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Internal friction in amorphous polystyrene at low temperature and high frequency (*)

J. Y. Duquesne and G. Bellessa

Laboratoire de Physique des Solides (**), Université Paris-Sud, 91405 Orsay, France

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Résumé. — Nous présentons l'observation, dans le polystyrène, d'un pic de frottement interne localisé autour de 80 K à 50 MHz. Ce pic présente beaucoup de similitudes avec celui observé dans le sélénium amorphe et est interprété dans le cadre du même modèle. Nous expliquons nos résultats à l'aide de processus de relaxation par activation thermique dont les énergies sont distribuées de façon constante entre 0 et 600 K. Nous suggérons que le pic observé est la résolution à haute fréquence de l'épaulement ε qui a été observé précédemment à beaucoup plus basse fréquence.

Abstract. — The existence in polystyrene of an internal-friction peak around 80 K at 50 MHz is reported. This peak displays many similarities with the peak observed in amorphous selenium. It is interpreted in the frame of the same model. We explain our results with thermal activated relaxation processes displaying a constant distribution of barrier heights between 0 and 600 K. We suggest that the observed peak is the resolution at high frequency of the ε -shoulder which has been reported previously at much lower frequency.

Many amorphous materials, such as fused silica [1], amorphous arsenic [2], amorphous PdSi [3] exhibit an internal-friction peak at low temperature ($T < 100$ K) and high frequency (1 to 100 MHz). Anderson and Bömmel suggested that thermal activated motions of some oxygen atoms could be the source of the internal friction in fused silica [1]. It was pointed out recently that thermal activated processes, with activation energies extending to zero, exist in amorphous selenium, which is polymeric [4]. Hence, it is interesting to clarify whether those processes are a particular feature of amorphous selenium or, on the contrary, a general feature of amorphous polymers. To our knowledge, there is no internal-friction measurement in amorphous polymers directly comparable with those existing in amorphous selenium, that is to say which are in the 10-100 MHz range and between 2 and 100 K. (However, there are internal-friction expe-

riments in the kHz range [5].) We report here such measurements performed with an ultrasonic method in amorphous polystyrene. This organic polymer is more complex than the selenium since it has heavy side groups (phenyl groups) whereas the selenium monomer is no more than a single atom. This complexity is responsible for the numerous internal-friction peaks at low frequency which exist in polystyrene below the glass transition temperature [5, 6].

The sample was obtained from commercial atactic polystyrene of mean molecular weight 321 000. It was melted down under vacuum and then cooled to room temperature. Acoustic measurements were carried out with a usual pulse method, using two X-cut quartz as transducers [7]. We did not determine the absolute value of the attenuation because of the non-perfect parallelism which plays a role difficult to precise, especially at high frequencies.

As shown in figure 1, the acoustic attenuation of amorphous polystyrene exhibits a large and well defined peak. The temperature location of this peak increases with increasing frequency and is 68, 73 and 83 K at 8.2, 26 and 52 MHz respectively (Fig. 2). The magnitude of the peak increases also with increasing frequency. In particular, it was impossible to locate the ultrasonic attenuation peak at frequencies higher than 52 MHz. It can be seen in figure 1 that the peaks are

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(**) Associé au Centre National de la Recherche Scientifique.

Fig. 1. — Attenuation of ultrasonic longitudinal waves as a function of temperature in amorphous polystyrene. The curves are arbitrarily shifted along the attenuation axis.

Fig. 2. — Temperature displacement of the internal friction peak as a function of frequency. The dashed lines δ and γ are from [5]. Δ shows the ϵ -shoulder presented in reference [5]. $\circ$ are from the present work. The continuous line is the theoretical curve obtained from numerical calculation starting from equation (2) and using for E_{MAX}/k_B and τ_0 600 K and 10^{-11} s respectively.

very broad and also that the attenuation is strongly varying at the lowest temperature. This latter property can be observed down to 4 K in figure 1 and down to 2 K in [8].

There is a great similarity between the acoustical properties of amorphous selenium and those of amorphous polystyrene, at low temperature and high frequency. Both materials exhibit a broad, large and well-defined peak whose temperature location increases with increasing frequency and for both materials the attenuation is very sensitive to the temperature down to 2 K. As in the case of amorphous selenium [4], these results may be interpreted in the frame of a thermal activation model. Thus the width of the ultrasonic attenuation peak involves a distribution of barrier heights and the strong variations of the attenuation of the lowest temperature reveal the existence of very small barrier heights. The simplest distribution of barriers that one can choose is a constant between 0 and a certain barrier cut-off E_{MAX} . Although the microscopic nature of the activated processes remains unknown, they can be described as the motion of some entity above potential barriers separating two equilibrium sites. The sound wave disturbs the equilibrium population of these sites. Then, equilibrium is re-established with a characteristic time τ , involving acoustic absorption. τ is related to the barrier height E according to the Arrhenius law :

$$\tau = \tau_0 \exp \frac{E}{k_B T} \quad (1)$$

where τ_0 is a characteristic time and T the temperature. This formula holds as long as the asymmetry of the double-well is small compared to E . The ultrasonic attenuation α due to a distribution of barrier height n_0 constant between 0 and E_{MAX} has been calculated previously with the assumption of a temperature independent relaxation strength ϵ [4]; it is found :

$$\alpha = \frac{k_B n_0 \epsilon}{2V} \omega T (\tan^{-1} \omega \tau_{\text{MAX}} - \tan^{-1} \omega \tau_0) \quad (2)$$

where V is the sound velocity (2.8×10^5 cm/s for longitudinal waves in amorphous polystyrene), ω is the ultrasonic angular frequency and τ_{MAX} is given by equation (1) for E equal to E_{MAX} . Equation (2) describes a peak in the attenuation whose location increases with increasing frequency. A good fit with the experimental variation is then obtained for E_{MAX}/k_B and τ_0 equal to 600 K and 10^{-11} s respectively (Fig. 2).

However, the accuracy of those numerical values is poor since the ultrasonic frequency range of our study is not very large. Equation (2) gives an attenuation peak larger than a pure Debye peak but still narrower than the experimental peak within a factor 2 [4].

A constant distribution of activation energy between 0 and E_{MAX} is obviously a very crude activation model and a more sophisticated distribution of double-well potential has been proposed recently [9]. Never-

theless, we stress here that our simple activation model does not require any low barrier cut-off to produce a peak in the attenuation and that the magnitude of the attenuation deduced from our model is in good agreement with the experimental data. (This latter property has been studied for amorphous selenium [4].) Lastly, the model we consider here implies at low temperature, an attenuation law proportional to the frequency and to the temperature which is indeed observed experimentally between 1.5 K and 4 K [8].

It is interesting to compare the present results with the internal-friction measurements at much lower frequencies. As the temperature is decreased from the glass transition temperature, four well defined mechanical relaxation peaks appear : the α , β , γ and δ peaks where α stands for the glass transition peak [5, 6]. Moreover, Yano and Wada have reported a shoulder ε in the internal-friction factor located at about 30 K at 34 kHz [5]. We have plotted in figure 2 the temperature location of the γ and δ peaks, the shoulder ε and the present experimental results. From the extrapolation of the frequency dependence of the temperature location of the δ peak, we can deduce that the δ peak should be located around 130 K at 26 MHz. In fact, we did not observe any peak in that range (Fig. 1). Further investigations between 100 kHz and 100 MHz could elucidate this point. Nevertheless, it is very attractive to associate the present experimental results with the ε -shoulder and to make the following assumption : at low frequency (10 kHz), the ε peak merges in the δ peak and appears as a shoulder [5]; then, as the frequency increases it grows into a resolved peak.

Indeed, the magnitude of an acoustical attenuation peak due to thermal activation processes is roughly proportional to the frequency and the peak height at 34 kHz deduced from the one at the 26 MHz is then consistent with the observed shoulder. This one has been reported for transverse waves [5] and the present results are obtained from longitudinal waves. Nevertheless, the small difference in the temperature location of the peak for transverse and longitudinal acoustic waves respectively should not invalidate our assumption. Obviously, new acoustic measurements in all the frequency range (from 100 kHz to 100 MHz) would be necessary to confirm this assumption.

To conclude, similar relaxation processes seem to exist in two very different amorphous polymers (selenium and polystyrene). In consequence they seem to be independent of the detailed chemical nature of the polymer and they could even be still present in the glassy state. Low activation energy processes with a wide distribution of barrier heights extending to very small values can explain our experimental results. Nevertheless, tunnelling relaxation processes through the potential barriers cannot be ruled out [9, 10]. Deviations from the Arrhenius' law or isotopic effects could reveal such tunnelling processes [10]. Hence, an accurate measurement of the temperature location of the peak *versus* frequency (in a very large frequency range) would be very interesting.

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