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Non-linear Viscoelastic Rheological Properties of PCC/PEG Suspensions

Hai-lin Yang, Jian-ming Ruan*, Jian-peng Zou, Qiu-mei Wu, Zhong-cheng Zhou, Yuan-yan Xie

State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

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The shear thinning and shear thickening rheological properties of PCC/PEG suspension were investigated with the increase of oscillatory amplitude stress at different constant frequencies. The results show that the complex viscosity was initially independent of stress amplitude and obvious shear thinning occurred, then dramatic shear thickening took place after reaching the minimum viscosity. Typically, in a constant frequency of 5 rad/s, the elastic modulus, viscous modulus, and $\tan\delta$ (δ is the out-of-phase angle) *vs.* the stress amplitude was investigated. It is found that the elastic modulus initially appeared to be independent of stress amplitude and then exhibited a rapid decrease, but the viscous modulus was independent of amplitude stress at lower amplitude stress. After reaching the minimum value the viscous modulus showed a rapid increase. On the other hand, $\tan\delta$ increased from 0.6 to 92, which indicates that the transition from elastic to viscous had taken place and $\tan\delta$ showed a steep increase when shear thickening occurred. Lissajous plots are shown for the dissipated energy *vs.* different maximum stress amplitude in the shear thinning and shear thickening regions. The relationship of dissipated energy *vs.* maximum stress amplitude was determined, which follows a power law. In the shear thinning region the exponent was 1.91, but it steeply increases to 3.97 in the shear thickening region.

Key words: Precipitated calcium carbonate, Suspension, Shear thickening, Dynamic oscillatory shear, Rheological response

I. INTRODUCTION

Shear thickening refers to when the viscosity of a fluid increases with increasing rates or stress of shear. Generally, this behavior is unacceptable because the rapid, sometimes discontinuous, increase in viscosity damages processing equipment. The change in microstructure leads to poor fluid and coating qualities. However, the micro-mechanism for this phenomenon still remains unclear. Early investigations attributed the change in rheological response from shear thinning to shear thickening behavior to an order-disorder transition (ODT) [1,2]. It was thought that the disruption of an ordered structure results in increased particle interactions, which leads to the increase of viscosity of the suspension. But, recently it was shown from simulations [3] and experiments [4,5] that reversible shear thickening results from the formation of clusters. Percolations of these clusters with increasing shear results in the formation of larger aggregates that can jam the flow, making discontinuous shear thickening behavior occur.

Many aspects play important roles in the occurrence of shear thickening of fluids, such as the polarity of the continuous phase [6,7], considerable volume fraction [8-

10], particle size [11,12], and medium of dispersed phase [13-15]. It is noteworthy that shear thickening behavior can be exploited in designing damping and controlling devices [16]. Interestingly, some researchers in USA took advantage of the shear thickening behavior under stress or strain of the silica suspensions in ethylene glycol, polyethylene glycol (PEG) and water to make novel advanced body armor materials [17-19]. It was reported that these novel materials could not only offer equivalent ballistic performance of existing body armor materials but also be more compact and flexible.

Calcium carbonate is a mineral widely applied in such industries as cosmetics, medicine, catalysis, ceramics, rubber, paint, and the paper industry. The precipitated calcium carbonate (PCC) suspensions being subject to macroscopic stresses are involved in many industrial processes used in work, filler and ceramic industries [20-22]. The rheological properties play an important role in these processes. As just mentioned, some researchers [23-27] have utilized the PCC suspension for impregnating Kevlar to make advanced body armor materials. But few investigations [23] have been done on the rheological properties of PCC in polar liquid, so it is significant to do some investigation on this system. The objective of this study focuses on oscillatory shear rheological properties under various constant frequencies and the energy dissipated for the stress shear. In addition, we will examine the dissipated energy which is clearly related to the breakup of the suspension struc-

* Author to whom correspondence should be addressed. E-mail: jianming@mail.csu.edu.cn

ture and discuss the rheological performance and the rheological mechanism of PCC suspension in terms of the system properties.

II. EXPERIMENTS

A. Materials

The starting materials used in this study were commercial. X-ray diffraction (XRD) analysis revealed that calcite was the only crystalline phase. It can also be observed by Jeol-6360LV for scanning electron microscopy (SEM) in Fig.1 that the morphology of PCC is cuboidal and the particle sizes are from 80 nm to 100 nm. The particles can easily fuse irreversibly to aggregates due to a high surface energy. The density of the PCC particles obtained by solution densimetry measurements at various weight fractions using a volumetric balance assuming ideal mixing in PEG at 25 °C is 2.6 g/cm³.

The continuous phase in the experiments material is PEG with average relative molecular mass of 200, which was supplied by Sinopharm Chemical Reagent Co. Ltd. The viscosity of PEG, a Newtonian liquid, is 0.03 Pa·s at temperature of 25 °C.

B. Sample preparation

In order to remove the absorbed water, the PCC powders were kept in vacuum at the temperature of 100 °C for 1 h prior to the experiments. The suspensions were prepared by adding the powder into the liquid in a blender and mixing for about 60 min and then homogenized by ultrasound for 10 min. The samples were made in batches of 100 mL and placed in vacuum at room temperature for more than 24 h to remove air bubbles. Because of high hydrophilic character of the particle surfaces, when the powder was dispersed in polar liquid PEG, the powder can preferentially be wetted by PEG. On the other hand, the absorbed polar liquid interacted with other suspending molecules through hydrogen bonds, which resulted in a nonfloculated sus-

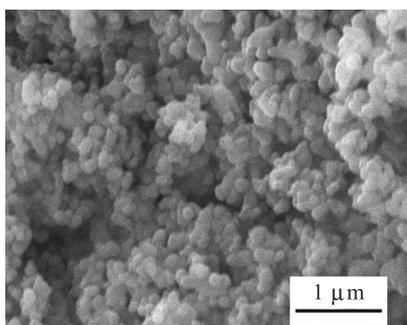


FIG. 1 SEM image of PCC particle powder.

pension. The volume fraction of the sample was held fixed at 40%.

C. Rheological experiments

A stress (strain) controlled rheometer AR2000ex (USA: TA company) was used to measure the rheological properties. A cone-and-plate fixture having a cone angle of 1° and a diameter of 40 mm was used. All the measurements were conducted at a constant temperature (25 °C). The stress-strain applied relation is given in the following formula:

$$\sigma(t) = \gamma[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)] \quad (1)$$

where σ , γ , ω , G' , and G'' are the stress, the strain amplitude, the frequency, elastic modulus, and viscous modulus, respectively. The measurement of the stress range investigated in this study was performed from 0.1 Pa to 1 kPa. In order to erase any previous shear histories and ensure the equilibrium of the structure, a steady preshear was applied at a shear rate of 1 s⁻¹ for 60 s followed by a 120 s rest period before any dynamic experiments.

III. RESULTS AND DISCUSSION

A. Oscillatory shear

The dynamic oscillatory stress sweeps under the constant frequencies were performed on PCC/PEG suspensions using the stress controlled rheometer with cone geometry, during which the shear thinning and shear thickening were observed in these systems. It can be observed from Fig.2 that with the increase of the dynamic oscillatory stress the complex viscosity (η^*) of these suspensions are initially nearly independent of the oscillatory shear stress amplitude σ at low stress (lower than 1 Pa). Furthermore, obvious shear thinning occurs, reaching a minimum viscosity at a critical value

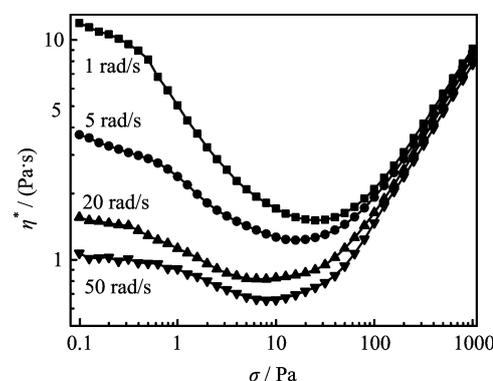


FIG. 2 Complex viscosity as a function of dynamic shear stress at constant solid loading of 40%.

of the oscillatory shear stress amplitude σ_c . Then the suspensions exhibit shear thickening behavior at higher stress, and the complex viscosity jumps to higher value. On the other hand, with the constant decrease in frequencies the shear thinning gets more and more notable, especially for sweeps under the constant frequency of 1 rad/s. It should also be pointed out σ_c shifts to lower value with the increase of constant frequencies. Moreover, in the whole stress region investigated, the more the constant frequencies are applied, the lower the viscosity is.

A typical correlation that the moduli (G' and G'') and $\tan\delta$ *vs.* σ with a constant frequency of 5 rad/s is illustrated in Fig.3. δ is the out-of-phase angle and $\tan\delta$ means the ratio value of G''/G' . It indicates that with the increase of dynamic σ the G' keeps slightly decreasing while the dynamic σ gets nearly to 1 Pa. Then the G' rapidly decreases, reaching a minimum and finally slightly increases. The G'' is independent of σ , but once σ_c is obtained, the G'' shows a dramatic increase to a high value. The $\tan\delta > 1$ indicates that the viscous effects dominate the elastic ones, while $\tan\delta < 1$ indicates that the elastic effects dominate the viscous ones. It is clear from Fig.3 that $\tan\delta$ shows a monotone increase in the range of stress investigated and the $\tan\delta$ increases from 0.6 to 92, which indicates when the transition from elastic to viscous occurs in the system. The system shows elastic characteristics at low stress (lower than 1 Pa) and transitions to viscous characteristics at higher stress (higher than 1 Pa). It is noteworthy to point out that once σ approaches to 100 Pa, $\tan\delta$ steeply jumps to a considerably high value.

Cluster theory can account for the phenomena mentioned above. Because of high hydrophilicity on the PCC particle surfaces and high surface energy, the PCC particles can bond themselves together forming "aggregates" and can be wetted by PEG easily. When they are dispersed in polar liquid PEG, the PEG can be absorbed by the aggregates and the absorbed PEG interacts with other PEG molecules through hydrogen bonds. At considerably low oscillatory shear stress amplitude, the PCC aggregates are prevented from further

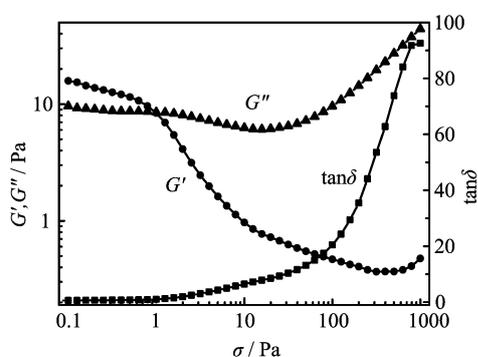


FIG. 3 G' , G'' , and $\tan\delta$ as function of dynamic stress at constant frequency of 5 rad/s.

aggregations by wear steric repulsive force and Brownian force, which keep the system balanced [20] as shown in Fig.2 and Fig.3. From Fig.3 it can be observed that at small stress amplitude (lower than 1 Pa) an equilibrium was obtained and G' keeps constant as the oscillatory shear stress increases. As the hydrodynamic force grows in magnitude, some of the aggregates are disrupted, which results in a decrease in viscosity, and the shear thinning occurs. But in the case that the hydrodynamic force dominates over the repulsive interactions at critical stress amplitude point, clusters are formed [28], composed of compact groups of particles or aggregates with shear forces driving particles nearly into contact [25], which blocks the flow of the fluid [1]. Then the viscosity shows a dramatic increase which corresponds to the shear thickening. The metastable and flow-induced clusters are unstable [29] so the clusters are dispersed in the system upon cessation of the hydrodynamic force, which makes shear thickening reversible.

The main reason for the metastable clusters increasing the viscosity is that the formation of clusters causes an increase of the effective volume fraction of disperse phase [5]. The metastable clusters are the PCC particles or aggregates, which have many holes. These holes would be occupied by the liquid phase and the entire structure would deform as a single entity, thereby increasing the effective volume fraction. The formation of clusters may be related to the suspension exposed to the constant frequency [5,30,31]. It is indicated from Fig.2 that with the increase of frequency the critical stress shifts to a lower value.

B. Dissipated energy

Intending to explore the difference in mechanical properties between thinning and thickening region, the constant frequency was held fixed at 5 rad/s while the maximum oscillatory stress amplitude was increased stepwise and the dynamic oscillatory measurements were analyzed in the following form. The energy dissipated by the shear thinning and thickening fluid can be obtained in terms of integrating the area contained in a plot of stress *vs.* strain for a dynamic oscillatory test. The flow mechanism can be understood from the shape of the resulting stress-strain curve (Lissajous plot). At 0.997 Pa of maximum imposed stress and 5 rad/s of the constant frequency, an elliptical hysteresis loop is recorded as shown in Fig.4. Figure 4 show the data taken at stress amplitude of 0.997 Pa corresponding to maximum strain (0.029) (shear thinning region), 15.84 Pa corresponding to maximum strain (2.78) (the critical shear thickening point), and 501.1 Pa corresponding to maximum strain (22.6) (shear thickening region), respectively. As can be seen, the area enclosed increases with increasing stress amplitude, indicating an increase in viscous dissipation. It can be observed from Fig.4 that the area enclosed increases with increasing

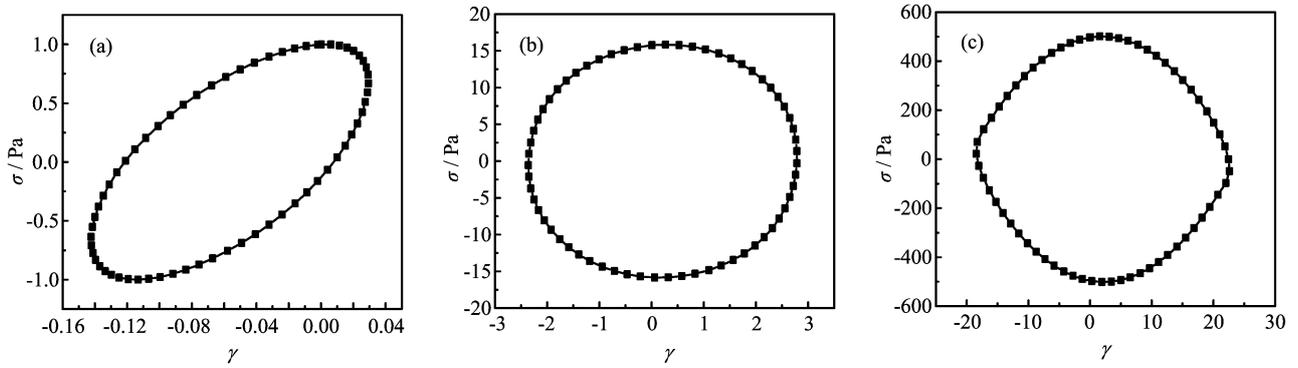


FIG. 4 Lissajous plot for PCC suspension at 40% and constant frequency of 5 rad/s. The applied amplitude of 1 Pa (a), 15.84 Pa at the critical stress (b), and 501.1 Pa above the critical stress (c).

oscillatory stress amplitude, indicating an increase in viscous dissipation. At low stress amplitude (0.997 Pa) the Lissajous loop is an elliptical shape. However with the increase of the stress amplitude the Lissajous loop deviates from an elliptical shape, especially for the maximum imposed stress amplitude (501.1 Pa) above the critical stress.

The dissipated energy E_d during an oscillation cycle can be determined from the Lissajous plot. E_d can be obtained by means of integrating the area contained in a plot of stress *vs.* strain for a dynamic oscillatory test as follows [14,20,32,33]:

$$E_d = \int_{\text{cycle}} \sigma(t) d\gamma = \pi G'' (\gamma_{\max})^2 \quad (2)$$

The relation is valid in the lower strain amplitude. For a linear viscoelastic material, G'' is independent of the maximum strain amplitude γ_{\max} and E_d is a quadratic function of the maximum strain amplitude, but at considerably high strain amplitude, G'' also changes with the γ_{\max} and the system deviates from linear viscoelasticity. An excess E_d is needed because of the shear thickening. E_d scales in strain amplitude as [5]:

$$E_d = K(\gamma_{\max})^\alpha \quad (3)$$

where K is the material constant, $\alpha=2+x$ and the 2 represents the linear viscous contribution, and the additional energy dissipation is quantified by the exponent x which depends on the suspension microstructure such as particle size, nature of the surface and continuous phase and solids concentration.

The relationship between E_d and γ_{\max} for the constant frequency of 5 rad/s (lg-lg plot) is plotted in Fig.5 and shows that the energy is an increasing function of maximum strain amplitude. The slopes at shear thinning and shear thickening region are both determined. The slope in the shear thinning region is 1.91+0.02, approaching to 2, which is consistent with Eq.(2). The results are also in agreement with the results of Wu *et al.* [34]. The system shows the characteristic of linear

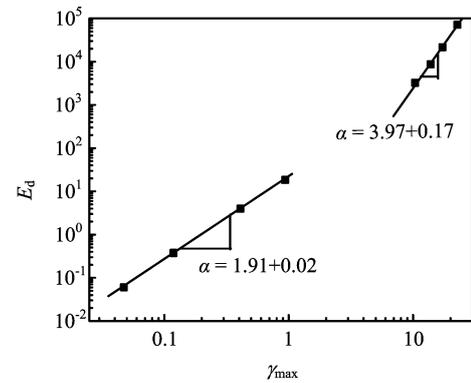


FIG. 5 The relationship between the dissipated energy E_d and the maximum strain amplitude γ_{\max} per a unit volume for one cycle for the constant frequency of 5 rad/s.

viscoelasticity. On the other hand, with the increase of γ_{\max} the slope increases steeply to 3.97+0.17 in shear thickening region, which means that at high γ_{\max} the system is more dissipative, which indicates that the system transits from linear viscoelastic to non-linear viscoelastic.

The results can be also qualitatively accounted for by the cluster theory. In the shear thinning region the system is linearly viscoelastic. The aggregates are disturbed to some extent by hydrodynamic force and plotting the E_d *vs.* γ_{\max} shows a quadratic function as usual. Once the critical stress amplitude is obtained, the clusters are formed which block the flow of the system. The temporary and metastable clusters get bigger and bigger as the hydrodynamic force grows. It can be concluded that power-law exponent of the energy *vs.* strain curve greater than 2 is due to an additional energy dissipation caused by the formation of the clusters in the system.

IV. CONCLUSION

Under different constant frequencies the PCC/PEG suspension of 40% exhibits shear thinning at lower shear stress amplitude and then shear thickening at higher shear stress amplitude. At critical stress amplitude, the occurrence temporary, flow-induced clusters leads to η^* dramatically increasing. The G' and G'' have different relationships over the range of the stress amplitude investigated.

The G' keeps constant at low stress amplitude and then decreases rapidly. The G'' appears to be independent of the stress amplitude at low stress amplitude, but it rapidly increased after reaching the critical stress amplitude. The change of $\tan\delta$ illuminates that the suspension changes from an elastic system to a viscous one. The $\tan\delta$ increases steeply after the stress amplitude gets to the critical stress amplitude.

Under the lower shear stress amplitude the slope of the energy dissipated E_d vs. the maximum strain amplitude γ_{\max} (lg-lg plot) is 1.91, but it jumps to 3.97 in the region of shear thickening. A reasonable explanation is that the formation of clusters due to the hydrodynamic force predominating over repulsive force causes additional energy dissipation.

V. ACKNOWLEDGMENT

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