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Glassy Polymers: Temperature Dependence of Viscoelastic Properties

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Temperature dependence of viscoelastic properties of glassy polymers is reviewed.

KEY WORDS Glassy polymers, viscoelastic properties, temperature effects.

Since the relaxation time values of polymers vary widely, the following expressions describe the components of the complex dynamic modulus of elasticity¹:

$$G' = \sum_{i=1}^N G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad (1)$$

$$G'' = \sum_{i=1}^N G_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \quad (2)$$

where G' is modulus of elasticity, G'' the loss modulus, ω the frequency, τ_i the relaxation time of i th process, and N is the number of events of mechanical relaxation in a polymer. G_i values for vitreous state depend upon the system of interactions in the polymer which is broken when the re-ordering of i th sort takes place.

Because of asymmetry of the interaction potential functions (anharmonicity), the components of G_i vary with temperature, as does the relaxation time τ_i . Therefore we can expect that in the following two ways the elasticity of glassy polymers shall be changed:

1. The modification of relaxation time spectrum (molecular mobility). As a result, the number of the terms in (1) such that $\omega \tau_i / 1 + \omega^2 \tau_i^2$ is changed.

2. The temperature dependence of power characteristics $G_i(T)$. It is very difficult to distinguish these two mechanisms on the level of each relaxation process. Therefore a number of assumptions have been made in the analysis of viscoelasticity temperature dependence. On the first stage it is assumed that the temperature dependence of G_i is weak. Under this condition, according to the calculations² the

temperature dependences of the components of the complex elasticity modulus relate as follows:

$$-\Delta G_T' = G'(T_1) - G'(T_2) \approx \frac{2a_0}{\pi} \int_{T_1}^{T_2} \frac{G''}{T} dT \quad (3)$$

or, since $G''/G' = \tan \delta$,

$$-\Delta \ln G_T' = \ln G'(T_1)/G'(T_2) \approx \frac{2a_0}{\pi} \int_{T_1}^{T_2} \frac{\tan \delta}{T} dT \quad (4)$$

with the parameter $a_0 = -(d \ln \tau_i / d \ln T)_\omega$ expressing the temperature dependence of the processes for which $\omega \tau_i$ undergo the transition between T_1 and T_2 . The expressions (3) and (4) resemble Staverman-Schwarzl relations³ for the frequency dependence of modulus components. The temperature dependence of elasticity modulus is directly related to the polymer relaxation spectrum, and it may be reduced from (3) and (4).

For the polymers with pronounced relaxation transitions, the values of a_0 at different temperature rates may be determined. In this case, the transitions may be regarded as the datum marks which provide a picture of the temperature behavior of relaxation time in different spectral ranges. In the vicinity of this or that most probable relaxation process the parameter $a_0 \approx a_{0i}$ ($i = \alpha, \beta, \gamma \dots$ processes) becomes

$$a_0 \approx a_{0i} = - \left(\frac{d \ln \tau_i}{d \ln T} \right) = \frac{d \ln \nu_{i\max}}{d \ln T} = - \frac{1}{T} \frac{d \ln \nu_{i\max}}{d(1/T)} = \ln \frac{\nu_{0i}}{\nu} \quad (5)$$

Hence, a_0 is a Y-intercept of the line tangent to $\ln \nu_{i\max}(1/T)$ curve at $y = \ln \nu$ (ν is the frequency of the measurement). The a_{0i} values obtained from the relaxation transition maps for a number of polymers⁴⁻¹⁰ at $\nu = 1$ Hz are shown in Figure 1. One can see that $a_{0i} = \text{const} \approx 30$ at low temperatures where the temperature dependence of relaxation time may be simply described as an exponent. As the glass transition temperature is approached, the temperature dependence of relaxation time of the co-operative processes is becoming much more complicated, and hence a_0 sharply increases.

To examine the equations obtained, the dynamic properties of the three linear polymers have been measured: poly(methyl-methylacrylate) (PMMA), poly(cyclohexylmethacrylate) (PCHMA), and poly(styrene) (PS). The measurements were taken on a torsion pendulum at 1 Hz in the temperature range from 100 K to T_g . The measured values of shear modulus G' and $\tan \delta$ are presented in Figure 2. This diagram also shows the temperature dependence of G' calculated according to (4). Apparently, the calculated values appreciably differ from those experimentally obtained, with the discrepancy being especially great in the case of PS, and being smallest in the case of PCHMA. The reason for this becomes clear as soon as the sizable difference between the internal friction spectra of the in-

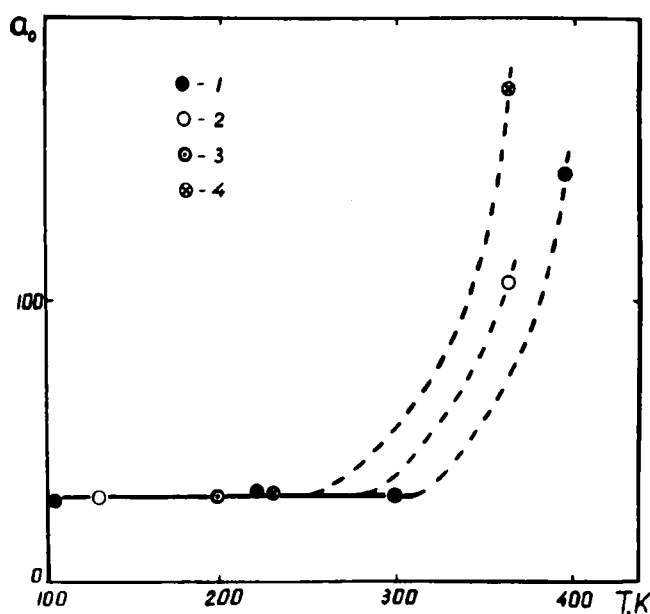


FIGURE 1 Temperature dependence of a_0 at 1 Hz. 1 = PMMA, 2 = PS, 3 = PCHMA and 4 = PVC.

investigated polymers is taken into account. Indeed, in the case of PS, where damping is very small, molecular mobility is responsible for just 25% of the total temperature-induced variation of the modulus, while for PMMA and PCHMA, both notable for their secondary transitions, this contribution amounts to 50 and 65%, respectively.

The next order of approximation deals with the temperature dependence of G_i . We assume that it is uniform for all i :

$$\frac{d \ln G_i}{dT} = \alpha_{G_i} \approx \alpha_G; \quad G_i = G_{i0} \exp \left(- \int_0^T \alpha_G dT \right) \quad (6)$$

This assumption is accurate if the components G_i are formed by the sufficiently great number of similar bonds (in our case, the weak intermolecular bonds). Then α_{G_i} is the average temperature coefficient over all bonds, and it would not substantially differ from the macroscopic α_G .

From (1, 2, 4, 6) follows the expression for the differential change in elasticity modulus with temperature:

$$-\Delta \ln G_T \approx \frac{2a_0}{\pi} \int_{T_1}^{T_2} \frac{\tan \delta}{T} dT + \int_{T_1}^{T_2} \alpha_G dT \quad (7)$$

The first term accounts for the temperature dependence determined by various relaxation processes, and the second term describes the contribution of the interaction temperature dependence.

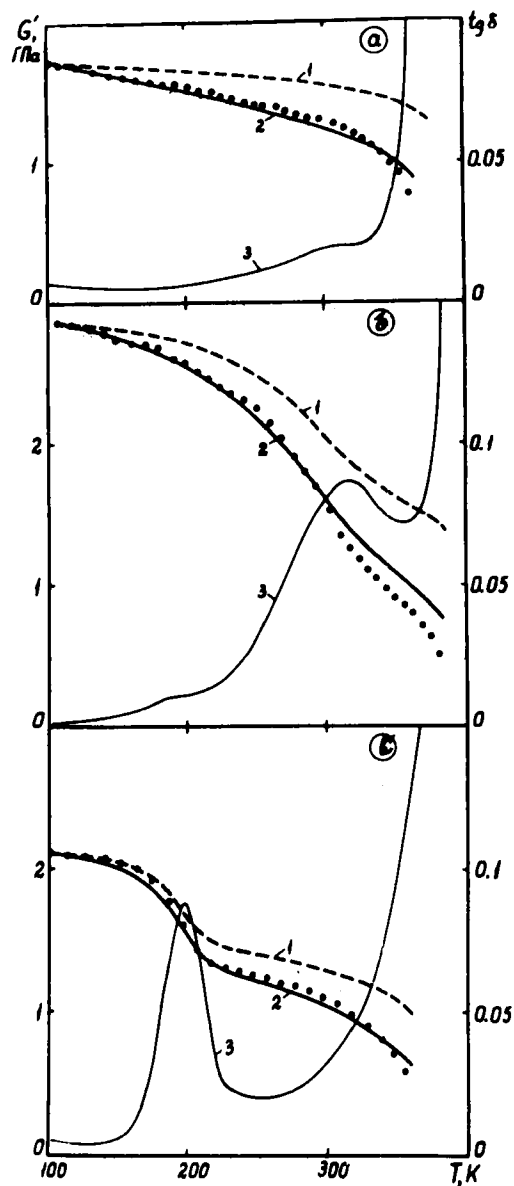


FIGURE 2 Temperature dependence of shear modulus and $\tan \delta$ (curve 3) at 1 Hz: $a = \text{PMMA}$, $b = \text{PS}$ and $c = \text{PCHMA}$. The series 1 were calculated according to Equation (4); the series 2 were calculated according to Equation (7). Dots stand for the measured values.

In the limit of $\omega \rightarrow \infty$ the relaxation processes do not influence the elasticity modulus. Therefore by measuring the modulus under the highest possible frequencies over a wide temperature range one can evaluate the second term in (7).

In this work, the acoustic properties of the polymers have been investigated with a technique described in earlier work,¹¹ which is based on Mandelstam-Brillouin scattering. This technique allows for measurement of the hypersonic velocity at ν

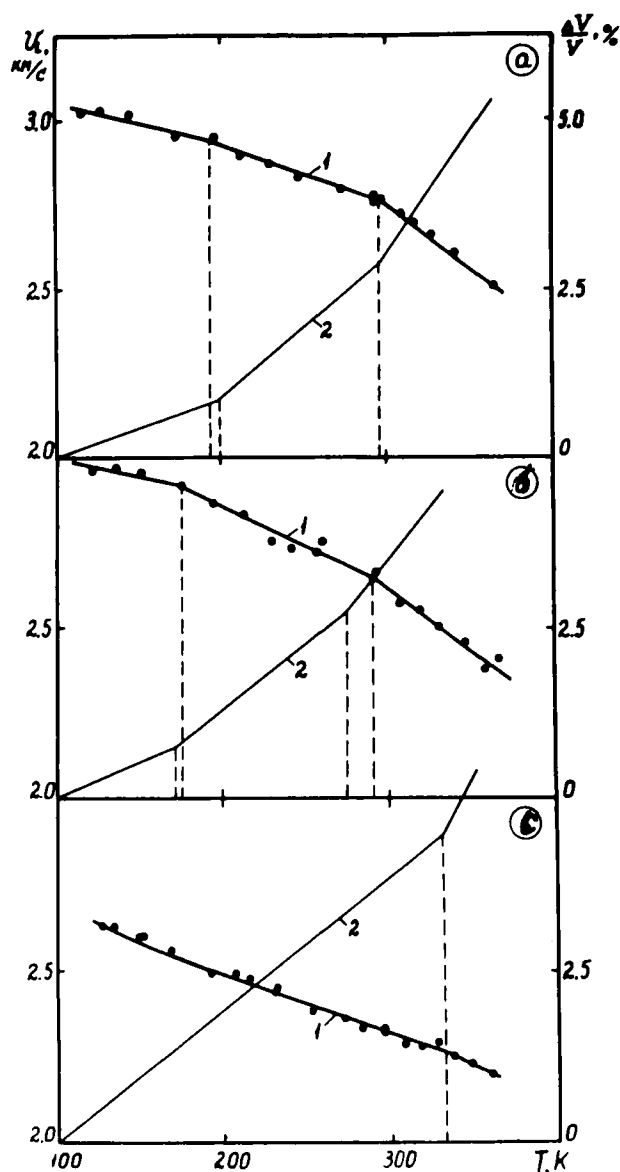


FIGURE 3 Temperature behavior of hypersonic velocity (1) and fractional volume modification (2): a = PMMA, b = PCHMA and c = PS.

$\approx 10^{10}$ Hz. Figure 3 shows the temperature dependence of the hypersonic wave velocity. As shown, the dependence is strong, and therefore a similar relationship holds for the elastic constants of the glassy polymers. The dependence may be regarded as a series of line segments with distinct 'bend' temperatures. Similar behavior of glassy polymers has been observed before^{12,13} in the ultrasonic measurements in the frequency range of 10^6 Hz. The 'transition' temperatures thus obtained are in good agreement with those obtained here with the hypersonic

measurements. Since there is no frequency shift, it is natural to suppose that the modifications of the vitreous polymer structure play the most important part in this type of 'transition'. Therefore the temperature dependence of volume $\Delta V/V(T)$ is likely to have the same sort of singularities as $V_L(T)$. Figure 3 also presents the thermal extension curves of the polymers. The typical temperatures of these curves are in satisfactory agreement with those corresponding to the 'bends' of the hypersound temperature dependence.

The second term in (7) may be evaluated as follows:

$$\int_{T_1}^{T_2} \alpha_G dT \approx 2 \ln \frac{\nu_L(T_1)}{\nu_L(T_2)} + \frac{\Delta V}{V} \quad (8)$$

After the appropriate substitution, the temperature dependence of elasticity modulus of the polymers was calculated anew. Figure 3 exhibits the good agreement of the calculated and measured results.

Thus, the analysis performed adequately provides both qualitative and quantitative description of the temperature dependence of the elasticity modulus of glassy polymers. Equation (7) explicitly shows the role played by the two mechanisms responsible for this dependence, namely the molecular mobility of the relaxation processes and anharmonicity. Presumably, their respective contributions would vary for different polymers and experimental environment.

In conclusion, let us make a few remarks on the problem of temperature/frequency correlation (TFC) of the viscoelastic properties of glassy polymers. To solve it successfully, first the contribution arising from the relaxation spectrum of the

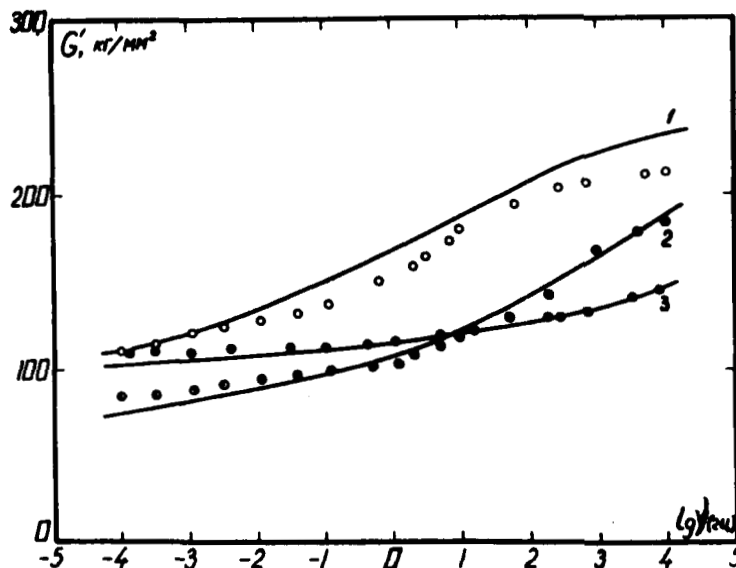


FIGURE 4 Frequency dependence of shear modulus: 1,2 = PMMA ($T = 293$ K, 333 K) and 3 = PVC ($T = 293$ K). Curves and dots stand for the calculated and measured data, respectively.

polymer must be reduced in accordance with Equations (3) or (7). Only then can this contribution undergo usual TFC treatment:

$$\frac{T_1}{T_2} = \frac{\ln \bar{\nu}_0/\nu_2}{\ln \bar{\nu}_0/\nu_1},$$

where $\bar{\nu}_0$ is the mean frequency factor in the temperature range from T_1 to T_2 . Note that far from the glass transition point $\bar{\nu}_0 = \neq \text{const} \approx 10^{13} \text{ c}^{-1}$). Knowledge of the temperature behavior of $\bar{\nu}_0$ is absolutely vital for TFC in the high-temperature region (closer to T_g), with the dependence in this case being especially strong.

Figure 4 shows the calculated frequency dependences of shear modulus of PMMA at 291 and 333 K, and poly(vinylchloride) (PVC) at 293 K. They were obtained from the aforementioned TFC expression and the temperature dependence of the viscoelastic properties of the materials investigated at 1 Hz. It is evident that over a rather wide range of frequencies (± 4 orders of magnitude) the calculated values adequately approximate the measured results.^{14,15}

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