Research and Applications of Shear Thickening Fluids

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Abstract:

Shear thickening fluids (STFs) have been studied extensively and generated enormous amount of patent filings due to their huge potential for commercial applications since their discovery. STFs draw more and more attentions as they have been considered as suitable materials for liquid body armour, sports and personal protection because of their unique properties. This paper presents a review of the state of the art in STF technology. The ingredient materials, fabrication methods and basic models to describe STF behaviors are discussed briefly. An outline of the patenting activities in the field of STF materials, including effects of the different particles and their volume fraction in the suspensions on the critical shear rate of shear thickening is presented. Most of the specific patent applications, particularly in body armor, as well as other industrial applications, such as smart structures, and devices with adaptive stiffness and damping, are also summarized. Recent advances, including the effects of particle surface properties, relationship to carrier fluids, electric or magnetic fields applied on the transition of STFs are included in the review. The possibilities of wider applications or designs depend upon a deeper understanding of the STFs, and the potential of novel STFs to protection applications provide an impetus for future research.

Keywords: body armour, damping, field activated, nanoparticles, Newtonian fluid, shear thickening fluids, smart structure, viscosity.

but with a higher viscosity, after the transition [9]. There has been some research into the dynamic properties of STFs. Laun *et al.* [9] reported the critical strain amplitude for dynamic shear thickening at a fixed angular frequency of a polymer latex dispersion. Raghavan *et al.* [10] investigated the shear thickening response of fumed silica suspensions under steady and oscillatory shear. Fischer *et al.* [1] investigated the dynamic properties of STF based on a vibrating sandwiched beam.

STFs have certain industrial uses due to the shear thickening behavior. The highly nonlinear behavior can provide a self-limiting maximum rate of flow that can be exploited in the design of damping and control devices. And various corporate and government entities are researching the application of shear thickening fluids for their uses in body armour. Such a system could allow the wearer flexibility for a normal range of movement, yet provide rigidity to resist piercing by bullets, stabbing knife blows, and similar attacks.

2. MATERIALS

A STF is composed of a carrier liquid and rigid, colloidal particles. A typical kind of particles is Colloidal silica and the most commonly used carrier liquid is polyethylene glycol. The tiny particles suspended in the liquid in a very high concentration (maximum 55-65 vol%) can be utilized for the shear thickening purpose. The actual nature of the shear thickening depends on physical parameters of the suspended phase: phase volume, particle size (distribution) and particle shape, as well as those of the suspending phase: viscosity, details of deformation (including shear or extensional flow, steady or transient, time and rate of deformation) [4]. For the last two decades, intensive research has been focused on the effects of the volume fraction of the particles in the suspension and particle dimension on the critical shear rate.

Extensive amounts of patenting activity have documented the effect of different particles and their volume fractions on the critical shear rate. The particles are generally selected from a number of the groups consisting of titanium oxide, calcium carbonate, cornstarch, polyvinyl alcohol-sodium borate mixtures, aqueous solutions of polymethacrylates and poly (alkyl methacrylates), gum arabic and borate ions, and

variety of fluids with different density matching, modified surface properties, roughness, shapes and measuring conditions, "discontinuous" shear thickening was always observed. Inductively, the discontinuous shearing thickening is general to all hard-particle suspension at near-sedimentation packing fractions provided that the shearing-thinning stresses are below a threshold [20].

Electrorheoloical (ER) or magnetorheological (MR) fluid are well known as kinds of smart materials respectively because their structural and rheological changes caused by an electric [22] or magnetic field [23] are typically reversible. Commonly, ER fluids are composed of insulating fluids and polarizable particles. ER fluids exhibit a tremendous increase in their shear viscosity, from a liquid-like to a solid-like state, when they are exposed to a relatively high electric field. It is caused by the formation of chain-like structures of the dispersed particles aligned along the electric field [24], which occurs within a few milliseconds [25]. Typical MR fluids are formulated by dispersion of magnetic particles in an inert (no magnetic) carrier liquid. This material shows a dramatic but reversible increase in shear viscosity in the presence of an external magnetic field. The dramatic change in shear yield stress is due to the magnetic polarization induced in particles, resulting in the dipole-dipole interaction forces between particles, which, in turn, lead to the formation of particle chains along the direction of magnetic field. ER fluids have been applied in various areas such as shock absorbers, engine mounts and clutches [26], while MR fluids show potential in applications of the design of dampers, brakes, polishing machines or torque transducers [27]. The recent research on the combination of ER or MR effects with shear thickening [20] has opened up possibilities for the designs of field-responsive shear-thickening fluids [28-30]. The applied fields would control the critical shear rate [30] only for weaker shear-thickening ($\varepsilon > 0$), where both the critical stress and shear rate vary with field. The critical shear rate is controlled by the particle packing fraction [31], whereas the critical stress can be tuned either passively with particle-fluid chemistry or actively with field [20].

and substantial increase in viscosity and shear stress. A viscoelastic damper, filled with a STF, was invented [34] to control the vibration of a structural member, a tank, a pipe, etc. The vibration might be caused by an earthquake or wind. The damper would produce minimum reaction force when the structural member and so on was slowly displaced as a result of the thermal deformation of the member itself or another member connected thereto. STF could present relatively small resistance when the speed of the motion is small and produces progressively resistance as the speed of the motion increases.

3.2 Smart structures

Based on the STF and STF devices, the smart structures used for industrial applications were also investigated. The patent [35] presented a method for minimizing damage to the downhole equipments. They used shear thickening fluid as a tamp in controlled pulse fracturing (CPF). The fluid would become more viscous and more resistant to flow up the production string or tubing when fluid velocities increased under the force generated by the ignited propellant. It would slow or even stop the upward movement of structures and the damage to the equipments would be lessened. The invention [36] presented a method to process composite structures with tailored stiffness and damping performance incorporating STF, preferably at the interface between two elements belonging to the same structure and moving to each other. The composite structure incorporating STFs according to this invention may advantageously be used in applications such as sports equipment, aeronautics, aerospace, consumer goods or in any other suitable field where the dynamic properties of the said structure need to be tailored.

Laun *et al.* [7] and Helber *et al.* [37] investigated the STF's application in mounting systems for industrial machinery. Some medical equipments can also use STF and STF devices to obtain special mechanical behaviors. The patent [38] invented a body limb movement limiter. The device was designed to use a shear thickening non-Newtonian fluid disposed within it for limiting movement. It could help limit movement of a person's joint such as shoulder, knee, elbow, ankle, hip, etc., so as to

material, being a dilatent compound or a lightweight version, incorporating Duolite spheres or a derivative. The dilatent material remained soft and flexible until it was subjected to the impact when its characteristics changed rendering it temporarily rigid. The carrier could be coated or impregnated with the dilatent compound in various ways. The patent [43] also described the use of dry dilatant agents in a fabric carrier to improve ballistic protection. In their approach, the dilatant agent is a polymeric powder which is applied to the fabric while suspended in a carrier fluid, and subsequently dried to leave behind the dilatant solid.

With emerging of the STFs, more and more patents have been filed to protect liquid body armors or sport protections using STF. Lee *et al.* [6] and Decker *et al.* [44] investigated the ballistic properties of woven aramid fabrics impregnated with a colloidal, discontinuous STF. The patents [45] and [46] invented an armor composite material, which contained a ballistic fabric impregnated with shear thickening fluid. The invented material offered a superior ballistic performance compared to the conventional ballistic fabric-based materials of the equal thickness. Furthermore, the STFs were enhanced and integrated into a flowable and deformable composite structure, which included reinforcement by "stiff" materials, i.e., materials with high compression strength and high bending modulus, such as, but not limited to, short inert fibres less than 1 cm [47].

There are also many similar patents about "liquid body armor", they almost have had the same process: First diluting the fluid in ethanol; saturating the Kevlar with the diluted fluid and placing in an oven to evaporate the ethanol; the STF then permeating the Kevlar, and the Kevlar strands holding the particle-filled fluid in place at the end. When an object strikes or stabs the Kevlar, the fluid immediately hardens, making the Kevlar stronger. The hardening process happens in mere milliseconds, and the armor becomes flexible again shortly afterward.

For such a novel liquid body armour based on STFs, the promising results have been shown towards improved protection and flexibility. However, the applications of the "liquid body armor" still suffer several drawbacks, which include evaporation, leakage of carrier fluids and air and/or moisture permeability for the comfort clothing

shapes and measuring conditions. The findings open up possibilities for new designs of smart suspensions that could combine shear thickening with particle surface properties, electro- or magnetorhelogic response, therefore, producing specific STFs for different applications, and certainly widening STFs potentials.

STFs are used as key materials for liquid body armour and sport protections because of their unique shear thickening property. Currently, research of STFs is being actively conducted around the world due to the huge potentials for commercial applications, particularly in the military area. A novel engineered material dee-three-oh (d3o) which employ shear thickening fluid based on a special gel has been developed by UK company d3o [51]. Such material is able to flow with you as you move but on shock lock together to absorb the impact energy. New STFs materials, based on novel carrier materials and fibre making techniques, will pave the way to the applications, not only overcoming the evaporation and leakage problems in conventional STFs, but also improving the wearing comforts because of the lightweight, and good permeability to air and moisture in the near future. Many polymeric materials behave like a fluid, but they have greater ability to retain physical shapes than a conventional fluid, and they do not evaporate easily. Along this line, for example, the shear curing gels or shear curing elastomeric materials with flexible behaviour would potentially be able to work as a STF in a greater range of environments, such as a wider temperature range from very cold to very hot, a broader humidity from very dry to very wet or at extreme conditions. The excellent stability and non-evaporating feature of these materials allow them to be used as alternatives to a fluid to host nanoparticles.

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1. INTRODUCTION

A shear thickening fluid (STF) is a material whose viscosity increases dramatically when the shear rate is above a critical value. It is an example of a non-Newtonian fluid and also termed a dilatant fluid. At low shear rates, the liquid has low viscosity and acts as a lubricant, and it flows easily; however, at higher shear rates, the hydrodynamic forces overcome repulsive interparticle forces and hydroclusters form. The liquid is then unable to fill the gaps created between particles, and friction greatly increases, causing an increase in viscosity. In addition, this increased viscosity is seen as being both 'field activated', due to the dependency on shearing rate, as well as reversible [1]. This can readily be seen with a mixture of cornstarch and water, which acts in counterintuitive ways when struck or thrown against a surface.

It has been demonstrated that reversible shear thickening results from hydrodynamic lubrication forces between particles, often denoted by the term "hydroclusters". The particles repel each other slightly, so they float easily throughout the liquid without clumping together or settling to the bottom. But the energy of a sudden impact overwhelms the repulsive forces between the particles, and they stick together to form hydroclusters. When the energy from the impact dissipates, the particles begin to repel one another again and the hydroclusters fall apart, so the apparently solid substance reverts to a liquid. Support for the hydrocluster mechanism has been demonstrated experimentally through rheological, rheo-optical and neutron experiments [2], as well as computer simulations [3].

Many earlier studies focused on determining this 'field activated' viscosity and other rheological properties of STF under a steady shear and/or an oscillatory shear flow. Steady shear research indicated the common feature of the STF materials rheograms is a sharp increase in viscosity that decays at higher shear rates, often referred to as a discontinuity [4-8]. This increase occurs at a critical shear rate. In addition, the suspension behaves as a Newtonian fluid during a large spectrum of shear rates, except for the transition shear rate period that causes the fluid's specific critical shear rate transition. These types of fluids have been characterized as Newtonian fluids with a low viscosity before the critical shear rate transition, and as quasi-Newtonian fluids,

guar gum and borate ions, synthetically occurring minerals, naturally occurring minerals, polymers and a mixture. Some of these shear thickening fluids are discussed in the patents [11-13] issued to Savins and Wagner *et al.* The concentration of the thickening compounds utilized should be sufficient to impart the desired shear thickening qualities and effect. The concentrations of polyvinyl alcohol and borate ions which can be used were discussed in one patent [11], while the concentrations of polymethacrylates and poly (alkyl methacrylates) were discussed in another patent [12]. Other useful shear thickening materials, and their concentrations can be found in the literature in which materials also include the category of dilatent materials and sometimes gels[14].

Many carrier fluids have been used, including water, ethylene glycol (EG) and polyethylene glycol (PEG). However, EG or PEG is the most widely used carrier fluid in STF due to its high stability, high boiling point and non-flammable properties. A typical STF was made of silica nanoparticles suspended in polyethylene glycol [15], so many reports describe this fluid as a form of nanotechnology. The carrier fluid was typically added to the powder, and a blender used to mechanically mix the two components. The concentration of the nanoparticles ranged from 40% to 60% [15].

The shear thickening effect is due to general mechanisms such as hydrodynamics [16, 17] or dilation [18, 19] and thus all suspensions are expected to show shear thickening under certain conditions [4].

Despite the longstanding expectation that shear thickening is a generic type of suspension behaviour [4, 16], very recently, apparent contradiction is found that shear thickening can be masked by a yield stress and can be recovered when the yield stress is decreased below a threshold [20]. In typical suspensions, attractions are often due to particle-fluid surface tension. An example is the common observation that cornstarch (a hydrophilic particle) shear thickens in water but not in hydrophobic liquids [21]. Apart from the surface properties (e.g. hydrophilic or hydrophobic), the surface roughness, the particle shape and the measuring conditions plays a role in being observed shear-thickening effect. It is found that a variety of suspensions consisting of particles including cornstarch, glass and polyethylene glycol (PEG), in a

3. APPLICATIONS

The STF has held promises in many industrial applications. Some patents protected certain applications while others invented certain shear thickening fluids with potentials of various applications. For example, one patent [32] described a shear thickening fluid used in conjunction with fabrics utilized in an expandable spacecraft. The combination of the fluid and the fabric allowed the fabric to resist penetration by hypervelocity particles in space. On the other hand, the other patent [33] studied the rheology of a colloidal PEG-based shear thickening fluid emulsified with silicone oil and found that a shear thickening response was observed in the viscosity-shear rate curves for volume fraction as low as 10% of STF in the silicone emulsion. Potential applications for such STF covered in the patent incorporated into pads for sport equipments: such as a mouthguard for improved energy dissipation, reducing the like hood of concussion or dental damage; gloves for reducing vibration or protecting the hands from jarring impact; directly into sports shoe designs for energy dissipative construction. The comfortable composites comprised of discrete droplets or co-continuous networks of STF could also be used in seat cushioning and neck supports in automobiles, airplanes and trains to provide more protection during accidents. Smart components could be fabricated where the stiffness or hardness of a flexible component can change as a result of deformation, such as from elongation, bending, torque, twisting, or compression. The materials could be used as a medium to control mechanical actuation of one object relative to another, etc [33].

The three main application streams, however, including devices with adaptive stiffness and damping, smart structure and body armor, will be reviewed in more details below.

3.1 Devices with adaptive stiffness and damping

The basic idea here is to use STF in a viscoelastic damper and to obtain adaptive stiffness and damping. A device filled with functional fluids, one of which was a shear thickening fluid to provide variable dampings[30]. When subjected to a predetermined shear rate, the shear thickening composition would undergo a dramatic

prevent the patient from subjecting the joint to sudden rapid acceleration and consequent force on the affected area. Such devices would help to prevent the attendant damage that could result from such rapid acceleration and work with varying degrees of efficiency.

3.3 Body Armor

Up to now, the widest application of the STFs has been for liquid body armors in military applications. Throughout the history, personal armour systems have been practical only when they have been able to provide significant protection against the prevailing threats whilst not impairing the wearer's ability to perform the tasks required to them. The materials which were used for current body armour applications were not capable to provide whole body protection due to their stiffness and bulky properties. The key issue is that if we provide the same level of protection as the torso with current body armour materials, they would be far too stiff and bulky to allow the wearers to carry out the normal movements of their arms and legs. Novel liquid body armour based on the STFs has shown promising prospects including towards improved protection and flexibility. Most liquid body armours in recent patents were formed by immersing a fibrous substrate or a porous media in a STF.

In contrast, in earlier year's patents, dry powders exhibiting dilatant property were used to increase volume and viscosity under ballistic impact or similar kinds. For example, the patent [39] used KEVLAR® fibers coated with a dry powder that exhibits dilatant properties. Dilatant properties refer to increases in both volume and viscosity under flow. In their work, the fibers demonstrated an improved ability to distribute energy during ballistic impact due to the enhanced inter-fiber friction. The patent [40] impregnated a low glass transition, viscous polymer fluid, as a liquid adhesive additive, acted as a friction modifier, into a fibre structure such as a polyaramid fabrics, and the patent [41] found the viscous polymers were effective in many different types of fibrous structures with a result of an optimal ballistic resistance and protection against blunt trauma in a body armor. The patent [42] reported a dimethyl-siloxane-hydro-terminated polymer, such as Dow Corning 3179

purpose. Most liquid body armours have been formed by immersing a fibrous substrate or a porous media in a STF. However, impregnated fibres or porous media have a disadvantage in that when the STF is exposed to the elements, the fabric performances suffer because of the STF evaporation and leakage. Therefore, the evaporation of the carrier fluid is indeed a key issue in the current STF research. For example, silicon nanoparticles suspending in an ethylene glycol fluid is a typical composition of STF. The EG is still easy to evaporate into the air, though its boiling point is as high as 197 centigrade. Considerable efforts have been made in recently years to solve this problem. One of the efforts included filling a hollow fibre with a STF [48]. However, a STF, by the nature, is not easily pumped into hollow fibres. In order to pump the STF into the fibres, the viscosity of the STF has to be decreased, but in this case the shear response of STF will be affected accordingly.

Another critical requirement for soft and comfort body armour is reasonably high permeability to air and moisture. It is expected that a body armour is not only very flexible but also permeable to air and moisture, so that they are comfort to wear, apart from the strong enough protection from being hurt. Research on STF-based liquid body armor is ongoing actively at the U.S. Army Research Laboratory, the University of Delaware [49], and the Massachusetts Institute of Technology (MIT) [50].

4. CURRENT & FUTURE DEVELOPMENTS

This paper presents a review of the state of the art in the STFs technology. There are growing needs to understand all aspects of the STFs, to model their behaviors and to improve applications by using optimal components and fabrication procedures or methods. The potential applications of the STFs are introduced by reviewing patent activities. The patent review indicates that researchers have been continually developing new STFs with new materials, or optimized conditions or novel manufactures to meet new and more demanding requirements. Perspectives on the applications of STF will provide an impetus for continuing research in this area.

Very recently, Eric Brown et al. [20] found that shear thickening can be controlled via changing surface properties of particles (e.g. hydrophilic or hydrophobic), roughness,

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