Amplitude-Dependent Dynamical Behavior of PVC

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SYNOPSIS

Results of the amplitude-dependent dynamical behavior of commercial poly(vinyl chloride) are presented. Both the loss factor (internal friction) and the storage Young's modulus are strain amplitude dependent when measured between room temperature and approximately 400 K at a frequency 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, or stress relaxation). It is suggested that these nonlinear effects are related to the α relaxation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The dynamical behavior of unplasticized poly(vinyl chloride) (PVC) has been studied by several authors. Becker,[1] for example, measured the real component of the dynamic modulus and the loss factor for frequencies between 2 and approximately 1000 Hz and temperatures between 277.5 and 426 K. By using the method of reduced variables and the Williams–Landel–Ferry (WLF) relationship,[2a] Becker obtained a temperature-dependent activation energy above the glass transition temperature. The activation energy decreased with temperature, reaching a value of 336 kJ/mol for temperatures above about 283 K. Becker reported a glass transition temperature T_g of 347 K in this material, as measured by dilatometric methods. The reported weight-average molecular weight was 35,000.

Sommer[3] also studied the dynamical behavior of unplasticized PVC. The real component of the dynamic modulus and the loss factor were reported for temperatures between 297 and 399.5 K and frequencies between 10^{-5} and 10^4 Hz. Sommer also used the time–temperature superposition, obtaining the corresponding spectra, and from a shifting of the spectra with temperature obtained a temperature-dependent activation enthalpy that increased with temperature, reaching a maximum of 335 kJ/mol at 353 K. Sommer reported the same T_g as Becker, and both probably used a similar material. More recently, data on the loss factor reported in the literature for PVC, measured as a function of frequency and at different temperatures, were interpreted in terms of the loss tangent distribution function.[4] A temperature-dependent activation enthalpy was obtained in this case, which varied from 20 to about 10 kJ/mol as the temperature changed from 360 to 380 K. All these data were measured above T_g.

Finally, some dynamic properties of PVC and other amorphous polymers have been reviewed by Schwarzl.[2b] The results just described assumed that the material behaves in a linear viscoelastic manner, and the amplitude-dependent dynamical behavior of polymers is seldom reported in the literature. Amplitude dependence of the dynamical properties have been observed in rubber compounds.[5] These effects were present both in the dynamic moduli and the loss tangent for strain amplitudes above 1×10^{-3}. Warnaka and Miller[6] observed a strain amplitude-dependent dynamic modulus, at room temperature, in filled silicone rubber. This amplitude dependence was strongly influenced by frequency, and nonlinear effects were observed at strains as low as 1×10^{-4}. Furthermore, these authors pointed out that nonlinearity or strain sensitivity of the dynamic moduli

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should be present in homogeneous amorphous polymers at low dynamic strains. More recently, data on the amplitude-dependent dynamical behavior of poly(methyl methacrylate) (PMMA) were reported.[7] Both the loss factor (internal friction) and the storage Young's modulus were found to be strain amplitude dependent when measured between room temperature and approximately 400 K at a frequency of 50 kHz. The data were interpreted in terms of a hyperbolic sine stress dependence of the strain rate, including an effective stress.

We present results on the amplitude dependence of the dynamic moduli and the damping of commercial PVC for strain amplitudes between approximately 1×10^{-7} and 1×10^{-4}. Both the strain amplitude and the temperature dependence of the dynamical response are considered from room temperature up to about 390 K and a frequency of 50 kHz.

EXPERIMENTAL

The material used was commercial PVC-CAW supplied by Simona AG (Kim, Germany). This material was fabricated according to DIN 4102-B1 standards in the form of 2-mm-thick sheets. The density and the static Young's modulus of the material, as indicated by the supplier, are $\rho = 1.42$ g/cm^3 and $E = 3.2$ GPa, at room temperature, respectively. The weight-average molecular weight determined by gel permeation chromatography is $M_w = 71{,}837$ with a polydispersivity of 1.832. The glass transition temperature, as determined by differential scanning calorimetry (DSC) at 10 K/min, is $T_g = 349.1$ K. Specimens 15.5-mm long and 5-mm wide were machined from the original sheets. Previous to the measurements, these specimens were located in a metallic capsule, introduced into an oil bath, and annealed in air during 2 h at 393 K. After this, the specimens were slowly cooled in the oil bath by shutting off the power of the oil heater.

The dynamic mechanical measurements were performed by vibrating the specimens longitudinally through a technique described in detail elsewhere.[7] This technique is based on the Marx oscillator where the specimen is cemented, with an instant adhesive, to a three-component oscillator formed by two piezoelectric crystals, driver and gauge, and a fused silica dummy buffer rod. The whole system vibrates at a frequency of 50 kHz. This setup allows measurements of the damping and the storage Young's modulus as a function of the strain amplitude at different temperatures. The detailed procedure used to obtain the damping and the storage Young's modulus of the specimen from the measured quantities is described elsewhere.[7] A fused silica dummy rod was used for the measurements, and the specimen was located into a furnace to change its temperature. To ensure homogeneity of temperature in the specimen, a dummy similar specimen, also cemented to a fused silica rod, was located near the specimen to be measured. Two thermocouples introduced near the ends of the dummy specimen were used to ensure homogeneity of temperature, and a third thermocouple, located near the specimen, was also used to sense the temperature. With this arrangement, it was possible to ensure homogeneity of temperature in the specimen, both axially and radially. Finally, all the measurements were performed mainly on heating and after a complete stabilization of the selected temperature, which was kept stable within ±0.5 K.

RESULTS

Figure 1 shows the damping and Figure 2 the storage Young's modulus as a function of the maximum strain amplitude applied to the specimen for various temperatures. It is seen that both the damping and the modulus are amplitude independent at very low strains and both become amplitude dependent at higher strains. Then, both quantities are divided in two parts: one amplitude independent and the other amplitude dependent, that is,

$$F_s = F_I + F_H \qquad (1)$$

where F_s is the damping (internal friction) of the specimen and F_I and F_H are the amplitude indepen-

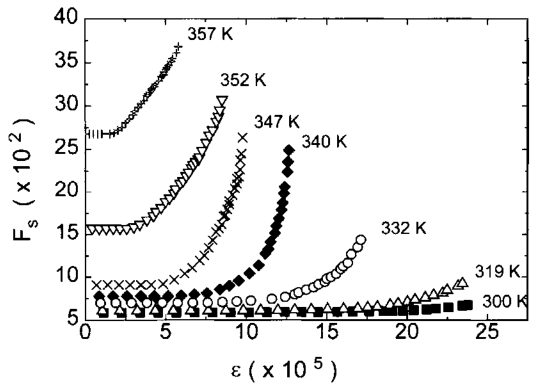

Figure 1 Damping (internal friction) of PVC as a function of strain amplitude at various temperatures.

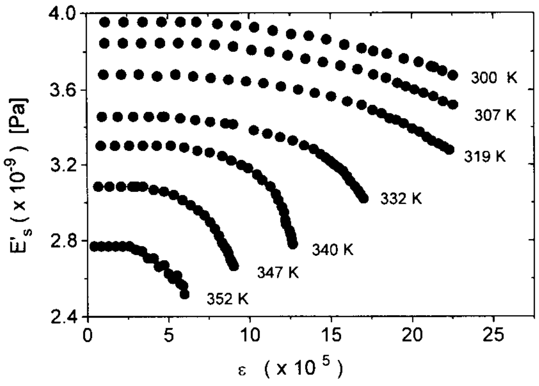

Figure 2 Storage Young's modulus of PVC as a function of the strain amplitude at various temperatures.

dent and the amplitude dependent parts, respectively.

A similar expression was used for the modulus. A procedure described elsewhere[8] was used to separate, with great accuracy, each contribution. The amplitude-dependent part of the modulus, or modulus defect, $d_{E'}$, is defined as

$$d_{E'} = \frac{E'_{s0} - E'_s}{E'_{s0}} \tag{2}$$

where E'_{s0} and E'_s are the storage Young's moduli of the specimen at low strain amplitudes and at any strain amplitude, respectively.

It should be pointed out that when the damping or the modulus defect are 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 stresses applied to the specimen are homogeneous. This is certainly not the case when measurements are made by means of a resonant technique, where nonhomogeneous stresses are applied to the specimens. A procedure was described[7] to reduce experimental curves of damping and modulus defect under nonuniform stress (strain) versus maximum strain amplitude to those intrinsic or true values that would be measured if the stress (or strain) distribution in the specimen where uniform. These corrections lead to the intrinsic damping and modulus defect curves shown in Figures 3 and 4, respectively. In what follows, the subscript c indicates intrinsic or true values of the corresponding quantities. Finally, Figure 5 shows the amplitude-independent damping F_I the amplitude-independent storage Young's modulus E'_I and the critical strain ϵ_c at which amplitude dependence starts, both in the damping and the modulus, as a function of temperature, respectively.

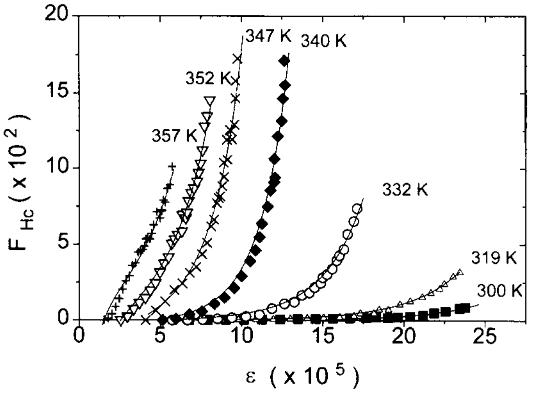

Figure 3 Intrinsic amplitude-dependent damping of PVC as a function of strain amplitude at various temperatures. The full curves represent the fitting by eq. (4).

DISCUSSION

The strain rate $\dot{\epsilon}$ under an applied stress σ is given in terms of the Ree–Eyring equation by

$$\dot{\epsilon} = \dot{\epsilon}^* \exp\left(\frac{-\Delta H}{kT}\right)\sinh\left(\frac{\bar{\sigma} V}{2kT}\right) \tag{3}$$

where ΔH and V are the activation enthalpy and the activation volume, respectively; $\dot{\epsilon}^*$ is a preexponential factor that includes entropic terms; k and T are Boltzmann's constant and the absolute temperature, respectively. $\bar{\sigma} = \sigma - \sigma_i$, being σ_i an internal stress. Equation (3) leads to an amplitude-dependent damping given by

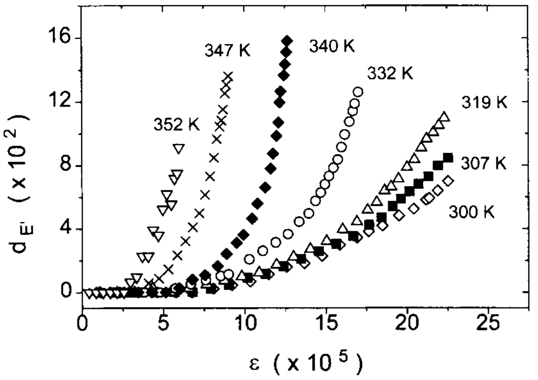

Figure 4 Modulus defect of PVC as a function of strain amplitude at various temperatures.

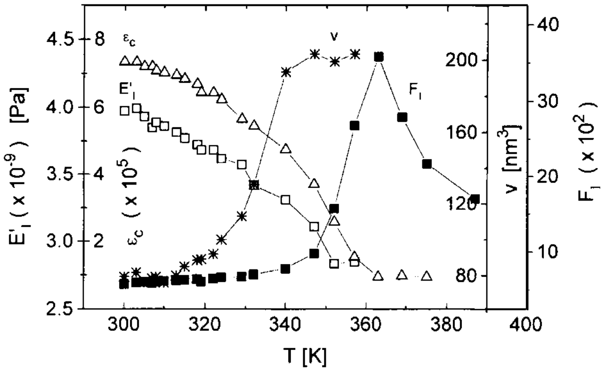

Figure 5 Amplitude-independent damping F_I, amplitude-independent storage Young's modulus E'_I, critical strain ϵ_c for the onset of amplitude dependence, and activation volume V for PVC as a function of temperature.

$$F_{Hc} = \frac{A}{\pi f_s \epsilon}\left(I_1(a\epsilon) - I_1(a\epsilon_c)\right) \tag{4}$$

where

$$A = \dot{\epsilon}^* \exp\left(\frac{-\Delta H}{kT}\right)\cosh\left(\frac{VE'_I\epsilon_c}{2kT}\right) \tag{5}$$

and

$$a = \frac{VE'_I}{2kT} \tag{6}$$

f_s is the resonant frequency of the specimen and I_1 is the integral form of the modified Bessel function of the first order. In the derivation of eq. (4), it was assumed that the storage Young's modulus does not depend on the strain amplitude. This assumption should not alter substantially the results because E'_s changes only slightly with strain. Equation (4) can be written as

$$F' = F_{Hc}\pi f_s \epsilon = AI_1(x) - AB \tag{7}$$

where

$$x = a\epsilon \tag{8}$$

and

$$B = I_1(a\epsilon_c) \tag{9}$$

A and B are constants at a given temperature because it is assumed they do not depend on strain. Then, a plot of F' against $I_1(x)$ should give a straight line of slope A and intercept AB, leading to A and a. In effect, through a computer program it is easy to find the range of x, at each temperature, where eq. (7) is obeyed. The full curves of Figure 3 show the quality of the fitting to the experimental data obtained in this way. Once a is known, it is possible to calculate the activation volume by using eq. (6) and the values of E'_I shown in Figure 5. The values of V obtained in this way are also shown in the same figure.

The values of A obtained by fitting the data to eq. (7) are shown in Figure 6 as ln A against $1/T$. This plot is not linear, indicating that $\exp(-\Delta H/kT)$ is not the dominant term in eq. (5). Furthermore, because the cosh term of this equation does not depend strongly on temperature, it might be possible that $\dot{\epsilon}^*$ is temperature dependent. This dependence can be found on assuming that ΔH is known. In fact, recently, ΔH was obtained by performing stress relaxation measurements in the same material,[9] leading to

$$\Delta H = 79.4 \text{ kJ/mol} \tag{10}$$

On using this value for ΔH, eq. (5) allows a calculation of $\dot{\epsilon}^*$ because the rest of the quantities are known. The results obtained are illustrated in Figure 6, showing that $\dot{\epsilon}^*$ is nearly constant up to about 350 K and then it increases very rapidly with temperature. It should be reminded that T = 349.1 K is the static glass transition temperature for this material. On comparing V from Figure 5 with $\dot{\epsilon}^*$ from Figure 6, it is seen that V saturates when $\dot{\epsilon}^*$ starts to increase. Furthermore, below T_g, $\dot{\epsilon}^* = 1 \times 10^8$ s^{-1}, which is a reasonable value when compared with Debye's frequency ($\approx 10^{13}$ s^{-1}).

Amplitude-Independent Damping

On assuming that the damping peak in F_I, shown in Figure 5, is produced by the α relaxation and that a single relaxation process is involved, then[10]

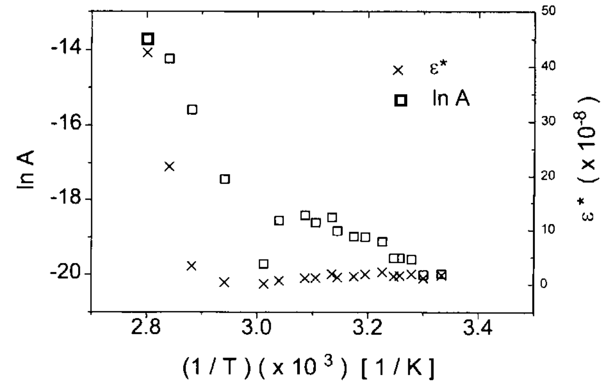

Figure 6 Parameters $\dot{\epsilon}^*$ and A of eqs. (3) and (5) as a function of the reciprocal of temperature.

$$F_I = \frac{\delta}{2\cosh(\ln \omega\tau)} \qquad (11)$$

where ω is the circular frequency, τ is the relaxation time, and δ depends only on temperature. Furthermore, if $\omega\tau \gg 1$, eq. (11) reduces to

$$F_I \approx \frac{\delta}{\omega\tau} \qquad (12)$$

Then, on assuming that

$$\tau = \tau_0 \exp(\Delta\bar{H}/kT) \qquad (13)$$

eq. (12) can be written as

$$\ln F_I = \ln(\delta/\tau_0\omega) - \frac{\Delta\bar{H}}{kT} \qquad (14)$$

Furthermore, on assuming that δ, τ_0, and ω are constants, a plot of ln F_I against $1/T$ should give a straight line of slope $\Delta\bar{H}/k$. In fact, a plot of ln F_I, from Figure 5, against $1/T$ for temperatures between 338 and 363 K gives a reasonable straight line, leading to

$$\Delta\bar{H} = 72.3 \text{ kJ/mol} \qquad (15)$$

This value is very close to the value given by eq. (10). A more detailed analysis of F_I must take into account that the peak shown in Figure 5 is not produced by a single relaxation process and a distribution of relaxation times is involved,[10] so that eq. (11) is a rough approximation. In any case, the close values for the activation enthalpies, given by eqs. (10) and (15), would indicate that the mechanisms involved in the α relaxation and in the amplitude-dependent damping are quite similar. Moreover, considering that the α transition occurs at the measured static T_g = 349.1 K for a frequency of 1 Hz, the corresponding T'_g at 50 kHz can be calculated by using WLF relationship[2a] as

$$T'_g = 349.1 + \frac{C_2 \log f}{C_1 - \log f} \qquad (16)$$

This equation, with $f = 5 \times 10^4$ Hz, $C_1 = 17.4$, and $C_2 = 51.6$ K for the values of the universal constants of the WLF equation, leads to

$$T'_g = 368.2 \text{ K} \qquad (17)$$

This temperature is very closed to that of the location of the maximum in the curve of F_I against T of Figure 5.

According to Schwarzl,[2c] the maximum of the β relaxation in PVC is located at T_β = 213 K at a frequency of 1 Hz. The activation enthalpy for this relaxation process is 59 kJ/mol. On assuming an Arrhenius temperature dependence of the relaxation time, that is, eq. (13), and that the damping is described by an equation similar to eq. (11), with δ independent from T, then the maximum of the β relaxation will occur, at 50 kHz, at the temperature

$$T_\beta = 315 \text{ K} \qquad (18)$$

In our case, the β relaxation is masked by the strong contribution of the α relaxation, as illustrated in Figure 7. In effect, this figure shows F_I against T together with an expanded view near the temperature given by eq. (18).

Storage Young's Modulus

The amplitude-independent storage Young's modulus is shown as a function of temperature in Figure 5. According to Gilbert et al.,[11] the drop in modulus caused by thermal expansion can be written as

$$E'_I = E'_0\left(1 - \alpha_m \frac{T}{T_g}\right) \qquad (19)$$

where α_m is a dimensionless coefficient and E'_0 is the value at 0 K. A fitting of the data of Figure 5 to eq. (19) leads to

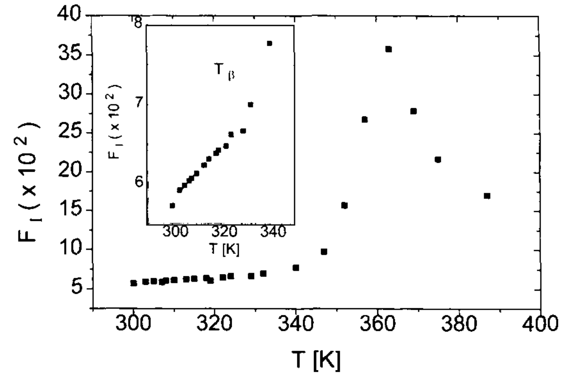

Figure 7 Amplitude-independent damping of PVC as a function of temperature together with an expanded view near the β relaxation.

$$E'_0 = 8.85 \text{ GPa} \tag{20}$$

and

$$\frac{\alpha_m}{T_g} = 1.8 \times 10^{-3} \text{ K}^{-1} \tag{21}$$

Equation (21) leads to

$$\alpha_m = 0.66 \tag{22}$$

by using the value of T_g given by eq. (17). It should be pointed out, however, that eq. (19) is only a first-order approximation of a more complex expression derived by Yannas and Luise,[12] when the intra- and intermolecular potentials in the chain are considered. α_m is related to the potential barriers and to the dimensions of the conformers, that is, each one of the monomers of the polymeric chain named strophons. On using the experimental data of Yannas and Luise,[12] it produces $\alpha_m = 0.8$, a value quite similar to the one given by eq. (22). Recent measurements of the static Young's modulus in the same PVC as the one used in this work lead to $\alpha_m = 0.9 \pm 0.1$.[13] It should be pointed out that eq. (19) was used for the dynamic Young's modulus even when it was deduced only for the static modulus. In effect, Yannas and Luise[12] did not consider the influence of frequency in their theory.

Activation Volume

As shown in Figure 5, the activation volume has a value of 80 nm^3 at room temperature and then it increases steadily with temperature, reaching a constant value of 200 nm^3 above T_g. Below 345 K, the activation volume can be described by the equation

$$V = 47 + \frac{1310}{349 - T} \text{ nm}^3 \tag{23}$$

showing that the activation volume is related in some way to the glass transition temperature. A similar result was encountered in PMMA.[7]

The activation volumes found in this work are much larger than those normally reported for glassy polymers,[14-24] which are 1 nm^3. The activation volumes reported in the literature, however, were obtained at much higher stresses, through tensile, stress relaxation, or creep experiments. Pink[16,22] and Pink et al.,[23,24] for example, measured the activation volume in PVC by means of tensile or stress relaxation tests. They obtained a stress-dependent activation volume that decreased from 5 to near 1 nm^3 as the stress increased. These data were obtained at room temperature or below. Furthermore, Pink[16] recognized that the activation volume might be temperature dependent, but until further evidence refutes it, in PVC it was considered only stress dependent. Cavrot et al.,[20] however, found a temperature-dependent activation volume for the thermally activated deformation of glassy polystyrene. In fact, V increased very rapidly above about 300 K, and its temperature dependence could be very well described by

$$V = 0.33 + \frac{27.2}{385 - T} \text{ nm}^3 \tag{24}$$

which is an equation similar to eq. (23). The critical temperature of 385 K is very close to the glass transition temperature for polystyrene. An equation similar to eqs. (23) and (24) was used recently to describe the temperature dependence of the activation volume in PMMA.[7] Furthermore, a recent analysis[25] of the temperature and strain rate dependence of the yield stress data of PMMA leads also to a temperature-dependent and stress-independent activation volume. According to Pink,[16] the activation volume of PVC decreases as the applied stress increases for stresses between 20 and 120 MPa and at room temperature. The maximum stress used in our experiments at this temperature is 0.1 MPa, which is much lower than those used with other techniques. The activation work in our case is $\sigma V = 10$ MPa nm^3 at most. The activation work in the case of Pink[16] was few MPa nm^3, that is, of the same order of magnitude. In the high-frequency experiments of this work, the activation volume must be much higher than in quasistatic conditions, in order that the sinh term of eq. (3) plays a role in the strain rate. Furthermore, the stresses applied at high frequency are very small and under the limit of detection of quasistatic conditions. Also, the strain rates are much smaller.

It is difficult at this point to explain the physical mechanisms leading to the high-activation volumes obtained experimentally in this work. It is clear that several monomers moving cooperatively are involved in the relaxation process, leading to the high measured activation volumes. A similar situation was encountered during measurements of the amplitude-dependent dynamical behavior of PMMA. Finally, it must be pointed out that Haward and Thackray[14] compared the Eyring activation volumes, that is, V obtained from the yield stress data with the volume of the "statistical random link." The latter was obtained from studies of solutions by assuming that the real chain can be represented by an equivalent chain with freely jointed links of a particular length. The authors showed that the activation volumes are very large in molecular terms and range from about 2–10 times that of a statistical random link. The results suggests that yielding involves the cooperative movement of a large number of chain segments than would be required for a conformational change in dilute solution. In the case of PVC, the volume of statistical link in solution is 0.38 nm^3, whereas the Eyring volume is 8.6 nm^3. This last value is smaller than the value of V measured near room temperature at high frequencies.

Internal Stress

The internal stress is given by

$$\sigma_i = E'_I \epsilon_c \tag{25}$$

This equation, with the values of E'_I and ϵ_c given in Figure 5, leads to the internal stresses shown in Figure 8. The internal stresses obtained at high frequencies are much lower than the values measured during tensile or compression tests. It was found in PMMA, for example, that a horizontal shift of −55 K and a vertical shift of 2.45 decades must be applied to the data at high frequencies, with respect to the values obtained during tensile or compression tests,[7,25] when the data are represented as log σ_i against T. With these shifts, the internal stresses obtained in quasistatic conditions and during dynamic measurements coincide. Lower values of σ_i are obtained at high frequencies due to the much higher sensitivity of the technique. No data on internal stresses are reported in PVC for a comparison with Figure 8. It is clear that more theoretical and experimental work is needed to establish a clear correlation between the high frequency and the quasistatic results. Even the mechanisms acting under quasistatic conditions are not clearly understood.

Finally, it should be mentioned that Boyd et al.[26] observed nonlinearity in the stress strain behavior in PVC under conditions where the strain is completely recoverable during creep experiments. The authors claim that the onset of stress saturation of the relaxed or equilibrium compliance associated with the localized group motion is a reasonable explanation for the phenomenon. Nonlinearity was associated with a secondary (β) relaxation process. A phenomenological model was presented recently by Rekson[27] to represent nonlinear viscoelastic relaxation. According to Ward,[28] however, the interpretation of nonlinear viscoelastic behavior is still unclear. We do not have, for example, a specific model to interprete the amplitude dependence of the storage Young' modulus.

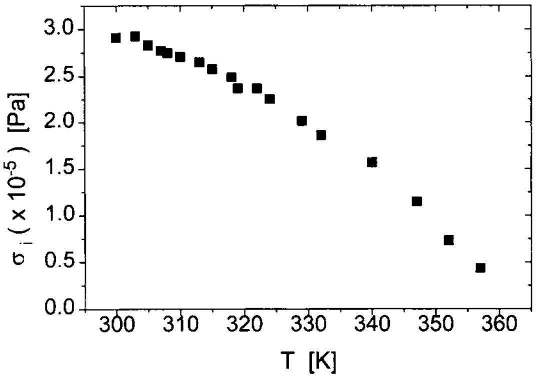

Figure 8 Internal stress for PVC, at high frequencies, as a function of temperature.

CONCLUSIONS

It was shown that the dynamic mechanical behavior of commercial PVC is temperature and strain-amplitude dependent. The amplitude-dependent damping can be described by assuming a hyperbolic sine stress dependence of the strain rate, indicating nonlinear viscoelastic behavior. Much larger activation volumes than those obtained through tensile, creep, or stress relaxation experiments were obtained from the damping data. Furthermore, the activation volume was found to depend on the temperature as $(T_c - T)^{-1}$, where T_c is close to the glass transition temperature measured by DSC. The amplitude-independent damping increased continuously, whereas the storage Young's modulus and the strain for the beginning of the amplitude dependence decreased continuously with the temperature, respectively. Finally, it is suggested that the mechanism controlling the nonlinear effects are related to those governig the α transition.

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