

## THE INFLUENCE OF CARBON NANOTUBE ADDITION ON THE SHEAR-THICKENING PERFORMANCE OF SUSPENSIONS

by

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*The shear thickening fluid as a protective material has received increasing attention, and its impact resistance and its rheological properties are controllable by integrating various kinds of additives to a single phase shear thickening fluid. In this paper, the rheological properties of shear thickening fluids with 26 wt.% fume silica, PEG200 and different mass fraction of multi-walled carbon nanotubes are investigated, and the effect of temperature from  $-5$  °C to  $55$  °C on steady state rheological properties of 1.0 wt.% multi-walled carbon nanotubes reinforced shear thickening fluids is studied. Finally a single yarn pull-out test is conducted to examine the influence of multi-shear thickening fluid on the shear strength and inter-yarn friction of fabrics. The results show that the addition of multi-walled carbon nanotubes can improve significantly the viscosity and shear thickening efficiency.*

Key words: *shear thickening fluids, rheology properties, viscosity, yarn pull-out*

### Introduction

Shear thickening fluid (STF) is a dense colloidal suspension liquid, whose viscosity increases abruptly as shear thickening occurs, and fabrics treated with STF are promising in impact resistance applications [1-3], such as in the high-tech fields of the body armor for ballistic and stab impact resistance [4, 5], the industry fields of vibration mitigation or shock absorbance [6]. The mechanisms of STF proposed so far are mainly the order-to-disorder theory [7-9], the hydro cluster theory [10-13], and the jamming theory [14-16], and all the three theories are based on the suspensions of single phases in a carrier liquid.

In recent years, due to the increasing interests to the applications of STF to energy absorption, amounts of other additives such as harder particles or functional nano particles were added into the silica and polyethylene glycol (PEG) based suspensions [17-22] to fabricate the multi-phase STF for tuning of rheological properties of STF, which gained considerable attention world widely. For increasing the ballistic performance, the multi-phase STF were fabricated by silicon carbide, silica and PEG [22-25], and demonstrated that the properties of additives had significant influence on the ballistic performance of multi-STF treated fabric. In the view of the contact rheology model [26], the stress transmission under high velocity impact is realized through contact interactions with particle interactions. In addition, the

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numerical modeling of the fabrics treated with multi-phase STF showed that the energy absorption capacity of the treated specimen was enhanced. Nakonieczna, *et al.* [2] reported that compared with the silica STF, the STF reinforced by CNT increased the ability of absorbing impact force. Ghosh *et al.* [18] studied the shear thickening phenomenon of adding cellulose nanofibers (CNF) into silica based STF and found that the hydroxyl groups of additives play an important role in enhancing the interaction between disperse phases. Ge *et al.* [22] studied the effect of SiC nanowires on the rheological behavior of STF and found that shear thickening viscosity increased almost 30% compared to that of the pure STF. Gurgen *et al.* [27] reported that the thickening behavior of silica based STF could be disrupted by adding SiC of different particle size. Laha *et al.* [28] demonstrated that more intense shear thickening behavior occurred in silica and silica-halloysite nanotube based STF than that of pure STF.

These previous works [17-28] showed that for utilizing STF in various fields, the tuning of rheological properties can be realized by integrating various kinds of additives to single phase STF. Moreover, the interactions between dispersed phases are also important to the rheological properties of STF. Based on those previous works, we explored the chemical structure of multi-phase STF consisting of MWCNT in the view of the hydroxyl groups and the interaction between disperse phase and disperse medium in this study according to the order-disorder theory [7, 9] and contact rheology model [26]. In addition, the influence of additives of MWCNT on the rheological behaviors of STF and the friction between the yarns of STF/UHMWPE fabrics are studied. The effect of temperature on the rheological properties of the CNT, silica and PEG STF were analyzed through rheological tests.

## Materials and methods

### Materials

The materials included fumed silica (Aladdin, Shanghai, China), with a specific surface area of 150 m<sup>2</sup>/g and an average particle size of 50-100 nm, multi-walled CNT (Aladdin, Shanghai, China), with diameter of 10-30 nm and length of 10-30 μm and PEG 200 (PEG200) (Sinopharm Chemical Reagent Co., Ltd, China) with molecular weight of 200, density of 1.125 g/cm<sup>3</sup> and purity of 99%. The fumed silica and multi-walled CNT were tested by using a Quanta-450-FEG field emission scanning electron. The UHMWPE plain woven fabric used in the test with a thickness of 0.59 mm and aerial mass of 240 g/m.

### Preparation of multiphase STF and composites

The STF were obtained by mixing fumed silica of 26 wt.% with polypropylene glycol-200 in the ultrasonic oscillator, lately the MWCNT with the amounts of 0.4, 0.6, 0.8, and 1.0 wt.% were added in the silica/PEG200 STF to form different multiphase STF by ultrasonic dispersing method. Then the composites were fabricated by impregnation of the UHMWPE plain woven fabric with the multiphase STF, as shown in fig. 1.

### Rheological measurements and single yarn pull-out tests

A stress-controlled rheometer with a cone plate system (MCR302, Anton Paar GmbH, Austria) is used to evaluate the rheological behaviors of multiphase STF. The diameter of the top cone and the cone angle is 25 mm and 2°, respectively, and the gap is 0.103 mm. The shear rate was increased from 0 s<sup>-1</sup> to 1000 s<sup>-1</sup> to obtain the thickening characteristic of the sample. The viscosity measurements were carried out at -5 °C, 5 °C, 15 °C, 25 °C, 35 °C, 45 °C, and 55 °C,

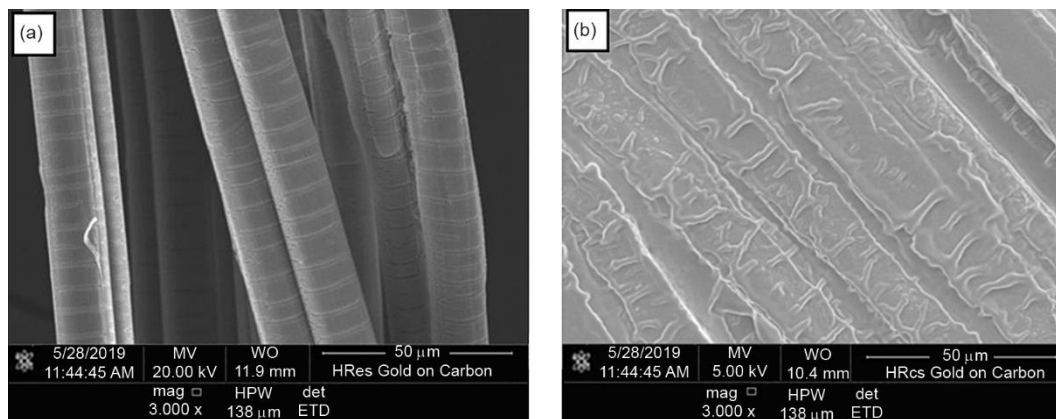


Figure 1. The SEM images of (a) neat UHMWPE fabric and (b) CNT/SiO<sub>2</sub>/PEG200/UHMWPE fabric

respectively, by the temperature-control device of the rheometer. The single yarn pull-out test is a direct way to evaluate the influence of STF on the friction between the yarns of STF/UHMWPE fabrics. The tests were conducted using INSTRON 5565 machine at the temperature of 25 °C with a tensile rate of 25 mm per minute.

## Results and discussion

### Steady state rheological analysis of MWCNT/silica STF

The viscosity versus shear strain rate curves of STF MWCNT, silica and PEG200 STF shown in fig. 2 indicate that each curve follows the same trend: the initial shear thinning, shear thickening onset beyond a critical shear rate and shear thinning. However, with the increase of mass fraction of MWCNT, the initial viscosity and the peak viscosity are increasing and the critical shearing rate is decreasing. The critical shearing rate of the silica STF is about 91.3 s<sup>-1</sup>, and the critical shearing rate of the STF with MWCNT is 73 s<sup>-1</sup>, 37 s<sup>-1</sup>, 19 s<sup>-1</sup>, and 15 s<sup>-1</sup>, respectively. From fig. 2, it is evident that the 1.0% MWCNT/silica STF showed the optimal shear thickening behavior.

Schematic representation of hydro cluster formation for MWCNT/silica STF is shown in fig. 3. It can be seen that the inter-particle distances are reduced with the addition of MWCNT in the suspension, and more binding sites to form hydrogen bond are provided in STF by the interaction between the hydroxyl groups of the MWCNT and the silanol group of silica, and between the ether oxygen radicals of PEG molecules and silica nanoparticles. The entanglement of the hydrogen bonds between two disperse phases and PEG forms *big particles group* in STF. When the STF at low shear rate, the silica particles and MWCNT were randomly suspended in the PEG200 in the form of big particles group and single particle at equi-

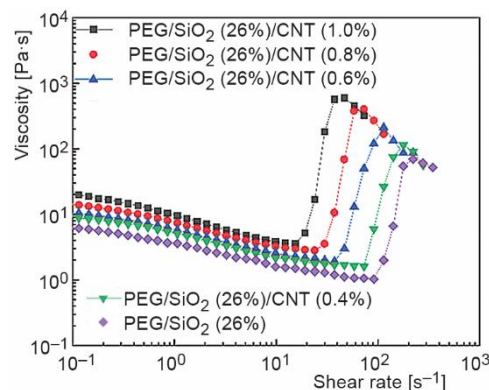
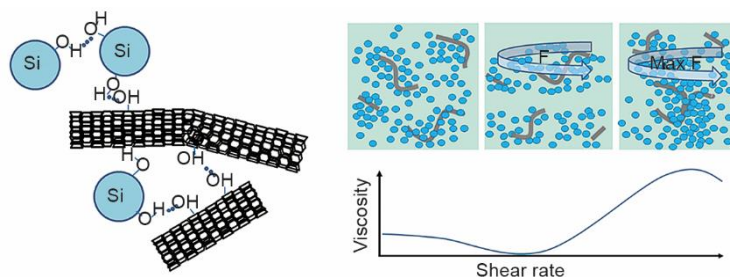


Figure 2. Rheological curves of STF based on 26 wt.% fumed silica and different mass fraction of MWCNT

librium as shown in fig. 3. As the shear rate increases, the equilibrium is disrupted, and the inter-particle repulsive forces acted on the big particles group and particles led to shear thinning exhibited as reduction of viscosity. As seen in fig. 3, the MWCNT can be regarded as a rope shape with a high length-diameter ratio, which facilitates forming the interactions between fume silicas and MWCNT in the multi-phase STF and the formation of contact networks in the suspension. When shear thickening onset, these particle contact points work together to enhance the STF viscosity. In addition, With the increase of the mass fraction of MWCNT, the number of the big particles group formed by the entangled silica and MWCNT increases in the STF, and extended contact networks strengthened by additive MWCNT provides more powerful contact forces. In view of contact rheology model, dense suspensions caused by additive MWCNT bring strong physical contacts of particles and the stress transmission in particles makes the major contribution to the viscosity increase.



**Figure 3. Schematic representation of hydro cluster formation for MWCNT/silica STF**

As represented in fig. 2, with the increasing of MWCNT mass fraction, the critical shear rate reduced significantly. The reason is that each particle can be considered as a subunit of the big particles group as shown in fig. 3, and the force networks are extended with the increasing of the big particles group amount, which is prominent in strengthening of shear thickening by the contact forces. Therefore, the particle agglomerations in the suspension become easier. In addition, because the existing of hydrogen bonds among PEG, MWCNT and silica, the disperse phases can be distributed randomly in the dispersing medium and the aggregation occurs more easily with the existing of the big particles group. In addition, the high aspect ratio of MWCNT had more possibility to contact the silica particles by interlocking to bear the external force from slipping and collapsing in the flow field. It can be exhibited by the lower critical shear rate required to occur shear thickening. All of this cause the shear thickening phenomenon of MWCNT/SiO<sub>2</sub>/PEG STF. With the shear rate increasing, the physical contacts of big particles group are increased, until the big particles group begin to split under the increasing force resulting in the collapse of the jamming clusters, then shear thinning to occur. It can be seen that the thickening ratio increases with the increasing of the mass fraction of MWCNT. It is related with the decreased average distance between silica nanoparticles due to the entanglement of MWCNT and silicas, and the MWCNT with a large aspect ratio contribute to more hydroxyl groups to participate in the forming of the hydrogen bonds between particles in the STF. It can be concluded that the additive of MWCNT in the suspension promotes the formation of particle clusters, resulting in the increased size and number of the hydro-clusters, and the agglomeration behavior is more easily to occur.

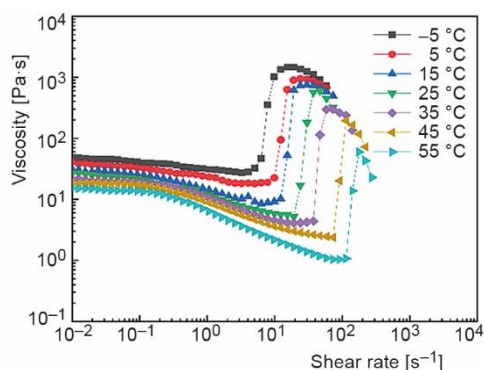
*The influence of temperature on the steady-state rheological properties of MWCNT/silica STF*

Figure 4 illustrates the characteristic of the rheological properties of 1.0% MWCNT/silica STF in temperature range of  $-5\text{ }^{\circ}\text{C}$  to  $55\text{ }^{\circ}\text{C}$ . It can be clearly seen that with the increase of temperature, the critical shear rates increase and the peak viscosity decreases. At  $-5\text{ }^{\circ}\text{C}$ , the peak viscosity of the suspension is  $1460\text{ Pa}\cdot\text{s}$ , which is 2.45 times higher than that of  $25\text{ }^{\circ}\text{C}$ , and the critical shear rate reduces from  $114\text{ s}^{-1}$  at  $55\text{ }^{\circ}\text{C}$  to  $5.07\text{ s}^{-1}$  at  $-5\text{ }^{\circ}\text{C}$ .

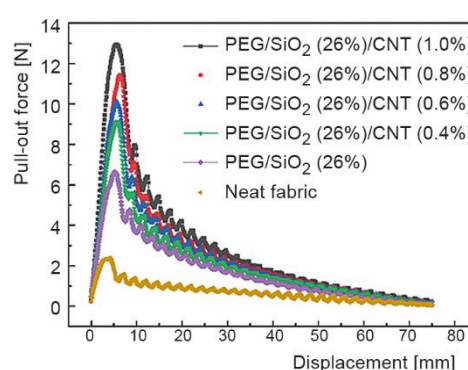
The reason is that the increasing temperature accelerates the rate of molecular motion and diffusion, the Brownian motion becomes stronger. As a result, the distance between molecules increases and the repulsive forces among particles are enhanced, and the particles aggregation become harder. The hydrogen bond interactions between silica particle, CNT and PEG were weakened. Therefore, to trigger particles aggregation forming *hydro clusters* require stronger hydrodynamic force corresponding to a higher shear rate, and the reduced viscosity of STF. In addition, it is clearly observed that the second shear thinning in the curve of reinforced STF at temperatures higher than  $25\text{ }^{\circ}\text{C}$  became sharp compared with that the curves at lower temperatures in fig. 4. It is related with the weakening of strength of hydrogen bonds due to high temperature. Therefore, strong hydro-dynamic forces could easily break the weak hydro-clusters formed by the limited hydrodynamic lubrication force, then the particle clusters began to collapse. As fig. 4 shows, the viscosity of the reinforced STF during the second shear thinning decreased quickly with the temperature increase.

*Pull-out test of fabrics impregnated MWCNT/silica STF*

From the previous works focused on the application of STF, it can be deduced that the energy absorption of fabrics is closely related to the inter-yarn friction, which can be evaluated by yarn pull-out tests. For comparing the influence of additive MWCNT on the inter-yarn friction of STF treated fabrics, the single yarn pull-out tests were carried out on the neat UHMWPE and UHMWPE treated by different STF. The force-displacement curves are shown in fig. 5.



**Figure 4. Viscosity curves of 1.0% MWCNT/silica STF from  $-5\text{ }^{\circ}\text{C}$  to  $55\text{ }^{\circ}\text{C}$**



**Figure 5. Pulling out force vs. displacement curve of UHMWPE fabrics treated different STF**

With the increase of the mass fraction ratio of CNT, the pull-out force of fabrics increased obviously in fig. 5, meaning that the inter-yarn friction of treated fabrics can be influenced prominently by the rheological properties of STF. The maximum pull-out force of

SiO<sub>2</sub>/PEG STF treated UHMWPE fabrics is about three times than that of the neat one of 2.3 N. Compared to neat fabric and the SiO<sub>2</sub>/PEG STF impregnated fabrics, the inter-yarn friction of the 1.0% CNT/SiO<sub>2</sub>/PEG STF treated fabrics were significantly enhanced exhibiting by a maximum pull-out force of 13 N as shown in fig. 5. It can be used to reflect the interlocking of fibers and yarns of fabric treated with STF. Figure 5 shows that the reinforced STF with CNTs is better at increasing the friction between the yarns during slipping, and each oscillation due to stick-slip motion is higher than that of the SiO<sub>2</sub>/PEG STF. These results indicated that the increasing number of MWCNT enhances the frictional forces between particles, which shows increase in the pull-out force.

### Discussion and conclusions

There might exist an alternative approach to study of the rheological property of the STF, for example, the fractal rheological model [29-32], the magnetic Reiner-Rivlin model [33], the Walters' B model [34], and Rabinowitsch model [35].

In the paper, MWCNT as disperse phase was added to the silica based STF to prepare multi-phase STF using for stab resistance materials. It is observed that the addition of MWCNT increases the peak viscosity and decreases the critical shearing rate effectively. The inter-yarn friction and the pull-out energy dissipation of multi-phase STF treated fabrics were well improved, especially the 1.0% CNT/SiO<sub>2</sub>/PEG STF. The addition of MWCNT to the silica based STF had obvious influence on the rheological properties and the enhancement of the pull-out forces.

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