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A thorough and critical review on Shear Thickening Fluids (STFs) is presented based on a literature survey. The rheological properties of STFs are discussed considering many factors affecting shear thickening behavior and the use of STFs in protective systems is reviewed. The main focus of this review is multi-phase STFs, relatively new to the literature (in the last five years). Multi-phase STFs include a second phase in suspensions and the influences of this additional phase on rheological behavior and protective applications are discussed extensively. Based on this extended review, STF do benefit protective applications, but the major contribution is not driven by the shear thickening behavior. Rather, STFs are responsible for the increase in friction along fabrics and enhanced fiber/yarn coupling in fabric based protective systems. As a result, of these effects, the load transfer is spread over a wider area and penetration depth is lowered in an impacted structure.

Disciplines
Engineering | Science and Technology Studies

Publication Details

This journal article is available at Research Online: https://ro.uow.edu.au/eispapers1/1015
Shear Thickening Fluids in Protective Applications: A Review
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Abstract
In the present work, a thorough and critical review on Shear Thickening Fluids (STFs) is presented based on a literature survey. The rheological properties of STFs are discussed considering many factors affecting shear thickening behavior. In addition, detailed reviews into the use of STFs, for the use in protective systems during recent years are extensively reviewed. The main focus of this review is multi-phase STFs, which are relatively new to the literature (in the last five years). Multi-phase STFs include a second phase in suspensions and the influences of this additional phase on rheological behavior and protective applications are discussed extensively. Based on this extended review, protective applications are benefited from STFs; however, the major contribution is not driven by the shear thickening behavior. STFs are responsible for the increase in friction along fabrics and enhanced fiber/yarn coupling in fabric based protective systems. As a result, of these effects, the load transfer is spread over a wider area and penetration depth is lowered in an impacted structure.

Keywords: Shear thickening fluids, smart fluids, multi-phase suspensions, rheology, nanoparticles, ceramic particles, carbon nanotubes, protection, energy dissipation.

1. Introduction
Shear thickening fluids (STFs) are dense colloidal suspensions exhibiting abrupt increase in viscosity with increasing shear rate [1]–[4]. The main favorable feature of STFs is that the process is reversible, which means the fluids turn to the initial liquid state after removing the loading from the medium. From past to
present, several investigations into STFs have been performed in order to understand the rheological behavior of these smart fluids and to utilize them in engineering applications. Initially, shear thickening was defined as a problem in industrial processes such as coating and mixing due to jamming in small openings, and overloading mixers thereby limiting process rate [5]. However, the unique characteristic of these fluids has been utilized in developing smart materials and structures more recently. STFs in protective applications have been in great demand since the beginning of the year 2000. In fact, the first study was performed in 1968 by Gates [6], but studies recessed for three decades and then the concept gained considerable attention by the researchers at the University of Delaware. The first studies suggested beneficial outputs for protective applications and the technology was supported by the U.S. Army Research Laboratory (ARL). In 2004, a patent application [7] was filed with the cooperation of University of Delaware and ARL. In the later years, hundreds of investigations were performed to improve the efficiency of protective systems in addition to increased lightness and flexibility. Beside protective applications, these smart fluids have been suggested to absorb shock waves from earthquake or severe wind conditions [8]. In machinery, STFs can be integrated within damper systems to optimize the dynamic performance of these systems [9], [10]. Structural components are combined with STFs to improve the vibration and damage resistance of whole systems [11]–[14]. In medical equipment, STFs are suggested to restrict the movement of shoulders, knees, elbows, ankles and hips to prevent these joints from sudden accelerations [15]. In more recent times, multi-phase STF systems including additive particles in the suspensions have been developed to take the advantage of additive particles. The best example of multi-phase STF is magnetorheological shear thickening fluid (MRSTF), which is a combination of STF and magnetorheological (MR) fluid [16]–[19]. In the last three years (2013-2016), additives of ceramic particles and carbon nanotubes have been investigated in multi-phase STFs in order to observe their influences on the rheology of these smart fluids and to adapt them for protective applications [20]–[25].

The purpose of this study is to provide a thorough review on literature related to the rheological properties of STFs and their applications in the field of protection. The mechanism of shear thickening phenomenon will be discussed in accordance with the hydro-clustering theory, order-disorder theory and a more recent model, the contact rheology model explaining the non-Newtonian property of these suspensions based on the contact of solid particles. The shear thickening mechanism is dependent on various factors such as particles, liquid medium, particle interactions, additives, temperature etc. and therefore, these factors are presented in this study. The influence of additive particles on the rheology of multi-phase STFs is also discussed. Furthermore, STFs in protective applications are given based on previous studies. We believe that this extended review paper will be beneficial in order to provide better understanding of STFs in the field of protective applications.

2. Shear thickening mechanism

STF is a kind of non-Newtonian fluid, where the shear stress is not linearly related with the shear rate. The viscosity of fluid increases as shear rate or applied stress increases on the medium [26]–[31]. Thickening behavior is observed in dense colloidal suspensions which are composed of solid particles (silica, calcium carbonate, etc.) and inert carrier liquids (water, ethylene glycol, polyethylene glycol, etc.). It should be noted that carrier liquids exhibit Newtonian behavior in pure form which indicates the prominence of solid particles in enabling the shear thickening mechanism. Figure 1 illustrates the particle interactions in STFs with increasing shear rate. It is seen from the schematic representation that particles are randomly suspended in a liquid medium due to dispersion at equilibrium. As the shear rate increases, particles form layered structures which causes shear thinning due to a reduction of viscosity. Beyond a critical shear rate
at which shear thickening begins, layered structures disorder and particle groups, namely hydro-clusters are formed being responsible for drastic increase in viscosity [3], [32].

Figure 1: Schematic illustration of shear thinning and shear thickening behavior of suspensions [33]. Copyright 2014. Reproduced with permission from Springer

The shear thickening mechanism was investigated by many researches and various models have been proposed in the literature. For example, Hoffman [34] made the pioneering study on the micromechanical structure of shear thickening; this study became the relevant basis of order-disorder theory. He proposed that below a critical shear rate, particles in suspension are in a layered order, however, beyond the critical shear rate, hydrodynamic forces acting on the particles become stronger and the layered orientation is disrupted; as a result of this process, layered particles disorder and the transition from order to disorder causes a drastic increase in suspension viscosity. Layered orientation in dense colloidal particle suspension was experimentally verified in a further investigation by Hoffman [35]. According to the order-disorder theory, shear thickening occurs only when the particles have a layered orientation because the viscosity increase is due to disordered particles within the suspension. Laun et al. [11], [36] conducted rheological and small angle neutron scattering (SANS) experiments for latex particles in glycols and the studies suggested that shear thickening is reversible, however, a critical strain rate is required to trigger it. This hypothesis was supported by Bossis et al. [37], it was stated that shear thickening behavior is not fully relying on an ordered orientation because thickening takes place due to particle clusters extending in different directions inside suspension while hydrodynamic forces dominate the particles. According to this approach, interactions between particles, either electrostatic or Brownian, make the suspension easily flow at low shear rates. However, at increasing shear rates, hydrodynamic forces begin to dominate suspension by suppressing the inter-particle repulsive forces and therefore, leading to formation of stress-bearing particle clusters which are called hydro-clusters. These units cause dramatic increase in viscosity by blocking the flowing and it is noteworthy that they are formed without requiring any particle orientation in suspension in contrast to order-disorder theory. This explanation for the thickening mechanism introduced the hydro-cluster theory and it was supported by neutron scattering, rheological and rheo-optical tests, as well as, computer simulations in various studies [3], [38]–[42]. In a later study of Hoffman [43], it was suggested that physical contacts of particles are possible after the transition in particle formation, from order to disorder and this causes the shear thickening phenomenon; this implied that contact forces are more likely involved in the thickening process and not just from hydrodynamic forces.

As well as the hydro-clustering theory, a new model, namely contact rheology model is suggested in recent studies [44]–[48]. It is stated that the hydro-clustering prevails suspensions at low shear rates due to contactless rheology because particle pressure is too small to withstand the repulsion between particles [44], [45]. In fact, pure hydrodynamic effect is only responsible for mild thickening at the onset of thickening but not the explanation of the strong shear thickening mechanism because stress transmission on a big scale is realized through contact interactions as suggested by Melrose et al. [49]–[51]. Contact forces grow stronger for the thickening point where the colloidal particles contact each other at high shear rates. For the further increase in the shear rate, contact forces generate force networks that dominate thickening where the hydrodynamic interactions are claimed to be insufficient. The influence of contact forces is pronounced along the suspension as the shear rate increases [48]. This change was also verified with a recent simulation work by Pednekar et al. [52], that particles are shown in a well-dispersed structure in pure Brownian condition. Upon introducing attractive forces, inter-particle contacts are
developed in the mixture. Contact networks have the ability to resist the applied shear forces and by means of this, suspension introduces viscosity growth and development of yield stress. It should be noted at this point that the major contribution to the viscosity increase, stems from inter-particle contacts rather than hydrodynamic interactions, and the mechanism works in a way where particle attraction only induces the formation of the contact networks; these extended branch-like structures exhibit resistance to shear deformation during flowing and ultimately enhance the viscosity to higher levels. In other words, hydrodynamic interactions are necessary and sufficient for mild viscosity increase but not the resistance to flow which generates the main thickening [52], [53]. In addition, particle concentration acts an important role in the contact rheology model because the possibility of contacted microstructure increases as the loading of colloidal particles increases in the suspension. Therefore, dense suspensions provide more opportunity for the contact forces to increase even at lower shear rates. Mari et al. [45] suggested that mildly dense suspensions are dense enough for contact forces to develop during thickening. In order to ascertain the contribution of contact forces in suspensions, Lin et al. [46] conducted shear reversal experiments on micro-sized particle suspensions; the contact forces were said to be zero at the reversal stage of the experiments, while assuming that the microstructure remained unchanged, and the hydrodynamic forces were identical in magnitude but reversed in direction. In this way, the qualitative difference between the hydrodynamic and contact forces was obtained to exhibit the discrete contributions upon reversal. Based on the results, contact forces seem more dominant than hydrodynamic forces in the thickening of the suspensions. In order to depict the relative contributions of hydrodynamic and contact forces, Figure 2 shows the viscosity characteristics of silica suspension in a glycerol and water medium, with a solid volume fraction of 49%. As shown in Figure 2a, the contribution of particle contacts to the thickening gradually increases whereas hydrodynamic contribution remains stable as the shear rate increases. The graph in Figure 2b shows the viscosity after shear reversal as a function of accumulated strain after reversal at four different shear rates. The viscosity immediately after reversal drops to a value of \( \eta_{rev}^0 \) which remains constant. This viscosity is taken to be the hydrodynamic contribution to the total steady state viscosity. Beyond the critical shear rate of 0.3 s\(^{-1}\), \( \eta_{rev}^0 \) increases and reaches a steady state value of \( \eta_{rev}^{\infty} \), which is the same as the steady state viscosity before reversal. Therefore, the difference between \( \eta_{rev}^{\infty} \) and \( \eta_{rev}^0 \) gives the contribution of contact forces to the viscosity increase. It is obviously seen that contact forces provide major contribution to the shear thickening mechanism in colloidal suspensions. Figure 3 shows the contact forces along a suspension with a particle loading of 50%. Non-contacted particles are drawn in gray lines joining the centers of the two involved particles while the red lines illustrate the particles in contact during thickening. Clearly, contacted particles develop contact networks that extend in the suspension. Although the shear reversal exhibits the influence of contact forces in shear thickening, this model neglects the Brownian forces which are well known for nanoparticle suspensions, especially, with a lower concentration of solid particles [45]. Brownian forces are seen in complex fluids where the particle size is smaller than one micron and they play an important role in creating effective repulsive stresses between neighboring particles [45], [54]. Under low shear rate conditions, the Brownian forces effectively separate particles, however, this influence weakens at high shear rates [55]. Accordingly, it was suggested in recent investigation into the Brownian motions that shear thickening is mostly driven by contact forces [56].

**Figure 2:** (a) Relative viscosity vs strain rate and (b) instantaneous relative viscosity after shear reversal vs strain at different shear rates for a suspension with silica volume fraction of 49% [46]. Copyright 2015. Reproduced with permission from the American Physical Society
3. Rheological properties of STFs

Rheological behavior of STFs exhibits systematical variations with respect to several factors [57]. In order to determine the rheological characteristics of STFs, most of the early studies focused on the variations in critical shear rate at which shear thickening onsets. Even though critical shear rate provides major understanding of rheological behavior of STFs, it is not enough to assure comprehensive knowledge in the field. For this reason, different parameters can be taken into account to have profound knowledge about STFs. The thickening ratio is defined as the ratio of maximum viscosity beyond the thickening point to viscosity at the critical shear rate and exhibits the intensity of thickening in the suspension. The thickening period is the difference between critical shear rate and the shear rate at maximum viscosity after the thickening point.

3.1. Effects of particle volume fraction

One of the major factors on the rheology of STFs is particle volume fraction which is defined as the fraction of total volume by particle volume. Previous studies [5], [58]–[61] reported a lower limit value for the thickening behavior of colloidal suspensions. Although the lower limit of particle volume fraction changes depending on the material properties in the suspension, Barnes et al. [5] stated that thickening generally onsets at a particle volume fraction of 0.5 based on their literature survey. Critical shear rate decreases with the increase of particle volume fraction. Hydrodynamic forces become greater in increased particle concentration suspensions due to reduced distance between particles, and therefore, less shear rate is required to overcome repulsive forces [62]–[65]. In light of the contact rheology model, contacted microstructure is pronounced and stress transfer is facilitated due to extended particle contact branches along the suspensions. The thickening ratio becomes higher and thickening period reduces which means that thickening grows stronger by increasing the particle volume fraction. Furthermore, STFs with high particle loadings lead to considerable increase in the viscosity due to restriction of particle motions in the suspensions [66].

3.2. Effects of particle aspect ratio

Figure 4 shows the influence of particle shapes on the rheological properties of STFs. It was found in early studies [5], [27] that rod shaped particles are the most effective particles to improve shear thickening among various particle shapes. In fact, the effect of particle shape is related to the aspect ratio of particles and with regard to this, Beazley et al. [67] stated that particles with high aspect ratios are more prone to increase the viscosity of STFs due to particle interlocking and rotational motion in the flow field. Wetzel et al. [58] noted that thickening can take place with lower particle loadings using higher aspect ratio particles. According to the rheological measurements, it is seen that particles with higher aspect ratios provoke increase of thickening ratio and decrease of thickening period for CaCO₃ based STFs. Higher aspect ratio particles have more possibility to contact neighbor particles during flowing and therefore, these particles are more prone to trigger the thickening behavior of STFs. Bossis et al. [37] suggested that hydrodynamic stresses are proportional to the cube of the larger dimension of hydro-clusters which means that elongated clusters contribute much more to the thickening behavior than spherical ones. Considering
each particle as a subunit of the hydro-clusters, it is possible to mention that higher aspect ratio particles are more beneficial for the thickening mechanism of STFs. Furthermore, regardless of thickening, entangled particles cause restriction for particle motions which lead to an increase in viscosity of the suspension.

Figure 4: Effect of particle shapes on the shear thickening effect [5]. Copyright 1989. Reproduced with permission from the Society of Rheology.

3.3. Effects of particle size

Particle size is another important factor on the rheological behavior of STFs. Previous investigations into the characteristics of STFs found that critical shear rate increases as the particle size reduces [5], [68], [69]. The role of the Brownian forces can be considered in the assessment of this trend, since they dominate nanoparticle suspensions and delay the thickening for higher shear rates, due to increased repulsive stresses between particles. Maranzano et al. [68] compared the flow curves of dispersions with five different particle sizes at a fixed volume fraction. They find that the thickening point of mixtures shifts to lower shear stresses with increasing particle size. This is because the Brownian stresses inversely change with particle size and they are readily overcome by lower shear stresses using coarser particles in suspensions. The results also exhibit that smaller particles in the suspensions enhance the viscosity of mixtures regardless of thickening.

3.4. Effects of particle size distribution

Barnes [5] stated that the critical shear rate increases if the particle size range becomes wider in colloidal particle suspensions. Regarding particle size, it was suggested that thickening onsets at lower shear rates by eliminating small size particles from suspensions. Figure 5 shows the effect of particle size distribution on various suspensions. The suspensions were prepared with two different sizes of particles (A: 9.5 μm and B: 0.7 μm) at a total solid volume fraction of 0.44. The ratio of solid particles (A:B) was varied as 0:100, 50:50 and 85:15 to observe the role of particle size distribution on the viscosity characteristics of suspensions. As represented in Figure 5, the suspension of pure B particles exhibits shear thickening at lower shear rates; however, shear thickening has not been observed as the coarser particles are involved in the suspensions under low shear rates. It can be deduced from these results that critical shear rate is reached at a lower stage by narrowing the particle size range while the thickening is postponed to higher order shear rates for the suspensions with wider particle size distributions [27], [70]. Olhero et al. [71] and Collins et al. [72] suggested that the broadening of particle size distribution such as adding coarser particles leads to a reduction in the shear thickening mechanism at higher shear rates. Moreover, D’Haene et al. [73] noted that replacing a small number of coarser particles by finer ones decreases the viscosity sharply. On the contrary, the change in viscosity is negligible when replacing a minor quantity of finer particles by coarser particles.

Figure 5: Effects of particle size distribution [70]. Copyright 1983. Reproduced with permission from Elsevier
3.5. Effects of particle-particle interactions

Another factor on the rheological characteristics of suspensions is particle-particle interactions. It was noted for shear thickening systems that particles may remain neutral or repel one another due to entropic or steric interactions. Deflocculated suspensions exhibit low viscosity at low shear rates, however, their viscosity increases by virtue of shear thickening at higher shear rates. Moreover, flocculated suspensions have high viscosity at low shear rates and shear thinning behavior is seen as the shear rate increases [5], [27].

3.6. Effects of particle hardness

Particle hardness is significant on the thickening behavior of STFs. Kalman et al. [74] investigated the role of particle hardness using hard silica and relatively softer poly-methyl-methacrylate (PMMA) particles in a poly-ethylene-glycol (PEG) medium. Harder particles are suggested for a shear thickening mechanism due to their advanced mechanical properties. The difference between hard and soft particles is pronounced under high shear rates where the particles mechanically contact each other as stated in the contact rheology model. It is suggested that soft particles could not withstand the increased stresses and therefore, particle deformations become prevalent under high shear rates. This deformation mechanism is believed to be associated with weakening of shear thickening which results in viscosity drop at high stresses [74], [75]. These results were further supported by Petel et al. [24], [25], in their investigations into suspensions with various hardness particles; according to their studies, particle crushing widely dominates suspensions relating to inter-particle contacts, despite the presence of the interstitial fluid and therefore, harder particles are more beneficial to withstand the inter-particle stresses.

3.7. Effects of particle roughness

Since the particle interactions play an important role in shear thickening behavior, particles with asperities represent a case in point. Although geometrical properties of particles were discussed in previous studies, few studies have been performed on particle roughness in the literature. In early investigations [76], [77], fumed and spherical silica particles were compared in terms of their rheological influences. Fumed silica is prepared by a flame hydrolysis process and the primary structure consists of branch shapes which increase the surface roughness of the particles. However, spherical silica includes smooth particles which have low asperities on their surfaces. Based on the results, fumed silica easily trigger the thickening mechanism upon forming hydro-clusters due to increased particle contacts arising from the branch shaped aggregates [78]. Fumed silica suspensions decrease critical shear rate and increase the viscosity of mixtures by the effect of increased occupied volume and particle contact points [79]–[83]. The increased occupied volume for fumed silica is explained by the open nature of fractal aggregates which allows fumed silica to occlude a significant amount of liquid [84].

3.8. Effects of particle modifications

Modification of particles is an alternative method for tailoring the rheological behavior of STFs. Yu et al. [85] treated silica particles using ball milling and a chemical method, to investigate their influences on the flow curves of suspensions. It is noted that silica particles after surface treatments exhibit much better
dispersibility in suspensions due to the reduced van der Waals forces between particles. As a result, each
treatment reduces the viscosity and slightly increases the critical shear rate of the suspensions. It is also
found that the surface treatments significantly increase the maximum particle volume fraction of STFs by
forming three dimensional cluster networks which hinder flocculation in suspensions. In order to increase
dispersibility in STFs, Hwang et al. [86] used multi-walled carbon nanotubes (MWNTs) coated by silica
particles through covalent bonding. Based on the rheological measurements, this modification process
reduces the critical shear rate for STFs. Regardless of thickening, viscosity of suspensions significantly
increases after the MWNT modification, due to the increase in total concentration of solid particles.
Joselin et al. [87] investigated the influences of functionalized silica particles, the functionalization
process was completed using a silane coupling agent which forms strong bonds between silica particles
and the liquid medium. Li et al. [88] investigated the role of acid treatment on the rheology of silica/PEG
based STFs. Suspensions were prepared using various amounts of nitric acid and their flow curves were
obtained through shear rheology. According to the results, acid treatment enhances the viscosity while
reducing the thickening ratio of suspensions for excessive concentration of nitric acid.

3.9. Effects of liquid medium

Liquid medium is important for the rheological behavior of suspensions. Previous studies [89]–[95]
investigated the rheological characteristics of STFs based on carrier fluids of various molecular weights. It
is found that higher molecular weight fluid based STFs exhibit higher viscosity which is explained by
longer molecular chains that hinder the relative movement of adjacent layers of fluid relative to each
other. Regardless of shear thickening mechanism, this trend is also observed in pure carrier fluids as given
in the viscosity chart of pure PEGs in Figure 6 [93]. As given in the same graph, PEG 600 based STF
provides stronger shear thickening behavior in comparison to the lower molecular weight liquid based
STFs. This is attributed to enhanced polymer adsorption onto particle surface through polar interactions
between silanol groups on particles and longer polymer chains that increase the extension of adsorption
[94]. In addition, lower critical shear rates are observed in suspensions by increasing the molecular weight
of carrier fluids due to the entanglement of chains which is an indicator of strong shear thickening. In
other words, hydro-clusters are extended with lower energy in high molecular weight liquid medium and
therefore, shear thickening begins at lower shear rates [96]. In the same manner, shear thickening is
achieved with lower amounts of solid particles using higher molecular weight fluids in suspensions [89].
In addition, the chemical composition of the carrier fluid is important on the rheology of suspensions.
Moriana et al. [97] investigated fumed silica based STFs using polyethylene glycol (PEG) and
polypropylene glycol (PPG) liquids which have a molecular weight of 400 g/mol. It was reported that
thickening behavior is found to occur at lower shear rates in PPG suspensions. Furthermore, PPG based
suspensions increase the thickening ratio with respect to PEG based suspensions. The degree of
polymerization which could influence the solvation layer thickness formed around the particles is smaller
in STFs with PPG. Therefore, suspensions require lower external forces to trigger shear thickening due to
smaller inter-particle distancing and weaker particle-particle repulsion. Another factor is difference in the
polymer structure of these fluids where an additional methyl branch is included within the PPG monomer
that is responsible for more rigid behavior under flow. Increase in the rigidity of polymer chains lead to
enhanced distance between adjacent chains and reduced entanglement allowing for easier rearrangement
while under shear flow. Hence, the shear thickening mechanism is enabled at lower shear rates due to
easier particle rearrangement.
3.10. Effects of temperature

The flow curve of STFs is heavily dependent on temperature. The viscosity of suspensions decreases as the temperature increases because the strength of hydrogen links between colloidal particles and liquid medium reduces at high temperatures. Furthermore, the Brownian motion of particles enhances and therefore, thickened structure is disordered by the effect of high temperatures [62]. On the other side, high temperature disrupts shear thickening by retarding the critical shear rate to higher values [98]. The disruption is also observed with an extended thickening period and a diminished thickening ratio while increasing temperature [62], [99]–[101]. Thickening occurs when the hydrodynamic forces overcome the inter-particle repulsive forces and thereby stimulating the formation of hydro-clusters. However, inter-particle repulsive forces increase at elevated temperatures and formation of the hydro-clusters requires larger shear rates. As a result, the critical shear rate of suspension increases at higher temperatures [62], [76], [102]. It is also important that solvent layers on particle surfaces become thinner when temperature increases and thereby enhancing the distance between particles while decreasing the effective volume fraction of particles in suspension. As a result of these, shear thickening behavior is disrupted at higher temperatures. Furthermore, the reduction in solvent layer thickness decreases the hydrodynamic diameter of particles and thus, hydrodynamic forces become insufficient to overcome repulsive forces. This effect also contributes to the weakening of thickening mechanism in STFs. As well as these influences, the viscosity of carrier liquid reduces by virtue of increased temperature and therefore, shear thickening mechanism suffers from this phenomenon. Due to thinner liquid medium at high temperatures, the prevalence of hydrodynamic forces lowers in suspension and thereby growing inter-particle distance which means that the formation of hydro-clusters and contact networks is delayed for larger shear rates [88].

4. Rheology of multi-phase STFs

Despite several studies into single-phase STFs, there have only been limited investigations in the literature about integrating particle additives to STFs. Multi-phase STFs are mixtures of single-phase STFs and various kinds of additives such as metal particles, ceramic particles and carbon nanotubes. These novel fluids provide an opportunity to obtain multi-functional composite systems which enable the tuning of rheological properties with respect to the application field. In order to investigate the rheology of multi-phase STFs, Gürgen et al. [20], [22] used various micron-sized ceramic particles in silica based STFs. It is suggested that ceramic particles inside the STFs disrupt the thickening behavior of suspensions, but the intensity of disruption varies depending on number of factors such as additive amount and particle size of additives. At excessive loadings of ceramic particles, volume fraction of silica falls below the effective limit and thus, suspension completely loses the shear thickening behavior as shown in Figure 7. The graph indicates that beyond the B₄C loading of wt%25 in the fumed silica based STF, shear thickening is completely removed and shear thinning behavior is observed; the rheology of the mixture is in the shear rate range of 0-1000 s⁻¹. Based on these results, it is stated that additive particles may disrupt the thickening behavior in two ways. The first is lowering silica percentage in mixtures by adding ceramic particles. The second is shortening hydro-cluster networks along suspensions due to interstitial additive particles. Gürgen et al. [22] suggested this second argument with the aid of early studies [37], [84]. According to these investigations, hydro-clusters, which are responsible for thickening mechanism, are
formed in chain-like structures and hydrodynamic forces are related to the longer dimension of chain-like clusters. This means that more extended hydro-clusters provide more powerful shear thickening behavior. In this light, micron-sized ceramic particles in mixtures occupy large volumes in nano-sized silica medium and thereby likely hindering the extension of hydro-clusters. As a result of this, it is possible to mention that contact networks of silica particles are more prone to be lowered in comparison to that of single-phase STFs which results in an attenuated shear thickening effect in regard to the contact rheology model. In addition, viscosity introduces a growth by virtue of increased density as the amount of ceramic particles increases in suspension [24], [66]. In terms of particle size of ceramic particles, coarser particles are more effective on the weakening of shear thickening in comparison to finer particles. It is possible to mention that coarser additive particles constitute larger distances between silica particles in the flow. However, size of additive particles approaches to silica particles by adding smaller size of ceramic particles and thus, hydro-clusters are less affected by the interstitial particle additives in suspensions. It is found that thickening ratio and viscosity decrease using coarser ceramic particles in suspensions. However, critical shear rate and thickening period exhibit no systematic variation considering the particle size of ceramic additives in suspensions [20].

*Figure 7: Rheological curves of multi-phase STFs with various amounts of micron-sized B₄C particles at 20°C [22]. Copyright 2016. Reproduced with permission from Elsevier*

Huang et al. [103] studied the tuning of the rheological properties of fumed silica/PEG based STFs using graphene oxide (GO) additives in the suspensions. In their multi-phase STFs, the amount of silica particles was kept constant at 15wt% and the loading of GO additives was varied from 0 to 0.3wt%. The rheological measurements exhibit that the addition of GO particles into suspensions leads to a remarkable increase of the viscosity regardless of shear thickening and shift of the shear thickening onset towards lower shear rates. Moreover, the thickening period is extended while thickening ratio gradually diminishes as the additives increases in the suspensions. The GO additives cause similar outputs with ceramic particles investigated by Gürgen et al. [20], [22] except for the critical shear rate. This difference is explained by the nature of GO additives by Huang et al. [103] that GO particles are sheet-like additives and therefore, GO particles have a larger hydrodynamic field effect than silica particles do, due to their large aspect ratios. For this reason, GO additives could cause more prominent congestion effect which means that hydro-clusters could be formed at lower shear rates. In addition, the interaction between the silica particles and GO additives are strong that the silica particles around the GO particles are more prone to aggregate on the GO surfaces as shown in Figure 8. However, the presence of GO particles in suspensions hampers the elongation of hydro-clusters and causes the silica clusters to be formed in small groups which lowers the viscosity increase in systems.

*Figure 8. SEM image of (a) single-phase STF and (b) multi-phase STF with GO particle [103]. Copyright 2015. Reproduced with permission from Hindawi*

Magnetorheological shear thickening fluids (MRSTFs) are very functional multi-phase STFs that are comprised of magnetorheological (MR) fluids and STFs. Similar to STFs, MR fluids are suspensions where magnetic particles are utilized as the solid phase. When these suspensions are subjected to a magnetic field, magnetic particles form particle chains in the direction of magnetic flux and therefore, the
viscosity of the suspension is altered [104]–[108]. The change can be as high as several orders of magnitude in a matter of milliseconds [109]. MR fluids are very attractive elements for mechanical systems such as shock absorbers, brakes, clutches and artificial joints [110]–[114]. In order to take the advantage of both MR fluids and STFs, combinations of these smart fluids are fabricated in recent investigations [16]–[19], [115]. In these studies, single-phase STFs are prepared distributing silica particles in a stable liquid medium such as PEG or EG and then, micro-sized particles generally, iron based particles are added as the second solid phase in suspensions. The rheological properties of MRSTFs are measured through steady shear experiments under various magnetic fields. In order to eliminate the effect of magnetic field and investigate the role of additive particles, we discuss the flow curves of MRSTFs under zero magnetic field conditions obtained in aforementioned studies. According to the results, iron based particles influence the shear thickening mechanism in a disruptive way similar to ceramic particles. According to Zhang et al. [16] and Li et al. [19], iron particles hinder the movement of silica particles and thus, hydro-cluster formation diminishes which results in reduced thickening ratio, delayed critical shear rate and extended thickening period in the rheology of fluids. The presence of iron particles lowers the concentration of silica particles in multi-phase system and this effect is also prominent in the weakening of shear thickening. On the other hand, iron particles have assistive influence for increasing the viscosity of MRSTFs regardless of the shear thickening behavior. In addition to thickening mechanism, Zhang et al. [17] investigated the sedimentation in multi-phase systems which is very important for the sustainability for the tuned properties of suspensions. Based on this study, the silica concentration of suspensions was varied while keeping the loading of iron particles constant. The samples were left undisturbed at room temperature for 24 h to observe the particle settling. After the resting, it is stated that liquid media provides a drag force to prevent particle sedimentation but, it is not able to avoid the particle movement absolutely. However, iron particles are fixed in their original position by elastic forces provided by matrix and the movement is restricted as the silica loading increases in suspensions. From this aspect, MRSTFs are more useful in comparison to MR fluids because, the inclusion of silica particles enhance the density of suspensions and thereby growing the drag forces acting on iron particles.

Passey [116] prepared multi-phase STFs, adding halloysite nanotubes with a diameter of 30 to 70 nm and a length of 1 to 3 μm in her thesis study. The constituent solid phase was chosen as fumed silica with the particle size of 7 nm whereas PEG200 was the liquid medium for the suspensions. The amount of additives was varied from 1 to 5 wt% to observe the influences of halloysite nanotubes on the rheology of STFs. Halloysite nanotubes decay the thickening mechanism of STFs similar with the ceramic and iron based particles discussed in early sections of this paper. The only difference is that halloysite nanotubes reduce the viscosity of the suspensions, contrary to the aforementioned additives. It is explained in the study that fumed silica and halloysite nanotubes are bonded together through strong hydrogen bonding and the bonds are not heavily affected by the weaker inter particle forces which can be in the form of Brownian forces or other stochastic particle-particle interactions. Upon increasing shear rate, hydrodynamic forces gradually dominate the suspension and the nanotubes align themselves in the same direction of layered fashion. Further increase in the shear rate results in hydro-cluster formations on halloysite nanotubes which interrupt the extension of clusters in the suspension and consequently, thickening behavior fades away. Critical shear rate exhibits systematic variation with the amount of additives and the increasing trend is explained by the interactions between the solid phases and carrier fluid. It is believed that required hydrodynamic forces to form clusters increase by adding halloysite nanotubes in suspensions because; the additive nanotubes enhance the surface area of particles due to their cylindrical geometry. In order to grow the hydrodynamic forces, the critical shear rate of the suspension is delayed for higher values.
Another investigation into multi-phase STFs was performed by Laha et al. [117] using halloysite nanotubes in spherical silica and PEG200 based STFs. The particle size of silica was 100 nm while the diameter of halloysite nanotubes varied from 50 to 200 nm and the length varied from 200 nm to 1.3 μm. According to the rheological measurements, it is suggested that critical shear rate reduces with increasing the content of halloysite nanotubes in suspensions. Furthermore, thickening ratio grows and thickening period decreases by adding more additive nanotubes in suspensions. These influences show that halloysite nanotubes improve the shear thickening behavior of STFs. In order to explain the role of additives, a two-dimensional hypothetical analysis was performed considering a rectangular space including one halloysite nanotube and randomly distributed 50 silica particles as illustrated in Figure 9a. Based on this analysis, silica particles agglomerate around the nanotubes to form hydro-clusters and therefore, the shortest distance between each silica nanoparticle and nanotube was calculated using Euclidean geometry. For the case of single-phase STF, the centroid of a silica was used as the base point for hydro-clusters and thus, this centroid was used to find the shortest distance from the other silica particles as depicted in Figure 9b. It is shown that the average travelling distance for silica particles is shorter in multi-phase system in comparison to single-phase system. In this light, it is suggested that forming of hydro-clusters is facilitated using nanotubes due to reducing the travelling distance of silica particles under loading. In addition to this, halloysite nanotubes are effective to increase the viscosity of STFs simply through high density effect. Even though Passey [116] and Laha et al. [117] used the same type of additives, the rheology of suspensions gives completely different responses. In the model of Laha et al. [117], additive nanotubes act as bases for hydro-clusters that spherical silica particles are collected around the nanotubes. However, fumed silica is not attracted by additive nanotubes and the fact remains that hydro-cluster formation is blocked by halloysite nanotubes, due to their presence intercepting the growth of silica networks according to Passey [116]. The interaction between halloysite nanotubes and silica could be differed with respect to the form of silica particles that spherical silica could be attractive while fumed silica could be repulsive for these additives. However, it is also noteworthy that fumed silica can be found in both hydrophilic and hydrophobic forms which directly influence the rheology of suspension. Hydrophilic silica due to the presence of the silanol groups exhibits strong thickening in low polarity medium through strong hydrogen bonding. However, hydrophobic silica becomes prominent as an effective thickener in highly polar medium [118]. Taking into account all of these, shape of silica may not be only factor that influences the interactions between silica and additives.

Hasanzadeh et al. [119] prepared a different multi-phase STF system using multi-walled carbon nanotubes (MWNTs) in fumed silica and PEG 200 based suspension. The length and diameter of MWNTs were 30 μm and 10–20 nm, respectively. The multi-phase suspensions with three different amounts (0.4, 0.8 and 1.2wt%) of MWNT additives were rheologically measured and compared with the single-phase STF. The results show that MWNTs have strong influences on the rheology of suspensions even though lower amounts of additives are used in the STFs. Based on the flow curves, critical shear rate increases and thickening ratio decreases by adding MWCTs in the suspensions. These outputs exhibit a disruptive effect on the shear thickening behavior, however, regardless of shear thickening, the inclusion of MWCTs lowers the viscosity of the suspensions in contrast to the other multi-phase STFs. The mechanism associated with MWNTs and shear thickening behavior is proposed in Figure 10. According to the proposed mechanism, shear thickening is influenced by the interactions between the silica nanoparticles,
carrier fluid and MWNTs. The silanol groups on the surface of silica particles forms hydrogen bonds with the internal oxygen atoms and the PEG hydroxyl groups. It is important at this point that both silica particles and PEG can serve as hydrogen bond donors and acceptors. When the MWNTs are included in the suspension, hydroxyl/carboxyl groups on the surface of MWNTs can form hydrogen bonds with PEG and silica particles. However, the hydrogen bonding is more prone to be formed with PEG rather than silica particles. This is verified through Fourier transform infrared spectroscopy (FTIR) that the number of hydrogen bonds in silica-MWNT-PEG suspension increases. In order to overcome the intense bonding between the MWNTs and PEG, the suspension requires increased level of shear forces and consequently, the thickening stage in the suspension is delayed for higher critical shear rates. In the same manner, the presence of MWNTs in STFs decreases the thickening ratio and thereby decimating the shear thickening behavior.

Figure 10. Shear thickening mechanism in MWCT based multi-phase STF [119]. Copyright 2016. Reproduced with permission from Springer

In the investigation of multi-phase STF rheology, Sha et al. [120] used graphene nanoplatelets (GNs) and carbon nanotubes (CNTs) as additives in suspensions. In addition to individual types of additives, GNs and CNTs were added together in spherical silica and PEG based STFs as shown in Figure 11. The GNs used in this study have an average length of 20 μm and diameter of >50 nm. The length and diameter of CNTs are 5-15 μm and 10-20 nm, respectively. The rheological curves of samples show that viscosity of suspensions grows as increasing the additives in the suspensions simply through the increased particle concentrations. Considering the type of additives, CNTs are more effective than GNs to increase the viscosity for the same additive loadings. In the GNs/CNTs systems that are comprised of both GNs and CNTs, the presence of CNTs dominates over the suspensions rather than GNs. According to the rheological results, viscosity increases more drastically as the ratio of GNs/CNTs decreases in the multi-phase STFs. In regard to thickening point in the suspensions, critical shear rate tends to decrease as the additives are included in the system which demonstrates an improvement on shear thickening behavior. Furthermore, CNTs are more effective to fulfil this tendency comparing these different additives in the suspensions. The difference of GNs and CNTs is explained in such a way that GNs act as bridges for aggregated silica particles in liquid medium and thereby linking the aggregated silica groups by forming hydrogen bonds. As a result of this process, shear thickening onsets lower shear rates by the effect of GNs. However, in the presence of CNTs, the interaction between silica particles and PEG determines the rheology of suspension since the interactions between silica particles are almost identical for GNs and CNTs as they have the same elements-carbon and the structures of C–C were similar for both GNs and CNTs. The relative lubrication force between CNTs and PEG are stronger than that between GNs and PEG because CNTs are long tubes and PEG has long chemical chains which mean that both have similar structures. On the other hand, GNs are sheet-like grains and the internal force of PEG-CNTs is much weaker than PEG-GNs. As a result, the phase separation readily takes place in CNT suspensions in comparison to GN ones and thus, CNTs are more beneficial than GNs for shear thickening behavior. On the other side, it is stated that the GNs are two-dimensional and soft fillers while CNTs are rigid rods in the STFs. Based on these structural properties, at higher shear rates, soft GNs could be deformed easily considering the contact rheology model. However, rigid CNTs could withstand the contact forces and provide more advances for shear thickening. It is also noteworthy that CNTs contribute to thickening mechanism in virtue of their winding effect by locating between the silica aggregations as seen in Figure 11c.
There are a limited number of studies, investigating the rheology of multi-phase STFs and each study expresses the role of additives in different ways. A classification of additive effects is not possible since the literature provides only case-dependent studies up to this time. As given in previous studies, some of the additives disrupt the thickening mechanism whilst some improve this behavior. To our understanding, the rheology of STFs is dependent on various factors such as material, geometry, mechanical properties and amount of additives in addition to the factors discussed in early sections. In order to procure a comprehensive understanding of additives in multi-phase STFs, more investigations should be performed using various types of additives in STFs.

5. STFs in protective applications

In recent years, there have been many attempts for understanding the rheological behavior of STFs and utilizing them in engineering applications. In addition to scientific papers, there are number of patent applications benefiting from STFs in various fields such as sport equipment, medical tools and machine mounting [121]. However, protective applications come to the fore among the potential applications due to the advanced contribution of these smart fluids to protective systems.

In the protective applications of STFs, these fluids are utilized with various materials to constitute composite systems. For body protection, in the most preferred cases, high performance fabrics such as aramid based Twaron, Kevlar, Technora and Ultra High Molecular Weight Polyethylene (UHMWPE) based Dyneema, Spectra become prominent to provide flexible structure for users [122], [123]. On the other hand, STFs are also considered for structural protection and therefore, various kinds of materials such as metallic plates are utilized as components in protective systems. In general, STFs for protection have been investigated under quasi-static, low-velocity and high-velocity conditions. In addition to these conditions, threat types have been varied using needles, knives, spikes and projectiles.

In the STF application procedure for fabrics, first of all, solid particles and liquid medium are mixed to disperse the colloidal particles homogenously in suspensions. The mixing stage can be completed using magnetic, mechanical or ultrasonic devices. However, ultrasonic method is suggested for the adequate dispersion of solid phase into a polymeric matrix [124]. Next, the suspension is diluted generally using excessive amounts of alcohol in suspensions since STFs are highly viscous fluids and therefore, the impregnation of fabrics is troublesome without dilution. After the dilution, fabrics are soaked into the diluted mixture by enabling the mixture to penetrate between fibers. After the wetting, fabrics are padded with a mangle to remove the excessive fluid and dried in a hot air medium to evaporate alcohol from the fabrics. Alcohol has no effect on the final STF treated fabrics and thereby being selected due to its low evaporation temperature [27]. In composite systems, STFs can be used in bulk form pouring them in pouches or containers to assemble these smart fluids with various components. Furthermore, cavities in multi-layer systems can be filled with STFs in structural protective applications.

For quasi-static and low-velocity conditions, early studies [125]–[142] used needles, knives, spikes or hemi-spherical rods to investigate the influences of STFs on the protection capacity of high performance fabrics. In order to discuss the role of STFs in fabrics, deformation modes of fabrics under various threats
should be understood. According to Houghton et al. [130], in needle penetration, the loading on needle reaches the first peak value prior to penetration and fabric exhibits a windowing effect where fibers are separated within the yarns without significant fiber breakage, thereby, creating an open area on the fabric. When the second peak load is reached, fabric introduces the maximum damaged zone size. For the further penetration stages, puncture loads are relaxed and fabric slides along constant diameter needle shank. Kalman et al. [74] stated that spike penetrators causes windowing effect as in the needle puncture process. However, higher puncture loads act on fabrics in spike attacks due to larger threat diameter. In knife attacks, fiber cutting prevails the failure mode of fabrics. The tip of knives make a small hole and blade edge cut the fabric along its length [127], [128]. On the other side, under rod-push conditions, contacted yarns are forced to move in the normal direction of fabric surface. In fact, the deformation mechanism is the same with the windowing effect; however, larger rod diameter causes yarn pushing in the direction of penetration to enlarge the yarn openings that allow the penetrator to slip through. Figure 12 shows the failure modes of fabrics under various threat conditions. Actually, these failure modes except for knife conditions are directly related to the inter-yarn friction of fabrics. Upon changing the boundary conditions or deformation rate for the fabrics, deformation modes can be varied. For example, Majumdar et al. [143], [144] fixed the fabric edges applying six bar pneumatic pressure in hemi-spherical rod impacts. The motions of contacted yarns are restricted due to their fixed ends along the fabric edges and therefore, yarns are subjected to tensile loadings. At this point, fiber tenacity becomes important to withstand the penetrator and fiber breakage is observed in the impacted area due to the elevated tensile stresses exceeding the tensile strength of fibers as shown in Figure 13. Regarding to knife threats, the failure mode in fabrics is attributed to the cutting resistance of fibers.

Figure 12: Failure of fabrics in (a) spike, (b) knife and (c) rod penetration. Copyright 2017. Adapted with permission from Taylor & Francis [21]. Copyright 2015. Adapted with permission from Taylor & Francis [89]

Figure 13: Fiber breakage in fabric with fixed edge boundary condition [145]. Copyright 2015. Reproduced with permission from Elsevier

For high-velocity conditions, ballistic tests are applied STF treated fabrics using handgun or gas compressed gun units as suggested in previous investigations [146]–[162]. As in quasi-static and low-velocity conditions, boundary conditions determine the deformation characteristic of fabrics. The fabric shown in Figure 14a was impacted with an approximate projectile velocity of 600 m/s. The fabric was placed on a clay backing material without fixing the edges. Therefore, the deformation on the fabric exhibited a wedge through phenomenon which is seen in targets with low in-plane constraints because projectile easily pushes the yarns ahead instead of breaking them. However, the edges of the fabric in Figure 14b was fixed using a frame and impacted with an approximate projectile velocity of 800 m/s. In this case, the movement of the impacted yarns were constrained due to the fixed end conditions and fibers were broken. In addition to boundary conditions, fiber strength at high strain rates is another factor in the protective performance of fabrics under ballistic impacts. In order to investigate the effect of STF treatment on the tensile strength of fabrics, Fahool et al. [134] applied tensile testing for neat and STF impregnated Twaron fabrics under two different tensile speeds. As shown in Figure 15, STF treated fabrics exhibit much higher modulus in comparison to neat ones which means that the energy absorption capacity of fabrics can be enhanced through higher sound propagation speed in the structure. Moreover,
the presence of STF provides improvement in tensile strength of fabrics and thereby increasing efficiency against attacking threats.

**Figure 14. Fabrics after ballistic impacts with (a) wedge through phenomenon and (b) fiber breakage. Copyright 2013. Adapted with permission from SAGE [148]. Copyright 2015. Adapted with permission from Elsevier [151]**

**Figure 15: Tensile test curves for neat and STF treated fabrics [134]. Copyright 2015. Reproduced with permission from Elsevier**

According to Srivastava et al. [27], plausible mechanisms of improved energy absorption in STF impregnated fabrics are given below as

- Energy dissipation due to shear thickening behavior
- Increased inter-yarn friction (yarn pull out energy)
- Better coupling and load transfer between fiber to fiber and yarn to yarn

Shear thickening behavior has been investigated through rheological measurements and thus, STFs have been integrated into various targets to take the advantage of increasing the thickening mechanism. Although STF treatments enhance the protection capacity of fabrics, the contribution of shear thickening behavior cannot be fully illuminated. Considering rheological behavior, the thickening of STFs in treated fabrics is possible even under quasi-static loadings. Because the required stresses to onset shear thickening are in the order of 10-100 Pa and it is likely that these stresses are generated in STFs around the impact point at very low deformation rates [63], [132]. In terms of inter-yarn friction, STFs are very effective to increase friction in woven structures. In fact, this influence provides the major contribution of STFs to the protection capacity of treated fabrics. Yarn pull-out test is extensively performed to observe the inter-yarn friction in fabrics. In the pull-out test, a single yarn from fabric is mounted in the upper grip of the tensile testing machine and the lower part of the fabric is fixed in the lower grip. The lower end of the single yarn remained free by creating an intentional cut below the yarn. Next, the single yarn is extracted applying various crosshead speeds until the single yarn is completely removed from the fabric. Load vs displacement curves indicate the inter-yarn friction along the fabrics. In general, pull-out forces increase as the single yarn is progressively straightened until the peak point is reached at the beginning of testing. When the pull-out force surpasses the static friction, it drops gradually from the peak point and oscillates while the free end of the single yarn passes each crossing yarn. Each oscillation exhibits local peaks in the graph due to stick-slip motion during pull-out. Last, the pulled yarn is completely removed from fabric. Figure 16 illustrates a typical pull-out test results while comparing neat and STF treated fabrics for different tensile speeds. Based on these curves, STF application enhances the inter-yarn friction and therefore, the interlocking of fibers and yarns is improved which results in better coupling and load distribution under impact. Gürgen et al. [21] carried out drop tower testing for neat and STF treated fabrics to investigate the stab resistance of composite systems. According to this study, the contribution of adjacent yarns to the impact resistance is enhanced using STF treatment in targets. Figure 17 shows the backing material of neat and STF treated fabrics under the spike impact energy of 7.36 J. It is clear that impact energy is concentrated on the impact point and thus, excessive depth of penetration is seen on neat fabric. The collapse of backing material is very small due to accumulated impact energy on the local point.
However, the energy is spread over a wider area and therefore, local damage is reduced due to the restricted motion of fibers on STF treated fabric. Based on this work, it is reported that depth of penetration in STF impregnated fabric is reduced approximately three times in comparison to neat fabric. In addition to inter-yarn friction, surface friction of fabrics is important for protective performance. Although surface friction is not crucial as the inter-yarn friction, it simulates the friction between fabric and attacking threat. In order to measure the surface friction of protective fabrics, ASTM D1894 or ASTM G99 standards can be applied. Figure 18 shows the surface friction of neat and STF treated fabrics and it is seen that STF application has a positive effect for the increase of surface friction which acts as an energy dissipation mechanism against impacting threat.

Figure 16: Pull-out test results for neat and STF treated fabrics [134]. Copyright 2015. Reproduced with permission from Elsevier

Figure 17: Deformation mark on the backing material of (a) neat fabric and (b) STF treated fabric after spike impact [21]. Copyright 2017. Reproduced with permission from Taylor & Francis

Figure 18: Surface friction test results for neat and STF treated fabrics [134]. Copyright 2015. Reproduced with permission from Elsevier

Kang et al. [135] improved the quasi-static penetration resistance of aramid based fabrics using fumed silica and EG based STF. The tests were carried out using a spike penetrator at the rate of 20 mm/min and the targets were prepared by assembling ten individual layers of fabrics. Loads on the penetrator were recorded with respect to the displacement as shown in Figure 19. Clearly, STF application enhances the penetration forces due to the fact that enhanced friction causes the interlocking of fibers within yarns and the fiber mobility is restricted, which acts as an important role in the improvement of protection capacity. Moreover, surface friction of fabric which is the frictional resistance between the spike and fabric contributes to penetration resistance as a secondary mechanism. Using the same testing method, Kalman et al. [74] investigated the role of particle hardness of solid phase in the penetration resistance of STF treated fabrics. For this purpose, hard colloidal silica particles and relatively softer PMMA particles were distributed in PEG200 medium and aramid based fabrics were impregnated with two different STFs. In the testing, a spike penetrator as suggested in the NIJ 0115.00 standard was used with penetration speed of 5 mm/min. According to the results, peak forces for neat fabric, PMMA-STF/fabric and silica-STF/fabric are approximately 20, 55 and 75 N, respectively. Failure mode in each sample is in the form of windowing effect which stems from the mobility of fibers. As given in the peak forces, STF applications restrict the fiber mobility by increasing inter-yarn friction and thereby requiring higher forces for penetration. It is also noteworthy that hard particle based STFs in comparison to softer based ones are more effective in the improvement of protection performance. This is attributed to the mechanical properties of particles which means that softer particles lead to lower resistance to bulk compression and thereby resulting in reduced effect on fabric mobility.
As in quasi-static conditions, STF treatment improves the penetration resistance of fabrics under dynamic conditions. Li et al. [91] used a load cell to measure the impact forces for neat and STF treated fabrics under knife and spike drop conditions in accordance with the NIJ 0115.00 standard. The results show that the depth of penetration is lowered in the fabrics impregnated with STFs; this proves the efficiency of STF treatment in protective applications. The dynamic load characteristics of fabrics are represented in Figure 20 and considering the STF influence on the impact forces, it is seen that STF treated fabrics require more forces to be perforated. The increase in the impact forces is attributed to restriction of yarns within fabrics which is provided by elevated inter-yarn frictions. The effect of STF treatment is also interpreted taking into account the threat types. As given in the force curves, STF treatment is more effective to improve the protection capacity against spike impactor in comparison to knife impactor. This arises from the discrepancy in the failure mode of fabrics which proves that enhanced friction is the major contribution of STF for the protection in fabrics. As suggested by Gürgen et al. [163], under spike impact, the windowing effect prevails the deformation mechanism, this stops the increasing inter-yarn friction. However, under knife impact, cutting is the primary deformation mode and thus, strength of fibers comes into prominence. Even though STF has contribution to the cutting resistance of fibers, it is not strong, as well as increasing the inter-yarn friction [91], [139]. Hence, this defines why the difference in impact forces between the neat and STF treated fabrics is larger under spike impact with respect to knife impact as shown in Figure 20.

Tan et al. [157] studied the ballistic resistance of aramid based fabrics impregnated with various kinds of STFs. In the fabrication of STFs, liquid medium is selected as water contrary to EG or PEG suggested in most of the earlier studies. The study focused on the ballistic limit of targets using spherical projectiles with diameter of 12 mm and a mass of 7 g. The results show that STF with the silica concentration of 40wt% exhibits the highest improvement for the ballistic limit of fabrics despite the STF with the silica loading of 50wt%. Furthermore, the fabrics containing only silica particles without liquid medium exhibit significant increase in the ballistic resistance even though shear thickening behavior does not occur in these fabrics. The mechanism behind the protection is attributed to the increased inter-yarn friction which enhances the coupling of neighbor yarns in the impact zone. Similarly, Park et al. [146] investigated STFs and STF treated fabrics with various configurations in order to reveal the role of shear thickening in the protective performance of fabric based targets. Based on this investigation, it is seen that shear thickening grows as the silica concentration enhances in the suspensions, however, the pull-out test results are not consistent with the rheological responses. The pull-out tests were repeated under eleven different tensile speeds and the fabric impregnated with the silica loading of 68wt% exhibited significantly higher pull-out forces in comparison to that of 69wt% for each pull-out speed. Therefore, Park et al. [146] concluded that the enhancement of maximum pull-out forces of STF treated fabrics compared to neat fabrics is due to the occupation of free volume within the fabric by STF, not the shear thickening effect. To prove this claim, they treated identical silica content STFs to fabrics with different add-on weights and measured the pull-out forces. It was suggested that pull-out forces increase by adding more STFs in the fabrics due to the reduction in free volume within the fabric rather than shear thickening effect. Fahool et al. [134] suggested
that the amount of STF deposited on the fabric during impact may not enable the formation of hydro-
clusters which means that shear thickening is not the plausible energy absorbing mechanism for STF
impregnated fabrics. Another study describing the role of shear thickening behavior in STF treated fabrics
was carried out by Gürgen et al. [163]. In this study, multi-phase STFs were fabricated using micron-sized
silicon carbide particles and aramid based fabrics were treated with these suspensions. Although carbide
particles disrupt the thickening mechanism of STFs, the stab resistance of fabrics increases adding carbide
particles into STF/fabric system. This inverse relationship between the rheological behavior of STFs and
stab resistance of fabrics indicates that shear thickening behavior does not have a major influence on the
protective characteristics of fabrics which are associated with the mechanical properties of sub-phases. It
is stated that carbide particles enhance the surface friction of fabrics associated with the fabric contact
with attacking threat and thereby contributing to the penetration resistance of the targets. Moreover, the
interlocking of yarns enhances owing to the carbide particles intercalated between yarns and fibers. In
addition to these frictional effects, high compressive strength and hardness of carbide particles contribute
to energy dissipation mechanism during impact. In concern with the impact behavior of STFs, Petel et al.
[24], [25] suggested that low velocity penetration resistance is dominated by the dynamic material strength
of suspension whereas at higher velocity conditions, penetration is prevailed by suspension density. In the
experimental stage of these studies, bulk suspensions in two different containers were subjected to ballistic
impacts using 17 grains (1.1 g) chisel-nosed mild steel NATO-standard FSP. The size of the first container
(capsule #1) was 50 mm of axial length and 25 mm of diameter whereas the size of the second container
(capsule #2) was 64 mm of axial length and 38 mm of diameter. The penetration resistance of suspensions
was evaluated considering the reduction in the projectile velocity which was calculated by the difference
between the impact velocity and residual velocity of projectile after leaving the container. During impact,
the formation of force chains restricts the fluid in STF to flow until force chains are broken which means
that the strength of particles in the chains come into prominence. In low velocity impacts, force chains are
disrupted through rotational and translational mechanisms of particles as long as the strength of particles
withstands the acting forces. However, in high velocity impacts, force chains can only be disrupted in case
of particle deformations such as fracture or crushing when the dynamic strength of particles is exceeded.
Therefore, as the particle concentration increases in the suspension which results in increased suspension
density, force chains are distributed through the increased number of particle contact branches and the
penetration resistance of suspension improves. On the other hand, the margin of low and high velocity
impacts was stated as approximately 300 m/s based on their experimental results which shows great
consistency with early studies [147], [157]. In these previous works, a loss of effectiveness is found
against steel projectiles above an impact velocity of 300 m/s. Figure 21 shows the impact velocity
responses for two STFs including different sub-phases. The term \( \Delta V \) represents the difference between
the impact velocity and residual velocity of the projectile while \( \Delta V/V_i \) gives the normalized velocity decrease
of the projectile which equals to 1 when mixture stops the projectile and this term reduces from 1 as the
residual velocity of the projectile increases.

**Figure 21: Impact velocity response for (a) single-phase STF with silica loading of 72.5wt% and (b)
multi-phase STF with silica loading of 50.2wt% and silicon carbide loading of 25.5wt% [24]. Copyright
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Numerical studies into STF treated fabrics point out that friction in fabrics is the major factor for the
protective behavior of fabrics regardless of shear thickening effect. Park et al. [151] investigated the
ballistic resistance of high performance fabrics impregnated with STF. In the numerical stage of the study,
fabric properties were modeled based on mechanical tests. To implement the role of STF for the fabrics, inter-yarn friction was considered as the only effect and Coulomb friction model was used in the finite element simulations according to the pull-out test results. Impact tests were carried out in the velocity range of 800-2000 m/s for fixed edge fabrics using 5.56 mm diameter 2017-T4 aluminum spherical balls. In the analyses, numerical results are compared with experimental results in terms of energy absorption and residual velocity. The results showed that friction based numerical simulations exhibit the influence of STF for protective fabrics despite some error percentages even observed in the neat fabric results. Therefore, it was stated that the assumption of inter-yarn friction provides adequate approximation of impact resistance of STF treated fabrics considering early studies which suggest that friction is the main contributor to energy absorption mechanism of woven fabrics. Furthermore, the experimental and numerical study on the protective characteristics of neat and STF treated fabrics suggested a positive influence by STF impregnation on the energy absorption capacity. Another numerical study was performed by Lee et al. [155] to model the impact response of STF treated high tenacity fabrics. As suggested by Park et al. [151], the inter-yarn friction along fabrics was increased for STF treated fabrics based on pull-out testing using Coulomb friction model in the finite element simulations. In the ballistic impacts, two-edge fixed fabrics were subjected to 7.62 mm spherical bullet shootings with the approximate velocity of 214 m/s. In the analysis of the results, deformation of woven structures was investigated in addition to residual velocity of projectile and energy dissipation rates. Figure 22 shows the local deformations on the neat and STF treated fabrics both in experiments and simulations. According to the results, numerical and experimental outputs exhibit good agreement each other which means that friction based approach for the ballistic resistance of fabrics is applicable and therefore, the contribution of STF is mainly dependent on the increase in the inter-yarn friction for fabrics.

Figure 22: Local deformations on (a) neat and (b) STF treated fabric both in experiments and simulations [155]. Copyright 2012. Reproduced with permission from Taylor & Francis

After introducing the investigations into the rheology of multi-phase STFs in literature in recent years, small number of researchers decided to utilize these novel suspensions in protective systems. There are only three publications on this concept and each study presents different results based on the additives. Hasanzadeh et al. [23] fabricated multi-phase STFs adding multi-walled carbon nanotubes (MWNTs) in fumed silica and PEG200 mixture. Based on the flow curves, the degree of shear thickening decreases with the addition of MWNTs as given an early study [119] performed by the same research group. In order to observe the effect of MWNTs on the inter-yarn friction, yarn pull-out test was carried out for high modulus polypropylene (HMPP) fabrics impregnated with single and multi-phase STFs. From the results, STF treatments provide an increase in inter-yarn friction with respect to no treatment condition however, the addition of MWNT to single-phase STF causes a mild decrease in the pull-out force. According to the quasi-static penetration test, the fabric treated with single-phase STF exhibits the highest penetration resistance among the specimens as shown in Figure 23. It is also noteworthy that the displacement for single-phase STF fabric is greater than the other ones which means that the largest deformation before puncturing is seen in the fabric with single-phase STF. On the other hand, MWNTs cause a reduction in penetration resistance of STF treated fabrics even multi-phase STF treatment yields beneficial results for protection in comparison to neat fabrics. The authors suggested that the single-phase STF provides higher increase in friction and correspondingly, the highest penetration resistance is achieved in single-phase STF treated fabric. Although the rheological results support the contribution of shear thickening effect, it is difficult to state this for the reason of enhanced penetration resistance. Moreover, it is noted considering
the SEM image of each specimen that the single-phase STF treated fabric has more continuity and integrity with well-distributed silica nanoparticles over the fabric surface and thus, applied stress is evenly spread over the fabric with the contribution of restricted adjacent yarns to the penetration point due to STF filled gaps in crossing yarns.

**Figure 23: Load vs displacement curves for each fabric under quasi-static penetration test [23]. Copyright 2016. Reproduced with permission from Elsevier**

It is also stated that deformation modes of the fabrics diverge by means of STF treatments. As shown in Figure 24, wedge through phenomenon governs the deformation in the penetration point of neat fabric. This deformation mode points out lower inter-yarn friction. It should be also noticed that the diameter of penetrator is significantly larger than yarn width and therefore, the opening between sliding yarns is not large enough to allow the penetrator to pass through as in windowing effect. On the other side, the fabrics impregnated with both single and multi-phase STFs exhibit fiber breakage in the penetration point which means that inter-yarn friction fulfills the demanded level. At this point, fiber strength is discussed which is directly related with the mechanical properties of fiber material and beside the point of STF treatments. From technical point of view, woven fabrics during impact exhibit various failure modes but among the failure mechanisms, enhanced inter-yarn friction has extreme contribution to dissipation of impact energy.

**Figure 24: Failure mode of (a) neat fabric, (b) single-phase STF/fabric and (c) multi-phase STF/fabric [23]. Copyright 2016. Reproduced with permission from Elsevier**

Second investigation concerning multi-phase STFs in protective applications was performed by Laha et al. [117]. In this study, multi-phase STFs were prepared adding halloysite nanotubes into silica based suspensions. In order to show the effect of multi-phase STFs on the protective capacity of fabrics, aramid based fabrics were treated with various mixtures and subjected to dynamic impact testing in which the fabric edges were fixed using grippers and a hemispherical impactor was dropped on the fabrics at a speed of 5.5 m/s. The results of impact testing is shown in Figure 25 where multi-phase STFs are more effective for energy absorption with respect to single-phase STF. Considering the amount of nanotubes in the fabrics, there is no systematic increase in the energy absorption capacity of fabrics with increase of additive loading. However, shear thickening mechanism systematically grows adding more nanotubes in suspensions. In the light of these results, it is difficult to associate the protection mechanism of STF treated fabrics to the shear thickening behavior of STFs. In fact, the failure modes of fabrics point out the prominence of yarn to yarn friction for fabrics subjected to impact. Figure 26 shows the deformation of impacted yarns for neat and STF treated fabrics and as stated the failure mode for neat fabric is wedge through phenomenon without a significant fiber breakage. However, wedge through effect is happened to a lesser extent and fiber breakage prevails the failure in comparison to neat fabric. This discrepancy in the failure modes of fabrics stems from the inter-yarn friction and enhanced friction due to STF treatment provides the contribution of secondary yarns to impact energy absorption which can be understood from relatively larger size of the dome in the deformed area of STF treated fabric as compared to neat one. Hence, energy absorption capacity is enhanced through increased friction using STF treatments.
Another recent work was performed by Gürgen et al. [163] to investigate the role of additive particles on the stab resistance of STF treated fabrics. In this study, silicon carbide particles with various sizes were utilized as the second phases in multi-phase STFs to take the advantage of carbide particles such as high hardness and strength in protective systems. The multi-phase STFs were prepared blending fumed silica and three different sizes of carbide particles in PEG400 medium. Based on the flow curves, carbide particles exhibit a disruptive effect for the shear thickening mechanism of STFs. Comprehensive investigations on multi-phase STFs with carbide particles are discussed in previous sections according to the same research team [20], [22]. In order to observe the effects of STFs on fabrics, surface friction and pull-out tests were carried out. Based on the surface friction results, single-phase STF significantly enhances the friction coefficient of fabric by virtue of sticky surface arising from the nature of STFs. Moreover, addition of carbide particles causes further increase for the surface friction where the additive particles participate as third bodies in the contact zone of fabric and threat. Presence of hard carbide particles hinder the motion of threat on fabric by creating asperities on the surface in addition to the sticky effect of STF. Furthermore, increased surface friction enables the growing of inter-layer friction in laminated targets and thereby restricting the lateral motion of yarns which stops the threat from penetrating. The pull-out test results are shown in Figure 27. Initially, pull-out force grows as the yarn is continuously straightened until the maximum point and then static friction limit is overcome which causes a gradual reduction in pull-out force. During this reduction, pull-out force oscillates while the extracted yarn passes each crossing yarn. Each oscillation exhibits local peaks in the force profile due to the stick-slip motion during the pull-out. It is seen that inter-yarn friction is significantly enhanced by STF applications on fabrics. Although single-phase STF enhances the maximum pull-out force approximately three times considering neat fabric, multi-phase STFs realize further enhancement in yarn to yarn friction of fabrics. Additive particles locate between fibers and yarns and thereby causing a pre-strained texture along fabrics and interlocking of fibers which result in increase of inter-yarn friction. In this light, coarser particles occupy larger volumes between fibers and thereby enhancing the aforementioned mechanism in inter-yarn friction.

In addition, the stab resistance of fabrics was investigated using a drop tower tube in accordance with NIJ 0115.00 standard. According to the drop tower test results as shown in Figure 28, STF treatments exhibit beneficial results in terms of protection capacity and multi-phase STFs enhance the improvement for further levels especially using coarser particles as the second phase in suspensions. The protection performance of fabrics is in compliance with the pull-out test results but the rheological results do not support it. Even though the shear thickening mechanism of single-phase STF is superior to that of multi-phase STFs, the fabric impregnated with this fluid exhibits lower penetration resistance in comparison to
multi-phase STF treated fabrics. Moreover, shear thickening behavior decreases as the particle size of carbide particles grows in multi-phase STF whereas the fluid with coarser additives is more effective to enhance the penetration resistance of fabrics. In this light, it is possible to mention that friction in fabrics is the major mechanism in energy dissipation under impacts and shear thickening effect is not related with the protection mechanism of fabrics. In concern with multi-phase STFs, material properties of additives determine the contribution level to fabrics protection. Considering carbide particles, in addition to their contribution to increasing friction, advanced hardness and strength of these particles provide an additional energy dissipation mechanism for impacted fabrics.

Figure 28: Drop tower test results for (a) spike and (b) knife impactor [163]. Copyright 2016. Reproduced with permission from Elsevier

Beside the flexible fabric applications, some early studies [160], [162], [164] integrated STFs into laminated composite materials using metallic or polymeric materials against high-velocity impacts. These composite structures are not flexible due to the nature of laminated components in targets however, STFs are employed for increasing the protection capacity and reducing the weight. Tan et al. [162] fabricated sandwich structures which are composed of two pure aluminum sheets and silica based bulk STFs between these plates. In order to report the influence of sheet thickness and STF rheology, the thickness of back side plates and the silica content of STFs were varied. The impact tests were carried out using a gas gun unit shooting a steel cylindrical projectile at the speed of 30 to 120 m/s. Based on the results, the shear thickening mechanism of STF increases its influence as the striking velocity increases in the tests. Figure 29 shows the failure mode of back side plates of composite structures including the 56wt% silica based STFs after the impacts at 80.1 m/s and 105.8 m/s respectively. Clearly, the plate shows shear and plug deformation at lower impact velocity whereas petalling governs the deformation at higher velocity impact. This is due to the shear thickening effect of STF that thickening at lower speeds, increase in the STF viscosity is not effective as expected and therefore, STF flows outward from the impact point and the projectile shears the plate. However, at higher impact velocity, thickening governs and extended hydro-clustering spreads the impact energy over a wider area and thus, petalling is formed on the impact zone. Moreover, residual velocity of projectile decreases as the silica loading increases in suspension. Haro et al. [160], [164] fabricated hybrid structures using aramid based fabrics between two aluminum alloy 5086 plates which are preferable for light armor systems. To observe the role of STF, the fabrics were impregnated with colloidal silica and PEG400 based STFs. The targets were subjected to ballistic impacts in accordance with NIJ 0108.01 standard using a rifle caliber 270 Winchester and ammunitions of 150 grains power-point. The results showed that STF-containing targets have better stability after several shots and target delamination is not observed due to the improved bonding between aluminum plates and fabrics treated with STF. On the other hand, targets without STF experience delamination at the interface of aluminum plates and fabrics as shown in Figure 30.

Figure 29: Failure mode of back side plate of composite structures including the 56wt% silica based STFs after the impacts at (a) 80.1 m/s and (b) 105.8 m/s [162]. Copyright 2016. Reproduced with permission from Elsevier
Cwalina et al. [125] investigated the STF application for standard extravehicular activity (EVA) space suit replacing the standard neoprene-coated nylon absorber layers with STF treated woven aramid fabrics. The fabrics were tested under hyper-velocity impact that represents the impact characteristic of micrometeoroids and orbital debris (MMOD). Impact experiments were performed on a 0.17 caliber light gas gun at NASA’s White Sands Remote Hyper-velocity Test Facility using spherical aluminum projectiles with the impact velocity of 4 to 8 km/s. The results suggested that EVA space suits containing STF/fabrics can propose plausible MMOD puncture protection whilst being lighter than standard EVA space suit. Therefore, STFs may be benefited for space researches in terms of both increase in protection and lightness. Another STF application regarding space researches is proposed for spacecraft being deployed on an extraterrestrial mass. A patent application [165] was filed for this application which offers STF treatment for the outer skin of inflatable spacecraft to reduce potential penetration of MMOD into the interior of module. Moreover, a bulk STF layer is optionally proposed under the outer skin of the module to enhance the protection capacity.

6. Possible applications of STFs

Due to the nature of STFs, these mixtures are intended to be adapted for engineering applications especially dealing with vibrations and shock loads. In order to reduce undesired vibrations in mechanical systems, STFs are replaced with viscoelastic liquids in viscoelastic liquid dampers. As reported in early publications, shear thickening behavior at high dynamic loadings provides higher stiffness/damping ratio and energy absorption capacity in comparison to this behavior at low velocity loadings [10]. In mounting applications, these suspensions are recommended to reduce resonance amplitudes. It is also stated that thickening behavior cannot be enabled below the critical thickening point even at high frequencies and thus, a gradual damping is realized in applications [12]. Structural elements integrated with STFs such as STF filled beams are beneficial against dynamic flexural loadings as strain or frequency changes. When STF filled beams are excited, vibrational response of system is significantly damped. The integration of STF into structural elements provides a significant damping in vibrational response and increase in resonant frequency [9]. Due to these beneficial influences of STFs, these complex suspensions can be candidate materials for the control of vibration and noise in civil engineering applications like seismic isolation of buildings and bridges or in mechanical engineering applications like energy dissipation devices [166]. In regard to shock loading applications where a major amount of energy is absorbed in a very short time, STFs are brought together with various structures such as open cell foams. Dawson [167] suggested flexible and low-density reticulated foams filled with STFs for vehicles and helmets to improve impact protection. In a recent study [14], micro-agglomerated cork sheets are engraved with various microfluidic patterns and filled with STFs. These novel composite materials are suggested as safety paddings for impact resistance applications such as motorcycle or bike helmets. STFs are also investigated against blast shock waves in very recent publications [168]. According to the pressure profiles and flow visualization in aforementioned study, STFs have a considerable influence on mitigating the strength of shock waves and therefore, energy dissipative structures such as barriers could take the advantage of shear thickening behavior of these mixtures. Ballantyne et al. [169] utilized STFs in protective eyewear against impact in sport applications. The conventional straps of a goggle were replaced with STF filled tubular straps and the google was mounted on a headform before the lacrosse ball impact tests. This novel straps
provides better protection in comparison to the conventional tethers especially against successive strikes which are likely to cause injuries and game stoppages. In medical applications, STFs are suggested to restrict the movement of shoulders, knees, elbows, ankles and hips to prevent these joints from sudden accelerations [15]. Given these studies, STFs have a wide range of application fields for future technology. In particular, applications dealing with vibration and shock response of systems could be heavily benefited from these smart fluids.

7. Conclusions

In the present work, the rheological properties of STF were reviewed. Since STFs have been very popular in protective applications for last decade, the role of STFs in protective systems was discussed based on early investigations. In addition, multi-phase STFs, which have been introduced into literature for last five years, were investigated according to the proposed rheological theories and models. Furthermore, multi-phase STF applications in the field of body protection was given based on very limited publications in literature. In the light of this extended review study, STFs provide an additional energy absorption capacity especially for woven fabric structures. However, it can be mentioned that the improvement is not directly related to shear thickening effect. It is possible to say that friction along woven fabrics is the primary energy dissipation mechanism and STFs improve this mechanism simply through increasing the friction. Moreover, by filling the gaps between fibers and yarns, STFs provide enhanced fiber/yarn coupling and therefore, load transfer is spread over a wider area and penetration depth is lowered in the structure.

Acknowledgements

S.Gürgen acknowledges the support of the Scientific and Technological Research Council of Turkey (TÜBİTAK) under Program 2211.