Influence of mechanical deageing and subsequent physical ageing on the loss curve of polycarbonate

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Mechanical damping spectra have been measured between the β and α transitions on specimens of polycarbonate deformed by traction or cold pressing in the pre-yield region and left thereafter to recover at room temperature for given periods of time. The deformation is always applied to samples previously aged for 2 years at room temperature after quenching from above the glass transition temperature. The deageing effect induced by small applied deformation is apparent on the damping spectra by the enhancement of two peaks: the α' peak precursor of the α transition and the α'' peak partially merging with the α' peak and at a lower temperature with the β loss process. Several experimental parameters such as the mode, amount of deformation and the recovery time after release of the stress are chosen to investigate the enhancement conditions and the relaxation behaviours of the α' and α'' loss processes. The location of the α' peak is well understood in terms of a classical formalism together with the hypothesis that a change in the structural temperature of the sample occurs as a result of the small deformation. At present, no interpretation of the α'' loss process has been proposed, but it is obvious from the present data that the existence of a strain-induced α'' loss process contributes significantly to the deageing and further physical ageing effects probed in the vicinity of room temperature by mechanical damping measurements.

(Keywords: polycarbonate; mechanical deageing; damping)

INTRODUCTION

This paper investigates the origin of the decrease in viscosity of polycarbonate (PC) specimens after release of a stress applied in the non-linear range of deformation before yielding[1,2]. The observed decrease in viscosity due to mechanical treatment is commonly termed rejuvenation[2-4] or deageing[2]. After deformation a progressive increase in viscosity takes place, whether the applied stress is maintained or suppressed and this process is termed physical ageing[1-3].

The term deageing is used in this paper to describe the effect of a small deformation for which the measured decrease in viscosity does not alter significantly the yield strength as outlined in this work and the term rejuvenation will be reserved to describe the mechanical treatment that produces a decrease in the yield stress[5]. Such a terminological distinction may be compared with the different terms used by Bauwens[6] to qualify the effect of thermal treatments on the mechanical behaviour of quenched PC: ageing is used to qualify the effect of treatments performed near room temperature that do not affect the yield strength, whereas annealing refers to thermal treatments between the glass transition temperature (T_g) − 50 K and T_g in which an increase of the yield stress is observed.

The origin of mechanical deageing and further ageing effects is not yet well established, the main point of controversy lies in the existence or not of a change of the structural state of the specimen[2,3,7,8]. It is usually emphasized that mechanical deageing results either from a strain-induced change of the average free volume or through modifications in the distribution function of the free volume[3,7], the subsequent physical ageing being in this case attributed to the relaxation of the excess free volume. It has also been shown that the increase of viscosity may occur during the first stage of physical ageing from the non-linear viscoelastic response of the sample[1] in agreement with the interpretation of Lee and McKenna[8].

In the present work, we have chosen to investigate the mechanical deageing phenomenon and further physical ageing by taking mechanical loss spectra of strained PC specimens; such measurements taken in a temperature range located between the β and α transitions are indeed very sensitive to the cooling conditions[3,9] as well as to plastic deformation[4,10]. From the loss spectra presented in this study it appears that mechanical deageing produced by a small deformation enhances the presence of two peaks: the α' peak also observed by Bauwens-Crowet and Bauwens[4] on the loss curve of PC samples annealed after high plastic deformation and modelled as the precursor of the α transition; the other enhanced peak is the α'' peak identified by the same authors and correlated in their study[9] to the cooling conditions of the sample from near or above T_g.

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EXPERIMENTAL

Experiments were carried out on test specimens machined from extruded sheets of Makrolon (bisphenol A polycarbonate, Bayer) 0.1 cm thick. All samples were heat treated above T_g (1 h at 165°C), quenched in iced water and thereafter left to age at ambient temperature. Mechanical deageing experiments were always performed on samples aged for at least 2 years at room temperature, after which the viscosity of the samples was constant during the time-scale used to investigate the viscosity changes induced by deformation and further recovery.

Mechanical deageing was accomplished mainly by tensile deformation performed at room temperature on an Instron tensile machine at a strain rate $\dot{\varepsilon}$ of $5.1 \times 10^{-6}\,s^{-1}$. Strip samples ($65 \times 5 \times 1\,mm^3$) were deformed to different applied strains ε_a (3, 2.3, 1.5 and 0.9%) in the non-linear range of deformation but below the yield point. Thereafter the stress was removed and the samples were left to age at ambient temperature or, for a few samples, at 8°C during given delay times after which the residual strain was measured. The engineering tensile strains were deduced from the length change in the non-linear range divided by the initial length. A few specimens ($55 \times 5 \times 1\,mm^3$) were cold pressed. As the maximum applied deformation could not be measured, the instantaneous residual deformation, ε_i, was evaluated after removal of the stress. The residual strain measured after several delay times at room temperature was deduced from the thickness change of the sample. The code number of the specimens and their mechanical deageing and strain recovery histories are given in *Table 1*.

The deaged specimens were submitted after several recovery times to internal friction measurements at two different frequencies (0.1 and 1 Hz) as a function of temperature usually from −50 to ~150°C, at a heating rate of 20 or 60 K h^{-1}. The mechanical damping measurements were performed on a torsional Metravib low frequency microanalyzer. Some specimens previously deaged by traction or cold pressing as described above were thereafter submitted to a second deformation by traction ($T = 23$°C, $\dot{\varepsilon} = 2.2 \times 10^{-4}\,s^{-1}$) to investigate the influence of prior deformation and recovery on the tensile curve shape before yielding and on the tensile yield strength. Such tests were carried out on small dumb-bell shaped samples having a width in the narrow range of 3 mm, a thickness of ~1 mm and a straight length of 15 mm.

RESULTS

Tensile curves

Tensile curves of different specimens are plotted in *Figure 1* to illustrate the known influence of ageing at ambient temperature[6,11] and the effect of small deformation on the yield stress level and on the shape of the tensile curve below the yield point. The tensile tests were carried out on samples submitted to the different treatments listed in *Table 2*. It may be seen from the curves in *Figure 1*, and from the results of *Table 2* that ageing at ambient temperature as well as the mechanical deageing applied do not significantly affect the yield stress level measured during a second deformation by traction. On the other hand, the shape of the tensile curve before yielding is influenced: ageing reduces the deformation before yielding (*Figure 1a*), whereas samples tested 20 h

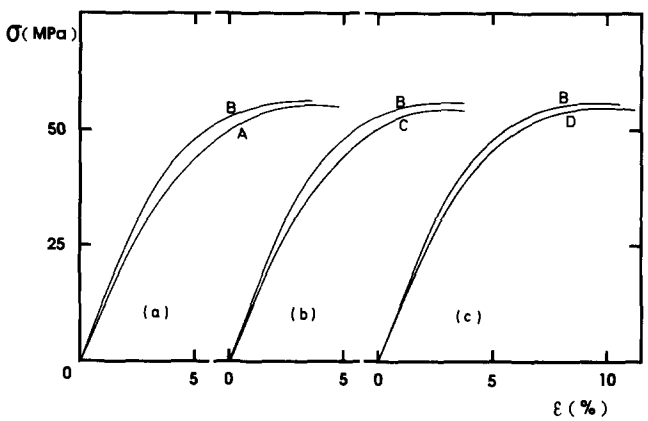

Figure 1 Influence of ageing and further mechanical deageing on the stress–strain curves of PC samples of *Table 2* submitted to a tensile test at $T = 23$°C and $\dot{\varepsilon} = 2.2 \times 10^{-4}\,s^{-1}$. Comparisons are made between the tensile curves of different samples: curve A, quenched sample; curve B, well aged sample; curves C and D, prior well aged samples deaged, respectively, by traction and by cold pressing in the pre-yield regime and left to recover for 20 h at room temperature

Table 1 Samples submitted to mechanical damping measurements

Sample	Ageing time (years)	Deageing conditions[a] (%)	Recovery time (h)	Recovery temperature (K)	Residual strain (%)	Structural temperature (K)
1	7 days					
2	2					415
Traction						
3	2	3	7 days	RT[b]	0.27	421.8
4	2	3	20	RT	0.42	425.4
5	2	3	20	RT	0.40	425.7
6	2	2.3	20	RT	0.20	420.2
7	2	1.5	20	RT	0.07	416.8
8	2	0.9	20	RT	0.05	416.3
9	2	3	20	281	0.54	428.9
Cold pressing						
10	2	3	20	RT	2.8	431.7
11	2	3	4 months	RT	1.5	424.4

[a]Traction, ε_a values; cold pressing, ε_i values
[b]RT, room temperature

Table 2 Samples of *Figure 1*

Sample	Ageing time (years)	First deformation	Recovery time (h)	Tensile yield stress σ_Y (MPa)
A	20 h			55.5
B	2			56.2
C	2	Traction to $\varepsilon_a = 3\%$	20	54.5
D	2	Cold pressing $\varepsilon_i = 3\%$	20	55.3

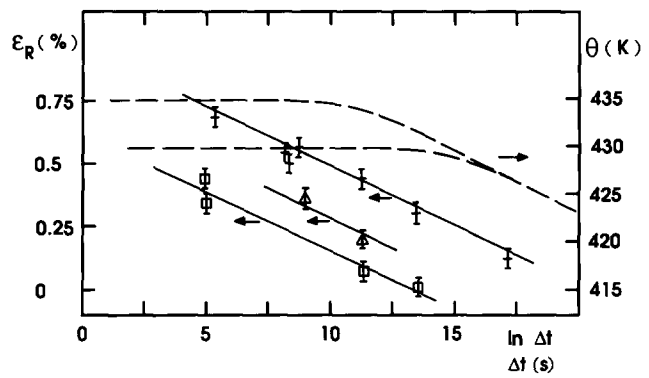

Figure 2 Plot of tensile residual strain *versus* the logarithm of the time Δt elapsed at room temperature after deformation to tensile strains of 3% (+), 2.3% (△) and 1.5% (□). On the right vertical axis are plotted the corresponding structural temperatures θ derived from relation (8). The broken lines are computed from equation (5) for two specimens with different structural temperatures. The parameters used are those adjusted to fit equation (7) to the temperature dependence of θ in the domain of the α' plateau

after predeformation, either by traction (curve C) or by cold pressing (curve D), present a greater strain before yielding than in their initial state of well aged samples (curve B).

Time dependence of the residual strain of deaged specimens

After deformation in the non-linear range before yielding, the samples were allowed to recover, usually at room temperature under zero stress for long periods, after which the residual strain was measured. In *Figure 2*, the residual tensile strain ε_R is plotted *versus* the logarithm of the elapsed time Δt, after tensile deformations up to 3, 2.3 and 1.5%. Error bars are drawn taking account of the uncertainty in the strain measurements. The linear dependence was in agreement with previous results[1] from tensile creep recovery experiments on PC. A set of parallel straight lines may be drawn to fit the data at different strain levels.

The residual tensile strain ε_R can be expressed by:

$$\varepsilon_R = -K \ln \Delta t + B \qquad (1)$$

where B and K are constants.

The value of K derived from the data of *Figure 2* is 0.46, a value consistent with the results of reference 1 where a mean value of 0.42 was obtained.

Mechanical damping curves

Effect of the elapsed ageing time after quenching. Let us briefly recall and illustrate the effect of the ageing time on the dynamic mechanical spectra of quenched specimens[9]: *Figure 3* displays the damping curves of two specimens aged, respectively, for 7 days and 2 years at room temperature after quenching. Both curves are characterized by an α' peak or plateau, precursor of the α glass transition. Below ~310K, the higher damping level observed for the specimen aged for 7 days results from the presence of another peak, the α'' peak identified by Bauwens-Crowet and Bauwens[9] as being linked to the cooling conditions from near or above T_g. It may be noted that when the ageing time is extended to 2 years the α'' peak has practically disappeared. In this last case, a very small α'' peak still remains but the damping level is very close to the background level taken as the mean minimum value reached for different specimens and drawn as a horizontal full line. The measured background levels equal to 6.8×10^{-3} at 0.1 Hz and 5×10^{-3} at 1 Hz are denoted by $\tan \delta_B$ on the damping spectra. On the curve referring to the specimen aged for 7 days, the α'' loss process partially merges with the α' peak.

Mechanical deageing of samples aged for 2 years. Throughout this paper, the mechanical deageing and further ageing effects are only investigated on specimens previously well aged (i.e. aged for 2 years after quenching), so that there will be no interference between the physical ageing phenomena that have occurred after quenching and the physical ageing taking place after mechanical deageing by deformation.

We have varied several experimental parameters such as the mode of deformation, the time elapsed after deformations realized in the same conditions, the amplitude of the applied strain and also for a few samples the temperature at which the specimen is left to recover after straining. The damping spectra of the deaged samples are usually compared with the loss curve of a well aged specimen (drawn as a broken line). Comments about the observed influences are given below for each figure. The code number of the loss curves refers to the code number of each specimen given in *Table 1*. The presented data are mainly given for damping measurements performed at a frequency of 0.1 Hz and a heating rate of 20 K h^{-1}, conditions for which the influences of the investigated parameters are the most noticeable.

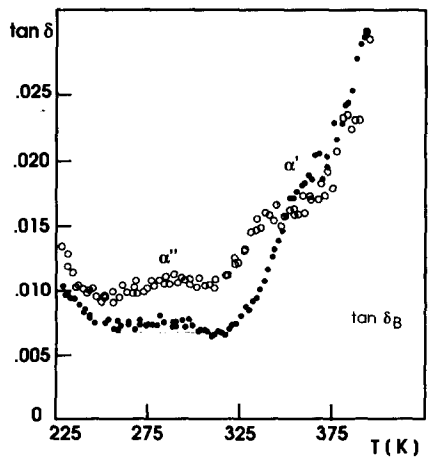

Figure 3 Mechanical damping spectra taken at a test frequency of 0.1 Hz and a heating rate of 20 K h^{-1} on samples 1 (○) and 2 (●) aged, respectively, for 7 days and 2 years at ambient temperature after quenching from above T_g. Both curves display the α'' and α' peaks

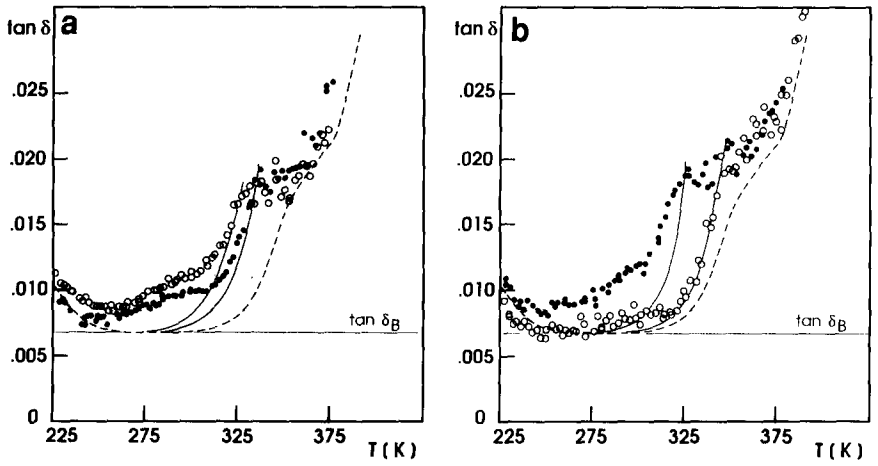

Figure 4 (a) Loss spectra of samples 3 (●) and 4 (○) submitted to the same applied tensile strain and different recovery times. (b) Loss spectra of samples 10 (●) and 11 (○) deformed to the same amount by cold pressing and left to recover for different times. The broken line refers to a well aged sample. All spectra are taken at a test frequency of 0.1 Hz and at a heating rate of 20 K h^{-1}. The solid lines are theoretical and calculated for each sample using equation (6) and related structural temperature given in *Table 1*

Figures 4a and *b* display the damping spectra of samples deformed, respectively, by traction and by cold pressing. After deformation, the specimens were left to recover at room temperature for different times ranging between 2 h and 4 months. The residual strains are given in *Table 1*. From the comparison of the data with the loss curve of a well aged sample, it appears clearly that mechanical deageing enhances the α' and α'' loss processes independently of the mode of deformation; the α' peak is shifted to lower temperatures and the amplitude of the α'' peak is raised. With increasing delay time after deformation the α' peak is shifted to higher temperatures, whereas the damping level in the α'' domain decreases.

Figure 5 shows the damping spectra of four samples strained by traction at different strain levels in the pre-yield region. Thereafter, all samples were left to recover under the same conditions, 20 h at room temperature. Such experiments were carried out to separate the influence of the strain from the effect of the recovery time. It can be seen that the temperature at which the α' peak appears decreases with an increase in the applied strain. In spite of the great scatter of the data in this region, it may be seen that the α' plateau level increases with increasing applied strain. In the low temperature domain of the α'' peak, where the α' peak does not merge with the α'' loss process, no significant difference is observed between the damping curves of the four deaged specimens, showing that in this domain and for the range of applied strains, the amplitude of the α'' loss process is independent of the applied as well as of the residual strain and appears to be mainly influenced by the recovery period Δt as shown also by the data in *Figures 4a* and *b*.

Figure 6 compares the damping spectra of specimens deformed by traction (curve 4) or cold pressing (curve 10) in the pre-yield regime. Both strained samples were left to recover at room temperature for 20 h. A greater shift of the α' plateau to lower temperatures and a higher plateau level is observed for the cold pressed sample. Note, the α'' peaks are very close appearing to be little influenced by the mode of deformation or by the amount of applied strain.

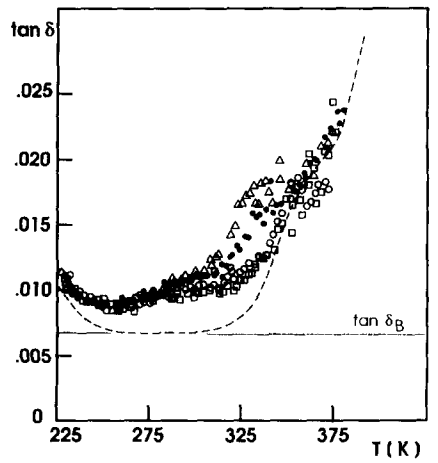

Figure 5 Loss spectra of samples 4 (△), 6 (●), 7 (○) and 8 (□) deformed to different strain levels and left to recover for 20 h at room temperature. The broken line is the loss curve of a well aged sample. The measurements were made at a test frequency of 0.1 Hz and at a heating rate of 20 K h^{-1}

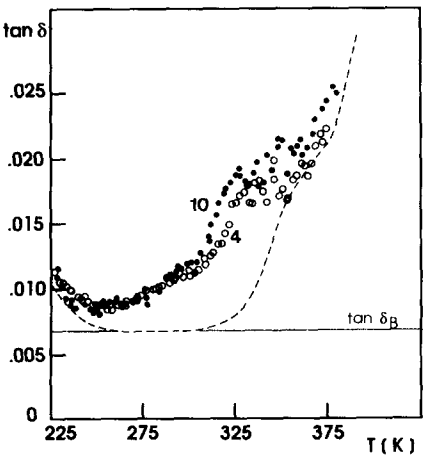

Figure 6 Loss spectra of samples 4 (○) and 10 (●), respectively, deaged by traction and by cold pressing and both allowed to recover for 20 h. The broken line refers to a well aged sample. The measurements were made at a test frequency of 0.1 Hz and at a heating rate of 20 K h^{-1}

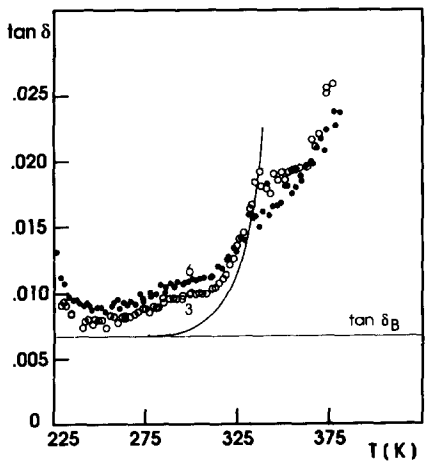

Figure 7 Mechanical damping spectra of samples 3 (○) and 6 (●) denoting close residual tensile strains resulting from different histories. The test frequency is 0.1 Hz and the heating rate is 20 K h^{-1}. The solid line is theoretical and derived from equation (6) where the structural temperature is taken as 421.8 K

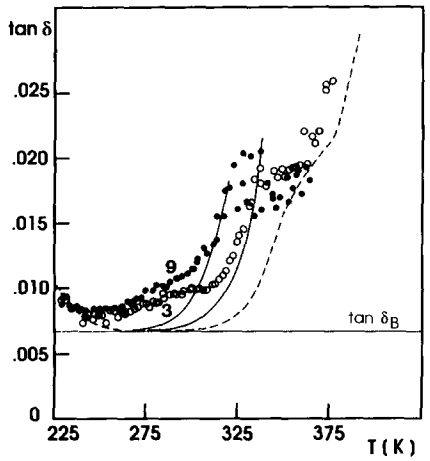

Figure 8 Loss spectra of samples 3 (○) and 9 (●) deformed to the same extent and left to recover for the same period (7 days), but at two temperatures (23°C for sample 3 and 8°C for sample 9). The broken line is the loss curve of a well aged sample. The curves were obtained under a test frequency of 0.1 Hz and at a heating rate of 20 K h^{-1}. The solid lines are calculated using equation (6) with structural temperature values referring to each sample (*Table 1*)

Figure 7 displays the loss curves of two samples submitted to different tensile deformations and to different recovery times leading to close values of residual strains (*Table 1*). Comparison of the loss curves in *Figure 7* shows that the onset temperature of the α' peak on both curves is very close, whereas the level of the α'' peak is lower for the specimen submitted to a longer recovery period after deformation. These results show clearly that the location of the α' peak may be linked to the residual strain independently of the recovery period, whereas the amplitude of the α'' peak depends mainly on the time elapsed during recovery under zero stress.

Figure 8 shows loss spectra of two specimens deformed by traction to a strain equal to 3% and left thereafter to recover for 7 days at two temperatures, 23°C (sample 3) and 8°C (sample 9). After recovery at 8°C the onset of the α' peak is located at a lower temperature, whereas the α'' peaks of both specimens coincide up to 260 K; above this temperature, the higher damping level of curve 9 in the α'' domain results from the onset of the α' peak as will be shown in further data analysis. A decrease of the ageing temperature from 23 to 8°C does not slow down the relaxation process of the α'' peak, in contrast to what happens for the α' loss process.

DATA ANALYSIS

On the basis of the above results, we have based our data analysis on the hypothesis that between the β and α transitions, the mechanical damping spectra of well aged PC specimens submitted to small deformations results from the superposition of two peaks, both enhanced by the deformation but whose relaxation is not governed by the same process.

α' peak

To describe the α' peak behaviour observed in the present work, we have extended to our data a formalism developed and successfully applied by Bauwens-Crowet and Bauwens[4,5] to the data of PC specimens rejuvenated by high deformation and annealed below T_g.

Basic equations. Let us recall briefly the basic ideas and the derived equations of the model proposed in references 4 and 5. The viscosity η of the polymer may be expressed through an Eyring type relation yielding at small stresses the following expression:

$$\eta = AT/2\gamma_0 v_d \exp[(\Delta S(\theta)/R) - (Q_d/RT)] \quad (2)$$

where γ_0 is the elementary shear, Q_d and v_d are, respectively, the activation energy and the frequency factor containing the entropy factor related to the initial structural state of the specimen, the subscript d referring to the deformation process, A is a constant and T is the test temperature. $\Delta S(\theta)$ is the change in the configurational entropy linked to the structural temperature θ which is the chief parameter in this model and denotes the temperature at which the structural state of the sample associated with a given treatment would be at equilibrium.

In the high frequency tail of the α transition, the mechanical damping may be described using a Williams–Watts formulation[4]:

$$\tan\delta = (G/2\pi f\eta)^m \quad (3)$$

where f is the frequency of the damping test, G is the shear modulus and m is a distribution parameter taken as a constant as in Struik's analysis[3].

The α' peak location on the damping spectrum is linked to the structural temperature θ. The configurational entropy $\Delta S(\theta)$ is taken as proportional to the structural temperature θ:

$$\Delta S(\theta)/R = C'\theta \quad (4)$$

A decrease of the structural temperature θ of a sample in a metastable state will result from an annealing thermal treatment, whereas an increase of θ will be produced by mechanical rejuvenation[13].

Damping measurements at increasing temperature produce an involuntary thermal treatment leading to a decrease of the structural temperature that may be calculated though a Davies and Jones type equation

yielding[4]:

$$d\theta = v_a(T_a - \theta)\exp(C'_a\theta - Q_a/RT_a)dt_a \quad (5)$$

where subscript a refers to the applied thermal treatment, and Q_a and v_a are, respectively, the activation energy and the frequency factor related to the annealing process carried out at a temperature T_a for a time t_a.

Let us assume in the present work that a small deformation applied in the non-linear pre-yield regime results for previously well aged samples in an increase $\Delta\theta$ of the structural temperature and that ageing at ambient temperature will produce a decrease of θ in similar ways as do rejuvenation and annealing treatments.

Numerical expression of the α′ peak. (1) Value of the dispersion parameter m related to the α' loss process. The dispersion parameter m of relation (3) may be easily deduced from the plateau levels of the α' peaks of a given specimen taken at two frequencies and at the same heating rate. As an example of the influence of the test frequency on the α' plateau level, the damping curves of specimen 3 are plotted in *Figure 9*. For all samples deformed by traction a mean m value of 0.21 is deduced, a value consistent with the parameter $m=0.22$ derived in a previous paper for PC samples undergoing tensile creep recovery[1]. A higher value equal to 0.27 is obtained for the specimens deaged by cold pressing. Let us mention that a constant dispersion parameter equal to 0.36 has been evaluated for specimens annealed after rejuvenation by large plastic deformation[4].

(2) Structural temperature θ of deformed samples. To obtain the structural temperature of each specimen, let us take in a first approach the value of θ characterizing the structural state of the sample at the onset of the α' plateau; below this temperature a very small decrease of θ with rising temperature takes place during damping measurements[4]. The θ values given in *Table 1* are adjusted to fit the damping data at the onset of the α' plateau to the tan δ expression given by relation (3); taking account of equations (2) and (4), with the same numerical values of most parameters used in reference 9, tan δ may be

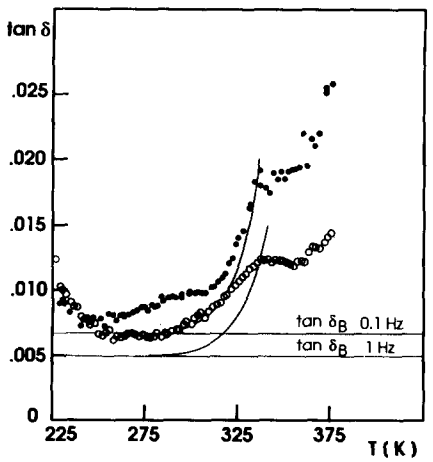

Figure 9 Loss spectra of sample 3 submitted to damping measurements at two testing frequencies, 0.1 Hz (●) and 1 Hz (○), but at the same heating rate of 20 K h^{-1}. The solid lines are derived from equation (6) taking account of the related test frequency and of the structural temperature given in *Table 1*

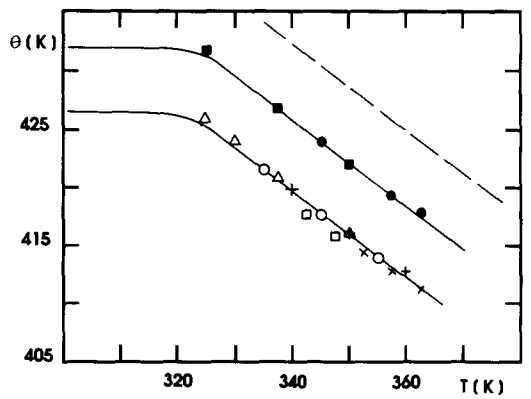

Figure 10 Temperature dependence of the structural temperature θ adjusted to fit relation (6) to the data in the α' plateau domain for samples 3 (+), 4 (○), 6 (×), 7 (□), 9 (△) deaged by traction and samples 10 (■) and 11 (●) deaged by cold pressing. The broken line is taken from reference 4 and derived from equation (7) with three parameters adjusted to fit d.s.c. data of PC specimens annealed after high plastic deformation. The solid lines are calculated using relation (7) where one parameter of the three has been adjusted for each kind of deaged specimen

expressed for a given test frequency f by:

$$\tan\delta = \tan\delta_B + [(5.62/fT)\times 10^{-111.2} \times \exp(0.83\theta - 3.8\times 10^4/T)]^m \quad (6)$$

The values of the dispersion parameter are evaluated in the present work: $m=0.21$ (deageing by tensile strain) and $m=0.27$ (deageing by cold pressing). The numerical values of the other parameters taken from reference 9 and used in relation (6) are: $G=10^3$ MPa, $Q_d=76$ kcal mol^{-1}, $C'_d=0.83\ K^{-1}$, $\gamma_0 v_d = 10^{115.2}\ s^{-1}$ and $A=5.7\times 10^{-3}$ MPa K^{-1}. The theoretical loss curves derived from relation (6) with θ values from *Table 1* are drawn on several damping spectra as a full line in the temperature range below the α' plateau.

(3) Temperature dependence of the structural temperature θ in the plateau domain of the α' peak. The data of *Figure 10* give for some specimens the temperature dependence of θ in the range of temperature corresponding to the α' plateau. The structural temperatures have been adjusted to give the best fit between the data obtained for each specimen at two frequencies and the theoretical damping expressed by relation (6). All θ values derived in the present work lie on two straight lines parallel to the theoretical broken line, reported from reference 4. The theoretical plot of θ *versus* the test temperature T at a constant heating rate v has been derived from equation (5) and is expressed as follows:

$$d\theta = v_a v^{-1}(T-\theta)\exp(C'_a\theta - Q_a/RT)dT \quad (7)$$

with the numerical values of the parameters adjusted to fit differential scanning data of samples annealed after rejuvenation[12]: $v_a = 10^{-95}\ s^{-1}$, $C'_a = 0.7\ K^{-1}$ and $Q_a = 64$ kcal mol^{-1}. From the parallelism between the data and the theoretical line taken from reference 4, it may be deduced that the same numerical value applies for the parameter C'_a, i.e. $0.7\ K^{-1}$. The other two parameters need to be adjusted. We have chosen to take an activation energy Q_a equal to 64 kcal mol^{-1}, a value successfully used in references 4 and 5 to describe the annealing process of specimens previously rejuvenated by cold pressing and by torsion above the yield point, so that

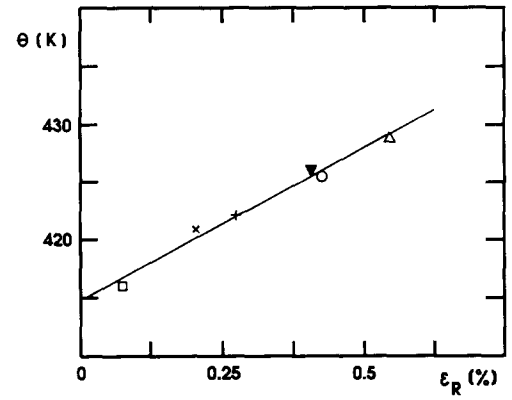

Figure 11 Structural temperatures θ of the specimens *versus* the residual tensile strains ε_R. θ is derived from the fit of relation (6) to the damping data at the onset of the α' plateau for samples 3 (+), 4 (○), 5 (▼), 6 (×), 7 (□) amd 9 (△)

the only adjusted annealing parameter in the present work is the pre-exponential factor: $\nu_a = 10^{-91.8}\ s^{-1}$ for the tensile strained specimens and $\nu_a = 10^{-93.6}\ s^{-1}$ for the cold pressed ones.

Link between the residual strain and the structural temperature. By plotting the derived structural temperature θ *versus* the tensile residual strain ε_R (*Figure 11*), a linear dependence is observed. From the data of *Figure 11*, θ may be expressed by

$$\theta = 415 + 26.5\varepsilon_R \qquad (8)$$

where ε_R is given as a percentage.

Let us recall that the residual strain depends linearly on the logarithm of the elapsed time (*Figure 2*), and, as a consequence of relationship (8), the structural temperature θ will also depend linearly on the logarithm of the time for recovery at ambient temperature. Such dependence may be predicted in a given range of time from an equation like relation (5) where the rate of change of θ depends exponentially on θ. We have plotted in *Figure 2* the structural temperatures associated with the measured tensile residual strains following relation (8). To describe the time dependence of θ at room temperature, equation (5) is used with the parameters derived to fit the temperature dependence of θ in the range of the α' plateau, the time t_a of equation (5) is here expressed by Δt the time elapsed after deformation.

The theoretical curve is drawn in *Figure 2* as a broken line. It may be seen that equation (5) will be convenient to describe the time dependence of θ taking the same parameter $C'_a = 0.7\ K^{-1}$ as used in the α' plateau range, but to predict the observed decrease of θ at room temperature for short ageing times, further recovery experiments carried out at different temperatures are needed to evaluate the two other appropriate parameters of relation (5).

α'' peak

First of all let us recall that it appears clearly (*Figures 4–10*) without any deconvolution of the α' and α'' loss processes that the amplitude of the α'' peak at low temperature is mainly governed by the time elapsed after deformation, no major effect of the applied or residual strain may be seen. It may also be observed (*Figure 12*) that the α'' loss process is, like the slope of the α' peak[4], independent of the heating rate, the damping measurements reported in *Figure 12* being performed at the same frequency.

Modelling of the α' peak allows a deconvolution of the damping spectra between the β and α transitions. In the range of temperature explored, the α'' peak may be obtained for each deaged specimen by subtracting from the loss curve at low temperature, the right tail of the β peak of a well aged PC sample (drawn as a broken line on several damping spectra) and at higher temperatures the modelled α' peak drawn as a solid line.

Due to the low damping level in the α'' domain with regard to the data scatter, only major changes in the shape of the α'' peak may be taken into account to illustrate the influence of some experimental parameters. After deconvolution of the damping spectra, we have retained the α'' peaks related to three different specimens, the damping data being taken for each specimen at two frequencies (1 and 0.1 Hz) and at a heating rate of 20 K h^{-1}. The three specimens were submitted to a tensile strain of 3% and thereafter left to age following the programme reported in *Table 1*. From the examples reported in *Figure 13* it appears that: there is a shift of the maximum of the α'' peak by increasing the frequency

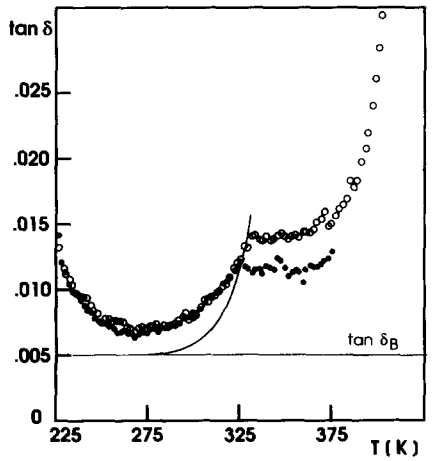

Figure 12 Loss curves of samples 4 (●) and 5 (○) submitted to the same mechanical deageing and further recovery treatments. The loss curves are taken at the same frequency (1 Hz) but at two heating rates, respectively, 20 K h^{-1} (●) and 60 K h^{-1} (○). The full line is calculated from relation (6) where the structural temperature is taken as 425.5 K

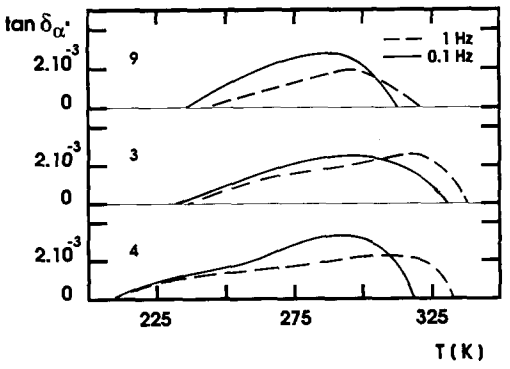

Figure 13 α'' peaks derived from the deconvolution of the loss curves of samples 3, 4 and 9 tested at two frequencies and at the same heating rate of 20 K h^{-1}

from 0.1 (solid line) to 1 Hz (broken line); the onset temperature of the α'' peak after a recovery period of 20 h lies on the right tail of the β peak below the domain of temperature usually explored in this work. The onset temperature lies in a range of ~210–215 K at both frequencies (sample 4); the extension of the recovery period to 7 days produces mainly a decrease of the amplitude of the left tail of the α'' peak as may be deduced from a comparison of curves 3 and 4; a decrease of the recovery temperature from 25 (sample 3) to 8°C (sample 9) does not slow down the relaxation process of the α'' peak, in contrast to what occurs for the α' peak (*Figure 8*).

At the present time no model for the α'' loss process can be proposed. Further experiments are needed as this work is limited to one kind of PC and a relatively narrow range of applied strains. Let us however point out that the conditions enhancing the α'' peak also produce either an excess of free volume fraction, e.g. cooling from near or above T_g[14] or affect the distribution function of the free volume, as shown by small-angle X-ray measurements on cold-drawn PC specimens[15]. Understanding the origin of the α'' loss process and a possible coupling with the free volume fraction requires further research.

DISCUSSION

The use of the formalism of reference 4 allows us to easily derive the slope of the α' peak related to lightly deformed specimens. However, some results deduced in the present paper from the data analysis of the α' peak may appear at first sight inconsistent with the implications of the model developed and applied in references 4 and 5 to describe the behaviour of PC specimens annealed after high plastic deformation. It will be shown below that the discrepancy may be removed by taking account of the inhomogeneous character of the strain when the specimen is lightly strained, a deduction already derived in an investigation[16] where the effects of mechanical rejuvenation were compared with the influences of annealing treatments on the α' plateau level and on the d.s.c. trace. Assuming the inhomogeneous character of the deformation, the specimen is divided in a first approach into two fractions: a rejuvenated β one and a remaining fraction $(1-\beta)$ for which no change of the configurational entropy has occurred. Using the same approach, some results of the present work related to the α' process will be discussed.

Yield stress and structural temperature derived from the α' peak location

The onset temperature of the α' peak is governed by the lower relaxation time related to the higher structural temperature θ and does not reflect the mean structural temperature $\bar{\theta}$ of the sample expressed following the simple approach outlined above by:

$$\bar{\theta} = \beta\theta + (1-\beta)\theta_0 \tag{9}$$

Let us now evaluate the yield strength of a specimen lightly strained and for which an increase of the structural temperature of ~10 K has been derived from damping measurements (*Table 1*). The correlation between the yield strength change $\Delta\sigma_Y$ and the change of the structural temperature $\Delta\theta$ has been established by Bauwens-Crowet and Bauwens[5] for specimens annealed after plastic deformation, yielding:

$$\Delta\sigma_Y = -ATC'(\theta-\theta_0) \tag{10}$$

with $A = 43.5\times10^{-4}$ MPa K^{-1} and $C' = 0.778$ K^{-1}.

A structural temperature increase of 10 K affecting the whole specimen would be responsible following relation (10) for a yield stress decrease at ambient temperature of 10 MPa, incompatible with the small decrease of ~1 MPa observed in *Figures 1b* and *c*. However, if one takes account of local configurational changes, the structural temperature θ of equation (10) has to be replaced by the mean value $\bar{\theta}$ yielding:

$$\Delta\sigma_Y = -ATC'(\bar{\theta}-\theta_0) \tag{11}$$

Taking account of relation (9), the yield stress decrease is then given by:

$$\Delta\sigma_Y = -ATC'\beta(\theta-\theta_0) \tag{12}$$

For the above conditions a deaged fraction equal to 10% may be derived from relation (12). This deaged fraction affects mainly the pre-yield deformation as observed in *Figures 1b* and *c*.

α' plateau level of a lightly deformed specimen

It appears from the data of *Figures 5* and *6* that a correlation exists between the maximum applied strain and the loss curve level in the range of the α' plateau. The damping level is raised when the applied strain is increased reaching as shown in reference 16 a maximum for specimens cold pressed to 40%. Let us consider a lightly strained sample for which at a given temperature ranging in the α' plateau, the deaged fraction is characterized by a structural temperature θ yielding a local viscosity η_θ. The measured viscosity derived from the α' plateau level at a given temperature by using relation (3), will be higher than the viscosity η_θ reached by the deaged fraction. Both viscosities may be linked by:

$$\eta_\theta = \eta\times\beta \tag{13}$$

Tan δ in the plateau measured at 0.1 Hz and 20 K h^{-1} on samples annealed after high plastic deformation is equal to $\sim2\times10^{-2}$ (ref. 4). In the present investigation samples cold pressed to 3% present a plateau at $\sim1.2\times10^{-2}$ for the same measurement conditions. From equation (3) and relation (13), the maximum plateau level reached after a deformation of 40% may be related to the plateau level of a 3% strained specimen by:

$$\tan\delta_{max} = \tan\delta_{3\%}\times(40/3)^m \tag{14}$$

For m equal to 0.27, relation (14) yields for the ratio $\tan\delta_{max}/\tan\delta_{3\%}$ a factor 2 consistent with the experimental value (1.7). The θ values deduced from a data analysis where only the deaged fraction is considered would lead for the above example to an increase $\Delta\theta$ of ~3 K.

Numerical value of the dispersion parameter m

The numerical values of the dispersion parameter deduced in the present investigation and in reference 1 are <0.33 which is the value mentioned in the literature for the α process[3] or its precursor the α' process[4]. We

are not sure that a physical meaning may be attributed to this lower measured value in the sense of a broader distribution function of the viscosity. It is possible that an underestimation of m results from the influence of factors such as the convolution of the α' and α'' peaks and also from the contribution of the fraction of matter unaffected by the deformation. Further research is needed to investigate the invoked possible influences.

The aim of the above discussion is to show that the effects of pre-yield deformation on the α' peak and on the yield strength are in quantitative agreement with the model established by Bauwens-Crowet and Bauwens[4,5] provided that only local configuration perturbations are taken into account for lightly strained specimens. In the present investigation where modelling of the α' peak has been considered to allow the deconvolution of the α' and α'' loss processes, we think that a data analysis where the specimen is treated as uniformly strained is more convenient to use as a first approach.

CONCLUSIONS

In the experiments listed, mechanical deageing and further ageing effects on the loss curve of PC specimens are due to the contribution of two processes, both enhanced by small deformation but whose relaxations are not controlled by the same mechanism: the α' loss process precursor of the α transition is well described by a model where the viscosity is a non-linear function of one main parameter, the structural temperature. This model extends to lightly deformed specimens allowed to recover at ambient temperature, the formalism established and used by Bauwens-Crowet and Bauwens in a series of papers about rejuvenation by high plastic deformation and annealing above 40°C; the α'' loss process that merges partially with the β and α' peaks has not yet been interpreted. Its amplitude is independent of the structural temperature governing the α' peak location and appears to be only influenced by the recovery period after straining irrespective of the deformation conditions.

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REFERENCES

1 Othmezouri-Decerf, J. *Polym. Commun.* 1991, **32**, 143
2 Smith, T. L., Levita, G. and Moonan, W. K. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 875
3 Struik, L. C. E. 'Physical Ageing in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
4 Bauwens-Crowet, C. and Bauwens, J.-C. *Polymer* 1990, **31**, 248
5 Bauwens-Crowet, C. and Bauwens, J.-C. *Polymer* 1988, **29**, 1985
6 Bauwens, J.-C. *Plastics Rubber Process. Applic.* 1987, **7**, 143
7 Yee, A. F., Bankert, R. J., Ngai, K. L. and Rendell, R. W. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 2463
8 Lee, A. and McKenna, G. B. *Polymer* 1990, **31**, 423
9 Bauwens-Crowet, C. and Bauwens, J.-C. *Polymer* 1990, **31**, 646
10 Trznadel, M., Pakula, T. and Kryszewski, M. *Polymer* 1988, **29**, 619
11 Othmezouri-Decerf, J. *Polymer* 1988, **29**, 641
12 Bauwens-Crowet, C. and Bauwens, J.-C. *Polymer* 1987, **28**, 1863
13 Bauwens, J.-C. *Colloid Polym. Sci.* 1992, **270**, 537
14 Pixa, R., Grisoni, B., Gay, T. and Froelich, D. *Polym. Bull.* 1986, **16**, 381
15 Muller, J. and Wendorff, J. H. *J. Polym. Sci., Polym. Lett. Edn* 1988, **26**, 421
16 Tastenoy, S. *Thesis*, Université Libre de Bruxelles, 1992