Amplitude Dependent Damping in Vinyl Polymers

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Abstract:The damping behaviour of several vinyl polymers—poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), polystyrene (PS) and impact polystyrene (PSi)—was studied both as a funtion of temperature and strain amplitude. The measurements were performed from room temperature up to the glass transition temperature and shows amplitude dependence at frequencies of the order of 50 kHz.
The data are interpreted in terms of a hyperbolic sine stress dependence of the strain rate, including an effective stress. The activation volume was found to depend on temperature, with values much larger than those given by the usual mechanical tests (tensile, creep and stress relaxation). It is suggested that the nonlinear effects are related to the α relaxation in these materials, since the activation enthalpy is quite similar to the one obtained from the maxima of this relaxation.

1 INTRODUCTION

The dynamical behaviour of vinyl polymers is normally assumed to be controlled by mechanisms acting in the linear viscoelastic regime [1] and only few data have been reported recently on non linear or amplitude dependent effects [2, 3]. It is the purpose of this paper to present the most salient features of the damping of four commercial vinyl polymers, showing that, even at very low strains, the damping is amplitude dependent between room temperature and their glass transition temperatures.

2 EXPERIMENTAL PROCEDURE

The internal friction measurements were performed by vibrating the specimens longitudinally through a technique described in detail elsewhere [2]. This technique is based on the Marx oscillator were the specimen is cemented, with an instant adhesive, to a three-components oscillator formed by two piezoelectric crystals, driver and gauge, and a fused silica dummy buffer rod. The whole system vibrates at a frequency of the order of 50 kHz. This setup allows measurements of the damping as a function of strain amplitude at different temperatures. All the specimens were annealed in air during 2 h at temperatures close to their glass transition temperatures, previous to the internal friction measurements, which were performed on heating and after a complete stabilization of the selected temperatures, kept stable within ±0.5 K.

3   RESULTS

The damping, F, can be divided in two parts: one amplitude independent, F_I, and the other amplitude dependent, F_{Hc}, that is

$$F = F_I + F_{Hc} \tag{1}$$

where F_{Hc} refers to the intrinsic damping, that would be measured if the stress (or strain) distribution in the specimen were uniform [2].An analogous separation can be made for the storage Young's modulus. Figure 1, for example, shows the results obtained in PVC where F_{Hc} is plotted against the maximum strain amplitude, ε_o, applied to the specimen. The curves of Fig.1 and those obtained in the rest of the materials could be fitted to the equation [2]

$$F = A[I_1(a\,\varepsilon_o) - I_1(a\,\varepsilon_c)] \tag{2}$$

where I_1 is the integral form of the modified Bessel function of the first order and ε_c is the critical strain at wich amplitude dependence starts. A and a are given by

$$A = [2\dot{\varepsilon}^* \exp(-\Delta H/kT)/\omega]\cosh(a\varepsilon_c) \tag{3}$$

and

$$a = v\,E_I'/kT \tag{4}$$

where v is the activation volume, ΔH the activation enthalpy, k Boltzmann's constant, T the absolute temperature and E_I' is the amplitude independent storage Young 'modulus. $\dot{\varepsilon}^*$ is the pre-exponential factor in the Ree-Eyring equation for the stress dependence of the strain rate, $\dot{\varepsilon}$, given by

$$\dot{\varepsilon} = \dot{\varepsilon}^* \exp(-\Delta H/kT)\,\sinh(\tilde{\sigma}\,v/2kT) \tag{5}$$

with, $\tilde{\sigma} = \sigma - \sigma_i$, being σ the applied and σ_i an internal stress. The quality of the fitting of the experimental data to eq.(2) is illustrated by the full curves of Fig.1.

Fig.2 shows the amplitude independent damping against temperature for all the specimens measured. The peaks due to the α relaxation can be easily noticed.
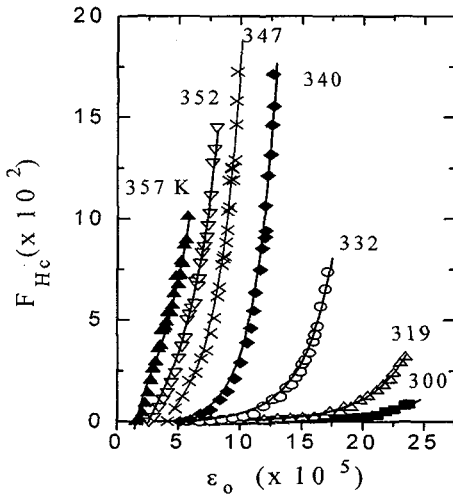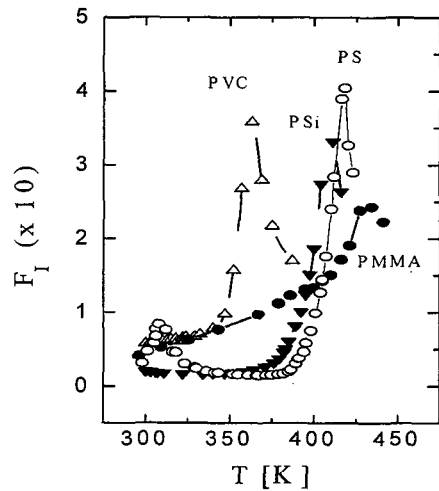

Fig.1: F_{Hc} for PVC

Fig.2: F_I for vinyl polymers

4 DISCUSSION

Figure 3 and 4 show the activation volumes and the internal stresses obtained by fitting the amplitude dependent damping to eqs. (2) to (4). v is much higher and σ_i is much lower than the values obtained through the usual mechanical tests (tensile, creep and stress relaxation) [4]−[8]. The activation work, that is, the product σ v is of the same order of magnitude as for quasistatic conditions [3]. In the high frequency experiments of this work, the activation volume must be higher in order that the sinh term of eq. (5) plays a role in the strain rate. In addition, the stresses applied at high frequency are very small and under the limit of detection of the usual tests. Also the strain rates are much smaller.
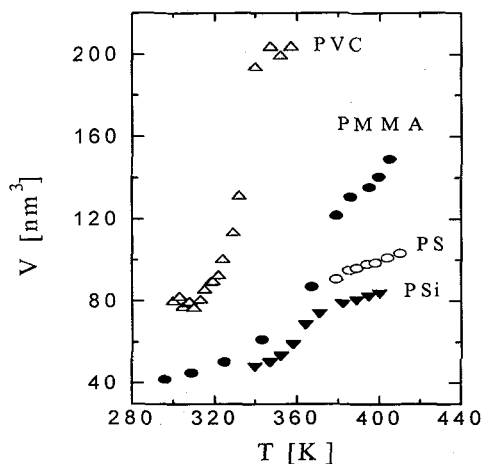

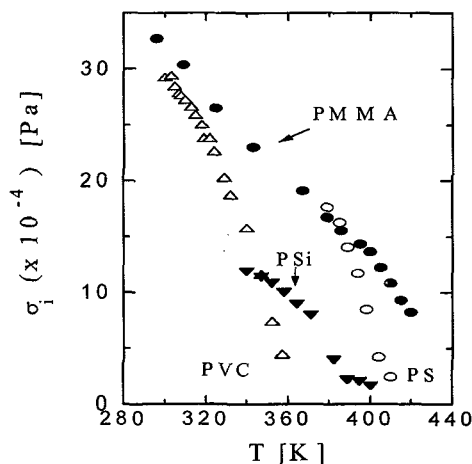Fig.3: Activation volumes for vinyl polymers. Fig.4: Internal stresses for vinyl polymers.

On assuming that the damping peaks of Fig.2 are produced by the α relaxation [9] and that a single relaxation time, τ, is involved, then for $\omega\tau \gg 1$.

$$\ln F_I = B - \Delta H/kT \qquad (6)$$

where B is a constant if $\omega \simeq$ constant. Then, a plot of $\ln F_I$ against $1/T$ for the increasing part of the peaks of Fig.2 should lead to straight lines of slope $\Delta H/k$. The values for ΔH obtained in this way are indicated in Table 1, except for PMMA where the β relaxation [9] influences the α peak. The value for ΔH in this material was obtained by fitting the amplitude dependent data to eqs. (2) to (4) [2].

Table 1: Activation enthalpies for vinyl polymers
in kJ/mol

PVC	PSi	PS	PMMA
73	96	124	114

A more detailed analysis of F_I must take into account that the peaks shown in Fig.2 are not

produced by a single relaxation process and a distribution of relaxation times is involved [10] so that eq.(6) is only a rough approximation. In any case the close values between the activation enthalpies obtained from F_I or F_{Hc} and trough tensile and stress relaxation experiments [7, 8], particularly in PVC and PMMA, would indicate that the mechanisms involved in the α relaxation and in the damping are quite similar. It is interesting to point out, however, that the yield points of PVC and PMMA could be described recently by an expression similar to eq.(5), but with $\sinh^n$, with n between 6 and 10 [6]−[8]. An analysis of the stress relaxation of PVC, below the yield point, interpreted in terms of linear viscoelasticity, leads to a cooperative mechanism involving five unities [7]. Then, the tensile and stress relaxation behaviour can be described in terms of n cooperative processes. Eq.(5) for high frequencies, however, is valid only for one process. It is difficult at this point to explain the physical mechanisms leading to F_I and F_{Hc} and to the high activation volumes obtained experimentally in this work. It is clear that several monomers moving cooperatively are involved leading to the high activation volumes.

Finally, the internal stresses obtained at high frequencies are much lower than the values measured in quasistatic experiments, even if the experimental data are scarce on this point. Lower values are obtained at high frequency due to the much higher sensitivity of the technique. Clearly, more theoretical and experimental work is needed to establish a clear correlation between the high frequency and quasistatic results. Even the mechanisms acting under quasistatic conditions are not clearly understood.

5   CONCLUSIONS

It was shown that the damping of four vinyl polymers is temperature and amplitude dependent. The amplitude dependent damping can be described by assuming a hyperbolic sine stress dependence of the strain rate, indicating nonlinear viscoelastic behaviour. It is suggested that the mechanisms controlling the damping are related to the α relaxation.

Acknowledgements

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