Preparation, characterization and properties of shear thickening fluid impregnated fabric composites

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Abstract: Shear thickening is a non-Newtonian flow behavior characterized by the increase of viscosity with the increase in applied shear rate. Due to this remarkable property of shear thickening fluid (STF), it has received extensively attention in armor protection fields. Through a process of impregnation, the STF in body armor has allowed further enhancement without hindering the flexibility of fabrics, which has led to the development of the concept of liquid body armor. In this paper, the STFs were prepared by mechanical stirring of silica nanoparticles dispersed in liquid polyethylene glycol. The rheological properties of as-prepared STFs were tested. Aramid and ultra-high molecular weight polyethylene fabrics were soaked in STF/ethanol solution to make STF/fabric composites. Knife quasi-static penetration tests were performed on the neat fabrics and STF/fabric composite targets for engineered knife on areal density basis. The results showed that compared with the neat fabrics, the STF impregnated fabrics exhibited better penetration resistance without affecting the fabric flexibility.

1. Introduction
Body armor is the defensive covering worn to protect the human body from injury in the battle field and other unsafe situations[1]. With the development of firearms, the weaponry has been consistently developed in order to become more effective and powerful for combat, and in conjunction, protection against such weapons has also been pursued. Nowadays, body armors are mainly of two types, namely hard armor and soft armor[2]. Hard body armors contain metal or ceramic plates, consequently making the armor hard and heavy, which restrict the movements of body parts of the wearer. Soft body armors are made of multiple layers of woven or laminated fabrics, and they are lighter in weight. Despite the low density, high strength and high energy characteristics of these fabrics, since 30-50 layers of fabrics are used in making them meet the protection requirements, the resulting products are lack of comfort. Over the years many attempts have been tried to improve the properties of body armors[3].

The idea of making flexible body armor has been around for some time. Compared to conventional body armor, liquid body armor system has been recently studied due to its lightweight, high flexibility and reduced layered fabric. During the last decade, liquid body armor based on the inclusion of shear thickening fluid (STF) has been intensively studied[4-8]. STF is a non-Newtonian fluid with remarkable properties. The STF behaves like a liquid when no forces applied, and it turns into a very stiff solid-like structure in the presence of high shear rates. The STF has been used in combination with protective fabrics to improve their ballistic, stab, and puncture protective properties[9-10]. Wagner et al
reported the ballistic penetration performance of composite composed of woven Kevlar fabric impregnated with a colloidal STF (57 vol.% of 450 nm silica in ethylene glycol)\cite{11}. The results demonstrated a significant enhancement in ballistic penetration resistance due to the addition of STF, without any loss in material flexibility. Kalman et al investigated the effects of particle hardness on the impact performance of STF treated fabrics by synthesizing a dispersion of polymethyl methacrylate (PMMA) particles\cite{12}. SEM micrographs of the damaged zone showed that, unlike the silica STF, the softer PMMA particles did not abrade the Kevlar. The ballistic results showed that the softer PMMA particles led to a reduced performance in comparison to the harder silica dispersions. Srivastava et al studied the influence of padding pressure and silica concentration in STF (40-60 wt.% of 278 nm silica in polyethylene glycol) on add-on%, yarn pull out force and impact energy absorption\cite{13}. The results confirmed the improvement in impact energy absorption capacity of Kevlar fabrics using STF. Kang et al developed an advanced stab proof material composed of STF (20 wt.% of fumed silica in ethylene glycol) and Kevlar fabrics\cite{14}. The STF impregnation significantly improved the stab resistance of Kevlar fabric against spike threats. Although a lot of interests have been shown by researchers in application of STF on body armor materials, some of the key application parameters like particle features have not been studied methodically.

In this study, silica nanoparticles in narrow size distribution were prepared by the modified Stöber method and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). A STF with high particle concentration (70 wt.%) was prepared by mechanical stirring of silica nanoparticles dispersed in liquid polyethylene glycol. Meanwhile, the effects of STF on the impact performance of treated Kevlar and ultra-high molecular weight polyethylene fabrics were also studied.

2. Experimental

2.1. Materials
Tetraethoxysilane [TEOS, 98%, Aladdin], absolute ethanol [99.9%, Aladdin], ammonium hydroxide [25%, Aladdin], polyethylene glycol (PEG) with molecular weight of 200 g mol\(^{-1}\) [PEG200, 98%, Aladdin] were directly used without any further purification process.

The fabrics used in the tests are plain-woven aramid and ultra-high molecular weight polyethylene (UHMWPE) fabrics. The aramid fabrics are purchased from DuPont Company (Kevlar 129, areal density of 200 g/m\(^2\)), and the UHMEPE fabrics (areal density of 180 g/m\(^2\)) used in this study are supplied by Hunan Zhongtai Special Equipment Co., Ltd., China.

2.2. Preparation of STF
The silica particles were synthesized using the modified Stöber method through hydrolysis of TEOS in ammonia solution. A certain amount of deionized water, absolute ethyl alcohol and ammonium hydroxide were mixed in a three-necked flask and stirred for 30 min. Then TEOS was added into the flask and the reaction was conducted for 6 h in a 50°C thermostatic waterbath. The silica particles were obtained by centrifuging and washing at room temperature. The colloid was dried in the vacuum oven for 24 h to remove the residual ethyl alcohol. At last, the product was heated to 800°C for a period to get the pure silica powder.

The STF was prepared by mechanical mixing method. The silica particles were added into the PEG slowly according to the weight percentage. The mixing process was kept for several hours until the particles were dispersed in the PEG fluid uniformly. To improve the stability of the fluid, the STF was put into the vacuum oven at 25°C and dried for about 24 h to remove the bubble.

2.3. Materials Characterization
The shape, size and size distribution of particles were characterized by SEM (QUANTA 200). The wide-angle XRD patterns of the particles were recorded using the X-ray diffractometer (PANalytical, X’Pert Pro). The functional groups on silica powders were detected by FT-IR (Thermo, ANTARIS II).
The rheological characterizations of the prepared STF were conducted by a rheometer (TA Instruments, Discovery HR-2). Steady rheological property refers to the relationship between viscosity and shear rate. Tests were carried out at 25°C in a steady flowing mode in the shear rate range of 0.01-1000 s⁻¹ with parallel plates having a diameter of 20 mm, and the gap size between the two plates was 0.50 mm.

2.4. Preparation of STF Treated Fabrics
The STF/fabric composites were prepared by impregnating process. Before impregnation, ethanol was added to decrease the surface tension of the dispersion to enable it to wet the fabric (STF: ethanol = 1:2). A high speed homogenizer was used to make the dispersion. The impregnation of the target was done by soaking the fabric specimen in the STF/ethanol solution for 10 min. The wet fabrics were squeezed using a 2-roll mangle to get rid of the excess amount of the solution and then the fabrics were put into the vacuum oven at 80°C for 2 h. At last, the STF treated fabrics were sealed as a unit with polyethylene film for later use.

2.5. Impact Resistance Tests
The test equipment was self-designed based on the universal tester (Instron 5966), as shown in Fig. 1. The knife was P1 blade used in National Institute of Justice (NIJ) of United States. One layer of fabric was clamped in a ring clamp with the outside diameter of 15 cm and the inner diameter of 5 cm. A sufficient force was used to clamp the specimen in order to avoid its slippage. Then the impactor was pushed into the center of the target at a rate of 200 mm/min. The data of load versus displacement was recorded during the impact process.

![Fig. 1 The test instruments for impact resistance](image)

3. Results and Discussion

3.1. Characterization of Silica Particles
Fig. 2 shows the SEM image of prepared silica particles. It can be seen that the particles exhibited the spherical shape and monodispersed with narrow size distribution. The average particle size of silica was about 200–300 nm. No obvious agglomeration was observed from these images.

The phase composition of silica particles can be deduced from XRD pattern. Fig. 3 shows the XRD pattern with only one broad amorphous diffraction peak in the range of 20-30°, which is the characteristic peak of silica. It is clear that the prepared silica is amorphous.
Fig. 2 SEM picture of silica particles
Fig. 3 XRD pattern of silica particles

Fig. 4 shows the FT-IR spectrum of silica particles. At the wave number of 795 cm\(^{-1}\) and 1055 cm\(^{-1}\), these are the symmetric vibration and asymmetric vibration of Si-O. The wave number of 950 cm\(^{-1}\) is the stretching vibration of Si-OH. The band at 1631 cm\(^{-1}\) is attributed to the vibration of O-H groups, which arise from the adsorption water by Si-OH. In the FT-IR spectrum, the absorption peaks of the anti-symmetric O-H bonds of the silicon hydroxyl groups and the bound water were not observed near 3419 cm\(^{-1}\), indicating that the hydroxyl content in the particles was low. Therefore, the prepared silica particles were hydrophobic.

3.2. Rheological Properties of STF

The rheological result of the prepared STF is shown in Fig. 5. As can be seen from the curves of viscosity and shear stress versus shear rate, the prepared STF showed distinct discontinuous shear thickening behaviors. A slight shear thinning behavior was observed initially when the shear rate was below the critical value, in which the viscosity decreased with increasing the shear rate. However, the viscosity then increased dramatically (shear thickening) when the shear rate was higher than the critical value. The maximum viscosity of the STF was up to about 650 Pa·s.

Fig. 5 The rheological curve of STF
3.3. Test Results of Impact Resistance
The test results of impact resistance are shown in Fig. 6. As can be seen in Fig. 6, the fabrics treated by STF supported a much higher loads than neat fabrics. After impregnation, the puncture strength of aramid fabrics increased from 14.1 N to 57.5 N (Fig. 6a). Although the area density of the fabric had also increased by about 30% (from 200 g/m² to 260 g/m²), the impact resistance performance of STF treated aramid with the same areal density as neat fabric was significantly improved by more than 3 times.

Fig. 6 Force-displacement curves for impact resistance test of neat fabric and STF treated fabrics
As for STF/UHMWPE fabric composites, similar results can also be obtained (Fig. 6b). The puncture strength of UHMWPE fabrics increased from 13.7 N to 22.7 N, and the impact resistance performance of STF treated fabric with the same areal density as neat fabric was improved by 18.5%. Compared with that of STF/aramid fabric, the impact performance of STF/UHMWPE fabric was not greatly improved. This may be due to the poor surface activity of the UHMWPE fibers as well as the chemical inertness. It was difficult to form an adequate infiltration with STF.

3.4. Micrographs of STF/Fabric Composites
SEM micrographs for aramid fabrics and STF/aramid composite can be seen in Fig. 7. The fibers in neat aramid fabrics showed a smooth appearance (Fig. 7a). However, the fibers in STF treated fabrics exhibited a quite different morphology. As can be seen from Fig. 7b, spherical-shaped silica particles were found to be on the fibers or embedded into the gaps between the fiber bundles.

Fig. 7 SEM pictures of neat aramid fabric (a) and STF/aramid composite (b)
According to the hydrocluster theory\(^{(15)}\), when the STF was impacted, the dispersed phase particles tended to aggregate, resulting in a rapid increase in the viscosity of the liquid. In this study, when the knife pierced the composite, the silica particles in the STF would form particle clusters between the aramid fiber bundles and on the fiber surfaces, resulting the increase in the friction between the fibers, thereby preventing the fibers from slipping and then absorbing more impact energy. At the same time, as a hard ceramic material, silica could also play a role in grinding the knife. These should be the reasons for the increased impact resistance of STF/fabric composites.

4. Conclusions
In this study, spherical and monodispersed silica nanoparticles in narrow size distribution were prepared by modified Stöber method. The XRD and FT-IR characterization showed that the particles
were hydrophobic silica with amorphous state. The STF with high particle concentration (70 wt.%) was prepared by dispersing silica nanoparticles in liquid PEG, which exhibited distinct discontinuous shear thickening behaviors. The maximum viscosity of the obtained STF was up to about 650 Pa·s. The STF/fabric composites were prepared by impregnating the aramid and UHMWPE fabrics in STF/ethanol solution. Knife quasi-static penetration tests indicated that the fabrics treated by STF had better impact resistance without affecting the fabric flexibility. Compared with that of neat fabric in the same areal density, the impact resistance performance of STF/aramid was significantly improved by more than 3 times.

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