Rheological characteristics analysis of shear thickening fluids based on response surface methodology

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Abstract

This paper analyzed the influence of various components and the external environment on the rheological properties of shear thickening fluid (STF). The single-factor experimental study was carried out with the silica particle size, the mass fraction of silica particles, the continuous phase’s average molecular weight, and the temperature as the influencing factors. Obtain the influence of various factors on the initial viscosity, critical shear rate, thickening period and thickening ratio of STF samples. According to the crossover relationship between the shear stress and the intermolecular force when the shear thickening occurs, the STF’s critical shear rate criterion is constructed. By introducing the mechanical balance between small molecules, the relationship between the particles’ volume fraction and the distance between particles in the suspension system is established. The influencing factors and formulas of the STF’s critical shear rate and shear capacity are deduced, which supports the conclusions obtained in the single-factor experiment. Based on the single-factor experiment conclusion, the mass fraction of silica particles, the average molecular weight of the continuous phase and the temperature are used as the influencing factors, and the critical shear rate, shear thickening ratio and maximum viscosity are the responses indicators. According to the Box-Behnken response surface methodology (RSM) design, 15 analysis experiments with three factors and three levels are carried out. Obtain the rheological characteristics of the STF and regression equation between each factor, based on the three-dimensional response surface graph and F-value in ANOVA result. We found that among the interaction effects, the interaction between the continuous phase’s average molecular weight and the temperature has the most significant impact on the critical shear rate of the STF. The interaction between the silica particles’ mass fraction and the continuous phase’s average molecular weight significantly impacts the shear thickening ratio of the STF. The interaction between silica particles’ mass fraction and the temperature has the most significant impact on the maximum viscosity of the STF. Finally, according to the response surface methodology experimental results and ideal STF rheological characteristics standard in engineering applications, when the mass fraction of silica particles is 35%, the average molecular weight of the continuous phase is 387, and the temperature is 20 °C. The critical shear rate of the STF system is 5.84 1/s, the shear thickening ratio is 102.8, and the peak viscosity is 1191.7 Pa·s, reaching the optimal theoretical value within the value scope.

1. Introduction

Shear thickening fluid (STF) is a kind of non-Newtonian fluid. When the shear strain rate reaches a certain threshold, the fluid’s viscosity will increase hundreds or even thousands of times instantly, realizing the transition from flowing fluid to quasi-solid state. When the shear stress disappeared, the material formed from quasi-solid to liquid [1]. The adaptability and reversibility of shear thickening fluid make it have broad application prospects in shock absorption and human body protection [2–6]. In recent years, researchers have
carried out a series of studies on the performance characterization [7–10], thickening mechanism [11–13] and practical application [14, 15] of STF and achieved fruitful results.

In STF-related applications, the core function mainly relies on STF’s unique rheological properties [16, 17]. The rheological properties of STF depend on the structure and composition of the system, which can be divided into the following four categories: dispersed phase, continuous phase, additives, and the external environment [18, 19]. Among them, the influencing factors of the dispersed phase include the type, mass fraction, morphology, size, and size distribution of the particles. The continuous phase mainly refers to the carrier fluid for preparing STF, and its influencing factors include type and concentration. Additives mainly refer to solid or liquid substances used to improve the performance of the STF system to modify the surface of the particles, increase the system’s stability, and improve the compatibility between the dispersed phase and the continuous phase [5, 20]. The external environment includes temperature, electric field, magnetic field, etc [21]. Liu [22] et al found that the particle size and content of silica significantly affect the shear thickening behavior, and the critical shear rate decreases as the content of silica particles increases. Li [23] et al indicated that the peak viscosity, loss (G″) and storage (G′) modulus of STFs with more hydroxyl groups and longer chain represented relatively slight change in comparison with the less and shorter ones as the increase of temperature. Aranya [24] et al found that an increase in the average molecular weight of the carrier fluid via the addition of PEG 1000 and PEG 3000 enhanced the dilatant behaviour of STF. Takshak [19] et al adopting Doolittle’s free volume theory approach proposed an empirical equation to describe the relative free volume-dependent viscosity, the shear stress-dependent viscosity, the shear rate-dependent viscosity, and the dimensionless Péclet number-dependent relative viscosity of shear thickening fluids. Liu [25] et al dispersed carbonyl iron powder (CIP) particles a shear thickening fluid, preparing a smart material with both shear thickening effect and magnetorheological properties. Its rheological properties and application potential were tested and analyzed.

Since the shear thickening fluid is a non-Newtonian fluid, there is no single rheological equation that can characterize the entire state of the STF. As the core characteristic of STFs application, the rheological properties’ qualitative change and quantitative prediction method are fundamental. In the current study, it is generally believed that in STF, the higher the viscosity thickening ratio and the earlier the thickening time, the better the product performance [26]. But this is not accurate in practical engineering applications. For example, in the field of protection, researchers pay more attention to the critical shear rate at which shear thickening occurs [27, 28]. Especially in the experiment of high-speed impact, scholars found that the effect of STF was not ideal under the condition of high-speed impact. In addition, in the field of vibration control, scholars pay more attention to the thickening ratio and initial viscosity of STF [29]. This will determine the compression stroke of the damper and the comfort and practicality of seats, vehicles, and medical devices using the damper [30]. Therefore, facing the above problems, we found that it is necessary to refine the rheological properties of STF through different indicators. At the same time, the indexes of rheological characteristics are analyzed by single factor experiment and response surface method, which will provide a reference for the engineering application of STF.

Therefore, some eigenvalues in the viscosity curve of STF are selected as rheological property indicators in this study. And the influence trends of the dispersed phase, continuous phase and external environment on the rheological properties of STF are discussed. The relationship between the intermolecular forces of the STF system was analyzed based on hydrodynamics. The experiment was carried out according to the Box–Behnken response surface design principle. The experimental results were fitted to obtain the weight of the interaction effect of the three factors on the three indicators.

### 2. Experiment preparation

#### 2.1. Material preparation

Materials used to prepare STF include silica particles (99.5%, Aladdin Biochemical Technologies) and polyethylene glycol (Aladdin Biochemical Technologies). To further explore the rheological properties of shear thickened fluid, four kinds of nano-silica particles with different particle sizes were selected as dispersed phases.

| Code | Particle size (nm) | Surface area (m²/g) |
|------|-------------------|---------------------|
| SiO₂−1 | 12 | 325 ±25 |
| SiO₂−2 | 20 | 300 ± 25 |
| SiO₂−3 | 200 | 200 ± 25 |
| SiO₂−4 | 400 | 110 ± 20 |
And three polyethylene glycols with different average molecular weights were selected as the continuous phase for research. The parameters of the chosen silica and polyethylene glycol are shown in tables 1 and 2.

Nano silica particles were dispersed into polyethylene glycol solvent by agitator dispersion instrument (AD500S-H) and stirred at a speed of 2000 r/min for 1 h. After that, an ultrasonic dispersion instrument (GS-010A) was used to conduct ultrasonic vibration on the stirred samples. Then the sample was placed in a vacuum drying oven for 24 h to remove the bubbles, and finally a stable dispersion system was obtained.

2.2. Experimental design

2.2.1. Single-factor impact experimental

To study the influence of various components on STF’s rheological properties, we prepared three types of STF based on the difference in the size of silica particles, the mass fraction of silica particles, and the average molecular weight of polyethylene glycol, as shown in table 3. Through the characterization test, the influence of every single factor on the rheological properties of STF is analyzed.

2.2.2. Multi-factor impact experimental

To evaluate the non-linear relationship between the impact factors, obtain the interaction between the elements and the optimal response value within the range. Based on the single-factor influence test, we take the mass fraction of silica particles, the average molecular weight of the continuous phase, and the temperature as the influencing factors. It takes the critical shear rate, shear thickening ratio, and maximum viscosity as the response indicators. According to the Box-Behnken Principle of Response Surface Design, 15 response surface analysis experiments with three factors and three levels are carried out. The Box-Behnken response surface test design table is shown in table 4.

The response surface design method is explained by the following quadratic polynomial, where \( Y \) is the response index, \( X_i \) and \( X_j \) are independent variables, \( \beta_0 \) is the constant term, \( \beta_{ij} \) and \( \beta_{i} \) are the estimated coefficients in the regression equation, and \( \varepsilon \) is the error. Design expert (Version 8.0.6, Stat-Ease, USA) software was used to design the response surface experiment and analyze the variance of the regression equation.

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{j=1}^{k} \beta_j X_j^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j + \varepsilon
\]

2.3. Testing and characterization

The steady-state rheological properties were measured by Anton-Paar MCR301 advanced rheometer. Conical rotor cp25–2, conical plate radius 25 mm. The upper cone of the rheometer is at an Angle of 2°, and the viscosity of the shear thickening fluid is measured at a shear rate of 0–1000 s\(^{-1}\). In order to eliminate the influence of loading, pre-shear with a shear rate of 1 s\(^{-1}\) for 60 s was applied before data collection. Control the shear rate
of each part of the sheared object to be consistent, only affected by the rotor angular velocity $\Omega$. According to the rotor’s feedback torque $M$, the shear stress $\tau$ is obtained, and the apparent viscosity $\eta$ is finally measured.
Figure 3. STF rheological properties under different mass fractions of silica particles.

Figure 4. STF rheological properties under different average molecular weight of polyethylene glycol.

\[ \dot{\gamma} = \frac{1}{\tan \alpha} \cdot \Omega \]  

(2)
3. Experimental results

In order to visually analyze the rheological properties of shear thickened fluid, several important parameters of rheological curve are selected: the initial viscosity, the critical shear rate, the thickening period T, and the thickening ratio TR. The critical thickening point is determined by the corresponding shear rate, where the slope of the apparent viscosity curve changes significantly, as shown in figure 1.

\[ \tau = \frac{3}{2\pi \cdot R_C} \cdot M \]  
\[ \eta = \frac{\tau}{\gamma} = \frac{3 \tan \alpha}{2\pi R_C^3} \cdot \frac{M}{\Omega} \]

**Figure 5.** STF rheological properties at different temperatures.

\[ T = \gamma_{max} - \gamma_C \]  
\[ TR = \frac{\eta_{max}}{\eta_C} \]

\( \gamma_C \): Shear rate at critical shear thickening point  
\( \eta_C \): Viscosity at critical shear thickening point  
\( \gamma_{max} \): Shear rate at the point of maximum viscosity  
\( \eta_{max} \): Maximum viscosity

3.1. Experimental results of single-factor rheological properties

Figures 2–5 show the influence of each single impact factor on the rheological properties of STF. The effect of the particle size of the silica particles is shown in figure 2. The influence of the mass fraction of silica particles is shown in figure 3, the effect of the average molecular weight of the continuous phase PEG is demonstrated in figure 4, and the impact of temperature is shown in figure 5.

From the viscosity curve of STF, it is not difficult to find that with the increase of shear rate, the viscosity change of the system can be divided into three stages: (1) Shear-thinning stage. The initial viscosity \( \eta_0 \) of STF was kept at a low level, and the apparent viscosity of the system decreased with the increase of the shear rate. This behavior is called the shear-to-thinness phenomenon in the field of non-Newtonian fluids. (2) Shear thickening stage. When the shear rate increases to the critical shear rate \( \gamma_C \), the viscosity of the system is the lowest in the
entire shearing process, subsequently, the viscosity increases sharply and reaches a peak, and STF undergoes a liquid-to-solid conversion at this stage. (3) The steady-state stage. The apparent viscosity of the STF system remained relatively stable after reaching the peak value until slippage occurred.

In figure 2, the silica particle mass fractions of the four STF samples remain unchanged at 25 wt.%, PEG200 is uniformly used as the continuous phase, and the room temperature is maintained at 20 °C. By controlling the size of silica particles, the viscosity curves of STF at particle sizes of 12 nm, 20 nm, 200 nm, and 400 nm were analyzed. According to the experimental data, STF-14 with a silica particle size of 400 nm has the lowest critical shear rate (10.9 1/s) and the highest peak viscosity (1680.8 Pa·s). In contrast, STF-11 with a silica particle size of 12 nm has the highest critical shear rate (31.6 1/s) and the lowest peak viscosity of the system (295 Pa·s). From the data in figure 2, it can be found that the larger the size of the silica particles, the higher the initial viscosity, the lower the critical shear rate, and the higher the peak viscosity of the system. The shear thickening ratio is positively related to the silica particle size. The thickening ratio of STF-14 with a silica particle size of 12 nm is 55.5 times, and the thickening ratio of STF-14 with a 400 nm dispersed phase particle size is as high as 120 times. On the other hand, the length of the shear thickening period is negatively correlated with the size of the silica particles. That is, the STF with larger dispersed phase particles can complete the thickening behavior faster. Therefore, the larger the size of the silica particles, the more evident and rapid the STF thickening system.

In figure 3, the silica particle size of the STF sample is kept at 12 nm, and PEG200 is uniformly used as the continuous phase, and the room temperature is maintained at 20 °C. By adjusting the mass fraction of the dispersed phase particles, the viscosity curve of the STF sample at 10%, 15%, 20%, 25%, and 30% mass fraction was analyzed. The other four samples all showed shear thickening, except for STF-21 with a 10% dispersed phase mass fraction. According to the experimental data, the initial viscosity and thickening ratio of the STF system increase with the increase of the silica mass fraction. The initial viscosity and thickening ratio of STF-25 containing 30 wt.% silica is as high as 28.8 Pa·s and 68 times, which is about 5.5 times and 6 times that of STF-22 containing 15 wt.% silica. The critical shear rate is negatively correlated with the mass fraction. The STF-22 containing 15 wt.% silica has the highest critical shear rate (102.4 1/s). The STF-25 with 30 wt.% silica has the lowest critical shear rate (8.6 1/s).

In figure 4, the silica particle size of the STF sample is maintained at 12 nm, the mass fraction of the dispersed phase is stable at 25%, and the room temperature is maintained at 20 °C. Using polyethylene glycols of different average molecular weights, the influence of the continuous phase on the rheological properties of the STF system was analyzed. It can be found that the higher the average molecular weight of PEG, the greater the overall apparent viscosity of the STF. The initial viscosity and peak viscosity of STF-33 are 38 Pa·s and 946 Pa·s, respectively. In comparison, the initial viscosity and peak viscosity of STF-31 is only 21.6 Pa·s and 295 Pa·s. The initial viscosity and shear thickening ratio are directly proportional to the average molecular weight of the continuous phase. In contrast, the critical shear rate and the length of the thickening stage are inversely proportional to the average molecular weight of the continuous phase. Therefore, the larger the average molecular weight of the continuous phase, the more obvious the thickening effect and the higher the overall viscosity of the system.

In figure 5, keeping the various components of the STF sample unchanged, by changing the temperature of the rheometer, the rheological characteristics of the STF system at 0 °C, 15 °C, 30 °C, 45 °C, and 60 °C are analyzed. It can be found that as the temperature increases, the initial viscosity of the system decreases, and the peak viscosity of the system decreases. As the time of the thickening stage passes, the length of the thickening
period increases. At a temperature of 60 °C, the STF critical shear rate shifted to 102.4 1/s, and the length of the thickening period was 110.1 1/s. It is about 7.7 times and 5.3 times that at 0 °C. Unlike other parameters, the thickening ratio of the system does not show a linear relationship with temperature changes. Instead, it peaked at 30 °C, reaching 36.6 times. Therefore, the increase in temperature will extend the shear thickening time and reduce the peak viscosity. At the same time, to ensure the best thickening effect of the STF system, the ambient temperature must be maintained at a moderate level.

To distinguish the effect of continuous phase rheological properties on STF shear thickening behavior, this paper tested the viscosity curves of pure polyethylene glycol solvents with different average molecular weights. It can be found from figure 6 that the viscosity of pure PEG solvent fluctuates slightly at the beginning of shearing, and then it is smooth, without shearing thickening. Therefore, the possibility of the shear thickening behavior of PEG solvent is ruled out.

3.2. Experimental results of multi-factor rheological properties

Based on the Ben-Behnken response surface design table, a 3-factor 3-level response surface analysis was performed on the shear thickening system. The silica particles in each STF system are controlled to be constant at 12 nm. The mass fraction of silica particles, the average molecular weight of the continuous phase, and the temperature are the influencing factors. The critical shear rate, the shear thickening ratio, and the maximum viscosity are the response indicators. The Ben-Behnken response surface design scheme and results are shown in table 5.

| Code | Silica concentration (wt.%) | Continuous phase average molecular | Temperature (°C) | Critical shear rate (1/s) | Shear thickening ratio | Maximum viscosity (Pa·s) |
|------|----------------------------|-----------------------------------|-----------------|--------------------------|-----------------------|------------------------|
| 1    | 30                         | 200                               | 20              | 8.6                      | 62                    | 1057                   |
| 2    | 35                         | 600                               | 40              | 11.4                     | 98.5                  | 289                    |
| 3    | 35                         | 200                               | 40              | 16.8                     | 56.3                  | 234                    |
| 4    | 25                         | 400                               | 60              | 81                       | 29                    | 103                    |
| 5    | 25                         | 200                               | 40              | 67                       | 31                    | 158                    |
| 6    | 25                         | 400                               | 20              | 24.5                     | 58.7                  | 730                    |
| 7    | 30                         | 600                               | 20              | 7.9                      | 97                    | 1147                   |
| 8    | 35                         | 400                               | 20              | 7                        | 102.8                 | 1287                   |
| 9    | 30                         | 400                               | 40              | 18                       | 49.4                  | 229                    |
| 10   | 30                         | 400                               | 40              | 17.7                     | 50                    | 227                    |
| 11   | 30                         | 400                               | 40              | 16.2                     | 48.5                  | 224                    |
| 12   | 25                         | 600                               | 40              | 22                       | 42.5                  | 207.3                  |
| 13   | 30                         | 200                               | 60              | 78                       | 34                    | 115                    |
| 14   | 35                         | 400                               | 60              | 27.3                     | 53                    | 156                    |
| 15   | 30                         | 600                               | 60              | 30.2                     | 45                    | 126                    |

4. Discussion

4.1. Analysis of the interaction between particles in the STF

In the suspension, the particles are affected by the interaction between the particles, showing two phenomena of dispersion and aggregation. In order to explore the mechanism of the thickening phenomenon, this paper analyzes the force between the dispersed particles in the STF system from the perspective of the interaction between particles. In the absence of external influences, the distribution of dispersed particles in the STF is mainly affected by the Brownian motion between the particles, van der Waals forces, and electrostatic repulsion on the surface of the particles [31]. The Brownian motion and the electrostatic repulsion between the particles tend to disperse the silica particles, and the Van der Waals force tends to aggregate the particles. Under external influences, the distribution of dispersed particles in the STF system is also affected by the lubricating force between the particles, which tends to aggregate the particles.

The van der Waals force between particles is the collective action of multiple atoms or molecules. The van der Waals forces between spherical particles with radius $R_1$ and $R_2$ are shown below. Where $F_{\text{van der Waals}}$ is the van der Waals force, $H$ is the distance between particles, $A$ is the Hamaker constant of the particles in vacuum, and $R_1$ and $R_2$ are the radius of spherical particles. In most cases, the adsorption layer on the surface of the particles in the dispersion system will increase the distance between the particles. At the same time, the Hamaker
constant of the adsorption layer material is usually smaller than the solid particles, so the van der Waals force between the particles is reduced [32]. In a shear thickening system with nano-silica as the dispersed phase and polyethylene glycol as the continuous phase, the van der Waals force between the nanoparticles can be ignored [33].

When the silica particles approach each other in the shear thickening suspension, and the electric double layers overlap, the homogeneous particles repel each other. At this time, an electrostatic repulsive force [34] is generated in the STF system, as shown in (8). Where \( \epsilon_0 \) is the vacuum dielectric constant, \( \epsilon_r \) is the relative dielectric constant, \( \psi_0 \) is the surface potential of the particle sphere, \( \kappa \) is the thickness of the electric double layer, \( a \) is the particle radius, and \( h \) is the distance between the two particles. Assuming that the distance \( h \) between two particles is tiny, (8) can be simplified to (9)

\[
F_{\text{rep}} = 2\pi \epsilon_0 \epsilon_r \psi_0^2 \frac{\kappa a \exp(-\kappa h)}{1 \pm \exp(-\kappa h)}
\]

(8)

\[
F_{\text{rep}} = \frac{2\pi \epsilon_0 \epsilon_r \psi_0^2 \kappa a}{2}
\]

(9)

After the STF is subjected to shearing, particles in laminar flow generate a lubricating force due to the removal of the fluid. The magnitude of the force is related to the distance between particles, liquid viscosity, shear rate and particle size, and the formula is shown in (10). Where \( F_{\text{hydrodynamic}} \) is the lubricating force, \( \eta_0 \) is the viscosity of the dispersion medium, \( a \) is the particle radius, \( \dot{\gamma} \) is the shear rate, and \( h \) is the distance between particles.

\[
F_{\text{hydrodynamic}} = \frac{6\pi \eta_0 a^2 \dot{\gamma}}{h}
\]

(10)

In summary, in the absence of external effects or low shear rate, the dispersed phase particles in STF are mainly affected by electrostatic repulsion, maintaining a stable layered structure distribution. As the shear rate increases, the lubricating force between particles increases, and the shear force the dispersed particles to leave their original stable positions. The stable layered structure in STF transforms to a disordered structure, thereby increasing the system’s viscosity. When the repulsive force between particles (9) and the intermolecular lubricating force (10) produced by shear are equal, the STF system is in the critical state of shear thickening transition, and the shear rate at this time is the critical shear rate.

\[
\dot{\gamma}_c = \frac{2\pi \epsilon_0 \epsilon_r \psi_0^2}{6\pi \eta_0 a} \cdot \frac{k}{2} \cdot \frac{h}{a}
\]

(11)

According to formula (11), the value of the critical shear rate is related to the particle size of the dispersed phase, the viscosity of the dispersion medium, and the ratio of the distance between particles in the dispersion system to the particle size \((h/a)\). Since particle concentration is one of the important controlling factors in the preparation of STF, it is of great significance to derive the relationship between the distance \( h \) between particles and the volume fraction \( \phi \). Based on the suspension shear thickening theory of Hoffman [35–37] et al, the
minimum distance between two particles in the same regular symmetric layer is assumed to be equal to the minimum distance between particles in adjacent layers. As shown in figure 7, the distance \(h\) between molecules is defined. According to the assumption, \(h = h_1 = h_2 = h_3\). The volume of the dispersed phase particles in the unit is \(2/3 \cdot \pi a^3\), and the volume of the unit interval is \(\sqrt{3}/4 \cdot (2a + h)^3\). The volume fraction of the dispersed phase in the suspension and the critical shear rate are shown below.

\[
\phi = \frac{2/3 \cdot \pi a^3}{\sqrt{3}/4 \cdot (2a + h)^3} = \frac{8\pi a^3}{3\sqrt{3} (2a + h)^3}
\]

(12)

### Table 6. The fitted model equations.

\[
Y_1 = 17.3 - 16.5A - 12.36B + 21.06C + 9.9AB - 9.05AC - 11.78BC + 7.89A^2 + 4.11B^2 + 9.76C^2
\]

\[
Y_2 = 49.3 + 18.68A + 12.46B - 19.94C + 7.68AB - 5.02AC - 6BC + 4.58A^2 + 3.2B^2 + 7C^2
\]

\[
Y_3 = 346.77 + 104.81A + 16.45B - 440.26C - 7.68AB - 5.02AC - 6BC + 4.58A^2 + 3.2B^2 + 7C^2
\]

**Y**: Critical shear rate; **Y**: Shear thickening ratio; **Y**: Maximum viscosity.

### Table 7. ANOVA result of response surface quadratic model for responses: Critical shear rate (\(Y_1\)), Shear thickening ratio (\(Y_2\)), Maximum viscosity (\(Y_3\)).

| Source                        | Sum of squares | DF | Mean square | F-value | P-value | Remarks |
|-------------------------------|----------------|----|-------------|---------|---------|---------|
| **ANOVA result of critical shear rate** |                |     |             |         |         |         |
| Model                         | 8795.37        | 9   | 977.26      | 112.12  | <0.0001 | Significant |
| A- Silica concentration       | 2178           | 1   | 2178        | 249.87  | 0.0006  | Significant |
| B- Continuous phase average molecular | 1222.65       | 1   | 1222.65     | 140.27  | 0.0013  | Significant |
| C-Temperature                 | 3549.03        | 1   | 3549.03     | 407.16  | <0.0001 | Significant |
| AB                            | 392.04         | 1   | 392.04      | 44.98   | 0.0011  | Significant |
| AC                            | 327.61         | 1   | 327.61      | 37.59   | 0.0017  | Significant |
| BC                            | 554.60         | 1   | 554.60      | 63.63   | 0.0005  | Significant |
| A^2                           | 229.71         | 1   | 229.71      | 26.35   | 0.0037  | Significant |
| B^2                           | 62.45          | 1   | 62.45       | 7.16    | 0.044   | Significant |
| C^2                           | 351.90         | 1   | 351.90      | 40.37   | 0.0014  | Significant |
| Residual                      | 43.58          | 5   | 8.72        |         |         |         |
| Lack of fit                   | 41.72          | 3   | 13.91       | 14.95   | 0.0633  | Not significant |
| Cor Total                     | 8838.95        | 14  |             |         |         |         |

| **ANOVA result of shear thickening ratio** |                |     |             |         |         |         |
| Model                         | 7955.68        | 9   | 883.96      | 145.37  | <0.0001 | Significant |
| A- Silica concentration       | 2790.04        | 1   | 2790.04     | 459.46  | <0.0001 | Significant |
| B- Continuous phase average molecular | 1242.51       | 1   | 1242.51     | 204.61  | <0.0001 | Significant |
| C-Temperature                 | 3180.03        | 1   | 3180.03     | 523.68  | <0.0001 | Significant |
| AB                            | 235.62         | 1   | 235.62      | 38.8    | 0.0016  | Significant |
| AC                            | 101            | 1   | 101         | 16.63   | 0.0096  | Significant |
| BC                            | 144            | 1   | 144         | 23.71   | 0.0046  | Significant |
| A^2                           | 77.28          | 1   | 77.28       | 12.73   | 0.0161  | Significant |
| B^2                           | 37.81          | 1   | 37.81       | 6.23    | 0.0548  | Not significant |
| C^2                           | 180.92         | 1   | 180.92      | 29.79   | 0.0028  | Significant |
| Residual                      | 43.58          | 5   | 8.72        |         |         |         |
| Lack of fit                   | 29.22          | 3   | 9.74        | 17.09   | 0.0538  | Not significant |
| Cor Total                     | 7986.04        | 14  |             |         |         |         |

| **ANOVA result of maximum viscosity** |                |     |             |         |         |         |
| Model                         | 1892000        | 9   | 210200      | 5066.33 | <0.0001 | Significant |
| A- Silica concentration       | 87885.28       | 1   | 87885.28    | 2117.88 | <0.0001 | Significant |
| B- Continuous phase average molecular | 2164.82       | 1   | 2164.82     | 52.17   | 0.0008  | Significant |
| C-Temperature                 | 1551000        | 1   | 1551000     | 37367.88| <0.0001 | Significant |
| AB                            | 117.72         | 1   | 117.72      | 2.84    | 0.1529  | Not significant |
| AC                            | 23901.16       | 1   | 23901.16    | 575.98  | <0.0001 | Significant |
| BC                            | 205.92         | 1   | 205.92      | 4.96    | 0.0764  | Not significant |
| A^2                           | 1337.6         | 1   | 1337.6      | 32.23   | 0.0024  | Significant |
| B^2                           | 501.85         | 1   | 501.85      | 12.09   | 0.0177  | Significant |
| C^2                           | 219000         | 1   | 219000      | 5287.6  | <0.0001 | Significant |
| Residual                      | 207.48         | 5   | 41.5        |         |         |         |
| Lack of fit                   | 194.56         | 3   | 64.85       | 10.03   | 0.092   | Not significant |
| Cor Total                     | 1892000        | 14  |             |         |         |         |
According to the analysis of the interaction force between the particles of the STF system, the critical shear rate of the shear thickening suspension can be explained by the formula (15), and the $F_{\text{hydrodynamic}}$ expression can explain the sudden increase in the viscosity of the system. In figure 2, as the silica particles increase from 12 nm to 400 nm, according to formula (15), the particle size increases and the critical shear rate $\gamma_c$ decreases. When the shear rate continues to increase beyond the critical point, the $F_{\text{hydrodynamic}}$ lubricating force increases with the particle size $a$, so the thickening effect of the shear thickening system is more obvious, the thickening ratio is higher, and the thickening period is short. In figure 3, the silica particles size and continuous phase of the STF sample remain unchanged, and the mass fraction of silica particles gradually increases from 10% to 30%. According to formula (15), the particle concentration $\phi$ increases, so the critical shear rate $\gamma_c$ decreases. In figure 4, the silica particles size is kept at 12 nm, the mass fraction of the dispersed phase is stable at 25%, and the average molecular weight of polyethylene glycol is changed. In figure 6, PEG 200 has the lowest apparent viscosity, and PEG 400 has the highest. According to formula (15), the viscosity of the dispersion medium $\eta_0$ increases with the continuous phase change, so the critical shear rate $\gamma_c$ decreases. When the shear rate continues to increase beyond the critical point, the $F_{\text{hydrodynamic}}$ lubricating force increases with the dispersion medium viscosity $\eta_0$, so the thickening ratio of the shear thickening system is high, and the thickening period is short.

It can be seen from figure 5 that the increase of temperature will increase the critical shear rate, increase the thickening time and decrease the thickening ratio of the shear thickening fluid. This is because the increase of temperature will lead to a significant decrease in the viscosity of polyethylene glycol, and the Brownian motion of nano silica particles and dispersed solvent molecules is more intense, and the repulsion between small molecules increases. In the process of shear thickening, the silica particles need to accumulate stronger dynamic contact to form particle clusters. Therefore, the increase of temperature affects the occurrence time and effect of shear thickening.

According to the grouping results of Ben-Behnken response surface design factors, the experimental data is subjected to quadratic polynomial fitting response surface analysis based on Design expert software (8.0.6, State-Ease, USA). Through data fitting, analyze the effect of silica particle mass fraction (A), continuous phase average molecular weight (B) and temperature (C) on the critical shear rate ($Y_1$), shear thickening ratio ($Y_2$) and maximum viscosity ($Y_3$). The regression equation is shown in table 6.

The regression equations affected by the critical shear rate ($Y_1$), shear thickening ratio ($Y_2$) and maximum viscosity ($Y_3$) are tested for variance, as shown in table 7. According to the model P-value, the model regression of the three response indexes of critical shear rate ($Y_1$), shear thickening ratio ($Y_2$) and maximum viscosity ($Y_3$) is highly significant ($P < 0.01$), and the lack of fit term is not significant ($P > 0.05$). The determination coefficient $R^2$ of the critical shear rate model is 99.51%, the adjustment determination coefficient $R^2_{\text{adj}}$ is 98.62%, and the prediction determination coefficient $R^2_{\text{pred}}$ is 92.40%. The determination coefficient $R^2$ of the shear thickening ratio model is 99.62%, the adjustment determination coefficient $R^2_{\text{adj}}$ is 98.94%, and the predicted determination coefficient $R^2_{\text{pred}}$ is 94.11%. The coefficient of determination $R^2$ of the maximum viscosity model is 99.79%, the coefficient of adjustment $R^2_{\text{adj}}$ is 98.76%, and the coefficient of determination of prediction $R^2_{\text{pred}}$ is 96.83%. It shows that the three models are established, the functional relationship is significant, and the model fits well.

According to the F-value in the variance test, the order of the influence of the three factors on the critical shear rate ($Y_1$), shear thickening ratio ($Y_2$), and maximum viscosity ($Y_3$) three response indicators is: temperature (C) > silica particles mass fraction (A) > average molecular weight of continuous phase (B). Meanwhile, we can sort the influence weight of a single factor and interactive factor of each index according to the f-value of the ANOVA result. In the analysis of the critical shear rate, the ratio of single factor influencing the level of silica particles mass fraction (A): continuous phase average molecular (b): temperature (c) is 1.8:1.2:9. The weight order of interaction factors is BC > AB > AC. The weight ratio is 1.2:1.7 (AB:AC:BC). In the analysis of the shear thickening ratio, the ratio of single factor influencing the level of A: B: C is 2.2 : 1 : 2.6. The weight order of interaction factors is AB > BC > AC. The weight ratio is 2.3:1:1.4 (AB:AC:BC). In the analysis of the maximum
viscosity, the ratio of single factor influencing the level of A: B: C is 40.6 : 1 : 716. The weight order of interaction factors is AC > BC > AB. The weight ratio is 1:202.8:1.7 (AB:AC:BC). Understanding the weight of single factor and interactive multi-factor can enable us to set schemes for different rheological indexes of STF faster when preparing STF with different standard characteristics.

Based on the results of response surface analysis, the three-dimensional interaction surface and contour lines of silica particle mass fraction, continuous phase average molecular weight, and temperature are drawn. In a three-dimensional response surface, the greater the surface slope, the more pronounced the interaction of the other two factors when a specific factor is fixed. The smoother the surface, the smaller the interaction of the two factors. It can be seen from figures 8–10 that the interaction between the average molecular weight of the continuous phase and the temperature has the most significant impact on the critical shear rate. The interaction between the mass fraction of silica particles and the average molecular weight of the continuous phase has the greatest effect on the shear thickening ratio. The interaction between the mass fraction of silica particles and temperature has the greatest impact on the maximum viscosity of the STF.

The optimal condition is confirmed through the software optimization module to find the extreme value of the response index. Since there are three response indicators, the best conditions in different response indicators are different. The desirability indicator is used to resolve conflicts between various indicators and find the best experimental conditions. The ideal STF system should have a low critical shear rate, high shear thickening ratio, and high peak viscosity in engineering applications. According to the desirability index, when the mass fraction of silica particles is 35%, the average molecular weight of the continuous phase is 387, and the temperature is 20 °C, the STF system has a critical shear rate of 5.84 1/s, a shear thickening ratio of 102.8, and a peak value of 1191.7 Pa·s, reaching the theoretical optimal value in the range of variable scope.
5. Conclusion

In order to analyze the rheological properties of the STF, this paper uses nano-silica and polyethylene glycol as the dispersed and continuous phases to prepare STF. Using silica particle size, silica particle mass fraction, continuous phase average molecular weight and temperature as the influencing factors, carry out single-factor influence research. Through the interaction between particles in the STF system, the critical shear rate formula of the STF is derived. Based on the single-factor experiment conclusion, the mass fraction of silica particles, the average molecular weight of the continuous phase and the temperature are used as the influencing factors, and the critical shear rate, shear thickening ratio and maximum viscosity are the responses indicators. According to the Box-Behnken response surface methodology (RSM) design, 15 analysis experiments with three factors and three levels are carried out. The regression equation between the index and each factor is solved by fitting. Finally, the interaction between the factors and the theoretical optimal value of the index is obtained. The specific conclusions are as follows:

1) In the single-factor experiment, the larger the size of the silica particles, the more evident and rapid the thickening effect of the STF system, the higher the initial viscosity, the lower the critical shear rate, and the higher the peak viscosity. The initial viscosity and thickening ratio of the STF is positively correlated with the silica mass fraction, and the critical shear rate is negatively correlated with the mass fraction. The larger the average molecular mass of the continuous phase, the more obvious the thickening effect and the higher the overall viscosity of the system. As the temperature increases, the initial viscosity of the system decreases, and the peak viscosity of the system decreases. As the time of the thickening phase is delayed, the length of the thickening period increases. Unlike other parameters, the thickening ratio of the system does not show a linear relationship with temperature changes, and it peaks at 30 °C, reaching 36.6 times. Therefore, in order to ensure the best thickening effect of the STF, the ambient temperature must be kept moderate.

2) In the STF system, when the repulsive force between the dispersed phase and the intermolecular lubricating force generated by shear are equal, the STF system is in a critical state when the shear thickening behaviour occurs. By introducing the mechanical equilibrium between small molecules, the relationship between the volume fraction of the dispersed phase and the distance between the dispersed phases in the suspension system is established. The critical shear rate formula of the STF system is deduced, which supports the conclusions obtained in the single-factor experiment.

3) Perform quadratic equation fitting analysis on the results of the Ben-Behnken response surface design test. Obtain the regression equation of silica particle mass fraction, continuous phase average molecular weight and temperature that responds to the critical shear rate, shear thickening ratio and maximum viscosity. According to the results of the variance test obtained from the regression equation, it can be seen that the order of the influence of the three factors on the three response indicators is: temperature > silica particle mass fraction > continuous phase average molecular weight. Based on the interaction three-dimensional surface diagram and the F-value, it can be seen that the weight order of interaction factors on critical shear rate is BC > AB > AC. The weight ratio is 1.2:1:1.7 (AB:AC:BC). The weight order of interaction factors on shear thickening ratio is AB > BC > AC. The weight ratio is 2.3:1:1.4 (AB:AC:BC). The weight order of interaction factors on maximum viscosity is AC > BC > AB. The weight ratio is 1:202.8:1.7 (AB:AC:BC). Finally, according to the ideal rheological characteristics of STF in engineering applications, the optimal STF is theoretically obtained within the variable range.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Declaration of conflicting interests

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References

[1] Zhao C et al 2020 Shear stiffening gels for intelligent anti-impact applications Cell Reports Physical Science 100266
[2] Gürgen S, Kushan M C and Li W 2017 Shear thickening fluids in protective applications: a review Prog. Polym. Sci. 78 48–72
[3] Zhang S et al 2018 Conductive shear thickening gel/polyurethane sponge: a flexible human motion detection sensor with excellent safeguarding performance Composites Part A: Applied Science and Manufacturing 112 197–206
[4] Sen S et al 2019 Numerical investigation of ballistic performance of shear thickening fluid (STF)-Kevlar composite Int. J. Mech. Sci. 164 105174
[5] Santos T F et al 2019 Influence of silane coupling agent on shear thickening fluids (STF) for personal protection Journal of Materials Research and Technology 8 4032–9
[6] Mawkhrieng U and Majumdar A 2020 Deconstructing the role of shear thickening fluid in enhancing the impact resistance of high-performance fabrics Composites Part B: Engineering 175 107167
[7] Chen K et al 2017 A hybrid molecular dynamics study on the non-Newtonian rheological behaviors of shear thickening fluid J. Colloid Interface Sci. 497 376–84
[8] Ge J et al 2018 The rheological properties of shear thickening fluid reinforced with SiC nanowires Results in Physics 7 3369–72
[9] Gong X et al 2017 Squeeze flow behavior of shear thickening fluid under constant volume Smart Mater. Struct. 26 065017
[10] Gürgen S, Li W and Kushan M C 2016 The rheology of shear thickening fluids with various ceramic particle additives Mater. Des. 104 312–9
[11] Cao S et al 2018 Stress relaxation in the transition from shear thinning to shear jamming in shear thickening fluid Smart Mater. Struct. 27 085013
[12] Haddie E K and Chen J 2019 Shear and extensional rheological characterization of thickened fluid for dysphagia management J. Food Eng. 245 18–23
[13] Liu M et al 2018 Shear thickening fluid with tunable structural colors Smart Mater. Struct. 27 095012
[14] Gürgen S and Kushan M C 2017 The ballistic performance of aramid-based fabrics impregnated with multi-phase shear thickening fluids Polym. Test. 64 296–306
[15] Gürgen S and Sofuoğlu M A 2019 Experimental investigation on vibration characteristics of shear thickening fluid filled CFRP tubes Compos. Struct. 226 111236
[16] Sheikh M R and Gürgen S 2022 Anti-impact design of multi-layer composites enhanced by shear thickening fluid Compos. Struct. 279 114794
[17] Nagy-György P and Hsiao C 2021 Predicting the damping characteristics of vibration dampers employing generalized shear thickening fluids J. Sound Vib. 506 116116
[18] Khodadadi A et al 2021 Impact characteristics of soft composites using shear thickening fluid and natural rubber—a review of current status Compos. Struct. 271 114092
[19] Shenude T, Niwas V J and Babai M 2021 An empirical equation for shear viscosity of shear thickening fluids J. Mol. Liq. 325 115220
[20] Fan Z et al 2020 Enhanced magnetic abrasive finishing of Ti–6Al–4V using shear thickening fluids additives Precis. Eng. 64 300–6
[21] Fu K et al 2020 Rheological and energy absorption characteristics of a concentrated shear thickening fluid at various temperatures Int. J. Impact Eng. 139 103525
[22] Liu L et al 2020 The influences of rheological property on the impact performance of kevlar fabrics impregnated with SiO2//PEG shear thickening fluid Thin-Walled Structures 151 106717
[23] Li D et al 2020 Effect of dispersing media and temperature on inter-yarn frictional properties of Kevlar fabrics impregnated with shear thickening fluid Compos. Struct. 249 112557
[24] Ghosh A, Majumdar A and Butola B S 2020 Modulating the rheological response of shear thickening fluids by variation in molecular weight of carrier fluid and its correlation with impact resistance of treated p-aramid fabrics Polym. Test. 91 106830
[25] Liu B et al 2022 Mechanical properties of magneto-sensitive shear thickening fluid absorber and application potential in a vehicle Composites Part A: Applied Science and Manufacturing 154 106782
[26] Zhang Q et al 2021 Processing technology and ballistic-resistant mechanism of shear thickening fluid/high-performance fiber-reinforced composites: a review Compos. Struct. 326 113806
[27] Mishra V D et al 2022 Ballistic impact performance of UHMWFP fabric impregnated with shear thickening fluid nanocomposite Compos. Struct. 281 114991
[28] Liu H et al 2022 High-impact resistant hybrid sandwich panel filled with shear thickening fluid Compos. Struct. 284 115208
[29] Zhao Q et al 2021 Vibration control of a rotor system by shear thickening fluid dampers J. Sound Vib. 494 115883
[30] Lin K et al 2020 Shear thickening fluid damper and its application to vibration mitigation of stay cable Structures 26 214–23
[31] Guy B M, Hermes M and Poon W C K 2015 Towards a unified description of the rheology of hard–particle suspensions Phys. Rev. Lett. 115 088304
[32] Emelyanenko K A, Emelyanenko A M and Boinovich L B 2019 Van der Waals forces in free and wetting liquid films Adv. Colloid Interface Sci. 269 357–69
[33] Raghavan S R, Walls H J and Khan S A 2000 Rheology of silica dispersions in organic liquids: new evidence for solvation forces dictated by hydrogen bonding Langmuir 16 7920–30
[34] Watanabe H et al 1998 Nonlinear rheology and flow-induced structure in a concentrated spherical silica suspension Rheol. Acta 37 1–6
[35] Hoffman R L 1972 Discontinuous and dilatant viscosity behavior in concentrated suspensions. I. observation of a flow instability Trans. Soc. Rheol. 16 155–73
[36] Hoffman R L 1974 Discontinuous and dilatant viscosity behavior in concentrated suspensions. II. Theory and experimental tests Journal of Colloid & Interface Science 46 491–506
[37] Hoffman R L 1982 Discontinuous and dilatant viscosity behavior in concentrated suspensions. III. Necessary conditions for their occurrence in viscometric flows Advances in Colloid & Interface Science 17 161–84