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EFFECT OF THERMAL HISTORY ON THE α' LOSS PEAK OF POLYCARBONATE

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Résumé - Il est connu que le pic de pertes des polymères vitreux apparaissant juste avant la transition vitreuse est très sensible aux traitements thermiques et mécaniques. Pour différents passés thermiques, nous avons mesuré le frottement intérieur du Polycarbonate à plusieurs fréquences dans un domaine de températures compris entre les transitions β et α . Nous avons tenté de modéliser le comportement observé en partant d'une théorie précédemment proposée pour rendre compte de la relaxation d'enthalpie d'échantillons recuits. L'accord avec l'expérience tend à prouver que le même mécanisme est responsable de la relaxation d'enthalpie et du pic α' . Ce modèle n'implique qu'un seul paramètre lié à la structure: une température de structure.

Abstract - The sub-T_g loss peak of glassy polymers is known to be very sensitive to mechanical and thermal treatments. After different thermal histories, the internal friction of Polycarbonate was measured at different frequencies in the temperature range between the β and α transitions. We attempted to model this behaviour, using a theory previously proposed to account for enthalpy relaxation exhibited by annealed samples. The agreement with the data seems to show that the same mechanism underlies both enthalpy relaxation and the α' loss peak. The model involves only one structure dependent parameter, a structural temperature, to account for the observed behaviour.

INTRODUCTION.

It has been known for some time that many glassy polymers reveal a loss peak at temperatures just below the glass transition /1/. The magnitude of this loss peak is highly sensitive to thermal treatments; decreasing upon annealing and increasing with quenching. The aim of this paper is, on one hand to measure the influence of time and temperature on the loss peak α' exhibited by quenched samples of Polycarbonate at low frequencies, on the other hand, to compare the data with a theoretical model previously proposed to account for the influence of thermomechanical treatments on the enthalpy relaxation.

THEORETICALEvolution of the structural state.

Previously /2/, we proposed to characterize the structural state of a polymer by the temperature θ at which it would be in equilibrium and to express the evolution of θ with time t and temperature T by the following relation:

$$d\theta = (T - \theta) J_1(T, \theta) dt \quad (1)$$

where J_1 denotes the frequency of configurational changes.

Quite generally, a frequency factor may be written:

$$J = \nu_0 \exp \left(\frac{T \Delta S(\theta) - Q}{R T} \right)$$

where ν_0 is the vibrational frequency, $\Delta S(\theta)$ the structural entropy, Q the activation energy and R the universal gas constant.

In a previous paper /3/, related to the enthalpy recovery of mechanically rejuvenated samples, we proposed the following relation in agreement with the D.S.C. data:

$$J_1 = \exp \left(73 + 0.7 (\theta - 416.6) - \frac{64000}{R T} \right) \quad (2)$$

This relation will be used in this paper.

Mechanical losses

Some time ago /4/, we proposed the Eyring model to account for the yield stress τ as a function of temperature and strain rate $\dot{\gamma}$; the basic relation of which may be written:

$$\dot{\gamma} = 2 \gamma_0 J_2 (T, \theta) \sinh \frac{\tau}{A T} \quad (3)$$

where γ denotes the elementary shear, J_2 the frequency factor and R/A the rheological volume.

For $\tau \gg AT$ this relation becomes:

$$\dot{\gamma} = \gamma_0 J_2 (T, \theta) \exp \frac{\tau}{A T} \quad (4)$$

while for $\tau \ll AT$:

$$\dot{\gamma} = \frac{2 \gamma_0 J_2 (T, \theta)}{A T} \tau$$

and the related newtonian viscosity is expressed by:

$$\eta = \frac{A T}{2 \gamma_0 J_2 (T, \theta)}$$

Previous data on the yield stress near T_g /5/ allow to adjust the parameters of relation (4). The fit on figure 1 was obtained by taking:

$$\gamma_0 J_2 = \exp \left(80.5 + 0.83 (\theta - 416.6) - \frac{76000}{R T} \right)$$

and

$$A = 8.7 \cdot 10^{-4} \text{ Kg mm}^{-2} \text{ K}^{-1}$$

Using a Maxwell model and the exponent m of the Williams-Watt treatment /6/ to account for a distribution of relaxation times, one obtains:

$$\text{tg } \delta = \left(\frac{G}{\omega \eta} \right)^m = \left(\frac{2 \gamma_0 G J_2 (T, \theta)}{A T \omega} \right)^m \quad (5)$$

where G is the shear modulus (100 Kg.mm^{-2}) and ω the angular frequency. In this relation, only m can be adjusted; the best fit is obtained with $m = 0.36$ which is close to the mean value of $1/3$ proposed by Struik /7/ for many materials.

It is now possible to compute $\text{tg } \delta$ for any thermal history.

EXPERIMENTAL.

Samples of Makrolon (Bayer) were ice-quenched from 165°C and, after 7 days at about 12°C, heated up to 137°C in a METRAVIB low frequency tester at a rate of 20°/h. During heating, the loss tangent was measured at three frequencies (1, 0.1 and 0.01 Hz). The same measurements were performed during cooling from 137°C at the same rate, immediately after heating.

OTHER DAMPING PROCESSES.

When a sample has been heated near T_g , the α' peak disappears and the remaining damping may be divided into three components: the tail of the β peak: $\text{tg } \delta_\beta$, the background: $\text{tg } \delta_B$, the beginning of the α transition: $\text{tg } \delta_\alpha$.

One obtains an acceptable fit with:

$$\begin{aligned}\text{tg } \delta_\beta &= \left(\nu \exp \left(\frac{10000}{R T} - 23 \right) \right)^{0.22} \\ \text{tg } \delta_B &= \left(\frac{4 \cdot 10^{-3}}{\nu} \right)^{0.2} \\ \text{tg } \delta_\alpha &= \left(\frac{1}{\nu} \exp \left(82.5 - \frac{76000}{R T} \right) \right)^{0.36}\end{aligned}$$

where ν is the frequency of the damping test.

RESULTS.

The model is compared with the data on figures 2 and 3 corresponding respectively to a quenched sample heated up to T_g , then immediately cooled. Agreement is good, provided one considers that in relation (5), m is the only adjustable parameter.

Furthermore, we computed the relation:

$$\mu = \frac{d \log \omega}{d \log t}$$

giving at constant losses and temperature the frequency shift versus the ageing time t , μ was found to equal 1.18 in agreement with Struik's results on creep /8/.

The model predicts that below 100°C and at constant frequency, $\text{tg } \delta$ only depends on the ageing time and not on the ageing temperature; consequently ageing appears to be athermal in this range of temperature as observed by Struik /9/.

DISCUSSION.

The model gives a good description of results when the thermal history consists of heating or cooling the sample at constant rate.

However, the plot of $\log \text{tg } \delta$ versus $\log \nu$ as a function of the ageing

time and temperature within a large range of frequencies gives a less accurate fit. We believe this to be due to oversimplifications in the model, in particular from the use of the Williams-Watt relation and an empirical expression of the background.

CONCLUSION.

The same model can be used to account with an acceptable agreement for the yield stress, the enthalpy relaxation and the α' loss peak of Polycarbonate. This probably means that the molecular movements involved are the same.

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Fig. 1 - Ratio of the engineering yield stress of Polycarbonate to temperature versus the logarithm of the strain rate. Straight lines are calculated from relation (4).

Fig. 2 - Logarithm of the loss tangent of quenched Polycarbonate heated at a rate of \$20^\circ/\text{h}\$. Curves are computed from relation (5).

Fig. 3 - Logarithm of the loss tangent of Polycarbonate cooled from 410 K immediately after heating. Curves are computed from relation (5).