurements are performed immediately after the annealing treatments while for curve b, the samples were allowed to age at room temperature before the loss curve was taken. In both cases curve a exhibits an α'' peak which tends to be erased on curve b.

CYCLIC LOSS CURVES BETWEEN 225 AND 413 K

At the end of a heating loss curve, θ has reached a value between 411 and 413 K for the samples considered here according to *Figure 2*. If a loss curve is then taken from 413 to 225 K, no θ change can occur during the measurements and therefore no α' peak may appear. An example of such a loss curve related to sample 7 is given on *Figure 6* (curve b). No α' peak is discernible but an α'' peak appears. Curve a on this figure has been presented

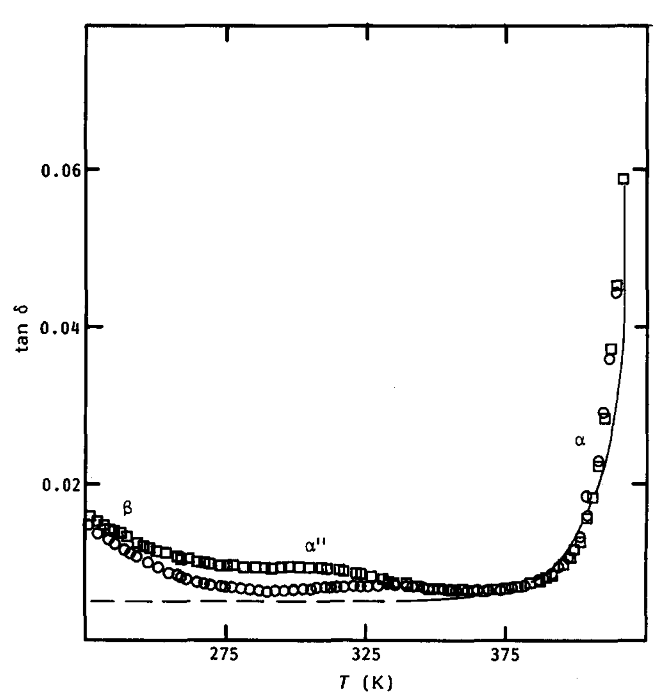

Figure 4 Loss curves related to samples 3 (□) and 4 (○) exhibiting both the α' and α'' peaks. Full lines represent the response of equations (3) associated with equation (1). The dashed line coincides with the background level

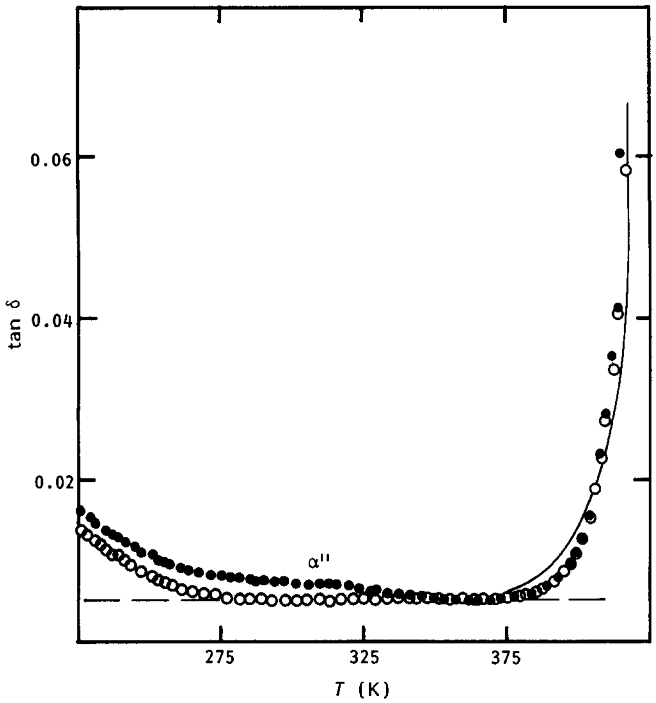

Figure 5 Loss curves related to samples 5 (●) and 6 (○). Full lines represent the response of equation (3) associated with equation (1). The dashed line coincides with the background level

previously[1]. Curves a and b constitute a heating and cooling cycle on the same sample. The α' peak appearing on curve a is not reversible. The cooling loss curve opposes the heating curve with regard to the occurrence of one peak or the other.

During a second heating and cooling cycle under the same conditions on the same sample, the loss curves prove reversibility; both curves coincide with curve b (same θ_a, same cooling rate).

From a theoretical point of view, apart from the α'' peak, a cooling loss curve does not differ from a heating curve related to the same θ_a value, provided this is low enough. Curve b on *Figure 6* can therefore be modelled using equations (3) and (4) with $\theta_a = 413$ K. The result is drawn as a full line on *Figure 6*.

Only one example of a cooling loss curve from 413 K is given because all such curves are identical, quite independent of the pretreatment of the sample related to the heating loss curve. Only the θ_a value (here, nearly the same for all the samples) influences such cooling curves, taken at the same frequency and cooling rate.

THE α'' PEAK

The α'' peak does not seem to depend directly on θ and therefore cannot be explained by our model at a first glance. However, let us grasp some peculiarities of this peak as they appear from our measurements.

α'' peak linked to cooling

The cooling loss curve from 140°C always exhibits the α'' peak which is also present on the heating loss curves of samples pre-treated at temperatures $T_a \geq 80°C = T_g - 65°C$ and cooled to room temperature before being tested.

But, first of all, the α'' peak is especially pronounced on the heating loss curves of samples quenched from above T_g. Such a peak has been considered by Struik[7] to be associated with the ageing effect observed on the creep compliance of quenched amorphous polymers. He has shown that in the case of PC, the height of this peak is more important after a quench of the sample from 155 to −150°C than after a cooling at 60 K/h within the same bounding temperatures[7,8]. In this aspect, the α'' peak seems to be related to free volume.

In *Figure 7*, we give the heating loss curve of sample 8, quenched and tested immediately after the quench

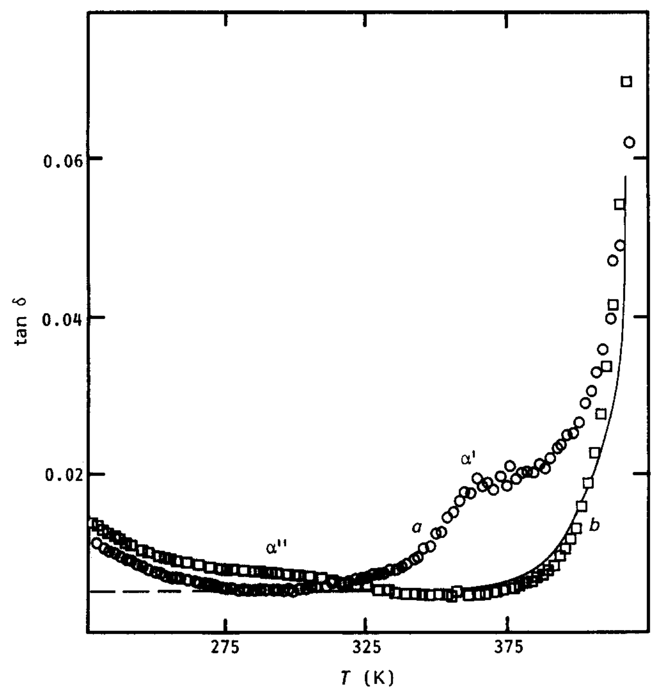

Figure 6 Example of a cyclic loss curve related to sample 7. Curves a (○) and b (□) represent the first run obtained on heating and the second run on cooling, respectively. The full line is theoretical

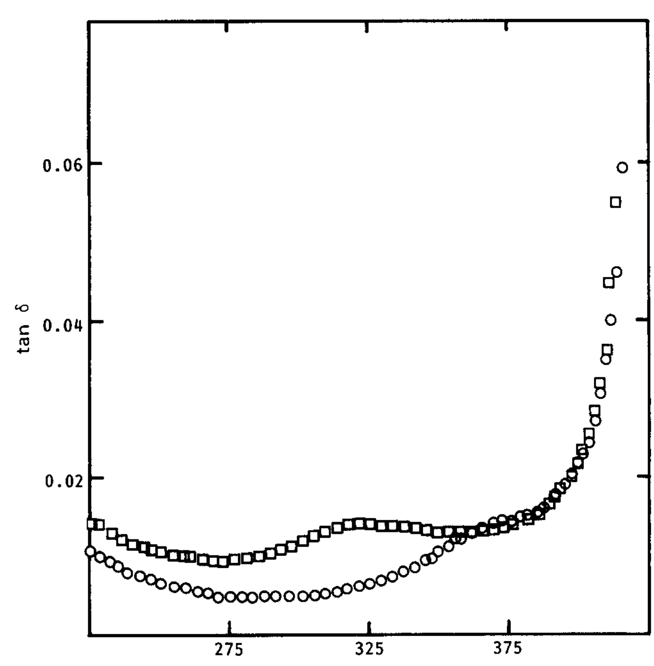

Figure 7 Loss curves obtained on quenched samples 8 (□) and 9 (○), not aged and aged for 6 years, respectively

(curve a). Between the β and α dispersions, a large broad peak is exhibited where we assume that α'' and α' merge.

α'' peak disappears with ageing

On curve b on *Figure 7* which is related to sample 9 which was quenched and aged for 6 years, the loss tangent reduces to the background level between 275 and 315 K. The α'' peak has vanished and the α' peak appears distinctly. Curve b on *Figures 4* and *5* are other examples which show that ageing at room temperature erases the α'' peak. The case of sample 6 with a low θ_a, aged 6 years, is particularly relevant (curve b on *Figure 5*). Neither the α' nor α'' peaks are exhibited and the value of the loss tangent coincides with the background level over a range of 100 K, from 275 to 375 K.

The α'' peak seems to be the only peak affected by ageing, as not only is the β peak insensitive to ageing[8], the α and α' peaks are also unaffected, as shown by the present measurements.

α'' peak erased by plastic deformation

It is worth noting that the α'' peak is completely erased from the heating loss curves related to samples rejuvenated by plastic deformation. Examples of such curves may be found in reference 1. We have also checked that the heating loss curve of cold rolled samples is identical to that of a sample first quenched and then cold rolled. No α'' peak appears.

ANNEALING AND AGEING

Physical ageing is defined by Struik[7] as a gradual approach to equilibrium under which many properties of amorphous polymers are changing with time. According to this author the temperature range in which ageing occurs (the ageing range) extends from T_β to T_g.

It has been emphasized previously[6] that such a definition covers a number of effects with different kinetics and which are not always quantitatively related to each other, for example, enthalpy relaxation and specific volume decrease[9] or free volume and embrittlement due to annealing[10]. It was then proposed to use the term ageing to describe the phenomenon extensively studied by Struik[7] using quenched samples and revealed by creep measurements at low stresses or damping measurements near but above T_β, and to characterize as annealing the effects of thermal pre-treatments near but below T_g on enthalpy relaxation and on the mechanical properties under the action of high stresses.

Using the concept of structural temperature, a clearer definition of both phenomena may be advanced: the annealing effects derive from a decrease of the θ value of the sample, while ageing effects occur at constant θ value. Our model[1–5] refers to annealing. The increase of the yield stress, the enthalpy relaxation, the occurrence and the shift of the α' peak on the heating loss curve have been correlated with the θ decrease.

Following our point of view, the annealing temperature range depends on the mechanical and thermal histories of the sample and must be defined as the range where the θ value of the sample (rejuvenated or not) is susceptible to decrease. Let us point out that for samples rejuvenated by plastic deformation and therefore characterized[5] by $\theta_{ir} = 460$ K, room temperature is included within the annealing range according to the graph in *Figure 1*. In contrast, the θ_{ir} of quenched samples, previously estimated[5] to reach about 421 K, is far too low to be affected by remaining at room temperature, even for 6 years. In the latter case ageing, but not annealing, can occur at room temperature.

However, the θ_{ir} of a quenched sample is high enough to be affected by heating during damping tests as shown in *Figure 2*. As a consequence, the related heating curve must exhibit an α' peak. This is merged with the α'' peak on the heating loss curve of a freshly quenched sample, but well isolated on the curve related to an aged quenched sample (see *Figure 7*).

The α'' peak of a quenched sample appears then to be affected by ageing at room temperature as opposed to the yield stress which has been found independent of ageing over 3 years[6]. This fact is fully confirmed by yield measurements performed on samples 8 and 9 with the same thermal histories as those related to curves a and b on *Figure 7*. No noticeable variation can be discerned, over 6 years later. However, deformation at yield is lower for sample 9 because the related Young's modulus, dependent on ageing, is higher.

Is the vanishing of the α'' peak the key to ageing of quenched samples at room temperature? This is difficult to say in so far as the peak is not modelled, but if that was the case, quenched PC should no longer age after a few years. In any case, the α'' and α' peaks seem to be affected by ageing and annealing, respectively.

Both peaks are located between the β and α dispersions and are therefore particularly discernible on the loss curve of PC samples because the β peak is well separated from the glass transition. For polymers whose α peak partially overlaps the β peak, some complications will arise.

CONCLUSIONS

The loss curve of PC is satisfactorily modelled in the low temperature side of the α peak, whether or not this curve entails an α' peak and whether it is measured on heating or cooling the sample. The concept of structural temperature may be useful for characterizing annealing and ageing phenomena: annealing effects derive from a decrease of θ, while ageing occurs at constant θ value. The data indicate that the α and α' peaks do not appear to be affected by ageing while the α'' peak does.

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