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Shear Thickening Fluids Based on Additives with Different Concentrations and Molecular Chain Lengths

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Shear thickening fluids (STFs) based on additives with different concentrations and molecular chain lengths were investigated. STF samples were prepared with silica and additive dispersed in polyethylene glycol (PEG) 400, where three types of additives with different molecular chain lengths of PEG4000, PEG6000, and PEG10000 were used. For PEG10000, different concentrations, including 0, 1%, 3%, and 5%, were selected to study the influences of additive concentrations. Rheological properties of the samples were measured with a rheometer. The results show that the shear thickening effect was significantly enhanced with the increase of the concentration and the molecular chain length of additives. The mechanism of enhancement was quantitatively explained with the formation of large particles clusters.

Key words: Shear thickening fluid, Additive, Polyethylene glycol, Concentration, Molecular chain length

I. INTRODUCTION

Shear thickening fluid (STF) is a kind of dispersion whose rheological property takes place an abrupt change when encountering a strike. The apparent viscosity of STF changes so dramatically at a high-speed impact that it may change from suspension to solid-like. Removal of impact, STF reverses its status to liquid-like rapidly again. Thus, the shear thickening effect is a reversible non-Newtonian behavior. A number of groups have conducted intensive studies of STF's rheological properties under steady and dynamical conditions. Steady-state measurement showed that there was a sharp increase in viscosity when shear rate exceeded a critical shear rate, then followed by the viscosity decreasing at higher shear rate [1−5]. Laun *et al.* reported the critical strain amplitude for dynamic shear thickening at a fixed angular frequency of a polymer latex dispersion, and briefly introduced the applications of these dispersions [6]. Raghavan *et al.* investigated the shear thickening response of a fumed silica suspension under steady and oscillatory shear, and the shear thickening behavior could be explained using a clustering mechanism [7]. The reversible shear thickening effect was attributed to hydrocluster mechanism, which

has been demonstrated experimentally through rheological, rheo-optical and neutron experiments [8], as well as computer simulations [9].

Base on the shear thickening effect, STFs have been used in the design of damping and control devices, like mountings for industrial machinery [6, 10]. In recent years, STFs have been exploited in bullet-proof material [11] and shock-proof materials [12, 13].

Rheological properties of STFs depend on a number of influencing factors. One key factor is particle, such as its size [3, 14], interactions [3] and types, which include silica [3−5], titania [15], calcium carbonate [16], and carbon nanofibers [17], *etc.* Another factor is dispersing medium [18, 19]. The interaction between particles and dispersing medium is connected with the molecular chain and functional groups of polymers, with which the performances of dispersion change subsequently [20]. Besides the particles and the dispersing medium, the additive as well as the interaction between particles and additive is another important factor influencing rheological properties of STFs [21]. When the long chains of additive come into contact with surface of bare particles, the bonds of polymer chains are formed between particles. Polymer chains adsorb particles to bind them together through polymer bridging [22, 23]. Owing to the long-range interactions, significant changes in rheological properties of dispersion can be observed.

In this work, silica and polyethylene glycol (PEG) 400 were employed to prepare STF samples, and high molecular weight PEG, in solid state, was used as ad-

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ditive. The rheological properties of STFs were tested by using a rheometer.

II. MATERIALS AND METHODS

A. Materials

The colloidal dispersions were composed of silica and PEG. Silica was used as a dispersed phase. Colloidal silica was prepared through the catalyzing of tetraethyl orthosilicate (TEOS, CP, Sinopharm Chemical Reagent Co., Ltd.) by ammonia solution (AR, 25%, Sinopharm Chemical Reagent Co., Ltd.). The reaction includes the hydrolysis of TEOS and the condensation of silicic acid [24]. Suspension was centrifugated and well washed, then silica was placed in a vacuum oven drying at 25 °C for 24 h prior to use. The dispersing medium was PEG400 (CP, Sinopharm Chemical Reagent Co., Ltd.), whose molecule weight was 400. Three PEG additives with different molecular weights of 4000, 6000 and 10000 were mixed with the PEG400 to form the STF mixture (CP, Sinopharm Chemical Reagent Co., Ltd). Then the mixture was placed in a ball mill grinding up to several hours. The silica was then added into the ball mill in the batches and then grinded for 24 h. All the samples were prepared with silica volume concentrations up to 50% while additive concentrations were 0, 1%, 3%, and 5% by weight, respectively. The STF samples were vacuumed for 2 h prior to rheological measurements.

B. Methods

Silica particles morphology was characterized by scanning electron microscope (SEM) (JEOL, type: JSM-6700F). Rheological properties were measured by using a rheometer (Anton Paar, Physica MCR301) with a cone plate with angle 2.007° and diameter 24.967 mm. In the rheological testing, the angular frequency sweep mode, with the angular frequency logarithmically increasing from 1 s^{-1} to 100 s^{-1} at a constant strain of 3, was employed to study the shear rate dependence on viscosity and modulus [25, 26]. In angular frequency dependent rheological measurement, the shear rate varies
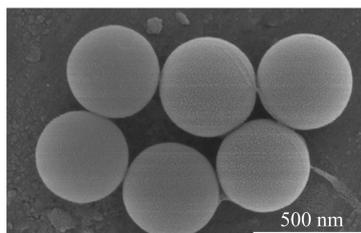

FIG. 1 SEM image of silica.

for each data point and the natural scale of shear rate is $\dot{\gamma}=\gamma_0\omega$ [27, 28]. Thus, the shear rate is swept from 3 s^{-1} to 300 s^{-1}. All the experiments were conducted at the room temperature of 25 °C.

III. RESULTS AND DISCUSSION

A. Characterization of the materials

The SEM image of silica used as the dispersed phase is shown in Fig.1. The particles are spherical and in good monodispersity. The average size of silica particles is about 420 nm. A summary of additive $HO(CH_2CH_2O)_nH$ (PEG4000, PEG6000, and PEG10000) parameters n are about 91, 136, and 227, repectively. The additives' degree of polymerization, n, is proportional to the molecular weight of PEG. The degree of polymerization is the number of repeated structural units in the polymer molecular chain. The larger the degree of polymerization is, the longer the molecular chain length of polymer is. As a consequence, the molecular chain length of additive is directly related to its molecular weight.

B. Rheological properties of STFs

Figure 2 shows the relationship between magnitude of complex viscosity and shear rate for samples at a particle concentration of 50% with PEG10000 at different concentrations: 0, 1%, 3%, and 5%, respectively. The shear rate is logarithmically swept from 3 s^{-1} to 300 s $^{-1}$.

It can be seen from Fig.2 that STF samples show quasi-Newtonian behavior and its magnitude of complex viscosity doesn't change much at relatively low shear rate. For each sample, as the shear rate increased to a critical value, the magnitude of complex viscosity has an abrupt and sharp increase and the onset of
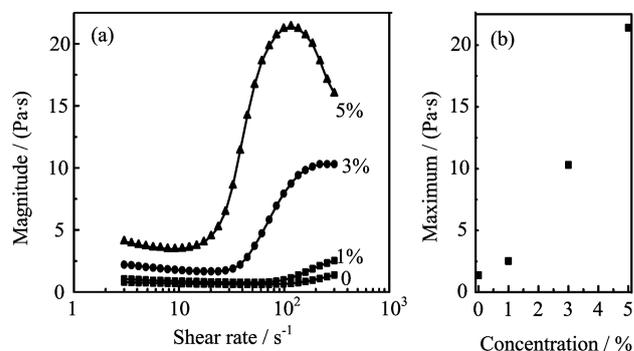

FIG. 2 (a) Magnitude of complex viscosity versus shear rate for samples with additives PEG10000 of different concentrations, and (b) the maximum of complex viscosity versus concentration of additive.

shear thickening occurs. With further increase of the shear rate, the magnitude of complex viscosity would go through a maximum value and then decay. Neglecting the changes of additive's concentration, the shear rate dependence on magnitude of complex viscosity shows a similar trend to results of Ref.[13]. This phenomenon can be explained by the shear rate dependence on microstructures. Because of the high concentration of particles, in the stationary state, particles in the colloidal dispersion are arranged in close-packed hexagonal layer structure. The silanol group on the surface of silica could combine with hydroxyl group in PEG to form hydrogen bond, so there are links among particles. When shear rate is relatively low, acting force on the particle is not strong enough to cause the offset of particle and the structure of dispersion doesn't change much. Accordingly, the magnitude of complex viscosity changes hardly at all and the sample is in a quasi-Newtonian fluid state. With the increase of shear rate up to a critical value, particles begin to move from the initial position and the layer structure is destroyed. As particles move, particles start to aggregate and form the particle clusters along the direction of shear due to the links among particles. With the increase of shear rate, the particle clusters become large and the magnitude of complex viscosity becomes great. The sample transforms from a quasi-Newtonian fluid state to a non-Newtonian fluid state. With the further increase of shear rate, links among particles become unstable because of the breakdown of hydrogen bond, thus the particle clusters begin to break which results in the decrease of magnitude of complex viscosity. Further theoretical and modeling work will be further investigated.

From Fig.2 it can also be seen that at an additive concentration of 1%, the curve of magnitude of complex viscosity versus shear rate is almost the same as that without additives. However, at an concentration of 3% or 5%, the curve of magnitude of complex viscosity versus shear rate is a little higher than that without additive at relatively low shear rate, and is much higher than that without additive at high shear rate. Figure 2(b) shows that the maximum of complex viscosity increases with the concentration of additive obviously. That is to say, with the increase of concentration of additive, the magnitude of complex viscosity obtained after the onset of shear thickening rapidly increases. In other words, the effect of shear thickening is stronger when the concentration of the additive, PEG10000, is larger. The molecular chain length of additive PEG10000 is far longer than that of dispersing medium PEG400, thus the range of particles connected by hydrogen bond is wider. As a result, the particles cluster of network structure is large and the obtained magnitude of complex viscosity is great. This enhanced effect is not obvious when the concentration of additive is very little, but it appears acutely with the increase of additive's concentration.

To further study the influence on additive of the shear

thickening effect, rheological properties of these samples at a particle concentration of 50% with additives at 5% of different molecular lengths: PEG4000, PEG6000, PEG10000, and none of additive, respectively were conducted and shown in Fig.3.

The trends of curves in Fig.3 are similar to those in Fig.2 and earlier works without the consideration of changes of additive's molecular chain length [13]. Irrespective of additive, when shear rate is relatively low, the flow is quasi-Newtonian. When the shear rate reaches a critical value, sample begins to exhibit the shear thickening effect, and magnitude of complex viscosity has a sharp increase. Figure 3 shows the effect of molecular chain length of additive on the viscosity behavior of colloidal dispersion. Magnitude of complex viscosity of sample with additive is slightly higher than that without additive at a relatively low shear rate, and markedly higher at a high shear rate. Figure 3(b) shows directly that the maximum of complex viscosity increases with the degree of polymerization. This suggests that the maximum of complex viscosity increases with the molecular chain length of additive. Therefore, the longer the molecular chain length of additive is, the more obvious the effect of shear thickening is. When the shear rate is relatively low, the long chains of additive would still be in state of flexible polymer coils. On the application of high shear fields, rotation and collision among the particles appear and the flexible polymer chain coils are highly extended. The range of particles connected by the bonds of polymer chains is wide with the long molecular chain, so particles aggregate into the large particle cluster of three-dimensional network structure. The large particle cluster can lead to high resistance to flow and the reached complex viscosity is great. In conclusion, the effect of shear thickening becomes strong with the increase of additive's molecular chain length.

The shear rate dependence of loss modulus of samples with PEG10000 at different concentrations was shown
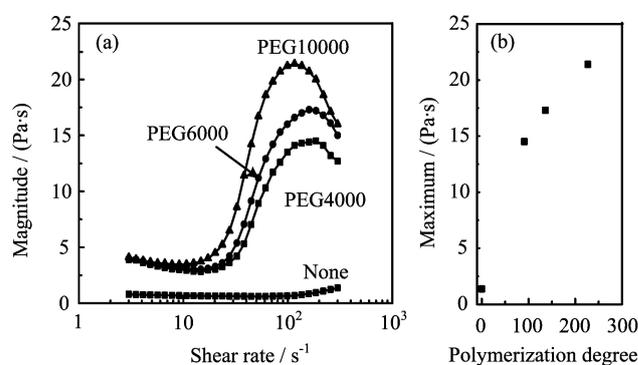

FIG. 3 (a) Magnitude of complex viscosity versus shear rate for samples with additives of different molecular chain lengths, and (b) the maximum of complex viscosity versus degree of polymerization.

in Fig.4. The experimental condition was the same as that in Fig.2. It can be seen that there is a platform of loss modulus at low shear rates, where the loss modulus remains unchanged basically. When the shear rate reaches a certain value, loss modulus begins to increase dramatically. Despite of the variation of additive's concentration, the shear rate dependence on loss modulus in general is in accord with work [13]. However, loss modulus of sample with PEG10000 at 1% changes very little in comparison with that without PEG10000. Moreover the rising trend of loss modulus of sample with PEG10000 at a larger concentration is more striking. The shear rate at which loss modulus begins to increase in Fig.4 is in accordance with that at which magnitude of complex viscosity begins to increase in Fig.2. Loss modulus is caused by viscous flow. When the force on particle reaches a certain value, particle moves from initial position and the relative displacement between particles occurs. Friction among particles becomes strong, and energy dissipation increases. The particle cluster becomes larger with the increase of concentration of additive. The larger the particle cluster is, the greater the energy dissipation is. This leads to the increase of the loss modulus.

Figure 5 shows the shear rate dependence on loss modulus of samples with additives of different molecular chain lengths at 5%. The same experimental condition was applied to that in Fig.3. It can be seen from Fig.5 that loss modulus changes little at low shear rates. When the shear rate exceeds the critical shear rate, loss modulus begins to increase rapidly. This phenomenon resembles the earlier works disregarding of the variation of additive's molecular chain length [13]. Loss modulus of sample with additive is a little larger than that without additive at low shear rate and much larger at higher shear rate. Moreover the longer the molecular chain length is, the sharper the rising trend of loss modulus is. The shear rate at which loss modulus begins to increase in Fig.5 coincides with that at which magnitude of complex viscosity begins to increase in Fig.3. In high shear flied, the extended flexible polymer chain coils cause a

wide range's aggregation of particles connected by bond with the long polymer molecular chain, so a large particle cluster is formed. That is to say, the formation of the large particle cluster is due to the long molecular chain of additive. The larger the particles cluster is, the larger the viscous force and friction among particles is. Consequently, the energy dissipated by viscous forces becomes large. Usually, the dissipated energy will result in large loss modulus. The increase of loss modulus corresponds to the enhancement of damping capacity in practical damping devices.

C. Modeling approach

A power law function, $\tau = k\dot{\gamma}^n$ $(n>1)$, is employed here to describe rheological properties of STF, where n symbolizes a non-Newtonian exponent. The higher the value of n is, the more obvious the non-Newtonian behavior is. When $n=1$, it represents a typical Newtonian fluid.

When the shear rate is relatively low, the shear stress is linear with shear rate and the Newtonian behavior appears. When shear rate exceeds the critical value, shear stress begins to increase sharply in a power-law. The curve changes from a Newtonian platform to a power-law zone. By minimizing errors between experimental results and model-predicting values, the two parameters k and n can be identified. Then the modeling-prediction data can be reconstructed.

Fitting parameters k and n of STFs with different concentrations of additive, PEG10000, are listed in Table I. From Table I it can be seen that the value of n increases with the increase of concentration of additive, PEG10000. When the concentration of PEG10000 gets large, non-Newtonian behavior becomes obvious and the shear thickening effect is strong. This has been demonstrated by experimental results in Fig.2, as the sample with PEG10000 at 5% had the most obvious shear thickening effect.

Fitting parameters k and n of STFs with additives,
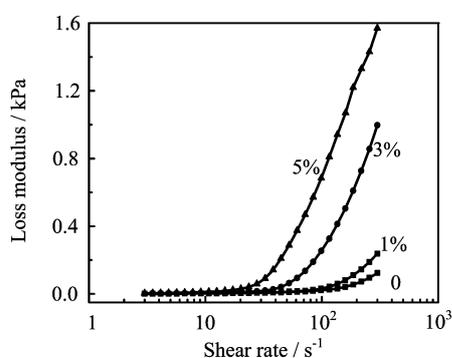

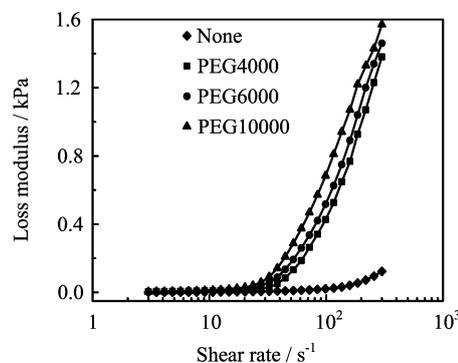FIG. 4 Loss modulus versus shear rate for samples with additives of different concentrations.

FIG. 5 Loss modulus versus shear rate for samples with additives of different molecular chain lengths.

TABLE I Fitting parameters k and n of STF with different concentrations of PEG10000.

Concentration of additive	k	n
0	0.59	1.06
1%	0.62	1.15
3%	0.91	1.35
5%	1.48	1.51

TABLE II Fitting parameters k and n of STF with different additives.

Additive	k	n
None	0.59	1.06
PEG4000	1.25	1.45
PEG6000	1.38	1.47
PEG10000	1.48	1.51

whose molecular chain length are different, are listed in Table II. From Table II it can be seen that the value of n increases with the increase of molecular chain length of additives. In the same conditions, when the molecular chain length of additive gets long, non-Newtonian behavior becomes obvious and the shear thickening effect is strong. This result is in agreement with experimental results in Fig.3, as the sample with PEG10000 had the most obvious shear thickening effect.

IV. CONCLUSION

STF samples with additives of different concentrations and molecular chain lengths were prepared. Their rheological performances were tested. The results indicate that concentration and molecular chain length of additive play important roles in the shear thickening effect.

The samples behave as Newtonian materials at low shear rates. When the shear rate exceeds the critical shear rate, samples exhibit the shear thickening effect. The trend of shear thickening of sample with larger concentration of PEG10000 is more striking, which suggested that the larger the concentration of additive is, the more obvious the shear thickening effect is. The trend of shear thickening of sample with PEG10000 as additive is more striking than that of sample with additive of shorter molecular chain length, which suggested that the longer the molecular chain length of additive is, the stronger the non-Newtonian behavior is and the more obvious the shear thickening effect is. In addition, energy dissipation is greater with the larger concentration and the longer molecular chain length of additive.

V. ACKNOWLEDGMENT

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