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MODIFICATION AND INTEGRATION OF SHEAR THICKENING FLUIDS INTO HIGH PERFORMANCE FABRICS

by

Jakub Mikolaj Szczepanski B.Eng. (Mechanical Engineering) Concordia University, 2009

A Thesis Presented to Ryerson University in partial fulfilment of the requirements for the Degree of Master of Applied Science in the Program of Mechanical Engineering

Toronto, Ontario, Canada, 2011 Jakub Mikolaj Szczepanski, 2011 This page is intentionally left blank.

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MODIFICATION AND INTEGRATION OF SHEAR THICKENING FLUIDS INTO HIGH PERFORMANCE FABRICS

Jakub Mikolaj Szczepanski

Master of Applied Science Department of Mechanical & Industrial Engineering Ryerson University, Toronto, Ontario, Canada, 2011

Abstract

Great interest has aroused in developing the next generation body armour based on the incorporation of a Shear Thickening Fluid (STF) into high performance fabrics (Kevlar®, UHMWPE). This innovative technology allows for the production of comfortable, flexible, lightweight, stab and ballistic resistant protective garments. The current research was undertaken to evaluate the stab resistance and the chemical properties of two types of high performance fabrics, Kevlar® and Ultra High Molecular Weight Polyethylene (UHMWPE), impregnated with several types of shear thickening fluids. The stab resistance properties of all samples were tested using drop tower and quasistatic testing apparatuses. Chemical compositions and microscopic structures were analyzed with Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy and Energy Dispersive Spectroscopy. The current study demonstrated the importance of incorporating Shear Thickening Fluid into woven high performance fibres. The results clearly display a significant enhancement in puncture resistance only of Kevlar® fabrics impregnated with different combination of STFs.

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List of Terminology

| Aliphatic | Organic, acyclic or cyclic, non-aromatic carbon compounds. | | | | |
|---|--|--|--|--|--|
| Amide | An organic compound that contains the functional group consisting of a | | | | |
| | carbonyl group (R-C=O) linked to a nitrogen atom (N). | | | | |
| Amine | Organic compounds and functional groups that contain a basic nitrogen atom | | | | |
| | with a lone pair. | | | | |
| Aromatic | Hydrocarbon characterized by general alternating double and single bonds | | | | |
| | between carbons | | | | |
| Denier | Unit of mass of fibres defined as grams per 9000 meters | | | | |
| Ether | Organic compounds that contain an ether group — an oxygen atom | | | | |
| | connected to two alkyl or aryl groups — of general formula R-O-R | | | | |
| Filament | Smallest component of a yarn | | | | |
| Inorganic | Considered to be of a mineral, not biological origin | | | | |
| compound | | | | | |
| Newtonian Fluid A fluid which has a linear relationship between shear stress and ve | | | | | |
| | gradient | | | | |
| Non-Newtonian | Any fluid whose behaviour is not characterized by the Navier-Stokes | | | | |
| Fluid | equations | | | | |
| Organic | Member of a large class of gaseous, liquid, or solid chemical compounds | | | | |
| compound | whose molecules contain carbon. | | | | |
| Rheology | The science of the deformation and flow of matter | | | | |
| Shear Rate | The change of shear strain per unit time | | | | |
| Shear Strain | Relative deformation in shear; term often abbreviated to shear | | | | |
| Shear Stress | The component of stress parallel to (tangential to) the area considered | | | | |
| Shear Thickening | ug The increase of viscosity with increasing rate of shear in a steady shear flow | | | | |
| Siloxane | Any chemical compound composed of units of the form R_2SiO , where R is a | | | | |
| | hydrogen atom or a hydrocarbon group | | | | |
| Yarn | Assembly of individual filaments | | | | |
| BET | Measurement of the specific surface area of a material | | | | |

List of Abbreviations

| СН | Hydrocarbon Group |
|--------------------|---|
| CH ₂ | Methylene Group |
| CH ₃ | Methyl Group |
| C-N | Cyanide Group |
| EDS | Energy Dispersive X-ray Spectroscopy |
| FTIR | Fourier Transform Infrared Spectroscopy |
| HNO ₃ | Nitric Acid |
| MW | Molecular Weight |
| N-H | Hydronitrogen Group |
| NH ₂ OH | Amonium Hydroxide |
| NIJ | National Institute of Justice |
| ODDMAC | Octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride |
| ODS | Octadecyltrimetoxysilane |
| PEG | Polyethylene Glycol |
| SEM | Scanning Electron Microscope |
| Si | Silicone |
| STF | Shear Thickening Fluid |
| TEM | Transmission Electron Microscope |
| TGA | Thermogravimetric Analysis |
| UHMWPE | Ultra High Molecular Weight Polyethylene |

Chapter 1. INTRODUCTION

1.1 Background

Today, most soft body armours are designated for the protection of individuals whose lives are constantly endangered such as military personnel, law enforcement officers and security personnel. However, according to crime statistics [1], ordinary citizens are equally at danger to fire arm attacks and more recently knife assaults.

Despite the fact that these modern soft body armours retain superior ballistic protection, their stab resistance properties are highly questionable. Current solutions to that problem carry several uncertainties. Stab resistant garments offered by DuPont under the trade name Kevlar Correctional® are costly and lack absolute stab protection. Also DuPont's product is not effective against ballistic threats, making it marginally useful only for correctional officers; thus, ignoring the remaining law enforcement personnel. Other knife resistant materials available on the market such as metal ring mesh, rigid plates and titanium foil are bulky, uncomfortable and inflexible [2].

Apart from being utilized by security, military and law enforcement services, body armours are not widely accepted by the public. Their high cost, difficulty to conceal and limited flexibility are among common concerns regarding regular usage of body armour.

In the light of recent publications regarding *liquid body armour*, a great interest has grown in developing the next generation body armour based on the incorporation of a non-Newtonian fluid (STF) into fabric armour (Kevlar®). This innovative technology can produce comfortable, stab and ballistic resistant protective garments. Also *liquid armour* technology is capable of overcoming some of the issues related to flexibility, weight, thickness (number of fabric layers), compactness and performance of currently produced personal body armour [3].

The non-Newtonian fluid responsible for the significant improvement of fabric armour is known as Shear Thickening Fluid (STF). This unique composition has exceptional characteristics. At low shear stresses, STF behaves like regular fluid. However, upon experiencing higher shear stresses, its viscosity rapidly increases. The phenomenon of shear thickening fluid is due to the suspension of highly concentrated oxide nanoparticles (silica) in solvent medium (polyethylene glycol) [3-9].

Although this recent innovation proved to be more effective than other body armour products, it is still far from being ideal [2, 6, 10-12]. Kevlar® material is still relatively heavy and less flexible when compared to other high performance fabrics. Shear thickening fluid based armour is not sufficient to protect the wearer against higher energy threats. Also the interface between STF and woven fibres can be significantly improved to achieve better adhesion.

Fabric armour utilizing woven Ultra High Molecular Weight Polyethylene (UHMWPE) fibres is known for its superior mechanical properties, lightweight and resistance to chemical degradation [13, 14]. Silane coupling agents are excellent surface modifiers that can enhance mechanical properties of STF by increasing interparticle friction [5, 15, 16]. Silanes are choice reagents in improving adhesion properties between fluids and fabrics, which will increase energy dissipation capabilities [6, 17, 18].

1.2 Statistics

According to FBI's statistics from 1990 to 1998, knives were more commonly used against officers in the United States than firearms. Almost 30.5% of all assaults on officers were caused by knives as compared to 30.2% caused by firearms.

FBI statistics also note that one is more likely to encounter an individual with a knife rather than a firearm, at a ratio of 8 to 1. On the top of that, other FBI reports show that 6 out of 10 victims die due to gunshot wounds as compared to 8 out of 10 that die due to knife attacks. Therefore, there is 20% greater chance of surviving a firearm attack than a knife assault [19].

Sadly, not only law enforcement officers are potential knife victims. Recent statistics from Royal London Hospital in England show that from January until November 2010 over 1,252 victims, including 50 children, were hospitalized due to stab wounds. Reports obtained from two schools in England showed that 15 teenagers under 16 years old, including a nine-year-old, were injured as a result of knife assaults [1].

Similar to statistics from England and the U.S., Canadian assaults with knives are more common than firearms (Figure 1.1). According to police, seven percent of all serious crimes in 2009 related to knife attacks or approximately 23,500 victims.



Figure 1.1 Percentage of all attacks by the type of weapons between 1999 and 2008 [20]

Figure 1.2 demonstrates, over a 30-year period, how knives have become weapon of a choice in homicide cases across Canada. Although, the homicide rate in Canada declined, the number of homicides committed with knife has significantly increased [20].



Figure 1.2 Percentage of homicides resulted from firearms and knives between 1974 to 2008 [20]

1.3 Scope

The purpose of this thesis is to undertake a new approach in the development of very light, cost effective and stab resistant personal body armour. The process of developing new body armour consists of several steps including; validation of shear thickening theory with Kevlar® fabrics, customization of shear thickening fluid by introducing coupling agents on the surface of silica nanoparticles, investigation of stab properties by performing drop tower tests and quasistatic tests and examination of chemical bonding by utilization of laboratory equipment such as Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy and Energy Dispersive X-ray Spectroscopy. The main objective of the current study is to demonstrate the significance of incorporating shear thickening fluid into high performance fabrics for enhancing stab resistance capabilities.

1.4 Current Thesis Outline

Chapter 1 includes a brief description of the background, purpose, scope and goals of this project. Chapter 2 includes a literature review of this concept, including all the important aspects of shear thickening phenomenon, as well as a detailed description of high performance fabrics. Chapter 3 introduces the methods and materials used in this research. It also describes principles behind each testing method, including a short description of experimental devices. Chapter 4 illustrates the results obtained from conducting several experiments such as Drop Tower testing, Quasistatic testing, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscope imaging and Energy Dispersive X-ray Dispersive Spectroscopy. Chapter 5 is devoted to discussion and comparison of the current study to previous studies. This chapter also contains general findings, as well as limitations and future considerations of the currently investigated concept. Final remarks and recommendation are presented in Chapter 6. This chapter summarizes all the aspects undertaken during the duration of this thesis project.

Chapter 2. LITERATURE REVIEW

2.1 Newtonian Fluids vs. Non-Newtonian Fluids

In order to gain a better understanding of shear thickening fluids some fundamental concepts of fluid mechanics associated with Newtonian fluids are presented. In general, all Newtonian fluids follow the linear law of fluid behaviour described by Equation 2.1 and illustrated in Figures 2.1 - 2.2 [21, 22]. Typical behaviour of Newtonian fluid subjected to shear stress is illustrated in Figures 2.3 (a) - 2.3 (b). The movement of the top surface, which is due to shear stress, causes shear strain rate to rise. This linear relation between shear stress and rate of shear strain applies only to Newtonian fluids [21-23].



Figure 2.1 Shear stress vs. Shear strain for. a). Several types of fluids [21], b). Purely viscous time-dependent fluids; rheopectic (b) [23]

$$\tau = \mu \frac{du}{dy} = \mu \frac{d\theta}{dt}$$
(2.1)

where τ [Pa] is shear stress, μ [Pa·s] is viscosity of the fluid and $d\theta/dt$ (γ) [s⁻¹] is shear strain rate which is equal to velocity gradient (du/dy).



Figure 2.2 Behaviour of a Newtonian fluid under applied force. a). Free body diagram, b). Boundary layer near wall [21]

Non-Newtonian fluids belong in the science of rheology [21]. In the literature, rheology is defined as the *science of deformation and* flow [24]. In other words, rheological fluids behave in such a manner that the shearing stress acting on them is not linearly associated with the rate of shearing strain (Figure 2.1). Another significant difference between Newtonian and non-Newtonian fluids is viscosity. In general, the property of viscosity for rheological fluids is undefined. However, for identifying non-Newtonian characteristics as well as for calculation purposes, a property called apparent viscosity was determined (Eq. 2.2) [23, 25].

$$\boldsymbol{\mu}_{a} = \frac{\tau}{\gamma} \tag{2.2}$$

where μ_a [Pa·s] is apparent viscosity, τ [Pa] is shear stress and γ is shear strain rate [s⁻¹].

According to the classification of fluids (Figure 2.3), substances that exhibit shear thickening transition fall under two categories of non-Newtonian, purely viscous fluids. The first category covers fluids that are time-independent and are shear thickening or dilatants (Figure 2.1 a). In the second category time-dependent fluids are referred to as rheopectic fluids (Figure 2.1 b) [23]. This research project covers only the non-Newtonian, time independent fluids.



Figure 2.3 Classifications of Fluids [22]

2.2 Shear Thickening Fluid

Lately, much attention is being directed toward non-Newtonian fluids that possess the ability to "stiffen up" in the manner of seconds. The main mechanism of this sudden phase change is known as a (reversible) shear thickening transition and is due to an increase in shear rate, which causes the fluid's apparent viscosity to rise, thus, making the fluid resistant to flow [3-9]. In other words, the applied force causes a reversible liquid to solid transformation. The fluids are reversible in such a manner that a decrease in the applied force will transfer the fluid (in solid state) back to a liquid state [8]. Shear thickening transition is also called rheological dilatancy [26]. Substances experiencing this unique transition consist of particles dispersed in solvent medium and exist under the name of shear thickening fluid (STF) [21].

The phenomenon of shear thickening transition can be explained by several theories but two of most widely known theories in the literature are the theory of "hydrocluster" formation and the order-disorder theory.

The "hydrocluster" theory is based on particle interactions in a liquid medium. Under applied shear stress, particles suspended in a fluid come into contact with each other, causing the hydrodynamic pressure to rise. This effect causes the liquid between the particles to shift out. As a result, the distance between the particles decreases causing hydrodynamic forces to rise (Figure 2.4) until they reach singularity. This hydrodynamic coupling, which exists only at high shear stresses, leads to "hydrocluster" formation [5, 27-29].



Figure 2.4 Relation between hydrodynamic forces and distance between particles [5]

The order-disorder theory describes the breaking of particle arrangements [4, 26, 29]. According to Hoffman, flow of particles at low shear rates is nothing more than a group of hexagonally packed layers moving in two dimensional order (sheets). At higher shear rates, that order disappears by breaking into three dimensional arrangements, which is due to action of shear forces that overcome the repulsive interparticle forces [8, 26, 29].

The main mechanism triggering shear thickening transition is known as critical shear rate. This property can be determined by experimental and theoretical methods. The experimental method is based on conducting a rheological test on shear thickening fluid. The theoretical technique consists of determining the critical shear stress by solving one of the following two equations (Eq. 2.3 or Eq. 2.4) [26].

$$\dot{\gamma} = \frac{2\pi \varepsilon_0 \varepsilon_r \psi_0^2 \kappa h}{6\pi \eta_0 a^2 a^3}$$
(2.3)

where \mathcal{E}_0 is the permittivity of vacuum, \mathcal{E}_r is the relative dielectric constant, Ψ_0 is the surface potential, η_0 is the medium viscosity, a is the particle radius; $1/\kappa$ is the Debye double layer thickness; and h is the distance between the particles.

$$N_{HE} = \frac{(12\pi \eta_0 a^2 \gamma)}{(2\pi \varepsilon_0 \varepsilon_r \psi_0^2 \kappa h)}$$
(2.4)

where N_{HE} corresponds to the balance between hydrodynamic and electrostatic forces. if $N_{HE} > 1$, shear thickening transition will take place.

As shown in Figure 2.5, the viscosity decreases before critical shear rate is reached. Further increases in shear rate, above its critical value, cause a sudden jump in viscosity until the shear rate reaches its maximum point noted as γ_m . As a result, a shear thickening transition can be observed in a particular region which begins beyond critical shear rate and ceases at maximum shear rate.



Figure 2.5 Viscosity vs. shear rate, shear thickening transition between critical shear rate and maximum shear rate [8]

Apart from achieving critical shear rates, there are other parameters that need to be controlled in order for a shear thickening transition to occur [5, 8]. These parameters can be divided into three groups: particle, continuous phase and flow field.

Properties related to particle's characteristics such as shape, size distribution, phase volume and interaction with other particles can impact its shear thickening properties. The next parameter is continuous phase viscosity of the medium solvent and last is classified into three types, rate and time of flow deformation [8].

Mainly publications guided by the above criteria were used in this current investigation. As previously mentioned a shear thickening fluid is a system compromising a high concentration of solid particles, usually in nano scale, suspended in liquid medium. Typical examples of shear thickening fluid are; silica suspended in ethylene glycol [3, 30], polyvinylchloride in dioctylphtalate [26], kaolin clay in glycerol [2], poly methyl methacrylate in polyethylene glycol [11], fumed silica in propylene glycol [8, 9] and silica suspended in polyethylene glycol [4, 6, 27]. The last compound is of special interest to this project.

Suspension of silica particles in polyethylene glycol has been widely investigated, analyzed and often reported in literature regarding shear thickening fluids. Extensive analysis of ballistic properties of several STF systems was undertaken by U.S. Army research laboratory with assistance of faculty of chemical engineering at University of Delaware. In their research, several volume fractions (wt.) of colloidal silica particles (120 nm average diameter) were suspended in polyethylene glycol with different molecular weights (200, 300, 400, 600 g/mol) and impregnated with Kevlar® fabrics. The results illustrated significant improvement in ballistic properties of Kevlar®/STF material as compared to neat Kevlar®. For instance, four layers of Kevlar® impregnated with STF absorbed as much energy as ten layers of neat Kevlar®. Also their study indicated good correlation between polyethylene glycol (200 Mw) and silica particles [6].

Another important investigation conducted by the same group was done to improve stab resistance properties of Kevlar® and Nylon fabrics. Incorporation of STF system compromising of colloidal silica (500 nm av. dia -48% wt) suspended in polyethylene glycol (200 Mw) demonstrated significant enhancement in puncture resistance of these materials [15, 27].

The same research group also analyzed stab resistance performance of another shear thickening composition based on colloidal silica (446 nm av. dia -40% wt) suspended in ethylene glycol [7, 12, 30].

Other STF's relevant to this study compromised of fumed silica dispersed in polypropylene glycol [8, 9]. Several volume fractions of fumed silica (14 nm) ranging from 3 to 10 wt% were suspended in polypropylene glycol. Selecting a polar solvent medium was necessary to achieve the formation of hydrogen bonds with surface hydroxyls that exist on silica aggregates [9, 31].

The key publication in the field of STF's was presented by a group of researchers who worked under the strict guidance of experts from the U.S. Army research lab and the University of Delaware. In this particular study, the comparison of shear thickening transitions of two most common types of silica particles namely; dry powder silica (15 nm) and colloidal silica (200 nm) were made. Sonochemical method was used to disperse numerous weight fractions of silica in the carrier fluid and analyzed by using different lab instrumentation, such as rheometer, TGA apparatus, SEM and TEM. According to the rheological tests (Figure 2.6) an ideal STF composition compromises 40 wt% of dry silica (15 nm) with polyethylene glycol [4].



Figure 2.6 Results of rheological test performed on several STF compositions, sample D indicates the most desirable STF combination [4]

2.3 Silane Coupling Agents

Silane coupling agents are silicon based compounds used for linking different materials by forming a chemical bond. Application of a silane coupling agent on a surface significantly improves mechanical properties of two bonding materials, usually organic with inorganic. Equation 2.5 and Figure 2.7 present chemical structure of silane coupling agent in general form [17].

$$X_3 SiR \tag{2.5}$$

where X is the hydrolyzable group such as alkoxy, acyloxy, inorganic materials (silica), Si is a silicon atom and R is representation of nonhydrolyzable organofunctional group that (PEG, PE, etc.) [32].



Figure 2.7 Molecular structure of silane coupling agent [66]

Figure 2.8 illustrates a typical chemical reaction taking place during formation of organosilane coupling agent. The process itself consists of four steps namely; hydrolysis, condensation, hydrogen bonding, bond formation.

The reaction starts with silane agent coming into a contact with moisture causing hydrolysis and the formation of silanols. In the next step, the newly formed silanols undergo a condensation process which causes oligomeric structures to be formed. At the same time, formation of hydrogen bonds to the inorganic materials occurs. It is also worth noting that during the condensation process, an additional reaction can take place between silanols and hydroxyls that are frequently encountered on inorganic surfaces. In the last step, additional condensation and dehydration occur creating inorganic materials chemically bound to organic functional groups [18].



Figure 2.8 Chemical reaction of silane coupling agents where X is represented by OR and R is replaced by Y [18]

2.3.1 Modification of Silica particles

Due to the poor adhesive properties of certain polymeric materials, modification with silica particles has been widely employed. The most common chemical compounds used in bonding silica particles to other materials are silane coupling agents [33].

According to literature several silane compounds, as well as different processing techniques, were developed and utilized to functionalize silica particles. These silane coupling agents include for example, methyltrimethoxysilane (MTMS), methyltriethoxysilane (MTES), vinyltrimethoxysilane (VTMS), vinyltriethoxysilane (VTES) [34], trimethoxy silylpropyl methacrylate (TPM) [33], octadecyltrimethoxysilane (ODS) [35-37], octadecyldimethyl trimethoxysilyl propyl ammonium chloride (ODDMAC) [38]. The most common techniques of silane deposition on silica surfaces are sol-gel [35], toluene absorption [36, 37] and grafting [39].

2.4 High Performance Fibres

Textile is the common name for any material that can be woven [13]. Over 100 textile fibres are used extensively by several industries in manufacturing fabrics for protection. Among them, 6 categories can be distinguished in terms of their mechanical strength (Table 2.1) [14].

| | Туре | Example | | |
|---|--|---------------------------|--|--|
| 1 | Highly extensible, elastomeric fibres | Lycra | | |
| 2 | Very brittle fibres | Rock wool | | |
| 3 | Widely used, natural and regenerated fibres | Cotton, Wool, Flax, Rayon | | |
| 4 | Tough fibres, moderately strong and extensible | Silk, Nylon, Polyester | | |
| 5 | Moderately strong, inextensible fibres | Glass, Ceramic fibres | | |
| 6 | High-modulus, high-tenacity fibres | Carbon, Aramid, UHMWPE | | |

 Table 2.1 Classification of textile fibres [14]

Fibre itself can be defined as material having long axis (width) much greater than its radius and commonly known as a filament. Single filaments are not meant for protection, they are only used for experimentation and laboratory testing. However, after being put together in the form of twisted (yarn) or untwisted bundles (tow) and woven into a fabric, their purpose and properties suddenly change. Weaving of these bundles can take several forms such as plain weave, basket weave, 4-harness-satin, 8-harness-satin, etc. Since the plain weave offers excellent fabric stability and low slippage between the yarns, it is considered as the most advantageous type of fibre arrangement for personal body armour [40].

High performance fibres also known as high-modulus and high-tenacity (HM-HT) fibres are the most common types of materials used for personal body armour, and their mechanical properties are listed in Table 2.2. The units used to represent tenacity (strength) and modulus (stiffness) are in Newton/tex, which is equal to units of energy to break, noted as kJ/g. In order to convert those units into GPa, N/tex must be multiplied by the density (g/cm³) [14]. Confusion might be caused by two equally preferred units representing the linear density of fibres. They are both very similar. Tex is expressed in terms of grams per 1000 meters, where denier is defined as grams per 9000 meters [13].

It is clearly seen in Table 2.2 that Aramid, Polybenzoxazole (PBO) as well as Ultra High Molecular Weight Polyethylene (UHMWPE) fibres retain the most desirable properties to achieve maximum ballistic and stab protection [13]. However, results of recent study regarding PBO fabric suggest that they are prone to moisture absorption, which leads to significant reduction in their mechanical properties [41].

| Fibre | Density g/cm ³ | Moisture % at 65% rh | Melting point °C | Tenacity N/tex | Modulus N/tex | Work to break J/g | Break ext % |
|-------------------|------------------------------|-------------------------|---------------------|-------------------|------------------|----------------------|----------------|
| Cotton | 1.52 | 7 | 185* | 0.2-0.45 | 4-7.5 | 5–15 | 6–7 |
| Flax | 1.52 | 7 | 185* | 0.54 | 18 | 8 | 3 |
| Wool | 1.31 | 15 | 100**/300* | 0.1-0.15 | 2–3 | 25–40 | 30-40 |
| Silk | 1.34 | 10 | 175* | 0.38 | 7.5 | 60 | 23 |
| Rayon | 1.49 | 13 | 185* | 0.2-0.4 | 5–13 | 10-30 | 7–30 |
| Nylon | 1.14 | 4 | 260*** | 0.35-0.8 | 1–5 | 60-100 | 15–25 |
| Polyester | 1.39 | 0.4 | 258 | 0.45-0.8 | 7–13 | 20-120 | 9–13 |
| Polypropylene | 0.91 | 0 | 165 | 0.6 | 6 | 70 | 17 |
| Para-aramid | 1.44 | 5 | 550* | 1.7-2.3 | 50-115 | 10-40 | 1.5-4.5 |
| Meta-aramid | 1.46 | 5 | 415* | 0.49 | 7.5 | 85 | 35 |
| TLCP (Vectran) | 1.4 | <0.1 | 330 | 2-2.5 | 45-60 | 15 | 3.5 |
| HMPE | 0.97 | 0 | 150 | 2.5-3.7 | 75–120 | 45-70 | 2.9-3.8 |
| PBO | 1.56 | 0 | 650* | 3.8-4.8 | 180 | 30-90 | 1.5-3.7 |
| Carbon | 1.8-2.1 | 0 | >2500 | 0.4-3.9 | 20-370 | 4–70 | 0.2-2.1 |
| Glass | 2.5 | 0 | 1000-12000**** | 1–2.5 | 50-60 | 10–70 | 1.8-5.4 |
| Ceramic | 2.4-4.1 | 0 | >1000 | 0.3-0.95 | 55-100 | 0.5–9 | 0.3-1.5 |
| Chemical res'tant | 1.3-1.6 | 0-0.5 | 170–375***** | 0-0.65 | 0.5-5 | 15-80 | 15–35 |
| Thermal res'tant | 1.25–1.45 | 5–15 | 200-500***** | 0.1–1.3 | 2.5-9.5 | 10–45 | 8–50 |

 Table 2.2 Mechanical properties of HM-HT fibres [14]

* decomposes (chars); ** softens; *** for nylon 66, nylon 6 at 216 °C; **** liquidus temperature; ***** various limiting temperatures

2.4.1 Kevlar®

Kevlar® is one of the most unique man-made fibres and is the signature product of Du Pont's polymer division. It is known for its high strength, toughness, high stiffness, thermal stability and low density (1.44 g/cm^3) [41]. This organic fabric belongs to a group of aromatic polyamides, which can be characterized by having at least 85% of amide groups connected to two aromatic rings and is formally called Poly[*p*-phenylene terephthalamide] (PPTA) (Figure 2.9) [14]. Many of PPTA molecular chains are linked together by hydrogen bonds, stack together to form a final fiber shape product that is known as Kevlar® (Figure 2.10) [41].



Figure 2.9 The molecular structure of Poly[*p*-phenylene terephthalamide] [13]



Figure 2.10 The molecular structure of Kevlar® fibre [41]

Kevlar® fibres are produced via a dry-jet wet-spinning process (Figure 2.11). It begins from dissolving an already polymerized substance of PPTA into sulphuric acid. Next step is to transfer the solution through an air-gap into the coagulating bath. The high molecular orientation of the final product is obtained through a combination of shear forces acting on the fluid in the spinning holes and by elongation that is taken place in the air gap. It is followed by heat treatment under tension, which enhances orientation as well as achieves higher modulus [14].



Figure 2.11 Schematics of dry-jet wet-spinning process [14]

In the early 70's the first synthetic fibres based on PPTA appeared on the market under the name of Kevlar® 29. At that time, Kevlar® 29 was considered as the revolution in ballistic-resistant materials. It was later followed by Kevlar® 49, Kevlar® 149, Kevlar® KM-2 and Kevlar® Correctional [13].

2.4.2 Ultra High Molecular Weight Polyethylene

Ultra High Molecular Weight Polyethylene (UHMWPE) is a special type of thermoplastic fabric consisting of highly crystallized units of ethylene (Figure 2.12) in a highly parallel oriented repeated order [13].



Figure 2.12 The molecular structure of UHMWPE [13]

To produce UHMWPE fibres, a process called gel-spinning (Figure 2.13) has been widely implemented. In this method, long molecules of ethylene are dissolved in a solvent and mixed. Afterwards, they take a form of a gel, which later is spun through a spinneret. Cooling followed by a rapid drawing of the fibres are the last steps before the final product is made [13].



Figure 2.13 Schematics of gel-spinning process [13]

UHMWPE is known for its exceptional properties. Apart from being ten times stronger than steel, it has the lowest density (0.97 g/cm³) among other HT-HM fibres [14]. When compared to aramid fibres, UHMWPE retain higher specific strength by 40% [14] and lower moisture absorption [13]. Also they are less susceptible to chemicals, retain better abrasion and fatigue resistance. Some of the drawbacks of UHMWPE are low creep resistance and poor compressive strength. Overall, UHMWPE is considered as the most advanced and superior material for armour applications. UHMWPE manufacturers include Dyneema® produced by the Dutch company DSM and Spectra® manufactured by Honeywell.
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Chapter 3. METHODS AND MATERIALS

3.1 General Approach

The current research was undertaken to develop several shear thickening fluids for two types of high performance fabrics, Kevlar® and UHMWPE, and to evaluate their stab resistance performance. Fourteen samples were prepared. Twelve of these samples were impregnated with several types of shear thickening fluid. Two controls, free of any treatments served only for comparison to the twelve that were functionalized. The stab resistant properties of all samples were tested using drop tower and quasistatic testing apparatuses. Chemical compositions and microscopic structures were analyzed with Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy.

3.2 Shear Thickening Fluid

Shear thickening fluid was prepared by a sonochemical method as outlined in section 2.2 [43]. This procedure consisted of ultrasonical mixing of three components, silica particles, polyethylene glycol (200 Mw), and ethanol alcohol in the weight ratio of 0.4:0.6:3 [43]. A Branson 450 digital sonifier acoustically agitated the mixture at 20 kHz (50% amplitude) [43] for about 1 hour. During the sonication process, the mixture was placed in container filled with ice to prevent heat generation (Figure 3.1). Addition of ethanol was provided to help reduce the surface tension and viscosity [6]. The next step was to impregnate the STF into 5 layers of high performance fabrics, dry them for 48 hours at room temperature and seal them in a polyethylene bag [43].



Figure 3.1 Schematics of the experimental set up

3.2.1 Polyethylene Glycol

Polyethylene glycol (PEG) with molecular weight of 200 g/mol is defined as low viscosity thermally stable polymer compound [43]. Its chemical structure is shown in Figure 3.2.



Figure 3.2 The molecular structure of Polyethylene Glycol [44]

Polyethylene glycol 200 is a non-toxic, water soluble substance [45] that hydrogen bonds well with Kevlar fibres [6, 11]. According to the literature, different molecular weight PEG polymer could be used and would not affect energy absorption of final product [6]. Polyethylene glycol 200 (Sigma Aldrich) used in this study has density 1.127 g/cm³ [44].

3.2.2 Silica

Silica or silicon dioxide (SiO₂) is the basic product of silicate and belongs to a group of ceramic materials. As shown in Figure 3.3, silica contains two oxygen atoms connected to silicon atom by double bond. The compound possesses a stable electronic structure due to the ratio of chemical elements which is 1:2.

O=Si=O

Figure 3.3 The molecular structure of Silica [46]

Silicon dioxide is also known for its hardness and good electrical insulating properties. Another advantage of silica corresponds to its low density due to a loose-packed molecular structure [47]. As an inorganic material, silica is an extremely compatible substrate for silane coupling agents. Silane creates very strong bonding structure at the surface of silica [18]. This study utilized two types of silica nanoparticles namely, dry powder silica and fumed silica.

3.2.2.1 Dry powder Silica

Dry silica nanopowder (10-20 nm) was acquired from Sigma Aldrich. Average values of BET surface area and density were given as 160 m²g and 2.4 g/mL respectively [48]. According to the literature, dry silica powder reduces the chance of water and moisture contamination during dispersion as well as reducing processing time [43].

3.2.2.2 Fumed Silica

Funed silica is the most appealing type of silicon dioxide to be used as reinforcement in stab resistance garment. Extremely cost effective, fumed silica has a surface area (200 m²/g), low density (2.3 g/mL) and available in nanometer scale (14 nm) [49]. This product is supplied as powder silica and was also purchased from Sigma Aldrich.

Suspension of fumed silica in several carrier fluids has been reported in literature. Synthesis of a similar fumed silica suspended in ethylene glycol was employed as a working mechanism in damping device [50]. Fumed silica is fabricated by *flame hydrolysis process of silicon tetrachloride in a flame of H*² *and O*² [31]. The significant advantage of fumed silica is the existence of a considerable number of hydroxyls groups on its surface. These groups can react with polar solvents (polyethylene) to create hydrogen bonds and are also the sites for functionalization with silane coupling agents [9].

3.3 Silane Coupling Agents

The idea of modifying silica particles was developed after an initial set of stab resistance testing performed on Kevlar and UHMWPE fibres impregnated with a standard shear thickening fluid. It appeared that STF had very small impact on UHMWPE fibres. In fact, STF did not hold the UHMWPE fibers together nearly as well as it did for Kevlar fibres. Later on it was revealed that despite the STF phenomena and its ability to increase the performance of abovementioned fabrics, the chemical and hydrogen bonds between the STF mixture and UHMWPE fibers was absent. Therefore, an approach of functionalizing silica particles with two different silane coupling agents such as octadecyltrimethoxysilane (ODS) and octadecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride (ODDMAC) was taken.

3.3.1 Octadecyltrimethoxysilane

A silane coupling agent that easily bonds to the surface of silica particles is octadecyltrimethoxy silane OTMS [51], ODTMS [52] or ODS [53]. The last acronym will be use throughout this thesis. Purchased from Sigma Aldrich, ODS has a density of 0.883 g/cm³ and molecular weight of 374.67 g/mol. As shown in Figure 3.4 the molecular formula is C₂₁H₄₆O₃Si [54].



Figure 3.4 The molecular structure of Octadecyltrimetoxysilane [38]

Silica nanoparticles were functionalized with octadecyltrimetoxysilane according to procedures found in literature. Seven grams of silica particles (one test sample) were dissolved in 700 mL of an ethanol-water mixture and mechanically stirred for 1 hour [55]. Ten minutes before the first step was completed, 25 mL of a toluene 5 mL of ODS [36] (1g of silica to 0.5 ml of silane) [55] was prepared. Afterwards, both solutions were mixed together for 24 hours at 25°C. In the final step, the solution was centrifuged for 5 min at 5000 rpm, washed with distilled water and dried [55]. Finally, the modified particles are introduced into the PEG solvent to form the STF. Figures 3.5 and 3.6 demonstrate the chemical structure of the final product.



Figure 3.5 The molecular structure of STF with ODS-treated silica particles on Kevlar®



Figure 3.6 The molecular structure of STF with ODS-treated silica particles on UHMWPE

3.3.2 Octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride

A second silane coupling agent selected to improve the penetration resistance of high performance fabrics was octadecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride, also known as ODDMAC [56]. This quaternary ammonium compound was also acquired from Sigma Aldrich. ODDMAC has a density of 0.889 g/cm³ and molecular weight of 496.28 g/mol. Figure 3.7 shows its molecular structure along with molecular formula which is $C_{23}H_{52}O_3SiCIN$ [56].



Figure 3.7 The molecular structure of Octadecyldimethyl[3-(trimethoxysilyl)propyl] ammonium chloride [56]

Modification of silica particles with ODDMAC starts by mechanically mixing 7 grams of silica particles with 15 mL and 142 mL of distilled water for 30 min. Hydrolysis reaction involving 1 mL of solution of HNO₃ was added, followed by the introduction of 5 mL of ODDMAC coupling agent [55] and stirred for 3 min at 60 °C. After the hydrolysis, condensation reaction

involving the addition of NH_4OH and stirring the mixture for 90 min. at 60 °C were undertaken. The solution was centrifuged for 5 min at 5000 rpm, and afterward the solution was washed with distilled water and recentrifuged. Finally the particles are removed, dried in oven for 5 hours, and ready for the use in STF (Figures 3.8 and 3.9) [34].



Fig. 3.8 The molecular structure of STF with ODDMAC-treated silica particles on Kevlar®



Fig. 3.9 The molecular structure of STF with ODDMAC-treated silica particles on UHMWPE

3.4 Digital Sonifier

The most effective technique to prepare shear thickening dispersion is through acoustic cavitation. This approach consists of alternating acoustic pressure which causes formations of cavities in the liquid. Ultrasonic agitators are known for their versatility, and are applicable in diffusion, wetting, dissolution, dispersion, and emulsification [43, 62]. This current study uses Branson Digital Sonicator model 450 (Figure 3.10).



Fig. 3.10 Branson Digital Sonicator model 450 [57]

3.5 High Performance fabrics

Two different types of woven fabrics were acquired for the current research. The first was Kevlar® 29 in the form of plain weave, supplied by Electro-pack located in Toronto, Canada. The second type is UHMWPE in the same form, provided by Jiangsu Safero Security Products Limited Company located in Dailou, China. Properties for both materials are given in Table 3.1. In addition, each testing sample consisted of five layers of only one type of fabrics cut in dimensions of 23 cm by 17.5 cm.

| Name | Density [g/cm ³] | Denier | Areal density [g/cm ²] | Tenacity [GPa] | Modulus [GPa] | Elongation [%] |
|------------|---------------------------------|--------|---------------------------------------|-------------------|------------------|-------------------|
| Kevlar® 29 | 1.44 | 3000 | 0.047 | 2.9 | 66.2 | 3.6 |
| UHMWPE | 0.97 | 1200 | 0.022 | 3.1 | 111.6 | 3.2 |

 Table 3.1 Properties of high performance fabrics used in the research

3.6 Drop Tower Testing

Drop test apparatus was designed and testing of samples was conducted according to National Institute of Justice NIJ Standard-0115.00. This stab resistance standard was developed to assess minimum requirements of potential materials that are capable to protect against slash and stab threats. NIJ Standard-0115.00 was established as an international regulation regarding testing and evaluation of protection levels of stab resistance garment. Several law enforcement organizations mainly from United Kingdom and the United Stated significantly contributed towards launching universal stab resistance standard that can be applicable anywhere in the world [59].

NIJ-0115.0 covers testing methods of two different protection classes support by three protection levels. Each protection class is intended to recreate a real life situation in terms of type of sharp weapons regularly used in stabbing attacks. First class is known as "Edged Blade" and it is defined as pair of knife blades (noted as S1 and P1) that are commonly encountered on "the street" (Figure 3.11-3.12). "Spike" class is described as improvised sharp weapons with pointed ends (noted as SP) encountered in correctional facilities (Figure 3.133) [59]. All the weapons classified in this section were reproduced exactly as they are illustrated on Figures 3.11-3.13 with additional internally threaded base. Again, thanks to the courtesy of Electro-pack.



Figure 3.11 NIJ-0115.0 Edge blade S1 [54]



Figure 3.12 NIJ-0115.0 Edge blade P1 [59]



Figure 3.13 NIJ-0115.0 Spike [59]

The next section of NIJ-0115.00 crucial to this study is devoted to backing material (Figure 3.14). Backing material outlined in NIJ standard has properties that are comparable to human flesh in terms of flexibility and impact absorption. This combination is compromised of four layers of 5.8 mm thick neoprene sponge, one layer of 31 mm thick polyethylene foam and two layers of 6.4 mm thick rubber and was used for this project [59].



Figure 3.14 Type and sequence of backing material for testing [59]

Another important element of the drop test apparatus that was borrowed from NIJ standard is design of a drop mass. A lot of attention was given to reproduce drop mass that was defined in the standard (Figure 3.15) [59]. However, due to the overall complexity and time constrain, some of the details were omitted. The drop mass used for this research consisted of steel body with similar shape to the standard one with externally threaded end for easy and quick change of stab weapons (S1, P1, SP). To experience a free fall drop, the mass was attached to a line and placed inside a transparent plastic tube which was restrained at the base of the fixture. It was assumed that the potential energy existing at certain heights will convert directly into kinetic energy with an estimated error of 1 Joule due to the friction between the drop mass and the plastic pipe.



Figure 3.15 Drop mass [59]

Protection levels are also very important part of NIJ standard. A study conducted by the Police Scientific Development Branch (PSDB) established three distinctive protection levels; however, only the first level was used in this project (Table 3.2). Each level presents a different magnitude of energy that can be produced by the male population during stabbing. The first protection level corresponds to 85 percent of the male population. In addition, testing should be performed twice for each protection level. Therefore, a testing sample needs to be evaluated with conditions outlined in Table 3.2 under categories called "E1" Strike Energy and "E2" Overtest Strike Energy. The first section refers to the energy that can be delivered by 85% of the male population with an allowable stab penetration up to 7 mm (0.28 in). The second category is E2 and it corresponds to level of energy indicated in E1 and increased by 50 % for safety precaution. At this condition, allowable stab penetration is limited to 20 mm (0.79 in) [59].

Table 3.2 Protection levels

| Protection | "E1" Str | ike Energy | "E2" Overtest | Strike Energy |
|------------|---------------|---------------|---------------|---------------|
| Level | J | ft• lbf | J | ft• lbf |
| 1 | 24 ± 0.50 | 17.7 ± 0.36 | 36 ± 0.60 | 26.6 ± 0.44 |

The drop test procedure consisted of placing a sample on backing material and supporting it with a duct tape. Next step was to select stab a weapon and mounting it to the drop mass. Afterwards the drop mass was positioned at a height that corresponded to a particular energy level. Values for different heights were calculated from equation 3.1 and were tabulated in Table 3.3. Finally the drop mass was released causing an impact on a sample.

$$U = mgh \tag{3.1}$$

where U [J] is potential energy, m [kg] is drop mass, g $[m/s^2]$ is gravity which is equal to 9.81 and h [m] is defined as height.

| Abbr. | Protectio n class | Description | Weight [kg] | Energy E1 [J] | Height [m] | Energy E2 [J] | Height [m] |
|-----------|----------------------|-------------|----------------|------------------|---------------|------------------|---------------|
| S1 | 1 - Edged | Figure 3.1 | 2.29 | 24.0 | 1.07 | 36.0 | 1.60 |
| P1 | blade | Figure 3.2 | 2.27 | 24.0 | 1.10 | 36.0 | 1.62 |
| SP | 2 - Spike | Figure 3.3 | 2.22 | 24.0 | 1.11 | 36.0 | 1.65 |

Table 3.3 Values for Energy and Height

3.7 Quasistatic Testing

According to National Institute of Justice, drop tower testing is sufficient enough to provide adequate results to evaluate potential stab resistance garment. However, quasistatic testing gives extra information regarding material's performance, its behaviour and stab resistance at low shear stresses. Also more data points are collected throughout the test; thus, the final results are much more comprehensive.

Quasistatic stab tests were performed on SFM United Tensile Testing Machine (Figure 3.16). Three screw-on stab weapons inserts (S1, P1, SP), the same as used in drop tower testing, were attached to upper grips of the testing frame. The weapons were connected one at the time. Backing material, as well as the testing sample was placed underneath. The frame with the mounted stab weapon was then pressed into the specimen until the load scale on the computer indicated a load of 5N. Next, the frame was set down at a rate of 5 mm/min until it reached a distance of 50 mm. Finally, the data was recorded and the penetration depth of the sample was evaluated and documented.



Figure 3.16 SFM United Tensile Testing Machine with mounted stab weapon (spike SP)

3.8 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is the most common technique of infrared spectroscopy [4]. Infrared (IR) is a part of electromagnetic spectrum located above microwave and below visible regions. FTIR works on the principle of sending IR radiation at certain frequencies through a sample and recording the output in form of wavelengths [60]. These wavelengths are associated with frequencies that exist in a molecule. Each molecule of any material consists of atoms, connected by chemical bonds, which tend to vibrate at particular frequencies. FTIR manages to activate these frequencies by IR irradiation [61]. In other words, the outcome generates a *molecular fingerprint* of the absorbed spectrum of a sample. This innovative process, shown on Figure 3.17, is able to easily indentify unknown materials along with their composition and overall quality [60]. Also FTIR is applicable for analysis of liquids, solids and gases [62].



Figure 3.17 a). Visual interpretation of principles of FTIR [60], b). FTIR Satellite by Thermo Scientific

An FTIR Satellite manufactured by Thermo Scientific was utilized in this study. The FTIR procedure starts with selecting the most suitable method of sample preparation. For analysis requiring interpretation of chemical bonds and structures of shear thickening fluid incorporated in synthetic fibres, the most applicable technique is KBr pellet. This method consists on forming a thin disk of ground fragments of the test sample mixed with KBr (potassium bromine) powder. Next, a clean background scan without any sample present in the holder is taken. Afterwards, the sample disk is inserted into sample holder and scanned with infrared light. The final results are given in form of a graph that can be printed out and scanned.

3.9 Scanning Electron Microscope

Scanning Electron Microscope (SEM) is the most common high resolution imaging apparatus. Numerous advantages such as high spatial resolution, various imaging features, user-friendliness and high-throughput control, place SEM ahead of other electron beam devices. Scanning Electron Microscope works on a mapping principle, which is similar to a fax machine. In other words, the SEM electron probe, as shown in Figure 3.8a, scans a surface of a sample in two-dimensional matter. Detected signals from the sample are amplified and utilized to modify the intensity of CRT (cathode-ray-tube) Electron Beam, which is responsible for mapping an image of the sample onto CRT display [63].



Figure 3.18 a). Schematics of principles of SEM imaging [63], b). Scanning Electron Microscope used in this research project - JOEL JSM – 6380 LV

The Scanning Electron Microscope used in this study is shown in Figure 3.18b. It was utilized for a better understanding of the phenomenon of shear thickening fluid and to examine damage sustained by the fabrics. Also, the images taken by the SEM assisted in verifying the quality of several STF compositions as well as distribution and infusion of STF into high performance fabrics. Another important feature that can be observed by SEM is agglomeration of silica particles into polyethylene glycol. SEM was operated by a highly skilled technician, also in charge of sample preparation. The procedure itself consisted of attaching a specimen to a base covered with copper tape. The next step includes coating the sample with gold to increase conductivity and to avoid charge build up by electrons [64].

3.10 Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDS) belongs to a group of electron probe X-ray microanalysis. EDS is a system attached to Scanning Electron Microscope (SEM) used for detection of chemical elements in a material. In other words, Energy dispersive X-ray spectroscopy detects and converts X-ray characteristics generated by primary beam of the SEM into electronic signal [65].

EDS is compromised of three major components: spectrometer, pulse processor and analyzer (Figure 3.19). The spectrometer is responsible for detecting X-rays emitted from a sample and creating an electronic signal out of it. Next, the electronic signal travels to the pulse processor which determines the energy associated with the X-Rays emission. Finally the analyzer receives the information from pulse processor and displays them in the form of an X-rays spectrum of the sample.



Figure 3.19 a)-c). Spectrometer, d). Pulse processor, e). Analyzer [63]

Overall, results obtained from EDS were processed in very short time, but with lower resolution than other electron probe X-ray microanalysis devices [63]. This particular technique was used to complement the Fourier Transform Infrared Spectroscopy testing presented in section 3.8. In addition, energy dispersive X-ray spectroscopy test was performed by the same technician who operated the scanning electron microscope method outlined in section 3.9.

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Chapter 4. RESULTS

4.1 Shear Thickening Fluid

Testing samples, composed of 5 layers of a material, were prepared according to procedures outlined in section 3.2, and are presented in Table (4.1). Masses of STF were obtained by subtracting weight values of samples composed of neat fabrics, from samples impregnated with STFs. The total areal density of sample 3 and sample 4 demonstrates the significant differences in the deposition of STF. The areal density of sample 3 increased by 0.0198 g/cm² after the impregnation, while the areal density of sample 4 increased only by 0.0074 g/cm². It seems that STF deposition worked more efficiently on samples made with Kevlar® than UHMWPE fabrics. Another variation was observed in samples compromised of different unmodified silica particles. Samples contained fumed silica were lighter by roughly 0.0020 g/cm². Also coupling agents had their impact on sample areal density. ODDMAC did not alter the weight of Kevlar® based samples, but it decreased the weight of UHMWPE samples by an average of 0.0025 g/cm² for Kevlar® STF (10-20) and by roughly 0.0035 g/cm² for Kevlar® STF (14).

| Sample | Description | Total | Weight of | Total Areal | STF Areal |
|--------|---------------------------|------------|-----------|------------------------------|------------------------------|
| No | Description | Weight [g] | STF [g] | Density [g/cm ²] | Density [g/cm ²] |
| 1 | KEVLAR | 89.50 | 0 | 0.0458 | 0.0000 |
| 2 | UHMWPE | 44.46 | 0 | 0.0227 | 0.0000 |
| 3 | KEVLAR STF (10-20) | 128.17 | 38.67 | 0.0656 | 0.0198 |
| 4 | UHMWPE STF (10-20) | 58.75 | 14.27 | 0.0301 | 0.0074 |
| 5 | KEVLAR STF (14) | 122.83 | 33.33 | 0.0628 | 0.0170 |
| 6 | UHMWPE STF (14) | 56.23 | 11.75 | 0.0288 | 0.0061 |
| 7 | KEVLAR STF (10-20) ODDMAC | 128.36 | 38.86 | 0.0657 | 0.0199 |
| 8 | UHMWPE STF (10-20) ODDMAC | 53.08 | 8.60 | 0.0271 | 0.0044 |
| 9 | KEVLAR STF (14) ODDMAC | 126.92 | 37.42 | 0.0649 | 0.0191 |
| 10 | UHMWPE STF (14) ODDMAC | 52.85 | 8.37 | 0.0270 | 0.0043 |
| 11 | KEVLAR STF (10-20) ODS | 129.34 | 39.84 | 0.0662 | 0.0204 |
| 12 | UHMWPE STF (10-20) ODS | 58.14 | 13.66 | 0.0297 | 0.0070 |
| 13 | KEVLAR STF (14) ODS | 129.68 | 40.18 | 0.0663 | 0.0205 |
| 14 | UHMWPE STF (14) ODS | 57.14 | 12.66 | 0.0292 | 0.0065 |

Table 4.1 Mass and areal density of testing samples impregnated with STF

4.2 Drop Tower Testing

Drop tower testing helped to evaluate the stab performance of fourteen samples exposed to three different stabbing weapons such as edge blade S1, edge blade P1 and spike SP. The energy level associated with the attacks was the same for all methods and corresponded to 85 percent of the male population. The results obtained from these three different drop tower tests are indicate that only one sample was able to pass the tests without any penetration. That sample is a combination of modified shear thickening fluid impregnated into Kevlar® woven fabric. The modified STF composition is made up of dry powder silica nanoparticles (10-20nm) functionalized with silane coupling agent known as ODDMAC incorporated into polyethylene glycol.

4.2.1 Edge blade – S1

The results obtained from an impact of edge blade S1 (Table 4.2) indicate that almost half of the samples were able to fully withstand level of energy associated with 85 percent of the male population. That group consisted of specimens based on combination of Kevlar® incorporated with different shear thickening fluids.

| Sample No | Description | Energy E1 [J] | Penetration Depth [mm] | Energy E2 [J] | Penetration Depth [mm] |
|--------------|---------------------------|------------------|---------------------------|------------------|---------------------------|
| 1 | KEVLAR | 24.0 | 25.0 | 36.0 | 100.0 |
| 2 | UHMWPE | 24.0 | 40.0 | 36.0 | 100.0 |
| 3 | KEVLAR STF (10-20) | 24.0 | 0.0 | 36.0 | 0.0 |
| 4 | UHMWPE STF (10-20) | 24.0 | 5.0 | 36.0 | 7.0 |
| 5 | KEVLAR STF (14) | 24.0 | 0.0 | 36.0 | 0.0 |
| 6 | UHMWPE STF (14) | 24.0 | 25.0 | 36.0 | 100.0 |
| 7 | KEVLAR STF (10-20) ODDMAC | 24.0 | 0.0 | 36.0 | 0.0 |
| 8 | UHMWPE STF (10-20) ODDMAC | 24.0 | 27.0 | 36.0 | 100.0 |
| 9 | KEVLAR STF (14) ODDMAC | 24.0 | 0.0 | 36.0 | 0.0 |
| 10 | UHMWPE STF (14) ODDMAC | 24.0 | 5.0 | 36.0 | 50.0 |
| 11 | KEVLAR STF (10-20) ODS | 24.0 | 0.0 | 36.0 | 0.0 |
| 12 | UHMWPE STF (10-20) ODS | 24.0 | 20.0 | 36.0 | 100.0 |
| 13 | KEVLAR STF (14) ODS | 24.0 | 0.0 | 36.0 | 0.0 |
| 14 | UHMWPE STF (14) ODS | 24.0 | 35.0 | 36.0 | 100.0 |

 Table 4.2 Experimental results of drop tower testing for edge blade S1

It is also worth to note that untreated Kevlar® fabrics exhibited poor stab resistance properties as compared to Kevlar impregnated with STF. Overall, all of the Kevlar® based samples impregnated with different STF exhibited zero penetration level. Samples compromised of UHMWPE/STF did not perform as well as the Kevlar®/STF. Although UHMWPE/STF samples with modified silica particles exhibited some stab resistance, their results were far from the results obtained by the samples composed of Kevlar®/STF with ODDMAC and ODS silane coupling agents. As a result, only sample 4 and sample 10 exhibited noticeable stab resistance properties. Sample 4 passed the drop test with penetration level of 7 mm (allowable is 20 mm at E2) but the penetration level by the sample 10 was found to be outside the allowable zone. Penetration level corresponding to an impact at energy E2 is much significant than an impact at energy E1. Therefore, the results obtained at energy level E2 are taken as the overall stab resistance performance.



Figure 4.1 Graphical representation of experimental results for edge blade S1

4.2.2 Edge blade –P1

Edge blade P1 exhibited the highest penetration level among all the stab weapons by going through most of the fourteen samples (Table 4.3). Two samples treated with the same silane coupling agent displayed similar properties. Kevlar® impregnated with STF having silica particles functionalized with ODDMAC performed extremely well under such a severe condition. Sample 7 (Kevlar® STF (10-20) ODDMAC) showed zero penetration level for both impact energies. Stab performance of sample 9 (Kevlar® STF (14) ODDMAC) was also improved but did not pass the test due to higher penetration depth than allowable. Comparable stab resistance properties can be observed at impact energy level E1. Samples based on Kevlar® fabrics showed better stab resistance at that particular energy level than UHMWPE based samples. Also, specimens containing silica particles functionalized with ODS exhibited lower stab resistance performance than systems consisting of untreated particles. In addition, dry silica particles achieved better results than fumed silica.

| Sample No | Description | Energy E1 [J] | Penetration Depth [mm] | Energy E2 [J] | Penetration Depth [mm] |
|--------------|---------------------------|------------------|---------------------------|------------------|---------------------------|
| 1 | KEVLAR | 24.0 | 40.0 | 36.0 | 100.0 |
| 2 | UHMWPE | 24.0 | 80.0 | 36.0 | 100.0 |
| 3 | KEVLAR STF (10-20) | 24.0 | 30.0 | 36.0 | 100.0 |
| 4 | UHMWPE STF (10-20) | 24.0 | 50.0 | 36.0 | 100.0 |
| 5 | KEVLAR STF (14) | 24.0 | 25.0 | 36.0 | 100.0 |
| 6 | UHMWPE STF (14) | 24.0 | 65.0 | 36.0 | 100.0 |
| 7 | KEVLAR STF (10-20) ODDMAC | 24.0 | 0.0 | 36.0 | 0.0 |
| 8 | UHMWPE STF (10-20) ODDMAC | 24.0 | 55.0 | 36.0 | 100.0 |
| 9 | KEVLAR STF (14) ODDMAC | 24.0 | 0.0 | 36.0 | 30.0 |
| 10 | UHMWPE STF (14) ODDMAC | 24.0 | 55.0 | 36.0 | 100.0 |
| 11 | KEVLAR STF (10-20) ODS | 24.0 | 35.0 | 36.0 | 100.0 |
| 12 | UHMWPE STF (10-20) ODS | 24.0 | 50.0 | 36.0 | 100.0 |
| 13 | KEVLAR STF (14) ODS | 24.0 | 55.0 | 36.0 | 100.0 |
| 14 | UHMWPE STF (14) ODS | 24.0 | 70.0 | 36.0 | 100.0 |

 Table 4.3 Experimental results of drop tower testing for edge blade P1



Figure 4.2 Graphical representation of experimental results for edge blade P1

4.2.3 Spike – SP

Spike testing also demonstrated the importance of STF enhancement on Kevlar® fabrics. All of Kevlar®/STF compositions showed excellent spike resistance properties (Table 4.4). Similar to other stab tests, combinations of UHMWPE/STF did not perform as well as Kevlar®/STF even at low energy level. All of the UHMWPE based samples experienced very little stab resistance enhancement and even lower in the presence of a silane coupling agent. Comparable results of UHMWPE based samples were observed between sample 4 (UHMWPE STF (10-20nm)) and sample 10 (UHMWPE STF (14) ODDMAC) at the lower energy level. Surprisingly, the same results were obtained for both types of silica particles. Besides that, sample 9 (UHMWPE STF (14) ODS) exhibited similar resistance to sample 2 (UHMWPE).

| Sample No | Description | Energy E1 [J] | Penetration Depth [mm] | Energy E2 [J] | Penetration Depth [mm] |
|--------------|---------------------------|------------------|---------------------------|------------------|---------------------------|
| 1 | KEVLAR | 24.0 | 40.0 | 36.0 | 100.0 |
| 2 | UHMWPE | 24.0 | 95.0 | 36.0 | 100.0 |
| 3 | KEVLAR STF (10-20) | 24.0 | 0.0 | 36.0 | 0.0 |
| 4 | UHMWPE STF (10-20) | 24.0 | 30.0 | 36.0 | 100.0 |
| 5 | KEVLAR STF (14) | 24.0 | 0.0 | 36.0 | 0.0 |
| 6 | UHMWPE STF (14) | 24.0 | 80.0 | 36.0 | 100.0 |
| 7 | KEVLAR STF (10-20) ODDMAC | 24.0 | 0.0 | 36.0 | 0.0 |
| 8 | UHMWPE STF (10-20) ODDMAC | 24.0 | 70.0 | 36.0 | 100.0 |
| 9 | KEVLAR STF (14) ODDMAC | 24.0 | 0.0 | 36.0 | 0.0 |
| 10 | UHMWPE STF (14) ODDMAC | 24.0 | 30.0 | 36.0 | 100.0 |
| 11 | KEVLAR STF (10-20) ODS | 24.0 | 0.0 | 36.0 | 0.0 |
| 12 | UHMWPE STF (10-20) ODS | 24.0 | 55.0 | 36.0 | 100.0 |
| 13 | KEVLAR STF (14) ODS | 24.0 | 0.0 | 36.0 | 0.0 |
| 14 | UHMWPE STF (14) ODS | 24.0 | 85.0 | 36.0 | 100.0 |

Table 4.4 Experimental results of drop tower testing for spike SP



Figure 4.3 Graphical representation of experimental results for spike SP

4.3 Quasistatic Testing

Quasistatic testing was performed on the same samples and under identical test conditions as the drop tower testing. The final results are summarized and tabulated in Table 4.5 which clearly illustrate the difference in material's behaviour under particular quasistatic test regime. It is evident from quasistatic testing that, Kevlar® STF (14) ODDMAC, Kevlar® STF (10-20) ODS as well as Kevlar® STF (10-20) ODDMAC demonstrated the highest level of stab resistance among other testing materials. Sample 9 (Kevlar® STF (14) ODDMAC) performed extremely well in edge blade S1 and edge blade P1 but not in spike SP testing. The next sample (Kevlar® STF (10-20) ODS) showed the best stab resistance in spike SP testing, the second best in edge blade P1 and decent in the edge blade S1. Sample no. 7 also showed improved stab resistance in all three tests, with final results being very close to the previous ones. Among UHMWPE based samples three compositions exhibited the highest stab resistance. Sample 4 (UHMWPE STF (10-20)) showed highest stab support in edge blade S1 testing. UHMWPE STF (14) ODDMAC demonstrated superior stab properties in edge blade P1 and sample 12 (UHMWPE STF (10-20) ODS) performed well in spike test SP.

| a i | | Velocity at | | Load [N] | |
|--------------|---------------------------|-------------------------|------------------|------------------|----------|
| Sample No | Description | penetration [mm/min] | Edge Blade S1 | Edge Blade P1 | Spike SP |
| 1 | KEVLAR | 5.0 | 316.77 | 195.72 | 138.85 |
| 2 | UHMWPE | 5.0 | 177.91 | 120.27 | 53.23 |
| 3 | KEVLAR STF (10-20) | 5.0 | 403.93 | 359.62 | 467.31 |
| 4 | UHMWPE STF (10-20) | 5.0 | 297.31 | 134.98 | 418.71 |
| 5 | KEVLAR STF (14) | 5.0 | 413.14 | 353.21 | 542.87 |
| 6 | UHMWPE STF (14) | 5.0 | 232.96 | 133.18 | 153.86 |
| 7 | KEVLAR STF (10-20) ODDMAC | 5.0 | 425.25 | 422.57 | 583.07 |
| 8 | UHMWPE STF (10-20) ODDMAC | 5.0 | 270.87 | 137.22 | 453.32 |
| 9 | KEVLAR STF (14) ODDMAC | 5.0 | 426.50 | 461.22 | 499.24 |
| 10 | UHMWPE STF (14) ODDMAC | 5.0 | 284.94 | 219.64 | 391.42 |
| 11 | KEVLAR STF (10-20) ODS | 5.0 | 394.37 | 424.33 | 605.82 |
| 12 | UHMWPE STF (10-20) ODS | 5.0 | 254.66 | 162.82 | 478.57 |
| 13 | KEVLAR STF (14) ODS | 5.0 | 364.57 | 353.11 | 509.45 |
| 14 | UHMWPE STF (14) ODS | 5.0 | 205.98 | 143.32 | 196.72 |

Table 4.5 Tabulated results of quasistatic testing for all stab treats

4.3.1 Edge blade – S1

Figure 4.4 shows the final results of samples tested against edge blade S1 stab weapon under quasistatic condition. Again Kevlar®/STF mixtures display superior stab resistance performance by supporting much higher loads than combination of UHMWPE/STF. Two Kevlar®/STF samples modified with ODDMAC coupling agent were able to withstand more than 400 N of load. Sample no. 7 (Kevlar® STF (14) ODDMAC) demonstrated the highest load resistance. The next sample (Kevlar® STF (10-20) ODDMAC) performed almost the same as the sample 7 with a load difference of 1.25 Newtons. Sample composed of UHMWPE fabrics and STF exhibited the most superior stab resistance properties of all UHMWPE based specimens. Only sample no. 12 (UHMWPE STF (10-20) ODS) experienced a sudden drop in applied load. This rapid decrease in stab resistance indicates that the samples experienced a penetration caused by failure of the fabric/STF composition.



Figure 4.4 Experimental results of quasistatic testing for edge blade S1

4.3.2 Edge blade – P1

Final results for edge blade P1 under the quasistatic mode are presented in Figure 4.5. Samples consisted of Kevlar® and STF showed similar trend to an applied force. In addition, specimens where ODDMAC silane coupling agent was used performed much better than the samples treated with ODS coupling agent. Graphical results presented in Figure 4.5 showed irregular trend for each of the UHMWPE/STF samples at certain load condition. An applied load at particular distance tends to break and starts to fluctuate. In some cases, beyond that breaking point, the resistance to the applied load decreases and the specimen is no longer able to support the load. That scenario was observed in UHMWPE STF (14) ODDMAC test sample. In other cases, the load supported by the sample at the breaking point is the same or little higher at the point where it reaches the end. This situation can be seen in behaviour pattern of most of the remaining UHMWPE/STF samples.



Figure 4.5 Experimental results of quasistatic testing for edge blade P1

4.3.3 Spike – SP

Spike testing results shown in Figure 4.6 for quasistatic test are quiet interesting. First of all, there is a significant difference in stab resistance between samples impregnated with shear thickening fluid and the sample that was not. Another interesting fact is the performance of UHMWPE/STF consisting of 14 nm silica particles alone and the one functionalized with ODS experiencing similar condition known as the breaking point. Beyond the breaking point both samples instantaneously experienced sudden loss of resistance to applied load. Also, surprisingly good performance in resisting spike penetration is observed in Kevlar® STF (10-20) treated with ODS as well as in Kevlar® STF (10-20) modified with ODDMAC. Another important finding, shown in Figure 4.6 is related to ODS silane coupling agent. It is evident, that this particular substance significantly increased resistance of both materials to the applied load. Also it is worth noting that there is better compatibility of ODS to dry silica powder (10-20 nm) than to the fumed silica.



Figure 4.6 Experimental results of quasistatic testing for spike SP

4.4 Fourier Transform Infrared Spectroscopy

The examination of samples by FTIR provided evidence for the structure of defined the types of chemical bonding present in prepared samples. Specimens compromised of neat Kevlar® and neat UHMWPE fabrics were omitted from the chemical analysis. Two tables were created to assist in interpretation of the final results. Table 4.7 shows the theoretical values of functional groups that are present in chemical compounds. Table 4.8 demonstrates the experimental data extracted from the FTIR graphs (included in appendix A). Peak wave numbers (cm⁻¹) along with their intensities were used to indicate the types of bonding structures present in the samples.

| Chem. compound | Group | Lit. Wave number [cm ⁻¹] | Intensity |
|----------------|--|--------------------------------------|---------------|
| | N-H amide & amine | 3500-3100 | medium |
| | CH stretch aromatic | 3150-3050 | strong |
| KEVLAR® | C=O amide | 1680-1630 | strong |
| | C-N amide | 1350-1000 | medium-strong |
| | CH aromatic o-o-p | 900-690 | strong |
| THNWDE | CH ₂ aliphatic | 2990-2850 | medium-strong |
| UNIVIVE | CH ₂ aliphatic | 1475-1450 | strong |
| | OH stretch | 3420-3250 | strong |
| PEG | CH ₂ aliphatic | 2990-2850 | medium-strong |
| | C-O-C ether | 1242-1070 | strong-medium |
| | C-O-C ether | 1710-798 | strong |
| | Si-CH ₂ | 1425-1400 | weak |
| SILICA | Si-CH ₂ | 1225-1200 | strong |
| | Si-O-Si siloxane | 1100-1000 | strong |
| | CH ₂ -CH ₃ aliphatic | 2990-2850 | medium-strong |
| | Si-CH ₂ | 1425-1400 | weak |
| ODS | Si-CH ₂ | 1225-1200 | strong |
| | Si-O-CH ₃ | 1200-1175 | medium |
| | Si-O- CH ₃ | 1115-1090 | strong |
| | CH ₂ aliphatic | 2990-2850 | medium-strong |
| | CH ₂ aliphatic | 1475-1450 | strong |
| ODDMAC | C-N | 1350-1000 | weak |
| ODDWAC | Si-O-CH ₃ | 1200-1175 | medium |
| | Si-O-CH ₃ | 1115-1090 | strong |
| | Si-O-Si siloxane | 1100-1000 | strong |

 Table 4.6 Literature assignments for known STF materials [60, 66]

| Chemical compound | Group | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 | Sample 8 | Sample 9 | Sample 10 | Sample 11 | Sample 12 | Sample 13 | Sample 14 |
|-------------------|----------------------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|----------------|-----------|
| | N-H amide & amine | 3300 | • | • | | • | • | • | 4 | 3356 | • | 3354 | • |
| | CH stretch aromatic | | | 3131 | | 3141 | | 3140 | | 3129 | | 3129 | |
| KEVLAR® | C=O amide | | | 1658 | | | | 1655 | | 1655 | | | |
| | C-N amide | 1112 | | 1093 | | 1091 | | 1092 | | 1090 | | 1095 | |
| | CH aromatic o-o-p | | | 820 | | 820 | | 820 | | | | | |
| THMMBE | CH2 aliphatic | 19 19 | 2922 | 10 | 2921 | 2921 | 2921 | | 2920 | 2922 | 2921 | 2921 | 2919 |
| TIMME | CH2 aliphatic | | | | | | 1467 | | 1470 | 3-13 | 1467 | | 1467 |
| 110000-00 | OH stretch | | | | | | 3356 | 3250 | 3300 | | 3366 | | 3355 |
| PEG | CH2 aliphatic | 2921 | 2922 | 2921 | 2921 | 2921 | 2921 | 2851 | 2920 | 2922 | 2921 | 2921 | 2919 |
| | C-O-C ether | 1112 | 1113 | 1093 | 1091 | 1091 | 1095 | 1092 | 1092 | 1090 | 1092 | 1095 | 1093 |
| | C-O-C ether | 1112 | 1113 | 1093 | 1400 | 1400 | 1400 | 1092 | 1400 | 1090 | 1400 | 1095 | 1093 |
| 1110 | Si-CH2 | 1400 | 1400 | 1420 | | | | | | | | | |
| SILICA | Si-CH2 | | | | | | | | | | | | |
| | Si-O-Si siloxane | 1090 | 1042 | 1093 | 1091 | 1092 | 1095 | 1092 | 1092 | 1090 | 1092 | 1095 | 1093 |
| £2 | CH2-CH3 aliphatic | | | | | | | | | 2922 | 2921 | 2921 | 2919 |
| | Si-CH2 | | | | | | | | | | | | |
| SODS | Si-CH2 | 94 | 9 - 52 | | | | | | | 8-03 | 3 | 8 92 8 8 | |
| | Si-O-CH3 | 10) | | | | | * | | | | | | |
| | Si-O-CH3 | | | | | | | | | 1090 | 1092 | 1095 | 1093 |
| | CH2 aliphatic | | | | | 2921 | 2921 | 2921 | 2920 | | | | |
| | CH2 aliphatic | | | | | 1467 | | | 1470 | | | | |
| JANUUD | C-N | -01 - | | | 2 | 1275 | 1275 | 1270 | 1250 | - | | | |
| NEWIGO | Si-O-CH ₃ | | | | | | | | | 8-8 | | 58 58 58 50 | () |
| | Si-O-CH3 | | | | | 1091 | 1095 | 1092 | 1092 | | | | |
| | Si-O-Si siloxane | 8 18 | 8 38 | | | 1091 | 1095 | 1092 | 1092 | 2-03 | 8-36 | s - 98 | |
| | | | | | | | | | | | | | |

Table 4.7 Experimental assignments for STF materials $[\rm cm^{\Lambda-1}]$

4.5 Scanning Electron Microscopy

SEM images of neat Kevlar® and neat UHMWPE fabrics (Figure 4.7) show no presence of STF on the surface of the fabrics. The next Figure (4.8), presents Kevlar and UHMWPE impregnated with STF (10-20). This Figure illustrates problem associated with adhesion and uniform dispersion of STF on both fabrics. The images show that the fabrics are not fully covered by the STF. A lower concentration of STF was found to be present on the samples composed of UHMWPE/STF (10-20) than system compromised of Kevlar/STF (10-20).



Figure 4.7 SEM images of. a). Neat Kevlar®, b) Neat UHMWPE



Figure 4.8 SEM images of. a). Kevlar®/STF (10-20), b) UHMWPE/STF (10-20)



Figure 4.9 SEM images of. a). Kevlar®/STF (14), b) UHMWPE/STF (14)

Figure 4.9 display a weak dispersion of STF, composed of 14 nm fumed silica. on UHMWPE fabrics. On the other hand, system compromised of Kevlar®/STF (14) shows better results, although, full uniformity is still missing. Another important finding, shown in Figures 4.9-4.12 is related to silica aggregates. Figures 4.10-11 illustrate much smaller silica aggregates than the one present on all the other images. Also, Figures 4.10-4.11 demonstrate significant improvement corresponding to the adhesion of STFs to both fabrics. It is also worth to note, the dispersion of STF became more uniform after modifying silica with silane coupling agents.



Figure 4.10 SEM images of. a). Kevlar®/STF (10-20) ODDMAC, b) UHMWPE/STF (10-20) ODDMAC



Figure 4.11 SEM images of. a). Kevlar®/STF (14) ODDMAC, b) UHMWPE/STF (14) ODDMAC

Sample 12 (UHMWPE (10-20) ODS) shown in Figure 4.12 (a) demonstrates good incorporation of STF between the fibres along with large silica agglomerates. Kevlar® STF (10-20) ODS, displays same silica agglomerates but the STF composition is not so highly present between the Kevlar® as well as it incorporated in UHMWPE fibres. Sample 13 (Kevlar® STF (14) ODS) and 14 (UHMWPE STF (14) ODS) illustrate the fabric structure (Figure 4.13). The deposition amount of STF on the surface of the fabrics is greater on sample 13 than sample 14.



Figure 4.12 SEM images of. a). Kevlar®/STF (10-20) ODS, b) UHMWPE/STF (10-20) ODS



Figure 4.13 SEM images of. a). Kevlar®/STF (14) ODS, b) UHMWPE/STF (14) ODS

4.6 Energy Dispersive X-Ray Spectroscopy

EDS microanalysis displays the final results in a graph form of x-ray counts vs. energy (in keV). Figure 4.14 shows elements that are usually present on neat fabrics carbon (C), oxygen (O) with some impurities sodium (Na). Figures 4.14-4.15 demonstrate existence of majopr elemental constitutes of STF composition; silica (Si), oxygen (O). Figures 4.16-4.20 illustrate the deposition of silane coupling agents onto silica surface by the presence of chlorine (Cl), and some impurities, sodium (Na) and calcium (Ca).



Figure 4.14 EDS spectrums of a). Neat Kevlar®, b) Neat UHMWPE



Figure 4.15 EDS spectrums of a). Kevlar®/STF (10-20), b) UHMWPE/STF (10-20)



Figure 4.16 EDS spectrums of a). Kevlar®/STF (14), b) UHMWPE/STF (14)



Figure 4.17 EDS spectrums of a). Kevlar®/STF (10-20) ODDMAC,

b) UHMWPE/STF (10-20) ODDMAC



Figure 4.18 spectrums of a). Kevlar®/STF (14) ODDMAC, b) UHMWPE/STF (14) ODDMAC



Figure 4.19 EDS spectrums of a). Kevlar®/STF (10-20) ODS, b) UHMWPE/STF (10-20) ODS



Figure 4.20 EDS spectrums of a). Kevlar®/STF (14) ODS, b) UHMWPE/STF (14) ODS

Chapter 5. DISCUSSION

5.1 General Findings from Current Study

Overall, this current research project, initiated through funding from an industrial sponsored OCE grant, is considered as a fundamental project for the developing of lightweight, inexpensive, thin, flexible, stab and ballistic resistant body armour. This study evaluated stab resistance performance of two types of high performance fabrics, Kevlar® and UHMWPE synthesized with several types of shear thickening fluids. SEM images illustrate the poor adhesion properties between STF and UHMWPE fibers. Also, the images displayed problems with uniform impregnation of STF into armour fabrics. The final results of stab resistance tests demonstrated increased performance of Kevlar® fabrics impregnated with shear thickening fluid composed of silica particles functionalized with octadecyldimethyl trimethoxysilyl propyl ammonium chloride. FTIR analysis showed an increase in bond formation on the surface of the nanoparticles. However, that modification process turned out to be insufficient to create the necessary linkage between STF and UHMWPE.

5.2 Expanded Commentary on Current Study

A series of experiments along with stab testing evaluation and chemical analyses significantly contributed toward the main objective regarding a development of innovative body armour. These key results assisted in assessing potential materials and processes for the project. Several ideas have been taken under the consideration; however, nanoparticles suspended in solvent medium impregnated with high performance fabrics appeared as the most attainable plan for making this project successful. In addition, a system composed of STF and Kevlar is already patented; therefore, another high performance material (UHMWPE) was selected to replace Kevlar. Unfortunately, the first set of stab tests revealed significant problems between STF and UHMWPE fabrics. The composition of STF/Kevlar performed according to the literature, showing enhanced stab resistance properties over neat Kevlar [2, 27, 43]. Afterwards a new initiative was established. Proven modification of silica particles with the most common silane agents was undertaken [34-39, 55]. Although the general objective was not reached, numerous important explanations and findings emerged from the current study and are presented.
Poor adhesion of STF composition to the UHMWPE fibres significantly affected stab resistance performance. Although, according to the literature [6], ethanol does not alter rheological properties, it influences adhesion to the fabrics. The recommended ratio of ethanol to STF was 3:1 but the final results indicate that the ratio should be decreased to improve adhesion capabilities. Also a reduced amount of ethanol can help to facilitate a higher STF concentration on the surface of the fibres. In addition, there are significant differences in the STF's areal density. Kevlar® impregnated fabrics retained roughly two and a half times higher concentration of STF than UHMWPE. This is another indication that amount of ethanol added to facilitate STF impregnation to the fibres should be controlled.

Silica particles used in the experiment exhibited significantly different stab resistance performance. Overall, samples containing a dry powder silica achieved slightly better results than fumed silica. Hardness of nanoparticles is considered as the main mechanism for that behaviour [7]. However, the cost of fumed silica is much lower than of dry powder silica which should also be taking under the consideration of a long run.

The performance of the Kevlar/STF was significantly increased by the addition of silane coupling agents. Both agents possess the ability to increase stab resistance properties; however, ODDMAC was to some extent more effective than ODS, especially considering the price.

The effectiveness of high performance fibers are also an important part. Fabrics constituted of higher denier are much likely to achieve lower penetration. The reason for that is larger number of filaments in the yarn, which assist in developing larger interface between STF and the fibers.

In general the Kevlar/STF performance dramatically improved after silica modification. Silane coupling agents are proven to increase stab resistance fabrics; however, this was true only for amides. The most desirable stab resistant characteristics are present in a modified STF composition made up of dry powder silica nanoparticles (10nm-20nm) that was functionalized with the silane coupling agent known as ODDMAC and incorporated into polyethylene glycol.

The purpose of functionalizing silica nanoparticles with ODDMAC lies in its superior coupling properties. ODDMAC quaternary, positively charged reactant which promotes greater hydrogen bonding and improves STF properties. In addition, the silane can be functionalized or modified to work with UHMWPE fibres under certain conditions.

5.3 Chemical Analysis

Two chemical analyses had essential impact on investigating chemical composition as well as bonding structures of prepared composites. FTIR analyses confirmed some important facts regarding chemical bonding that exists between different chemical compounds. Some of these functional groups associated with particular chemical compound could not be found on the IR spectrum. The disappearance of these peaks mainly occurred in the region between the 1700 cm⁻¹ to 700 cm⁻¹. According to the theory, this problem is due to strong siloxane compounds Si-O-Si and Si-CH₂ groups that cause a high scattering in that particular range [67]. A major reason for the high compatibility between STF and Kevlar fibres lies in the presence of C-N amine, N-H amide and C=O amide bonds on the Kevlar surface. Another important fact is the existence of two peaks located roughly at 2380 cm⁻¹ and 2285 cm⁻¹ after introducing silane coupling agents on Kevlar surface. The strong intensity of these peaks in the IR spectrum of samples with modified silica particles ODDMAC rather compared to the ODS samples. The examination by FTIR analysis provided evidence for the structure of N=C=O and C=N aromatic nitriles. The assignment for 2385 cm⁻¹ and 2285 cm⁻¹ respectively was within the range of literature values of 2270 cm⁻¹ and 2230 cm⁻¹ [66].

EDS analysis confirmed the chemical elements of compounds used in this research project. Some minor impurities (Na, Ca) were observed, but were too small to affect fabric/liquid systems.

5.4 Stab Resistance Analysis

The stab resistance investigation, carried out on fourteen samples illustrated different failure mechanisms that have occurred under six impact conditions.

Spike impact tests revealed the same failure mechanism, responsible for fabric failure in several publications called windowing [11, 68]. It is evident in this study that windowing appears mostly on samples compromised of neat fabrics or UHMWPE impregnated with STF. Composition of Kevlar/STF exhibited small windowing but the samples were not fully penetrated. This phenomenon corresponds to yarn constrain in the woven fabrics also known as inter-yarn and fabric-projectile friction. Due to the inherent low coefficient of friction fibres tend to slide over each other causing pushing the yarns aside during stabbing instead of breaking [69]. Shear thickening fluid dispersed between the fibres increases inter-yarn and fabric-projectile

friction, which eventually leads to significant improvement in energy dissipation properties. Also, an additional energy is absorbed due to fiber fracture instead of fiber separation [3]. Another improvement is observed in samples having silica particles functionalized with silane coupling agents. It is evident that ODDMAC coupling agent creates higher friction between the fibres than ODS. In addition, surfactants can influence shear thickening transition due an increase in inter-particle friction [5].

Another failure regime, known as shearing, was encountered during edge blade S1 and edge blade P1 impact testing. The analysis demonstrated increased penetration caused by testing weapon with two identical sharp edges known as edge blade S1. The stab resistance to spike and edge blade P1 was almost the same which concludes that the geometry of stab device greatly influences the penetration depth.

It is evident that samples composed of Kevlar fabrics were much stronger than samples compromised of UHMWPE due to denier difference. Therefore, the stab performance of Kevlar and UHMWPE based samples required separate analyses and cannot be compared to the literature.

The final results for Kevlar based compositions showed significant enhancement in stab resistant properties. Samples impregnated with STF composed of modified silica retained low penetration depth and developed high load stab resistance capabilities. On the top of that, zero penetration level was achieved by combination of dry powder silica nanoparticles coated with ODDMAC coupling agent, mixed with polyethylene glycol and dispersed in Kevlar.

Systems compromising of UHMWPE fabrics and STF exhibited low stab resistance capabilities. The majority of the samples failed both sets of impact tests. Only sample 4 (UHMWPE STF (10-20)) showed an acceptable resistance to edge blade S1 in drop tower test, but failed all the other tests. The results obtained from quasistatic testing confirmed weak compatibility between the STFs and UHMWPE fabrics. It was observed that penetration of several UHMWPE composites, under quasistatic load conditions, occurred at the breaking point. This point can be seen as the sudden drop in applied load followed by a constant or fluctuating load values until it reached the end point.

5.5 Limitations and Future Considerations

At the onset of this project, virtually no stab testing equipment was available at Ryerson except for the tensile machine used for Quasistatic testing. Therefore, several testing instruments needed to be fabricated such as the Drop Tower device and adjustable stab weapons. Also rheological testing were not performed due to the absence of available sophisticated rheological equipment. In addition, the combination of Kevlar and STF compromised of silica suspended in polyethylene is already patented. Also, fabrics used in this study were not comparable due to the denier difference. Overall, high performance fibres in woven form are considered as military products. Therefore, they are more difficult to obtain than other fabrics.

Polyethylene glycol is an effective STF solvent medium that adheres well to Kevlar®; unfortunately, not so well to UHMWPE surface. Therefore, selecting a carrier fluid that exhibits better compatibility with UHMWPE can improve their stab resistance.

Applying properties of polyamide to increase compatibility of STF with UHMWPE fibres can be done by coating UHMWPE fibres with nylon. This process can be achieved by dissolving pellets of Nylon 6.6 in 15% calcium chloride and methanol and in phenol [70].

Surface improvement on UHMWPE woven fibres can be performed by process called gas plasma treatment. It works on a principle of modifying top molecules of the material to meet desirable chemical characteristics or surface energies [71].

According to the literature, the addition of a certain vinyl silanes coupling agents can be used to crosslink polyethylene chains. The process known as grafting uses peroxide and heat to attach the vinyl silane to the polyethylene backbone, producing silane grafted polyethylene. Further crosslinking of grafted polyethylene can create a silane crosslinked product [72]. Similar procedures can be applied to UHMWPE fibres. Vinyl silane coupling agent can be added to ethylene and solvent during mixing. This page is intentionally left blank.

Chapter 6. CONCLUSION

This current study demonstrated the importance of incorporating a shear thickening fluid into woven high performance fibres. The results clearly displayed a significant enhancement in puncture resistance of Kevlar® impregnated with different combination of STFs.

Shear thickening fluids composed of silica particles functionalized with silane coupling agents demonstrated better stab resistance during Drop Tower and Quasistatic test than without. Also SEM images illustrated better adhesion of STFs with modified silica to the high performance fabrics. FTIR analysis demonstrated additional chemical bonding created by silane coupling agents on the surface of composites.

It was evident from the experimental results that none of the shear thickening fluids prepared for this research worked on the UHMWPE fibres as well as they did on Kevlar® fibres. However, it has been proven that shear thickening composition is capable of becoming a significant element for the production of thinner, flexible and patentable body armour. Therefore, further research on improving compatibility between shear thickening fluid and UHMWPE fibres should be guided towards fabric modification not silica. This page is intentionally left blank.



APPENDIX A: Results from Fourier Transform Infrared Spectroscopy

APPENDICES

Figure A1-1 FTIR analysis of sample 3-Kevlar STF (10-20)



Figure A1-2 FTIR analysis of sample 4-UHMWPE STF (10-20)



Figure A1-3 FTIR analysis of sample 5-Kevlar STF (14)



Figure A1-4 FTIR analysis of sample 6-UHMWPE STF (14)



Figure A1-5 FTIR analysis of sample 7-Kevlar STF (10-20) ODDMAC



Figure A1-6 FTIR analysis of sample 8-UHMWPE STF (10-20) ODDMAC



Figure A1-7 FTIR analysis of sample 9-Kevlar STF (14) ODDMAC



Figure A1-8 FTIR analysis of sample 10-UHMWPE STF (14) ODDMAC



Figure A1-9 FTIR analysis of sample 11-Kevlar STF (10-20) ODS



Figure A1-10 FTIR analysis of sample 12-UHMWPE STF (10-20) ODS



Figure A1-11 FTIR analysis of sample 13-Kevlar STF (14) ODS



Figure A1-12 FTIR analysis of sample 14-UHMWPE STF (14) ODS

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