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Rheological properties of particle suspensions in a polymeric liquid

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Abstract

The rheological characteristics of a particle-suspended Boger fluid are reported. Non-shear thinning, highly elastic polymer solutions were obtained from a mixture of high-molecular-weight polyisobutylene (PIB) and low-molecular-weight polybutene (PB). Kaolinite was chosen as the suspended particles. The shear viscosity and first normal stress difference of the kaolinite-suspended PIB/PB solution exhibit characteristics similar to those of Boger fluids. In contrast to polymer melts with nearly spherical particles, the elasticity of this system increases with the addition of particles, and a qualitative interpretation based on PB (the solvent) as a 'shielding' agent is given. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Boger fluid; Particle suspension; Rheological property

1. Introduction

Since Boger et al. [1,2] reported the remarkable rheological properties (non-shear thinning, highly elastic) of a viscoelastic fluid consisting of a small amount of dissolved polyacrylamide in corn syrup, various Boger fluids (a certain class of polymeric solutions) have been used by many investigators [3–9] to study the effect of elasticity, without shear thinning, on flow fields. Choplin et al. [10] found that a lubricant, Emkarox, and a solution of polyacrylamide in mixtures of glycerine and water were better model fluids for this purpose. Recently, Solomon and Muller [11] have formulated a series of Boger fluids based on monodisperse polystyrenes, varying in polymer solvent quality and molecular weight, which they have systematically characterized. Using solutions of high-molecular-weight, nearly monodisperse, linear polystyrene in oligomeric polystyrene, they studied shear-induced migration of polymers in a cone and plate geometry. They also prepared polystyrene-based Boger fluids in mixed solvents of oligomeric polystyrene with either dioctyl phthalate or tricresyl phosphate and studied transient extensional behavior.

Rheologically, a Boger fluid satisfies the 'second-order fluid model', possessing both high elasticity and a constant, high viscosity at room temperature. The second-order fluid model is a constitutive equation obtained by keeping only the first two Taylor-series terms of the retarded motion expansion [12]. Furthermore, Prilutski et al. [4] described a Boger fluid using a molecular model (Hookean dumbbell dissolved in a Newtonian solvent) which is analogous to the Oldroyd-B model from a continuum viewpoint. Mackay and Boger [13] found that the Oldroyd-B model failed to describe the behavior of these fluids in oscillatory flow, since the solvent possessed a slight amount of elasticity. Furthermore, numerous studies using Boger fluids, such as lateral translational motion of both a single particle and suspended particles [3,14,15], and rod-climbing characteristics, have also been reported [12,16].

Despite these investigations, rheological characterization of particle-suspended Boger fluids has rarely been reported and will be treated in this communication. In our study, the shear viscosity and first normal stress difference of particle-suspended polymer solutions were examined. Note that a mixture of polyisobutylene (PIB) and polybutene (PB) is chosen as the polymer solution because it has been well described by the second-order fluid model [5,12].

2. Experimental

High-molecular-weight PIB (Vistanex, MM grade L-80, $M_v = 9.9 \times 10^5$) [17], obtained from Exxon Chemicals, was prepared in low-molecular-weight PB with the suspended kaolinite (Ka) ($[Al_2Si_2O_5(OH)_4]_2$) particles. The PB (Daelim Chemicals, Korea) is a chemically stable liquid

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with relatively high zero-shear-rate viscosity (104 poise at 30°C), and the Ka is a common clay mineral having a two-dimensional structure, a mean particle size of 4 μm and a specific gravity of 2.6.

Even though PIB is compatible with PB, it is difficult to dissolve PIB in PB without a cosolvent. A low-viscosity solution of PIB in PB was prepared by dissolving the desired amount of PIB into reagent-grade toluene, which is not only volatile but also a good solvent for both PIB and PB. Separately, small pieces of PIB were dissolved in toluene by stirring with a magnetic stirring bar in a sealed glass flask for at least 24 h at room temperature. This solution was then mixed with PB (1 l beaker) and subsequently placed on a magnetic stirring heating plate at 30°C for two days. The Ka was dried in an oven and sieved prior to use. To make the dispersion process easier, we reduced the viscosity of the solution by adding toluene and then dispersed particles in this PB/toluene solution, using a high-speed mixer at 1000 rpm for 1 h.

The PIB/toluene solution was then added to the particle-suspended PB/toluene mixture in the 1 l beaker, being stirred occasionally with a glass rod for at least one week. A low-speed rotation was maintained to minimize the mechanical degradation of the PIB. Finally, the toluene was removed with a rotary evaporator and a vacuum oven. The rheological properties of the Ka particle-suspended PIB/PB solutions were then measured using a mechanical spectrometer (RMS-800) in a cone and plate geometry at 30°C.

3. Results and discussion

Fig. 1 shows the shear viscosity (η) of the particle-suspended PIB/PB solution as a function of shear rate ($\dot{\gamma}$), indicating typical Boger fluid viscosity characteristics without suspended particles (0% Ka). Even though shear-thickening behavior appears in the high shear rate region ($\dot{\gamma} > 2\ \mathrm{s}^{-1}$) for a 10% v/v concentration of Ka particles, the PIB/PB/Ka composites predominantly show time-independent, high and constant values of η. There is experimental evidence that some suspensions exhibit shear-thickening behavior; using an optical technique to measure diffraction patterns, Hoffman [18] observed that there was a change in flow patterns of particles (from an ordered to a disordered array) at the shear rate at which the discontinuity in effective viscosity was actually observed. This appears to indicate that the rheological properties of concentrated suspensions depend on the state of dispersion of the rigid particles suspended in the continuous medium.

Fig. 2 shows the first normal stress difference (N_1) as a function of $\dot{\gamma}$ for PIB/PB solutions with four different Ka particle concentrations. For the solution without Ka (0% Ka), Fig. 2 shows typical Boger fluid characteristics for N_1 by exhibiting a quadratic dependence on $\dot{\gamma}$ over a broad range of $\dot{\gamma}$. By applying the upper convected Maxwell model to characterize the rheological properties of second-order fluids [9,13], N_1 was obtained as $N_1 = 2\eta\lambda\dot{\gamma}^2$. Here, λ is the relaxation time of the PIB/PB/Ka composite system. The Ka-suspended PIB/PB solutions also show second-order behavior, with high elasticity.

In addition, Fig. 2 illustrates that the first normal stress difference increases with particle concentration. However, it has been shown that the plots of first normal stress difference versus shear rate for polymer melts filled with various particles are not enough to show how the addition of inert solid particles to a polymeric system affects the melt elasticity [19]. This is due to the fact that the shear rate (i.e., velocity gradient) may not be continuous at the interface between the

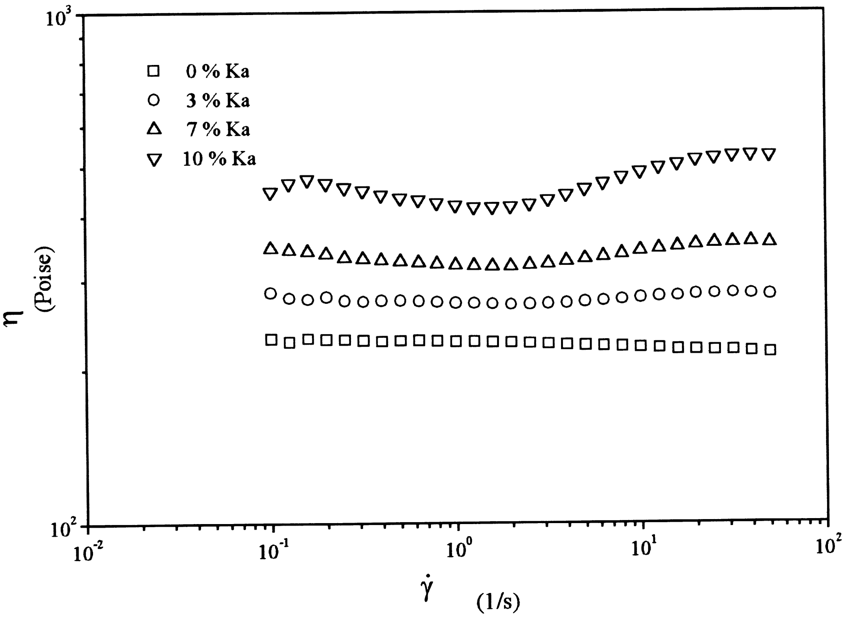

Fig. 1. Viscosity (η) as a function of shear rate ($\dot{\gamma}$) for four different Ka particle concentrations.

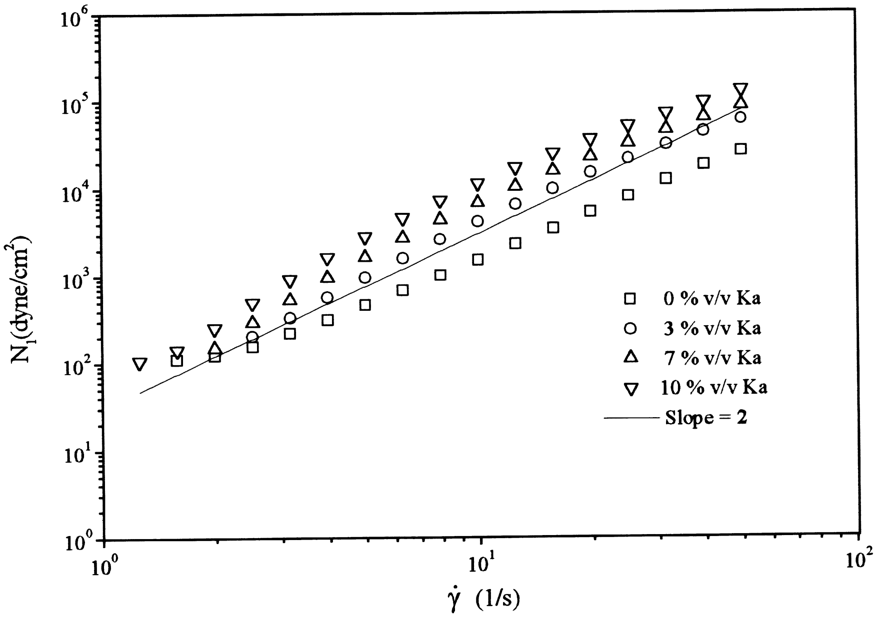

Fig. 2. Log–log plot of N_1 vs shear rate ($\dot{\gamma}$) for four different Ka particle concentrations.

phases, whereas shear stress may be continuous at the interface when no slippage occurs between the phases.

For calcium carbonate filled polypropylene melts at 200°C at various filler concentrations, Tanaka and White [20] found that N_1 increases with filler concentration; however, when N_1 is plotted against shear stress (τ_s), instead of against shear rate, the effect of filler concentration on N_1 is seen to indicate a trend opposite to that of N_1 versus shear rate. It was further seen that the extrudate swell decreases with an increase in filler concentration, supporting the correlation of N_1 with τ_s [21]. The experimental results that polymers with high filler concentrations have smaller N_1 than those with low filler concentrations when N_1 is plotted against τ_s are observed for various other systems such as TiO_2 in resinous or polymer solutions [22], carbon black in polystyrene melts [23] and calcium carbonate in polypropylene [24].

On the other hand, from plots of N_1 versus τ_s for polystyrene melts filled with glass fiber, Czarnecki and White [25] observed that N_1 increases with filler concentration, showing a trend opposite to the one observed when nearly spherical particles such as carbon black and TiO_2 were used

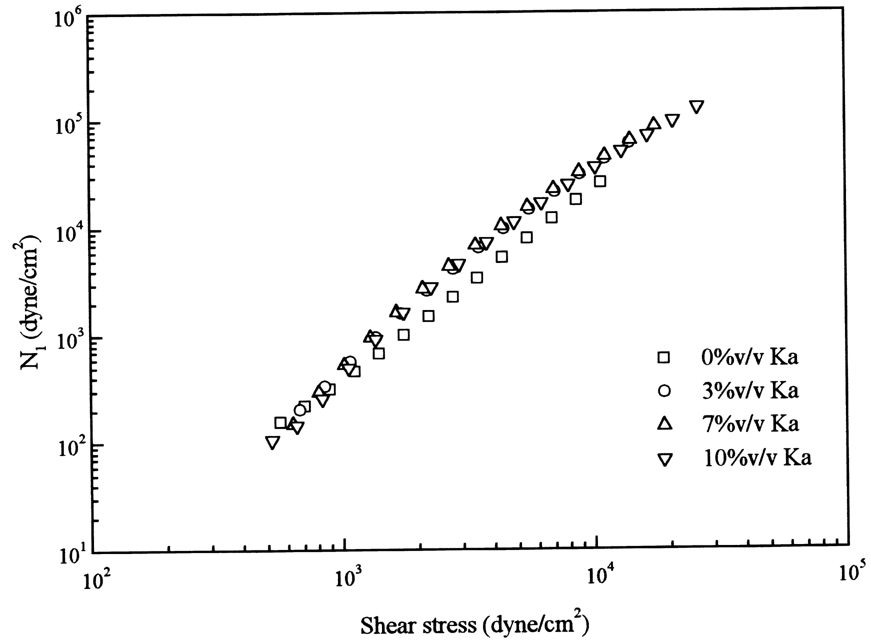

Fig. 3. Log–log plot of N_1 vs shear stress (τ_s) showing a universal correlation between Ka/PIB/PB composites.

as filler. They noted that the normal stresses of melts containing long, flexible particulates depend on the fiber length-to-diameter ratio. The increase in N_1 in the presence of long, flexible particulates should not be a surprise, because even Newtonian liquids can exhibit normal stress effects when glass fibers are suspended in them [26,27].

Fig. 3 shows a plot of N_1 versus shear stress for particle-suspended Boger fluids. N_1 is found to increase with addition of Ka particles in comparison to the solution without Ka (0% Ka). Even though the dependency of both viscosity (or shear stress) and normal stress on $\dot{\gamma}$ changes with the volume fraction of Ka particles, there appears to be a universal correlation between the Ka/PIB/PB composites, as seen in Fig. 3. We see that the three sets of data for the different Ka particle concentrations collapse into one curve. However, whether this indicates a real universal correlation, or whether the particle concentrations in this study are not high enough to see the concentration effect, is under investigation. Nevertheless, in contrast to the fact that the addition of nearly spherical inert solid particles to a polymeric liquid decreases the melt elasticity, and N_1 decreases as the filler concentration increases [19,20,28], we find an increase of N_1 with filler addition for our Ka particle suspension Boger fluid system. Note that even though Ka particles have a two-dimensional structure, they can be treated as nearly spherical compared to glass fiber.

The observation that polymers with high filler concentrations of nearly spherical particles have smaller first normal stress differences than those with low filler concentrations can be attributed to the fact that the filler itself can increase the rigidity of the polymer [19].

We believe that there is a different interaction between particles and polymers as compared to the interaction between the Ka particles and the PIB/PB solution. In polymer melts, polymer chains interact directly with the particles. The mobility of the polymer chains is reduced; thus the rigidity of the polymer increases. The fact that polymers with high filler concentrations of nearly spherical particles have smaller normal stresses than those with low concentrations can be explained by this increase in rigidity. In the particle-suspended PIB/PB solutions, the high-molecular-weight PIB is in a different environment. Here, we must focus on the role of the solvent, PB. Since PB is a polymer and occupies most of the system, it may exclude the approach of particles into PIB chains. Therefore, it is expected that PB takes on the role of a ‘shielding’ (or ‘screening’) material. As a result, the effect of the particles on the rigidity of PIB may not be as important as the increase of the rigidity of the solvent with increased particle concentration.

In conclusion, from this rheological characterization of a PIB/PB/Ka composite solution, we found that particle-suspended Boger fluids also show typical Boger fluid characteristics by exhibiting high elasticity and constant viscosity. Also, in contrast to polymer melts with nearly spherical particles, the elasticity of this system is observed to increase with particle addition. Testing for the universal correlation of rheological properties for this complex fluid system as shown in Fig. 3, using many different particles, is currently under investigation and will be published elsewhere.

Acknowledgements

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References

[1] Boger DV. J Non-Newtonian Fluid Mech 1977/1978;3:87.
[2] Boger DV, Nguyen H. Polym Eng Sci 1978;18:1037.
[3] Boger DV, Binnington R. Trans Soc Rheol 1977;21:515.
[4] Prilutski G, Gupta RK, Sridhar T, Ryan ME. J Non-Newtonian Fluid Mech 1983;12:233.
[5] Karis TE, Prieve DC, Rosen SL. J Rheol 1984;28:381.
[6] Walters K, Rawlinson DM. Rheol Acta 1982;21:547.
[7] Choi HJ, Prieve DC, Jhon MS. J Rheol 1987;31:317.
[8] Quinzani LM, McKinley DH, Brown RA, Armstrong RC. J Rheol 1990;34:705.
[9] Binding DM, Jones DM, Walters K. J Non-Newtonian Fluid Mech 1990;35:121.
[10] Choplin L, Carreau PJ, Ait Kadi A. Polym Eng Sci 1983;23:459.
[11] Solomon MJ, Muller SJ. J Rheol 1996;40:837.
[12] Choi HJ, Shon HS, Lee HJ, Jhon MS. Int J Polym Anal and Char 1996;3:75.
[13] Mackay ME, Boger DV. J Non-Newtonian Fluid Mech 1987;22:235.
[14] Leal LG. Ann Rev Fluid Mech 1980;12:435.
[15] Feng J, Joseph DD. J Fluid Mech 1996;324:199.
[16] Beavers GS, Joseph DD. J Fluid Mech 1975;69:475.
[17] Choi HJ, Jhon MS. Ind Eng Chem Res 1996;35:2993.
[18] Hoffman RL. J Colloid Interface Sci 1974;46:419.
[19] Han CD. Multiphase flow in polymer processing. New York: Academic Press, 1981.
[20] Tanaka H, White JL. Polym Eng Sci 1980;20:949.
[21] Minagawa N, White JL. J Appl Polym Sci 1976;20:501.
[22] Mewis J, de Bleyser R. Rheol Acta 1975;14:721.
[23] Lobe VM, White JL. Polym Eng Sci 1979;19:617.
[24] Han CD. J Appl Polym Sci 1974;18:821.
[25] Czarnecki L, White JL. J Appl Polym Sci 1980;25:1217.
[26] Newab MA, Mason SG. J Phys Chem 1958;62:1248.
[27] Mewis J, Metzner AB. J Fluid Mech 1974;62:593.
[28] Chan Y, White JL, Oyanagi Y. J Rheol 1978;22:507.