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Superposition of Small Strains on Large Deformations as a Probe of Nonlinear Response in Polymers

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The incremental response $\Delta G(t)$, obtained by superposing a deformation, $\Delta\gamma$, on a large deformation, γ_1 , has been determined in step shear experiments for a polyisobutylene solution and for a poly(methylmethacrylate) glass in torsion. For both systems $\Delta G(t)$ at γ_1 was found to be smaller than the linear viscoelastic modulus, $G(t)$, at zero prestrain. $\Delta G(t)$ was found to increase with increasing time, t_e , after imposition of the large deformation. It was also observed that the "apparent relaxation spectrum" associated with $\Delta G(t)$ narrows and shifts to shorter times when compared to the spectrum associated with the linear viscoelastic modulus, $G(t)$. The results for the solution are well described by the nonlinear constitutive equation of the BKZ elastic fluid theory. It is found that $\Delta G(t)$ for the glass falls between the behavior predicted by the BKZ theory and the linear viscoelastic behavior.

INTRODUCTION

With the advent of sophisticated servo-controlled and computer commanded testing machines, there has been a considerable amount of recent activity (1 to 8) in which small strains superimposed upon large deformations are used to probe the response of polymeric materials. Although the experiments themselves are quite interesting, we find that the common practice of treating the superposed response as if it were a linear viscoelastic property and relating this to molecular relaxations, glassy structure, etc. to be quite ambiguous as we will show below.

There are two important findings which describe the effects of mechanical deformation on the incremental response [$\Delta E(t)$ or $\Delta E^*(\omega)$] of polymer glasses. First, $\Delta E^*(\omega)$ is found to decrease with increasing deformation (3 to 5) and to increase with increasing time, t_e , after the imposition of the large deformation. Second, the relaxation spectrum associated with the superposed response is found to increasingly shift to shorter times and to narrow as the deformation increases or t_e decreases (4). Such results have been interpreted in terms of mechanically-induced physical aging, changes in segmental mobility, or change in glassy structure (1, 4, 5).

The purpose of this paper is to show that although there may be structural changes associated with the mechanical deformation of polymer glasses, the superposition of small

strains on large as a probe of such changes gives ambiguous results. We show this by carrying out experiments on a concentrated solution of polyisobutylene (PIB) and on a poly(methylmethacrylate) (PMMA) glass. We rationalize the results in the context of the single integral non-linear viscoelastic constitutive equation of Bernstein, Kearsley, and Zapas (9) (BKZ).

ANALYSIS

For simplicity we shall use the incompressible, isothermal form of the BKZ (9, 10) theory and consider the class of motions limited to simple shearing histories.

In a two step stress relaxation history in which the material, being at rest for all times $\tau < -t_e$, at time $\tau = -t_e$ is subjected to a step in shear strain γ_1 , and then at $\tau = 0$ is subjected to a second step $\gamma_2 = \gamma_1 + \Delta\gamma$, we have

$$\gamma(\tau) = 0 \quad \text{for } -\infty < \tau \leq -t_e$$

$$\gamma(\tau) = \gamma_1 \quad \text{for } -t_e < \tau \leq 0$$

$$\gamma(\tau) = \gamma(t) = \gamma_2 \quad \text{for } 0 < \tau \leq t$$

and the BKZ theory gives the shear stress $\sigma(t)$ as (10, 11):

$$\sigma(t) = K(\gamma_1 + \Delta\gamma, t + t_e) + K(\Delta\gamma, t) - K(\Delta\gamma, t + t_e) \quad (1)$$

where $K(\gamma, t)$ is the single step stress relaxation response.

In this paper we are interested in histories for which $\Delta\gamma$ is much smaller than γ_1 , i.e., $\Delta\gamma \leq 0.1 \times \gamma_1$.

Then the incremental modulus is (11):

$$\Delta G(t, t_e) = \Delta \sigma(t) / \Delta \gamma \quad (2)$$

$$= \phi'(\gamma_1, t + t_e) + G(t) - G(t + t_e)$$

where $\Delta \sigma(t) = \sigma(\gamma_1 + \Delta\gamma, t) - \sigma(\gamma_1, t + t_e)$ and $G(t) = \lim_{\Delta\gamma \rightarrow 0} \frac{K(\Delta\gamma, t)}{\Delta\gamma}$ is the small strain (linear) relaxation modulus and $\phi'(\gamma, t + t_e) = dK(\gamma, t + t_e)/d\gamma$ is the instantaneous slope of the isochronal stress-strain curve at time $t + t_e$ and strain γ . (Similar equations apply for torsional histories (10) where now γ is the maximum strain on the cylinder and G is the apparent torsional modulus, etc.).

Examination of Eq 2 immediately tells us several things. First, if one is in the linear viscoelastic range, then since $\phi' = G$ the incremental modulus (response) is simply equal to $G(t)$ as if no prestrain had been applied. Second, as $t_e \rightarrow \infty$, $\phi'(\gamma_1, t + t_e) = G(t + t_e) = 0$ for all levels of deformation and again the response is that $\Delta G(t, t_e) = G(t)$, i.e., the linear response as if no prestrain had been applied. Third, in the non-linear range, if no strain hardening occurs $\phi'(\gamma_1, t + t_e) \leq G(t + t_e)$ and, therefore, $\Delta G(t, t_e) \leq G(t)$. Thus, the incremental modulus at short times, t_e , is smaller than the small strain (linear) modulus and as the time, t_e , increases $\Delta G(t, t_e)$ approaches $G(t)$. This is one of the major features of the incremental response described in the introduction. Closer examination of Eq 2 shows that as the level of deformation increases, the incremental modulus decreases when one has a monotonically decreasing slope for the isochronal stress strain behavior. Finally, since for a given time, t , after imposition of the small strain, $G(t)$ is a constant while $\phi'(\gamma_1, t + t_e)$ and $G(t + t_e)$ vary, the shape of any "incremental relaxation spectrum" can be expected to vary as well.

EXPERIMENTAL

The data in this paper were obtained on a 16 percent solution of polyisobutylene (Vistanex L-200, Enjay Chemical Company¹) in a white mineral oil (Primol 355) or on a commercial grade PMMA used in previous studies (12), but now seven years older. Single step and multiple step stress relaxation experiments were carried out at $23.5 \pm 0.5^\circ\text{C}$ in laboratory air. The PIB was studied using a cone and plate geometry in a Rheometrics Mechanical Spectrometer* (RMS) to which a two function variable voltage external power supply had been added. The cone angle was 0.04 radians, the plate diameter was

72 mm. Torque response was recorded continuously on a chart recorder. The PMMA experiments were carried out using a tension-torsion servo-hydraulic system interfaced with a mini-computer as described previously (12).

The experiments to study the incremental response to a small deformation superposed on a large one were carried out in a manner similar to those reported by others (4, 5, 11, 13) and with the format proposed by Struik (14) for physical aging after a quench (see Fig. 1). The large deformation was applied at time $t_e = 0$. Each small incremental strain was applied for a total time of about $0.1 t_e$, so that errors introduced in extrapolating the baseline relaxation for $\sigma(\gamma_1, t + t_e)$ would be small. The incremental strains were applied at time intervals that approximately doubled with each test. Thus, the minimum time interval between the end of the next was $9 t_1$, where t_1 is the duration of application of the previous incremental strain. In this way, each small deformation step could be treated as if the prior step had not been performed.

RESULTS

Polyisobutylene (PIB)

Figure 2 depicts the single step stress relaxation data for the PIB solution as isochronal plots of $\log \sigma$ versus $\log \gamma$. From these data one obtains the values required in Eq 2 to calculate $\Delta G(t, t_e)$ at different strain levels, γ , and times, t and $t + t_e$.

Figures 3 and 4, are plots of the incremental modulus $\Delta G(t)$ versus the time, t_e , after imposition of the large deformation γ_1 , for values of γ_1 of 2.700 and 9.352. Also shown are the predictions from equation (2). At the lower values of deformation the agreement between the experimental data and the predictions are within the experimental error. However, at $\gamma_1 =$

Fig. 1. Schematic of strain history and stress response used in determining the incremental modulus $\Delta G(t) = \Delta \sigma(t) / \Delta \gamma$.

* Certain commercial materials and equipment are identified in this article to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards or that the materials and equipment identified are necessarily the best available for the purpose.

Fig. 2. Single step stress relaxation isochrones for a 16 percent polyisobutylene (PIB L-200) solution in Primol 355 at $T = 23.5^\circ\text{C}$.

Fig. 3. Incremental modulus, $\Delta G(t)$ versus time, t_e , after imposition of large deformation, γ_1 . $\gamma_1 = 2.700$; $\Delta\gamma = 0.265$. Solid lines: BKZ predictions; Points with dashed lines: Experimental Results. 16 percent PIB L-200 in Primol 355 at 23.5°C .

9.352 experimental values of ΔG are 10 to 15 percent lower than those predicted from Eq 2 at small values of t_e . The differences decrease as t_e increases and the values of $\Delta G(t)$ approach the limiting values, i.e., the small strain modulus $G(t)$.

Figure 5 shows the effect of the magnitude of the deformation γ_1 , on $\Delta G(t)$ as a function of time, t_e , after the imposition of the large deformation for the 0.5 second isochrone of $\Delta G(t)$. As can be seen $\Delta G(0.5)$ decreases with increasing γ_1 and increases with increasing t_e . This is

Fig. 4. Incremental modulus $\Delta G(t)$ versus time, t_e , after imposition of large deformation, γ_1 . $\gamma_1 = 9.352$; $\Delta\gamma = 0.455$. Solid lines: BKZ predictions; Points with dashed lines: Experimental Results. 16 percent PIB solution in Primol 355 at 23.5°C .

Fig. 5. 0.5 second isochrone for the incremental modulus, $\Delta G(0.5)$ versus time, t_e , after imposition of large deformation, γ_1 , for different values of γ_1 , as indicated. 16 percent PIB L-200 in Primol 355 at 23.5°C .

one of the major effects of deformation on incremental modulus of glasses described in the introduction.

Figure 6 shows the incremental relaxation modulus versus time on log-log scales at different values of t_e for $\gamma_1 = 5.064$. Also shown for comparison is the small strain modulus, $G(t)$ ($t_e = \infty$). It is readily noted that the apparent relaxation behavior for the incremental modulus is different than that of the small strain modulus. A description of such behavior has been given by Yee, *et al.* using the Williams-Watts function to describe the data for small incremental strains superposed on large strains. The Williams-Watts relaxation function is given by

$$G(t) = G_0 e^{-(t/\tau)^\beta} \quad (3)$$

where β describes the width of the relaxation spectrum and τ is a relaxation time. In the instance of Yee, *et al.* (4) for polycarbonate, it was found that τ for $\Delta G(t)$ decreases relative to that for $G(t)$, and that β increases indicating that the spectrum is narrowing. Table 1 presents values used to fit the apparent Williams-Watts spectrum associated with $\Delta G(t)$ for the data presented in Fig. 6.

The results presented in Table 1 show that the apparent incremental spectra for the PIB solution shift to shorter times and narrow with respect to the spectrum associated with the linear modulus.

Poly(methylmethacrylate (PMMA))

Figure 7 depicts experimental and predicted responses for $\Delta G(t)$ for PMMA with $\gamma_1 = 0.05$ and $\Delta\gamma = 0.005$. There are several things to be noted from this plot. First, the experimental incremental response shows the typical behavior relative to the linear viscoelastic response, i.e., it is smaller than $G(t)$, shifted towards shorter times, and increases with increasing t_e . Also we notice immediately that the incremental response predicted by the BKZ theory can be described in the same way, except that the BKZ predictions are much smaller than the experimentally observed response.

Fig. 6. Incremental relaxation modulus, $\Delta G(t)$ versus time, t , for different values of time, t_e , after imposition of the large deformation, γ_1 . $t_e = \infty$ refers to small strain modulus of unperturbed material. $\gamma_1 = 5.064$, $\Delta\gamma = 0.266$. 16 percent PIB L-200 in Primol 355 at 23.5°C.

Table 1. Williams-Watts* Parameters for the Incremental Modulus at Increasing "Aging" Times, t_e , After Imposition of the Large Deformation, γ_1 , for a 16 percent Polyisobutylene Solution in Primol 355.

γ_1	$\Delta\gamma$	t_e/s	τ/s	β
0	0.244	—	0.149	0.208
5.064	0.266	15	0.060	0.259
		30	0.080	0.252
		60	0.091	0.237
		120	0.095	0.224
		240	0.110	0.210
		480	0.138	0.216

* $\Delta G(t) = G_0 e - (t/\tau)^\beta$, where $G_0 = 827$ Pa.

Fig. 7. Incremental relaxation modulus, $\Delta G(t)$ versus time, t , for different values of time, t_e , after imposition of the large deformation, γ_1 . Comparison of linear response, $G(t)$ with the experimental results (points) and the BKZ predictions. $\gamma_1 = 0.05$, $\Delta\gamma = 0.0050$. PMMA at 24°C.

The point of interest here is that the material incremental response relative to the BKZ response is the opposite of the response relative to a linear viscoelastic response. This leads to ambiguity in assigning molecular or structural interpretations to the incremental response.

CONCLUSIONS

Superposition of small strains on large strains can be studied in terms of an incremental modulus, $\Delta G(t)$, which is observed to differ from the small strain modulus, $G(t)$, determined from experiments at zero prestrain. It is shown that the primary effects of the prestrain, which are observed in polymer glasses, are also seen in a concentrated polymer solution (16 percent PIB in Primol 355), i.e., (1) the incremental modulus at a given time, t_e , after superposition of the large strain both decreases with increasing deformation and increases with increasing t_e and, (2) the apparent incremental relaxation spectrum shifts to shorter times and narrows relative to that of the spectrum representing the small strain relaxation response. We have shown that these features of the incremental (superposed) response are described by the BKZ theory of an elastic fluid to within 15 percent for all deformation histories studied.

On the other hand, the incremental response of the PMMA glass is not well described by the nonlinear viscoelasticity theory, but interpretation in terms of molecular or structural behavior is inverted if one uses the BKZ theory as the point of departure rather than the linear viscoelasticity theory. Interestingly, the material response for the polymer glass is less nonlinear than the BKZ fluid theory would predict.

These results lead us to conclude that, while experiments using small deformations superimposed on large ones are interesting, simple analysis of the incremental response as a linear viscoelastic probe of molecular or state behavior can be ambiguous, and that the experiments

must be, at a minimum, analyzed within the context of an appropriate nonlinear model. Preferably any conclusions should be supported by the more direct, and perhaps less ambiguous, measures of polymer molecular or state quantities, such as small molecule permeability (15) or volume (16) measurements on deformed samples, etc.

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