입자분산 폴리아이소부틸렌 Boger 용액의 막대상승현상 및 유변학적 특성고찰

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Rod-climbing Phenomenon and Rheological Characterization of Particle suspended Polyisobutylene Boger Solution

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Introduction

Polymeric and viscoelastic liquids climb a rotating rod, and this phenomenon is known to be associated with flow-induced normal stresses that exist in non-Newtonian fluids. In the rod-climbing, a polymeric liquid is sheared, inducing normal stress 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. This well-known phenomenon is usually referred as the 'Weissenberg effect', and the most intensive studies in this field have been carried out by Joseph and his research group (1973, 1977). The mathematical description can be obtained as a series of powers of the angular frequency ω. Beavers and Joseph (1975) showed that polymeric liquids used in their experiments have a second-order range, i.e. a range in which the height of climb is linear in ω^2. In the second-order theory, there is only one viscoelastic parameter, the climbing constant (β). And it was shown that the values of this parameter, and ever its dependence on temperature, could be determined from measurements of the height of climb.

From this study, we systematically confirmed the normal stress effect on polymeric liquids at low shear rate from the height prediction based on the second-order fluid constitutional relationship (Nuñez et al., 1994). The climbing constants, β, of particle suspended polyisobutylene(PIB)/polybutene(PB) solutions possessing Boger fluid characteristics (no shear-thinning and highly elastic) were correlated with the rheological properties measured by rheometers.

Theory

The climbing constant has been derived from the perturbation studies by Kaye (1973), and Joseph and Fosdick (1973). By a perturbation method, the free surface is expressed as follows (Joseph et al., 1973) :

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

where ω is the angular frequency (rev/s) of the rotating rod, and $h_0(r)$ is the static rod climb, and the higher order term $O(\omega^4)$ is neglected. With surface tension, the height rise function is obtained as follows :

$$h(a,\omega) \cong h_o(a) + \frac{4\pi^2 a}{\sigma\sqrt{S}}\left[\frac{4(3\alpha_1+2\alpha_2)}{4+\kappa} - \frac{\rho a^2}{2+\kappa}\right]\frac{\omega^2}{2} \tag{2}$$

where $\kappa=a(S)^{1/2}$, $S=\rho g/\sigma$ and $h_o(a)$ is a static climb. From the observation of h with ω^2, the slope of the line is identified as

$$\frac{dh}{d\omega^2} = \frac{2\pi^2 a}{\sigma\sqrt{S}}\left[\frac{4\beta}{4+\kappa} - \frac{\rho a^2}{2+\kappa}\right] \tag{3}$$

and then, β is calculated with the known values of σ and $(dh/d\omega^2)_{\omega\to 0}$ as follows :

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

β is related to the first and second normal stress difference coefficient, Ψ_1 and Ψ_2 of the fluid by (Choi, 1991; Nuñez et al., 1994)

$$\beta = 3\alpha_1 + 2\alpha_2 = \Psi_1/2 + 2\Psi_2 . \tag{5}$$

For many polymeric systems, Ψ_2 is negative and much smaller than Ψ_1. For simplicity, the approximation $\Psi_1/\Psi_2 \cong -0.1$ is used, and Eq. (5) becomes

$$\beta = 0.3\Psi_1 . \tag{6}$$

With this relation, the theoretical value of N_1 is obtained as follows :

$$N_1 = \Psi_1\dot{\gamma}^2 = \frac{10}{3}\beta\dot{\gamma}^2 . \tag{7}$$

The relationship between rheological parameters in the lower limit of frequency and shear rate, based on the Cox-Merz rule (1958) is expressed as follows

$$\lim_{\dot{\gamma}\to 0}\frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} = \lim_{\omega\to 0}\frac{2G'(\omega)}{\omega} = \frac{10}{3}\beta = \Psi_{1,0} . \tag{8}$$

Experimental

The PIBs were Vistanex polyisobutylene MM L grades obtained from Exxon Chemicals (USA), and the solvent was polybutene (PB, Daelim Chemicals, Korea), which is chemically stable liquids with moderate to high viscosities (12 ~ 40 Pas). To investigate the effect of particle on the Boger fluid, we dispersed three types of particles; i.e. kaolinite, α-Fe_2O_3 and γ-Fe_2O_3. The kaolinite[$Al_2Si_2O_5(OH)_4$] is the most common clay mineral having two dimensional silicate structure. The mean particle size is 4μm and its specific gravity is 2.6. The α-Fe_2O_3 (non-magnetic) is Bayferrox 130M grade (mean particle size 0.17 μm, specific gravity 5.0) from Bayer Co., and the γ-Fe_2O_3 (magnetic) is HR-359 grade (mean particle size 4.2μm, specific gravity 6.0) from Magonx Co..

PIB was dissolved in PB with cosolvent (toluene). Then, particles were added in the mixture. Finally, toluene was removed using a vacuum oven.

Various experimental conditions such as polymer molecular weight, polymer concentration, solvent viscosity, rod size, particle concentration, particle type and temperature were applied. We also measured rheological properties (η, G', G", N_1 etc) of particle suspended PIB/PB solutions using rheometers (RMS-800, Physica MC-120 and ARES) at 30 ℃.

Results and Discussion

Higher polymer concentrations (i.e. higher elasticity) exhibit higher climbing heights, showing that the restoring force induced by the anisotropic structure of deformed polymer fluid exposed flow grows up with concentration. The relationship between β and concentration can be considered from the theory developed by Brunn (1980), who adopted Brinkman's analysis for the dumbbell model polymer in a second order fluid. The linear correlation between β and concentration is introduced as follows using Brunn's theory

$$\frac{\beta}{\eta_S^2 C} = B(1 + 0.75C[\eta]) \tag{10}$$

where, B, a constant at given temperature and molecular weight, is $M[\eta]^2/RT$. The climbing constants increase with the PIB molecular weight (Fig. 1). Eq. (10) also explains the effects of solvent viscosity and temperature.

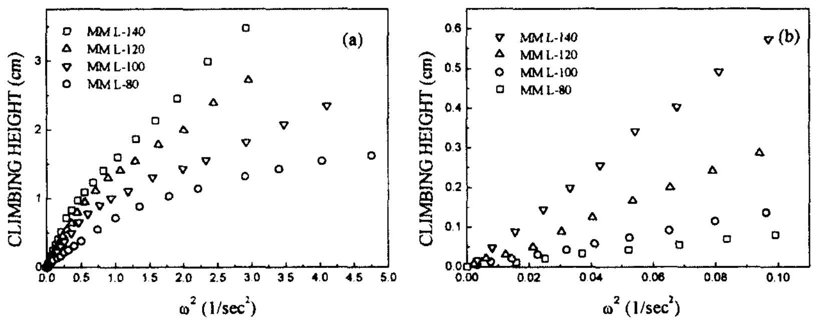

Fig. 1 Effect of polymer molecular weight (0.25wt% in PB) on the climbing height with 1.0cm diameter rod at 30℃. (a) α-Fe_2O_3 (0.03v/v) (b) γ-Fe_2O_3 (0.03v/v).

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, we find an increase of N_1 with filler addition for particle suspended Boger fluid system (Choi et al., 1999). In addition, in the case of magnetic particle (γ-Fe_2O_3) system, the climbing height is higher than the non-magnetic particle systems (Fig. 1). The magnetic particles usually form floc structure in the suspending medium due to particle interactions and have higher viscosity at the same volumetric concentration (Choi et al., 2000).

The comparison between the climbing constants and the values from rheometers (simple shear mode and dynamic mode) was also conducted. The result showed that theoretical prediction from climbing constant, β is well correlated with each other especially in the low shear rate and low frequency region as given in Fig. 2.

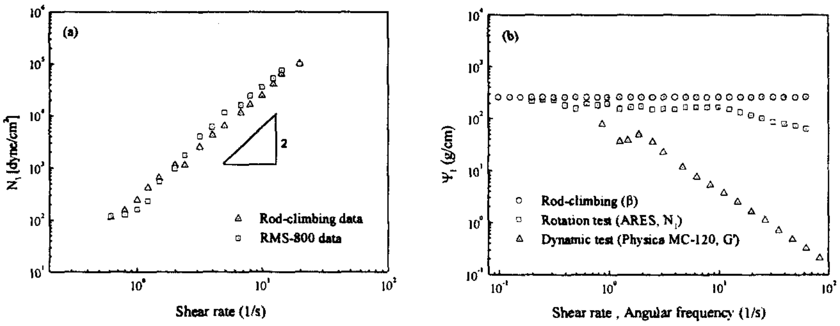

Fig. 2 (a) Comparison of first normal stress difference (N_1) of RMS-800 data with that of the rod-climbing for PIB MM L-140 0.2wt% in PB-kaolinite 0.07v/v at 30℃.

(b) Comparison of normal stress difference coefficients (Ψ_1) for PIB MM L-140 0.25wt% in PB/α-Fe_2O_3 0.03v/v from different methods.

Conclusion

The rod-climbing constants are found to be increased with polymer concentration and polymer molecular weight, rod-size, solvent viscosity and rod-size but decreased with temperature. In addition, for particle suspended systems, contrasting to polymer melt, β is increased with particle concentration due to the screening effect of solvent on particles. The first normal stress differences calculated from the second-order theory were well correlated with the measured ones. Therefore, from the climbing height of free surface near the rod, we can get a more simple and precise measure of the elastic nature of the fluid in a low deformation rate region.

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