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Long term physical ageing of polycarbonate at room temperature: dynamic mechanical measurements

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The loss peak, called α', appearing as a shoulder in the left wing of the α peak in dynamic mechanical measurements is used to follow the very long term ageing at room temperature of samples of Polycarbonate rejuvenated by cold rolling or by quenching prior to ageing. This peak shifts to higher temperature with increasing ageing time t_a. An approximate linear increase with ln t_a is found with a similar slope of about 8 K/decade for both kinds of samples. The shape and the magnitude of the peak are strongly dependent on the treatment given to the samples before ageing. It is assumed that ageing at room temperature and below results from an activated process additive to the annealing process prevailing at higher temperatures up to T_g. This ageing process which depends of the pretreatment is characterized by a lower activation energy than the annealing one. Taking these assumptions into account, experimental data are shown to agree reasonably with the predictions of a model previously proposed. © *1999 Kluwer Academic Publishers*

1. Introduction

Dynamic mechanical measurements (DMM) are of use to follow ageing behaviour and can yield information about molecular motions in glassy polymers. As first pointed out by Struik [1], the ageing range of bisphenol-A Polycarbonate (PC) is very wide, extending over more than 100 K between T_β, the temperature of the highest secondary transition and T_g, the glass transition temperature. This polymer is therefore suitable to study physical ageing processes unlike polymers whose secondary and main transitions overlap. Within the ageing range, the loss tangent curve of PC (i.e., the data giving tan δ as a function of temperature at constant frequency) may exhibit intermediate peaks highly sensitive to the ageing conditions. This paper is concerned with the highest temperature intermediate peak, labelled α' in previous papers [2–5], appearing as a shoulder in the low temperature tail of the α peak related to the glass transition (Fig. 1). The α' peak, first observed by Illers and Breuer [6], has been reported by several authors, both in mechanical and dielectric techniques as reviewed in [7]. Previous papers [4, 5] give a theoretical interpretation derived from a model based on the assumption that annealing and deformation processes in glassy polymers follow from activated processes, the kinetics of which appear to be close but not identical [8]. The shape and the magnitude as well as the position of the α' peak on the loss curve were predicted depending on the frequency and the heating rate values. An acceptable fit was found with data related to PC samples initially cold rolled and annealed at temperatures from 40 to 120 °C prior to testing. It follows from theoretical considerations that the α' peak is part of the α peak and therefore can never be completely separated. Also it can never take place on loss curves obtained on cooling the sample from the T_g range. This peak results from an involuntary thermal treatment occurring during the course of the measurements. Therefore it depends on an annealing process which was assumed to be the same as that correlated with enthalpy relaxation measured in differential scanning calorimetry (DSC) experiments performed in the T_g range [9]. It is considered that this annealing process does not depend on the thermal or mechanical history of the sample. Does this process still act at room temperature or is it overcome by another process of lower activation energy as suggested by Bauwens [10]? The present paper attempts to answer this question. The DMM behaviour of cold rolled and quenched PC samples aged for different times at room temperature is investigated. The shift of the α' peak as a function of the ageing time is measured and compared with that of exothermal peaks obtained in DSC experiments. The shape and the position of the α' peak on the loss curve is evaluated using the previously proposed model together with different assumed ageing processes.

2. Theoretical

2.1. The model

The basic idea of the previous approach, supported by experimental results, is that annealing and deformation processes are activated processes the kinetics of which are close. Therefore these processes are characterized

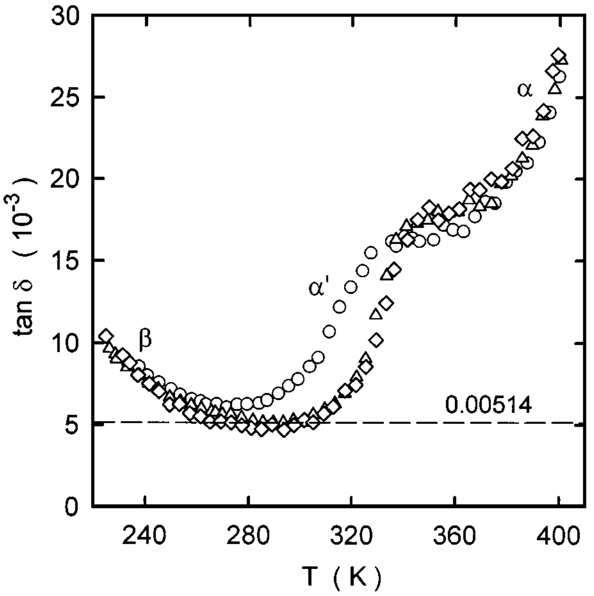

Figure 1 Examples of loss curves exhibiting the α' peak related to cold rolled samples unaged (○), aged 5 days (△), pre-annealed 2 h at 313 K and then aged 5 days at room temperature (◇). Note the baseline value of 5.14×10^{-3} on the last two curves.

by an activation energy Q, a pre-exponential factor ν and an entropic term. Until now, it is viewed that these parameters keep a constant mean value for a given process (i.e. no distribution function has yet been considered). Nevertheless, such a crude model, relying on basic classical equations chosen as simple as possible, namely the Eyring equation of non-Newtonian viscosity, the Davies and Jones equation and the Williams-Watts treatment, is able to give a straightforward prediction of data obtained in various fields such as yield stress, enthalpy relaxation and DMM. Moreover, it is assumed that in glassy polymers, ageing or annealing phenomena induce structural changes governed by the decrease of θ the structural temperature of the sample. This concept, originally proposed by Tool [11], often called fictive temperature in the literature, denotes the temperature related to the thermodynamical equilibrium of the sample. A simple linear relation is assumed between θ and the entropy change $\Delta S(\theta)$ produced by annealing or deformation:

$$\Delta S(\theta)/R = C'\theta \qquad (1)$$

where R denotes the universal gas constant. The value of C' related to the annealing process is slightly different from that related to the deformation process as outlined previously [4].

In this paper subscripts a and d refer to the annealing and deformation parameters respectively. Also annealing will denote a process which occurs not too far below T_g and ageing a process which occurs during storage and use at room temperature and below. Until now, the model was only concerned with annealing effects.

TABLE I Parameters of the annealing and deformation processes

Annealing process	ν_a (s^{-1})	C'_a (K^{-1})	Q_a (kcal mol^{-1})		
	10^{-95}	0.7	64		
Deformation process	$\gamma_0\nu_d$ (s^{-1})	C'_d (K^{-1})	Q_d (kcal mol^{-1})	A (MPa K^{-1})	G (MPa)
	$10^{-115.2}$	0.83	76	5.59×10^{-3}	981

2.2. Annealing process

The structural temperature θ is calculated as a function of the annealing conditions (annealing temperature: T_a and annealing time: t_a) by numerical integration of a Davies and Jones type equation [12]

$$\begin{aligned} d\theta &= (T_a - \theta)\nu_a \exp(C'_a\theta - Q_a/RT_a)\,dt_a \\ &= (T_a - \theta)10^{-95} \exp\big(0.7\theta - 6.4 \times 10^4/RT_a\big)\,dt_a \end{aligned} \qquad (2)$$

with the values of the parameters previously used and recalled in Table I. They were adjusted using enthalpy relaxation measurements obtained on samples annealed for various times at temperatures near T_g from 110 to 140 °C [9]. The response of Equation 2, i.e. θ against $\ln t_a$ at constant T_a is given for a series of T_a values in Fig. 1 of [5] and at 281 and 295 K in Fig. 14 of the present paper (dashed lines). A linear dependence is found at each T_a. Let θ_i characterize the structural state of a sample prior to ageing and $\theta(t_a)$ that of the sample aged during t_a at room temperature. Provided $\theta_i > \theta(t_a)$ holds, $\theta(t_a)$ may then be obtained, it does not depend on the thermal or mechanical history of the sample prior to annealing.

2.3. Deformation processes

2.3.1. Yield processes

The deformation process at yield was assumed to be governed by the Eyring equation of non-Newtonian viscosity. For example, the tensile yield stress σ_t may be written:

$$\sigma_t/T = A_t(\ln\dot{\varepsilon} - \ln\gamma_0\nu_d - C'_d\theta + Q_d/RT) \qquad (3)$$

where $\dot{\varepsilon}$ denotes the strain-rate, T the test temperature, γ_0 the elementary shear and A_t a constant characteristic of tensile experiments (it was not possible to separate γ_0 from ν_d). Such a linear dependance of σ_t versus $\ln\dot{\varepsilon}$ at constant T has been observed [13] allowing to conclude that Equation 3 fits the data within a wide range of experimental conditions (temperature and strain-rate). But, near and below T_g where yield stresses are rather low, although the structure of Equation 3 seems to hold, other values of the parameters A_t, $\gamma_0\nu_d$ and C'_d are required. It was then assumed that two different deformation processes with the same activation energy Q_d, called α_1 and α_2 respectively may take place at yield, α_2 being the most probable at moderate and low stresses [14]. Parameters related to the α_2 process where determined previously [4, 5] and are recalled in Table I.

2.3.2. Linear deformation process

The deformation process implied in DMM takes place under very small stresses. In such case, the non-Newtonian viscosity becomes Newtonian and may be expressed by:

$$\eta = AT/2\gamma_0\nu_{\mathrm{d}} \exp(C'_{\mathrm{d}}\theta - Q_{\mathrm{d}}/RT) \qquad (4)$$

where A is a constant, evaluated previously [4], which parallels A_{t} in torsion. Parameters are those of the α_2 deformation process. The loss tangent is described through a generalized Maxwell model and expressed by:

$$\tan\delta = (G/2\pi f \eta)^m \qquad (5)$$

as in the Williams-Watts treatment [15] used by Struik [1]. G denotes the shear modulus and f the frequency of the damping test. The stretching exponent m is about 1/3 according to Struik [1] who proposed this value for many materials including glassy polymers. A value of $m = 0.36$ was found previously [4]. As first crude approximation, G is taken as constant throughout the whole test and for all the tests.

2.4. The α' peak origin

The plot of $\tan\delta$ against increasing T, calculated using Equations 4 and 5 assuming a constant θ value of the sample, gives a peak with a classical shape which does not exhibit any plateau on the low temperature tail [4]. But if a decrease of θ is considered during the course of the measurements, it may be assumed that within a given range of temperatures:

$$C'_{\mathrm{d}}\theta - Q_{\mathrm{d}}/RT = \text{const} \qquad (6)$$

implying that the decrease of the entropic term equals the increase of the enthalpic one in the deformation process. Such a condition entails a plateau like shape of the loss curve; this is the origin of the α' peak. Of course, the θ decrease depends on the heating rate v. Equation 2 may be rewritten as a function of v and the current temperature T of the test as:

$$d\theta = 10^{-95} v^{-1} (T - \theta) \exp(0.7\theta - 6.4 \times 10^4/RT)\, dT \qquad (7)$$

with the numerical values of the annealing process parameters. Equations 4 and 5 together with the numerical integration of (7) from $\theta(t_{\mathrm{a}})$ allow to obtain theoretical loss curves using the parameters listed in Table I. Fig. 2 shows a couple of such curves (dotted lines) related to $T_{\mathrm{a}} = 295$ K and $t_{\mathrm{a}} = 5$ and 50 days respectively. The corresponding $\theta(t_{\mathrm{a}})$ values i.e. 442.3 and 439 K respectively are obtained by numerical integration of Equation 2 from $\theta_i = 460$ K, a sufficiently high value assumed previously [4, 16].

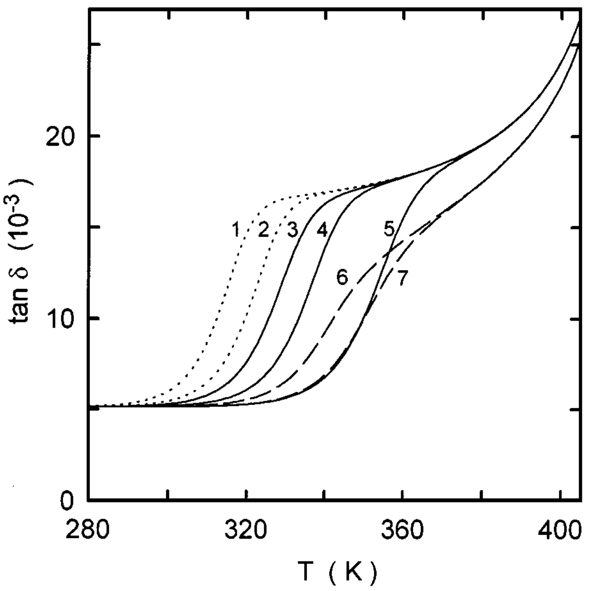

Figure 2 Theoretical loss curves related to samples aged at 295 K for various t_{a}: 5 days (curves 1 and 3), 50 days (curves 2 and 4), 500 days (curves 6), 5000 days (curves 5 and 7). In all cases the parameters of Equations 4 and 5 are those listed in Table I, $m = 0.36$ and a baseline of 5.14×10^{-3} is considered. Curves 1 and 2 are related to the annealing process expressed by Equations 2 and 7. Curves 3, 4 and 5 are related to Equations 10 and 11 appropriate for aged c.r. samples. Curves 6 and 7 are related to Equations 12 and 13 appropriate for aged q. samples.

2.5. The α' peak shift

The α' peak position is defined from the loss curve by the onset temperature T_{p} using the intersection of the baseline and the inflexional tangent as shown in Fig. 3. According to the model, this position only depends on the θ value acquired by the sample prior to testing in DMM. Therefore, in the case of samples aged or annealed at constant T_{a} for different t_{a}, the α' peak must shift towards higher temperatures with increasing t_{a} (Fig. 2). For each increase of t_{a} by a factor of 10, θ will be 3.25 K lower according to Equation 2. This θ shift value of 3.25 K/decade which derives from that of

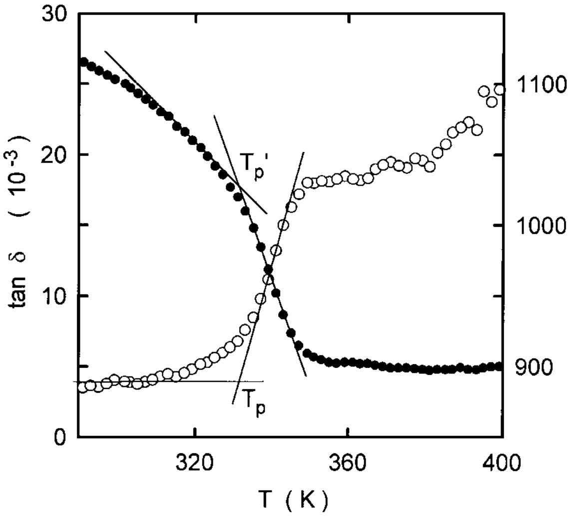

Figure 3 Typical loss curve (○) for aged cold rolled samples (300 days at 295 K). The location of the α' peak is defined by T_{p}, the intersection of the baseline and the inflexional tangent. Shear modulus (●) for the same sample, the α' transition is defined by T'_{p} the intersection of the tangents as shown.

$C'_a = 0.7\,\mathrm{K}^{-1}$ appearing in the entropic term of Equation 2 remains nearly the same for annealing treatments at constant T_a from 281 K up to 373 K.

Two different samples aged or annealed during t_a and $t_a + \Delta t_a$ are characterized by $\theta(t_a)$ and $\theta(t_a) - \Delta\theta$ and therefore T_p and $T_p + \Delta T_p$ respectively. At T_p and $T_p + \Delta T_p$, it may be considered that $\theta(t_a)$ does not vary yet during DMM measurements and moreover that the molecular mobility (and therefore the viscosity η) always reaches an identical value, a condition which reduces to:

$$C'_d\theta(t_a) - Q_d/RT_p = C'_d(\theta(t_a) - \Delta\theta) - Q_d/R(T_p + \Delta T_p) \quad (8)$$

taking (4) into account and assuming that $\Delta T_p/T_p \ll 1$. Therefore, in a series of loss curves related to samples with different t_a, i.e. different $\theta(t_a)$, a shift of:

$$\Delta T_p \cong T_p^2 R(C'_d/Q_d)\Delta\theta(t_a) \quad (9)$$

may be approximated from (8). Relation (9) ought to be fitted by the data.

3. Experimental

A necessary condition for ageing is a high θ_i value. As previously [4, 5], we propose to call rejuvenated samples those which fulfil this condition. Rejuvenation was achieved by cold rolling and by quenching. The position and the shape of the α' peak appearing on the loss curve was examined as a function of the ageing time and the structural state of the samples before ageing.

3.1. Samples

Commercially available Makrolon (Bayer) was used in this study. Samples were cut from the same sheet 2 mm thick which has been stored at room temperature for a very long time (about 10 years). All the samples have the same cross section of 1 by 5.5 mm and a gauge length of 35 mm. The mechanically rejuvenated samples (c.r. samples) were prepared from a strip rolled 50%, the length was parallel to the rolling direction. A few c.r. samples were annealed before ageing 2 h at 40 and 60 °C respectively. The quenched samples (q. samples) were obtained as follows: a strip was first thinned down, the samples were machined and annealed above T_g at 165 °C for 1 h and then rapidly immersed in a ice-water bath. All the samples were aged at room temperature for long times varying from a few days to a few years.

3.2. Dynamic mechanical tests

Internal friction and shear modulus were measured at a constant frequency of 1 Hz as a function of temperature from −50 to 140 °C using a torsional Metravib low frequency microanalyser. A heating rate of 60 K/h was used throughout.

4. Data analysis

4.1. DMM on aged c.r. samples

Fig. 1 and Figs 3–6 show examples of loss curves related to c.r. samples aged at room temperature. These loss curves clearly reveal an α' peak with similar shape and height as those observed previously. The horizontal part of the loss curve appearing between the β and α' peaks is taken as baseline or background level.

Previously, a mean value of 5.14×10^{-3} was found to be remarkably reproducible. Although this value agrees with the data of Figs 1, 4 and 6 other loss curves yield somewhat different baselines from 3.75×10^{-3} to 5.14×10^{-3} (in the case of the unaged sample of Fig. 1, the baseline can not be detected because the β

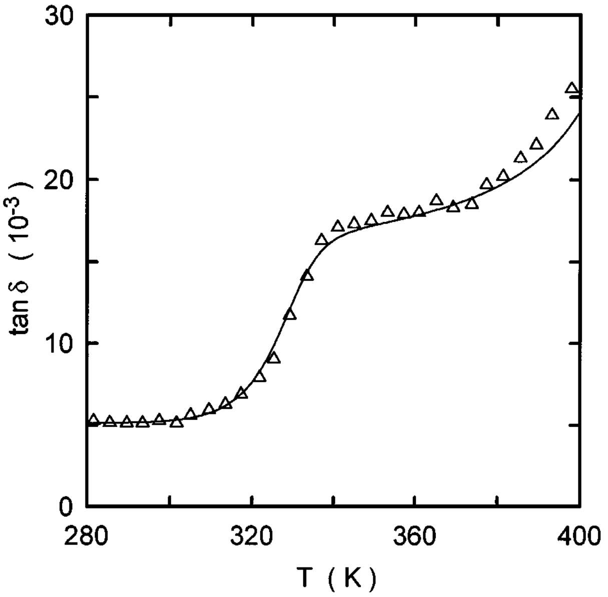

Figure 4 Loss curve related to a c.r. sample aged 5 days at 295 K (data: Δ). Theoretical curve (full line) calculated using Equations 4, 5, 10 and 11, $m = 0.36$, baseline: 5.14×10^{-3}.

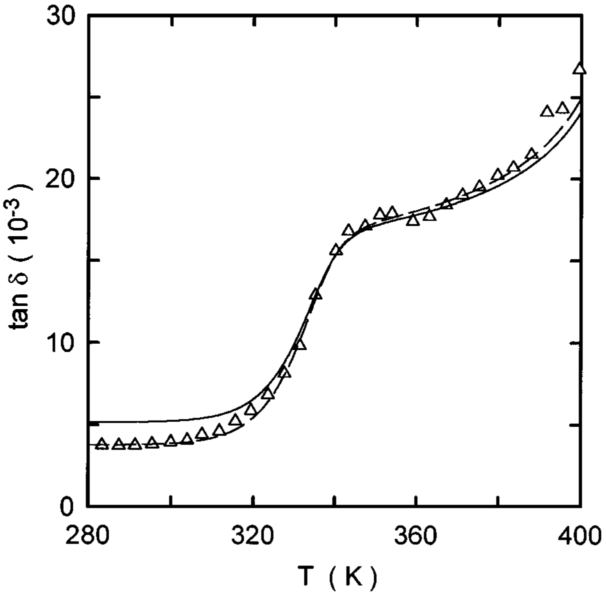

Figure 5 Loss curve related to a c.r. sample aged 20 days at 295 K (data: Δ). Theoretical curves calculated using Equations 4, 5, 10 and 11 and (full line) $m = 0.36$, baseline $= 5.14 \times 10^{-3}$ or (dashed line) $m = 0.35$, baseline $= 3.75 \times 10^{-3}$.

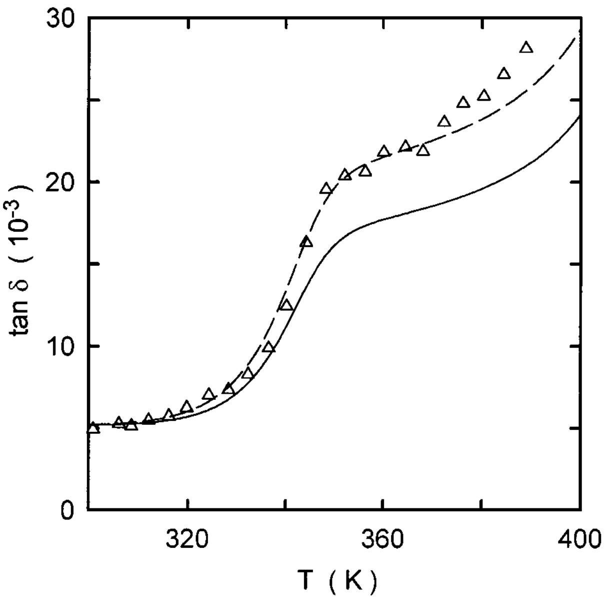

Figure 6 Loss curve related to a c.r. sample aged 197 days at 295 K (data: △). Theoretical curves calculated using Equations 4, 5, 10 and 11, a baseline of 5.14×10^{-3} and $m = 0.36$ (full line) or $m = 0.338$ (dashed line).

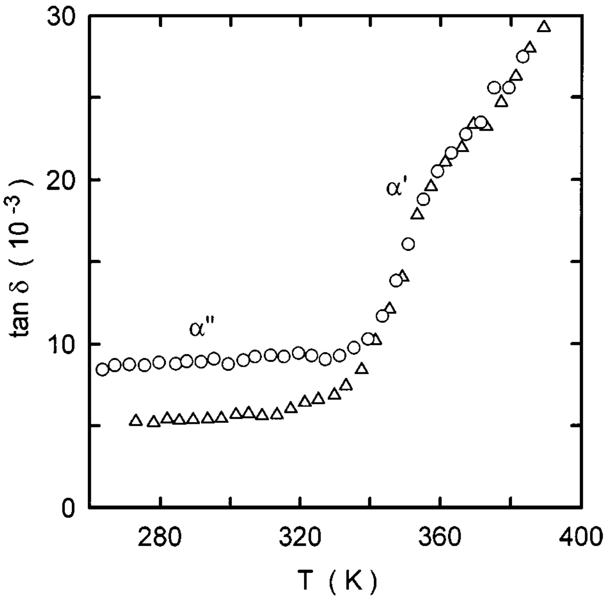

Figure 7 Loss curves of 2 c.r. samples annealed 2 h at 333 K and cooled to room temperature. One (○) is tested in DMM immediately after cooling, the other (△) is aged 48 days at room temperature. Both α' peaks coincide. The related θ values are given in Table III.

and α' peaks overlap). Therefore uncertainty remains in positioning the baseline in a theoretical approach. The same problem arises with the α' peak height, the level of which may vary. Loss curves related to different t_a do not "fit together" as nicely as previously or in the theoretical set of curves in Fig. 2.

It is experimentally checked that ageing occurs only on samples characterized by a sufficiently high θ_i value. Loss curves related to c.r. samples annealed 2 h at 40 °C and then aged coincide with those of c.r. samples not annealed and aged during the same time, an example is given in Fig. 1. The curves related to the aged samples are identical but distinct from that related to an unaged sample. Conversely, c.r. samples annealed 2 h at 60 °C tested immediately and 48 days after annealing respectively, exhibit the same α' as Fig. 7 shows. Ageing did not affect the α' peak in this case because the θ_i value acquired after annealing is already too low to evolve at room temperature in the considered range of ageing times. These experimental statements agree with the calculated θ_i values as it will be shown below. Although the α' peak is not affected by ageing in the last example the loss curve is still influenced through the magnitude of the α'' peak [5, 17]. Such a peak which is small compared to the α' peak takes place between the β and α' peaks for q. samples or when c.r. samples are annealed and cooled before being tested. This peak tends to vanish with increasing ageing time (see Fig. 3 of [17]).

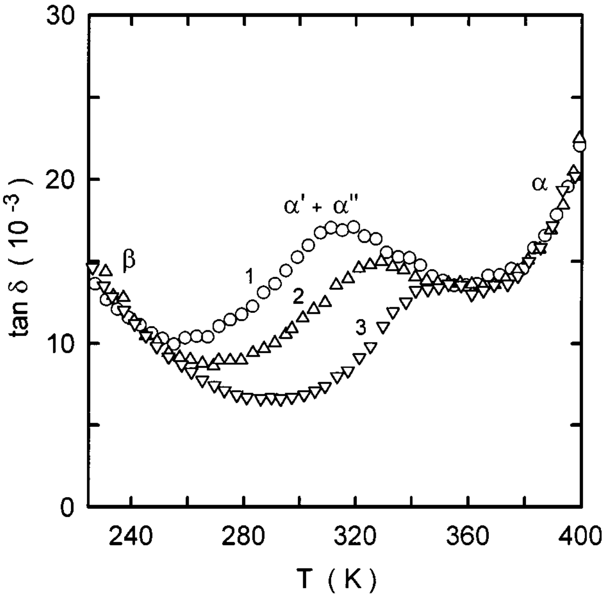

Figure 8 Loss curves of q. samples: unaged (○), aged 1 day (△), aged 3 days (▽) at room temperature.

4.2. DMM on aged q. samples

Loss curves related to q. samples unaged and aged 1 and 3 days respectively are shown in Fig. 8. Obviously, the shape differs from that of c.r. samples; curves 1 and 2 exhibit a marked maximum which looks like a real distinct peak rather than a shoulder in the α peak. We assume that in such cases a prominent α'' peak, linked to quenching, overlaps both the β and α' peaks. This assumption is supported by the fact that β, α'' and α' are separated in loss cuves of aged q. samples tested at a lower frequency [17]. As both the α'' peak height decreases and the α' peak position shifts towards the right with increasing ageing time, long term aged q. samples exhibit well shaped α' peaks; examples are shown in Figs 8–12. In such cases a vanishing α'' peak overlaps only the α' peak foot and/or raises the level of the baseline. For q. samples aged longer than 2 years it may be considered that α'' disappears from the loss curve. Let us point out that the α' peak height related to q. samples is about 20% lower than that of c.r. ones.

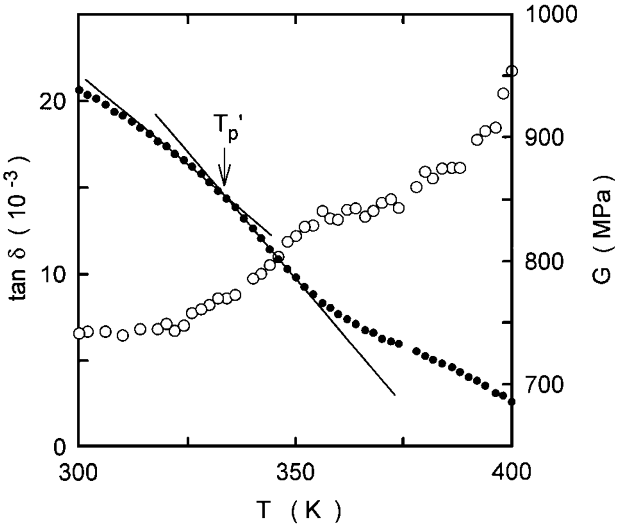

Figure 9 Typical loss curve (○) of a q. sample aged for a very long time (18 months). Shear modulus (●) for the same sample. The location of the α' transition is defined by T_p' the intersection of the tangents at the modulus drop.

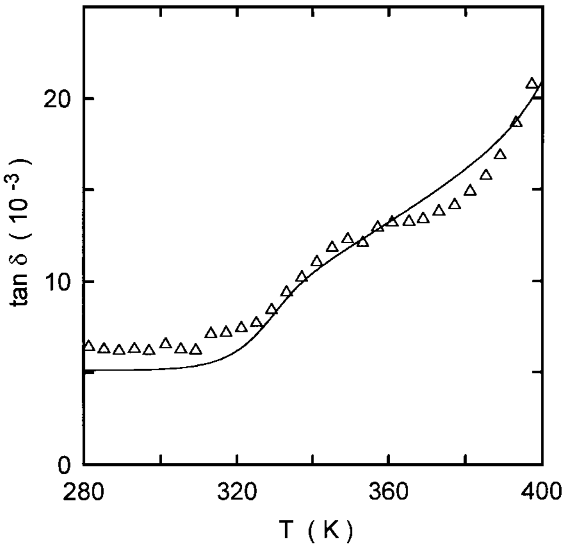

Figure 10 Loss curve related to a q. sample aged 30 days at 295 K (data: △). Theoretical curve (full line) calculated using Equations 4, 5, 12 and 13, a baseline of 5.14×10^{-3} and $m = 0.37$.

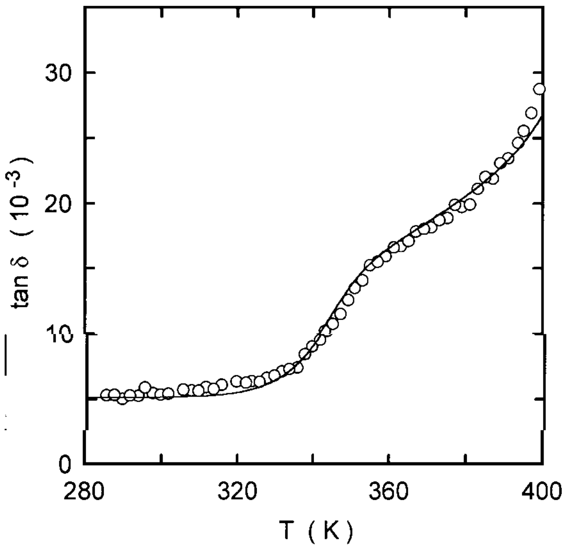

Figure 11 Loss curve related to a q. sample aged 3 years at 295 K (data: ○). Theoretical curve (full line) calculated using Equations 4, 5, 12 and 13, a baseline of 5.14×10^{-3} and $m = 0.342$.

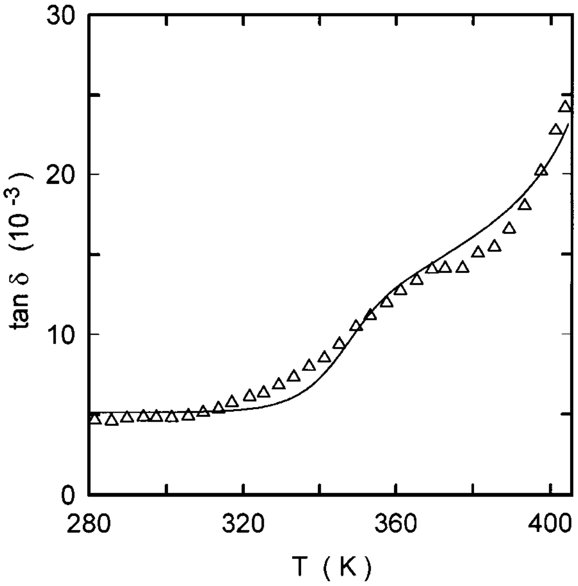

Figure 12 Loss curve related to a q. sample aged 6 years at 295 K (data: △). Theoretical curve calculated using Equations 4, 5, 12 and 13, a baseline of 5.14×10^{-3} and $m = 0.37$.

4.3. Evaluation of the α' peak shift

The shift of the α' peak as a function of ageing time is assumed to be evaluated from the onset peak temperature T_p (Fig. 3). However, because of the uncertainty of detecting the baseline, especially in the case of q. samples, we tried to find another procedure for α' peak shift determination. A small but rather well defined shear modulus drop parallels the α' peak as shown on Fig. 3. From this drop T_p', which seems to correlate with T_p, is determined graphically as indicated on Fig. 3. Both quantities are estimated for each c.r. sample and plotted as a function of $\ln t_a$ in Fig. 13. A single linear relationship is found indicating that T_p' is of use as well as T_p to follow the α' peak shift. The gradient yields a shift

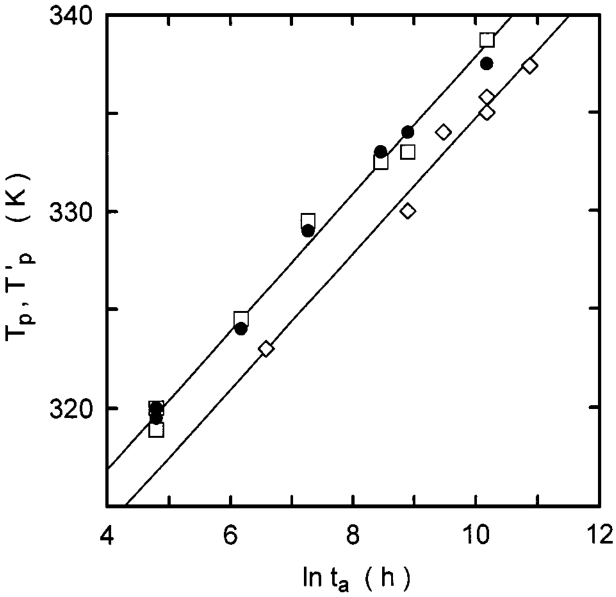

Figure 13 The α' peak position as a function of $\ln t_a$ at room temperature determined by T_p, the onset peak temperature, for c.r. samples (□) and by T_p', the modulus drop temperature, for c.r. samples (●) and for q. samples (◇).

of 8 K/decade. In the case of q. samples T'_p alone was estimated (see an example on Fig. 9) and also plotted versus $\ln t_a$ on Fig. 13. Again a linear increase is found with a similar slope (7.9 K/decade) as for c.r. samples.

As the T_p variation covers only 20 K from 320 to 340 K, the factor in Equation 9 may be considered as constant which leads to an approximate linear relationship between T_p and $\ln t_a$ as checked in Fig. 13. Let us evaluate the T_p shift from (9) for the median value $T_p = 330$ K using the deformation parameters recalled in Table I and assuming a θ shift value of 3.25 K/decade according to Equation 2. Under such conditions a T_p shift of 7.73 K/decade is obtained in acceptable agreement with those evaluated from the data.

5. Calculation results: comparison with the data

5.1. Loss curves of aged c.r. samples

Let us come back to Fig. 2 where the loss curves (dotted liness) are displayed calculated using Equations 2, 4, 5 and 7 with the parameters listed in Table I. Although a suitable shape of the α' peak is obtained, the position deviates from experimental data. This was already the case previously for c.r. samples annealed 2 h at 40 °C, the calculated curves lying on the left of the data but no more than experimental uncertainty (see Fig. 4 of [4]).

Unfortunately, the deviation becomes more pronounced in room temperature ageing. It then appears that $\theta(t_a)$ which fixes the peak position is too high at 295 K, this can be overcome by associating $\theta(t_a)$ with an ageing process of lower activation energy than the annealing one expressed by Equation 2. In fact, it is assumed that this ageing process prevailing at room temperature is additive to the annealing one. Let subscripts a1 refer to this ageing process parameters. Then Equations 2 and 7 become

$$d\theta = (T_a - \theta)\big(10^{-95}\exp\big(0.7\theta - 6.4\times 10^4/RT_a\big) + \nu_{a1}\exp(C'_{a1}\theta - Q_{a1}/RT_a)\big)\,dt_a \qquad (10)$$

and

$$d\theta = v^{-1}(T - \theta)\big(10^{-95}\exp(0.7\theta - 6.4\times 10^4/RT) + \nu_{a1}\exp(C'_{a1}\theta - Q_{a1}/RT)\big)\,dT \qquad (11)$$

respectively. Parameters of this ageing process need to be adjusted to give a quantitative account of the experimental data: loss curve and T_p dependence on $\ln t_a$. As Equation 2, Equation 10 yields a linear $\theta(t_a)$ versus $\ln t_a$ dependence, a similar slope is required in order to fulfil (9); it is then assumed that $C'_{a1} = C'_a = 0.7\ \mathrm{K}^{-1}$. Therefore, this parameter is fixed and the other two ageing parameters: ν_{a1} and Q_{a1} are allowed to vary until a best fit of (5) is obtained to the data of Fig. 4 (c.r. sample aged during 5 days) giving the optimum values of $\nu_{a1} = 10^{-118.2}$ and $Q_{a1} = 3\times 10^4$ cal/mol. These ageing parameters are listed in Table II.

Theoretical loss curves calculated using (4), (5), (10) and (11) are displayed in Fig. 2 (full lines) for several ageing times to be compared with those calculated using Equations 2, 4, 5 and 7 (dotted lines).

TABLE II Ageing parameters

c.r. samples	ν_{a1} (s^{-1})	C'_{a1} (K^{-1})	Q_{a1} (kcal mol^{-1})
	$10^{-118.2}$	0.7	30
q. samples	ν_{a2} (s^{-1})	C'_{a2} (K^{-1})	Q_{a2} (kcal mol^{-1})
	$10^{-102.9}$	0.7	51

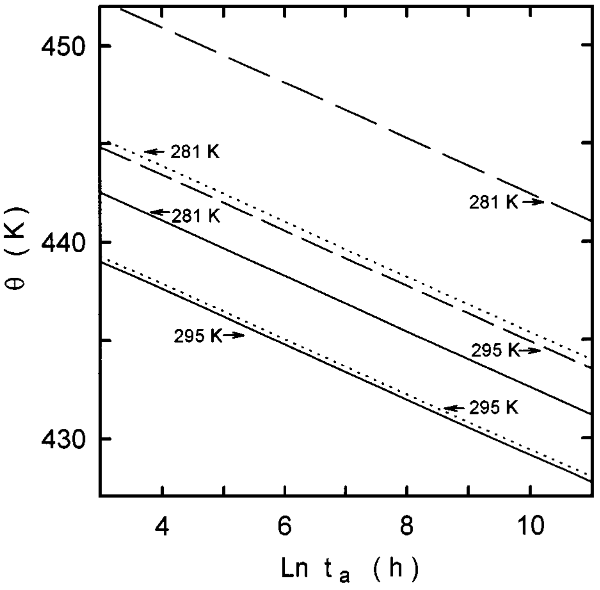

Figure 14 Calculated θ value as a function of $\ln t_a$ at 295 and 281 K for the annealing process (dashed line) using Equation 2, for the ageing process suitable for the c.r. samples (full lines) using Equation 10, for the ageing process suitable for the q. samples (dotted lines) using Equation 12.

Fig. 14 is a plot of $\theta(t_a)$ versus $\ln t_a$ at 281 and 295 K, calculated using Equation 2 (dashed line) as well as Equation 10 (full line) in order to compare the effects of both the annealing and ageing processes.

Also Equation 10 allows evaluation of θ_i values of c.r. samples annealed before ageing, results are listed in Table III and compared to the ageing $\theta(t_a)$ values at 295 K. From inspection of Table III, it can be derived that the α' peak related to c.r. samples annealed 2 h at 40 °C will shift by ageing at 295 K while that of c.r. samples annealed 2 h at 60 °C will not be affected by ageing as experimentally checked above.

Let us point out that the ageing term of Equation 10, which prevails at 295 K, decreases with increasing T_a or T so as to vanish at about 333 K, the annealing term remains then predominant at high temperatures

TABLE III Calculated θ values using Equation 10 (c.r. samples)

T_a (K)	t_a (h)	θ_i (K)	$\theta(t_a)$ (K)
313	2	437.8	
333	2	430.9	
295	120		436.5
295	1152		433.3

in agreement with previous results. Also, this is the reason why at 295 K only the position but not the shape of the α' peak depends on the ageing term because the peak starts at about 320 K or above for the samples considered here.

Loss curves for ageing times longer than 5 days are calculated in the same way and with the same parameters values. Examples are given in Figs 5 and 6 (full lines). The peak position is correctly predicted for ageing times up to 3 years as well as the peak shape. However, because the baseline and the peak magnitude seem to vary from one specimen to another, a better fit may be obtained by considering that the baseline value and m are experimental parameters characterizing specimen properties rather than characteristic material ones. It should be recalled that m may be determined using the peak heights measured on the same specimen at two different frequencies [4]. A better fit is obtained using a baseline of 3.75×10^{-3} together with $m = 0.35$ in Fig. 5 and a baseline of 5.14×10^{-3} and $m = 0.338$ in Fig. 6 (dashed lines). Although a weak dependence of the peak position and shape on m value is observed, deviations remain within experimental uncertainties.

5.2. Loss curves of aged q. samples

Neither the shape nor the height of the α' peak related to aged q. samples can be predicted using Equations 5, 10 and 11 suitable for c.r. samples. According to the model, the annealing process as well as the deformation one do not depend on the mechanical or thermal history of the sample. It is then assumed that q. samples are distinguished from c.r. samples by their own ageing process additive to the annealing one. Let us denote it by subscripts a2. Therefore in such cases Equations 10 and 11 become:

$$\mathrm{d}\theta = (T_\mathrm{a} - \theta)\big(10^{-95}\exp\big(0.7\theta - 6.4 \times 10^4/RT_\mathrm{a}\big) + \nu_\mathrm{a2}\exp(C'_\mathrm{a2}\theta - Q_\mathrm{a2}/RT_\mathrm{a})\big)\,\mathrm{d}t_\mathrm{a} \qquad (12)$$

and

$$\mathrm{d}\theta = v^{-1}(T - \theta)\big(10^{-95}\exp(0.7\theta - 6.4 \times 10^4/RT) + \nu_\mathrm{a2}\exp(C'_\mathrm{a2}\theta - Q_\mathrm{a2}/RT)\big)\,\mathrm{d}T \qquad (13)$$

respectively. For the same reason as above it is assumed that:

$$C'_\mathrm{a2} = C'_\mathrm{a1} = C'_\mathrm{a} = 0.7\,\mathrm{K}^{-1} \qquad (14)$$

in agreement with the straight lines slopes of Fig. 13. The other parameters are adjusted to obtain a best fit to experimental data. Results are listed in Table II where the parameters of both ageing processes may be compared. Examples of calculated loss curves are given in Figs 10–12 together with the data. The baseline in all cases is fixed at 5.14×10^{-3} in agreement with the data related to ageing times exceeding two years, for which it can be assumed that the α'' peak has vanished. For shorter ageing times the baseline is masked by the α'' peak. The m value differs slightly from one to another sample lying between 0.348 and 0.37. Except for Fig. 11 where a rather satisfactory fit is obtained, the quantitative agreement between the theoretical curve shape and the data is not as good as in the case of c.r. samples. Moreover, this agreement is lacking for ageing times shorter than one month. Theoretical loss curves calculated at 295 K using (4), (5), (12), (13), Tables I and II and $m = 0.36$ are displayed on Fig. 2 (dashed lines) to be compared with those related to c.r. samples (full lines). Although the shape and the height of the peak differ in both cases, the positions are similar for equal t_a. This is consistent with the $\theta(t_\mathrm{a})/\ln t_\mathrm{a}$ dependence quite close in both cases at 295 K as it can be seen in Fig. 14 where the related straight lines are calculated using (10) (full lines) and (12) (dotted lines) respectively. Of course, such a coincidence can not occur at lower T_a because both ageing processes differ by their activation energies and pre-exponential factors (see the straight lines calculated for $T_\mathrm{a} = 281$ K in both cases on Fig. 14).

6. Discussion

The shift of the α' position seems to be independent of the pretreatment of the sample, reaching about 8 K/decade. This is consistent with the model prediction expressed by (9) which implies that this shift is determined by the kinetics of the deformation process through $C'_\mathrm{d}\Delta\theta(t_\mathrm{a})/Q_\mathrm{d}$ and the $\theta(t_\mathrm{a})$ shift value both independent of prior history. The last quantity derives from the assumed condition (14) and was found to equal 3.25 K/decade. A correlation may be established between the α' peak shift and that of sub-T_g exotherms exhibited by DSC traces obtained on PC samples rejuvenated by compressing and annealed below T_g for different t_a at constant T_a [9]. Such exotherms appear roughly in the same range of temperatures as the α' peak in the present study. A linear dependence between the position of the exotherm and $\ln t_\mathrm{a}$ was found through the data as it can be seen on Fig. 4 of [9]. A mean value of the gradient may be estimated yielding a shift of 8.27 K/decade. Molecular motions in DSC experiments are related to the annealing process which differs from the deformation one but remains close to it. It may even be deduced from Table I that:

$$C'_\mathrm{a}/Q_\mathrm{a} \cong C'_\mathrm{d}/Q_\mathrm{d} \qquad (15)$$

The corresponding $\theta(t_\mathrm{a})$ in DSC experimentss derives from (14) too. No wonder then that similar values are found for curves shifts in both DMM and DSC measurements, this can be looked on as a consequence from the proposed model.

Wimberger-Friedl and de Bruin [18] have investigated the specific volume change in PC for several years at room temperature. The volume recovery curve they produce giving the specific volume versus $\log t_\mathrm{a}$ is characterized by a flat first part followed by a sharp transition to a much steeper part. The transition occurs at approximately 6 months. No correlation with such a transition has been observed in our results, but perhaps more experimental data are needed in this ageing time range to reveal this trend. However, let us point out that Washer [19] has shown that the decrease of free volume is far too low to induce the $\theta(t_a)$ variation implied in enthalpy relaxation and yield stress increase upon annealing, but his statements lean on data performed near and below T_g at short times and are related to a flat recovery curve.

The Q_{a1} and Q_{a2} values adjusted by curve fitting to the data require to be checked by measurements performed at temperatures lower than 295 K. Othmezouri-Decerf [20] by investigating the α' peak shift of q. samples aged at 281 and 295 K, finds an activation energy of about 5.1×10^4 cal mol^{-1} in full agreement with the present study, but the Q_{a1} value has yet to be experimentally confirmed by independent measurements.

The α' peak is found to be highly sensitive to annealing, ageing and deageing [17] effects in PC samples but it can be wondered if the occurrence of such a peak is a general feature in glassy polymers. The problem is that most often DMM measurements reported in the literature are related to samples tested immediately after a rapid quench or conversely to samples annealed near T_g. In the former case the α' peak is obscured by the presence of the α'' peak, while in the latter case it has shifted so as to be merged with the α peak. The best conditions to detect the α' peak are ageing for long times well below T_g because then the α'' peak vanishes, low frequency measurements because both peaks are better separated and the magnitude of the α' peak increases with decreasing frequency, high plastic deformation before ageing which was found to erase the α'' peak. For example, an α' peak (not recognized as such by the authors) can be seen on the loss curve of a sample of poly (methyl methacrylate) (PMMA) aged 30 days at room temperature after rapid cooling (see Fig. 1 of [21], specially the insert on a linear scale) but is not discernable in the case of quenched samples unaged or annealed near T_g.

7. Conclusions

The main conclusion to this work is that ageing at room temperature induces a shift of the α' peak towards higher temperatures. The shift seems to be independent of the mechanical or thermal history of the sample and is similar to that of sub-T_g exotherms appearing in DSC traces. On the other hand, the shape, the magnitude and the position of the α' peak on the loss curve are dependent on the pretreatment given to the sample. The α' peak appearance may be rather well predicted using a model previously proposed provided one assumes that three different kinds of activated processes are implied, namely:

(1) the deformation process, the parameters of which are derived from yield stress measurements performed near T_g,

(2) the annealing process prevailing in the high temperature range of the loss curve, the parameters of which are derived from DSC measurements,

(3) the ageing process prevailing at room temperature and below, the parameters of which are adjusted by curve fitting.

Both the deformation and annealing processes are considered to be independent of the history of the sample while the reverse is assumed for the ageing process. Two different ageing processes are then assumed here to be related to c.r. and q. samples respectively. They are supposed to be additive to the annealing process and of lower activation energy. This is enough to account for different peak shapes, magnitudes and positions for both kinds of samples, which are then linked to the same deformation process, the same annealing process and the same mean m value.

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