Effect of Surface Modification of Silica Nanoparticles with Thiol group on the Shear Thickening Behaviors of the Suspensions of Silica Nanoparticles in polyethylene glycol (PEG)

Shuchi Sharma*, Yogesh Kumar Walia**, Gunjan Grovera, Sanjeev K. Vermaa,b.

*Career Point University, Hamirpur, 176041, India
**Terminal Ballistics Research Laboratory, DRDO, Chandigarh, 160030, India

skv002002@gmail.com

ABSTRACT. The Fine-tuning of Shear Thickening Fluids (STFs) by surface modification of silica particles has fascinated scientist's interest worldwide as it results in performance enhancement of STF based on armor systems. In the current study, surface modified Silica nanoparticles (average diameter of 600 nm) possess thiol functional groups which were attained through a reaction with 3-mercaptopropyl trimethoxysilane in absolute ethanol at 90 °C. Shear thickening fluid of Thiol functionalized Silica nanoparticles were prepared by sonochemical method in polyethylene glycol (PEG-200). The rheological parameters of STFs (modified and unmodified silica Nano particles) were measured using Rheometer MCR 52, Anton Par, Germany. The shear thickening behavior of thiol-based STF shows shear thickening at a higher shear rate compared to only silica-based STF with the decrease in viscosity maximum.

Keywords: Bullet Impact; Shear Thickening Fluid; Strain-Thickening; Particle Dispersion; Rheology.

1. INTRODUCTION:

The guardians of our country are provided with body armors, which are designed to weaken slashing or penetrating attacks by resisting the low-velocity bullet penetration. Multiple layers of high modulus, high strength, and low-density fabrics eg. Kevlar & Dyneema have been reported to be used for making soft armor panel (SAP) for protection against 9 x 19mm ammunition[1-4]. However, increases the weight of the armor observed because of large number of layers of ballistic materials, thereby posing restrictions to the comfort and mobility of the user. A lot of work has been reported in literature cites for the reduction in the areal density of the armor. One such potential method is application of liquid armor or shear thickening fluid (STF) on high strength fabric like Kevlar. [5, 6].

A large number of reports have been published on shear thickening phenomena of colloidal suspensions [7-9]. Under sudden impact the liquid armor or the colloidal suspension of hard particles in polymer matrix converts to a solid-alike state, however, at low shear rates STF flows easily because of lower viscosity. A number of methods have been put forward in literature to elaborate the Non-Newtonian behavior of concentrated suspensions. In one of the early studies, a rise in viscosity is proposed by Hoffman because of order-disorder transition of particles [10, 11].

Nonetheless, shear-induced hydro clusters formation is the most widely accepted mechanism, in which inter particle repulsive forces was completely overcome by hydrodynamic lubricating forces that results to increase in viscosity. This simulation studies, rheological and optic-SANS supported this hypothesis. [12-15]. The possibility to control rheological property of STFs for desired applications makes STF a suitable candidate for a lot of applications in different fields such as damping devices,
body armors, medical devices smart structures etc [16–21].

The shear thickening behaviour of STF depends on different parameters such as particle shape, particle size, particle concentration, and polydispersity of dispersed particles, the method of preparation of STF and the molecular weight of polymeric matrix. The ST behavior of STF is considerably influenced by the surface properties of dispersed particles [22-29]. The surface modification of silica nanoparticles significantly alters particle–media and the particle-particle interactions. Thus, shear thickening fluids consisting of surface-modified silica nanoparticles has bee in interest worldwide specially for its energy absorption behavior with potential application in base protective system.

Mahfuz et al. prepared STF using surface-modified silica particles with aminopropyl triethoxy silane and its application to Kevlar fabric was analyzed [30,31]. The performance of the resulting armor composites was observed to improve significantly in comparison to that of the neat fabric. Butola et al reported that a reduction in surface hydroxyl group increases the energy absorption behavior of shear thickening fluids [32,33]. This paper includes the synthesis of thiol-modified Silica Nanoparticles based shear thickening fluid and its rheological behaviors in continuation of our earlier research works related to fine-tuning of shear thickening fluids. To the best of our knowledge, the STF of Thiol modified Silica particles has not been reported in literature. This study also believes in the development of STF based armor systems [1, 2, 15, 34-36].

2. EXPERIMENTAL:

2.1 Materials

The spherical silica nanoparticles of particle size 600nm and PEG 200 were used for the synthesis of the Shear Thickening Fluids. The average particle size of unmodified and surface-modified silica nanoparticles was measured through DLS (Fig. 1a), and also through SEM (Fig. 1b). 3-Mercaptopropyltrimethoxysilane (MPTMS) was used for the modification of dispersed particles (silica particles 600nm). The absolute ethanol 99.9 % was used in synthesis of STFs.

2.2 Synthesis of Thiol-modified Silica Nanoparticles.

Thiol-modified Silica nanoparticles with different concentration of surface thiol groups were synthesized by dispersion of the nanoparticles (10g) in a solution of 3- Mercaptopropyltrimethoxysilane (MPTMS) (25-100 mmol) in toluene (400.0 mL) as shown in table 1. The mixture was reflux for 12 hours. The final centrifuged product was left for another 2 hours and than washed with toluene, ethanol, and dried under vacuum. Ellman’s reagent and Emmett–Teller (BET) surface area is used to determine the quantity of thiol group (–SH) per particle of functionalized silica nanoparticles.

**Table 1.** Mercaptopropyltrimethoxysilane (MPTMS) mmols added to silica nanoparticles of average particle size 600nm.

| S. No. | Sample Code. | Silica Nanoparticles -600nm (grams) | MPTMS (mmol) |
|-------|--------------|-------------------------------------|--------------|
| 1     | Silica-SH-25 mmol | 10                                | 25           |
| 2     | Silica-SH-50 mmol | 10                                | 50           |
| 3     | Silica-SH-75 mmol | 10                                | 70           |
| 4     | Silica-SH-100 mmol | 10                                | 100          |
2.3 Synthesis of Shear thickening fluid

In this study, shear thickening fluid with 70 wt% of modified and unmodified silica nanoparticles were synthesized using sonochemical & homogenization method with ethanol solvent. The treated and untreated silica nanoparticles (70% w/W) were dispersed in ethanol (excess) using homogenisation at 5000 rpm for 10 minutes followed by sonication at a frequency of 24 kHz, 75 W/cm² for 10 min. After it the polyethylene glycol (PEG-200) (liquid, 30 % w/W) was added and the mixture is homogenised for 10 minutes at 5000 rpm followed by sonication. The reaction mixture was maintained below 40°C. Ethanol was evaporated under vacuum and product is collected as pale yellow or white coloured liquid.

2.4 Rheology of Shear thickening fluid

ST behavior of the synthesized STF samples was analyzed by rheological studies with MCR-52 Rheometer, Anton Paar, Germany, with cone angle of 1 º in cone-plate geometry plate diameter of 40 mm and a gap of 0.08 mm. All the rheology experiments were performed at 25 °C with shear rate in the range of 0 - 2000/s. All the STF samples were subjected to 6 seconds pre-shearing at 0.1 to 1 S-1 to set up an equilibrium structure of the sample and to remove any air bubble in the system.

3. RESULTS AND DISCUSSION

The dispersed silica nanoparticles of average size 600 nm were treated with different concentration of Mercaptopropyltrimethoxysilane (MPTMS) (25-100 mmol) to achieve different concentration of surface thiol groups (Table 2). Mercaptopropyltrimethoxysilane is usually used for surface modification of nanoparticles with thiol groups as shown in figure 1. Huang and co-workers functionalized mesoporous silica materials with MPTMS [34].

Figure 1. Schematic representation of surface modification of silica nanoparticles with thiol functional group.

The morphology and average diameter of unmodified and modified silica nanoparticles (Silica- SH-100mmol) was studied by SEM (Scanning Electron Microscope) analysis as shown in Figure 2. It was observed that functionalization of silica nanoparticles doesn’t result to significant change in particles size.
Figure 2. SEM analysis on unmodified and modified Silica Particles with thiol group

The BET (Brunauer–Emmett–Teller) surface area of unmodified silica particles and thiol functionalized silica nanoparticles were evaluated. Based upon the results it was further utilized along with Ellman’s reagent 5,5'-dithiobis-(2-nitrobenzoic acid)] (DTNB) (figure 1) to calculate the number of thiol groups per silica nanoparticles (Table 2) [35].

The surface charges of unmodified and modified silica particles dispersed in ethanol were evaluated using the zeta potential at pH of 6.7. The unmodified silica shows zeta potential of -7.1 ± 2 mV due to the deprotonation of surface hydroxyl groups (Table 2). Whereas, after modification with M3-Mercaptopropyltrimethoxysilane (MPTMS), the zeta potential of the thiol functionalised silica particles was observed at -11.1 to -17.4 mV.

Table 2. Zeta potential/surface area and Thiol group per particles of modified and unmodified shear thickening fluids.

| S. No. | Sample                | Zeta Potential (mV) | Surface area per particle (nm²) | Thiol (-SH) group per Particle |
|--------|-----------------------|---------------------|---------------------------------|-------------------------------|
| 1      | Unmodified Silica     | -7.1 ± 2            | 5.20 x 10⁵                      | 0                             |
| 2      | Silica-SH-25mmol      | -11.1 ± 2           | 4.50 x 10⁴                      | 1.20 x 10⁶                    |
| 3      | Silica-SH-50mmol      | -14.2 ± 2           | 4.35 x 10⁴                      | 1.90 x 10⁶                    |
| 4      | Silica-SH-75mmol      | -17.1 ± 1           | 4.20 x 10⁴                      | 2.21 x 10⁶                    |
| 5      | Silica-SH-100mmol     | -17.4 ± 1           | 4.15 x 10⁴                      | 2.23 x 10⁶                    |
Table 3. Rheological parameters of surface modified shear thickening fluids of different Thiol concentration

| S. No | Sample Name          | Critical Shear Rate (s⁻¹) | Critical Viscosity (Pa.s) | Shear Max (s⁻¹) | Viscosity Max (Pa.s) |
|-------|----------------------|---------------------------|---------------------------|-----------------|----------------------|
| 1     | Unmodified Silica    | 2.23                      | 7.7089                    | 81.7            | 238                  |
| 2     | Silica-SH-25mmol-70% | 4.82                      | 4.5176                    | 37.7            | 187.39               |
| 3     | Silica-SH-50mmol-70% | 13.5                      | 2.007                     | 48.8            | 143.84               |
| 4     | Silica-SH-75mmol-70% | 16.1                      | 3.4073                    | 48.8            | 128.47               |
| 5     | Silica-SH-100mmol-70%| 29.2                      | 2.9346                    | 106             | 67.433               |

Figure 3. Steady state viscosity as a function of shear rate of STF of unmodified and surface functionalised silica particles.
Figure 4. Viscosity max profile and Critical shear rate of the STFs with different SH concentration.

The steady viscosity as a function of shear rate from 0 to 1000 s\(^{-1}\) of STF of unmodified and surface functionalised silica particles was depicted in Figure 3. It can be seen that all the STFs of both kind of particles show a similar rheological behaviour to the applied shear stress. At lower shear rates the viscosity of STFs decreases. It is followed by a spontaneous rise in viscosity after critical value of shear rate. It exhibits shear thickening response of both kind of shear thickening fluids. This is an important aspect for the impact energy absorption of shear thickening fluids. Steady-shear rheological analysis (Figure 3) also shows the effect of –SH on the steady shear response of the synthesized STFs. It was observed from Figure 3 & 4 and Table 3 that with increasing –SH concentration of modified silica nanoparticles, a fall in the maximum viscosity and rise in shear rate was observed. The maximum viscosity value decreases from 238 to 67.43 Pa.s as the thiol concentration on the surface of silica particles was increased to 2.23 x 10\(^6\) per particle. It was also observed that the critical shear rate value increases from 2.23 to 29.2 sec\(^{-1}\) with increase in thiol concentration on silica nanoparticles.

In case of the thiol modified silica nanoparticles, the STF formed shows lesser attraction between hydrophilic polyethylene glycol and hydrophobic thiol modified silica particles. This results in increase in critical shear rate (29.2 s\(^{-1}\)) with the lowering of the peak viscosity (67.43 Pa.s) for the onset of shear thickening of STFs. Previous studies have reported that the hydroxyl density on silica influences the inter-particle interactions of particles [30-32]. It is understandably obvious from Fig. 3 that modified silica based STF shows significant increase in the critical shear rate profile compared to that of silica- based STFs. In our study, it was found that the STF of -SH functionalized silica nanoparticles have shown a lesser inter-particle attraction as compared to unmodified silica particles due to lower surface hydroxyl density. It will result to increase in value of critical shear rate. Butola et al [36] also found increase in performance of shear thickening fluid with decrease in surface hydroxyl group. It was also observed that with the decrease in surface OH group, the viscosity max of the STF decreases with increase in critical shear rate. The critical shear rate is one of the important parameter for ballistic performance of armor panels. The STF with higher shear rate maintain the flexibility of armor panels and results in shear hardening at higher shear rate. The developed STF of thiol modified silica particles with higher critical shear rate and lower surface hydroxyl group is therefore a plausible candidate for STF based armor systems.
4. CONCLUSION

This study opine a method in which silica nanoparticles of different concentration with surface thiol groups were synthesized by the reaction of silica nanoparticles with average particle size of 600nm and MPTMS. Shear thickening fluid of thiol functionalized silica nanoparticles were characterized using steady state rheology. It was observed that thiol functionalized silica nanoparticle based STFs shows shear thickening at higher shear rate compared to unmodified silica nanoparticles. Therefore, the STFs of modified silica NP is well-advised as more suitable fluid for STF based armor system.

Conflict of interest

The authors declare that they have no conflict of interest.

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