Nonlinear Mechanical Spectrometry of Poly(methyl methacrylate)

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SYNOPSIS

Data on the damping spectra of commercial poly(methyl methacrylate) (PMMA) are reported, both at low (of the order of 1 Hz) and at intermediate (of the order of 50 Hz) frequencies. It is shown that the damping does not only depend strongly on temperature and frequency but also on the strain amplitude applied to the specimen. In other words, the dynamic mechanical behavior of PMMA is nonlinear and cannot be described in terms of linear viscoelasticity. Finally, some aging effects in the damping, measured at low frequencies, are also reported. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Several works have been published on the dynamic mechanical behavior of poly(methyl methacrylate) (PMMA), and various reviews have been written on relaxation processes in amorphous glassy polymers, including PMMA.[1,2] The dynamic mechanical behavior (storage and loss moduli, loss tangent) has been interpreted mainly in terms of linear viscoelasticity, appropriate for small strains, and the study of nonlinear viscoelastic and plastic phenomena has been restricted mainly to large deformations, like those reached in stress–strain curves and creep.[3] Recently, Muzeau et al.[4,5] have reported the shear modulus and loss spectra of PMMA over a frequency range from 2×10^{-4} to 1 Hz. These data were interpreted in terms of a distribution function of relaxation times, meaning that linear viscoelasticity was involved. Boyd et al.[6] have reported nonlinearity in stress–strain behavior under conditions where the strain is completely recoverable, during creep experiments in PMMA. This nonlinearity was associated by these authors with a secondary (β) relaxation process and was evident at strains of the order $\frac{1}{2}$–1%.

The nonlinearity should be reflected in the dynamic mechanical behavior of the material through a strain amplitude dependence of the dynamic moduli and the loss tangent (damping). In fact, some results on the amplitude dependence of the dynamic moduli and the damping of commercia PMMA, for strain amplitudes between 1×10^{-7} and 6×10^{-5}, at frequency of the order of 50 kHz and for temperatures between 293 and 400 K, have been reported very recently.[7] The data have been interpreted in terms of Ree–Eyring equation, that is,

$$\dot{\varepsilon} = \dot{\varepsilon}^{*}\exp(-\Delta H/kT)\sinh(\bar{\sigma}v/kT) \quad (1)$$

and

$$\bar{\sigma} = \sigma - \sigma_i \quad (2)$$

where $\dot{\varepsilon}$ is the strain rate, σ is the applied stress, ΔH is the activation enthalpy, v is the activation volume, $\dot{\varepsilon}^{*}$ is the preexponential factor, σ_i is the internal stress, k is Boltzmann' constant, and T is the absolute temperature. Equation (1) leads to an amplitude-dependent (nonlinear) damping, F_H, given by

$$F_H = (2\dot{\varepsilon}^{*}/\varepsilon\omega)\exp(-\Delta H/kT)\cosh(vE'_I\varepsilon_c/2kT) \times [I_1(vE'_I\varepsilon/2kT) - I_1(vE'_I\varepsilon_c/2kT)] \quad (3)$$

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where ω is the oscillation frequency, ε is the maximum strain amplitude applied to the specimen, E'_I is the amplitude independent storage Young's modulus, ε_c is the strain at which amplitude dependence begins, that is, the strain below which the damping and the dynamic moduli are amplitude independent, and I_1 is the modified Bessel function of the first order. Both υ and ε_c were found to be strongly temperature dependent and a value of 114 kJ/mol was obtained for ΔH.

It is the purpose of this study to show that the dynamical behavior of commercial PMMA is amplitude dependent also at low frequencies, that is, of the order of 1 and 60 Hz. Furthermore, the dynamical response does not only depend strongly from the applied stress or strain but also from the frequency of the excitation.

EXPERIMENTAL

Two types of torsion pendulum were used for the measurements of the damping and the storage shear modulus. One of the pendulum, which is of the inverted type and was described elsewhere,[8] operates at a frequency of the order of 1 Hz and allows a continuous variation of the moment of inertia, in such a way that it is possible not only to measure the damping and the storage modulus but also their partial derivatives with respect to the moment of inertia, at constant temperature. This pendulum operates both in free decay and in sustained oscillations.[9] In the second pendulum, operating at frequencies of the order of 100 Hz, the damping is measured in sustained oscillations. For the sustained oscillation mode the damping, F_{SO}, is given by

$$F_{SO} = (K/f^P)V \tag{4}$$

where $\omega = 2\pi f$, V is a voltage proportional to the energy supplied to keep the oscillating system in a steady state, K is a constant for a given apparatus, and p depends on the quantity that is maintained constant during the experiments.[10] In most equipment, like in our case, the amplitude of the oscillation is kept constant and $p = 2$.

The material used was commercial PMMA, named Vicalon, supplied by a local firm. This material was fabricated by molding according to ASTM 0788-84 standards. According to the supplier, the material had a content of free monomers of methyl methacrylate lower than 1% and a density at room temperature of 1.19 g/cm^3. The molecular weight of this material is $M_w = 2.7 \times 10^6$ and the polydispersity index is $p_i = 1.84$. The glass transition temperature, at 50 kHz, is of the order of $T_g = 404$ K.[7]

Specimens in the form of rods of 1.5 mm in diameter and 30 mm long were used for the measurements at low frequencies and 1.125 mm diameter and 20 mm long at intermediate frequencies.

RESULTS

Figure 1 shows the damping versus temperature obtained at different maximum strain amplitudes, which are indicated on each curve. These data were obtained at low frequencies and in sustained oscillations. It is important to notice the strong amplitude dependence of the damping, which decreases as the strain amplitude increases. This nonlinear behavior is evident even at strain amplitudes as low as $1 \times 10-5$. The curves shown were measured at a heating rate of the order of 0.5 K/min between successive temperatures and the specimen was maintained for 20 min at each temperature before initiating the steps in the strain amplitude. The curves indicated in Figure 1 represents the measured damping versus temperature at different maximum strain amplitudes, applied to the surface of the specimen. When the damping is amplitude dependent, a correction must be made to the measured curves. In effect, on comparing the experimental results with the theoretical models, it is assumed that the stress (or strain) applied to the specimen is homogeneous. This is not the case when the damping is measured with a torsion pendulum, where the specimen is subjected to an inhomogeneous strain, which is zero at the center of the specimen and maximum on its surface. This maximum strain amplitude is the one indicated in Figure 1.

Procedures have been developed[11-15] to reduce experimental curves of damping under nonuniform strain to those given the intrinsic or true values, that is, the damping that would be measured if the strain distribution in the specimen where uniform. In the case of torsion and sustained oscillations the intrinsic damping, F_I, is given by

$$F_I(\varepsilon_0) = F(\varepsilon_0) + (\varepsilon_0/4)\left.\frac{\partial F(\varepsilon_0)}{\partial \varepsilon_0}\right|_T \tag{5}$$

where $F(\varepsilon_0)$ is the measured damping at a maximum strain amplitude ε_0 and F_I is the intrinsic value at an uniform strain ε_0. The procedure to obtain F_I is the following: at each temperature, the damping is measured at a certain maximum strain ε_0 and, sub-

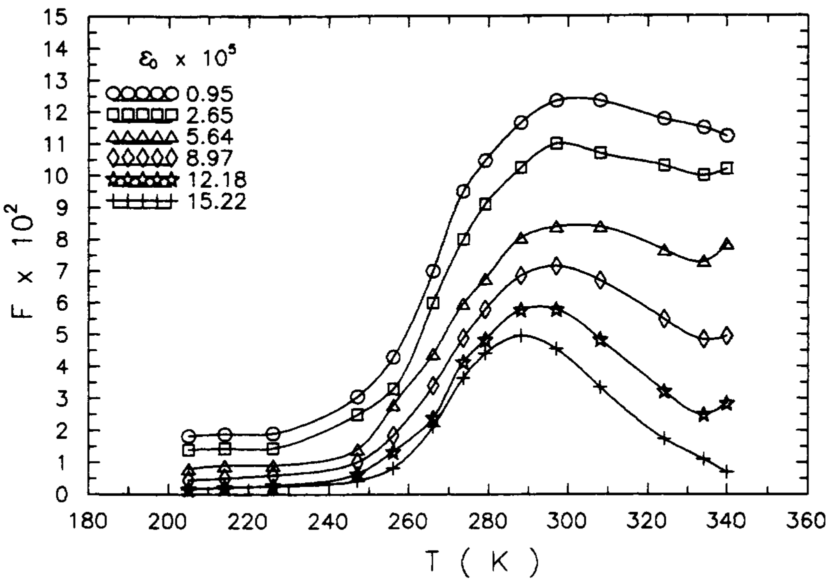

Figure 1 Damping against temperature, at different maximum strain amplitudes, in commercial PMMA. The data were obtained at a frequency of the order of 1 Hz.

sequently, a small increment of strain is made $\Delta\varepsilon_0$ which leads to a small increment of the damping ΔF. Then, $\partial F/\partial\varepsilon_0|_T \simeq \Delta F/\Delta\varepsilon_0|_T$ and F_I can be calculated by using Eq. (5). The procedure is repeated for different values of ε_0.

Figure 2 shows the intrinsic damping versus temperature, at different strain levels. These are the curves that should be compared with any theoretical model used to describe the nonlinear behavior of the material. In the same figure are also indicated the values obtained for a slightly different moment of inertia of the pendulum, I_2, as compared with the values obtained for another moment of inertia, I_1, used to obtain the data shown in Figure 1. It is evident from Figure 2 that as the strain increases a clear peak can be distinguished, since the high-temperature background damping decreases as the strain increases. Figure 3 shows the damping max-

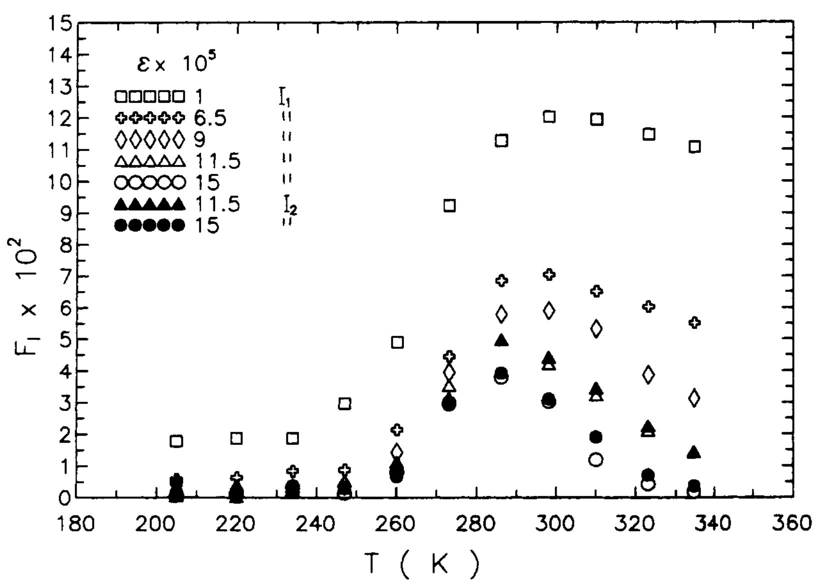

Figure 2 Intrinsic damping against temperature, at different strains and for two different moments of inertia.

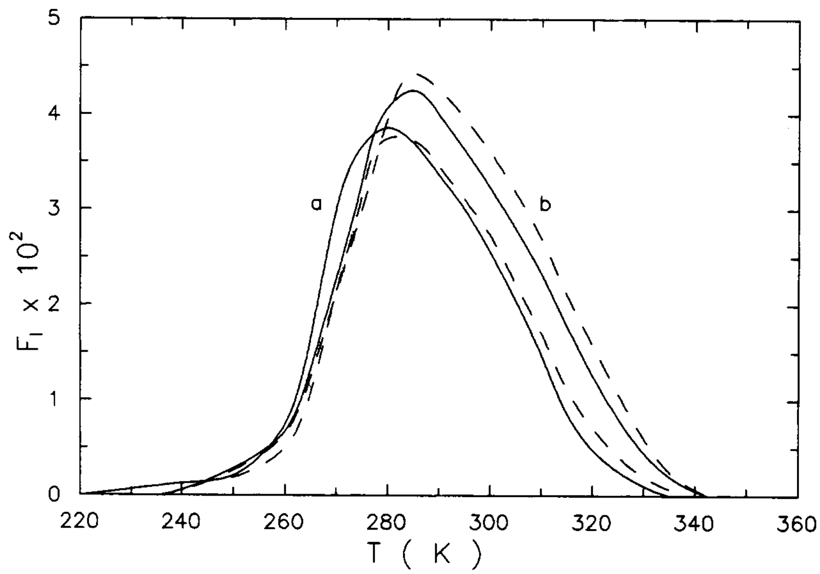

Figure 3 Damping peak obtained from the data of Figure 2 after subtracting out a small background. (a) $\varepsilon = 15 \times 10^{-5}$, (b) $\varepsilon = 11.5 \times 10^{-5}$. The full curves correspond to the moment on innertia I_1 and the broken ones to the moment of inertia I_2.

ima at two different strains and for two slightly different moments of inertia. A small background was subtracted out to show the peaks more neatly. Figure 4 illustrates the variations of the square of the free oscillation frequencies against temperature, for the two moments of inertia. No strain dependence of f^2 was detected, within experimental error.

The hysteresis effects observed in the damping due to successive heating and cooling cycles is shown in Figure 5. These curves were obtained at the moment of inertia I_1 and a strain of 6.5×10^{-5}. Curve *a* was measured during the first heating and is the same as the one shown in Figure 2 for the same strain. Curve *b* was obtained on cooling, after keeping the specimen for about one hour at a temperature of the order of 345 K. Finally, curve *c* was measured during a subsequent heating, after keeping the specimen for about one hour at a temperature of the

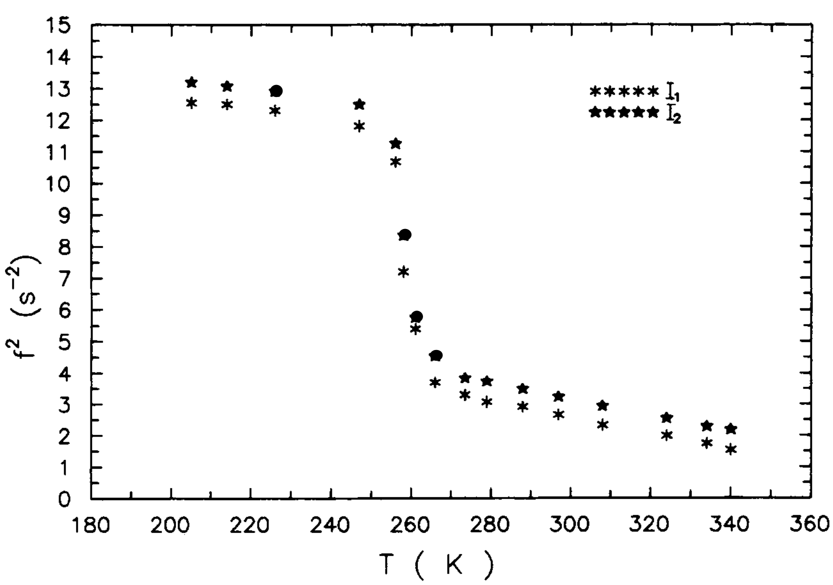

Figure 4 Square of the oscillation frequency against temperature for the two moments of inertia.

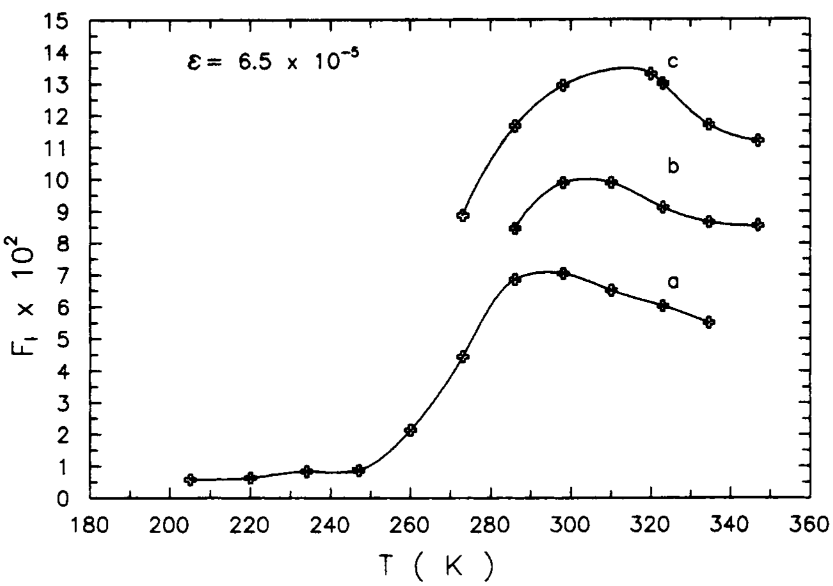

Figure 5 Hysteresis effects observed in the damping at low frequencies and a strain of 6.5×10^{-5}. (a) First heating, (b) on cooling, after one hour at 345 K, (c) on heating, after one hour at 270 K.

order of 270 K. It is evident that thermal cycling of the specimen produces hysteresis effects in the damping.

Figure 6 illustrates the results obtained at intermediate frequencies, where the measured damping is plotted as a function of the maximum strain amplitude. This specimen was heated at a rate of 15 K/h, during each measurement as a function of the strain amplitude. Finally, the results obtained, also at intermediate frequencies, for the measured damping against temperature and at a maximum strain amplitude of 1×10^{-4} are illustrated in Figure 7. Also shown in the same figure is the square of the free oscillation frequency, which does not change

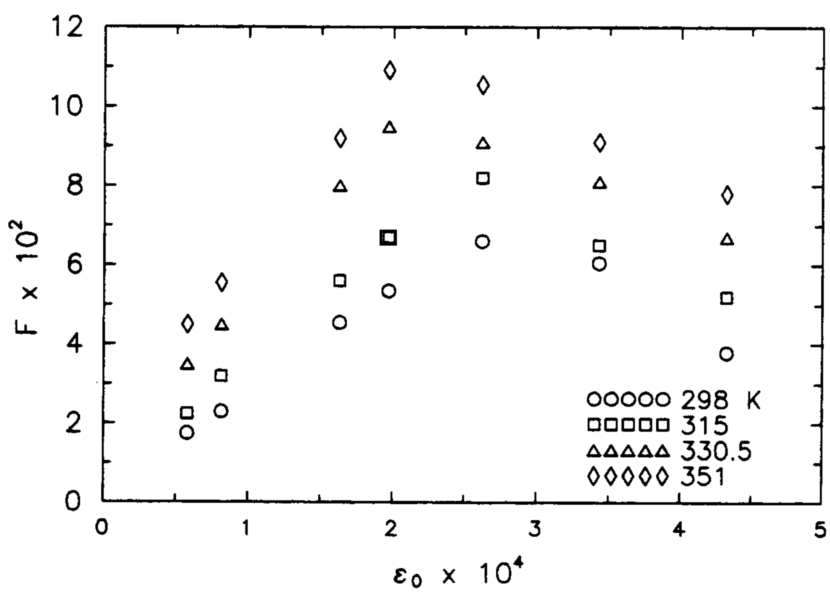

Figure 6 Measured damping against maximum strain amplitude, at different temperatures. Data obtained at intermediate frequencies.

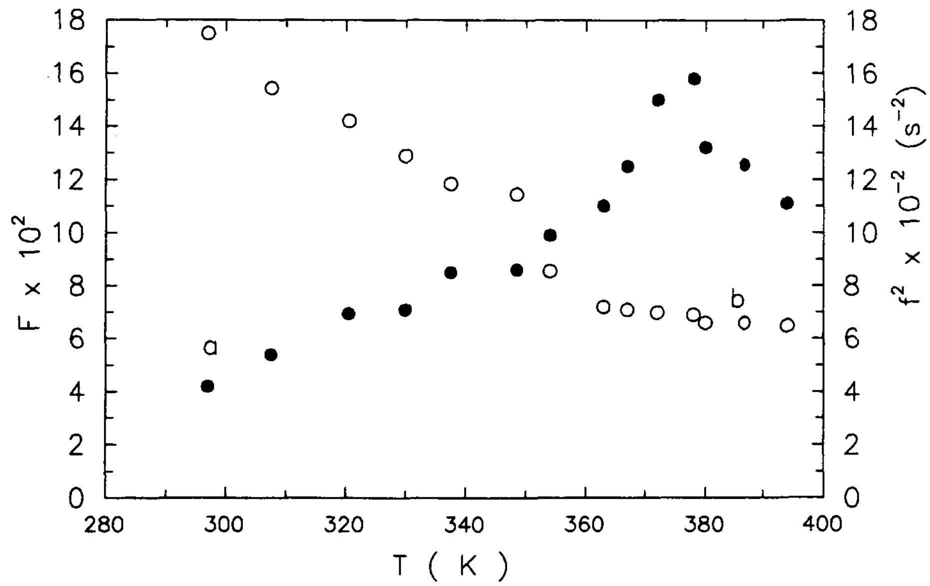

Figure 7 Measured damping (solid circles) and square of the oscillation frequency (open circles) against temperature, for a maximum strain of 1×10^{-4}. Data obtained at intermediate frequencies.

with the strain amplitude within experimental error. The data of Figure 7 were obtained at a heating rate of 15 K/h.

DISCUSSION

According to Figure 2 a peak is clearly distinguished in the damping as the strain increases. This peak was indicated in Figure 3 for two strains and two slightly different moments of inertia. In the case where the damping peak can be described in the framework of linear viscoelasticity and even when a distribution of relaxation times is present, it can be shown that it can be described by[16]

$$F = \frac{\alpha(T, \omega)}{2} \cosh\{\ln[\omega(T)\tau(T)]\} \qquad (6)$$

where $\tau(T)$ is the average relaxation time in the frequency domain, which depends only of the temperature and $\alpha(T, \omega)$ is a parameter which depends on the frequency, the relaxation strength and the temperature. Differentiating Eq. (6) with respect to ω leads to

$$\left.\frac{\partial \ln F}{\partial \ln \omega}\right|_T = \left.\frac{\partial \ln \alpha(T, \omega)}{\partial \ln \omega}\right|_T - \tanh[(\ln \omega(T)\tau(T)] \quad (7)$$

As shown in Figure 4, a small change in the moment of inertia implies a small change in the oscillation frequency of the pendulum. On assuming that $\alpha(T, \omega)$ depends only slightly from ω, then $\partial \ln \alpha(T, \omega)/\partial \ln \omega|_T \simeq 0$ and Eq. (7) reduces to

$$\ln \tau(T) = \operatorname{arctanh}\left[-\left.\frac{\partial \ln F}{\partial \ln \omega}\right|_T\right] - \ln \omega \qquad (8)$$

Then, for each of the peaks of Figure 3, measured at two different strains and at two different moments of inertia, it is possible, at each temperature, to calculate $-\partial \ln F/\partial \ln \omega|_T \simeq -\Delta \ln F/\Delta \ln \omega|_T$ from the data of Figures 3 and 4, and, consequently, to calculate $\ln \tau$ by using Eq. (8). Figure 8 shows the results obtained by using the procedure just described. The open circles indicate the values obtained for a strain of 15×10^{-5} and the open triangles those for a strain of 11.5×10^{-5}. The situation in which no solutions were found for $\ln \tau$, at a given temperature, is indicated by a dagger or a double dagger, for $\varepsilon = 15 \times 10^{-5}$ and $\varepsilon = 11.5 \times 10^{-5}$, respectively. According to Figure 8, τ is not described by an Arrhenius relationship of the type

$$\tau = \tau_0 \exp(\Delta H/kT) \qquad (9)$$

where τ_0 is the preexponential factor and ΔH is the activation enthalpy. Only in a limited range of temperatures and for $\varepsilon = 15 \times 10^{-5}$, it can be stated that τ can be described by Eq. (8), as shown by the broken

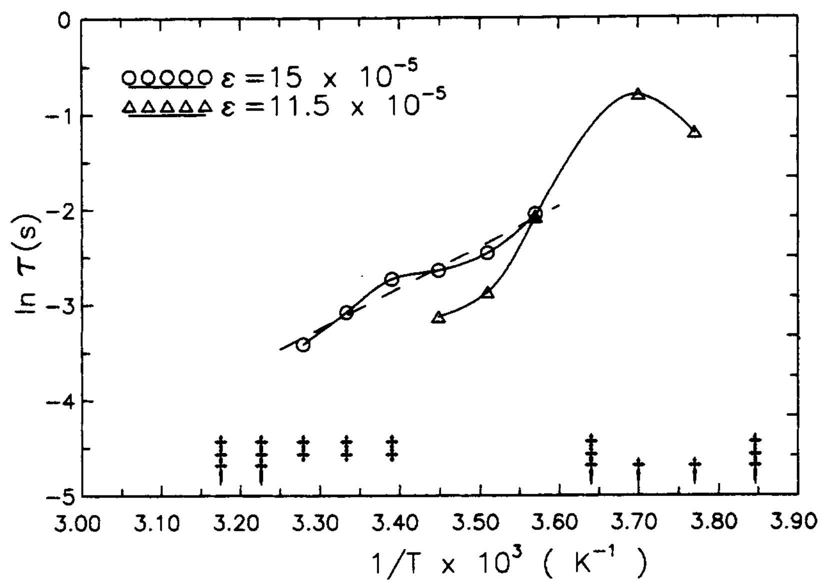

Figure 8 Relaxation time against the reciprocal of the temperature, as obtained from Figures 3 and 4 by using Eq. (8). The single and double daggers indicate the temperatures at which no solutions were found at $\varepsilon = 15 \times 10^{-5}$ and $\varepsilon = 11.5 \times 10^{-5}$, respectively.

straight line of Figure 8. This straight line, obtained through a least-square fitting to the data leads to

$$\Delta H = 34.7 \text{ kJ/mol and } \tau_0 = 3.11 \times 10^{-8} \text{ s} \quad (10)$$

In summary, it is evident from Figures 3 and 8 that the damping peak cannot be described in terms of linear viscoelasticity.

An interesting point to be considered refers to the value of the storage shear modulus of PMMA, near room temperature. In a torsion pendulum, operating in free oscillations, the storage shear modulus, G', is related to the oscillation frequency by

$$f^2 = G'r^4/8Il\pi \quad (11)$$

where r is the radius of the cylindrical specimen of length l, and I is the moment of inertia of the pendulum. I can be obtained by locating a specimen of known shear modulus and dimensions and measuring the oscillation frequency. A niobium specimen, whose G' is very well known and is independent from the frequency, was used in our case in both pendulums. This procedure leads to the following values for G' in PMMA at 295 K:

$$G' = 2.90 \text{ GPa} \quad \text{at } f = 41.83 \text{ Hz} \quad (12)$$

and

$$G' = 0.24 \text{ GPa} \quad \text{at } f = 1.67 \text{ Hz} \quad (13)$$

In longitudinal excitations, in the same material and at the same temperature, a value of 5.55 GPa was obtained for the storage Young's modulus, E'.[16] This leads to $G' \simeq E'/3 = 1.81$ GPa at 50 kHz.

According to Muzeau and Perez,[5] the storage shear modulus of PMMA ($M_w = 126{,}000$, $p_i = 1.8$, and $T_g = 375$ K) at 300 K is 0.65 GPa at 1 Hz, as obtained with a torsion pendulum. This value is quite similar to the one given by Eq. (13). Houssay et al.[17] reported a value of 0.016 GPa for G' at 1.7 Hz and $T = 300$ K, in a material with $M_w = 2.23 \times 10^5$, $p_i = 2.29$, and $T_g = 380$ K. According to Lefebvre and Escaig[18] $G' = 1.63$ GPa at 7.8 Hz, at the same temperature and in a material with the same characteristics. Finally, according to Read,[19] $G' = 1.2$ and 1.6 GPa at 1 and 40 Hz, respectively, at room temperature. The values given by Read, which did not report the characteristics of the material, were calculated from Young's modulus and Poisson ratio obtained from tensile nonresonance data. The results just described show that there are important disagreements in the literature about the real value of G' for PMMA and on its frequency dependence. It should be noticed, for example, that the material used in this work has a molecular weight much higher than the one employed by Muzeau and Perez, even if the values for G' are quite similar, when measured at practically the same frequency. It is clear that more work is needed in this field.

On comparing the data of Figure 1, obtained at low frequencies, with those of Figure 6, measured at intermediate frequencies, it is seen that the damping decreases with strain at low frequencies, while the opposite behavior is observed at intermediate frequencies, in the region of temperatures and strains where the data overlap. In other words, the damping is strongly influenced by the strain amplitude, the temperature and the frequency. Equation (3), used to describe the amplitude-dependent damping at high frequencies (50 kHz),[7] cannot be used for the data at low and at intermediate frequencies. In fact, this equation describes a damping which increases monotonously with strain, which is not the case for the data reported in this work. A theory for the nonlinear damping of PMMA should be developed, including all the variables that affect the nonlinear dynamic mechanical behavior. In addition, it is clear that more experimental data are needed. Finally, it is important to point out that Heijboer,[20] several years ago, has given a complete mapping of the damping of PMMA as a function of both the frequency and the temperature. According to Figure 3 of this paper, the damping behavior, as a function of temperature, changes substantially at frequencies between about 0.4 and 100 Hz. No important changes with frequency are observed above 100 Hz. The author, however, does not report any amplitude dependence of the damping and no information was given on the characteristics of the material.

Venditti and Gillham[21] have reported recently aging phenomena in the shear modulus of PMMA (M_w = 93264, p_i = 2.01, and T_g = 389 K at 1 Hz), at aging temperatures down to 261 K. Muzeau et al.[22] have observed aging phenomena in two types of PMMA (M_n = 40000, T_g = 396 and M_n = 67000, T_g = 404 K) and in the damping, on annealing at temperatures as low as 296 K.

CONCLUSIONS

The dynamic mechanical response of commercial PMMA shows nonlinear effects. This is reflected in the strong amplitude dependence of the damping, both at low (of the order of 1 Hz) and at intermediate frequencies (of the order of 50 Hz). The damping, measured as a function of temperature, decreases with strains at low frequencies while the opposite behavior is observed at intermediate frequencies. A damping peak observed near 280 K, at low frequencies, is strongly amplitude dependent and cannot be described in terms of linear viscoelasticity. Finally, hysteresis effects were observed in the damping, measured at low frequencies, at temperatures as low as 260 K.

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