Investigation of the glass transition on atactic polystyrene by isothermal internal friction measurements

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 abstract. — This article presents the first results obtained on atactic polystyrene thanks to a new method, allowing isothermal internal friction measurements. The wide range of available frequencies allows us to show that the glass transition in polystyrene corresponds to a single relaxation time process, due for example to a stress induced reorientation of the chain bonds that make up the macromolecules. The temperature dependence of the relaxation strength seems to indicate the presence of a pseudo critical temperature ($T_c = 175 K$), well below the glass transition temperature, corresponding to a second order thermodynamic transition.

1. Introduction. — Relaxation processes associated to the glass transition in amorphous polymers have been widely studied by dynamic mechanical techniques [1, 2, 3]. That glass transition is generally associated with large scale chain backbone motions through rotational isomerisation of the links between adjacent carbon atoms. The corresponding anelastic strain is certainly of entropic nature, as in the case of the relaxation due to the stress induced diffusion of interstitial atoms in a B.C.C. crystalline matrix [4].

With the commonly used low frequency internal friction techniques [5, 6], relaxation times can be determined only on a very narrow temperature range because of the high thermal activation associated with the $\alpha$ loss peak (corresponding to the glass transition).

The aim of this paper is therefore to present results obtained from atactic polystyrene thanks to a new method allowing isothermal internal friction measurements on a wide frequency range.

2. Experimental method. — Samples in the form of flat bars ($50 \times 4 \times 2 \text{ mm}^3$) of atactic polystyrene moulded under pressure at 180 °C and annealed at 140 °C, have been tested on an apparatus allowing isothermal internal friction measurements, previously described [7].

The working principle of the apparatus will be shortly recalled. It is an inverted torsional pendulum with a high eigen frequency (a few hundred hertz), set into torsion vibrations at frequencies low enough to permit neglect of inertial forces. The internal friction is then obtained directly by the measure of the phase lag between the driving current and the strain on the sample, brought about by an optical method.

Testings were carried out in air in order to minimize the gradient of temperature on the sample, with maximum shear strains included between $5 \times 10^{-6}$ and $5 \times 10^{-5}$.

The necessity to control the temperature in a very precise way (better than 0,1°) did not allow us to operate at frequencies lower than 0.001 Hz. Towards the high frequencies, it was necessary to set a limit up to 60 Hz in order to maintain the inertial forces negligible.
3. Experimental results. — The variations of the damping (phase lag \( \phi \)) and of the vibration amplitude of a sample held at 101.9 °C are shown in figure 1. One can notice the presence of a very high relaxation peak as well as the large corresponding modulus effect. The peak seems to be larger than a single relaxation time one and slightly dissymmetrical, but this is simply due to the importance of the relaxation strength. As a matter of fact, it may be seen in figure 2 that the real and imaginary components of the dynamic modulus:

\[
J_1 = \frac{A}{\sqrt{1 + \tan^2 \phi}} \\
J_2 = \frac{A \tan \phi}{\sqrt{1 + \tan^2 \phi}}
\]

approximately follow Debye's relations, characteristic of a single relaxation time process. One can also note that the peak in figure 2, has been shifted towards the low frequencies, compared to the one in figure 1, and it is advisable to take this shift into account before using internal friction results.

Figure 3 shows internal friction peaks obtained at different temperatures. It can be seen that a variation of 18 °C in temperature is sufficient to shift the damping maximum on about 4 decades in frequency. Therefore, a very accurate temperature control is required because of the importance of the thermal activation. In figure 4, one can also check that the relaxation is caused by perfectly linear effects, for the low strain amplitudes considered here, since a large variation of the applied stress does not alter the results.

In figure 5 the measured relaxation times are plotted versus the reciprocal absolute temperature. The transition temperature being related to the vibration
Fig. 4. — Influence of the stress amplitude on the internal friction peak.

Fig. 5. — Variations of the relaxation time with the measurement temperature (x : this work, A Yano et al.).

frequency, the lowest temperature used has been chosen as $T_g$, the transition temperature

$T_g = 91.8 \, ^\circ\text{C}$.

In figure 5, the relaxation times are rapported to $\tau_0$ the relaxation time obtained at 91.8 $^\circ\text{C}$. The results are also compared to the W.L.F. equation with universal constants [8]. It may be seen that the experimental results are best fitted by an Arrhenius plot corresponding to an apparent activation enthalpy :

$$H_a = 147 \text{ kcal/mole}.$$

An experimental point obtained by Yano et al. [9] at 10 kHz, is also reported to be compared to our results. From figure 2 it may be seen that the usual transition temperature given in the literature ($T_g = 102 ^\circ\text{C}$) corresponds to a frequency :

$$N_\omega = 0.19 \text{ Hz},$$

close to the value extrapolated from viscosity measurements : 0.15 Hz [10].

On figure 3, it could be noted that the relaxation strength is strongly temperature dependent, and figure 6 shows that a critical temperature $T_c$ of Curie Weiss type, may be deduced from that variation :

$$\varphi = \frac{A}{T - T_c},$$

with :

$$T_c = 175 \, \text{K}.$$

Such a temperature can correspond to the pseudo critical temperature introduced by Kauzmann [11] and can be the glass transition temperature associated with an infinitely slow cooling rate. Such a temperature can correspond to a true second order thermodynamic transition below which an equilibrium crystalline phase appears.

Fig. 6. — Variation of the relaxation strength with the measurement temperature.

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References