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Relaxation strength and distribution function of an internal friction peak

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Abstract

A procedure based on the mechanical properties of a modified anelastic element (MAE) has already been developed to get a functional dependence of the real and imaginary components of the dynamical modulus or compliance. The MAE is essentially a standard anelastic element except for its characteristic time, which depends on the frequency. The analysis of this dependence provides an analytical description of not only the dynamical properties but also the distribution function.

In this work it is shown that the procedure can be extended to internal friction peaks, yielding not only the parameters of the distribution function but also the relaxation strength. This procedure is applied to various materials and the results are compared with a previous method proposed in the literature.

1. Introduction

In linear viscoelastic materials with a relaxation strength $\Delta \ll 1$ the internal friction F is practically equal to the imaginary component of the dynamical modulus or compliance, namely G_2 or J_2 respectively. In this case F is characterized by Δ and by the distribution function derived from G_2 or J_2. Nevertheless, recently it has been demonstrated that even for large values of Δ a distribution function can be associated with F [1].

Since the distribution function is related to structural micromechanisms, several researchers have concentrated on determining Δ and the parameters of the distribution from internal friction peaks measured as a function of temperature [2] or frequency [3]. In particular, the former peaks have been treated by Nowick and Berry, who developed a methodology [2] applicable to symmetrical internal friction peaks in order to determine the mean characteristic time τ_m and the halfwidth β of a log–normal distribution. This distribution, which is statistically appropriate, has the disadvantage that the mechanical properties derived from it cannot be written in terms of known functions but must be calculated numerically. Because of this, a model based on the standard anelastic solid (SAS) (ref. 4, p. 48) but with a characteristic time that depends on the frequency was introduced to provide simple analytical expressions for the dynamical moduli or compliances. Moreover, this modified anelastic element (MAE) leads to a symmetrical distribution function which is very similar to a log–normal distribution [5].

It is the purpose of this paper to show that the MAE can also be used to describe internal friction peaks, enabling us to calculate the relaxation strength as well as the parameters of the distribution. The methodology developed to determine these parameters will be applied to peaks measured as a function of temperature and frequency in various materials.

2. Theory

In a previous paper it has been shown that the real and imaginary components of a linear viscoelastic material can be expressed as [5]

$$G_1(\omega, T) = G_u(T) - \frac{G_u(T) - G_r(T)}{1 + [\omega\tau_\epsilon(T)]^{2\gamma(T)}} \tag{1}$$

$$G_2 = \frac{\tilde{\gamma}(T)[G_u(T) - G_r(T)]}{2\cosh\{\tilde{\gamma}(T)\ln[\omega\tau_\epsilon(T)]\}} \tag{2}$$

where G_u and G_r are the unrelaxed and relaxed moduli respectively, $\tau_\epsilon(T)$ is the mean time of the distribution function and γ or $\tilde{\gamma}$ – which both vary between zero and unity and may depend on the temperature – characterizes the halfwidth of the distribution. Even when γ and $\tilde{\gamma}$ are not strictly equal, their difference is negligible, particularly for $0.5 \leqslant \gamma, \tilde{\gamma} \leqslant 1$. This interval corresponds to symmetrical distributions similar to log–normals with $0 \leqslant \beta < 3$ [5].

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Taking into account that the internal friction F is the ratio between G_2 and G_1 and that the relaxation strength is $\Delta=(G_u-G_r)/G_r$, eqns. (1) and (2) lead to

$$F=\frac{\gamma}{2\cosh[\gamma\ln(\omega\tau_\epsilon)]}\Bigg/\left(\frac{1+\Delta}{\Delta}-\frac{1}{1+(\omega\tau_\epsilon)^{2\gamma}}\right) \quad (3)$$

On defining

$$\tau_t=\tau_\epsilon(1+\Delta)^{1/2\gamma} \quad (4)$$

and

$$\alpha=\frac{\gamma\Delta}{(1+\Delta)^{1/2}} \quad (5)$$

eqn. (3) can be rewritten as

$$F=\frac{\alpha}{2\cosh[\gamma\ln(\omega\tau_t)]} \quad (6)$$

It should be noticed that eqn. (6) has the same form as the internal friction of an SAS but with a characteristic time that depends on the frequency as

$$\tau_t(\omega, T)=[\tau(T)]^{\gamma}\omega^{\gamma-1}$$

i.e. eqn. (6) gives the analytical form of the internal friction of an MAE.

Eqns. (4)–(6) are not sufficient to determine either the strength of relaxation or the parameters of the distribution, τ_ϵ and γ. Effectively, this determination is based on a set of equations that depend upon how the internal friction data are measured, *i.e.* at a constant temperature or at a constant moment of inertia.

For instance, by using a forced oscillating system, F can be measured together with G_1 over a wide interval of frequency at a fixed temperature. In this way, if $G_1(\omega)$ reaches the asymptotic limits for very high and low frequencies G_u and G_r respectively, then Δ is calculated straightforwardly. Hence, on considering that the maximum of the internal friction peak is $F_{max}=\alpha/2$, the parameter γ is derived using eqn. (5). Finally, τ_t arises directly from eqn. (6).

On the other hand, by employing a freely oscillating torsional pendulum, the internal friction and the frequency of oscillation, f, can be measured at different temperatures but at a fixed moment of inertia, I. In this situation the dynamic modulus G_1 is related to the angular velocity $\omega=2\pi f$ according to $G=kI\omega^2$, k being a geometrical constant. Hence eqn. (1) can be rewritten as

$$\omega^2(T)=\omega_u^2-\frac{\omega_u^2(T)-\omega_r^2(T)}{1+[\omega(T)\tau_\epsilon(T)]^{2\gamma(T)}} \quad (7)$$

The temperature dependences of ω_u and ω_r are determined from the asymptotes of $\omega(T)$ at low and high temperatures, respectively. Unlike in the previous analysis, $\gamma(T)$ cannot be determined from the maximum since it varies with temperature; thus additional measurements must be included. By using a torsional pendulum with a variable moment of inertia [6], it is possible to measure the partial derivative of F with respect to ω at a constant temperature. Thus eqn. (6) leads to the equation

$$\left.\frac{\partial\ln F}{\partial\ln\omega}\right|_T=-\gamma(T)\tanh\{\gamma(T)\ln[\omega\tau_t(T)]\} \quad (8)$$

which together with eqns. (4)–(7) constitutes a system of equations yielding the values of Δ, γ and τ_ϵ at each temperature.

3. Applications

Firstly, it is interesting to notice that eqn. (6) has been proposed empirically for various materials [5]. For instance, Gaudaud and Woirgard [7] described the internal friction of phosphorous-doped silicon by

$$F=\tilde{\Delta}\frac{(\omega\tau_m)^a}{1+(\omega\tau_m)^{2a}} \quad (9)$$

a being a constant which is equivalent to the parameter γ of the MAE, while $\tau_m=\tau_t$. Both parameters are derived directly from eqn. (4) assuming that $\alpha\approx\tilde{\Delta}$.

Secondly, it should be pointed out that in order to apply this procedure, the experimental data of F, ω and $\partial\ln F/\partial\ln\omega$ must be accurately measured. However, in their work [2] Nowick and Berry remarked that accuracy is not usually attained in measurements of $\omega(T)$. Moreover, very accurate data found in the literature gave only the internal friction and frequency dependence on temperature but not the partial derivative. Because of this, a set of precise measurements are being performed using the torsional pendulum with a variable moment of inertia [6]. Meanwhile, in order to solve the system given by eqns. (4)–(8), the simulated data shown in Fig. 1 are proposed both for $F(T)$ and $\omega(T)$. Figure 2 shows the excellent agreement between the values of $\gamma(T)$ and $\Delta(T)$ calculated from the system and those proposed. Also, it is determined that $\ln\tau_t=\ln\tau_o+\Delta H/kT$, *i.e.* the proposed temperature dependence of τ_t.

Another application is based on the set of internal friction peaks illustrated in Fig. 3, which can be treated in terms of an MAE. These peaks correspond to forced oscillation measurements in atactic polystyrene (PS) at various temperatures and were described using a log-normal distribution function [9] with $\beta=1.6$ by applying the methodology developed by Nowick and Berry [2]. Since $\Delta\gg1$ for PS, the inflection point of G_1 at $\omega=\tau_\epsilon^{-1}$ is to the left of the peak centred at $\omega=\tau_t^{-1}$. Thus in the frequency range where the whole

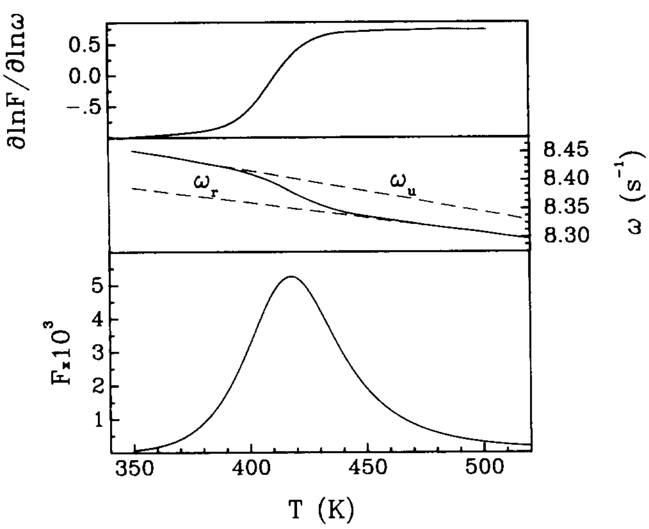

Fig. 1. F, ω and $\partial \ln F/\partial \ln \omega$ *vs.* temperature calculated from eqns. (6)–(8) respectively with $\gamma(T) = -2.35\times10^{-3}T + 1.82$ and $\ln \tau = -30 + 1.17\times10^{4}/T$. $\omega_u(T)$ and $\omega_r(T)$ are represented by the dashed lines.

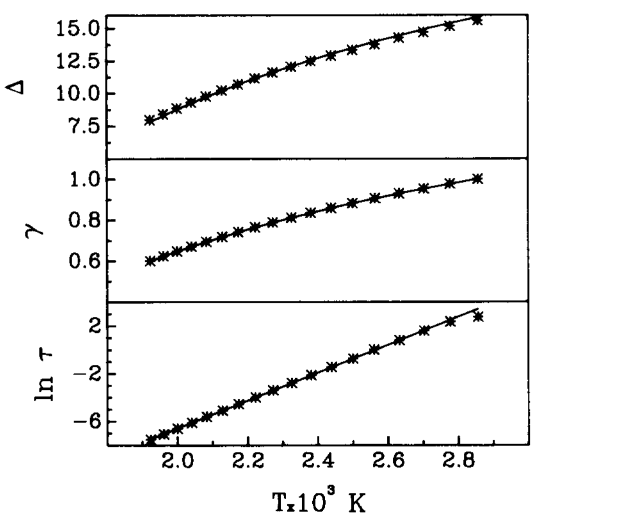

Fig. 2. Temperature dependence of parameters γ and Δ corresponding to the peak shown in Fig. 1. The full curves represent the simulated values for these parameters.

internal friction peak is measured the curve of $G_1(\omega)$ does not exhibit its inflection point. That is, the measurements of G_1 are not sufficiently extended to guarantee the values of G_u and G_r at each temperature. Thus eqn. (1) cannot be considered, so it is intended to determine the parameter γ from the limit of eqn. (8), *i.e.*

$$\left.\frac{\partial \ln F}{\partial \ln \omega}\right|_T = \pm\gamma \tag{10}$$

where the plus and minus signs correspond to the limits at very low and high frequencies respectively. For each peak the asymptotes are not clearly defined and only a mean value can be calculated at each temperature.

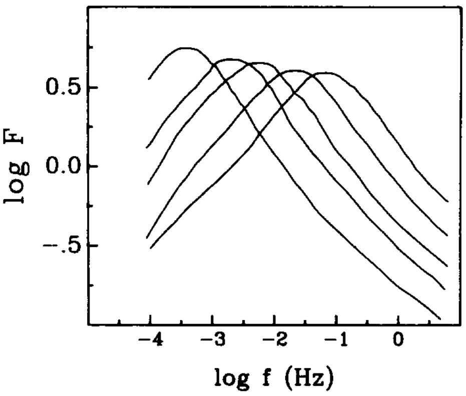

Fig. 3. Internal friction peaks measured at various temperatures in atactic polystyrene [8].

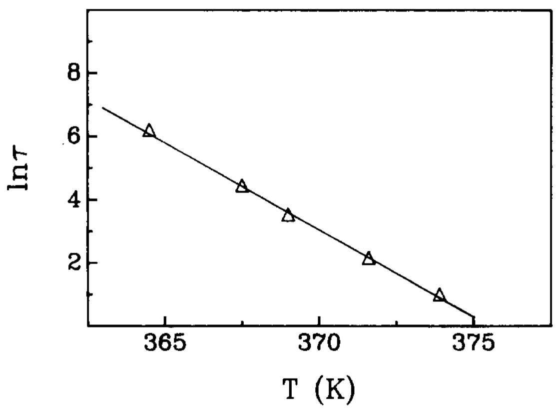

Fig. 4. Temperature dependence of characteristic time τ_t. The straight line corresponds to eqn. (11).

These values lead to $\gamma = 0.65 \pm 0.5$, which is independent of the temperature. This value of γ corresponds to a symmetrical distribution function of halfwidth $\beta = 1.6 \pm 0.3$ [10], which includes the value derived from Nowick and Berry's procedure. Once γ is known, the evaluation of eqn. (8) at the intermediate frequencies leads to the values of τ_t presented in Fig. 4. These characteristic times depend on the temperature according to

$$\tau_t = \tau_o \exp\left(\frac{\Delta H}{k(T - T_c)}\right) \tag{11}$$

where ΔH is the activation enthalpy, τ_o is a pre-exponential factor, T_c is a critical temperature and k is Boltzmann's constant. Both the activation enthalpy $\Delta H = 21.6$ kJ mol^{-1} and the critical temperature $T_c = 300.6$ K derived from the values of τ_t at various temperatures are coincident with those determined by Povolo [9] on assuming the validity of the Williams–Landel–Ferry relationship [11]. Furthermore, it is also established that Δ depends on the temperature as $\Delta \propto (T - T_c)^{-1}$, indicating that the ordering energy is also allowed to depend on the existing state of order.

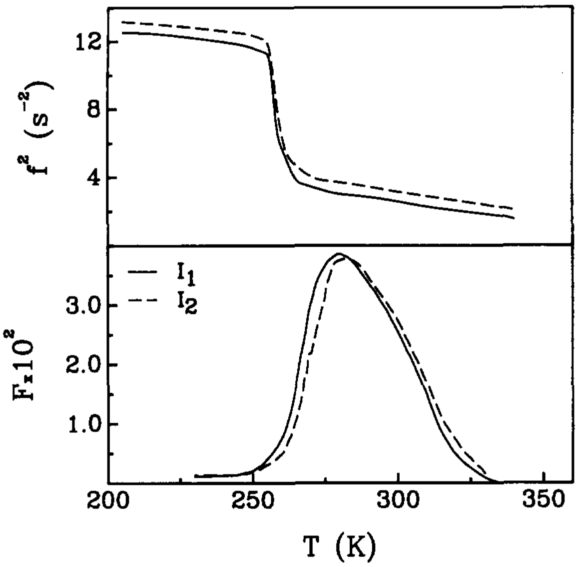

Fig. 5. Intrinsic damping and square of oscillation frequency *vs.* temperature in PMMA for two slightly different moments of inertia, I_1 and I_2.

Finally, the dynamical data measured by Povolo and Lambri [12] in atactic poly(methylmethacrylate) (PMMA) and presented in Fig. 5 are considered. As mentioned in Section 2, when the internal friction peak is measured as a function of temperature, the partial derivative $\partial \ln F/\partial \ln \omega$ must also be measured in order to determine Δ and the parameters of the distribution. Because of this, Fig. 5 shows one peak and the corresponding curve of frequency measured at one moment of inertia, I_1, while the second peak and the respective frequencies correspond to another moment of inertia, I_2. According to eqn. (8), if the procedure of the MAE is valid, $|\partial \ln F/\partial \ln \omega|_T$ must be lower than $\gamma(T)$. However, the derivative calculated from Fig. 5 takes values greater than 20. This apparent contradiction is due to the non-linear behaviour of PMMA. Effectively, Povolo and Lambri [12] measured internal friction peaks at a fixed temperature but at different strain amplitudes and found that the damping is strain dependent.

4. Discussion

It has been shown how the temperature dependence of the relaxation strength and the parameters of a symmetrical distribution function can be calculated from a single internal friction peak if G_1(T) and $\partial \ln F/\partial \ln \omega$ are also measured. It should be noticed that in principle this procedure could be applied to curves measured as a function of temperature or frequency, but for $\Delta \gg 1$ it is difficult to get these parameters from the latest curves. Effectively, as pointed out in the previous section, the limits ω_u and ω_r are found only if the measurements cover many orders of magnitude of frequency. Since this is not empirically possible, γ may be calculated from the limits of the partial derivative. These limits correspond to the tails of the internal friction peak where there is much more error, particularly at high frequencies where the background increases. Consequently, it is much more appropriate to employ the torsional pendulum with a variable moment of inertia, measuring the internal friction and the frequency as a function of temperature at two slightly different moments of inertia. Effectively, because of the thermal activation, the interval of temperature needed to determine both G_u and G_r can be swept in any laboratory. Furthermore, the improvement of a variable moment of inertia allows one to measure the dependence on frequency through $\partial \ln F/\partial \ln \omega$.

Even considering data determined as a function of frequency, the various applications show that the procedure of the MAE gives a relaxation strength, a characteristic time and a halfwidth of the distribution function which are very similar to those derived by Nowick and Berry. A detailed comparison between their procedure and that of the MAE will be given in a forthcoming paper. In particular, that paper will show that $\gamma \approx [r_2(\beta)]^{-1}$, where $r_2(\beta)$ is the relative peak width defined by Nowick and Berry (ref. 4, p. 99).

However, the method proposed in this paper enables us to calculate the temperature dependence of the relaxation strength and of the parameters of a symmetrical distribution function from a single internal friction peak measured together with ω and $\partial \ln F/\partial \ln \omega$.

Finally, from the data of PMMA it was shown that the procedure of the MAE gives absurd results when a non-linear viscoelastic material is treated.

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