Rejuvenation and annealing effects on the loss curve of polycarbonate: 1. Structural temperature dependence

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The effect of annealing rejuvenated samples of polycarbonate below T_g (at 40 and 60°C) has been investigated by damping measurements. Rejuvenation was achieved by cold rolling. The rejuvenated samples were annealed for different times prior to testing. Loss curves were measured at constant frequency on heating the samples from -50 to 140°C at two constant heating rates. These curves exhibit a broad α' peak appearing as a plateau region on the low temperature side of the α peak. The location of α' on the loss curve was found to be strongly dependent on the annealing conditions of the rejuvenated samples, while the level of the plateau region was affected by the heating rate and the frequency of the damping test. Experimental results are quantitatively interpreted by means of a model supported by classical equations using the concept of structural temperature. This temperature, denoted by θ, is evaluated as a function of the annealing conditions, the heating rate and the temperature of the test. The origin of the α' peak is attributed to a decrease of θ during damping measurements obtained on heating the sample. Most of the parameters used to check the response of the model in the present investigation have been adjusted previously with other types of data, namely yield stress and enthalpy relaxation.

(Keywords: polycarbonate; annealing; rejuvenation; structural temperature; damping)

INTRODUCTION

Internal friction measurements were undertaken to check experimentally some implications of a model previously proposed[1–4]. This model relies on basic classical equations chosen as simple as possible and takes into account the effect of annealing below T_g on the yield behaviour and enthalpy relaxation of polycarbonate (PC). It is extended here to take the loss curve into account. The basic ideas of this model are discussed below.

The chief parameter to be adopted in annealing investigations is θ, the structural temperature, i.e. the temperature at which the structure of the sample in a metastable state related to a given thermal or mechanical history would be in equilibrium. As in previous papers[3,4], a simple linear relation is chosen for the entropy change $\Delta S(\theta)$ produced by annealing or by deformation:

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

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

The parameter 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[5]:

$$d\theta = \nu_a(T_a - \theta)\exp(C'_a\theta - Q_a/RT_a)\,dt_a \tag{2}$$

where subscript a refers to annealing, ν_a and Q_a are constants and denote the frequency factor and the activation energy of the annealing process respectively.

The deformation process at yield depends on the Eyring non-Newtonian viscosity which under small stresses reduces to Newtonian viscosity expressed by:

$$\eta = AT/2\gamma_0\gamma_d \exp(C'_d\theta - Q_d/RT) \tag{3}$$

where deformation is denoted by subscript d and the test temperature by T. A is a constant and γ_0 is the elementary shear.

We propose to describe the loss tangent through a generalized Maxwell model expressed by:

$$\tan\delta = (G/2\pi f\eta)^m \tag{4}$$

as in the Williams–Watts treatment[6]. G denotes the shear modulus and f the frequency of the damping test. The exponent m is about 1/3 according to Struik, who proposed this value for many materials, including amorphous glassy polymers[7].

Samples with a high θ value are called rejuvenated samples. In such cases θ may be influenced over a large range of annealing conditions below T_g, including room temperature[4]. If internal friction is measured, at constant frequency, on heating a rejuvenated sample up to T_g, the sample is submitted to an involuntary thermal treatment during the course of the measurements. As a consequence, θ decreases and the loss curve must reflect this change according to the model. It is the purpose of the present paper to give the response of the model in such conditions and to check it experimentally.

EXPERIMENTAL

Samples

We have chosen to rejuvenate the material by plastic deformation produced by cold rolling. Samples, which were machined from a sheet of Makrolon (Bayer) rolled

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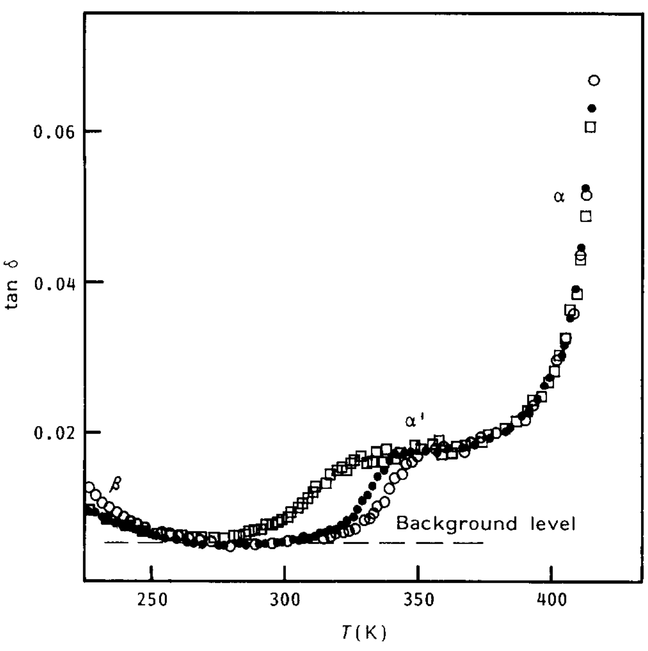

Figure 1 Examples of loss curves obtained on rejuvenated samples having different thermal histories; □, not annealed; ●, annealed 2 h at 40°C; ○, annealed 16 h at 40°C. The curves are related to the same testing frequency, 1 Hz, and the same heating rate, 60 K/h

50%, had a gauge length of 35 mm and were 1 mm thick and 5.5 mm wide. The length was parallel to the rolling direction. Before being tested the samples were pre-annealed at 40°C for various times and at 60°C for 2 h in order to give them different initial θ values. Thermal treatments were performed in a dry oven.

Damping tests

Internal friction was measured at two different constant frequencies (0.1 and 1 Hz) as a function of temperature from −50 to 140°C using a torsional Metravib low frequency microanalyser. Two different heating rates were used: 20 and 60 K/h.

DATA ANALYSIS

Let θ_a denote the initial structural temperature acquired by the sample prior to the damping tests. Examples of loss curves related to rejuvenated samples with different thermal histories and therefore characterized by different θ_a values, are given in *Figure 1*. On the left of the graph, the high temperature side of a peak can be discerned; this is the β peak associated with the local chain motion[7,8]. Such a peak was found not to be affected by thermal history[9] and therefore, according to the model, is not θ dependent. Therefore it will not be considered in the present paper.

Between the β and α dispersions, the loss curve exhibits an intermediate plateau region called α' in previous papers[10,11]. We consider this plateau as belonging to the low temperature side of the α peak related to the glass transition. Clearly, the location of α' on the loss curve depends on the thermal and mechanical history of the sample. It is shifted toward higher values with increasing T_a and t_a, i.e. with decreasing θ_a. We can therefore imagine that for low θ_a values, α' disappears from the loss curve. Two different cases must then be considered. These are discussed below.

The rejuvenation and annealing conditions prior to the test lead to a high θ_a value susceptible of decreasing during the course of the measurements on heating the sample. Let us assume that in such cases, for the deformation process, the decrease of the entropy term equals the increase of the enthalpy one, which implies that:

$$C'_d\theta - Q_d/RT = \text{constant} \qquad (5)$$

Then from equations (3), (4) and (5) and for a first approximation, the model predicts that the loss curve, at constant frequency, must exhibit a plateau.

The annealing conditions are such that rejuvenation recovers completely. This leads to a low θ_a value which will not be affected by heating the sample in the glassy range during the test. As a consequence, α' disappears from the curve. Such loss curves will be treated later in the second part of the paper. On *Figure 2*, four curves are given related to samples annealed at the same T_a for 2 and 20 h and tested at 0.1 and 1 Hz. Clearly the level of the α' peak is frequency dependent. As the position of α' in curves B and C is the same although the annealing times and the frequencies differ by a factor of ten, it can be concluded that an increase by the same factor of the annealing time or the frequency of the test has the same effect. This shift rate μ as defined by Struik[7] for creep measurements, equals unity within experimental errors.

NUMERICAL VALUES OF THE PARAMETERS

Numerical values of the parameter values are listed in *Table 1*.

Constants related to the loss tangent expression

Shear modulus. As a first approximation, the shear modulus is taken as constant throughout the whole test and for all the tests. It is therefore insensitive to frequency, temperature and heating rate changes. A mean value of the shear modulus data obtained together with the loss curve is considered.

Background level. Between the β and α' peaks the loss tangent curves exhibit a minimum value which is frequency

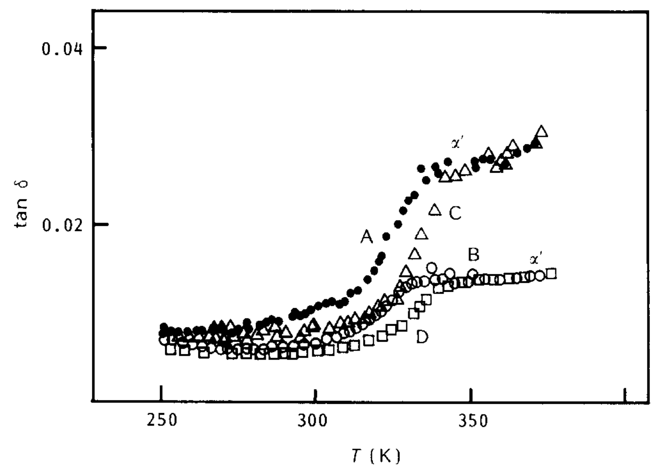

Figure 2 Loss curves of rejuvenated samples annealed at 40°C for 2 h (●, curve A; ○, curve B) and for 20 h (△, curve C; □, curve D). A testing frequency of 0.1 Hz was used to obtain curves A and C; curves B and D are related to 1 Hz. The heating rate was 20 K h^{-1} for all the curves. The positions of α' in curves B and C coincide

Table 1 Numerical values of the parameters

Parameters related to the loss tangent expression		
G (kg mm^{-2})	Background level	m
100	at 1 Hz: 5.14×10^{-3} at 0.1 Hz: 7.91×10^{-3}	0.36
Annealing parameters		
ν_a (s^{-1})	C'_a (K^{-1})	Q_a (kcal mol^{-1})
10^{-95}	0.7	64
Deformation parameters		
Traction or torsion (α_1 process)		
$\gamma_0\nu_d$ (s^{-1})	C'_d (K^{-1})	Q_d (kcal mol^{-1})
10^{-115}	0.83	76
Traction (α_2)	Torsion (α_2)	Traction-compression (α_1)
A_t (kg mm^{-2} K^{-1})	A (kg mm^{-2} K^{-1})	c
8.7×10^{-4}	5.7×10^{-4}	1.3

Table 2 Calculated θ values as a function of the annealing conditions

T (°C)	t (h)	θ (K)
40	2	439.3
40	16	436.5
40	20	436.2
60	2	431

dependent but not affected by thermal pre-treatments (see *Figure 1*). This value is taken as the background level.

Exponent m. This parameter is determined from curves A and B in *Figure 2*, which are related to the same annealing conditions. A mean value is taken for the level of the plateau and the background in both cases and the latter is subtracted from the former to obtain $\tan\delta_{0.1\,\mathrm{Hz}}$ and $\tan\delta_{1\,\mathrm{Hz}}$. Then from equations (3), (4) and (5):

$$m=\log(\tan\delta_{0.1\,\mathrm{Hz}}/\tan\delta_{1\,\mathrm{Hz}}) \qquad (6)$$

A value of 0.36 is found for equation (6), which is close to 1/3 as proposed by Struik[7].

Annealing parameters

The structural temperature of a cold rolled sample not yet annealed, i.e. the largest θ_a value in the present investigation, is not known. We may expect that it does not differ a lot from 460 K, the θ_a value of a sample rejuvenated by plastic deformation in torsion which was measured previously[4]. We therefore adopted this value as the integration limit which does not require to be known with accuracy provided it is high enough. The θ_a values related to the annealing pre-treatments are listed in *Table 2*. They are obtained by step-by-step numerical calculation from 460 K of equation (2) where the values of the parameters are exactly the same as those adjusted in a previous paper[3] using enthalpy relaxation measurements. The step was taken equal to 0.5 K.

Deformation parameters

The numerical values of the deformation parameters namely A, $\gamma_d\nu_0$, C'_d and Q_d are also obtained using previous results already published. Let us recall that one of the relations upon which the model relies is the Eyring equation which may be written as:

$$\dot{\gamma}=2\gamma_0\nu_d\exp(C'_d\theta-Q_d/RT)\sinh\tau/AT \qquad (7)$$

where $\dot{\gamma}$ and τ denote the shear strain rate and the shear yield stress respectively. For $\tau\gg AT$, relation (7) becomes:

$$\dot{\gamma}=\gamma_0\nu_d\exp(C'_d\theta-Q_d/RT)\exp\tau/AT \qquad (8)$$

while for $\tau\ll AT$:

$$\dot{\gamma}=2\gamma_0\nu_d\exp(C'_d\theta-Q_d/RT)\tau/AT \qquad (9)$$

In the last case the viscosity becomes Newtonian and is expressed by equation (3). Extensive data giving τ as a function of $\dot{\gamma}$ at different T are lacking in the literature, but the tensile yield stress has been studied as a function of the strain rate $\dot{\varepsilon}$ in a wide range of temperatures, including the T_g range, by one of us[12]. It was shown that two different deformation processes, called α_1 and α_2, respectively, may take place at yield; α_2 being the most probable at low stresses. For clarity, we reproduce on *Figure 3* the tensile yield stress data related to the α_2 process taken from this previous paper. Let us point out that low yield stresses data can only be obtained near T_g. In order to unify the notations, we give the following expression for the yield stress:

$$\sigma_t/T=A_t(\ln\dot{\varepsilon}-\ln\gamma_0\nu_d-C'_d\theta+Q_d/RT) \qquad (10)$$

which proceeds from equation (8) rewritten in the case of traction. A_t is a constant which parallels A. The best fit of equation (10) to the data of *Figure 3* gives the numerical value of the parameters related to the α_2 process. It was not possible to separate γ_0 from ν_d. The value of A_t has already been given in an earlier paper[13], while that of Q_d was found to be the same as for the α_1 process[1,2,14]. The constant A related to shear stresses may be evaluated for each process as a function of A_t and the ratio c of the yield stress in compression to the yield stress in traction, as:

$$A=2cA_t/3^{1/2}(1+c) \qquad (11)$$

already established in previous papers[15,16]. The ratio c has been measured for the α_1 process only[15]. Assuming that Newtonian viscosity is related to the α_2 process, most probable at low stresses, an approximate value of

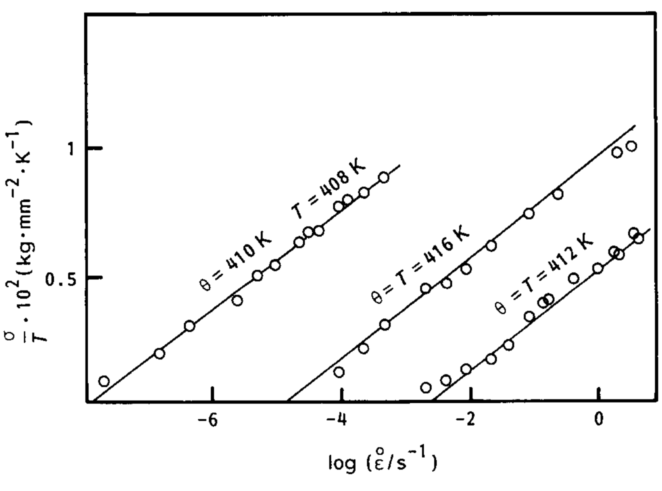

Figure 3 Ratio of the yield stress to the temperature of the test against the logarithm of the strain rate. Data are taken from a previous paper[12], full lines are a best fit of equation (10) to the data

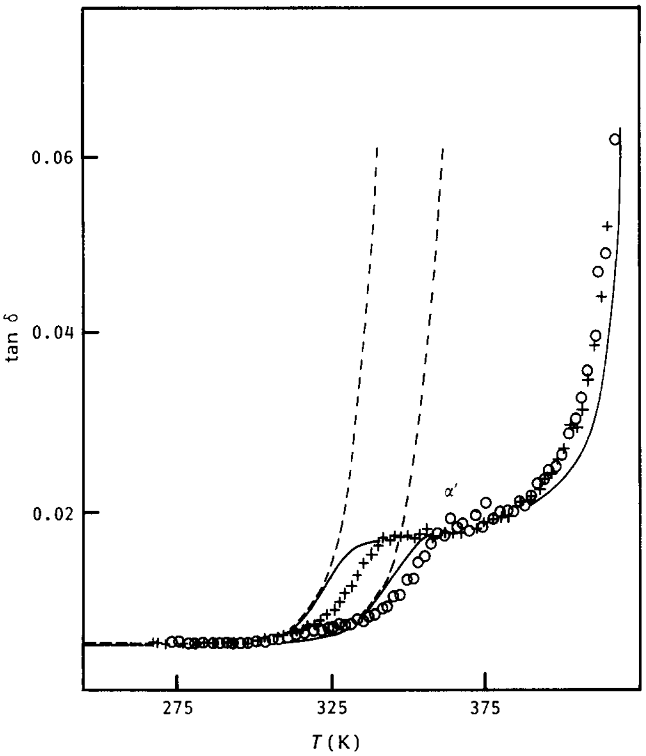

Figure 4 Loss curves related to rejuvenated samples annealed for 2 h at 40°C (+) and 60°C (○), tested at 1 Hz and a heating rate of 60 K/h. Dashed lines are calculated from equation (12) assuming that θ remains constant during the tests; full lines are calculated from equation (12) assuming a decrease of θ during the test. θ is calculated by numerical integration of equation (13) and *Table 2*

A may be obtained using equation (11) with A_t related to the α_2 process and c to the α_1 process, for want of a better estimate. Let us point out that an accurate value of A is not required because it appears with the exponent 0.36 in the expression of the loss tangent.

ORIGIN OF THE α' PEAK

Let us consider two samples characterized by the following θ_a values: 431 K and 439.3 K respectively (see *Table 2* for the related annealing conditions). By combining equations (3) and (4) and taking into account the value of the parameters given in *Table 1*, the numerical expression of the low temperature side of the α peak at constant frequency (1 Hz for example) may be obtained and written as follows:

$$\tan\delta = 5.14\times10^{-3} + ((5.62\times10^{4}/T)10^{-115} \times \exp(0.83\,\theta - (3.8\times10^{4}/T))^{0.36} \tag{12}$$

Assuming that for each sample, θ_a is not affected by heating during the damping measurements, the theoretical loss curve can be easily computed from equation (12) with $\theta = \theta_a$. Such a curve, plotted for each sample on *Figure 4* (dashed lines), is not dependent on heating rate and does not exhibit any α' peak. Equation (2) may be written as a function of the heating rate v and the current temperature T of the test, as:

$$d\theta = 10^{-95}\, v^{-1}(T-\theta)\exp(0.7\theta - (3.2\times10^{4}/T))\,dT \tag{13}$$

with the numerical values of the annealing parameters given in *Table 2*. *Figure 5* gives θ as a function of T for the two considered samples heated at 20 and 60 K/h. The graph is obtained by numerical integration of equation (13), from θ_a. On this figure, a critical temperature can be discerned for each sample and heating rate, above which θ begins to decrease. Below this temperature, the integration of equation (13) leads to a negligible decrease of θ which remains nearly equal to θ_a. Heating the sample in this range does not affect the θ value. Now, taking equation (13) into account, let us compute equation (12) in order to obtain the low temperature side of the α peak

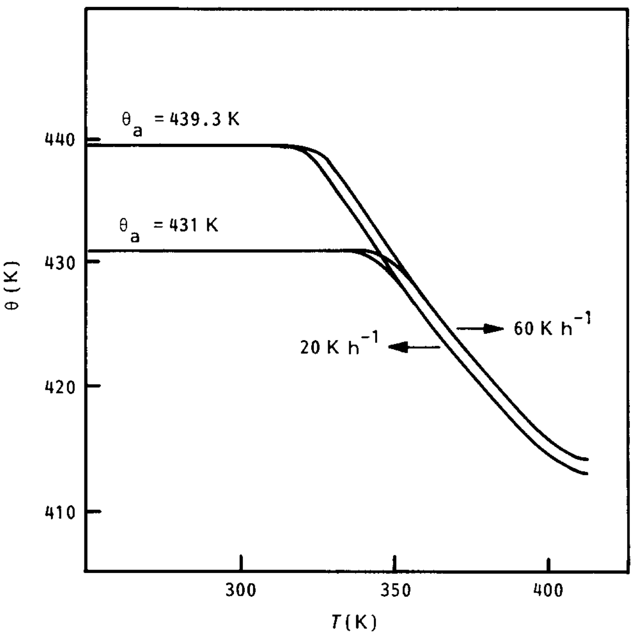

Figure 5 Theoretical plot of θ as a function of the test temperature for two different heating rates and for the two samples related to the loss curves of *Figure 4*

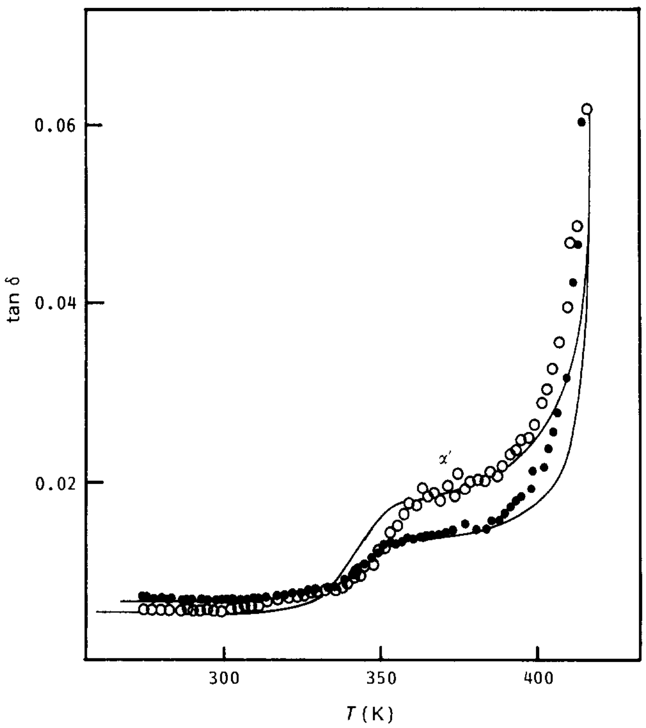

Figure 6 Loss curves related to rejuvenated samples annealed in the same conditions (2 h at 60°C), tested at the same frequency (1 Hz) but at two different heating rates: 60 K/h (○) and 20 K/h (●). Full lines are calculated from equations (3), (4), (13) and *Tables 1* and *2*

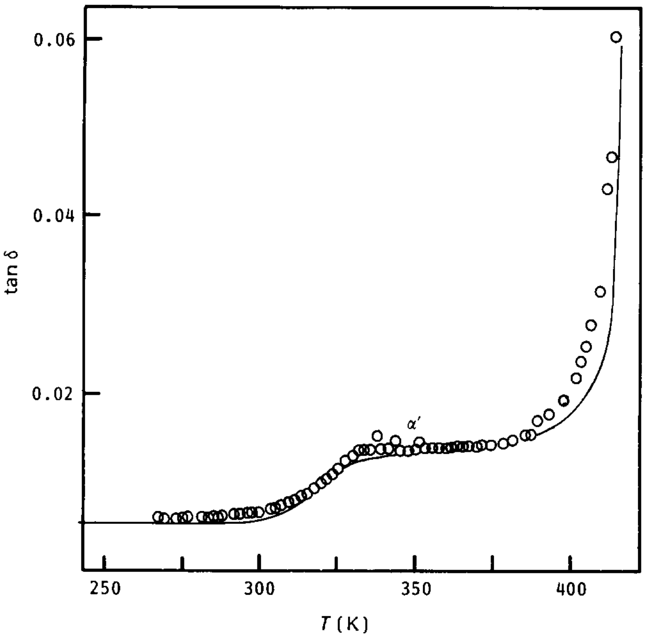

Figure 7 The same data as curve B of *Figure 2*, but here compared with the theoretical curve (full line) calculated from equations (3), (4), (13) and *Tables 1* and *2*

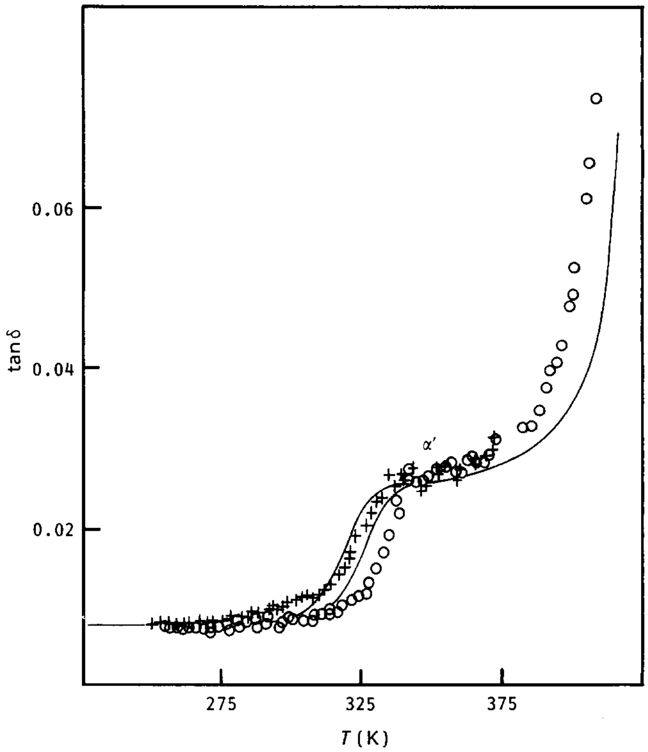

Figure 8 The same data as curves A and C of *Figure 2*, but here compared with the theoretical curves (full lines) calculated from equations (3), (4), (13) and *Tables 1* and *2*

related to samples, the θ of which is affected during damping measurements. Theoretical loss curves (full lines) are plotted on *Figure 4*. They exhibit an α' peak, the level and shape of which agree rather well with the data.

Of course, the model implies that α' is not a reversible peak. At the end of a loss curve obtained on heating the sample up to the T_g range, θ has a very low value which will not be affected on cooling. Damping curves obtained on cooling the sample from the T_g range cannot exhibit any α' peak. This implication of the model is in agreement with experimental results published in the early work of Illers and Breuer[17] and later in a previous paper by ourselves[10].

COMPARISON OF THEORETICAL AND EXPERIMENTAL RESULTS

The checking of the model by the data of *Figure 4* is promising. Let us give some other examples related to other annealing pre-treatments, heating rates and testing frequencies.

On *Figure 6*, the effect of changing the heating rate is shown both experimentally and theoretically. Although the loss curves are related to samples characterized by the same θ_a value and tested at the same constant frequency, the level of α' differs, indicating a significant heating rate effect.

On *Figure 7*, an example is given of a particularly good agreement between the data and the response of the model. Examples of loss curves obtained at 0.1 Hz are presented in *Figure 8* and compared with the theoretical full curves.

Let us point out that, except for m and G, all the parameters have been previously adjusted using other types of measurements: enthalpy relaxation and tensile yield stress near the glass transition.

CONCLUSIONS

A model allowing yield and annealing processes to be discussed within a common formalism is extended here to describe the loss curve quantitatively. The accuracy of the fit is promising and reinforces the basic idea that θ is the main parameter to be adopted in annealing investigations.

The decrease of θ on heating the sample offers an explanation of the origin of the α' peak appearing on the loss curve of rejuvenated samples and makes it possible to account for heating rate effects.

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