EFFECT OF SOLID LOADING AND AGGREGATE SIZE ON THE RHEOLOGICAL BEHAVIOR OF PDMS/CALCIUM CARBONATE SUSPENSIONS

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Abstract - The purpose of this study is to examine the effect of solid loading and aggregate size on the rheological behavior of PDMS (polydimethylsiloxane)/CC (calcium carbonate) suspensions. Mixtures containing 10 to 40 vol% of CC were prepared; the effect of shear rate and particle content on aggregate size and rheological properties was studied. Rheological properties including viscosity, loss modulus, storage modulus and yield stress were measured using rotational and oscillatory rheometry. Casson's equation was found to satisfactorily model the samples' stress response as a function of shear rate for different solid content. While solid content did not have any effect on the aggregate size, shear rate did influence the aggregate median diameter. It was observed that suspensions with higher aggregate size had a higher viscosity. In general, for a given volume fraction, a small change in the aggregate size had a significant impact on the viscosity, particularly at low shear rates.
Keywords: Rheological behavior; Aggregate size; PDMS/CC suspensions.

INTRODUCTION

Suspensions and colloids are of considerable industrial and daily life importance. Blood, paint, ink, oil, and food are a few examples indicating the diversity of technological significance of these systems (Larson, 1999).

Rheological study of suspensions and colloidal dispersions provides valuable information for efficient utilization, transport and handling of such materials in industrial applications. Therefore, the rheological behavior of colloids and suspensions has been the subject of interest for many researchers (Krieger and Dougherty, 1959, Russel, 1987, van der Werff et al., 1989, Shikata and Pearson, 1994, Liu and Tseng, 1998, Le Meins et al., 2002, Olhero and Ferreira, 2004). The rheological properties of suspensions are affected by a number of parameters, including particle

concentration, particle shape and size, particle size distribution, rheological characteristics of the matrix fluid and also aggregate size (Russel, 1987, Liu and Tseng, 1998, Jancer, 1999, Shenoy, 1999, Selomulya, 2001, Tseng and Lin, 2003, Grizzuti and Pasquino, 2008).

One of the determining factors in the rheological behavior of filled systems is the formation and structure of aggregates and agglomerates. While aggregates are a number of particles bonded by strong chemical forces, agglomerates are a number of aggregates bonded by mostly weak physical forces (Teleki et al., 2008). The important role of particle and aggregate size in determining the rheology of filled systems has been reported by Tseng and Lin and also George et al. (Tseng and Lin, 2003, George et al., 2004), although Chong et al. (1971) suggested that the rheological behavior of suspensions is independent of filler size.

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Studies of the relationship between aggregate size and rheology have generally focused on the effect of initial particles size at the beginning of every process. It is common that aggregate size changes during mixing and other flow processes. Recently, there have been articles considering the effect of aggregate size on the rheological behavior of filled systems (George et al., 2004, Kaully et al., 2007, Colomer et al., 2005).

The present work focuses on the study of aggregate sizes formed in a mixing process and its relation to the rheological behavior of suspensions. The suspension samples were made from a medium viscosity liquid (PDMS100) and micron sized calcium carbonate particles with different volume fractions and mixed at different shear rates.

EXPERIMENTAL

In the next section, experimental issues including details of samples and sample preparation are given. It is then followed by a thorough discussion of the experimental results.

A- Materials

A silicone fluid, dimethylpolysiloxane, (PDMS100) supplied by Wacker-Chemie GmbH was used as the fluid and had a dynamic viscosity of about 96 mPa.s at 25°C as reported by the manufacturer. Treated commercial calcium carbonate with the trade name of 1T-SW, supplied by OmyaPars Company, was dispersed with different filler concentrations. More details are given in Table 1.

1T-SW powder was micron-sized, with a mean particle size of 1.8 micron as reported by the manufacturer.

B- Sample Preparation

Samples were prepared by direct loading and mixing in a stirred vessel with a volume of 250 mL using a high shear Sawtooth impeller. Samples of 10, 20, 30 and 40% calcium carbonate volume fraction were prepared at a 5000 rpm rotation speed to study the effect of solid volume fraction. Samples with 30% volume fraction were prepared with mixing at different rotation speeds to study the effect of rotation speed on aggregate size and rheological properties. The impeller ran at different speeds, from 500 rpm to 5000 rpm for 20 minutes. The batch volume was 200 mL and the corresponding average shear rates were estimated from equations proposed by Camp and Stein (1943) and Clark (1985). Reynolds numbers were calculated by the following equation:

$$Re = \rho ND^2 / \mu \tag{1}$$

where μ, N, D and ρ are the fluid viscosity, rotation speed, impeller diameter and fluid density, respectively. Reynolds numbers and shear rates for different cases are presented in Table 2 and range from 93.44 to 934.43 and from 24.3 to $769\,s^{-1}$, respectively.

Table 1: Characteristics of matrix and dispersing particles

	PDMS	Calcium Carbonate
Density (kg/m^3)	963	900
Molecular weight (kg/mol)	5	-
Viscosity at $25'C$ (mPas)	96	-
Refractive index at $25'C$	1.403	1.56
$d_{50}(\mu m)$	-	1.8
$d_{98}(\mu m)$	-	8
d_{90}/d_{10}	-	13
Type	hydrophobic	hydrophobic

Table 2: Calculated average shear rate and Reynolds number for each rotation speed

Rotation speed(rpm)	Average shear rate(1/s)	Reynolds number
500	24.3	93.44
1000	68.77	186.88
2000	194.42	373.77
3000	357.35	560.66
4000	550	747.55
5000	769	934.43

Sample Characterization

Two types of assessment were performed on the samples; a) particle size measurement and b) rheological measurement in order to know if there had been a change in aggregate size distribution and if that change had any effect on rheological behavior of the samples.

Rheological Measurements

The rheological behavior of the samples was analyzed with an Anton Paar MCR301 rheometer, in both rotational and oscillation modes in coaxial cylinder geometry. The tests were carried out at room temperature starting with an amplitude sweep test to determine the linear viscoelastic limit of samples. Then, a small amplitude oscillatory shear test was performed in the linear region. Finally, steady state tests were carried out to measure the viscosity in the shear rate range of $0.01\,\mathrm{s}^{-1}$ to $1000\,\mathrm{s}^{-1}$.

Particle Size Measurements

Aggregate sizes were measured after mixing by using a Shimadzu SA-CP3 Particle Size Analyzer in the centrifugal mode and the median aggregate diameter of each sample was reported. Acetone was used to dilute the samples, lowering the viscosity to the instrument requirements. The dilution process was made cautiously to avoid any change in aggregate sizes. All particle size measurements were performed immediately after the mixing and again after several days to make sure that there was no aging effect.

RESULTS AND DISCUSSION

In the following sections, the effects of solid content and mixing shear rate on aggregate size are discussed. The results of rheological measurements have been used to study the influence of solid content and aggregate size on the rheological behavior of samples.

A- Study of Aggregate Size Distribution in Suspensions

Results of aggregate size distribution studies are presented in two sections as follows:

A1- Effect of Solid Content

Table 3 presents the median aggregate size for different contents of calcium carbonate. Size measurements did not show any significant change for various volume fractions in the range of 10 to 40 vol%. This can be attributed to equal improvement in the rate of aggregation and breakage, as had been assumed in some earlier modeling efforts (Kim and Kramer, 2005). However, Selomulya et al. (2001) reported formation of larger aggregates of polystyrene latex at higher solid content. It may be concluded that changes in aggregate size due to the solid content are system dependent and may be different in different ranges.

Table 3: Particle size measurement results for samples with different solid contents at a rotation speed of 5000 rpm

Sample	Median diameter d_{50} (µm)
Pure CC	32.5
10%vol -5000 rpm	32
20%vol -5000 rpm	33
30%vol -5000 rpm	30
40%vol -5000 rpm	30

A2- Effect of Shear Rate

Table 4 shows the median diameter of aggregates as a function of rotation speed for suspensions filled with 30 vol% calcium carbonate particles. In comparison with other studies (Selomulya et al., 2001; Colomer et al., 2005), our results did not exhibit a unique trend of increasing or decreasing median aggregate size as the rotation speed and, accordingly, the shear rate is increased. Colomer et al. (2005) showed that, upon increasing the shear rate, aggregate size increased in an aqueous solution of polystyrene sulfate latex, although their shear rates and loading were low. On the contrary, Selomulya et al. (2001) reported a drop in the aggregate size of aqueous solutions of polystyrene latex with shear rate growth at higher shear rates, although they did not observe a unique trend in the aggregate size upon increasing shear rate in the primary stages of mixing after 20 minutes. As it can be seen in Table 4, our results showed a minimum for aggregate median size when shear rate steps up in the mixing process.

This can be attributed to a change in the flow regime, changing from laminar to turbulent state. When the Reynolds number is below 10, the flow field is laminar, while full turbulent flow is achieved above 10^4. By increasing the rotation speed from 500 rpm to 5000 rpm, the flow regime gets far from the laminar regime. Since the studies were separately done in laminar and turbulent flow regimes, the fluctuations in the aggregate size can be associated

with a change in flow regime, passing from laminar to turbulent regime.

This phenomenon shows that increasing the shear rate or input energy in the transient regime is not necessarily followed by a decrease in aggregate sizes for a suspension and that the opposite may occur.

Table 4: Particle size measurement results for samples with 30% volume fraction at different rotation speeds

Sample	Median diameter d_{50} (μm)
30%vol -500 rpm	30
30%vol -1000 rpm	22
30%vol -2000 rpm	25
30%vol -3000 rpm	26
30%vol -4000 rpm	28
30%vol -5000 rpm	30

B- Study of the Rheological Properties of Suspensions

The main objective of this study was to illustrate the effect of solid content and aggregate size on the rheological behavior.

B1- Effect of Particle Content

The particle content in suspensions clearly influences the rheological behavior. The presence of particles in filled systems results in higher viscosity, shear thinning behavior, and appearance of yield stress (Kaully et al., 2007). Hence, several researchers focused on the suspensions' rheology as a function of solid loading and monoparticle size (Mooney, 1951, Thomas, 1965, Farris, 1968, Patzold, 1980, Cohen and Metzner, 1981, Cheng, 1984, Kaully et al., 2007). In the present study, the viscosity, stress response, and dynamic moduli of samples of different volume fractions were taken into consideration.

In Figure 1, the steady shear viscosity of suspensions, η, with different solid volume fractions, ϕ, is given as a function of shear rate, $\dot{\gamma}$. Increasing the solid content, the viscosity increased, particularly at low shear rates. Higher viscosity of suspensions is mainly due to the existence of local structures in the media that immobilize the fluid, preventing it from participating in the hydrodynamic flow field. In all samples, shear thinning behavior was observed. Higher filler content intensified the shear thinning behavior. Quemada (1998) proposed that the structure breakdown is the reason for shear thinning

behavior in non-Brownian concentrated suspensions. The higher the filler content in the samples, the more aggregates in the system, the more susceptibility to break and the more shear thinning behavior.
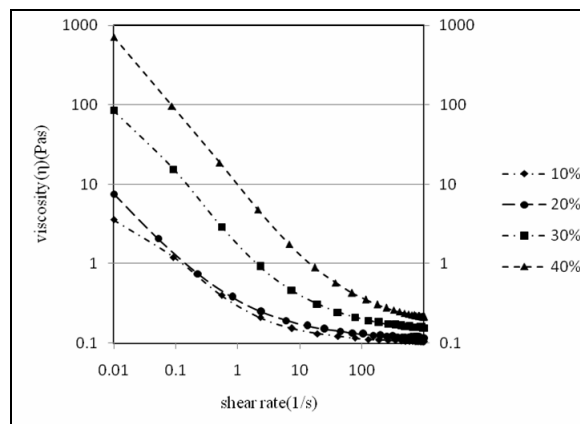

Figure 1: Steady shear viscosity against shear rate for suspensions with various volume concentration of calcium carbonate

At a higher volume fraction of particles, an increase in the filler content results in a higher rate of viscosity increase. Therefore, the viscosity difference between the samples with 30% and 40% of filler is higher than the difference between 20% and 30% or 10% and 20% of calcium carbonate. This is because the former is getting closer to the maximum volume fraction of particles.

As shown in Figure 1, for suspensions with different filler content, the viscosity reaches the lowest value at high shear rates. The high shear rate viscosity was plotted against particle volume fraction in Figure 2.
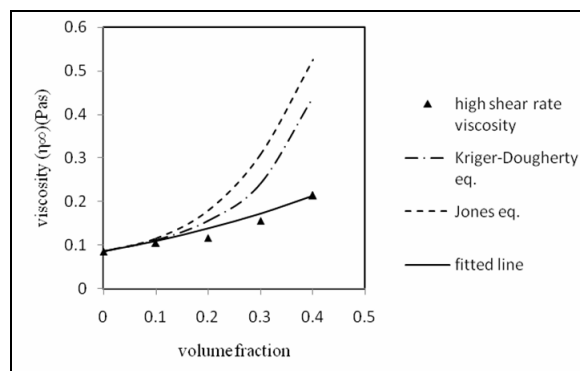

Figure 2: High shear rate viscosity as a function of calcium carbonate volume fraction in PDMS; the solid lines are the values predicted by the models presented

Einstein and Batchelor considered the motion of a single particle and pairs of particles in the fluid equations, respectively. Their models cannot be employed to predict viscosity in our samples because ternary and multi-particle collisions become important in the suspensions containing more than 10 vol% of solid particles (Batchelor, 1977, Labanda et al., 2004). Einstein and Batchelor models are valid for dilute and semi-dilute suspensions. Jones and Dole (1929) and Krieger and Dougherty (1959) developed models for more concentrated suspensions but the measured viscosity values were lower than their predictions. The prediction was in good agreement only for the 10% suspension. The Jones and Krieger-Dougherty equations, which were obtained semi-empirically, are as follows (Jones and Dole, 1929, Krieger and Dougherty, 1959):

$$\eta = \eta_0(1 + [\eta]\phi + 5\phi^2 + 53\phi^3)$$
(2)

Jones equation

$$\eta_\infty = \eta_0(1 + \phi/\phi_m)^{-[\eta]\phi_m} = \eta_0(1 + \phi/0.605)^{-1.5125}$$
(3)

Krieger – Dougherty equation

where ϕ, η and η_0 are the particle volume fraction, suspension viscosity and fluid viscosity, respectively. $[\eta]$ is the intrinsic viscosity, having a typical value of 2.5 for monodisperse dispersions of hard spheres, and ϕ_m is the maximum particle packing fraction, which varies from 0.495 to 0.54 under quiescent conditions and is approximately 0.605 at high shear rates (Chen et al., 2007). In equation 3, η_∞ is the viscosity at high shear rates. Assuming the aggregates to be hard spheres and considering the high shear rate viscosity, the right hand side of equation 3 was obtained. The equation fitted to our results, also depicted in Figure 2, was as follows:

$$\eta_\infty = \eta_0(1 + \frac{5}{2}\phi + 3\phi^2 + 0.5\phi^3)$$
(4)

Compared to the Jones equation, equation 4 indicates that viscosity has a weak dependency on the cube of the volume fraction, while the coefficient of ϕ^2 is in the range of the Jones equation.

Figure 3 presents the stress values versus shear rate for samples with different solid content, showing good conformity with Casson's equation. Casson's equation is (Casson, 1959):

$$\sigma^{0.5} = \sigma_{yield}^{0.5} + k\dot{\gamma}^{0.5}$$
(5)

where σ, σ_{yield}, $\dot{\gamma}$ and k are shear stress, yield stress, shear rate and fitting parameter denoting viscosity, respectively. The values of σ_{yield} and k for each sample are given in Table 5.
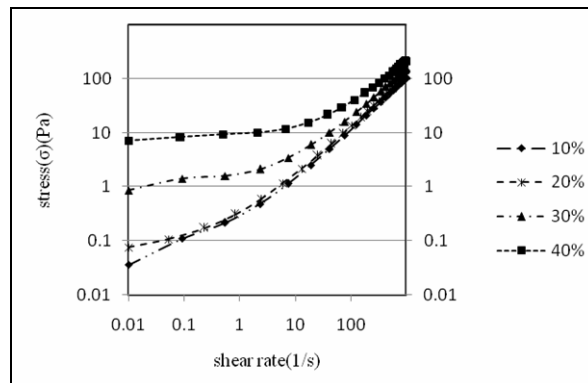

Figure 3: Shear stress as a function of shear rate for various volume fractions of particles in suspensions

Table 5: σ_{yield} and k **values for prepared samples**

Sample	$\sigma_{yield}^{0.5}$	k
10%vol -5000 rpm	0.205	0.317
20%vol -5000 rpm	0.258	0.334
30%vol -500 rpm	0.671	0.377
30%vol -1000 rpm	0.504	0.371
30%vol -2000 rpm	1.046	0.362
30%vol -3000 rpm	1.147	0.361
30%vol -4000 rpm	1.218	0.355
30%-5000 rpm	0.887	0.365
40%-5000 rpm	2.486	0.380

Increasing the volume fraction of calcium carbonate results in an increase in yield stress because of the higher number of local structures formed. Since the volume fraction of particles did not have much influence on aggregate diameter (see Table 3), it can be concluded that the volume fraction of CC was proportional to the number of aggregates. Thus, the higher the number of aggregates in the system, the higher the stress required to break up the networks.

Results of small amplitude oscillatory strain rheometry are presented in Figures 4 and 5 in terms of loss and storage moduli versus frequency. The loss and storage moduli of samples were approximately constant over the applied frequency range, increasing with the filler content. Increase of dynamic moduli for high solid content has also been reported by Palierne (1990) and Grizzuti and Pasquino (2008).

Figure 6 depicts the values of the storage modulus plateau against particle volume fraction.

Scaling concepts introduced by De Gennes for polymer melts and gels have been applied (Buscall et al., 1988, Shih et al., 1994) to suspensions and it has been shown that there is a power law type relationship between values for the storage modulus plateau and the particle volume fraction. In agreement with scaling concepts, the experimental results showed the power law

equation, $G' = 1830\phi^{4.122}$.

Figure 7 shows the complex viscosity of suspensions as a function of frequency. This graph confirms the shear thinning behavior. The Cox-Mertz rule was checked and, in contrast to Kaully et al. (2007), it was not valid for any of the samples due to structural changes in the steady shear tests.
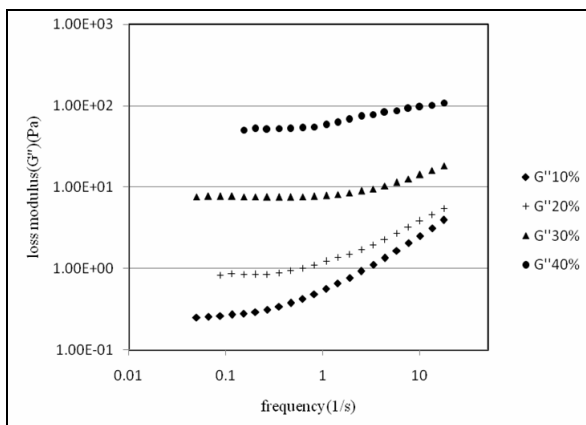

Figure 4: Samples' loss modulus against frequency for various volume fractions of calcium carbonate
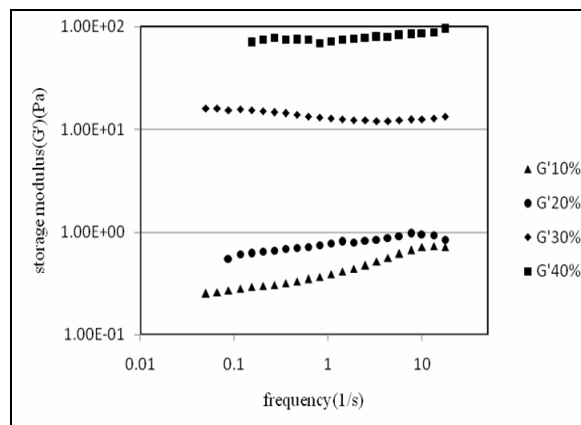

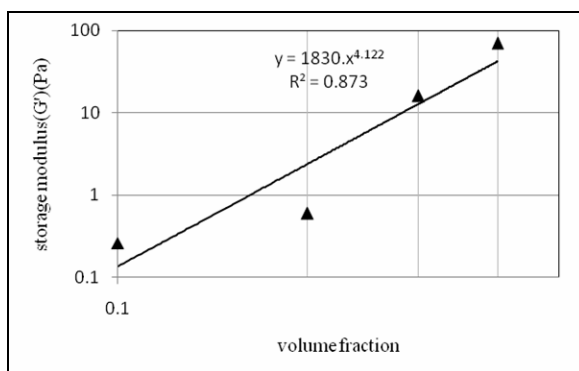**Figure 5:** Samples' storage modulus against frequency for various volume fractions of calcium carbonate

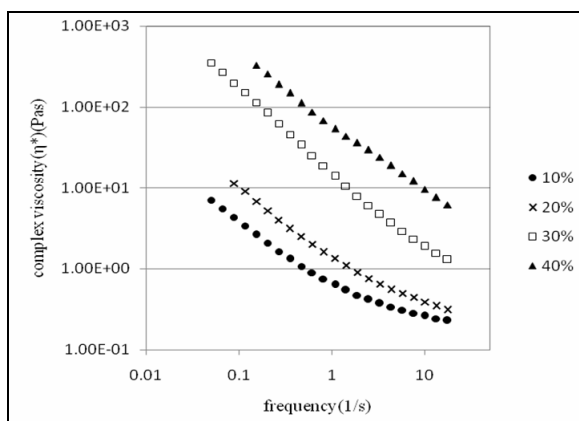**Figure 6:** Storage modulus in the plateau region against volume fractions of calcium carbonate and fitted line

Figure 7: Complex viscosity of suspensions against frequency for various volume fractions of calcium carbonate prepared at 5000 rpm

B2- Effect of Aggregate Size

Apart from the effect of particle content and number of aggregates on the rheological behavior of suspensions, aggregate size, determined with the Particle Size Analyzer, was found to have a great influence on the viscosity of the samples. In previous studies, the effect of particle size was taken into consideration and the rheological behavior of a bimodal particle size distribution has also been examined (Kaully et al., 2007). The aggregate sizes for the samples with 30% solid content are presented in Table 4. Figure 8 shows the viscosity of the samples with 30% solid content versus shear rate that were mixed with different speeds. Kaully et al. (2007) reported that the viscosity is unaffected by particle size up to roughly 40 vol% of calcium carbonate in PDMS and found that fine filler suspensions exhibit much higher viscosity at a given loading, but made no argument about the aggregate size composed of monoparticles in the system. On the other hand, Quemada (1998) proposed the effective volume fraction concept to show the structural variation at a constant solid content and illustrated that structure breakdown leads to a drop in the viscosity. As shown in Figure 8, small changes in aggregate size can have a large impact on suspension viscosity. Increasing the aggregate size resulted in higher viscosity, markedly at low shear rates. When the shear rate increases, the sensitivity to the local structure size decreases and approximately vanishes at high shear rates. The shear rate ranges from 24.3 to $769\,s^{-1}$ in our experiments and mixing time was 20 minutes. Shear deformation in dynamic tests $(\gamma = \overset{\bullet}{\gamma}/\omega)$ was much lower than what was in the mixing process. Therefore, shear thinning was attributed to the breakdown of agglomerates composed of aggregates that had been obtained at the end of the mixing process and could be formed by short-range interactions in the period after the mixing process and before the rheometry tests. A relationship was found between the aggregate size obtained after the mixing process and the suspension viscosity in the rotational tests. The results may be explained in terms of agglomerates composed of bigger aggregates greater in size than those formed from smaller aggregate attachment, leading to more fluid captivity and thus higher viscosity. George et al. (2004) studied the effect of aggregate size of alumina particles in distilled water on sediment bed rheological properties. They produced two different aggregate sizes in low and high salt aggregation conditions and they found that increasing the aggregate size causes higher yield stresses.
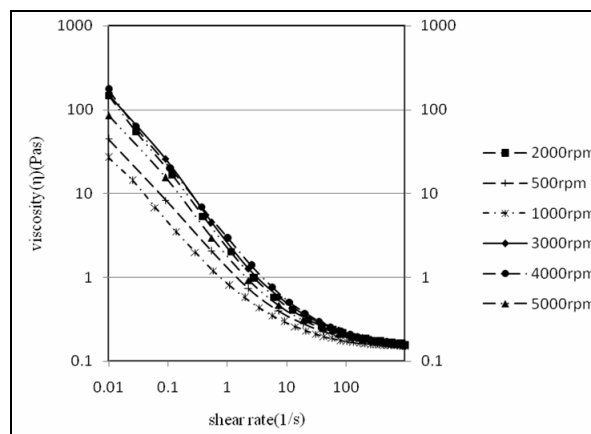

Figure 8: Shear steady viscosity of 30 vol% suspensions as a function of shear rate

The viscosity difference in suspensions filled with 30% vol of calcium carbonate was higher at lower shear rates. Passing a critical shear rate, no matter how a sample is prepared, the viscosity values increase up to the same value. This is due to the fact that the viscosity of a suspension with constant particle content depends strongly on the aggregate size and amount of imposed strain. The aggregate size is determined by the prior processes performed on the suspension and the shear deformation value is dictated by circumstances of application. The viscosity of a suspension, therefore, can be tailored through adjusting the aggregate size in prior processes and adjusting the shear strain, which can be applied in a defined geometry.

CONCLUSION

Samples of PDMS/CC suspensions were prepared with different solid volume fractions and with different average mixing shear rates. Study of aggregate size in samples showed that, while solid content did not influence the median aggregate size significantly, average mixing shear rate had a strong effect on median aggregate size. Rheological measurements showed shear thinning behavior for all prepared samples, while shear thickening was not observed at high shear rates up to 1000(1/s). Increasing the volume fraction of calcium carbonate caused high viscosities in the system due to a higher number of aggregates formed in the mixing process. Equations 4 and a power law type equation ($.G' = k\phi^n$.) were considered for modeling of the high shear rate viscosity and low frequency storage modulus of samples, respectively. In addition,

Casson's model properly explained the stress response of the prepared samples. At a constant solid loading, the aggregate size has a great influence on the viscosity of suspensions particularly at lower shear rates. Bigger aggregates cause higher viscosity in suspensions due to the higher effective volume of particles and more immobilized liquid inside the local structures. The viscosity of a suspension can be influenced by aggregate sizes formed in earlier processes and the shear strain, which can be applied in a defined geometry.

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