Effect of multi-phase STF on the high-speed impact performance of shear-thickening fluid (STF)-impregnated Kevlar Composite Fabrics

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Abstract. Shear thickening is a non-Newtonian flow behavior, characterized by an increase in viscosity with the applied shear rate. Due to this superior performance of shear thickening fluid (STF), it has received a great deal of attention in the field of armor protection. In this paper, the properties of nanoscale silica STF systems are modified by the addition of nanocellulose (CNF). The rheological properties of the prepared STFs were tested. Kevlar fabrics were immersed in multiphase STF solutions to make STF/fabric composites. The results showed that the addition of nanocellulose (CNF) enhanced the steady-state and dynamic aspects of the shear-thickening fluid. The rheological properties of the shear-thickening fluid were strongest when the content of nanocellulose added was 0.2%, and the single yarn extraction force of the Kevlar composite was much stronger than that of the pure Kevlar without STF. The CNF-modified STF enhances the impact resistance of the composite.

1. Introduction
Shear thickening fluid (STF) is a dense suspension whose viscosity increases rapidly with increasing shear rate or shear stress. When subjected to a high-velocity impact, STFs change from a liquid to a solid-state and return to their initial liquid state when the external force is removed [1,2]. Many national and international research institutes are engaged in the study of STFs for puncture-resistant products. Wagner et al. reported the ballistic penetration properties of composites consisting of Kevlar woven fabrics impregnated with colloidal STF (57 volume % of 450 nm silica in ethylene glycol) [3]. The results showed a significant improvement in ballistic penetration due to the addition of STF, without any loss of flexibility of the material. Inspired by Wagner, Lee et al. conducted an in-depth study on the mechanical properties of Kevlar/STF. Experimental tests and numerical simulations show that Kevlar/STF has better impact resistance than pure Kevlar fibers. Hassan et al. investigated the ballistic impact properties of STF-impregnated Kevlar fabrics and found that the addition of STF significantly enhanced ballistic penetration strength without reducing flexibility [4]. Majumdar et al. demonstrated the deformation and energy absorption patterns of STF-treated and untreated Kevlar woven fabrics upon impact and found that in the untreated Kevlar fabric, only the primary yarns were involved in load sharing and thus energy absorption. Park et al. also fabricated STF-treated high-performance fabrics and showed that STF treatment has an important impact on the protective properties of the fabric [5]. Srivastava et al. investigated the effect of filling pressure and silica concentration in STF (40-60 wt. % silica in 278 nm silica in polyethylene glycol) on the additional percentage, yarn pull-out force, and impact energy absorption [6]. The results confirmed that the use of STF improved the impact energy.
absorption of Kevlar fabrics. Kang et al. developed an advanced anti-puncture material consisting of STF (20% by weight of fumed silica in ethylene glycol) and Kevlar fabric [7]. The STF impregnation significantly improved the anti-puncture properties of the Kevlar fabric against the threat of spikes. In the present study, the effect of CNF on the performance of the STF system was investigated by blending STF modified by adding different amounts of CNF (0%, 0.1, 0.2%, 0.3%, 0.4%) and characterized by scanning electron microscopy (SEM). The effect of multiphase STFs on the impact resistance of treated Kevlar fabrics was also investigated.

2. Experimental

2.1. Materials
Fumed silica nanoparticles (AEROSIL 200) with a particle size of 12 nm and a specific surface area of 200 m²/g were purchased from Evonik Company. Polyethylene glycol with a molar mass of 200 g/mol (PEG 200) was purchased from Macklin Company. Alcohol had a purity of 99% provided by Beijing Tongguang Fine Chemical Co., China. Nanocellulose (99.5%, width 10 ~ 50 nm, length 0.5 ~ 3 μm) were supplied from CHEMKEY Reagent Co. Kevlar filaments were supplied from DuPont. Corporation.

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 by 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 STF0.

2.3. Preparation of Multi-phase STF
A multiphase shear-thickening solution was prepared by a variable frequency double planetary ball mill. The formulations for the different component contents are shown in Table 1.

| Serial number | Different mass ratios of Nanocellulose (CNF) and STF |
|---------------|-----------------------------------------------------|
|               | The mass ratio of additives and STF (%)   | Original STF mass (g) | Mass of Additives (g) |
| 0             | 0                                    | 40                  | 0                   |
| 1             | 0.1                                  | 40                  | 0.04                |
| 2             | 0.2                                  | 40                  | 0.08                |
| 3             | 0.3                                  | 40                  | 0.12                |
| 4             | 0.4                                  | 40                  | 0.16                |

2.4. Preparation of Multi-phase STF Treated Fabrics
Multi-phase STF/fabric composites were prepared by an impregnation process. Before impregnation, ethanol was added to reduce the surface tension of the dispersion so that it can wet the fabric (STF: ethanol = 1:1). A high-speed homogenizer was used to prepare the dispersions. Complete the target impregnation by soaking the fabric sample in the STF/ethanol solution for 10 minutes. Squeeze the wet fabric with a 2-roller grinder to remove the excess solution and place the fabric in a vacuum oven at 80 °C for 26 h. Finally, seal the STF-treated fabric with the polyethylene film as a single unit for later use.
2.5. Characterization
The shape, size, and size distribution of the particles were characterized by SEM (JEOL JSM-6366LV). The functional groups on the silica powder were detected by FT-IR (TENSOR 27).

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 the 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 a dispersing medium.

2.5.1. Fabric Single Yarn Extraction Force Test. The test equipment was self-designed based on the universal tester (Instron 5966). Cut the multiphase STF Kevlar composite into the shape. The force-displacement curves of the specimens were obtained by the data acquisition system after the lower end of the specimen was clamped in the center of the lower fixture of the tensile testing machine and a single yarn was separated from the upper end of the specimen and clamped in the center of the upper fixture, with the length of 1cm.

2.5.2. Impact Resistance Tests. Impact testing was performed with a drop hammer impact tester DIT302E. The specimens (10 cm × 10 cm) were clamped with a fixture, and the specimens were held with 6 atmospheres of compressed air to prevent the specimens from slipping off. The overall weight of the drop hammer was 10 kg, the head of the punch was hemispherical, 15 mm in diameter, and the impact energy was 20 J. The impact point was the center of the specimen. The impact point is the center of the specimen. The force and energy changes with time and displacement are recorded simultaneously during the impact.

2.5.3. Anti-Stab Performance Test. Anti-Stab performance test is the same test with drop hammer impact tester DIT302E, the impact hammer for tool, fixture fixed specimen, size 15cm × 12cm, other conditions as impact test.

3. Results and Discussion

3.1. Characterization of multi-phase STF

![Figure 1 SEM picture of multi-phase STF](image)

(a) STF0; (b)CNF-STF

The SEM picture of different STF systems is shown in Figure 1. The STF0 and CNF-STF systems are shown in Figure 1(a) and Figure 1(b). Although the purchased fumed silica particles had a native particle size of 12 nm, scanning electron microscopy (SEM) observed that they were not completely dispersed, which was a result of particle agglomeration due to the high surface area and intermolecular hydrogen
bonding of nanoscale SiO\textsubscript{2}. The agglomeration scale of STF0 produced by ultrasonication and mechanical agitation is roughly in the range of 200 nm to 800 nm, as shown in Figure 3(b), after dispersing CNF on STF0, silica particles can be observed agglomerating and adhering to the nanocellulose in the scale of 200-400 nm. The dispersion of nanocellulose by the planetary ball mill has reached the nanoscale and is almost monofilamentally dispersed.

3.2. Rheological Properties of multi-phase STF

![Figure 2 The rheological curve of multi-phase STF](image)

The rheological result of the prepared STF is shown in Figure 2. The added nanocellulose system exhibits the same shear thickening properties as STF0 and shows the discontinuous thickening (DST) phenomenon. It is noteworthy that the critical shear rate \( \gamma_c \) of the multi-phase STF system decreased from 29.33 s\(^{-1}\) (0% CNF) to 9.502 s\(^{-1}\) (0.2% CNF) and then increased to 11.98 s\(^{-1}\) (0.4% CNF) with increasing mass fraction of nanocellulose. The maximum value of 9.275 Pa\·s (0.2% CNF) was decreased to 6.106 Pa\·s (0.4% CNF), and the maximum thickening viscosity \( \eta_m \) was increased from 212.2 Pa\·s (0% CNF) to 447.0 Pa\·s (0.3% CNF), and then gradually decreased to 273.5 Pa\·s (0.4% CNF). On the whole, the shear thickening responsiveness of the system was advanced and the shear thickening performance was enhanced after the addition of CNF. The best enhancement effect was observed at CNF content of 0.2 wt% and 0.3 wt%.

3.3. Test Results of Impact Resistance

| Serial number | Maximum single yarn withdrawal force (N) | Weight gain (%) |
|---------------|------------------------------------------|-----------------|
|               | 50mm/min | 400mm/min | 800mm/min | | 50mm/min | 400mm/min | 800mm/min |
| 0             | 5.749    | 5.091     | 6.965     | / | /         | /         | /         |
| 1             | 20.273   | 17.109    | 21.540    | 23.57 | 65.166 | 49.423 | 73.521 |
| 2             | 26.524   | 19.870    | 28.356    | 24.37 | 22.466 | 23.901 | 28.38 |
| 3             | 30.212   | 22.466    | 23.901    | 28.38 | 22.180 | 30.430 | 30.80 |
| 4             | 29.552   | 22.180    | 30.430    | 30.80 | / | / | / |

| Serial number | Reinforcement (N) | Unit Weight Gain Strength (N) |
|---------------|-------------------|-------------------------------|
|               | 50mm/min | 400mm/min | 800mm/min | 50mm/min | 400mm/min | 800mm/min |
| 0             | 0.836    | -0.369    | 2.753     | /         | /         | /         |
| 1             | 15.359   | 11.649    | 17.329    | 65.166    | 49.423    | 73.521    |
Table 2, Table 3 shows the data for each test sample tested and processed. Each STF number in the sample name corresponds to the formulation table in Table 1. The weight gain represents the percentage increase in the mass of Kevlar composite STF compared to the original Kevlar mass, the reinforcing force is the value of the single yarn extraction force of each composite material minus the value of the single yarn extraction force of pure Kevlar, and the unit weight gain reinforcing force is the ratio of reinforcing force to weight gain.

First of all, it can be seen visually that the maximum single yarn extraction force of Kevlar without composite STF is almost the same at the three tensile speeds. But after laminating STF, the extraction force at 400mm/min for almost all specimens is less than the force at 50mm/min, and the value rises again at 800mm/min because the STF is in the shear thinning region at 400mm/min.

From the calculation of the reinforcing force data, it can be seen that the extraction force of STF composite aramid yarns with nanocellulose was the highest among all experimental controls. At a tensile speed of 50 mm/min, the extraction force of STF (0.3% CNF) was increased to a maximum of 25.298 N. At a tensile speed of 400 mm/min, the extraction force of STF (0.3% CNF) was increased to a maximum of 17.005 N. At a tensile speed of 800 mm/min, the extraction force of STF (0.4% CNF) + KF was increased to a maximum of 25.298 N. The maximum value is 26.218 N. This is 5.15 times, 3.11 times and 6.22 times higher than that of pure aramid, respectively.

The STF (0.2% CNF) was the most enhanced in the whole experimental group at 50 mm/min, 400 mm/min, and 800 mm/min, with 88.676N, 59.130N, and 99.075N, respectively.

3.4. Anti-Stab Performance Test

Figure 3 Force-Time Curve of CNF-STF Kevlar Composites for Drop Hammer Impacts

From the force-time curve of CNF-STF Kevlar composites in Figure 3, it can be seen that the general trend of the data of each component is more or less the same, and the fallen hammer force first increases and then decreases to zero, but the difference is the time of the peak force. As the mass fraction of CNF added in the system increased, the peak force appeared at 17.938ms (0% CNF), 20.842ms (0.1% CNF), 22.554ms (0.2% CNF), 18.516ms (0.3% CNF), 19.486ms (0.4% CNF) in order. The peak forces were 3.990 kN (0% CNF), 3.823 kN (0.1% CNF), 3.766 kN (0.2% CNF), 4.019 kN (0.3% CNF), and 4.690 kN (0.4% CNF).

|   | 2    | 3    | 4    |
|---|------|------|------|
|   | 21.610 | 25.298 | 24.638 |
|   | 14.410 | 17.005 | 16.719 |
|   | 24.144 | 19.689 | 26.218 |
|   | 88.676 | 89.142 | 79.996 |
|   | 59.130 | 59.921 | 54.285 |
|   | 99.075 | 69.378 | 85.124 |

Table
The force-displacement curve of CNF-STF Kevlar composites shows that the general trend of the data of each component is about the same, the impact force increases to the maximum and then decreases to zero, the difference is the displacement of the peak force. The maximum displacement of the composites after impact increases and then decreases with the increase of the CNF mass fraction in the system, but the maximum displacement of the composites with CNF is all greater than that of the two-component STF with 0% CNF. Synergistically sharing the impact force, deforming the composite material as a whole, expanding the local force into an overall force, and protecting the fabric from fracture and damage.

3.5. Puncture Resistance

Table 4 Comparison of puncture resistance before and after composite CNF-STF

| Maximum penetration force (N) | Reinforcement (%) |
|-------------------------------|------------------|
|                               | Pre-Compound     | After compound  |
| Kevlar                        | 14.1             | 15.2            | 7.80%           |

The main purpose of this experiment is not to study the puncture resistance of fiber materials, but to briefly test the maximum dynamic puncture force of each material to obtain a puncture cutting surface, and then observe the microstructure of the cutting surface through an electron microscope, in the hope of observing more different from the structure of the impact specimens, and have some reference value for impact protection materials. As shown in Table 4, the puncture resistance of the fabric was enhanced after lamination with CNF-STF.

3.6. Kevlar composite CNF-STF before and after puncture cross-sectional morphology comparison

Figure 5 Kevlar composite CNF-STF pre- and post-puncture cross-sectional electron micrographs
(a) Kevlar (b) Kevlar composite CNF-STF
As shown in Figure 5, there is a tendency of micro fibrillation at the fracture of uncompounded pure Kevlar after the dynamic puncture, and the fracture position of the fiber varies greatly, this phenomenon shows that pure Kevlar is punctured and cut at the same time with obvious fiber slip and stretching, resulting in uneven cross-section. The CNF-STF composite Kevlar fracture morphology is flatter, with almost no tearing cross-section. The reason is that when the composite fibers encounter shear force, the thickening properties of CNF-STF are expressed, and the viscosity increases dramatically to a solid-like state, which prevents the relative slip between fibers, and the relative slip is transformed into a deformation of the yarn as a whole.

4. Conclusion
A multiphase shear thickening fluid with fumed silica as dispersion phase and PEG200 as dispersion medium was prepared by ultrasonic method and mechanical stirring method, and a multiphase shear thickening fluid was prepared by adding CNF-STF dispersion phases with different contents and different components using a variable frequency double planetary ball mill. Fabric Composites. The addition of nanocellulose (CNF) enhances the steady-state and dynamic aspects of the shear-thickening fluid. The rheological properties of the shear-thickened fluid are strongest at a mass fraction of 0.2%. CNF-STF enhances the impact resistance of the composites. The fracture pattern of CNF-STF composite Kevlar is flat, with almost no tear cross-section. This can be attributed to the fact that when the composite fiber encounters shear, the thickening properties of CNF-STF are exhibited, and the viscosity increases dramatically to a solid-like state, preventing relative slip between fibers, which leads to overall yarn deformation.

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