Confirmation of Plazek's Slight Shoulder in the Shear Retardation Spectrum of Poly(vinyl acetate) at the Dynamic Glass Transition

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Plazek reported a slight shoulder in the shear retardation spectrum, $L(\log \tau)$, of poly(vinyl acetate) (PVAC)[1] and polypropylene (PP)[2] just at the same position where the shear loss modulus ($G''(\omega)$) has its glass transition maximum ($\omega\tau = 1$). He did not decide whether this is a real effect or "caused by experimental uncertainty"[1] or "by temperature-reduction errors".[2] On the other hand, this shoulder was assumed, in the framework of a study on the fine structure of the main transition in polymers,[3,4] to be a direct indicator of the "proper" glass transition manifested by the G'' maximum, the dielectric loss maximum (ϵ''), and others. The aim of this paper is an experimental confirmation of this shoulder and its comparison with G'', ϵ'', and heat spectroscopy data.

Experimental Section. A carefully dried PVAC sample ($M_w = 5.6 \pm 0.3 \times 10^5$, $M_w/M_n = 3.7 \pm 0.2$, $T_g = 38 \pm 1$ °C from a DSC equal area construction for $\dot{T} = 10$ K/min) was investigated in the relevant frequency and temperature range with the aid of a dynamic analyzer RDA II and a dynamic stress analyzer DSR from Rheometrics Scientific, by a broad-band dielectric spectrometer from Novocontrol, and by specific heat spectroscopy according to Birge and Nagel[5,6] in a periodic calorimeter.[7] The relative mean uncertainty of the original shear data is not larger than 10%, corresponding to about the symbol size of Figure 2, below. Details of the sample preparation, the time−temperature program, and the comparability of the temperatures in the different devices will be published elsewhere.[8] The retardation spectrum L was calculated from the shear data by means of a nonlinear regularization program by Honerkamp and Weese.[9]

Results and Discussion. Figure 1 shows three isothermal shear retardation spectra calculated from shear frequency sweeps at the temperatures 41.5, 43.5, and 45.4 °C, with no temperature reduction. Each of the three curves demonstrates the slight shoulder that cannot, therefore, be caused by temperature-reduction errors.

The original data of the real part compliance (J') at these temperatures are shown in the upper part of Figure 2. The lower part of Figure 2 shows $\log(-\mathrm{d}J'/\mathrm{d} \log \omega)$, smoothed with five-point splines. A slight indication of the shoulder can be detected also in this representation. [Similar results are obtained for repeated measurements, for a PVAC sample with higher water content, and for a commercial polystyrene sample. It seems that the occurrence of the shoulder does not depend on polydispersity.] Since the differentiation is a local procedure, the slight shoulder in L cannot be generated by the steep slope of the J^* values in the main transition that could be, in principle, reflected by the nonlocality properties of the regularization program.

Figure 3 shows the sensitivity of this slight shoulder in a 56.6 °C master curve (from about 300 data) against a manipulated variation of the experimental data. The

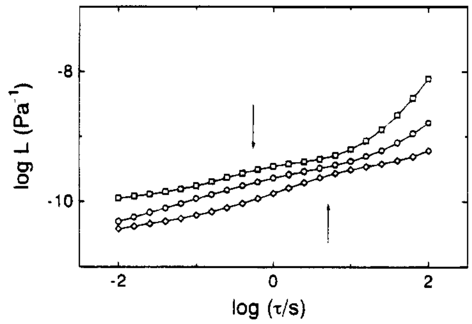

Figure 1. Shear retardation spectrum of PVAC: (□) 45.4, (○) 43.5, (◇) 41.5 °C. The arrows show the position of the slight shoulder. The *log* symbol always means $\log_{10}$ (logarithm on basis 10).

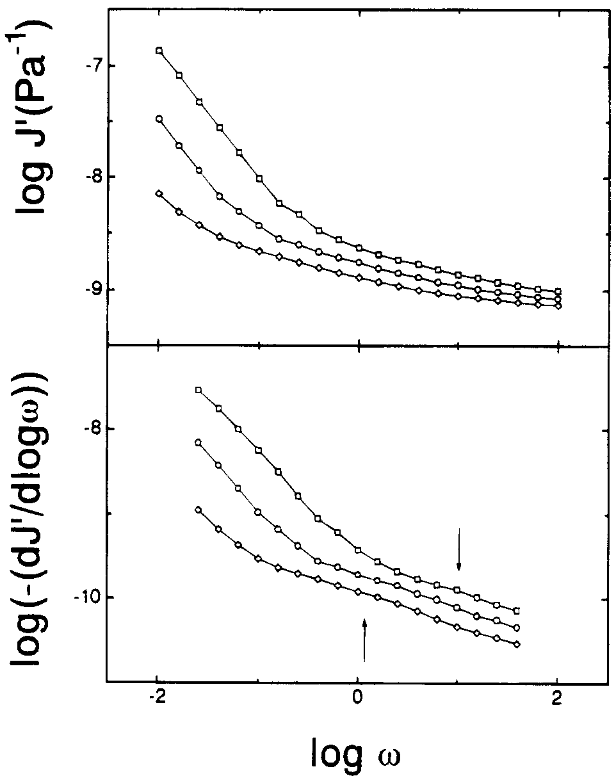

Figure 2. Original data of the real part of dynamic shear compliance, J' (upper part), from which the spectrum of Figure 1 was calculated. The lower part shows a smoothed differentiation of these curves.

shoulder resisted the following data manipulations: addition of random errors of ±10 and ±20% to each experimental point, a rarefaction of the data down to 10% (i.e., only any tenth point was used, in sum about 30 data), and a combination of rarefaction and ±10% randomization. The shoulder is only lost by a combination of rarefaction plus the ±20% randomization. The shoulder is also resistant to a data cutoff for $\log \tau/a_T < -2.5$ (not shown in Figure 3). We conclude from this stability that the slight shoulder cannot be caused by experimental uncertainty.

Figure 4 shows the master curves for the real and imaginary part of the dynamic shear modulus, $G^* = G' + i\omega G''$, the shear loss factor, $\tan \delta = G''/G'$, and the shear retardation spectrum L reduced to $T_0 = 56.6$ °C with a WLF equation, $\log(f/\mathrm{Hz}) = 10.9 - 451/(T/\mathrm{K} - 275.6)$, $f = \omega/2\pi$. The $\tau\omega$ conversion was again done by $\omega\tau = 1$. The frequency range of the shear data is 10^{-2}−10^{+2} rad/s, and the temperature range, 41.5−148.5 °C.

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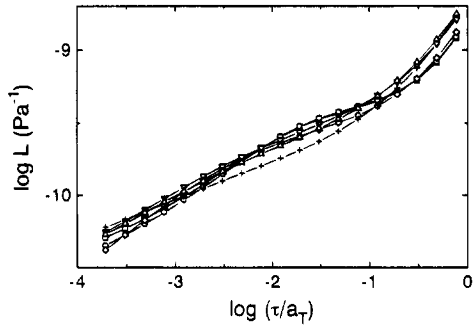

Figure 3. Stability against manipulated data variation of a L master curve (T_0 = 56.6 °C): (□) from the original master curve, (○) from the master curve with a random error of ±10%, (◇) from the master curve with a random error of ±20%, (△) from the master curve rarefied down to about 10% of the data, (▽) from the rarefied master curve with a random error of ±10%, (+) from the rarefied master curve with a random error of ±20%.

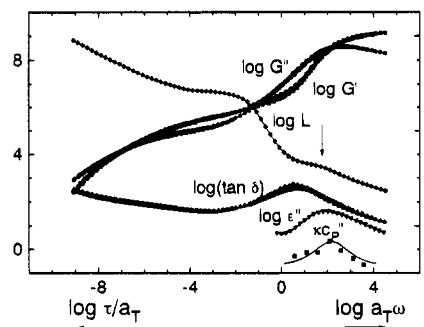

Figure 4. Comparison of shear modulus (log G', log G''), shear loss factor (log(tan δ)), dielectric function (log ϵ''), and heat spectroscopy ($\kappa c''_{\mathrm{P}}$, linearly presented) with the slight shoulder in the shear retardation spectrum (log L). Arbitrary units, also for the dimensionless variables such as tan δ and ϵ'', and $\omega\tau = 1$.

For comparison, the dielectric loss, ϵ'', was measured at T = 58 °C and WLF corrected from this temperature to T_0. The imaginary output of heat spectroscopy was measured directly at T = 56.6 °C. Since the experimental real part $\kappa c'_{\mathrm{P}}$ is more precise than the imaginary part $\kappa c''_{\mathrm{P}}$, the $\kappa c''_{\mathrm{P}}$ curve was calculated from the real part by using the Kramers–Kronig relation via a fit with a Havriliak–Negami function.[8] Figure 4 demonstrates that the usual signals of a dynamic glass transition in equilibrium (no freezing-in) are about at the same position as Plazek's slight shoulder.

Conclusions. According to the fluctuation dissipation theorem, the natural frequencies (or times) of the spontaneous system fluctuations are identified[3,4,10] with the external frequencies (or relaxation times) at which the system can absorb energy. The slight L shoulder is, therefore, a direct consequence of the fluctuations which produce also the other (dielectric, caloric) signals of the proper glass transition. The large step of G', J', or L in the main transition of polymers is therefore caused by other molecular modes (possibly confined flow and modified Rouse modes[4]). These modes are slower (and larger[10]) than the modes producing the proper glass transition. There is no contradiction of this thesis to the general relation $G^*(\omega)\,J^*(\omega) = 1$, with J^* the shear compliance, if the flank sensitivity of this relation is taken into account. The flank sensitivity means that very small (percent range) systematic variations of $G^*(\omega)$ in the crossover from the main to the plateau zone can, just from the $G^*J^* = 1$ relation, produce very large changes in the J^* values there.[3]

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