Slipping in Stress Relaxation in Shear Estimated by Damping and Stress-Strain Behavior of Polyisobutylene

by

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In this article the slipping of less entangled polyisobutylene (PIB) melts and solutions in shear is investigated by the damping as well as the stress growth behavior. The obtained data are also compared with those of the moderately and highly entangled PIB systems. The concentrated solutions do not show the slipping at the sample-fixture interface probably because the stress level on the stress-strain curves is very low even at large preset strains. The less entangled melts do not show strong damping, although they show a stress peak whose value amounts to the critical stress of the moderately and highly entangled PIB samples. It is suggested that little slipping occurs for the melts of the less entangled PIB due to the existence of the fast stress relaxation processes.

Key words:

Slipping, Damping function, Stress relaxation, Modulus, Polyisobutylene

1 Introduction

Rotational rheometers are now widely used to investigate rheological properties of polymer liquids. For this type of rheometers, slipping at sample-fixture interface sometimes occurs. The slip strongly affects the reliability of the experiments and thus extensive studies have been made by many research groups¹⁻³⁾.

Nonlinear viscoelasticity of polymer liquids is one of the important topics in polymer rheology, and has still been studied intensively⁴⁾. It is well recognized that the slip also strongly affects the nonlinear viscoelasticity. To investigate the nonlinear viscoelasticity the damping function is often employed. The damping function $h(\gamma)$ is defined by using following equation:⁴⁻⁶⁾

$$G(t, \gamma) = G(t)h(\gamma) \quad (1)$$

Here, $G(t, \gamma)$ is called the relaxation modulus and is a function of time t and strain γ , and $G(t)$ is the linear relaxation modulus. Equation (1) holds for polymer liquids at long times⁴⁻⁶⁾. The quantities, $G(t, \gamma)$ and $G(t)$ are determined by the stress relaxation experiments. The Doi-Edwards (DE) theory⁵⁾ gives a prediction of $h(\gamma)$, which well explains the damping behavior of moderately entangled polymers with narrow molecular weight distributions. For highly entangled polymers in shear, however, stronger damping than the DE prediction⁵⁾ has been reported. We have examined the damping behavior of highly entangled high density polyethylene (HDPE) samples, and show that the damping actually becomes stronger in shear but becomes almost identical to the DE prediction in uniaxial elongation^{7,8)}. Similar behavior has been observed for highly entangled

polyisobutylene (PIB) melts^{9,10)}.

For the PIB melts, stress-strain curves were prepared by using the stress and strain data in the strain application process before stress relaxation (SR) in shear, and the curves differing in γ formed an envelope^{9,10)}. According to the experimental procedure by Isono et al¹¹⁾, an adhesive was used to obtain a tight sample-fixture interface, i.e., non-slipping interface, and investigated how the adhesive affected the damping as well as stress-strain behavior. The PIB samples without adhesive showed stronger damping and also had stress-strain envelopes showing the saturation of stress. The stress level for saturation remained almost constant, regardless of the molecular weight. We concluded that the saturation of stress originates from slipping and the stronger damping is also due to slipping^{9,10)}.

The aim of this study is to investigate the damping as well as the stress-strain envelopes for less entangled PIB melts and concentrated solutions, and compare the results of the less entangled PIB with those with moderately and highly entangled PIB melts.

2 Experimental

Two types of PIB, S-15 and S-30, were supplied by BASF, Germany. The sample code, number-average molecular weight (M_n), weight-average molecular weight (M_w) and the ratio M_w / M_n for the PIB samples are summarized in Table 1, where M_n and M_w are transferred from the supplier's datasheet. The quantity n_e in Table 1 represents the average number of entanglements per chain. Here, the molecular weight between entanglements (M_e) for

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Sample	M_n	M_w	M_w/M_n	n_e
S-15	1.5×10^4	7.5×10^4	5.0	2
S-30	4.0×10^4	2.0×10^5	5.0	4

Table 1 Number average molecular weight (M_n), weight average molecular weight (M_w), the ratio of M_w to M_n , and the number of entanglements calculated by $n_e = M_n / M_e$.

PIB melts¹²⁾ was assumed to be 8,900 and n_e was calculated by $n_e = M_n / M_e$. Rheological measurements were made for four samples: two kinds of melt samples and two kinds of concentrated solutions. Decalin (non-volatile solvent) and tetrahydrofuran (THF; volatile solvent) were initially used to prepare the solution samples, but THF was finally removed from the solutions. The final polymer concentration of the solutions was 67 wt% for the S-15 solution and 63 wt% for the S-30 solution. There exists little entanglements in these solutions according to the calculated n_e , but we confirmed that the solution samples show the rubbery plateau. For the dynamic viscoelasticity measurements of the melts disk-shaped specimens were made by compression molding at temperature (T) of 100 °C.

Dynamic viscoelasticity and SR experiments in shear were made by using an ARES rheometer (TA Instruments, USA) with a parallel-plate (8mm in diameter) geometry. Before and after SR measurements, dynamic storage and loss moduli (G' and G'' , respectively) as a function of the angular frequency (ω) were measured at γ of 0.1 and the reproducibility of dynamic viscoelasticity after SR measurements was confirmed for all samples. The SR measurements were carried out in the γ range of 0.1 to 1.5. The temperature for the measurements was chosen to be 50 °C for the melts, and 0 °C for the solutions. On the basis of Eq. (1), $h(\gamma)$ was experimentally determined by using $G(t, \gamma)$ and $G(t)$ in the long time region, where $G(t)$ was assumed to be $G(t, \gamma)$ at $\gamma = 0.1$. It was also confirmed that $G(t)$ thus defined coincides well with $G(t)$ calculated by the following equation¹¹⁾ with dynamic viscoelasticity data.

$$G(t) = [G'(\omega) - 0.4 G''(0.4\omega) + 0.014 G''(10\omega)]_{\omega=1/t} \quad (2)$$

For the SR measurements in ARES, a step-like preset strain is applied to the samples for the relaxation tests. We checked the operation of the ARES and found that the rise time (τ) for the time (t)-dependent strain curve, which can be defined as the time duration from 10% to 90% of the preset strain, is rather short and is independent of preset strain magnitude. In this study the stress (σ) versus γ curves were prepared by using the σ and γ data in the above strain application process.

Fig. 1 (a) $G(t, \gamma)$ curves at various γ for the melt of S-30, (b) $G(t, \gamma)$ curve at $\gamma = 0.1$ and $G(t)$ calculated by Eq. (2) for the melt of S-30.

Fig. 2 $G(t, \gamma)$ curves vertically shifted to $G(t, \gamma)$ curve at $\gamma = 0.1$ for the melt of S-30. The shift factor corresponds to the damping function $h(\gamma)$.

3 Results and discussion

Figure 1(a) shows the SR curves of the S-30 melt at 50 °C. The curves slightly move downwards with increasing γ but the shape of the curves remains unchanged. In Fig. 1(b) the SR curve at $\gamma = 0.1$ and the linear relaxation modulus calculated by Eq. (2) with G' and G'' before stress relaxation measurement are shown for the S-30 melt. Although the calculated curve is rather short in length, the relaxation curve at $\gamma = 0.1$ appears to coincide well with the calculated one. Because the above coincidence was observed for the other

Fig. 3 Damping function $h(\gamma)$ for PIB. Data on PIB-1, PIB-2 and PIB-3 are replotted for comparison. Solid curve represents the prediction by the DE theory calculated with the independent alignment approximation (IAA).

melt and solution samples, the relaxation curve at $\gamma = 0.1$ was regarded as the curve of linear relaxation modulus for all samples. The damping function $h(\gamma)$ for the S-30 melt was obtained from the vertical shift factor between the SR curves at $\gamma > 0.1$ and at $\gamma = 0.1$. Figure 2 summarizes all shifted curves for the S-30 melt, as an example. A good superposition appears for all curves. The similar results are obtained for the other PIB samples.

Figure 3 shows $h(\gamma)$ of all PIB samples examined in this study. The figure also contains the curves for the moderately entangled PIB ($n_e = 22$ for PIB-1) and highly entangled PIB ($n_e = 67$ for PIB-2 and $n_e = 350$ for PIB-3) obtained in the previous study^{9,10}, and the theoretical prediction by the DE theory⁵ for the readers' convenience. All data points in the figure were obtained in the parallel-plate geometry which is expected to give weaker γ -dependence of h than the cone-plate geometry¹³. The "without-adhesive" samples of PIB-2 and PIB-3, which had no "adhered" interface, show the steeper decrease of $h(\gamma)$ than the DE prediction, and this strong damping was attributed to the slipping at the sample-fixture interface. However, the PIB-2 and PIB-3 with an adhesive (i.e., PIB-2 and PIB-3 pasted to metal plates with an adhesive) do not show the steeper change, although the data points at large strains are quite limited for PIB-3 due to the overloading of the rheometer. Thus, how strong the damping is becomes a measure of the possibility that the slip occurs at the interface. The PIB samples examined in this study, which are all less entangled, are not so strong in damping and are almost identical to or even weaker than the DE prediction. This might be basically due to the small number of entanglements and the broader molecular weight distribution, but also suggests that no large scale of slip occurs at the interface for the melts and solutions of S-30 and S-15.

In Fig. 4 rise curves of γ and σ are shown for the S-30

Fig. 4 Rise curves of γ and σ for the stress relaxation measurements for S-30. (a) Preset strain is 0.1. (b) Preset strain is 0.7. (c) Preset strain is 1.5.

melt. The value of γ in each panel means the preset strain at which the stress relaxation measurement is performed and thus corresponds to the final constant τ value on the rise curve. As can be seen from the figure, τ of the t vs γ curve appears independently of the preset values, and is lying around 50 ms for the three preset values. Concerning the σ curves, not only a fast rise in response to the rise of γ but also a clear decay are observed at all γ examined. Figure 5 shows the similar plots for the S-15 melt. A marked decay of stress is observed in the t -domain of 0.05 to 0.1 s for all γ examined in contrast to the highly entangled PIB without adhesive which shows a large decay of σ at high strains but little decay appears at small strains⁹. This fast decay for the S-15 melt originates from the lower molecular weight of the sample.

Figure 6 shows the σ - γ curves obtained in the strain application process before the SR measurements. For the

Fig. 5 Rise curves of γ and σ for the stress relaxation measurements for S-15. (a) Preset strain is 0.1. (b) Preset strain is 0.7. (c) Preset strain is 1.5.

Fig. 6 σ vs γ curves in the course of strain application for the stress relaxation experiments. Data on PIB-1, PIB-2 and PIB-3 are again plotted for comparison. For readers' convenience, this figure also contains the data for

moderately and highly entangled PIB samples^{9,10}) other than those obtained in this study. The data points included in the figure are those on each of the rise and decay curve at $t \leq 0.01 \text{ s}$. Each curve corresponds to an envelope of the curves at different preset strains. The σ - γ curves of "without adhesive" samples of PIB- i ($i = 1, 2, 3$) never exceed the stress level of about $2 \times 10^5 \text{ Pa}$. This stress level was considered to be the critical stress for slipping^{9,10}). In addition, leveling-off or maximum of σ occurs at relatively small γ , ranging from 0.6 to 0.7. Concerning the "with-adhesive" samples, PIB-2 clearly shows a continuous increase of σ even beyond the critical value, although the behavior of PIB-3 remains unclear because the rheometer turned to overload at large preset strains.

The solutions of S-30 and S-15 run almost on the same trace with several peaks. The emergence of these peaks is because the fast relaxation exists. For the envelopes, the maximum of σ lies around $7 \times 10^4 \text{ Pa}$. This maximum value is much smaller than the critical value for the melts, although the above critical value may be basically applicable only to melts. The envelopes for the melts of S-30 and S-15 become almost identical and also have several peaks. It should be noticed that clear peaks on the envelopes are due to the fast relaxation and are observed only for the melts and the solutions of S-15 and S-30. The maximum value of σ for the envelopes becomes almost identical to the critical value of slipping for melts. Although this appears to indicate that the slipping occurs for the melts, we think little slipping existing even at high strains. The slipping appears as a fast decay of stress at large strains on the rise and decay curve^{9,10}) and the similar behavior is clearly observed for the S-15 melt (Fig.5). However, the fast decay occurs even at small strains for the S-15 melt. In addition, no large difference exists in the degree of relative stress reduction between large and small strains. It should be remembered again that no strong damping was observed for the melts of S-30 and S-15 as shown in Fig. 3. These suggest that for the melts of S-30 and S-15 little slipping occurs even around the threshold: At least, the stress reduction by slipping is suppressed by the fast stress relaxation due to low molecular weights.

4 Conclusion

Slipping of less entangled PIB melts and solutions in shear was investigated by the damping as well as stress-strain behavior. The results obtained in this study were also compared with those of the moderately and highly entangled PIB melts. The concentrated solutions did not show the slipping at the sample-fixture interface probably because the stress level on the σ - γ curves is very low even at large preset strains. The less entangled melts showed a peak on the σ - γ curves whose value amounts to the critical stress for the

moderately and highly entangled PIB, but did not show the strong damping. These suggest that little slipping occurred for melts of S-30 and S-15, probably due to the existence of the fast relaxation processes.

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