JOURNAL OF MATERIALS SCIENCE **34** (1999) 2351 – 2359

Investigation of the low temperature ageing kinetics of glassy polycarbonate by mechanical damping spectroscopy

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Polycarbonate samples were submitted to ageing at room temperature or at 8 °C after quenching from above T_g or de-ageing by pre-yield tensile deformation. Loss curves were measured in the temperature range located between the β and the α transitions. These curves exhibit an α' peak on the low temperature side of the α peak. The position of the α' peak is clearly dependent on the history of the sample: the α' peak located in the low temperature range after quenching or mechanical de-ageing is shifted to higher temperatures during further ageing. The time and temperature dependence of the α' peak location has shown that the kinetics of the α' relaxation near and below room temperature is controlled by a lower activation energy process than the annealing process prevailing near T_g and already identified. A classical formalism modified by taking into account two α' relaxation processes prevailing either at low or higher temperatures yields a good description of the α' loss curves of most samples aged for a long term at room temperature, but fails to describe the α' peaks of specimens submitted to another ageing history. To model the loss curves of such specimens the relaxation time spectrum involved in the description of the α' peak is assumed to be dependent on the history of the sample and on the current test temperature.

1. Introduction

The well known physical ageing process involves the spontaneous decrease of molecular mobility of polymeric glasses when held at constant experimental conditions below the glass transition temperature. It has been shown in several works [1–8], that the application of a deformation in the non linear pre-yield range may erase part of the previous ageing, a process that we have previously termed mechanical de-ageing [7]. De-ageing of previously aged glassy polymers produces an instantaneous decrease of the viscosity of the sample, whether the applied stress is maintained or suppressed. The decrease in viscosity induced by deformation is then followed by a progressive increase, the physical ageing process being reactivated by the mechanical treatment.

As in previous work [6, 7], the ageing and de-ageing of glassy polycarbonate will be followed through the evolution of the mechanical damping properties known to be significantly dependent on thermal and mechanical treatments [2–15]. It has been observed [7] that mechanical de-ageing affects the loss curves of PC specimens in a similar way as does quenching from above T_g [10, 14], or high plastic deformation [12, 13]; the loss curves of such specimens may exhibit two intermediate peaks in the range of temperature between the α glass transition and the highest secondary transition β: the α' peak located at the low temperature side of the α glass transition and the α'' peak observed between the α' and β relaxations (examples are given in Fig. 1a and b).

To describe the α' damping data of de-aged and subsequently aged PC specimens we used in previous work [7] the formalism proposed and successfully applied by Bauwens *et al.* to PC specimens annealed near but below T_g after plastic deformation [13, 14, 16]. A satisfactory description could be obtained for the onset slope of the α' peak, but the numerical equation derived from the α' relaxation kinetics near T_g failed to predict the position of the α' peak for specimens aged at room temperature after quenching or mechanical de-ageing.

The main purpose of the present work is to investigate the low temperature α' relaxation kinetics by submitting PC specimens either quenched from above T_g or mechanically de-aged, to ageing treatments at room temperature and at 8 °C during times ranging from a few hours to several months. The influence of various de-ageing and ageing conditions on the damping behaviour of PC specimens is also explored. A model to predict the α' loss curves is proposed on the basis of the same formalism as the one used in a previous investigation but modified by taking into account two α' relaxation processes [15] and a relaxation time spectrum involved in the modelling of the α' peak dependent on the prior history of the sample and on the current test temperature [17].

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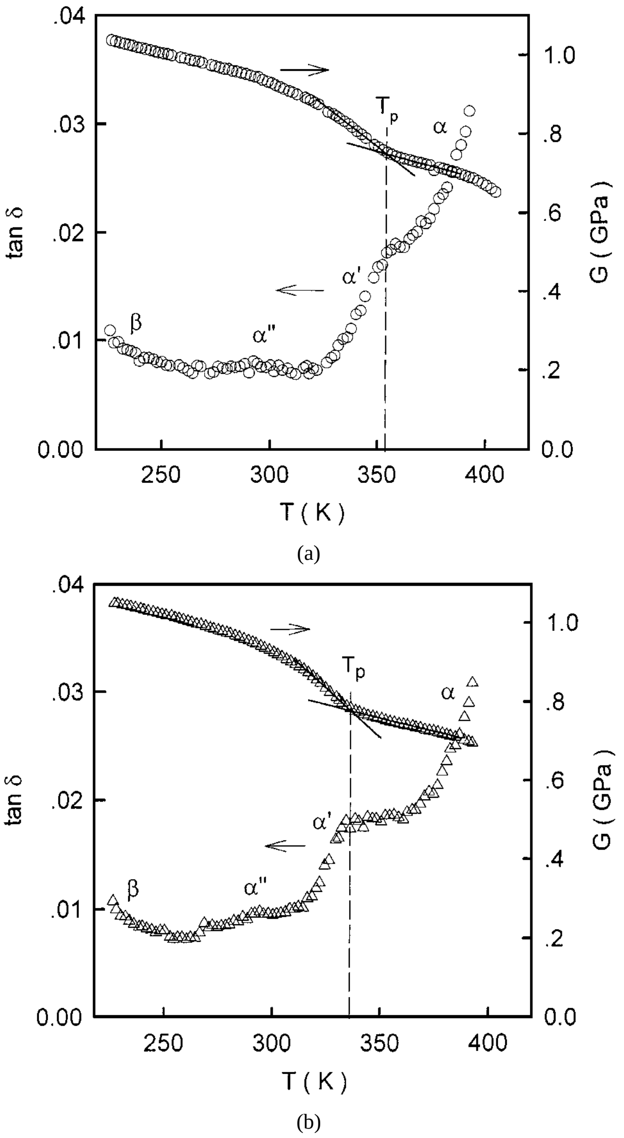


Figure 1 Examples of loss curves exhibiting the α' and the α'' peaks. The shear modulus curves are also given. The onset of the α' plateau located at T_p is derived from the intersection of the tangents at the shear modulus slope change: (a) sample 2 (○) aged for 4 years at room temperature after quenching from above T_g; (b) sample 5 (△) aged for 2 years at 8 °C after quenching from above T_g.

2. Experimental

As in previous work [7], experiments were carried out on specimens machined from the same extruded sheet of Makrolon (bisphenol A polycarbonate, Bayer) 1 mm thick.

Two kinds of samples were submitted to mechanical damping measurements:

- samples were quenched in iced water after a thermal treatment above T_g (1 h at 165 °C) and left thereafter to age at ambient temperature or at 8 °C for times ranging from 20 h to four years.
- samples aged two years at ambient temperature after quenching (i.e., well aged specimens) were submitted to mechanical de-ageing by tensile deformation at ambient temperature, and aged for various durations at room temperature or at 8 °C.

TABLE I Samples investigated

Code number	Tensile (%) strain	Ageing conditions		Structural temperature
		Time	Temperature	
		Quenched samples		
1		8 days	RT^a	436 K
2		4 years	*RT*	428 K
3		15 days	281 K	441.1 K
4		5 months	281 K	437.8 K
5		2 years	281 K	435.4 K
		Well aged samples		
6	3	7 days	*RT*	436.2 K
7	3	45 days	*RT*	433.6 K
8	3	4 months	*RT*	432.2 K
9	2.3	45 days	*RT*	433.6 K
10	3	15 days	281 K	439.5 K
11	3	7 months	281 K	437.4 K
12	2.3	20 hours	281 K	444.1 K
13	2.3	8 days	281 K	439.7 K
14	2.3	7 months	281 K	437.4 K

[a] *RT*: Room temperature.

The tensile tests were carried out on an Instron tensile machine at ambient temperature and at a strain rate $\dot{\varepsilon}$ of $5.1 \times 10^{-6}\ \mathrm{s}^{-1}$. Strip samples of $65 \times 5 \times 1\ \mathrm{mm}^3$ were strained in the range of deformation below the yield point. The engineering tensile strain was evaluated from the length change in the non elastic range divided by the gauge length.

The de-ageing conditions and the ageing history of the specimens are listed in Table I, together with their code numbers. The dynamic mechanical measurements were performed using a Metravib torsional low frequency microanalyser on samples having a gauge length of about 35 mm, 1 mm thick and 5 mm wide.

The evolution of the torsional modulus *G* and of the mechanical damping tan δ with temperature was usually followed between −50 °C to about +150 °C at a heating rate of $20\ \mathrm{K\,h}^{-1}$ and at two frequencies, 0.1 and 1 Hz.

3. Results

Representative examples of the influence of experimental parameters on the mechanical damping behaviour are given below. As in a previous paper [7], only data taken at a frequency of 0.1 Hz are displayed. The kinetics of the α' relaxation in the experimental conditions explored will be derived from the location of the α' peak as a function of ageing time and temperature.

3.1. Quenched specimens

As observed previously [7, 10, 14, 15], quenching from above T_g promotes the appearance of two intermediate peaks (see Fig. 1a and b): the α' peak lying on the low temperature side of the α peak, the α'' peak located between the α' peak and the β peak and partially merging with both.

The damping data of Fig. 1a and b are given to show the effect of the ageing temperature for long term ageing treatments: two specimens were left to age after quenching during comparable long terms, four years at ambient temperature (Fig. 1a) and two years at 8 °C

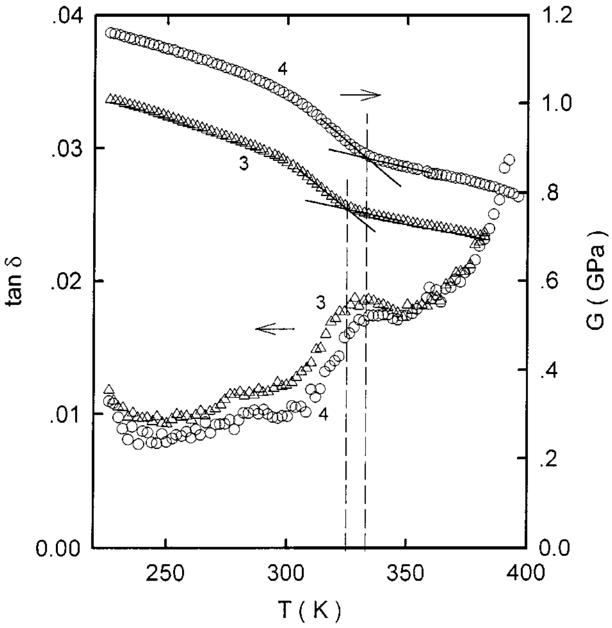


Figure 2 Effect of ageing time on quenched samples. Loss spectra and shear modulus curves of samples 3 (△) and 4 (○) respectively aged for 15 days and 5 months at 8 °C after quenching. *G* scale is correct for sample 3 (△), the shear modulus curve of sample 4 (○) is shifted upwards by 0.1 GPa for clarity.

(Fig. 1b) respectively. It may be seen that an α'' peak of small amplitude still remains on both loss curves in the same temperature range. As clearly shown on Fig. 1b, the presence of an α'' peak partially merging with the α' peak prevents location of the onset temperature of the α' peak. Moreover the mechanical damping background taken as the minimum damping level reached between the β and α transition [13] remains undetermined in this work due to the presence on all loss curves of an α'' peak located between the β and α' peaks and partially merging with both.

On Fig. 2, a comparison is made between two samples aged for 15 days and 5 months respectively at 8 °C after quenching. It may be seen that increasing the ageing time at low temperature produces a significant shift of the α' peak to higher temperatures and a decrease of the amplitude of the α'' peak, a behaviour similar to the one observed for specimens aged at ambient temperature [7].

Note that the amplitudes of the α'' peaks are particularly prominent on loss curves of the PC sheet used in our experiments in comparison to the damping data of samples machined from other PC plates also provided under the label Bayer Makrolon [18].

It will be seen throughout this work that the α'' peak always present on the damping data will not only affect the shape of the loss curves but also the shape of the torsional modulus curves leading for these last curves to a smooth and progressive decrease in the range of onset of the α' peak as illustrated for example on Figs 1 and 2. This fact leads to a high uncertainty about the evaluation of the α' peak onset temperature in the present work in contrast to the results obtained by Bauwens-Crowet in [15]. On the other hand, the clear change of slope of the modulus curve in the range of onset of the α' plateau allows us to derive a better defined temperature that we call T_p (see Fig. 1a and b). In order to investigate the kinetics of the α' relaxation throughout this work, we intend to follow the shift of the α' peak through the shift of the temperature T_p derived from the modulus curve and associated with the start of the α' plateau.

3.2. Mechanically de-aged specimens

Mechanical de-ageing was always carried out on well aged specimens (i.e. specimens aged at least two years at ambient temperature after quenching) in order to avoid the interaction between the ageing process after quenching and the process resulting from the imposed deformation. As shown previously [7], deformation of well aged specimens in the pre-yield range produces a shift of the α' peak to lower temperatures and an increase of the α'' peak amplitude. As for quenched specimens, further ageing will produce the opposite effects, i.e. a shift of the α' peak to higher temperatures and a decrease of the α'' peak amplitude.

Fig. 3 shows the influence of the ageing temperature on the damping spectra of two specimens de-aged by 3% tensile deformation and aged for similar times: 4 months at room temperature and 7 months at 8 °C respectively. As observed for quenched samples, a decrease of the ageing temperature by about 15 °C reduces the kinetics of the α' relaxation process.

The data of Fig. 4 illustrate the effect of increasing ageing time on the damping spectra of two specimens de-aged by a tensile strain of 2.3% and left to age at 8 °C for 20 h and 7 months respectively. It may be seen that a significant shift of the α' peak to higher temperatures takes place as the ageing duration at this low temperature is increased by a factor of 30.

The data of Fig. 5 display the effect of the amplitude of deformation on the loss curve shape. Two samples

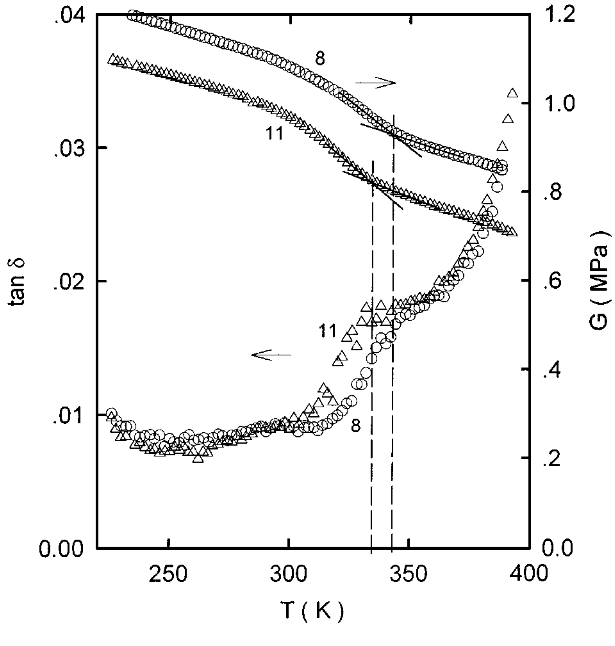


Figure 3 Effect of ageing temperature on de-aged samples. Loss spectra and shear modulus curves of samples 8 (○) and 11 (△) submitted to the same applied tensile strain of 3% and aged for comparable times at room temperature (○) and at 8 °C (△) respectively. *G* scale is correct for sample 11 (△), the modulus curve of sample 8 (○) is shifted upwards by 0.1 GPa for clarity.

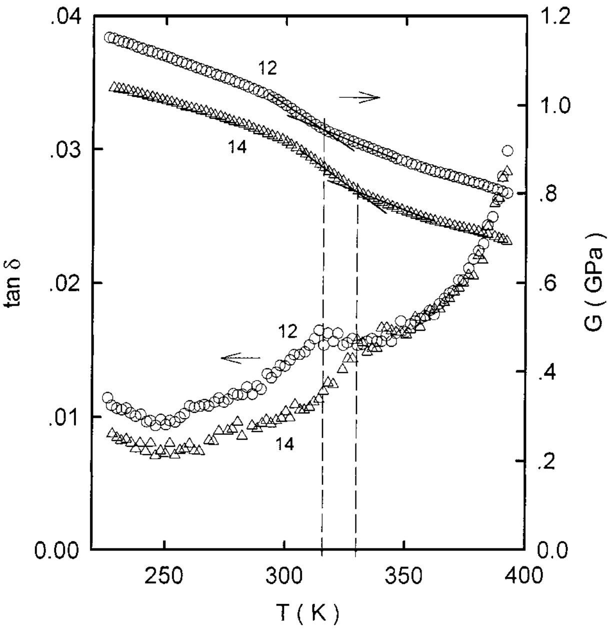


Figure 4 Effect of ageing time on de-aged samples. Loss spectra and shear modulus curves of samples 12 (○) and 14 (△) strained 2.3% and left to age at 8 °C for different times. *G* scale is correct for sample 14 (△), the modulus curve of sample 12 (○) is shifted upwards by 0.1 GPa for clarity.

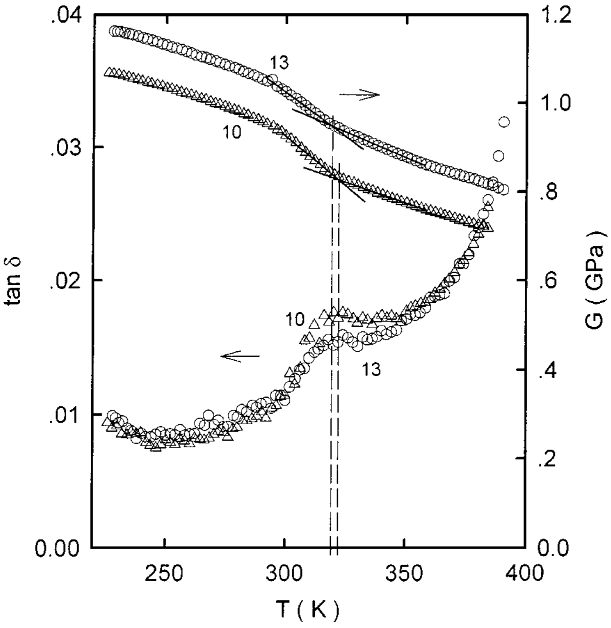


Figure 5 Effect of the amplitude of tensile deformation. Loss spectra and shear modulus curves of samples 10 (△) and 13 (○) submitted to slightly different amounts of tensile strains (3% and 2.3% respectively) and aged under similar conditions. *G* scale is correct for sample 10 (△), the modulus curve of sample 13 (○) is shifted upwards by 0.1 GPa for clarity.

were strained to 2.3 and 3% and then aged for 8 days and 15 days respectively at 8 °C. As previously put forward [7], a decrease in the amplitude of the deformation leads to a systematic small decrease of the height of the α' plateau; on the other hand, the onset temperatures of the α' plateau are close together as may be derived from the slope change of the modulus curves in the range of the α' plateau.

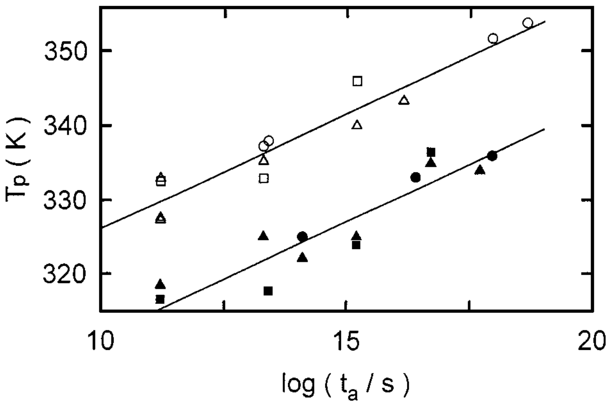
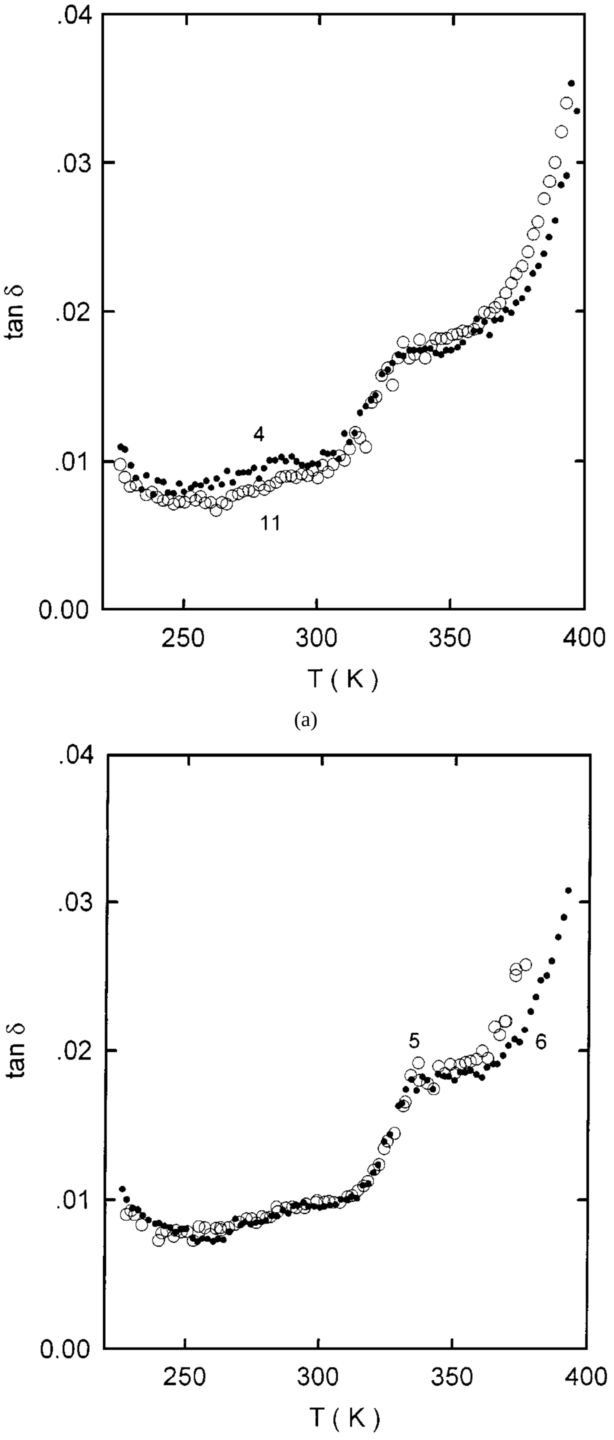


Figure 6 The temperature T_p related to the α' plateau location is plotted as a function of ln t_a for samples aged at room temperature after quenching (○), tensile straining to 2.3% (□) and 3% (△) and for samples aged at 8 °C after quenching (●), tensile straining to 2.3% (■) and 3% (▲).

3.3. Kinetics of low temperature physical ageing

The temperatures T_p derived from the torsional modulus curves were determined for a variety of specimens and are plotted on Fig. 6 as a function of the logarithm of the time t_a elapsed after quenching or after mechanical de-ageing by tensile deformation 2.3 and 3%. Although the data are dispersed, it may be clearly seen that at both ageing temperatures those related to the quenched specimens and to the mechanically de-aged specimens display the same logarithmic dependence on ageing time t_a. From the data of Fig. 6, it may be deduced that deformation of well aged specimens to a stress level near the yield point is able to shift the α' peak back to the same low temperature as does quenching, the kinetics of the α' relaxation for quenched or mechanically de-aged specimens being thereafter the same at each ageing temperature, independent of the prior history of the sample. Such behaviour may be set in parallel with the differential scanning calorimetry data of PVC presented by Berens and Hodge [19]. It is clearly put forward in reference [19] that the position of the endotherm sub-T_g peak that has been shifted to low temperatures by several different pretreatments is, during further ageing, dependent only on ageing time and on ageing temperature.

The slope of the parallel straight lines drawn through the data is 7.1 K/decade, a value consistent with the results obtained by Bauwens-Crowet [15] for aged quenched and cold rolled PC specimens which gave shifts of about 8 K/decade. Assuming a mean room temperature of 295 K, an activation energy of around 213 kJ mol^{-1} (52 kcal mol^{-1}) has been derived from the shift of the α' peak. Note that this activation energy value, deduced from the kinetics of low temperature ageing, is lower than the value of 262 kJ mol^{-1} (64 kcal mol^{-1}) successfully used for ageing treatments performed near T_g [13]. This result supports the hypothesis made by Bauwens-Crowet in a recent paper [15] about the existence of a second α' relaxation process prevailing at low ageing temperature, in addition to the already identified annealing process prevailing near T_g.



(a)

(b)

Figure 7 Examples of damping data for samples displaying same T_p values. (a) Damping spectra of samples aged at 8 °C during about the same time after quenching (sample 4 (●)) and straining to 3% (sample 11 (○)). The α' peaks coincide as the θ values given in Table I. (b) Quasi identical loss curves related to samples characterized by different de-ageing and ageing histories, but by close T_p and θ values: sample 5 (○) aged 2 years at 8 °C after quenching, sample 6 (●) aged 7 days at room temperature after straining to 3%.

3.4. Comparison of quenched and mechanically de-aged specimens

On Fig. 7a, a comparison is made between the damping data of samples aged at 8 °C for about the same times, respectively 5 months for the quenched specimen and 7 months for the specimen strained to 3%. From the comparison of the loss curves, it appears clearly that the onset temperatures of the α' plateau are the same for both specimens.

Let us consider two samples characterized by different histories but by close T_p values around 435 K (see Fig. 6): it may be seen on Fig. 7b that the specimen strained to 3% and aged for seven days at ambient temperature displays the same onset temperature for the α' plateau as the quenched one aged for two years at 8 °C.

The above examples confirm the independence of the kinetics of the α' relaxation process on the prior de-ageing treatments applied in our experiments.

From the loss curves plotted on Fig. 7a and b, it may also be pointed out that de-ageing by 3% tensile deformation does not affect significantly the α' plateau height of the quenched and aged sample, whereas de-ageing by 2.3% deformation leads to a lower plateau height (see Fig. 5).

4. Data analysis and discussion

4.1. Model equations

The purpose of the present data analysis is to model the α' peak assuming that the α'' and the α' peaks are governed by different processes.

As in previous work, the basic model used is the one developed by Bauwens *et al.* and applied to the data of PC specimens quenched or rejuvenated by high deformation and thereafter annealed in the range from $T_g - 35$ K to T_g [13] or aged for a long time at ambient temperature [14, 15]. The model is applied here to describe the mechanical damping behaviour of PC specimens slightly deformed in the pre-yield range and aged at or below room temperature. We summarize below the model reviewed in reference [15].

The chief parameter of the model proposed by Bauwens *et al.* is a structural temperature θ reflecting somehow the structure of the glassy polymer and defined as the temperature at which the structural state of the sample having had a particular thermal or mechanical history would be at equilibrium. The structural temperature is assumed to be the parameter governing the viscosity of the glassy polymer.

Annealing below T_g may produce a configurational change leading to a decrease of θ, while plastic deformation always produces a configurational change associated with an increase of θ. A simple linear relation is chosen to express the configurational entropy $\Delta S(\theta)$ as a function of θ

$$\Delta S/R = C'\theta \tag{1}$$

where R is the gas constant and C' is a constant.

As in a previous paper [7], we assume that like high deformation and annealing, pre-yield deformation and ageing at or below room temperature are able to produce configurational changes of the specimen leading to changes of its structural temperature.

The amount of decrease of θ with time t_a at a given temperature T_a is expressed through a Davies and Jones type relationship [13]

$$d\theta = (T_a - \theta)J\,dt_a \tag{2}$$

where J denotes the frequency of configurational change of the sample.

In the range of temperatures covering annealing treatments performed near T_g, the temperature dependence of the structural temperature θ is satisfactorily described using the following equation for J [14]

$$\begin{aligned} J &= \nu_a \exp(C'_a\theta - Q_a/RT) \\ &= 10^{-95}\exp(0.7\theta - 6.4 \cdot 10^4/RT) \end{aligned} \quad (3)$$

where the subscript a refers to the annealing process. The values of the parameters related to the annealing process are those used in reference [14], where relation (2) with the numerical Equation 3 allows a good fit of the data for PC specimens annealed after high deformation or quenching.

As shown in references [7] and [15], the use of Equation 3 to express J does not allow prediction of the evolution of the structural temperature observed in experiments where PC specimens are submitted to ageing treatments near or below room temperature after having been quenched or deformed. In order to describe the temperature dependence of θ in a large temperature range covering annealing and ageing treatments, Bauwens-Crowet has assumed in a recent paper [15] that J is governed by two relaxation processes each prevailing either at low temperature or near T_g, the ageing process prevailing at low temperature being characterized by a lower activation energy than the annealing process. Following such hypothesis J may be expressed by

$$\begin{aligned} J &= 10^{-95}\exp(0.7\theta - 6.4 \cdot 10^4/RT) \\ &\quad + \nu_{ag}\exp(C'_{ag}\theta - Q_{ag}/RT) \\ &= 10^{-95}\exp(0.7\theta - 6.4 \cdot 10^4/RT) \\ &\quad + 10^{-102.9}\exp(0.7\theta - 5.1 \cdot 10^4/RT) \end{aligned} \quad (4)$$

The subscript ag refers to the process prevailing during low temperature ageing treatments. The numerical values of the parameters related to the ageing relaxation process are the ones used in reference [15] to fit the data of PC specimens quenched and aged for a long term at room temperature. The same value has been taken for C'_a and C'_{ag} (i.e. 0.7 K^{-1}) to yield a similar slope for the dependence of θ versus $\ln t_a$ in a large temperature range. Note that the value of the lower activation energy Q_{ag} is close to the value derived in this paper from the shift of the temperature T_p linked to the onset of the α' plateau.

From Equations 2 and 4, the amount of decrease of the structural temperature of a specimen treated at a temperature T_a for a time t_a is given by

$$\begin{aligned} d\theta &= (T_a - \theta)\big[10^{-95}\exp\big(0.7\theta - 6.4 \cdot 10^4\big/RT_a\big) \\ &\quad + 10^{-102.9}\exp\big(0.7\theta - 5.1 \cdot 10^4\big/RT_a\big)\big]\, dt_a \end{aligned} \quad (5)$$

The numerical Equation 5 has been used to describe the evolution of the structural temperature both for the quenched specimens and for the mechanically de-aged ones, in agreement with the conclusions derived from Fig. 6 about the independence of the α' relaxation kinetics on the prior history of the sample.

The value of θ after quenching or de-ageing is unknown, but if the initial value of θ is sufficiently high prior to ageing its evolution described by relation (2) does not depend on it [14]. An initial θ value around 450 K was chosen here to take account of the evolution of θ as a function of ageing time at 295 and 281 K. The theoretical θ values of the PC specimens were evaluated using Equation 5 and are given in Table I.

In the model proposed by Bauwens *et al.* [13, 14], the mechanical damping on the high frequency side of the α peak is expressed using a Williams-Watts formulation

$$\tan\delta = (G/2\pi f \eta)^m \quad (6)$$

where f is the frequency of the damping test; G the shear modulus of PC in the glassy state is taken equal to 981 MPa, η represents the viscosity of the polymer and m is a distribution parameter taken constant and equal to 0.36 in references [13] and [14]. The viscosity η of the glassy polymer is described through an Eyring type relation reducing at low stresses to

$$\eta = AT/2\gamma_0\nu_d \exp[C'_d\theta - (Q_d/RT)] \quad (7)$$

γ_0 denotes the elementary shear of the deformation process referred by the subscript d, Q_d and ν_d are respectively the activation energy and the frequency factor, C'_d is a constant. The parameters for this formula were evaluated by Bauwens *et al.* from numerous data obtained through a variety of experiments as outlined in reference [15]. Identical values to the ones of reference [15] are used for most parameters, yielding:

$Q_d = 312$ kJ mol^{-1} (76 kcal mol^{-1}), $C'_d = 0.83$ K^{-1} and $A = 5.59 \cdot 10^{-3}$ MPa K^{-1}, a slightly different value is chosen in the present paper for the parameter $\gamma_0\nu_d$ taken here equal to $10^{-115.3}$ s^{-1} in order to obtain a better fit with the damping data.

From (6) and (7) and using the above parameters, $\tan\delta$ may be expressed for a test frequency equal to 0.1 Hz by

$$\begin{aligned} \tan\delta &= \tan\delta_B + [(5.59/fT)\, 10^{-115.3} \\ &\quad \times \exp(0.83\theta - 7.6 \cdot 10^4/RT)]^m \end{aligned} \quad (8)$$

where $\tan\delta_B$ is the background level.

The theoretical plot of $\tan\delta$ as a function of increasing temperature gives a flat peak the location of which is dependent on the θ value acquired by the sample prior to damping measurements [7, 15]. If the structural temperature is high enough prior to testing, its value may decrease during the measurements on heating the sample. The decrease of θ during the damping measurements at a constant heating rate v may be derived from relations (2) and (4), yielding

$$\begin{aligned} d\theta &= (T - \theta)v^{-1}[10^{-95}\exp(0.7\theta - 6.4 \cdot 10^4/RT) \\ &\quad + 10^{-102.9}\exp(0.7\theta - 5.1 \cdot 10^4/RT)]\, dT \end{aligned} \quad (9)$$

A decrease of the structural temperature during the damping measurements may lead to a plateau on the theoretical loss curves as shown in references [13] and [14].

4.2. Theoretical loss curves compared with the data

In the comparison of the experimental results with the model calculations, Equations 5, 8 and 9 with a single set of constant parameters will be used, as such numerical equations yield a quite satisfactory description of the α' peak [13–15]; the only fitted parameters will be the distribution parameter m and the background level $\tan\delta_B$. Let us recall that $\tan\delta_B$, defined as the minimum damping level, cannot be evaluated from the data of the present work due to the fact that the α'' peak located between the α' and β peaks raises the base-line. The other fitted parameter, the exponent m, may be regarded as a measure of the breadth of the relaxation time distribution involved in the description of the α' peak; it is admitted that such a distribution parameter may be linked to the prior history of the sample and may vary from sample to sample; on the other hand, to derive a satisfactory fit in the α' peak range, a temperature dependence of the distribution parameter will be taken into account to describe most data.

4.2.1. Application of the model taking a constant value for m

The loss curves drawn in full lines on Figs 8–10 were computed from the numerical Equations 5, 8 and 9 taking m equal to 0.36; the background levels adjusted to obtain the best fit with the data are given in the figure captions. A good description of the loss curves of Figs 8–10 related to PC specimens aged for a long term at room temperature is obtained in complete agreement with the results displayed in reference [15].

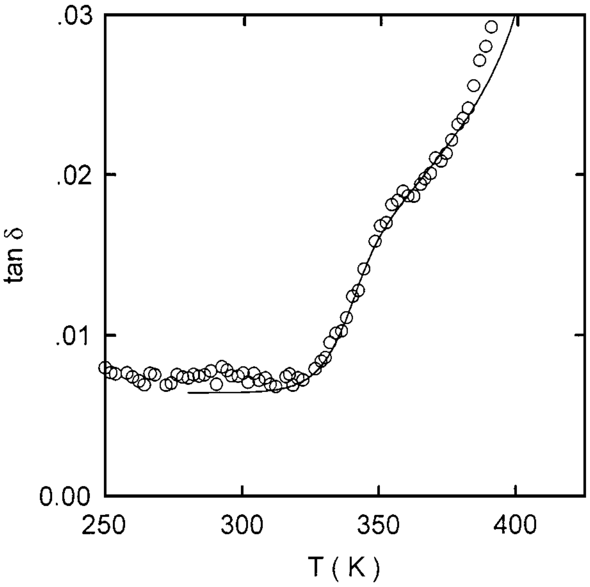


Figure 8 Loss spectrum of sample 2 aged for 4 years at room temperature after quenching. The theoretical full curve is calculated using Equations 5, 8 and 9. $m = 0.36$; $\tan\delta_B = 0.0065$.

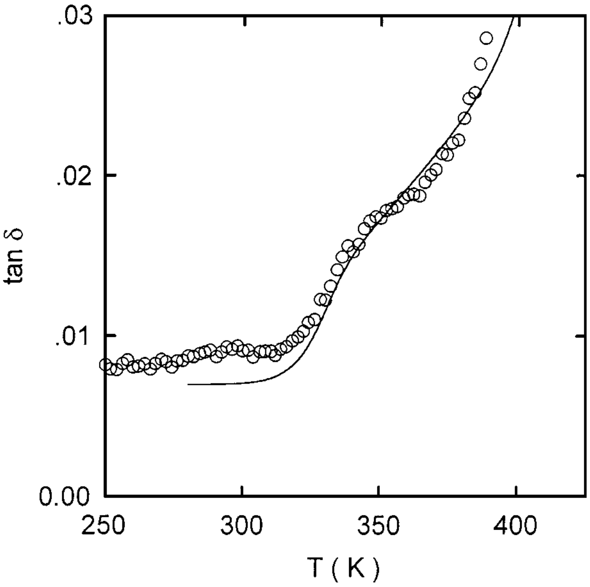


Figure 9 Loss spectrum of sample 8 strained to 3% and aged for 4 months at room temperature. The theoretical full curve is calculated using Equations 5, 8 and 9. $m = 0.36$; $\tan\delta_B = 0.007$.

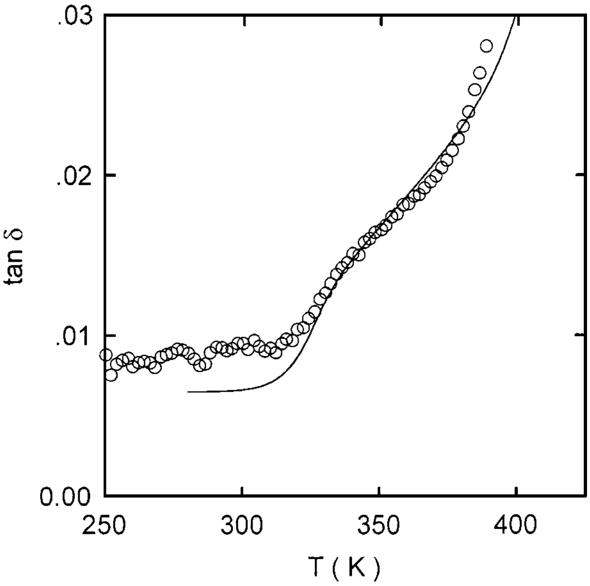


Figure 10 Loss spectrum of sample 9 strained to 2.3% and aged for 45 days at room temperature. The theoretical curve in full line is calculated using Equations 5, 8 and 9. $m = 0.36$; $\tan\delta_B = 0.0065$.

On the other hand, as may be seen on Fig. 11, no satisfactory modelling of the loss curve of sample 1 aged for a short time at room temperature after quenching could be obtained by using Equations 5, 8 and 9 either with $m = 0.36$ (full line), or taking $m = 0.335$ to fit the onset of the α' peak (dotted line).

Similarly the damping curve of sample 7 (Fig. 12) characterized by the same structural temperature $\theta = 433.6$ K as sample 9 (Fig. 10), but de-aged through a slightly higher amount of tensile strain, could not be modelled by using Equations 5, 8 and 9 with a somewhat lower value for m; here again the α' plateau and the loss curve at higher temperature are not described by the dotted line corresponding to $m = 0.33$ and chosen to fit the slope of the α' peak onset; the full line drawn by taking $m = 0.36$ is given for comparison.

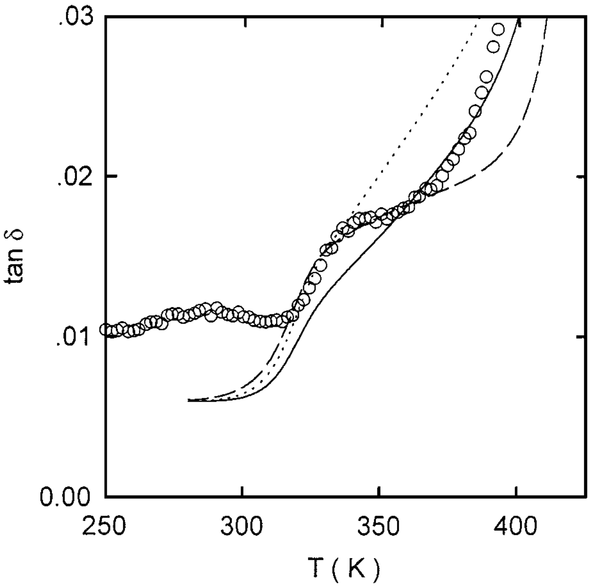


Figure 11 Loss curve of sample 1 aged for 8 days at room temperature after quenching. Theoretical curves were calculated using Equations 5, 8 and 9 taking $m = 0.36$ (full line), $m = 0.335$ (dotted line) and m derived from Equation 10 with fitting parameters of Table II (broken line); $\tan \delta_B = 0.006$.

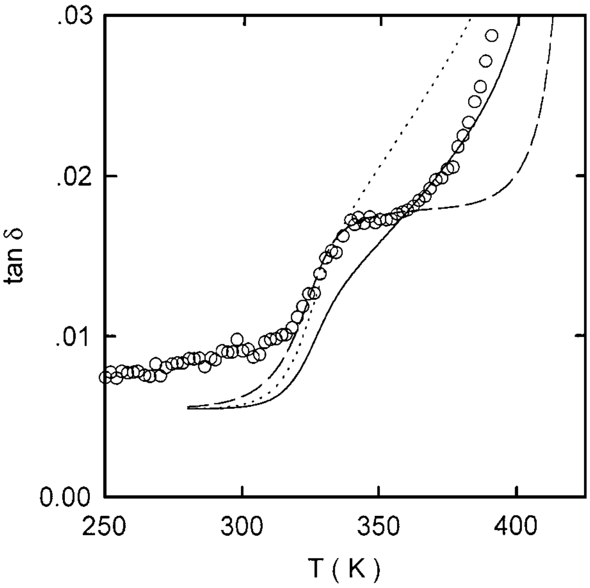


Figure 12 Loss curve of sample 7 strained to 3% and aged for 45 days at room temperature. Theoretical curves were calculated using Equations 5, 8 and 9 taking $m = 0.36$ (full line), $m = 0.33$ (dotted line) and m derived from Equation 10 with fitting parameters of Table II (broken line); $\tan \delta_B = 0.0055$.

Taking into account the fact that in paper [15], the author uses other ageing parameter values for the samples rejuvenated by high deformation than for the quenched ones, we have applied a least-squares search routine on parameters Q_{ag}, ν_{ag} and m to fit the data in the α' domain for sample 7 and others de-aged by 3% tensile deformation; a satisfactory description of the α' loss peak could never be obtained.

4.2.2. Application of the model taking into account a temperature dependent distribution parameter

In order to derive a better description of the α' plateau, we have assumed that the distribution parameter m may vary slightly with temperature, as mentioned in the review paper of Williams [17] about the use of Williams-Watts type equations.

TABLE II Fitting parameters of relation (10)

Code number of the sample	K_1	$K_2(\mathrm{K}^{-1})$
1	0.054	$0.85 \cdot 10^{-3}$
4	0	10^{-3}
5	−0.005	10^{-3}
7	−0.072	$1.2 \cdot 10^{-3}$

In a first approximation, the following hypotheses are made:

- the numerical Equations 5, 8 and 9 are valid, the only variable parameters being the distribution parameter m and the background level
- the value of m is linked to the prior de-ageing treatment, to the ageing conditions and to the current test temperature
- the value of m will increase with temperature during the damping measurements A linear dependence of m with the current test temperature T will be taken into account in this first crude approach, yielding

$$m = K_1 - K_2 T \tag{10}$$

where K_1 and K_2 are fitting parameters.

Typical illustrations of the kind of fit obtained by using Equations 5, 8–10 with the fitting parameters of Table II are shown as broken lines on Figs 11–14. In view of the quite simple proposed approach a satisfactory fit of the data in the range of the α' plateau is obtained, but the description of the loss curve using a linear temperature dependence for m is no longer valid

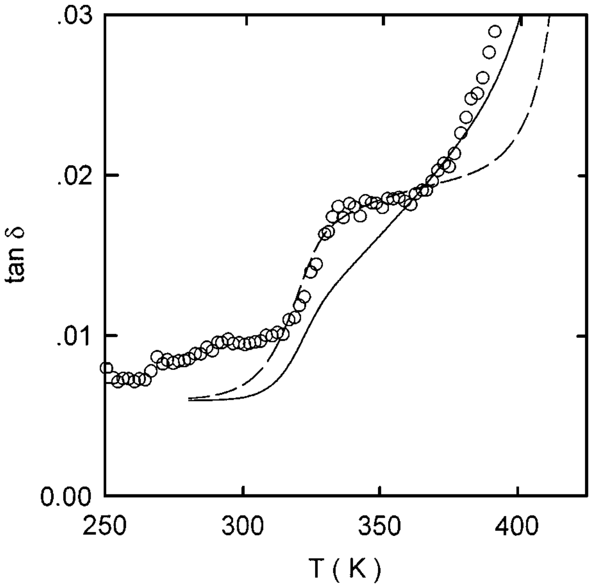


Figure 13 Loss curve of sample 5 aged for 2 years at 8 °C after quenching. Theoretical curves were calculated using Equations 5, 8 and 9 taking $m = 0.36$ (full line) and m derived from Equation 10 with fitting parameters of Table II (broken line); $\tan \delta_B = 0.006$.

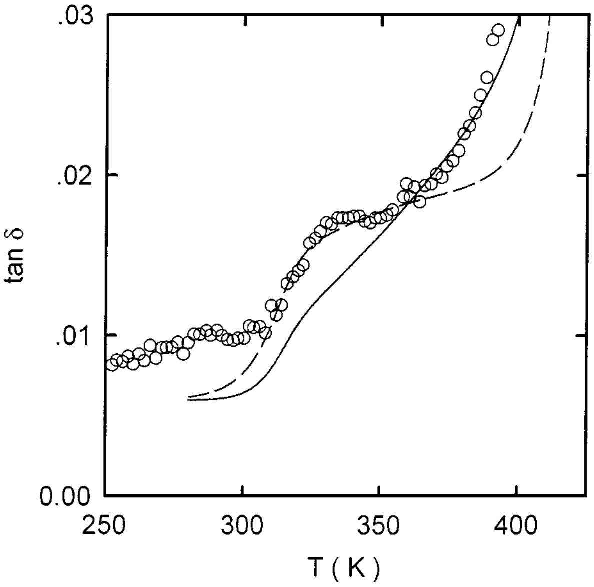


Figure 14 Loss curve of sample 4 aged for 5 months at 8 °C after quenching. Theoretical curves were calculated using Equations 5, 8 and 9 taking $m = 0.36$ (full line) and m derived from Equation 10 with fitting parameters of Table II (broken line); $\tan \delta_B = 0.006$.

in the α peak range, where the full curve taking a constant value for m yields a better fit to the data.

It must be noticed that this last proposed treatment can only be applied to loss curves displaying an α'' peak of small amplitude as it is necessary to fit the parameters of relation (10) at the onset slope of the α' peak. Obviously to test the validity of the proposed option, further experiments are needed to investigate the presumed dependence of the distribution parameter on prior history and on temperature.

5. Conclusions

With regards to the α' peak location nonlinear deformation close to yielding is able to erase long term room temperature ageing of previously quenched specimens. Further physical ageing at room and lower temperature manifests itself by a shift of the α' peak to higher temperatures.

The kinetics of the low temperature α' relaxation process appear to be independent of the prior history of the sample whereas the height of the α' plateau is influenced by the de-ageing and ageing conditions.

From the shift of the α' peak, an apparent activation energy around 213 kJ mol^{-1} (52 kcal mol^{-1}) has been derived in the low temperature ageing range.

The location of the α' peak of specimens aged at low temperature after quenching or mechanical de-ageing may be predicted by the formalism established and used by Bauwens *et al.* and extended by taking into account two α' relaxation processes prevailing either at high or low temperature.

The α' loss peak shape is well described for most specimens aged for a long term at room temperature, expressing the mechanical damping in the α' range by a Williams Watts relation with a constant distribution parameter.

A proposition assuming that the distribution parameter is dependent on the previous history and also on the test temperature is advanced and applied to describe loss curves, for which an agreement is lacking between the data and the predicted damping curves taking into account a constant distribution parameter.

Acknowledgements

I am grateful to Professeur J. C. Bauwens for enlightening comments, to C. Bauwens-Crowet for stimulating discussions and suggestions and to N. Heymans for helpful comments and suggestions.

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Received 28 September
and accepted 16 November 1998