A new view on improving the preparation efficiency of shear thickening fluid

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Abstract. In this paper, the relationship of rheological properties, particle size and particle size distribution of dispersed phase silica at different blending times during the preparation of STF was studied in detail. It is found that with the increase of blending time, the initial viscosity \( \eta_0 \) of STF decreases, the critical shear rate \( \gamma_c \) increases, the maximum thickening viscosity \( \eta_m \) decreases, the thickening ratio decreases and the shear thickening effect of the system shows a weakening trend. On the other, the volume average particle size of silica decreases gradually and finally reaches a stable value. The particle size distribution changed from double-interval distribution to single-interval distribution. The variation of shear thickening properties with blending time was explained by combining Cluster and Jamming theory. It is considered that the preparation of STF can be completed when the suspension is transparent and has a uniform viscosity. It is believed that this will play an important role in improving the efficiency of STF preparation and will be of great help to realize industrialized production of STF in the future.

1. Introduction

Shear thickening fluid (STF) is a dense suspension of micron or nanoscale particles dispersed in a polar medium. When subjected to low-speed shearing, the viscosity of this concentrated suspension shows a slight downward trend, and the state is a flowable liquid. When the shear rate exceeds a certain threshold, its viscosity rises sharply with the increase of the shear rate, and the physical state change to a solid state. When the shearing action is undone, it can return to the original liquid state [1-2].

Shear thickening fluid is a new type of intelligent material, which has the characteristics of energy dissipation of liquid and high strength of solid without external electric field or magnetic field. Its application in damping equipment, human body protection, sports equipment and other fields can show significant advantages and broad prospects [3-4]. Especially when shear thickening fluid is combined with high strength fiber fabric, the impact resistance of protective clothing is doubled [5-6].

At present, the preparation methods of STF system are mainly divided into two methods: stirring method and ultrasonic method. Since the dispersed phase silica is mostly nano/micron scale, the volume of silica added to prepare STF is huge. It is generally added step by step, and the addition is continued after the former silica is substantially dissolved. As the viscosity of the system increases, the dissolution rate toward the back becomes slower. The problem is that it often takes a long time to complete the blending. In fact, the shear thickening performance of the system has been clearly observed in the later stages of the overall blending, only waiting for the further homogenization of the blends. In the last stage, it is observed that the initial viscosity of the suspension system decreases continuously. If the viscosity is no longer reduced as the end point of blending, it will take a lot of time,
and it is inconvenient to strictly quantify the viscosity to be stable. In this study, it was found that there is a corresponding relationship of the viscosity of STF and the volume average particle size and blending time in the final blending stage. This article presents a new perspective on improving the efficiency of STF preparation.

2. Materials and Methods

2.1 Materials
Fumed silica nanoparticles (AEROSIL 200) with particle size of 12 nm and specific surface area of 200 m$^2$/g were purchased from Evonik Company. Polyethylene glycol with a molar mass of 200 g/mol (PEG 200) was purchased from Macklin Company. Silica was used as a dispersed phase. PEG used as continuous phase of colloidal suspension.

2.2 Preparation of STF
The STF of silica nanoparticles was prepared by gradually and continuously adding fumed silica nanoparticles into PEG 200, blending by a mechanical agitator and an ultrasonicator (DONGSEN DS-100S) at the same time. The combination of ultrasonic and mechanical agitation can increase blending speed and enhance the blending effect.

The concentration of silica in the suspension was selected 20%. After the silica is completely added, the blending is continued until the STF system has no visible agglomeration meanwhile the STF is colorless and transparent. The STF in this state is defined as the initial 0 minute state. After that, the blending was continued. Pause every 30 minutes, take out the amount needed for characterization, and record the STF as 30 minutes, 60 minutes and 90 minutes respectively. The operation was continued until the rheological properties and volume average particle size characterized tend to remain unchanged.

2.3 Characterization.
The rheological behavior of STF was characterized by Bohlin Gemini HR nano Rotonetic drive 2 Rheometer, using two parallel plates with 20 mm in diameter and 1 mm in gap.

The dispersion state of fumed silica nanoparticles within the PEG as well as the size and the distribution of the aggregates were evaluated by the particle size analyzer: Malvern MS2000 HYDRO 2000MU. Water as dispersing medium.

Scanning electron microscope images were captured by (JEOL JSM-6366LV). The samples prepared for SEM were diluted with alcohol. All samples were deposited on the high conductive silicon wafer.

3. Results and Discussion

![Figure 1. Relationship between viscosity and shear rate at different blending times.](image-url)
Figure 1 shows the relationship between viscosity and shear rate of STF at different blending times. The initial viscosity $\eta_0$ is defined as the system viscosity when the shear rate is equal to 0.1 s$^{-1}$ (large fluctuations in data due to external environmental influences at 0.01 s$^{-1}$), representing the system viscosity at a shear rate close to zero. The critical shear rate $\gamma_c$ is the shear rate corresponding to the trigger time of shear thickening, which indicates the difficulty of shear thickening. The smaller the $\gamma_c$, the easier the shear thickening will occur. The maximum thickening viscosity $\eta_m$ is the maximum after the thickening point, which represents the corresponding viscosity when the shear thickening effect reaches the strongest. The thickening ratio is the ratio of $\eta_m$ to the critical viscosity $\eta_c$ at the critical shear rate $\gamma_c$, indicating the thickening strength of the STF. The data are listed in Table 1.

| time [min] | $\eta_0$ [Pa·s] | $\gamma_c$ [s$^{-1}$] | $\eta_c$ [Pa·s] | $\eta_m$ [Pa·s] | thickening ratio $\eta_m/\eta_c$ |
|------------|------------------|-----------------------|-----------------|-----------------|-------------------------------|
| 0          | 12.366           | 11.991                | 4.0555          | 567.03          | 139.818                       |
| 30         | 9.4090           | 19.093                | 2.9696          | 413.97          | 139.403                       |
| 60         | 7.6601           | 27.064                | 2.3858          | 354.89          | 148.751                       |
| 120        | 5.9824           | 38.363                | 1.9303          | 282.16          | 146.174                       |
| 180        | 3.6037           | 54.378                | 1.6370          | 190.65          | 116.463                       |
| 240        | 2.8260           | 97.257                | 1.2626          | 73.192          | 57.9693                       |
| 270        | 2.7171           | 102.80                | 1.2400          | 53.922          | 43.4855                       |
| 300        | 2.0904           | 195.48                | 0.9190          | 24.722          | 26.9010                       |
| 330        | 2.1095           | 219.40                | 1.0716          | 25.491          | 23.7878                       |

It can be seen from Table 1 that as the blending time increases, the initial viscosity $\eta_0$ of the STF system decreases, the critical shear rate $\gamma_c$ increases, the maximum thickening viscosity $\eta_m$ decreases, and the thickening ratio increases slightly at first and then decreases rapidly. Overall, the shear thickening effect of the system is weakened as the blending time increases. The reason for this phenomenon needs to be explained by combining the average particle size and particle size distribution of silica.

![Figure 2. Curve of volume average particle size versus blending time.](image)

As shown in figure 2, as the blending time increases, the volume average particle size of silica gradually decreases from 4.600 μm to a stable 0.123 μm. The particle sizes of 300 minutes and 330 minutes are almost identical, indicating that the silica dispersion of the system has reached a steady state after blending 300 minutes, no longer changing.
The change trend shows that the slope at both ends is larger, the slope at the middle section is smaller, and the platform area appears approximately. The reason for this phenomenon is that the system has a large particle size agglomeration at the beginning, and the content is massive. Large particle size agglomeration is relatively easy to separate, so the dispersion effect of ultrasonic blending is more obvious, resulting in a rapid decline of average particle size at the beginning. After that, the content of large size silica agglomeration decreases gradually, the average volume size decreases gradually, but the deceleration slowed down. This is because the volume of silica content decreases and the probability of shearing is reduced during stirring. The slow decrease of volume average particle size lasted from 60 minutes to 240 minutes, and then suddenly decreased again. This phenomenon needs to be explained in conjunction with figure 3.

Figure 3. Comparison of particle size distribution under different blending times.

The particle size distribution of STF system for initial 0 minute, middle 180 minutes and final 330 minutes is compared in Figure 3. In fact, the particle size distribution was measured every 30 minutes, and only three time points were selected to indicate the trend. It can be seen that there are two distribution regions of particle size at initial blending time of 0 minute, 0.052~0.55 μm and 3.311~52.481 μm. The volume fraction of the two distribution areas is 74.11% and 25.89% respectively. The peak values of volume fraction were 0.158 μm and 15.136 μm, respectively. After 180 minutes of blending, the volume fraction in the range of 0.052~0.55 μm increased to 92.35%, and the proportion in the range of 3.802~39.811 μm decreased to 7.65%. After 330 minutes of blending, only 0.052~0.275 μm remained in the range of particle size distribution, and the particle size with the largest volume content was 0.105 μm. It can be concluded that the main target of ultrasonic-stirring blending is silica agglomerated particles with a size of more than 1 μm, and particles with a particle size below 0.55 μm are difficult to continue segmentation.

The abrupt increase of the volume average particle size reduction rate in the final stage of blending appearing in figure 2 above, can be explained in conjunction with figure 3. It is attributed to the fact that the volume average particle size presents two distribution regions, and the difference between the large size and the small size is nearly 100 times. The calculation method of the volume average particle size determines that as long as there is a small amount of large particle size distribution, the calculated average value is significantly increased. When the silica agglomeration of large size completely disappears by ultrasonic-stirring blending, the particle size distribution concentrates in the range of 0.052~0.55 μm, and then the average particle size calculated by mathematical formula will suddenly decrease.
The size and distribution of silicon dioxide in figure 3 are confirmed by the SEM images of figure 4. It can be seen that silica dispersed in PEG at 0 minute has a small particle size distribution, but there are large agglomerations in size of micron, and the scale of agglomeration is quite different. After 330 minutes blending, the average particle size decreases obviously, the large agglomeration disappears and the particle size distribution becomes more concentrated.

Referring to figures 2 through 4, the reason why the shear thickening performance in figure 1 decreases as the blending time increases can now be explained. When STF is prepared, the earlier the silica is added, the longer the dispersion time is, the better the dispersion effect is. The silica added later has less time to be subjected to ultrasonic and mechanical shear force, which results in larger particle size, so there are two particle size distribution regions in the system.

However, from the experimental data, the presence of a low content of large particle size agglomeration has an enhanced effect on shear thickening. It can be easily explained by using the existing theory about the particle cluster mechanism and “jamming” [4]. The existence of large particle size occupies a larger space, which can increase the collision probability between particles. It makes the particle cluster easier to form, and the formed particle agglomerates become larger, thereby producing a chain effect. It is more likely to cause “jamming” in a limited space, causing a sharp increase in flow resistance. Macroscopically, the initial viscosity $\eta_0$ of STF increases, the critical shear rate $\gamma_c$ decreases, and the maximum thickening viscosity $\eta_m$ of the system increases. With the increase of blending time, the larger particle size is dispersed, and it is more difficult to occur either in particle clusters or in “jamming”. The effect of shear thickening naturally decreases. However, the specific range of large particle size, and the multiple relationship between small particle size and the content range of the two should be further studied.

In addition, it is worth mentioning that the rheological curves in figure 1 show DST (discontinuous shear thickening) phenomena from the initial 0 minute to the final 330 minutes. Previous researchers believe that CST (continuous shear thickening) phenomena should occur in the particle-solvent system with nano-size and low concentration [7-9]. This is noteworthy, and we will continue to study it in the future.

4. Conclusions
During the preparation of STF was studied in detail, silica can be regarded as the third component additive, and the existence of larger size aggregates is beneficial, which makes it easier for STF to produce clusters and “jamming” phenomenon under the shear action, and effectively enhances the shear thickening performance. The preparation of STF can be completed just by adding to the calculated value and blending until the system is transparent and has uniform viscosity.
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