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# Effect of Filler Particle Size on the Rheological Properties of Suspension. I. CaCO₃ Suspended in an Aqueous HEC Solution

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**Abstract** : Suspensions of six samples of calcium carbonate ($CaCO_3$) with different average particle sizes in 1.5 wt% aqueous solution of hydroxyethyl cellulose (HEC) were prepared. The effect of filler particle size on such rheological properties as viscosity and yield value was investigated. The smaller $CaCO_3$ particles exhibited the greater tendency of particle agglomeration. Unlike the aqueous HEC solution which shows Newtonian flow region, suspension systems exhibited a yield behavior. At the same filler concentration, suspension including smaller $CaCO_3$ particles gave higher viscosity and greater yield value than that including larger $CaCO_3$ particles. Further the value of yield stress was increased with increasing $CaCO_3$ concentration. The Mooney equation gave a qualitive explanation of the effect of particle size of $CaCO_3$ on the suspension viscosity.

## INTRODUCTION

Up to now a number of studies on the rheological properties of suspensions containing rigid particles have been disclosed, and lots of rheological models have also been proposed[1~7]. However, there is only a little systematic work on the suspension systems of non–Newtonian fluids although the primary interest of industry is in the rheological properties of suspensions of particles in polymeric materials[8~11]. In the dispersed flow of particulate-filled poly-

meric systems, the average size of dispersed particles may have a profound influence on the rheological properties through the change in dispersing and packing fashion of particles[11,12]. Therefore, it may be of practical importance to grasp a relationship between the macroscopic rheological properties of suspensions and the microscopic structure of particle size.

Two classes of clacium carbonate with different average particle sizes were selected, and mixed at several ratios. They were finely dispersed in an aqueous solution of hydroxyethyl cellulose

(HEC) which shows a non–Newtonian flow be-havior, and the viscosity behavior of the sus-pension was discussed in terms of sedimentation volume of filler and rheological model.

## EXPERIMENTS

### Materials and Formulations

As a suspending medium an aqueous sloution of HEC whose weight average molecular weight is about 50,000(1.5 wt%) was used, and calcium carbonates with different average particle sizes were tested. The experimental formulations in-vestigated are given in Table 1.

### Experimental Procedure :

The particle size and size distribution were determined by a particle analyzer, Sedigraph 5000 ET (Micromeritics Co., U.S.A.), and the sed-imentation volume was measured by the method suggested by Freundlich et. al.[13,14] The formulated components were mixed in a polyethylene bag by hand[15]. The viscosity of suspension was me-asured with a Haake Rotovisco RV2 (Haake Mess–Technik GmbH u. Co., West Germany). The volume fraction, $\varphi_f$ was calculated from the following equation :

$$\varphi_f = \frac{W_f/\rho_f}{(W_f/\rho_f)+[(1-W_f)/\rho_p]}$$

in which, $W_f$ is the weight fraction of filler, $\rho_f$ is the density of filler, and $\rho_p$ is the density of polymer solution.

Table 1. Experimental Formulations

| Suspension number | Mixing ratio of large to small particles (L/S) | Average particle size (microns) |
|---|---|---|
| S–1 | 0/10 | 2.0 |
| S–2 | 2/8 | 3.7 |
| S–3 | 4/6 | 5.4 |
| S–4 | 6/4 | 7.1 |
| S–5 | 8/2 | 8.8 |
| S–6 | 10/0 | 10.5 |

## RESULTS AND DISCUSSION

### Assessment of Particle Microstructure:

The particle size and size distribution of two basic grades of calcium carbonate tested are given in Fig.1. The measured average particle size of "S"grade containing smaller particles was $2\,\mu$m and that of "L" grade containing larger particles was 10.5 $\mu$m. The tendency of small particles to agglomerate is well characterized by relative sedimentation volume. The relative sedimentation volume (RSV) was obtained from the expression

$$RSV = SV/BV$$

in which, SV is the sedimentation volume of filler and BV is the bulk volume of filler. The surface area of particles is increased with decreasing par-ticle size, which is closely related to the ma-gnitude of electrical dipoles on the surface of calcium carbonate. Therefore, the ability to form a net–work and the strength of that network may increase as the size of the filler particles decreases.[16] In consequence, smaller particles gave rise to higer relative sedimentation volume as they form bulkier network resulting from st-ronger interparticle interactions as given in Fig.

### Rheological Properties of Suspensions

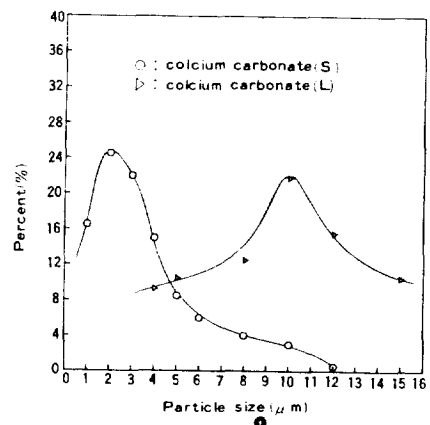Fig. 3 gives viscosity curves of suspension, S–3, showing the effect of volume loading level



Fig. 1. Particle size distribution curves of two grades of calcium carbonate tested.

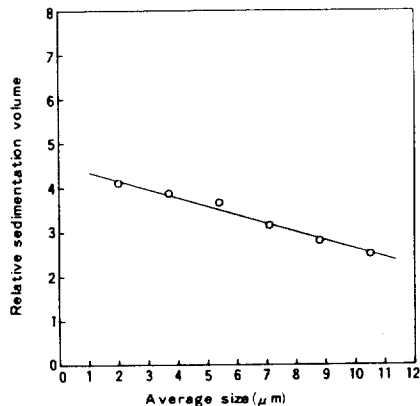B. C. Kim, K. U. Kim, K. S. Kim, and Y. S. Kim



Fig. 2. Relative sedimentation volume versus average size of calcium carbonate particles tested.
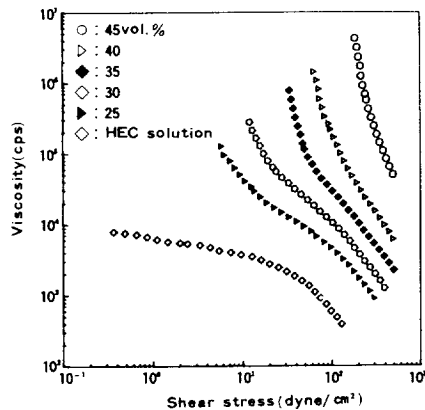


Fig. 4. Plots of viscosity versus shear stress of HEC solution and suspension, S-3, at several filler concentrations.
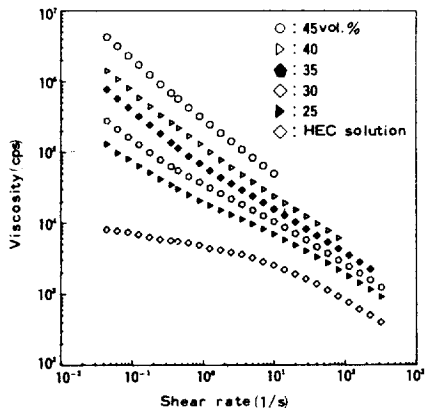


Fig. 3. Viscosity curves of HEC solution and suspension, S-3, at several filler concentrations.
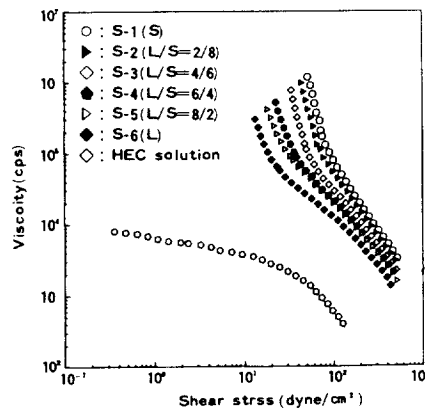


Fig. 5. Plots of viscosity versus shear stress of various suspensions at filler content 35 vol.%.

of filler. It is worth noting that the viscosity of suspensions was decreased over the entire range of shear rates tested while the viscosity of HEC solution showed a Newtonian flow region at low shear rates. Further, the dependence of viscosity on shear rate was more pronounced for the suspensions with higher concentrations at the same average particle size[11]. In general, the degree of interparticle interactions may increase as the concentration of filler increases. This may result in a formation of a continuous three-dimensional network at high concentrations, which may partly be destroyed upon deformation. Therefore, the viscosity of suspensions with high filler con-

centrations was very high particularly at low shear rate range as shown in the figure.

As a rule, the linear decrease of viscosity with increasing shear rate in the low shear rate range is an indication of yield stress[10,11]. The viscosities were replotted against shear stress in Fig.4, which clearly shows the existence of yield stress.

To investigate the effect of particle size on the viscosity of suspensions at the same filler concentration, viscosities of various suspesions including different average particle sizes are plotted against shear stress in Fig.5. At the same filler concentration smaller CaCO$_3$ particles gave

higher viscosity and exhibited greater degree of shear-thinning at low shear stresses. This implies that the yield stress is greater for the suspensions including smaller filler particles.

To estimate the magnitude of yield stress the root shear stress is plotted against the root shear rate in Figs.6 and 7 according to the MTMO equation[17] :

$$\tau^{1/2} = \tau_y^{1/2} + k_s(\eta_a/\eta_0)^{1/2}\dot{\gamma}^{1/2}$$

in which, $\tau$ denotes shear stress, $\tau_y$ yield stress, $k_s$ a constant, $\dot{\gamma}$ shear rate, $\eta_0$ and $\eta_a$ zero-shear and apparent viscosities of medium, respectively. The yield values so determined are listed in Table 2. Since the yield stress is the resistance of structure to the initial deformation it may be proportional to the strength of phy-

sical aggregates of particles. As already mentioned, the higher relative sedimentation volume of smaller filler particles suggests a stronger tendency to aggregate and to form stronger networks. Further, the interparticle interactions increase with increasing filler concentration. As a result, the yield value was increased with increasing filler concentration and with decreasing particle size as shown in the figures.

For the viscosity of suspensions, Mooney derived the following equation[18] :

$$\ln(\eta_s/\eta) = \frac{K_E \varphi_f}{1-(\varphi_f/\varphi_m)}$$

in which, $\eta_s$ is the suspension viscosity, $\eta$ is the viscosity of HEC solution, $K_E$ is Einstein coefficient which is very close to 2.5, $\varphi_f$ is the volume fraction of filler, and $\varphi_m$ is the maximum packing fraction of filler.

In real suspension systems agglomeration of particles takes place due to the interparticle interactions. Further, polydispersity, non-sphericity and non-uniform dispersion also violate the original assumptions.[1] Therfore it is almost impossible to fit the experimental data to the theoretical curve quantitatively. However, it may be plausible to account for the effect of average particle size on the suspension viscosity at least in qual-

Table 2. Yield Values (dyne/cm²) of Suspensions

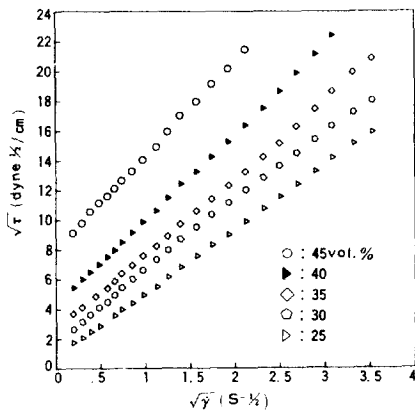| Filler content (vol %) Suspension No. | 25 | 30 | 35 | 40 | 45 |
|---|---|---|---|---|---|
| S-1 | 4.7 | 11.1 | 39.5 | 92.9 | 257.2 |
| S-2 | 4.0 | 9.0 | 32.4 | 77.8 | 203.2 |
| S-3 | 2.6 | 7.0 | 23.8 | 49.1 | 159.7 |
| S-4 | 1.8 | 6.1 | 15.3 | 41.6 | 114.2 |
| S-5 | 1.4 | 4.4 | 12.1 | 31.0 | 86.2 |
| S-6 | 1.0 | 3.2 | 7.4 | 19.0 | 64.6 |



Fig. 6. Onogi plots of suspension, S-6, showing the effect of filler concentration on yield value.
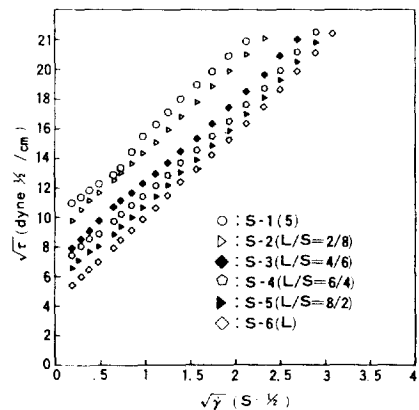


Fig. 7. Onogi plots of various suspensions at filler concentration 40 vol.% showing the effect of particle size on yield value.
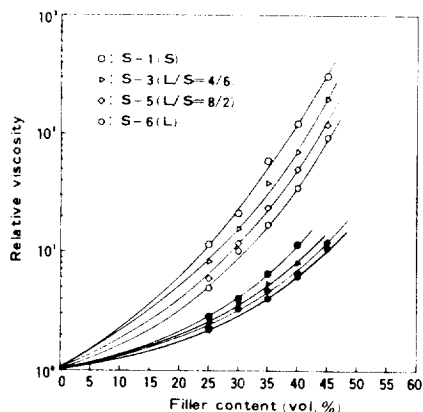
Fig. 8. Plots of relative viscosity versus filler concentration at two shear rates for several suspensions (open symbols at 0.176 s$^{-1}$ and closed symbols at 19.910 s$^{-1}$).

itative way. It is evident that agglomeration of filler particles will increase the viscosity at the same filler concentration througt the increase of "apparent" volume fraction of filler.[19] That is, the smaller CaCO$_3$ particles may create more immobile layer because they give rise to greater particle agglomeration due to the stronger interparticle interactions. Since the suspension viscosity is a function of apparent volume rather than true volume, agglomeration increased the suspension viscosity at the same usage level of filler.[20] Referring to the Mooney equation also indicates that the smaller CaCO$_3$ particles give higher viscosity at the same filler concentration because formation of immobile layer reduces $\varphi_m$ as shown in Fig.8.

## CONCLUSIONS

1. The smaller calcium carbonate (CaCO$_3$) particles gave greater tendencies of agglomeration. Suspension containing smaller CaCO$_3$ particles gave higher viscosity and greater yield value at the same filler loading.

2. The value of yield stress was increased with increasing CaCO$_3$ concentration.

3. The Mooney equation gave a qualitative explanation of the effect of particle size of filler on the viscosity in the real suspension systems.

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