Analysis of temperature-dependent longitudinal ultrasonic properties of amorphous polymers

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The temperature dependence of the components of the longitudinal moduli $M'(T)$ and $M''(T)$ was derived from ultrasonic measurements at 1 MHz. The measurements were performed in polybutadiene ($M_w = 13\,000$) and poly(phenylmethylsiloxane) ($M_w = 4100$). The temperature dependence of M' and M'' was calculated in the framework of linear viscoelasticity using the Kohlrausch–Williams–Watts (KWW) relaxation function and including the temperature dependence of the mean relaxation time described by the Vogel–Fulcher–Tamman–Hesse equation. The only adjustable parameter was the KWW parameter β. We also considered the possibility of a temperature-dependent β parameter to describe the data.

(Keywords: temperature dependence; ultrasonic properties; amorphous polymers)

INTRODUCTION

The glass–rubber transition from the melt to the glassy state has to be analysed from a dynamical point of view as suggested by its dependence on time. The main transition or dynamic glass transition in amorphous bulk polymers is thought to be substantially a relaxation phenomenon accompanied by collective motions of macromolecular chains. These relaxation mechanisms are not in general a single exponential, and different assumptions are used to explain the non-exponential decay. First it is possible to assume[1] a relaxation time distribution $H(\tau)$ with a characteristic average time $\bar{\tau}$ and one or two parameters describing the broadness of the distribution. Second there exist theories connected to the so-called 'non-exponential decay'[2] which lead to the experimentally observed broadening of the relaxation function in the temperature or frequency domain. In both cases the temperature-dependent time τ may be identified: with the frequency ($\tau = 1/2\pi f_{\max}$) of the maximum loss modulus, determined by frequency-dependent measurements at a given temperature; or with the measuring frequency ($\tau = 1/2\pi f_{\exp}$) at the temperature of the maximum loss modulus, determined by temperature variation.

If the time–temperature superposition can be applied to the process under consideration, it should be possible to convert one experiment into the other. It is a well established fact that the temperature dependence of the average relaxation time for homogeneous amorphous polymers above the thermal glass transition temperature, T_g [i.e. in the range $\sim(T_g + 10\text{ K})$–$(T_g + 100\text{ K})$] can be well described by the Vogel–Fulcher–Tamman–Hesse (VFTH) equation[1]:

$$\bar{\tau} = \tau_0 \exp \frac{B}{T - T_0} \tag{1}$$

The difference in the characteristic times obtained from relaxation (longitudinal modulus M^*) and retardation (longitudinal compliance $D^* = 1/M^*$) experiments is negligible for measurements of longitudinal viscoelastic properties above T_g. This is because $M' \gg M''$ and the dispersion in M' is small, which means $\log(M'_\infty/M'_0) \ll 1$, where M'_∞ and M'_0 are the high and low frequency limits of the real part of the longitudinal modulus. Therefore it is possible to experimentally determine the temperature dependence of the characteristic time $\bar{\tau}$ over a broad temperature and frequency range by combining different methods which are sensitive to longitudinal properties, e.g. photon correlation spectroscopy, ultrasonics, Brillouin scattering[3–6].

The aim of this work is to describe the temperature dependence of the real and imaginary parts of the longitudinal modulus at a fixed measuring frequency. The temperature dependence of M' and M'' are calculated based on the Kohlrausch–Williams–Watts (KWW) function[7,8]:

$$\varphi(t) = \exp -\left(\frac{t}{\bar{\tau}}\right)^{\beta} \tag{2}$$

for the time-dependent modulus, including the VFTH equation for temperature dependence of the mean relaxation time. We used the non-exponential decay because it is known to give a satisfactory fit for experimental data and furthermore there is a physical motivation in the framework of the coupling model of Ngai[2]. It should be noted that the calculations are restricted to the temperature range where the VFTH equation is valid.

GENERAL

From the temperature dependence of both the ultrasonic absorption $\alpha(T)$ and velocity $c(T)$ for longitudinal wave propagation one can calculate the temperature dependence of the real and imaginary parts of the longitudinal

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modulus[9] $M^* = M' + iM''$:

$$M^* = \frac{\rho c^2}{(1 - i\alpha c/\omega)^2} \tag{3}$$

where ρ is the density and $\omega = 2\pi f$.

For longitudinal waves it is usual to assume $\alpha c/\omega \ll 1$. Therefore the following relations were applied to calculate $M'(T)$ and $M''(T)$:

$$M' = \rho c^2; \qquad M'' = 2\rho c^3 \alpha/\omega \tag{4}$$

In order to describe experimental data of dynamic measurements it is necessary to transform the time-dependent KWW function (equation (2)) into the frequency domain. An analytical and numerical transformation of the dipole correlation function into the frequency-dependent complex dielectric permittivity was proposed several years ago[10]. In our case the KWW function has to be connected to the longitudinal modulus. Following the approach of linear viscoelasticity[1] the generalized modulus $\chi(t)$ can be expressed using the KWW function:

$$\chi(t) = \chi_0 - (\chi_\infty - \chi_0)\exp[-(t/\bar{\tau})^\beta] \tag{5}$$

where χ_0 and χ_∞ are the limits of the generalized modulus for $t \to \infty$, $\omega \to 0$ and $t \to 0$, $\omega \to \infty$, respectively.

Formally, it is possible to apply this equation to the longitudinal modulus. After Fourier transformation we obtain:

$$M^*(\omega) = M'_\infty + (M'_\infty - M'_0)\int_0^\infty \exp(-i\omega t)\frac{\mathrm{d}}{\mathrm{d}t} \times \exp\left[-\left(\frac{t}{\bar{\tau}}\right)^\beta\right]\mathrm{d}t \tag{6}$$

By partial integration and separation into real and imaginary parts, we have:

$$M'(\omega, \bar{\tau}) = M'_0 + (M'_\infty - M'_0)\omega \times \int_0^\infty \exp\left[-\left(\frac{t}{\bar{\tau}}\right)^\beta\right]\sin\omega t\,\mathrm{d}t \tag{7}$$

$$M''(\omega, \bar{\tau}) = (M'_\infty - M'_0)\omega \times \int_0^\infty \exp\left[-\left(\frac{t}{\bar{\tau}}\right)^\beta\right]\cos\omega t\,\mathrm{d}t \tag{8}$$

For the description of the temperature dependence of the modulus we have to introduce the temperature dependence of the relaxation time which can be expressed by a VFTH equation (equation (1)). Because analytical solutions for the integrals in equations (7) and (8) exist only for special values of β, one has to use numerical methods to calculate them. Useful approximations for numerical calculations are given in reference 10.

EXPERIMENTAL

The ultrasonic absorption and velocity were measured at a frequency of 1 MHz over a temperature range of 170–370 K. At temperatures below 220 K a nitrogen gas stream was used to cool the sample with a temperature stability of ±0.5 K. At higher temperatures conventional liquid thermostatic techniques were applied.

The experiments were performed by a pulse technique using one transmitting transducer and two fixed receiving transducers to realize different acoustic path lengths under the same acoustic conditions. We estimated the delay time and the attenuation by the use of a pulse-overlap method. The accuracy for ultrasonic velocity is ~2–3% and the absolute error of the absorption is ~10 m^{-1}. The error in absorption measurement increases at temperatures near T_g caused by internal thermal stresses and microcracks in the sample. Therefore the absorption measurements are performed only above T_g.

Two amorphous polymer melts were studied, a polybutadiene (PB) and a poly(phenylmethylsiloxane) (PPMS) sample. The PB had a weight and a number average molar mass (M_w, M_n) of 13 000 and 8600, respectively. Its chemical microstructure, obtained by nuclear magnetic resonance, was 71% 1,2-vinyl, 20% 1,4-*trans* and 9% 1,4-*cis*. The T_g value estimated by differential scanning calorimetry was 222 K.

The PPMS had $M_w = 4100$ and $M_n = 2750$. The T_g value was ~235 K.

RESULTS AND DISCUSSION

The temperature dependence of the ultrasonic absorption and velocity of PPMS and PB are given in *Figures 1* and *2*. For both samples the typical step in ultrasonic velocity and the maximum in ultrasonic absorption indicating the dynamic glass transition[9] are clearly evident.

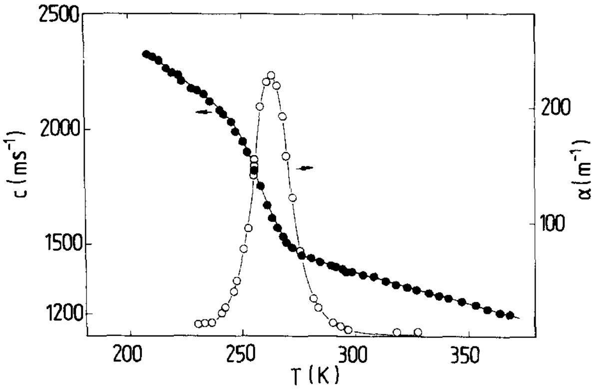

Figure 1 Temperature dependence of the ultrasonic absorption α and velocity c of PPMS at 1 MHz

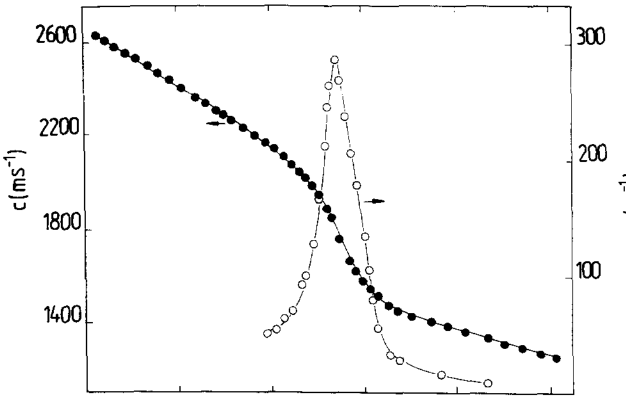

Figure 2 Temperature dependence of the ultrasonic absorption α and velocity c of PB at 1 MHz

Table 1 Parameters for the calculation of $M'(T)$ and $M''(T)$ using the KWW function

	$c_\infty{}^a$ $(T=0\text{ K})$ (m s^{-1})	$\frac{\Delta c_\infty{}^a}{\Delta T}$ $(\text{m s}^{-1}\text{ K}^{-1})$	$c_0{}^b$ $(T=0\text{ K})$ (m s^{-1})	$\frac{\Delta c_0{}^b}{\Delta T}$ $(\text{m s}^{-1}\text{ K}^{-1})$	$\rho_0{}^c$ $(T=293\text{ K})$ (kg m^{-3})	$\frac{\Delta\rho^c}{\Delta T}$ $(\text{kg m}^{-3}\text{ K}^{-1})$	T_g^{dyn} (K)
PB	3875	7.4	2260	2.9	896	0.75	263
PPMS	3555	6.2	2360	3.1	1115	0.8	266

[a] $c_\infty(T)=(\Delta c_\infty/\Delta T)T+c\ (T=0\text{ K});\ M'_\infty(T)=\rho(T)c^2_\infty(T)$

[b] $c_0(T)=(\Delta c_0/\Delta T)T+c\ (T=0\text{ K});\ M'_0(T)=\rho(T)c_0^2T$

[c] $\rho(T)=-(\Delta\rho/\Delta T)(T-293\text{ K})+\rho_0$

Using equation (4) we calculated the values of $M'(T)$ and $M''(T)$. The temperature dependence of the density was shown to be linear above T_g (*Table 1*). For temperatures below T_g we assumed a temperature extension coefficient of one-half of that in the polymer melt as a typical value for polymers[1]. The error caused by that assumption should be $<1\%$ for $T=T_g-10$ K.

The values of $M'(T)$ and $M''(T)$ are given in *Figures 3* and *4*. Some experimental parameters are needed for the calculation of the theoretical curves for $M'(T)$ and $M''(T)$. The parameters of the VFTH equation obtained by independent measurements[4] (photon correlation spectroscopy, ultrasonics) are $\log[\tau_0(s)]=-13.6\pm0.7$, $B=1175\pm110$ K, and $T_0=193\pm5$ K for PB and $\log[\tau_0(s)]=-13.2$, $B=920$ K, and $T_0=198$ K (only ultrasound) for PPMS. The temperature dependence of M'_∞ and M'_0 can be obtained from linear extrapolation of the temperature dependence of $M'(T)$ well below and above the dynamic glass transition. All parameters are listed in *Table 1*.

The results of the calculation are represented in *Figures 3* and *4*. The three lines show the influence of the parameter β on the calculated curves. In the case of PB and PPMS a good fit is achieved for $\beta=0.6$ and 0.5, respectively. The M' data fit very well in the whole temperature region, whereas for M'' there are deviations in the low temperature range. These deviations are especially significant for PB and may be explained as additional secondary relaxations. From measurements of the dynamic shear modulus of *cis*-PB[11] the influence of secondary relaxations have been obtained in a similar temperature and frequency range. On the other hand, internal thermal stresses may lead to additional experimental error at low temperatures. In some references, a temperature-dependent distribution parameter is suggested[12,13]. Comparing the β parameters, estimated from photon correlation spectroscopy measurements[4] and from temperature- and frequency-dependent ultrasonic measurements[5] (*Figure 5*), we found the temperature dependence of $\beta=0.095(T-T_0)$. This relationship was introduced for calculating M' and M''. The results are shown in *Figures 6* and *7*. It was possible to achieve a better fit between the experimental data and the theoretical curve for PPMS in the low-temperature region. It should be noted that by this procedure the theoretical curves are calculated using only experimental values without any adjustable parameter.

On the other hand we have for both samples a significant deviation of experimental data from the calculated curve at higher temperatures. From the point of view of polymer dynamics this deviation can be explained by the contribution of subchain motions

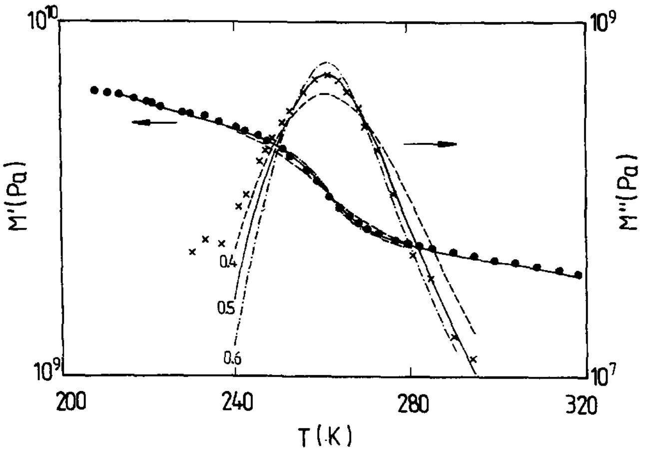

Figure 3 Temperature dependence of real M' and imaginary M'' parts of the longitudinal modulus of PPMS at 1 MHz. The broken lines are calculated from equations (1), (2), (7) and (8) for different distribution parameters β

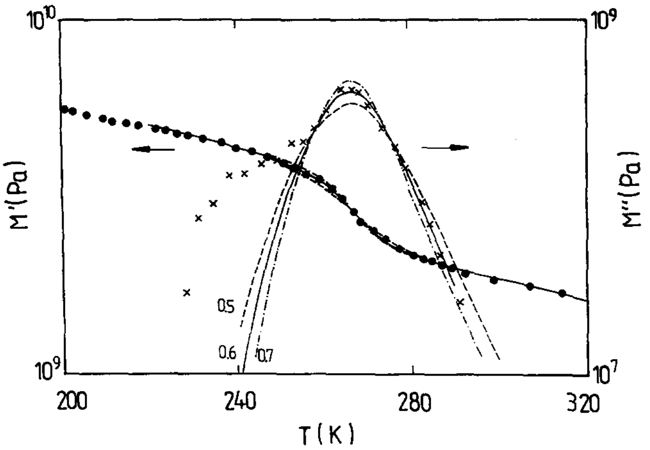

Figure 4 Temperature dependence of real M' and imaginary M'' parts of the longitudinal modulus of PB at 1 MHz. The broken lines are calculated from equations (1), (2), (7) and (8) for different distribution parameters β

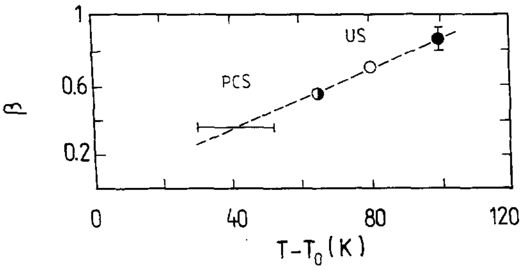

Figure 5 Temperature dependence of the KWW parameter β from photon correlation spectroscopy and ultrasonic measurements [○, PB-$\alpha(T)$; ◐, PPMS-$\alpha(T)$; ●, PB-$\alpha(f)$]. The broken line represents $\beta=0.095(T-T_0)$

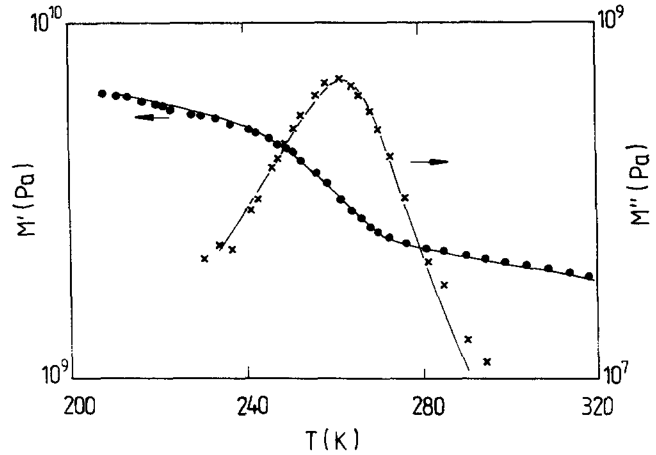

Figure 6 Temperature dependence of real M' and imaginary M'' parts of the longitudinal modulus of PPMS at 1 MHz. The lines are calculated with a temperature-dependent β parameter

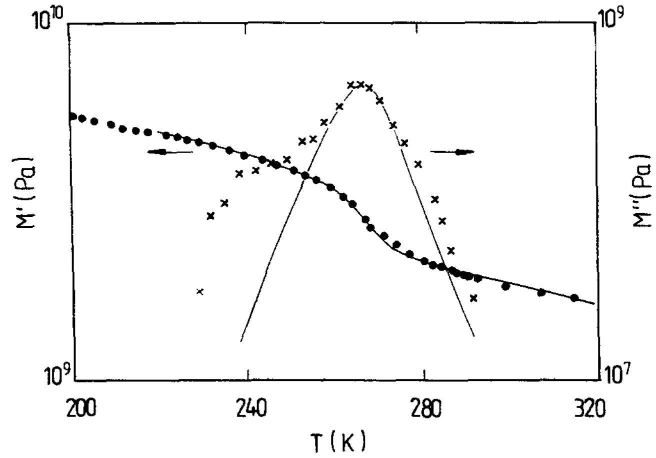

Figure 7 Temperature dependence of real M' and imaginary M'' parts of the longitudinal modulus of PB at 1 MHz. The lines are calculated with a temperature-dependent β parameter

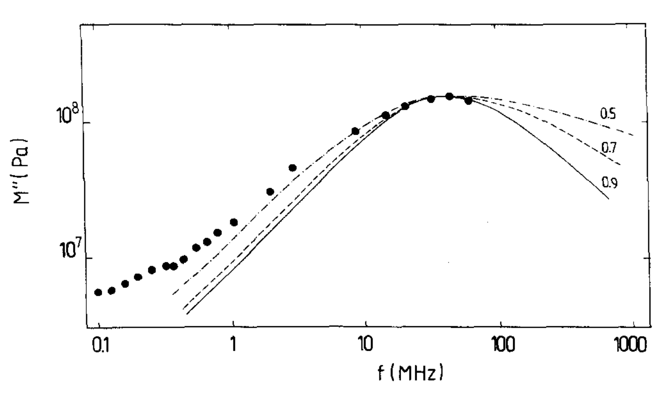

Figure 8 Imaginary M'' part of the longitudinal modulus as a function of frequency f. Curves are calculated from the transformed KWW function for different β values

(Rouse-like modes and/or entanglement effects) to the loss mechanisms. Of course this type of motion is not represented by the KWW function, which describes the phenomenon of the dynamic glass transition. In the case of frequency-dependent measurements[5] at temperatures far above T_g it can be shown that it is possible to interpret the frequency dependence of the loss modulus by superimposing a Rouse-like relaxation time spectrum on a nearly single exponential relaxation mechanism due to the dynamic glass transition.

A similar deviation was found in the low-frequency region by comparing[5,14] the experimental frequency dependence of M'' with the calculated curves by using the transformed KWW function. We suggest that the deviations in *Figure 8* are also connected to slower modes which are not involved in the KWW equation. A more detailed discussion of those motions is given elsewhere[14].

CONCLUSIONS

It has been shown that the temperature dependence of the real M' and imaginary M'' part of the longitudinal modulus can be described satisfactorily by a combination of the transformed KWW function (that is the Fourier transform of $\mathrm{d}\{\exp[-(t/\bar{\tau})^{\beta}]\}/\mathrm{d}t$ and the VFTH equation for the temperature dependence of the mean relaxation time. We also attempted to include the temperature-dependent distribution parameter β, obtained from ultrasonics and photon correlation spectroscopy. Deviations can be explained by additional relaxation processes (secondary relaxations, subchain motions, entanglements) which are not involved in the KWW function. This is also supported by comparing the transformed KWW function with frequency-dependent measurements.

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