Rod-Climbing in a Particle-Suspended Polymeric Liquid

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ABSTRACT: The rod-climbing experiment and its relationship to the first normal stress difference of kaolinite particle-suspended polyisobutylene (PIB)/polybutene (PB) systems possessing Boger fluid characteristics (no shear-thinning and highly elastic) were investigated. The rod-climbing constants of the kaolinite/PIB/PB system obtained from the second-order fluid model increased with particle concentration and PIB molecular weight, indicating that the elasticity of the PIB/PB increases as kaolinite particle concentration increases. The first normal stress difference obtained from the rod-climbing constant is also correlated with that measured value using RMS-800, a mechanical spectrometer, for the particle-suspended PIB/PB system. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 572–575, 2000

Key words: rod-climbing; polyisobutylene; second-order fluid; first normal stress difference; Boger fluid

INTRODUCTION

It is well known that polymeric and viscoelastic liquids will climb a rotating rod, and this phenomenon is known to be associated with flow-induced normal stresses that do not exist in Newtonian fluids. In the rod-climbing experiment, a polymeric liquid is sheared, inducing normal stresses perpendicular to the planes of shear. The free surface of the liquid is then deformed in the direction of the rod axis, and the fluid climbs the rod. Hence, rod-climbing is a solely viscoelastic phenomenon. Since Weissenberg[1] explained this phenomenon via the normal stress concept, many researchers have scrutinized this rod-climbing phenomenon both theoretically and experimentally.[2–5] By assuming that the velocity is independent of the coordinate along the axis of the cylinder, the free surface remains relatively horizontal, and the two material functions in the Reiner-Rivlin theory are constants, Serrin[2] achieved Weissenberg's result. In addition, Coleman et al.[3] computed the value of the normal stress from Couette flow in an infinite cylinder for a rheologically simple fluid. The overthrust of the normal stress on the fictitious plane of constant pressure is the basis for the approximate estimation of the direction of climbing. However, they did not consider gravity and surface tension.

Despite the difficulty in calculating the free surface profile from a given rheological equation of state, Joseph and Fosdick[6] developed a quantitative rod-climbing theory for low cylinder speeds by determining the shape of the free surface for a rheologically simple fluid resulting from a perturbation from a state of rest. Joseph and coworkers[7,8] further considered surface effects to gain agreement with measured shapes.

Furthermore, from this precise rod-climbing analysis, some important rheological parameters of a viscoelastic liquid can be obtained,[9,10] including the rod-climbing constant β related to the

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elasticity of polymeric liquids. The shape of the free surface, derived from the perturbation method, is found to be expressed in the following form:

$$h(r, \omega) = h_0(r) + h_2(r)\omega^2 + O(\omega^4), \qquad (1)$$

where ω is the angular frequency of the rotating rod (rev/s), $h_0(r)$ is the static rod climb, and the higher order term $O(\omega^4)$ is neglected. When a rod of radius a is rotated slowly at an angular speed ω, the resulting velocity field satisfies the condition in which the fluid response is described asymptotically by a second-order fluid. Adopting the two-parameter expansion procedure into the governing equation for the height rise function $h_2(r)$, Joseph et al.[7] obtained a very accurate approximate solution. They showed that, for slow rotation, the fluid level at the rod surface rises to a height:

$$h \cong h_0(a) + \frac{4\pi^2 a}{\sigma\sqrt{S}}\left[\frac{4\beta}{4+\kappa} - \frac{\rho a^2}{2+\kappa}\right]\frac{\omega^2}{2} \qquad (2)$$

where $\kappa = a(S)^{1/2}$, $S = \rho g/\sigma$, σ is the surface tension, ρ is the density of the liquid, and g is the gravitational acceleration. From eq. (2) and the observation that the value of h varies linearly with ω^2 in the rod-climbing experiment, β can be calculated with the known values of σ and $(dh/d\omega^2)_{\omega\to 0}$ as follows:

$$\beta = \frac{4+\kappa}{4}\left[\frac{\sigma(S)^{1/2}}{2a\pi^2}\left(\frac{dh}{d\omega^2}\right)_{\omega\to 0} + \frac{\rho a^2}{2+\kappa}\right] \qquad (3)$$

In addition, using the second-order fluid model, it has been found that experimental rod-climbing results correlate closely with the first (Ψ_1) and second (Ψ_2) normal stress difference coefficients.[9] Note that various second-order fluids possessing both a constant high viscosity and high elasticity at room temperature have been studied. However, not many studies have been performed on particles suspended Boger fluid systems. Choi et al.[11] investigated the lateral migration of a rigid sphere in torsional flow of a polyisobutylene (PIB)/polybutene (PB) solution and correlated the critical shear rate with the relaxation time of the polymer solution. Kaloni and Stastna[12] theoretically studied the rheological behavior of a dilute suspension of rigid spherical particles in a second-order fluid. Recently, Choi et al.[13] measured the rheological properties of a particle-suspended Boger fluid and found that, in contrast to polymer melts with nearly spherical particles, the elasticity of this system increases with increased particle concentration.

EXPERIMENTAL

The polymer solutions used in this study were made of high molecular weight PIBs (Vistanex MM grades L-100 and L-140, Exxon Chemicals), low molecular weight PBs (Daelim Chemical, Korea), and kaolinite ($[Al_2Si_2O_5(OH)_4]_2$), as the suspended particle, which is the most common clay mineral having a two-dimensional silicate structure (4 μm mean particle size and 2.6 specific gravity). A small amount of PIB was added to the PB with reagent toluene, which is a volatile and good solvent for both PIB and PB as a cosolvent. Because it is difficult to dissolve PIB in PB directly without a cosolvent despite the fact that PIB is compatible with PB, small pieces of PIB were dissolved in toluene by stirring in a sealed glass flask at room temperature for at least 24 h. The solution of PIB in toluene was then mixed with PB in a 1-L beaker and stirred occasionally for at least 2 days. Once kaolinite particles were suspended in these PIB solutions, a low rotation speed was used to minimize degradation. The kaolinite was dried in an oven and sieved before use. Finally, the toluene was removed using a rotary evaporator. Non-shear–thinning, highly elastic particle-suspended polymer solutions consisting of PIB and PB were obtained.[13]

The essential part of the rod-climbing apparatus is a rod with a circular cross-section, which is free to rotate about a vertical axis immersed in a large circular glass vessel of fluid. These rods can be rotated up to 200 rpm. A digital tachometer (Hanyoung SM3) with an accuracy of ± 0.5 rpm was used to measure the rotation speed of the rod. The temperature of the fluid was maintained at 30.0 ± 0.2°C in a water bath. The climbing height of the fluid was determined with the aid of a cathetometer (Gaertner Science Co., Chicago, IL), with a reproducibility of 0.001 cm.

Note that, as mentioned by Beavers and Joseph,[8] both the vessel and rod were coated with Scotch Gard to establish a 90° contact angle between the fluid and the rod and also between the fluid and the vessel [therefore, $h_0(a) \cong 0$ in eqs. (1) or (2)].

RESULTS AND DISCUSSION

Rheological characteristics have been investigated for various kinds of Boger fluids such as polyacrylamide in mixtures of glycerine and water,[14] and PIB in PB and in kerosene,[15] polystrene-based Boger fluids[16] and PIB in PB.[17,18] These Boger fluids are known to be well described by the following second-order fluid model:

$$\underset{\approx}{\tau} = \alpha_0 \underset{\approx}{\dot{\gamma}} + \alpha_1 \frac{\mathcal{D}\underset{\approx}{\dot{\gamma}}}{\mathcal{D}t} + \alpha_2 \{\underset{\approx}{\dot{\gamma}} \cdot \underset{\approx}{\dot{\gamma}}\}, \tag{4}$$

where $\mathcal{D}/\mathcal{D}t$ is the Jaumann or corrotational derivative. α_i (i = 0,1,2) are coefficient characterizing material properties,[19] which correspond to those from the retarded-motion expansion.[9,19] Furthermore, the constants α_1 and α_2 are related to the zero shear rate values of N_1 and N_2 by the following equations[9,19]:

$$N_1 = -2\alpha_1\dot{\gamma}^2 \equiv \Psi_1\dot{\gamma}^2$$

$$N_2 = (2\alpha_1 + \alpha_2)\dot{\gamma}^2 \equiv \Psi_2\dot{\gamma}^2 \tag{5}$$

where $\dot{\gamma}$ is the shear rate, $\alpha_1 = -\Psi_1/2$ and $\alpha_2 = \Psi_1 + \Psi_2$. Therefore, from these relations, β is expressed as follows[20]:

$$\beta = 3\alpha_1 + 2\alpha_2 = \Psi_1/2 + 2\Psi_2 \tag{6}$$

Figure 1 gives a plot of climbing height vs the square of the rotational speed for different kaolinite concentrations (ϕ = 0, 0.03, 0.06, and 0.10) in 0.2% w/w PIB L-100 in PB. The rod-climbing height increases with the suspended particle concentration, indicating that the elasticity of the PIB/PB increases with the addition of kaolinite particles; however, the addition of inert solid particles to polymer solutions, in general, decreases the melt elasticity. This phenomenon can be explained by the fact that the filler itself increases the rigidity of the polymer chain to restrain the motion. The opposite behavior observed in this study can be explained by the fact that the suspended particle acts like a solvent viscosity enhancer for Ψ_1 and Ψ_2,[17] and also that PB takes on the role of a "shielding" material.[13]

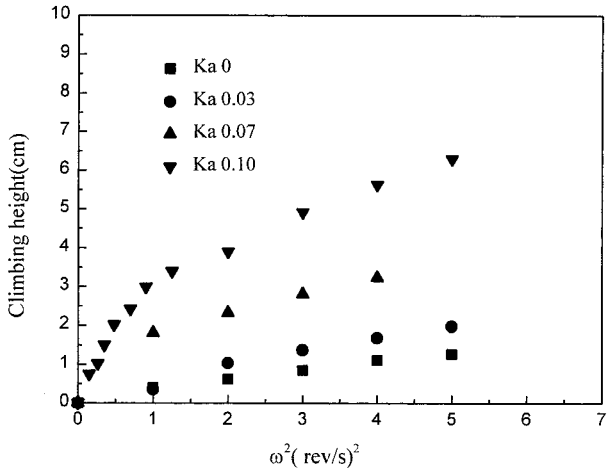

Figure 1 Effect of kaolinite particle concentration (PIB MM L-100, 0.2% w/w in PB) on the rod-climbing height using a 1.0-cm diameter rod at 30°C.

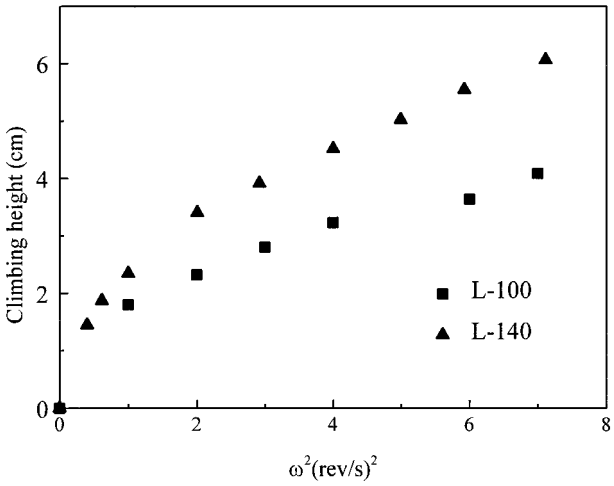

Figure 2 Effect of PIB molecular weight for (PIB MM L-100 and L-140 0.2% w/w in PB-kaolinite 0.07 v/v) on the rod-climbing height using a 1.0-cm diameter at 30°C.

The rod-climbing experiment was also performed for different PIB molecular weights, MM L-100 and 140. The rod-climbing height increases, as the polymer molecular weight increases as shown in Figure 2. The relationship between β and polymer molecular weight was obtained from the theory developed by Brunn,[21] who adopted Brinkman's analysis for the dumbbell (polymer) model in a second-order fluid as follows[17]:

$$\beta = \frac{M\eta_S^2[\eta]^2 c(1 + 0.75c[\eta])}{RT}. \tag{7}$$

Equation (7) indicates that β is proportional to the molecular weight of the polymer, which cor-

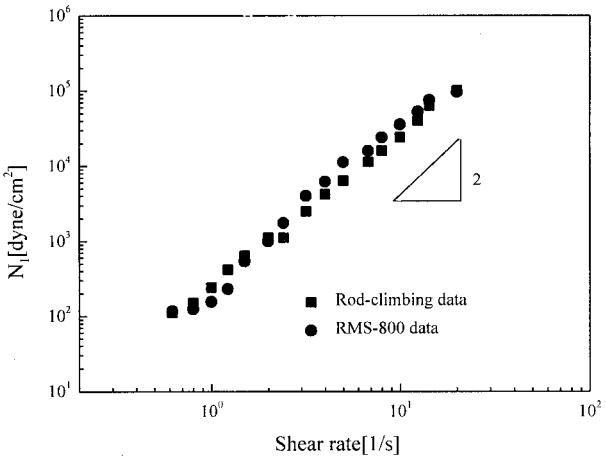

Figure 3 Comparison of first normal stress difference (N_1) of RMS-800 data with that of the rod-climbing for PIB MM L-140 0.2% w/w in PB-kaolinite 0.07 v/v at 30°C.

responds to the fact that the elasticity of polymer solution increases with PIB molecular weight.

The N_1 values computed from the rod-climbing experiments were found to agree well with those measured with the conventional rotational rheometer for either heavy crude oils[19] or PIB/PB.[17] To apply this concept to the particle-suspended Boger fluid system, the N_1 of the system was measured with a mechanical spectrometer (RMS-800) at 30°C and then compared with that from the rod-climbing experiment as shown in Figure 3. The results show typical Boger fluid characteristics for N_1 by exhibiting a quadratic dependence on $\dot{\gamma}$ over a broad range of $\dot{\gamma}$ both from the rod-climbing experiment and from the rheometer. Note that β is related to the rheological properties of the fluid by: $\beta = 3\alpha_1 + 2\alpha_2$.

For many polymeric systems, it is well known that Ψ_2 is negative and has an absolute value much smaller than that of Ψ_1. For simplicity, the approximation $\Psi_2/\Psi_1 \cong -0.1$[20] has been made, and eq. (6) becomes

$$\beta \cong 0.3\Psi_1. \tag{8}$$

Thus, from the measured values of the rod-climbing height, the value of β is determined, and Ψ_1 can then be obtained from eq. (8). First normal stress difference coefficients for low shear rate can be obtained as follows

$$\lim_{\dot{\gamma}\to 0} \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} = \Psi_1 \cong \frac{10}{3}\beta. \tag{9}$$

In conclusion, from the rod-climbing experiment the climbing constant and first normal stress difference of particle-suspended PIB solutions are investigated, and the climbing constants are found to increase with PIB molecular weight and kaolinite concentration. Among the rheological properties, N_1 values computed from the climbing constant were compared with those measured using the RMS-800, and it was found that they are well correlated with each other in the low a shear rate region.

REFERENCES

1. Weissenberg, K. Nature 1947, 159, 310.
2. Serrin, J. Z. Angew Math Mech 1959, 39, 295.
3. Coleman, B. D.; Markovtz, H.; Noll, W. Viscometric Flows of non-Newtonian Fluids: Springer Tracts in Natural Philosophy; Springer-Verlag: Berlin, 1966; Vol. 5.
4. Giesekus, H. Rheol Acta 1961, 1, 403.
5. Kaye, A. Rheol Acta 1973, 12, 206.
6. Joseph, D. D.; Fosdick, R. L. Arch Rat Mech Anal 1973, 49, 321.
7. Joseph, D. D.; Beavers, G. S.; Fosdick, R. L. Arch Rat Mech Anal 1973, 49, 381.
8. Beavers, G. S.; Joseph, D. D. J Fluid Mech 1975, 69, 475.
9. Joseph, D. D.; Beavers, G. S.; Cers, A.; Dewald, C.; Hoger, A.; Than, P. T. J Rheol 1984, 28, 325.
10. Liao, T. Y.; Hu, H. H.; Joseph, D. D. J Non-Newtonian Fluid Mech 1994, 51, 111.
11. Choi, H. J.; Prieve, D. C.; Jhon, M. S. J Rheol 1987, 31, 317.
12. Kaloni, P. N.; Stastna, V. Polym Eng Sci 1983, 23, 465.
13. Choi, H. J.; Vinay, S. J., III; Jhon, M. S. Polymer 1999, 40, 2869.
14. Choplin, L.; Carreau, P. J.; Ait Kadi, A. Polym Eng Sci 1983, 23, 459.
15. Binnington, R. J.; Boger, D. V. Polym Eng Sci 1986, 26, 133.
16. Solomon, M. J.; Muller, S. J. J Rheol 1996, 40, 837.
17. Choi, H. J.; Shon, H. S.; Lee, H. J.; Jhon, M. S. Int J Polym Analysis Char 1996, 3, 75.
18. Quinzani, L. M.; McKinley, D. H.; Brown, R. A.; Amstrong, R. C. J Rheol 1990, 34, 705.
19. Bird, R. B.; Armstrong, R. C.; Hassager, O. Dynamics of Polymeric Liquids: Fluid Mechanics; Wiley: New York, 1987; Vol. 1.
20. Nunez, G. A.; Ribero, G. S.; Arney, M. S.; Feng, J.; Joseph, D. D. J Rheol 1994, 38, 1251.
21. Brunn, P. J Rheol 1980, 24, 263.