2016

Fabrication, characterisation and optimisation of shear thickening fluids

Alain David Moriana

University of Wollongong

UNIVERSITY OF WOLLONGONG
COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author.

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

Recommended Citation

Moriana, Alain David, Fabrication, characterisation and optimisation of shear thickening fluids, Master of Philosophy (Materials Engineering) thesis, School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, 2016.
https://ro.uow.edu.au/theses/4779

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au
FABRICATION, CHARACTERISATION AND
OPTIMISATION OF SHEAR THICKENING FLUIDS

By
ALAIN DAVID MORIANA

A dissertation submitted in partial fulfilment of the
requirements for the award of the degree of

MASTER OF PHILOSOPHY
(MATERIALS ENGINEERING)

From
UNIVERSITY OF WOLLONGONG

FACULTY OF ENGINEERING AND INFORMATION SCIENCES
August 2016
# TABLE OF CONTENTS

Acknowledgements ............................................................................................................ 4
Abstract ............................................................................................................................... 5
List of Figures ...................................................................................................................... 6
List of Tables ....................................................................................................................... 9
Notation ............................................................................................................................... 10
Abbreviations ...................................................................................................................... 11
1. Introduction .................................................................................................................. 12
2. Literature Review ........................................................................................................ 13
   2.1. Introduction .......................................................................................................... 13
       2.1.1. What is shear thickening? .............................................................................. 13
       2.1.2. Components of STF ...................................................................................... 13
   2.2. Parameters affecting shear thickening .................................................................. 14
       2.2.1. Main particle composition ............................................................................ 15
       2.2.2. Particle shape ............................................................................................... 16
       2.2.3. Particle surface chemistry .......................................................................... 17
       2.2.4. Particle size ................................................................................................... 18
       2.2.5. Carrier liquid (liquid-particle reaction, chemistry) ...................................... 19
       2.2.6. Molecular weight ......................................................................................... 19
       2.2.7. Carrier fluid chemistry ............................................................................... 21
       2.2.8. Additives ....................................................................................................... 22
       2.2.9. Temperature .................................................................................................. 23
   2.3. Mechanisms of STF .............................................................................................. 24
       2.3.1. Order-disorder transition (ODT) ................................................................. 24
       2.3.2. Hydrocluster ............................................................................................... 26
       2.3.3. Other theories ............................................................................................. 28
   2.4. Modelling of STF .................................................................................................. 29
   2.5. Applications of STF .............................................................................................. 33
       2.5.1. Impact resistance ......................................................................................... 33
       2.5.2. Dampening control ..................................................................................... 37
       2.5.3. Other applications ...................................................................................... 38
   2.6. Chapter Summary ................................................................................................ 39
3. Quantifying rheological behaviors with material properties of shear thickening fluids .... 40
   3.1. Materials ............................................................................................................... 40
       3.1.1. Fumed silica particles .................................................................................. 40
3.1.2. Carrier fluids ................................................................. 41

3.2. Method 42

3.2.1. STF fabrication ............................................................... 42
3.2.2. Properties measurement of STF ....................................... 42

3.3. Results 43

3.3.1. Characterisation of STFs .................................................. 43
3.3.2. Modelling of STFs’ thickening behaviour .......................... 49

3.4. Relating material variables with rheology of STFs 59

3.4.1. Weight fraction .............................................................. 59
3.4.2. Primary particle size ...................................................... 62
3.4.3. Carrier fluid chemistry .................................................. 63

3.5. Validity with the Modified Cox-Merz Rule 65

3.6. Chapter Summary 67

4. The Effects of additives on shear thickening fluids .......................... 69

4.1. Materials 69

4.1.1. STFs ............................................................................ 69
4.1.2. Boron nitride (BN) particles, BN2.0 .................................. 70
4.1.3. Boron nitride (BN) particles, TubularBN .......................... 73
4.1.4. Titanium dioxide (TD) particles ...................................... 75

4.2. Method 76

STF + ADDITIVE fabrication and characterisation ............................ 76

4.3. Results 77

4.3.1. Characterisation of STF with increasing temperature ............ 77
4.3.2. STF + BN2.0 ................................................................. 79
4.3.3. STF + TubularBN ......................................................... 82
4.3.4. STF+TD ..................................................................... 85

4.4. Discussion 88

Effect of material properties of additives on the thickening performance 88

4.5. Chapter Summary 91

5. Conclusion ............................................................................ 92

6. References ............................................................................. 94

7. Appendix A ........................................................................... 99

8. Appendix B ............................................................................ 100

9. Appendix C ........................................................................... 101

10. Appendix D ........................................................................ 102
ACKNOWLEDGEMENTS

Many people have assisted me in the past 2 years that have resulted in producing my final dissertation and I would therefore like to acknowledge them personally.

Much appreciation is also given to my supervisor Prof. Weihua Li who assisted me with purchasing relevant materials, constant support, and encouragement and going out of his way to ensure that the final dissertation and results are meaningful and worth being proud of.

Thanks also go to Dr. Vitor Sencadas for his impressive knowledge of all things polymers, helping me diagnose relationships between results and variables and assisting me in using theory to explain trends in results.

Many thanks to the Intelligent Polymer Research Institute (IPRI) at Innovation Campus at University of Wollongong, specifically Dr. Zhenguo Huong and Dr. Feng Xiao for supplying the boron nitride variants and relevant material information used in testing, allowing for potential further modifications to shear thickening fluids.

I would also like to thank my Co-supervisor Dr. Tongfei Tian for his constant support, helping me settle into the world of academia and allow me to regularly check my results, postulations and draft works by him, both in person and whilst abroad. His knowledge of all non-Newtonian fluids helped set the foundations for the work presented here.

The author acknowledges Evonik Industries for supplying fumed silica samples for testing and Sigma-Aldrich® for supplying the various carrier fluids used for testing.

Finally, I would like to thank my parents, Rafael and Maria Moriana, and my sister Lara Moriana who have spent the last 2 years supporting me through the problematic times and their constant love and support helped make the last 2 years a significant, yet positive, statement on my life so far.
ABSTRACT

This thesis focuses on quantifying the effect of ingredients within shear thickening fluids (STFs) with resultant rheological behaviours for their potential use in practical applications. This was done by firstly using steady shear testing to measure the rheology of STFs fabricated by several carrier fluids of poly(ethylene glycol) and poly(propylene glycol) of varying molecular weights and fumed silica with different particle sizes. It was discovered that larger particles increased the thickening effect, critical shear rate and the specific carrier fluid used affected the overall shear thickening effect and the critical shear rate. It was found that the fumed silica at larger particle size (OX50), increased the thickening effect and critical shear rate and the type of carrier fluid used affected the shear thickening performance and the critical shear rate. It was also found that there existed an optimum weight fraction of fumed silica which showed maximum shear thickening performance. An explanation was then proposed to correlate factors such as varying particle size, carrier fluid chemistry and weight fraction to resultant rheological behaviours. A mathematical model was also proposed that correlated temperature and weight fraction to specific rheological parameters.

In two selected STFs from the initial experiment (“PEG400 + 45 wt% OX50” and “PPG400 + 35 wt% OX50”), various additives (Tubular and platelets of boron nitride and titanium dioxide) were used in attempt to improve shear thickening performance. Boron nitride (BN) particles, in particular, showed improved temperature stability of rheological behaviour during steady shear testing at 0.5 wt% in PEG400 + OX50. It was proposed that the superior thermal conductivity and hydrophilic nature of BN allowed for heat to rapidly evacuate from the STF during testing.

These findings have significant impact in helping to understand the effects of particles and carrier fluid chemistry on the shear thickening effect and assisting in ‘tailoring’ STFs for specific applications to maximise shear thickening for above mentioned applications.
LIST OF FIGURES

Figure 2.1 Typical viscosity curve of a shear thickening fluid. Experimental data shown is corresponding to a suspension of Aerosil®R816 in polypropylene glycol at 5% (v/v) and 25°C [29].......................................................... 14
Figure 2.2 The effect of shape on shear thickening for weight fraction of 20% [30].............................. 16
Figure 2.3 Shear thickening behaviour of colloidal silica with PEG200 (poly(ethylene glycol) with molecular weights 200 g/mol) for steady shear flow with different particle size [7]..........18
Figure 2.4 Shear rate sweep curves of CaCO₃ and SiO₂ suspensions at 15, 25 and 35 wt.% concentrations: (top) PEG200–contained; (bottom) PEG400–contained [55]................................. 20
Figure 2.5 Rheology of fumed silica dispersions in oligomers with different end-functionalities under steady shear rheology in: PEG-diacylate 400, PEG-monomethyl ether monomethacrylate 400, and PEG-monobutyl [36]................................. 22
Figure 2.6 Steady-shear experimental results as a function of temperature for 15 wt% A200 fumed silica in PEG200 (left) and 22.5 wt% A200 fumed silica in PEG200 (right) [62].............. 24
Figure 2.7 Visual approximation of the microstructure of a STF under various stages of steady flow [64]..........................................................................................................................25
Figure 2.8 Comparison of function simulation and experimental data [77]........................................31
Figure 2.9 Comparison of function simulation and experimental data of 20% STF (left) and 26% STF (right) [78].......................................................................................................... 32
Figure 2.10 Comparison of front Kevlar® layers for (left) unimpregnated and (right) impregnated target after ballistic testing [2].................................................................................. 34
Figure 2.11 SEM images for (a) Neat Nylon fabrics; (b-d) STF/Nylon composite [9]...................... 35
Figure 2.12 Steady shear results of the MRSTF sample based on 15 wt% STF and the STF sample [25]................................................................................................................. 38
Figure 3.1 Representative TEM images of (a) A90 and (b) OX50.................................................. 41
Figure 3.2 Viscosity measured as a function of shear rate under steady shear conditions for STF containing PEG400 + A90 (a), PPG400 + A90 (b) and PPG725 + A90 (c)......................... 43
Figure 3.3 Viscosity measured as a function of shear rate under steady shear conditions for STF containing 25 wt% A90 using different carrier fluids ............................................ 44
Figure 3.4 Viscosity measured as a function of shear rate under steady shear conditions for STF containing PEG400 + A130 (a) and PPG400 + A130 (b) ......................................................... 45
Figure 3.5 Viscosity measured as a function of shear rate under steady shear conditions for STF containing PEG400 + OX50 (a) and PPG400 + OX50 (b) ......................................................... 46
Figure 3.6 Viscosity measured as a function of shear rate under steady shear conditions for STF containing 45 wt% OX50 using different carrier fluids ......................................................... 47
Figure 3.7 Viscosity measured as a function of shear rate under steady conditions under varying temperatures for STFs containing (a)STFPEG and (b) STFPPG................................. 47
Figure 3.8 Shear thickening ratio (a) and critical shear rate (b) measured as a function of testing temperature of STFPEG. Lines denote trend line with equation and regression adjacent. Error lines are the maxima/minima of repeated tests.......................................................... 47
Figure 3.9 Shear thickening ratio (a) and critical shear rate (b) measured as a function of testing temperature of STFPPG. Lines denote trend line with equation and regression adjacent. Error lines are the maxima/minima of repeated tests.......................................................... 49
Figure 3.10 Steady shear tests of PEG400 + OX50 measuring viscosity as a function of shear rate (a) and shear stress (b). Labels are the specific material parameters extracted from each steady shear test ................................................................. 50
Figure 3.11 Varying thickening parameters as a function of weight fraction of PEG400 + OX50 (left column) and PPG400 + OX50 (right column) mixtures, shear stress (a and b), viscosity (c and d) and shear rate (e and f). Lines represent the modelling data for comparison. .................. 53
Figure 3.12 Varying thickening parameters as a function of weight fraction of PEG400 + A90 (left column) and PPG400 + A90 (right column) mixtures, shear stress (a and b), viscosity (c and d) and shear rate (e and f). Lines represent the modelling data for comparison .......... 54
Figure 3.13 Three-dimensional representation of STF models as functions of weight fraction and temperature for PEG400 + OX50 (a, c and e) and PPG400 + OX50 (b, d and f). Red series denotes critical values and blue series denotes maximum values for corresponding rheological trait ................................................................. 57
Figure 3.14 Three-dimensional representation of STF models as functions of weight fraction and temperature for PEG400 + A90 (a, c and e) and PPG400 + A90 (b, d and f). Red series denotes critical values and blue series denotes maximum values for corresponding rheological trait ................................................................. 58
Figure 3.15 Diagrammatic representation of the possible STF composition at optimum weight fraction (a), below the optimum weight fraction (b) and above the optimum weight fraction (c). Blue circles represent fumed silica aggregates within the STF carrier fluid. .................... 60
Figure 3.16 Thickening performance (a) and critical shear rate (b) measured as a function of weight fraction mixed with A90 fumed silica under steady shear conditions. ............... 61
Figure 3.17 Monomer unit for (a) PEG and (b) PPG ................................................. 61
Figure 3.18 Thickening performance (a) and critical shear rate (b) measured as a function of weight fraction mixed in PEG400 carrier fluid under steady conditions. .............. 62
Figure 3.19 Thickening performance (a) and critical shear rate (b) measured as a function of weight fraction mixed with OX50 fumed silica under steady shear conditions........... 64
Figure 3.20 Dynamic frequency tests conducted on STFPEG (a) and STFPPG (b). Each data series represents the strain amplitude (γ0) ........................................................................................................... 66
Figure 3.21 Correlation of steady and dynamic shear test data of STFPEG (a) and STFPPG (b) using MCM rule. Each data series represents the strain amplitude (γ0) when applicable........ 67
Figure 4.1 XRD pattern of BN2.0 samples received. X-axis represents 2-theta (2θ) and y-axis is the Counts per second. ........................................................................................................ 71
Figure 4.2 FTIR spectrum analysis of BN2.0. X-axis represents the inverse of wavelength (cm⁻¹) and y-axis as Transmittance (%). ................................................................. 72
Figure 4.3 TEM images of BN2.0 ............................................................................ 73
Figure 4.4 XRD pattern of TubularBN samples received. X-axis represents 2-theta (2θ) and y-axis is the Counts per second. ................................................................. 73
Figure 4.5. FTIR spectrum analysis of TubularBN. X-axis represents the inverse of wavelength (1/cm) and y-axis as Transmittance (%). ................................................................. 74
Figure 4.6 TEM images of TubularBN .................................................................... 75
Figure 4.7 Representative TEM image of the TD particles used. ................................. 76
Figure 4.8 Viscosity measured as a function of shear rate under steady shear conditions of PEG400 + 45 wt% OX50. Each series denotes the testing stage temperature during testing.... 77
Figure 4.9 Thickening performance (a) and yıc (b) measured as a function of testing temperature of PEG400 + 45 wt% OX50 control sample. Lines denote trend line with equation and regression adjacent .............................................................................. 78
Figure 4.10 Viscosity measured as a function of shear rate under steady conditions under varying temperatures for STFs containing 0.5 wt% BN2.0 (a), 1 wt% BN2.0 (b) and 3 wt% BN2.0 (c).

Figure 4.11 Thickening performance (a) and $\gamma c$ (b) measured as a function of testing temperature of STF+BN2.0. Each series denote the weight fraction of BN2.0 added to the STF.

Figure 4.12 Viscosity measured as a function of shear rate under steady conditions under varying temperatures for STFs containing 0.5 wt% TubularBN (a), 1 wt% TubularBN (b) and 3 wt% TubularBN (c).

Figure 4.13 Thickening performance (a) and $\gamma c$ (b) measured as a function of testing temperature of STF+TubularBN. Each series denote the weight fraction of TubularBN added to the STF.

Figure 4.14 Viscosity measured as a function of shear rate under steady conditions under varying temperatures for STFs containing 0.5 wt% TD (a), 1 wt% TD (b) and 3 wt% TD (c).

Figure 4.15 Thickening performance (a) and $\gamma c$ (b) measured as a function of testing temperature of STF+TD. Each series denote the weight fraction of TD added to the STF.

Figure 4.16 Diagrammatic representation of the possible changes in STF+BN2.0/TD with increasing temperature. Blue circles represent fumed silica aggregates, red ovals represent BN2.0 particles and black lines are PEG400 polymer chains.
LIST OF TABLES

Table 3.1 Material properties of A130, A90 and OX50 [85].................................................. 41
Table 3.2 Material properties of PEG400 [86], PPG400 [87] and PPG725 [88]...................... 42
**NOTATION**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pe}$</td>
<td>Pèclet number</td>
</tr>
<tr>
<td>$a$</td>
<td>Hydrodynamic radius</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>Shear rate, s$^{-1}$</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Diffusivity, m$^2$/s</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant, J/K</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature, K</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>Carrier fluid viscosity, Pa·s</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity, Pa·s</td>
</tr>
<tr>
<td>$\eta^*$</td>
<td>Complex viscosity, Pa·s</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency, rad/s</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>Shear strain amplitude, %</td>
</tr>
<tr>
<td>$\dot{\gamma}_c$</td>
<td>Critical shear rate, s$^{-1}$</td>
</tr>
<tr>
<td>$h$</td>
<td>Interparticle distancing, nm</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Weight fraction, %</td>
</tr>
<tr>
<td>$G'$</td>
<td>Storage modulus, Pa</td>
</tr>
<tr>
<td>$G''$</td>
<td>Loss modulus, Pa</td>
</tr>
<tr>
<td>$\omega \gamma_0$</td>
<td>Dynamic shear rate, s$^{-1}$</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>STFs</td>
<td>Shear thickening fluids</td>
</tr>
<tr>
<td>ODT</td>
<td>Order-disorder theory</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of Polymerisation</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly(ethylene glycol)</td>
</tr>
<tr>
<td>PPG</td>
<td>Poly(propylene glycol)</td>
</tr>
<tr>
<td>NATO-standard</td>
<td>North Atlantic Treaty Organisation standard</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
</tr>
<tr>
<td>MRSTF</td>
<td>Magnetorheological shear thickening fluid</td>
</tr>
<tr>
<td>MRF</td>
<td>Magnetorheological fluid</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller theory</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>MCM</td>
<td>Modified Cox-Merz</td>
</tr>
<tr>
<td>BN</td>
<td>Boron nitride</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>TD</td>
<td>Titanium dioxide</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

Shear thickening fluids (STFs) are a novel compound with significant potential applications in the field of impact and vibrational absorption. The main behaviour of STFs is its ability of increasing viscosity greatly with increasing shear force past a certain point and its ability to revert to its unloaded state, making STFs reusable in applications. Recent research on STFs focused on impregnating Kevlar® fabrics with STFs in order to improve its stab resistance [1-9] and to reduce the amount of layers required for maximum penetration resistance.

However, it is apparent that there is a significant gap in research which is the limitations associated with STFs’ use in studies related to applications. There is limited research conducted into the relation between the different rheological behaviours and the STF’s ability to adsorb impact energy. One could assume that by increasing the magnitude of thickening, the STF would be more effective at absorbing applied impact energy. The critical shear rate at which shear thickening occurs is another significant point to consider as it states how sensitive the STF is to have the onset of shear thickening in different applications. Other factors needed to be considered for applications include service temperature and the effect of additives.

This project aims to bridge this gap by observing the effects of varying material parameters within STF solutions and their resultant rheological behaviours for potential uses in practical applications. Initially, analysis of current research and findings was undertaken in order to build the foundation for later experimental work in this project. With this, we were able to evaluate the optimum composition to attain favourable rheological abilities and map the resultant shear thickening ability as a function of STF composition, allowing for coordination between potential mechanical applications and the rheological properties required from it. A secondary objective was to observe the effect of additives to STF and monitor their effect on the rheological behaviour under different conditions.
2. LITERATURE REVIEW

2.1. Introduction

2.1.1. What is shear thickening?

Shear thickening fluids (STFs) are non-Newtonian fluids in which viscosity is dependent on the applied shear rate. Specifically for STFs, once a certain shear rate has been surpassed, the viscosity increases dramatically often ten or hundredfold. This phenomenon is also completely reversible once the applied shear force is removed, which makes STFs reusable. Current understanding of this shear thickening effect has surmised that the particles within the STF are the root cause of this discontinuous shear thickening phenomenon. Two main theories have been proposed that explain this shear thickening phenomena including the clustering of nearby particles to form ‘hydroclusters’ which increase resistance of fluid motion [10-16] and the other consisting of a transition from an organised layered formation of particles into a disorganised state which results in increased viscosity often denoted as the “Order-disorder theory (ODT)” [17, 18]. Due to this unique phenomenon, they are considered to have significant potential in applications of impact and vibrational energy adsorption. Current applications include impregnating STFs within Kevlar fibres to decrease the penetration depth from knife-shaped or spike-shaped penetrations [1-6, 8, 9, 19, 20], vibrational dampening [21, 22] and as a passive effect in combination with other polymeric materials such as magnetorheological fluids [23-26], electrorheological fluids [27] and as an electrolyte in electrode cells [28].

2.1.2. Components of STF

Most STFs exhibit three differing phenomena with increasing shear force: Thinning, thickening then thinning again. The essential components of STFs that are significant to engineers are labelled below in Figure 2.1.
Figure 2.1 Typical viscosity curve of a shear thickening fluid. Experimental data shown is corresponding to a suspension of Aerosil® R816 in polypropylene glycol at 5% (v/v) and 25°C [29]

The shear rate at which thickening begins to occur is often recorded as the critical shear rate (\( \dot{\gamma}_c \)) and is often important for engineers as it denotes the shear force required for certain STFs to begin thickening. At the peak of thickening, the shear rate is also recorded, known as the maximum shear rate (\( \dot{\gamma}_{\text{max}} \)) in which thinning begins with increasing shear force. The thickening performance used is a fraction of the maximum viscosity over the viscosity at the critical point (\( \eta_{\text{max}}/\eta_c \)). For potential applications, it would be preferential to maximise \( \eta_{\text{max}}/\eta_c \) and to quantify both \( \dot{\gamma}_c \) and \( \dot{\gamma}_{\text{max}} \) in order to exploit the thickening region for certain applications within this shear rate region.

2.2. Parameters affecting shear thickening
The parameters that affect rheological behaviour of STFs were first postulated in 1989 by Barnes [30] in a review of over 100 articles published before then. In Barnes’ review, he gathered that the main contributing factors that affect the shear thickening effect of STFs relate to particles such as size distribution, volume, shape, interparticle forces and, to a lesser extent, the chemistry of the carrier fluid. Since then, STF research and experimentation have used these findings as a basis for improving the rheological behaviours of STFs as well as attempting to quantify the effect of changing particle chemistry. Previous and current literature was reviewed and categorised below.

2.2.1. Main particle composition

There are many types of primary particles used in STFs over the last few years include titanium dioxide [31-34], calcium carbonate [35], fumed silica aggregates [36], alumina [37, 38], aqueous kaolin clay suspensions [39] and silica carbide [38, 40]. Titanium dioxide is favoured due to its increased yield stress and complex viscosity at high temperatures and its thermal conductivity [32]. Chadwick et al. [33] attempted to fabricate Titania with ethylene glycol and observed that minimal thickening occurred at higher shear stresses. These findings were also similar to those by Zupančič et al. [34]. Petel et al. [40] investigated the effect of particle strength in the ballistic resistance of STFs. They found that the addition of silica carbide to their STF consisting of colloidal silica and ethylene glycol increased the incident velocity of a projectile due to the carbide’s increased particle yield strength. It is implied from the previous articles that using alternative primary particles will reduce the passive thickening effect but could be considered to be used as an additive to STFs in order to adopt some of the favourable material properties of the additive (Thermal conductivity, yield strength, etc.)

Much work has been completed by changing the type of particles used in STFs. A favourable outcome is to use particles in which their material properties translate into improved rheological behaviours. One option for primary particles used in STFs was carbon nanotubes (CNTs). CNTs are a favourable particle option due to their hydrophobic nature, strong interactions between adjacent CNTs [41], ability to enhance mechanical strength and electrical conductivity of the STFs [42]. However,
shortcomings including interparticle entanglement make it difficult to defloculate once shear stresses are removed, making it less reusable for mechanical applications.

### 2.2.2. Particle shape

Barnes [30] initially believed that the shape of the particles within STFs affected the shear thickening performance of STFs considerably as exhibited in Figure 2.2.

![Figure 2.2 The effect of shape on shear thickening for weight fraction of 20% [30]](image)

The difference in particle shape on the resultant rheological behaviour has been investigated previously by Bergström [37] by using silica carbide whiskers with differing aspect ratios. He found that particles with differing size ratios induced shear thickening at lower weight fractions when compared to spherical particles at higher weight fraction. It was believed that the different shaped particles resulted in misalignment during flow resulting in entanglement of the whiskers in addition to hydroclustering. These findings were similar to those using calcium carbonate rods with differing length and diameter ratios by Egres and Wagner [35], using plate-like nanoparticles with exceptional aspect ratios (~2200) [43] and controlling non-
spherical particles called “Superballs” [44]. Therefore, the shape and aspect ratio of the primary particles used is an important factor in materials selection in order to optimise the thickening effect for practical applications, with more spherical particles exhibiting the weakest shear thickening effect [39, 45].

2.2.3. Particle surface chemistry

Much research has been conducted into quantifying the effect of varying surface chemistry of the particles on the resultant shear thickening effect. Research into the difference between hydrophilic and hydrophobic fumed silica particles was conducted by Uneo et al. [46]. Their results showed that the hydrophilic silica particles with hydroxyl end groups on the surface exhibited sharp thickening regions whilst the hydrophobic counterparts with methyl end groups showed shear thinning behaviour. The reactive surface of the hydrophilic surface induced a relationship between the carrier fluid and particles that allowed for flow at lower stress and clustering past a critical point. Raghavan et al. [47] and Yang et al. [48] further supported these findings by stipulating that hydrophobic silica is more likely to thin due to poor interaction between silica surface and the carrier fluid, resulting in the formation of a three dimensional network or ‘gel-like behaviour’ resulting in decreasing viscosity with increasing shear rate.

Focusing on various fumed silica particles, Wang and Wunder [49] identified that between two different types of fumed silicas. The silica with the larger primary particle size attained lower effective surface area and therefore a lower hydroxyl surface density, essentially making larger fumed silica particles less reactive.

The effect of changing effective surface area of fumed silica was analysed by Gun’ko et al. [50] using water adsorption-desorption, mass spectrometry and Fourier transform infrared spectroscopy. They found that with increasing effective surface (and hence decreasing particle size) resulted in increased aggregation of primary silica particles into longer chains and adsorption capacity, increased water adsorption and decreased surface hydroxyl group density. The significance of these findings can help to understand that consequences of using smaller fumed silica particles can include higher atmospheric
moisture adsorption above carrier fluid-surface hydroxyl bonding which may have a negative effect when STFs are in open exposure to moisture or open atmosphere.

The porosity of primary particles was examined by He et al. [51] and observed and proposed increasing porosity of colloidal silica nanoparticles increases the effective surface area which resulted in thickening at lower particle weight fractions. These could implicate fewer materials to attain optimum rheological behaviour in certain mechanical applications.

2.2.4. Particle size

As previously mentioned, Barnes identified changing particle size can significantly affect the shear thickening region of STFs [30]. Prior experiments work has been completed to quantify the effect of changing particle size on the rheological behaviour, with most focusing on colloidal silica with increasing size [4, 7]. A common example of the difference in particle sizes on the rheology can be seen in Figure 2.3.

![Figure 2.3 Shear thickening behaviour of colloidal silica with PEG200 (poly(ethylene glycol) with molecular weights 200 g/mol) for steady shear flow with different particle size [7]](image-url)
The common result is that increasing particle size could result in decrease the shear thickening effect as does the critical shear rate.

2.2.5. Carrier liquid (liquid-particle reaction, chemistry)

To a lesser extent, the influence of carrier fluid chemistry and material properties also affect the shear thickening properties. Initially it was believed that only the fluid viscosity affected the shear thickening effect [30] or even independent of carrier fluid viscosity [52], but more present works have dispelled these notions [16, 31, 36, 53-57]. This will be explained in the following two subsections.

2.2.6. Molecular weight

The molecular lengths of the polymers that constitute the carrier fluid also have a significant effect as observed by previous works [16, 36, 53, 55-58]. A common comparison of differing molecular weights is for poly(ethylene glycol) (PEG) with different molecular weights (200, 400 and 600 g/mol), but with consitant particles sizes and weight fraction in each STF. The results showed decreased critical shear rate with increasing molecular weights [53]. Baharvandi et al. [55] observed when comparing STFs containing PEG200 and PEG400 (see Figure 2.4).
There was little difference in the critical shear rate but the STF containing the higher molecular weight exhibited higher thickening ratios, “Influence of increasing molecular weight is not as considerable as the effect of particle-particle interaction on the enhancement of penetration resistance performance” [55]. Liu et al. [57] observed that increased weight fraction of silica (40 wt%) in PEG200 was required for noticeable shear thickening to occur while inversely approximately half the weight fraction (20
wt%) was required in PEG400 for similar, if not greater, shear thickening performance. Their explanation for this trend was that PEG400 attained less hydrogen bonding potential between silica surface and carrier fluid, resulting in increased mobility of the silica to participate in hydrocluster formation. From previous works so far, there is no proportional statement that can encompass the effect of increasing the molecular weight of the carrier fluid and the resultant shear thickening effect, rather treat it as a ‘case by case’ situation when mixed with various particles.

2.2.7. Carrier fluid chemistry

The effect of changing carrier fluid polymer composition has also been investigated to see visible differences in rheological behaviour. Shan et al. [54] tested PEG and poly(propylene glycol) (PPG), both at 400 g/mol with 14 nm fumed silica and found STFs containing PPG exhibited significantly increased thickening performance (~110 times) with decreased critical shear rate (30 s\(^{-1}\)) whilst STFs with PEG exhibited lower thickening ratios (~11 times) but with increased critical shear rate (50 s\(^{-1}\)). The only significant difference separating both STFs is an extra methyl chain within PPG polymer chains which may have an effect with rheological behaviour, but currently only speculation.

In an thorough examination in the effect of differing carrier fluid chemistry done by Raghavan et al. [36], they concluded that a relationship between the carrier fluid polymer chains and the surface chemistry existed in terms of the number of hydrogen bonds that existed between them. A comparison of the rheological behaviour of several STFs with differing carrier fluid chemistries can be seen in Figure 2.5.
2.2.8. Additives

As discussed previously, it would be ideal to use particles in STFs that have superior properties such as increased temperature conductance, increased particle strength, etc. However, using them as primary particles in solution may not translate into shear thickening behaviour so consideration could be given into using these alternative particles as an additive to suitable STFs so that they may ‘adopt’ some of the additive’s favourable properties. The use of surfactants is a favourable option as it was found to
improve the shear thickening effect by up to 5 times in certain STF mixtures [59] by altering the particle’s surface chemistry or by altering hydrodynamic forces and interparticle repulsion forces.

Carbon nanotubes (CNT), whilst relatively ineffective when used as a primary particle in STFs, could be a candidate as an additive [41, 60, 61]. Due to its hydrophobic nature and strong interactions between other CNTs, it would make a separate phase within the STF [41]. Sha et al. [60] attempted to mix CNTs within STFs consisting of PEG200 and colloidal silica and observed the addition of less than 3 wt% of CNTs results in decreased thickening effect, decreased critical shear rate and increased overall viscosity of the STF. Possible due to the CNT’s flexibility and length, they would interfere with the primary particles under shear flow, which can result in early breakup of hydroclusters during shear thickening.

Titanium dioxide is another possible additive due to its increased thermal conductivity and increased yield strength [32-34]. Although not favourable as a primary particle in STFs as tested by Zupančič et al. [34], the increased yield strength would make it favourable in high impact energy applications and hence could be added as a 2nd phase in STFs.

The significance of using additives in STFs is a relatively unpopular research field and could be considered as an area with more potential to be investigated in order to augment beneficial material properties to obtain high-performing STFs.

2.2.9. Temperature

The effect of temperature on the STFs’ rheological behaviour has only been recently studied and reported. In several articles that were reviewed [54, 57, 62, 63] the result of increasing temperature resulted in decreased overall viscosity of the STFs, increased critical shear rate and decreased shear thickening effect as exampled in Figure 2.6.
Figure 2.6 Steady-shear experimental results as a function of temperature for 15 wt% A200 fumed silica in PEG200 (left) and 22.5 wt% A200 fumed silica in PEG200 (right) [62]

Liu et al. [57] suggested that with increasing temperature, the hydrogen bonding between carrier fluid polymer and particle surface groups is weakened. This resulted in increased interparticle repulsion forces and therefore more external shear forces to enact hydroclustering and hence shear thickening. They further speculated that when heated to 80°C, the STF exhibited gel-like behaviour, resulting from interparticle bonding forming permanent entanglements amongst each other, forming a three dimensional network, much like a gel microstructure.

It is apparent that the temperature in which the STF is used and tested has a significant effect on the resultant rheological behaviour of the STF and should be carefully considered when choosing a specific mixture for certain applications and their service temperature.

2.3. Mechanisms of STF

2.3.1. Order-disorder transition (ODT)
One of the common theories explaining shear thickening phenomenon in solution is the transition from an ordered and layered formation of particles into a disorganised mixture of particles which results in an increased viscosity past a certain shear stress.

Bender and Wagner [10] utilised rheological and optical measurements to observe particle motion prior to and during shear thickening and observed the formation of thin, loosely formed layers. Once the critical shear rate was reached, the layers become unstable as the hydrodynamic forces between particles dominate and form clusters which increase resistance to flow. A diagrammatical representation of this phenomenon can be viewed in Figure 2.7.

![Diagram of shear thickening process](image)

**Figure 2.7 Visual approximation of the microstructure of a STF under various stages of steady flow [64]**

The formation of this ordered layer prior to thickening is predictable by utilising the Péclet number [12, 64, 65], which can be calculated in the Equation 2.1.

\[
P e = \frac{a^2 \dot{\gamma}}{D_0}
\]  

(2.1)

where \( a \) represents the hydrodynamic radii, \( \dot{\gamma} \) is the shear rate and \( D_0 \) is the diffusivity, which can be further defined in Equation 2.2.
\[ D_0 = \frac{kT}{6\pi\eta_0 a} \] (2.2)

where \( k \) is Boltzmann’s constant, \( T \) is temperature and \( \eta_0 \) is the viscosity of the carrier fluid. Bergenholtz et al. [65] conducted low-shear testing on dilute STFs both analytically and numerically to quantify the shear thinning effect with \( Pe^2 \) values less than one. They suggested the low \( Pe \) numbers are due to the decrease in collision-based particle motion, otherwise known as Brownian motion.

2.3.2. Hydrocluster

The most accepted and followed theory that explains the shear thickening effect of STFs is the formation of hydroclusters within the STF which impede viscous flow. Boersma et al. [11] utilised computer simulations of monodispersed spheres in layers within a STF and observed the disordered layers. Their explanation is that the increased shear forces resulted in dominating hydrodynamic interparticle forces to form hydroclusters. As a modification of the Péclet Number equation, Frankel et al. [66], found an equation that can summarise the hydrodynamic interparticle forces that exist between two particles (Equation 2.3).

\[ F_{hydrodynamic} = \frac{6\pi\eta_0 a^3\dot{\gamma}}{h} \] (2.3) [35]

where \( h \) is the interparticle distance.

This hydrocluster theory is also supported by Chellamuthu et al. [12] where clusters were observed to be formed along flow direction using small-angle light scattering measurements under both linear and oscillating shear conditions. The Modified Cox-Merz (MCM) rule, a relationship which connects both steady and oscillatory rheological results, was also used as displayed below (Equation 2.4):

\[ \eta(\dot{\gamma}) = \eta'(\omega \gamma_0) \] (2.4)

where \( \eta(\dot{\gamma}) \) represents the viscosity as a function of shear rate under steady shear flow and \( \eta'(\omega \gamma_0) \) is the complex viscosity as a function of the product of angular frequency (\( \omega \)) and strain amplitude (\( \gamma_0 \)). The significance of this relationship could allow for approximation of corresponding performance under different shear conditions of STFs.
However, the MCM rule was only accurate at very high strain amplitudes. Further investigation into the relationship between steady and oscillating shear conditions of STFs were completed by Fisher et al. [67] and concurred with the previous findings that the MCM rule was applicable for their STFs at very high strain amplitudes ($\gamma_0=300\%$). Another common thread between the findings were the regions before and after thickening were independent of $\gamma_0$, suggesting that shear thinning in STFs is present regardless of the type of shear forces used prior and after the thickening effect. This needs to be considered when exploiting the thickening effect of STFs in mechanical applications as shear forces not within the region of thickening would result in thinning and completely nullify any energy absorption properties.

Temperature of the STF has a significant effect on the formation of hydroclusters. Lee et al. [15] measured the viscosity of STFs at decreased temperatures, which resulted in the thickening effect occurring at lower shear rates. They proposed that as particle motion is proportional to particle diffusivity, the formation of ordered layers proposed in the ODT were not stable or present resulting in the formation of hydroclusters more readily.

However, Lee et al. [52] argues that interparticle hydrodynamic forces did not affect the onset of shear thickening under oscillating shear forces. They also found that other factors including the carrier fluid viscosity, angular frequency and particle size do not affect these forces. These suggestions contradicted a majority of papers and recent research that suggested otherwise from Chellamuthu et al. [12] and Boersma et al. [11].

The motion of hydroclusters was also possibly dispelled by Lin et al. [68]. They tested a STF by instantaneously reversing the shear stress to its opposite polar to observe hydrodynamic and contact forces between particles. Their results suggested that the shear thickening phenomenon originates from clustering via physical interparticle contact rather than contactless hydrodynamic forces. The significance of these findings could affect the overall choice of materials used in STFs as potentially no carrier fluid polymer chains will flow within formed hydroclusters under shear stress.
2.3.3. Other theories

Other reasons behind shear thickening phenomenon have also been proposed in other scientific articles. Bergström [37] observed that a STF containing rod-shaped silicon carbide whiskers exhibited shear thickening at very low weight fractions compared to a STF containing spherical alumina particles at very high weight fractions. He believed that rather than hydrodynamic clustering, the anisotropic whiskers rearrange under flow and become entangled with adjacent whiskers to form stronger hydroclusters at lower shear forces. The significance of these early findings can allow for increased performance of shear thickening behaviour with fewer particles due to the added entanglement phenomenon during the hydrocluster formation. This entanglement theory was also explored further by Fall et al. [69] by observing the change in viscosity of corn-starch in water, which is a well-known STF. They believed that the thickness of STF used is proportional to the shear rate at which thickening occurs and the thickening ability is traced back to the suspension’s entanglement of particles, resulting in jamming and thus thickening occurs. The STF’s ability to expand in volume under shear stress is impeded due to this jamming effect. Firth et al. [70] incorporated the ODT with their findings and suggested that when shear rate was past the critical value, the particles within the STF were removed from the ordered structure and jammed/entangled with each other to increase viscosity.

One rather unique theory was given by Van Hecke [71] implying that the thickening effect was due to the compressive forces instead of shear forces. He suggested that “below the rod’s impact site, a rapidly growing solidification front spread and formed a solid zone” [71]. The theory was reminiscent of hydrocluster formation as shear force was still applied parallel to the impact object, inducing shear stresses to the STFs.

A modification to this entanglement theory in which the carrier fluid polymer length was more prevalent in the thickening phenomenon was mentioned as ‘polymer bridging’ few findings [72-74]. Kamibayashi et al. [72] observed a STF containing fumed silica and diluted poly(ethylene oxide) (PEO) with very large molecular weights resulted in enhanced shear thickening performance. It was suggested that the increased length of the PEO polymer chains resulted in additional entanglement of adjacent PEO chains to resist viscous flow. These findings were further supported by works from
Khandavalli and Rothstein except with the added theory that “Under shear flow, the free ends of polymer chains adsorbed onto particles at equilibrium can adsorb onto more neighbouring particles and can create a larger particle clusters bridged by polymer chains.” [73, 74]. This theory could result in increased thickening performance at high shear stresses but could also result in little to no reversibility if hydrogen bonding between particles and polymer chains are formed, leading to a permanent 3D-network similar to a gel or solid after testing.

Other proposed modifiers to hydrocluster theory was suggested by Boersma et al. [11] that particles and carrier fluids exhibiting Van der Waals forces in unison resulted in sharper thickening transitions. These forces were said to increase the strength of these hydroclusters with increasing shear forces. This could be considered when fabricating STFs in order to maximise the rheological behaviour for specific applications.

An additional mechanism present in certain STFs during thickening is the presence of an additional layer surrounding the particles in suspension, otherwise referred to as a ‘solvation layer’ [75]. Krishnamurthy et al. [76] expanded on this solvation layer theory by predicting its existence results in increased critical shear stresses required for hydrocluster formation and increased thickening performance. Raghavan and Khan [75] discovered that when poly(propylene glycol) (PPG) was mixed with fumed silica, the PPG reacted with the surface groups of silica to form a layer around each silica particle which promoted deflocculation and interparticle distance. This mechanism can be considered plausible as it would encompass the hydrophilic nature of fumed silica and result in increased shear forces to encourage hydrocluster formation due to increased energies required to bring silica particles close enough.

2.4. Modelling of STF

Several attempts have been made previously in an attempt to create a mathematical relationship that can account for the rheological properties of STFs as a function of varying material parameters. Significant attempt at mathematically modelling STFs by Galindo-Rosales et al. [29] was to propose three separate equations for each stage of the thickening process: Initial shear thinning (Stage I), shear thickening (Stage II) and post-thinning (Stage III) which can be summarised as (Equation 2.5):
where \( \eta_c \) and \( \dot{\gamma}_c \) are the critical viscosity and shear rate respectively, \( \eta_{\text{max}} \) and \( \dot{\gamma}_{\text{max}} \) are the maximum viscosity and shear rate respectively. “\( \dot{K} \) is a constant directly related to time dimension and are responsible for the transitions between the plateaus and the power law, while the dimensionless exponents \( n_i \) are related to the slopes of the power-law regimes” [29]. However these material parameters are unique and dependent on the STF’s composition amongst other material variables. These models were then utilised by Tian et al. [77] with STF mixtures consisting of ethylene glycol and fumed silica with BET-surface area (The surface area that effectively absorbs foreign particles) of 200 m\(^2\)/g with increasing temperature in order to mathematically predict the viscosity as a function of temperature and shear rate between temperatures, 20°C ≤ \( T \) ≤ 80°C. By combining experimental data to produce the material parameters at each Stage (I, II and III) at different temperatures, they were able to produce accurate mathematical models for their STF mixtures as shown below in Equation 2.6 [77],

\[
\eta_I(\dot{\gamma}) = \eta_c + \frac{\eta_0 - \eta_c}{1 + \left( \frac{\dot{\gamma}}{\dot{\gamma}_c} \right)^{n_I}}, \quad \text{for } \dot{\gamma} \leq \dot{\gamma}_c,
\]

\[
\eta_{II}(\dot{\gamma}) = \eta_{\text{max}} + \frac{\eta_c - \eta_{\text{max}}}{1 + \left( \frac{\dot{\gamma}}{\dot{\gamma}_{\text{max}}} \right)^{n_{II}}}, \quad \text{for } \dot{\gamma}_c < \dot{\gamma} \leq \dot{\gamma}_{\text{max}}, \quad (2.5)
\]

\[
\eta_{III}(\dot{\gamma}) = \frac{\eta_{\text{max}}}{1 + [K_{III}(\dot{\gamma} - \dot{\gamma}_{\text{max}})]^{n_{III}}}, \quad \text{for } \dot{\gamma}_{\text{max}} < \dot{\gamma},
\]

\[
\eta_I(\dot{\gamma}) = 1130 T^{-1.629} + \frac{1480 T^{-1.533} - 1130 T^{-1.629}}{1 + \left[ (0.8 + 0.015 T) \left( \frac{\dot{\gamma}^2}{\dot{\gamma} - 0.0473 T^{1.629}} \right) \right]^{(1.4-0.017)}}
\]

\[
\eta_{II}(\dot{\gamma}) = 1240000 T^{-2.624} + \frac{1130 T^{-1.629} - 1240000 T^{-2.624}}{1 + \left[ (0.133(7-14)^{-0.9}) \left( \frac{\dot{\gamma} - 0.0473 T^{1.629}}{\dot{\gamma} - 0.295 T^{1.7134}} \right) \right]^{(1.4+0.017)}} \quad (2.6)
\]

\[
\eta_{III}(\dot{\gamma}) = \frac{1240000 T^{-2.624}}{1 + [0.02 e^{-0.037(\dot{\gamma} - 0.295 T^{1.7134})}]^{(1.2+0.005 T)}}
\]

The comparison of the proposed mathematical models and the experimental data used by Tian et al. [77] can be seen below in Figure 2.8.
The proposed model fits relatively well and has the potential to predict rheological behaviour and shear thickening patterns, however these are limited only to ethylene glycol and fumed silica STFs, more experimental data would be required to determine whether this mathematical model is transferrable to other mixtures with differing particles and carrier fluid chemistry. In later work, Tian et al. [78] again elaborated their previous mathematical model to incorporate weight fraction as a variable by utilising weight fractions 20 – 26 wt%. Their end models looked significantly different from their previous attempts and were as follows (Equation 2.7).

\[ \text{Equation 2.7} \]
Relatively more complex compared to their previous proposed models, the comparison against experimental data can be seen below in Figure 2.9.

\[
\eta_1(\dot{\gamma}) = \exp((-(0.01T+1.2) \log(0.0028 \exp(26.795 \phi) \\
+ ((40 \phi - 6.7) + (40 \phi - 6.7) - (0.0028 \exp(26.795 \phi))/
(1 + [\exp(0.405465 + 34.65736 \times (\phi - 20\%))]^{1.5}} \\
+ 3.75 \phi + 0.0225T - 0.1875 \phi T - 0.45))))
\]

\[
\eta_2(\dot{\gamma}) = \exp(((0.01T+1.2) \log(0.0484 \exp(35.275 \phi) \\
+ (0.0028 \exp(26.795 \phi) - 0.0484 \exp(35.275 \phi))/
(1 + [\exp(-5.116 + 34.65736 \times (\phi - 20\%))]/(\dot{\gamma} - 0.0052568 \exp(-27.46 \phi)) \dot{\gamma}]^{1.5}) \\
+ 3.75 \phi + 0.0225T - 0.1875 \phi T - 0.45))))
\]

\[
\eta_3(\dot{\gamma}) = \exp(((0.01T+1.2) \log(0.0484 \exp(35.275 \phi))/
(1 + [\exp(-5.80914 + 34.65736 \times (\phi - 20\%))]/(\dot{\gamma} - 0.0052568 \exp(-27.46 \phi))]^{1.5})) \\
+ 3.75 \phi + 0.0225T - 0.1875 \phi T - 0.45))]
\]

(2.7) [78]

**Figure 2.9** Comparison of function simulation and experimental data of 20% STF (left) and 26% STF (right) [78]
As well fitting as the models appeared to be, the values used were able to predict the viscosity during all 3 stages of steady shear providing the temperature range between 20-60°C and weight fractions 20-26 wt%. These experimental modelling equations could have the potential to be expanded and extrapolated further to include other dependents such as particle size, carrier fluid molecular weight, and so on, in order to encompass a large range of STFs.

2.5. Applications of STF

The thickening properties of STFs are quite and useful in mechanical applications that involve energy absorption from projectiles and vibrational motions. Applications such as stab and bullet impact resistance [1-9, 40, 55, 79-81], vibrational dampening control in sound insulation [82] and mechanical vibrations [21, 22] and as a second phase in other materials [23-28, 83] have been previously explored and improved for eventual application in real-world applications.

2.5.1. Impact resistance

One of the most common applications and research conducted into specific fields is in the use of penetration resistance of projectiles ranging from knife to bullet impacts. One specific application in the utilisation of STF’s is in the form of impregnating STF’s into woven fabrics to decrease penetration depth. Lee et al. [2] investigated impregnating Kevlar® fabric with ethylene glycol and spherical silica STF mixture and also the change in penetration depth of a 22 calibre, low-velocity ballistic projectile. They identified that the same performance was observed between 14 multiple neat Kevlar® sheets layered with 4 Kevlar® sheets all impregnated with STFs. Photographs comparing both fabrics after ballistic testing can be seen in Figure 2.10.
They also postulated that energy adsorption is proportional to the volume of STF impregnated on the Kevlar® fabric essentially reducing the required Kevlar® fabric required for suitable protection from low-velocity ballistic projectile. Wetzel et al. [3] then further examined the effect of adding STF to Kevlar® and determined that the addition of STF provided coupling and load transfer on an inter-filament and inter-yarn level which, in turn, modified the fabric’s response to become more effectively loaded under impact. Another interpretation implied that the increased performance was due to additional friction forces induced from increased surface coverage of silica on the fabric surface [3]. This friction theory was also supported by Lee et al. [1] and Park et al. [79] via computational modelling based on experimental data of ballistic impacts on Kevlar®/STF mixtures, they believed that the friction between the fibres was primarily due to the presence of STF droplets thickening to rubber-like consistency which increased the friction between fibres under impact stress.

Hassan et al. [9] explored the use of alternative Nylon fabric impregnated with STF consisting of Nano sized silica particles and discovered a marginal decrease in penetration depth of low impact forces from spike and knife shaped projectiles to forces below 7.5 J, as opposed to Kevlar fabric with STF which was measured to effectively work at impact energies below 5 J. The presence of STF on Nylon via SEM imagery can be seen below in Figure 2.11.
Current findings have suggested the use of STFs containing colloidal silica in fabrics pertaining to penetration resistance are effective in the case of low impact energy situations such as knife or stab attacks.

The ratio of diluting STF prior to impregnation also has a direct effect on the resultant penetration resistance on Kevlar®/STF composites. Zhao et al. [6] observed the difference in stab performance when diluting STFs with ethanol before impregnating on Kevlar® fabric. It was discovered that more dilute mixtures of STF:ethanol- at 1:1 ratio produced better stab resistance at higher impact energies than those of ratios at 1:0.5. It was suggested that increased dilution of STF allowed for more efficient impregnation of STF droplets in-between Kevlar® fibres and thus a larger contribution of STF thickening during impact.

As research into the effect of impregnating STF into fabrics has been clearly established, the effect of other material property variables on penetration resistance is still an opportune point for research. Work conducted by Petel et al. [40] primarily focused on fluid density and particle strength and their effects on ballistic resistance of STFs alone. By using an experimental setup consisting of firing a projectile similar to
that of a NATO-standard (Ammunition created for North Atlantic Treaty Organisation standards) bullet into a container with the various STFs and measuring the change in velocity before, during and after impact, they observed that STF containing colloidal silica in ethylene glycol was effective at decelerating or even stopping projectiles, possibly due to the silica’s particle strength. At higher velocities, they postulated that the particle strength was less effective and the bulk mixture density of the STF dominated deceleration of projectile penetration. By adding silica carbide particles to this STF, they observed that the increased yield strength of the new particles increased the incident velocity range at which penetration resistance was still possible. This effectively increased the impact energy range of this modified STF mixture. Their conclusion was that the addition of colloidal silica was effective at decelerating low velocity impact whilst the addition of silica carbide effectively increased the range to include medium to higher velocity impact forces. This is significant evidence showing that particle strength also has an effect in the thickening process of impact-like projectile motion and should be considered during the material selection process for fabricating STFs.

Changing carrier fluid also has an effect on the stab-resistant properties of Kevlar®/STF composites. Gong et al. [8] found that by using ethylene glycol, PEG200 and PEG500, the STFs containing smaller molecular weights mixed with colloidal polystyrene-ethylacrylate (PSt-EA) exhibited increased puncture resistance with decreasing molecular weight carrier fluid. The decrease in molecular weight of carrier fluids in STFs exhibited increased $\dot{\gamma}_c$ and increased shear thickening effect. This was also correlated with Baharvandi et al. [55] further stating that “Influence of increasing molecular weight is not as considerable as the effect of particle-particle interaction on the enhancement of penetration resistance performance”.

Much research has been conducted in this promising mechanical application and has been proven somewhat to enhance the performance of impact-resistant fabrics. It would be beneficial to correlate rheological behaviours based on material properties and penetration resistance performance in order to create soft-body armours that require minimal material for maximum protection.
2.5.2. Dampening control

One of STF’s favourable features is its ability to thicken under both impact forces and vibrational or dynamic shear loading conditions. This makes STF a potential in applications for vibrational energy adsorption such as mechanical or even audial insulation. One potential application was investigated by Fischer et al. [21] by combining STF consisting of 12 nm fumed silica particles, PPG and beams consisting of poly(vinyl chloride) (PVC) substrate. It was found that over a critical vibrational frequency and amplitude, shear thickening was induced which decreased the relative deflection of the STF/PVC beam. However, when the frequency was more than a certain value, the dampening effect decreased and actually resulted in increased deflection, possibly due to the gel-like behaviour typically exhibited in STFs after the thickening period. This limited the possibility of using STFs in vibrational dampening in this application to specific compositions to ensure the dampening to be induced within vibrational frequencies and amplitudes within shear thickening range. Another similar application is the composite material consisting of multiple parallel fibres in combination with a STF to observe the dampening effect induced with the addition of STFs by Neagu et al. [22]. Similarly, the dampening effect was found to be dependent on the rheological behaviours of the PEG mixed with 500 nm spherical silica particle STF. Wang et al. [82] performed another similar experiment by infusing a STF consisting of PEG200 and a combination of spherical silica and tetrapod-shaped zinc oxide whiskers and instilled them into glass fibre fabrics. It was found that for a double layer of this composite the material decreased the sound between 10.25-13.84 dB with an incident sound of 75 db (13.67-18.45% reduction) [82].

It is apparent that there is a ‘window’ of thickening for all STFs in which dampening is effective and to optimise its use in vibrational applications, it is important to measure the frequency and amplitude of the application and to use a STF in which dampening is assured to activate.
2.5.3. **Other applications**

Other potential applications have been investigated with adding STF liquids into other applications in order to use the thickening component as a passive feature to varying other applications for added protection. Potential applications include the addition of iron carbonyl particles to STF consisting ethylene glycol and 14 nm fumed silica to create a magnetorheological shear thickening fluid (MRSTF) as done by several groups [23-26]. There was an advance for fumed silica as the addition that was to reduce the sedimentation of iron particles in solution at rest. They found that with the addition of STF components with iron particles resulted in a shear thickening effect under shear conditions as well as magnetorheological effects whilst under a magnetic field. However, the addition of iron particles did result in a decrease of the shear thickening effect as shown below in Figure 2.12.

![Figure 2.12 Steady shear results of the MRSTF sample based on 15 wt% STF and the STF sample [25]](image)

Tian *et al.* [24] went further and found that by increasing the applied magnetic field resulted in increased $\tau_c$ and $\dot{\gamma}_c$, and the critical magnetic field required for shear thickening was greater than the critical magnetic field for striped and lamellar MRF structures.
It appears that the benefits of implementing a shear thickening element to magnetorheological fluids (MRFs) include particle deflocculation and the addition of a passive shear thickening effect under shear flow, at a cost of reduced shear thickening performance and increased magnetic fields to activate the magnetorheological function of the MRSTF.

A novel hybrid application is the addition of STF components into the electrolytes of lithium ion batteries. Ding et al. [84] discovered the effect of adding fumed silica particles to bare electrolyte resulted “Exhibit a shear thickening effect under pressure or impact” [84] and “The fluids show higher ionic conductivities and comparable redox stability windows to the commercial liquid electrolytes” [84]. The added benefit of increasing electrical efficiency as well as impact resistance makes the concept of STFs very versatile when combined to other applications to employ impact resistance and potentially alter the original behaviour of the material.

2.6. Chapter Summary

The review has been effective into distinguishing the possible theories for shear thickening behaviour in STFs, different material parameters that affect shear thickening and the current applications in which STFs are useful in. However, it is apparent that there is a significant gap in research which is the limitations associated with STF use in studies related to applications. There is limited research conducted into the relation between the different rheological behaviours and the STF’s ability to adsorb impact energy. One could assume that by increasing the magnitude of thickening, the STF would be more effective at absorbing impact energies. The critical shear rate of STF is another significant point to be considered as it states how sensitive the STF is to thickening in different applications. Other factors needed to be considered for applications include service temperature, water adsorption, deterioration and the effect of additives.
3. QUANTIFYING RHEOLOGICAL BEHAVIORS WITH MATERIAL PROPERTIES OF SHEAR THICKENING FLUIDS

As mentioned previously, there is a significant gap between the rheological behaviours of a STF and its ability to be effectively utilised in mechanical applications. To bridge this gap, we must maximise and quantify the effect of all variable material properties of the STF related to particles and carrier fluids to the resultant thickening performance and parameters. The ultimate aim would be to predict several of these thickening parameters for certain mixtures to allow for future projects and to utilise and adopt certain STF mixtures based on the required thickening parameters for the applications.

In this chapter, several material parameters were varied and quantified with respect to the resultant thickening behaviour such as particle weight fraction, carrier fluid chemistry and molecular weight, primary particle size and BET-surface area. A mathematical model was also proposed as an attempt to encapsulate several significant rheological points, both prior and after the thickening region, with various weight fractions and temperatures. A graphical summary of various rheological components such as viscosity, shear rate and shear stress at which shear thickening begins and ends was also made by using above mentioned mathematical models. The final goal was to present the thickening phenomenon as a function of weight fraction as a ‘phase diagram’ to allow for mechanical engineers to reference and use when determining what composition of STF they would use for their specific application.

3.1. Materials

3.1.1. Fumed silica particles
Fumed silica particles were used for fabricating STFs due to their known ability to induce shear thickening at lower weight fractions when compared to spherical nano silica particles [26]. Three types of fumed silica were used in this experiment: AEROSIL® 130 (A130), AEROSIL® 90 (A90) and AEROSIL® OX 50 (OX50) which were all supplied by EVONIK Industries AG. All fumed silica particles were
hydrophilic in nature, sensitive to moisture adsorption. The materials properties for all fumed silica variants can be viewed below in Table 3.1.

Table 3.1 Material properties of A130, A90 and OX50 [85]

<table>
<thead>
<tr>
<th>Particle name</th>
<th>Primary particle size (nm)</th>
<th>BET-surface area (m²/g)</th>
<th>Tapped density (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A130</td>
<td>16</td>
<td>130±25</td>
<td>50</td>
</tr>
<tr>
<td>A90</td>
<td>20</td>
<td>90±15</td>
<td>80</td>
</tr>
<tr>
<td>OX50</td>
<td>40</td>
<td>50±15</td>
<td>130</td>
</tr>
</tbody>
</table>

Prior to STF preparation, all fumed silica variants were placed in a vacuum chamber for approximately 24 hours at 110°C to ensure the moisture to be removed. Transmission Electron Microscopic (TEM) images were taken for fumed silica batches A90 and OX50 and are shown in Figure 3.1.

![Figure 3.1](image1.png)  
**Figure 3.1** Representative TEM images of (a) A90 and (b) OX50

### 3.1.2. Carrier fluids

PEG was used as carrier fluid with molecular weights of 400 g/mol. PPG was supplied in two molecular weights, 400 and 725 g/mol. All carrier fluids were supplied by Sigma-Aldrich. The main properties of PEG and PPG are presented in Table 3.2.
Table 3.2 Material properties of PEG400 [86], PPG400 [87] and PPG725 [88]

<table>
<thead>
<tr>
<th>Polymer name</th>
<th>Molecular weight (g/mol)</th>
<th>Degree of polymerisation</th>
<th>Density at 25°C (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG400</td>
<td>400</td>
<td>9.09</td>
<td>1.13</td>
</tr>
<tr>
<td>PPG400</td>
<td>400</td>
<td>6.90</td>
<td>1.01</td>
</tr>
<tr>
<td>PPG725</td>
<td>725</td>
<td>12.50</td>
<td>1.01</td>
</tr>
</tbody>
</table>

3.2. Method

3.2.1. STF fabrication

For each STF, certain amounts of fumed silica were added to the various carrier fluids with a certain weight fraction (from 20 to 55 wt%). The silica was mixed with carrier fluid mechanically until all fumed silica particles were satisfactorily blended into the carrier fluid in order to ensure an enhanced mixture of particles within the fluid. Once mixed, the mixture was placed in a vacuum chamber for one hour to remove any trapped air bubbles, and then an additional mechanical stirring step was requested to ensure adequate distribution of silica within the STF.

3.2.2. Properties measurement of STF

Testing was completed with a parallel-plate Rheometer (MCR 301, Anton Paar, Germany) under steady shear and dynamic conditions with increasing angular frequency. A 20 mm diameter testing geometry (PP-20) was used with a gap of 0.8–1.0 mm to ensure adequate filling of the STF over the testing disk. Viscosity was measured as a function of shear rate within the range of 0.1–1000 s⁻¹ at 20°C. Several tests were also completed under oscillating motion, or dynamic testing, with varying strain amplitude, $\gamma_0$, and increasing angular frequency, $\omega$. The advantage of testing under dynamic conditions is to replicate vibrational motion at low or high frequencies to simulate wither mechanical vibrations or frequencies in the range of sounds.
3.3. Results

3.3.1. Characterisation of STFs

Preliminary testing was completed on various weight fractions of both fumed silica batches in PEG400 and PPG400 to determine the optimum weight fraction of each batch that exhibit the highest shear thickening behaviour. Fumed silica particles A90 was blended with PEG400, PPG400 and PPG725 in weight fractions between 20-40 wt% and the resultant steady shear test results are shown below in Figure 3.2.

![Figure 3.2 Viscosity measured as a function of shear rate under steady shear conditions for STF containing PEG400 + A90 (a), PPG400 + A90 (b) and PPG725 + A90 (c)](image)

All STF mixtures showed decreasing viscosity with increasing shear rate (‘Shear thinning’) when \( \dot{\gamma} < 1 \text{ s}^{-1} \) which is expected rheological behaviour prior to thickening. As weight fraction increases in PEG400 + A90, differing rheological behaviours are
observed. Most notably, the thickening performance increases between 20 and 25 wt\%.
However, at 30 wt\% only minute thickening was observed and overall thinning
behaviour was exhibited. This general thinning behaviour with increasing shear rate is
typically indicative of gel-like behaviour associated with the formation of a three-
dimensional network within the STF and the absence of particle flow. The weight
fraction at which this behaviour was observed in future STF mixtures were labelled as
“oversaturated”, and thickening behaviour was no longer apparent.

In PPG400 + A90 (Figure 3.2b), it is apparent that with increasing the weight fraction
from 20 to 25 wt\%, the thickening performance increases significantly whilst $\dot{\gamma}_c$
remains relatively constant. From this, we can infer that the influence of the carrier fluid
PPG400 is significant on the thickening performance of STFs, particularly when the
weight fraction is held constant. Several STFs were fabricated using 25 wt\% of A90
particles in different carrier fluids were measured and are displayed in Figure 3.3.

![Figure 3.3 Viscosity measured as a function of shear rate under steady shear
conditions for STF containing 25 wt\% A90 using different carrier fluids](image)

This comparison supports the earlier inference that the carrier fluid has a significant
effect on the rheological behaviour and thickening performance of the STF. By
increasing the molecular weight of PPG from 400 to 725 g/mol, it becomes
oversaturated. One possible explanation is that the increased polymer chain length of
PPG725 molecules could result in entanglement with adjacent PPG polymer chains within the STF solution under shear stress, resulting in both an overall increased viscosity and gel-like behaviour due to the difficulty to propagate under varying shear rates. Due to this unfavourable result, STFs containing PPG725 carrier fluid were not further explored due to their poor thickening performance and rheological behaviour as a potential option for mechanical applications.

STF mixtures containing A130 particles were mixed with both PEG400 and PPG400 carrier fluids at varying weight fractions. The results are displayed below in Figure 3.4.

![Figure 3.4 Viscosity measured as a function of shear rate under steady shear conditions for STF containing PEG400 + A130 (a) and PPG400 + A130 (b)](image)

It is apparent there is a significant difference in rheological behaviour in changing fumed silica particles from A90 to A130. For instance, thickening behaviour was observed in PEG400 + A130 at lower weight fraction and oversaturation occurred at 20 wt%. Although the thickening performance was relatively poorer than in PEG400 + A90, fewer silica particles were required to observe thickening (to a certain degree). In STFs containing PPG400 + A130, the thickening effects was considerably unstable as the viscosity increased gradually past the critical point as opposed to sharply as observed in previous mixtures and previous research articles. The decreased particle size of A130 has a significant effect on the thickening effect of STFs. Wang and Wunder both quantified the differences of two types of fumed silica sizes and observed that “state of aggregation/agglomeration therefore increases with decreasing particle size” [49]. Gun’ko et al also stated “aggregation of primary particles…decrease…with
decreasing specific surface area” [50]. Increased degrees of aggregation in smaller particles are proportional to increased aspect ratios and increased chances of interparticle clustering or ‘hooking’ to form a three-dimensional or ‘gel’ network.

STF mixtures containing OX50 were then mixed into PEG400 and PPG400 at varying weight fractions and their resultant rheological behaviours are shown in Figure 3.5.

![Figure 3.5: Viscosity measured as a function of shear rate under steady shear conditions for STF containing PEG400 + OX50 (a) and PPG400 + OX50 (b)](image)

Similar trends found in the STFs containing A90 particles can also be seen in STFs containing OX50. In both STFs, the optimum weight fraction was found to be 45 wt% which showed a good combination of $\dot{\gamma}$ and thickening performance, increasing weight fraction further resulted in deterioration of thickening, trending more towards gel-like behaviour (Figure 3.5).

From these preliminary results, two STF mixtures were chosen based on their superior rheological behaviours: PEG400 + 45 wt% OX50 and PPG400 + 45 wt% OX50 henceforth known as STF_{PEG} and STF_{PPG} respectively (Figure 3.6).
The effect of changing temperatures, during testing, was also explored for both STF mixtures. Prior to testing, the measuring plate in rheometer was heated to a specific temperature then held constant during the testing. Both STF\textsubscript{PEG} and STF\textsubscript{PPG} were tested under temperatures 20, 40, 60 and 80°C and the results are shown below in Figure 3.7.

For both STFs, it is apparent that the overall viscosity of each STF decreases with increasing temperature. This was expected as increasing the temperature of liquids...
generally decrease the overall viscosity as the carrier fluid polymer chains become more energetic and allow for easier flow. Another interesting finding is the decrease in thickening performance and increase in \( \dot{\gamma}_c \) with increasing temperature. One possible explanation for this behaviour is that the combination of increased excitation of carrier fluid chains and particle motion could result in increased external shear stresses required to overcome interparticle repulsive forces and distancing and induce hydrocluster formation. For easier comparison, \( \dot{\gamma}_c \) and the ratio of thickening \( (\eta_{max}/\eta_c) \) was extracted from each test under differing testing temperatures and plotted as a function of temperature, which can be viewed in Figure 3.8.

![Figure 3.8](image)

**Figure 3.8** Shear thickening ratio (a) and critical shear rate (b) measured as a function of testing temperature of STF\textsubscript{PEG}. Lines denote trend line with equation and regression adjacent. Error lines are the maxima/minima of repeated tests.

For STF\textsubscript{PEG} it becomes apparent that there is a decreasing exponential trend of thickening performance with increasing temperature and an increasing exponential trend of \( \dot{\gamma}_c \) with increasing temperature. These findings were also apparent when measuring the corresponding rheological figures in STF\textsubscript{PPG} with increasing temperature in Figure 3.9.
Figure 3.9 Shear thickening ratio (a) and critical shear rate (b) measured as a function of testing temperature of STF_{PPG}. Lines denote trend line with equation and regression adjacent. Error lines are the maxima/minima of repeated tests.

This unique proportional relationship between both thickening performance and $\dot{\gamma}_c$ with testing temperature was considered when attempting to mathematically model the testing and material parameters for potentially prediction of the thickening behaviours for various STFs.

### 3.3.2. Modelling of STFs’ thickening behaviour

One common thread between the different postulations of both jamming and entanglement has very similar features and characteristics of hydrocluster formation theory and ODT. We suggest that it is possible for a combined theory encompassing all previously mentioned theories to explain the thickening process prior and during this phenomenon: Prior to thickening ($\dot{\gamma} < \dot{\gamma}_c$), the shear forces applied to the STF dominate Brownian motion of the particles, restricting particle motion and formation into ordered layers that result in decreased viscosity, or shear thinning.

At and after the onset of thickening ($\dot{\gamma} \geq \dot{\gamma}_c$), the interparticle hydrodynamic forces surpass interparticle repulsive forces and distancing, resulting in the clustering of adjacent particles from the layered arrangement into significantly enlarged hydroclusters that increase viscous flow with increasing shear force.
Several significant points were extracted from each steady shear test for four STF mixtures: PEG400 and PPG400 combined A90 and OX50 mixtures under varying weight fractions. This was to try to quantify the changes in performance with changing weight fraction in order for future research works to utilise when selecting a STF to use for their specific mechanical application. Several parameters were recorded for each data series: the critical and maximum shear stress ($\tau_c$ and $\tau_{max}$), critical and maximum viscosity ($\eta_c$ and $\eta_{max}$) and critical and maximum shear rate ($\dot{\gamma}_c$ and $\dot{\gamma}_{max}$). These parameters are extracted accordingly as displayed in Figure 3.10.

Figure 3.10 Steady shear tests of PEG400 + OX50 measuring viscosity as a function of shear rate (a) and shear stress (b). Labels are the specific material parameters extracted from each steady shear test.

Each thickening parameter was extracted initially from a range of weight fractions between 25-55 wt% OX50 mixed with PEG400 at 20°C and was plotted as a function of weight fraction as displayed in Appendix A.

By observing the experimental data of the varying weight fractions of PEG400 + OX50, there are trends that can help to develop a STF phase diagram that can allow us to understand at which stresses and rates the STF will thicken for a given weight fraction. The gap in-between the critical and maximum shear stress and shear is indicative of when the specific PEG400 + OX50 will begin to thicken, i.e. when it becomes active. One possible application is that the analysis of the shear stresses applied for a certain application and determining whether any given PEG400 + OX50 mixture will begin thickening within that given stress or rate. The gap in-between the critical and
maximum viscosities are indicative of the thickening performance, or alternatively the ability of the STF to absorb applied shear forces. It would be ideal to maximise this viscosity gap however when combined, the shear stress and rate at which thickening occurs changes with weight fraction. These differing factors should be considered when selecting a STF mixture for use in certain applications.

The thickening parameters for PPG400 + OX50 were also extracted between weight fractions of 30-55 wt% at 20°C and are displayed in Appendix B.

Similar to Appendix A, the gaps in-between the various figures represent the parameters in which thickening is active when certain shear stresses and rates are applied. For completeness, the thickening parameters for PEG400 + A90 and PPG400 + A90 are also extracted and are displayed in Appendix C.

Comparing PEG400 + OX50 and PPG400 + OX50 mixtures:

- **Shear stress:** The $\tau$-range in which thickening occurs in PEG400 + OX50 is relatively higher as the $\tau_c - \tau_{max}$ gap is smaller than that of PPG400 + OX50. One could infer that PPG400 + OX50 is more sensitive to thickening at lower shear stresses and continually thicken over a larger range of $\tau$.

- **Viscosity:** The $\eta_c - \eta_{max}$ gap, indicative of the degree of thickening, is relatively larger for PPG400 + OX50 than STFPEG. This indicates that the former STF option has a larger thickening performance and is able to absorb more shear stresses when applied.

- **Shear rate:** Similarly to shear stress, the $\dot{\gamma}$-range in which thickening occurs in PEG400 + OX50 is relatively higher as its $\dot{\gamma}_c - \dot{\gamma}_{max}$ gap is smaller than that of PPG400 + OX50. One could infer that PPG400 + OX50 is more sensitive to thickening at lower shear rates and continually thicken over a larger range of $\dot{\gamma}$.

From the raw data, a line-of-best fit was created along the experimental data for PEG400 + OX50, PPG400 + OX50, PEG400 + A90 and PPG400 + A90 to calculate the various thickening parameters as a function of weight fraction. For PEG400 + OX50 (Equation 3.1):

$$\dot{\gamma}_c = 288.33e^{-0.069\phi}$$

$$\dot{\gamma}_{max} = 87698\phi^{-2.015}$$
\[ \eta_c = 0.0131 e^{0.1399 \phi} \]
\[ \eta_{max} = (3 \times 10^{-12}) \phi^{8.5525} \]
\[ \tau_c = 3.8041 e^{0.0707 \phi} \]
\[ \tau_{max} = (3 \times 10^{-7}) \phi^{6.5423} \]  \hspace{1cm} (3.1)

where \( \phi \) is the percentage weight fraction. Similar models were produced for PPG400 + OX50 (Equation 3.2):

\[ \dot{\gamma}_c = 165.06 e^{-0.094 \phi} \]
\[ \dot{\gamma}_{max} = (1 \times 10^8) \phi^{-4.244} \]
\[ \eta_c = (1 \times 10^{-5}) e^{0.3309 \phi} \]
\[ \eta_{max} = (6 \times 10^{-13}) \phi^{9.3097} \]
\[ \tau_c = 0.0018 e^{0.2367 \phi} \]
\[ \tau_{max} = (7 \times 10^{-5}) \phi^{5.0627} \]  \hspace{1cm} (3.2)

As well as PEG400 + A90 (Equation 3.3):

\[ \dot{\gamma}_c = 0.9954 e^{0.0607 \phi} \]
\[ \dot{\gamma}_{max} = (832.08) \phi^{-1.172} \]
\[ \eta_c = (0.0186) e^{0.2768 \phi} \]
\[ \eta_{max} = (1 \times 10^{-6}) \phi^{6.0347} \]
\[ \tau_c = 0.0185 e^{0.3376 \phi} \]
\[ \tau_{max} = (0.0012) \phi^{4.8651} \]  \hspace{1cm} (3.3)

And PPG400 + A90 (Equation 3.4):

\[ \dot{\gamma}_c = 39.707 e^{-0.123 \phi} \]
\[ \dot{\gamma}_{max} = (14943) \phi^{-2.256} \]
\[ \eta_c = (0.0244) e^{0.2252 \phi} \]
\[ \eta_{max} = (3 \times 10^{-7}) \phi^{6.6468} \]
\[ \tau_c = 0.9675 e^{0.1022 \phi} \]
\[
\tau_{max} = (0.0046)\phi^{4.3943}
\]  

(3.4)

These proposed models were then plotted against experimental data for comparisons’ sake and can be seen below in Figures 3.11 and 3.12.

Figure 3.11 Varying thickening parameters as a function of weight fraction of PEG400 + OX50 (left column) and PPG400 + OX50 (right column) mixtures, shear stress (a and b), viscosity (c and d) and shear rate (e and f). Lines represent the modelling data for comparison.
Although not perfect, it can be useful in approximating the shear stress and rate at which thickening commences and the degree of thickening that occurs. These models are also limited to test conditions when $T = 20^\circ$C. The regression was taken on all proposed models comparing them to the raw experimental data (Appendix D).
To further expand the proposed models, data from tests conducted at 40, 60 and 80°C were also analysed and the relevant models for each thickening parameter were also created. Collating the coefficients from each model, a more detailed version of each model was developed as a function of both weight fraction and temperature. The updated models for PEG400 + OX50 (Equation 3.5) were:

\[
\begin{align*}
\dot{\gamma}_c &= [356e^{-0.02857}] e^{[\phi(0.0746\ln T - 0.2929)]} \\
\dot{\gamma}_{\text{max}} &= [(9 \times 10^6)T^{-1.177}] \times \phi^{[0.8377\ln T - 4.8525]} \\
\eta_c &= [0.0705T^{-0.568}]e^{[\phi(0.3566T - 0.306)]} \\
\eta_{\text{max}} &= [(5 \times 10^{-15})T^{1.9469}] \times \phi^{[9.5291e^{-0.0047}]} \\
\tau_c &= [834.24T^{-1.86}]e^{[\phi(0.0199T^{0.428})]} \\
\tau_{\text{max}} &= [(5 \times 10^{-8})T^{0.828}] \times \phi^{[8.0874T^{-0.078}]} 
\end{align*}
\]

(3.5)

For PPG400 + OX50 (Equation 3.6):

\[
\begin{align*}
\dot{\gamma}_c &= [539.92e^{0.00537}]e^{[\phi(0.0452\ln T - 0.2537)]} \\
\dot{\gamma}_{\text{max}} &= [(1 \times 10^{15})T^{-4.754}] \times \phi^{[1.9263\ln T - 10.591]} \\
\eta_c &= [(2 \times 10^{-9})T^{2.8948}]e^{[\phi(1.3664T^{-0.483})]} \\
\eta_{\text{max}} &= [(8 \times 10^{-10})T^{2.472}] \times \phi^{[9.4881e^{-0.00077}]} \\
\tau_c &= [(1 \times 10^{-7})T^{3.5804}]e^{[\phi(0.6374T^{-0.403})]} \\
\tau_{\text{max}} &= [(2 \times 10^{6})T^{-7.417}] \times \phi^{[2.0551T^{0.274}]} 
\end{align*}
\]

(3.6)

Also for PEG400 + A90 (Equation 3.7):

\[
\begin{align*}
\dot{\gamma}_c &= [0.4416e^{0.06357}]e^{[\phi(-0.033\ln T + 0.1463)]} \\
\dot{\gamma}_{\text{max}} &= [1559.9T^{-0.193}] \times \phi^{[0.0108\ln T - 3.0737]} \\
\eta_c &= [0.0979T^{-0.393}]e^{[\phi(1.1016T^{-0.489})]} \\
\eta_{\text{max}} &= [0.0534T^{-3.331}] \times \phi^{[5.5618e^{0.00229}]} \\
\tau_c &= [8 \times 10^{-6}T^{3.1309}]e^{[\phi(2.5306T^{0.2014})]} \\
\tau_{\text{max}} &= [243.57T^{-3.783}] \times \phi^{[2.5306T^{0.2014}]} 
\end{align*}
\]

(3.7)
And for PPG400 + A90, these equations are (Equation 3.8):

\[
\begin{align*}
\dot{\gamma}_c &= [28.451e^{0.0335T}]e^{\phi(0.04221\ln T - 0.2597)} \\
\dot{\gamma}_{\text{max}} &= [21.073T^{2.183}] \times \phi^{0.0229\ln T - 2.3529} \\
\eta_c &= [19.642T^{-2.25}] \times \exp[\phi(0.156T^{0.1227})] \\
\eta_{\text{max}} &= [1 \times 10^{-12}T^{3.6572}] \times \phi^{8.5434e^{-0.009T}} \\
\tau_c &= [5.0465T^{-0.545}]e^{\phi(0.0221T^{0.4942})} \\
\tau_{\text{max}} &= [6 \times 10^{-5}T^{1.468}] \times \phi^{7.484T^{-0.166}}
\end{align*}
\]

(3.8)

The updated models provided a greater fit to the experimental data when:

- PEG400 + OX50: 25 ≤ wt% ≤ 55 and 20 ≤ T(°C) ≤ 80
- PPG400 + OX50: 30 ≤ wt% ≤ 55 and 20 ≤ T(°C) ≤ 80
- PEG400 + A90: 10 ≤ wt% ≤ 30 and 20 ≤ T(°C) ≤ 80
- PPG400 + A90: 10 ≤ wt% ≤ 40 and 20 ≤ T(°C) ≤ 80

The following models were plotted onto three-dimensional scatter plots and can be seen in Figures 3.13 and 3.14.
Figure 3.13 Three-dimensional representation of STF models as functions of weight fraction and temperature for PEG400 + OX50 (a, c and e) and PPG400 + OX50 (b, d and f). Red series denotes critical values and blue series denotes maximum values for corresponding rheological trait.
Figure 3.14 Three-dimensional representation of STF models as functions of weight fraction and temperature for PEG400 + A90 (a, c and e) and PPG400 + A90 (b, d and f). Red series denotes critical values and blue series denotes maximum values for corresponding rheological trait.
In this format, it is ideal to encompass the thickening regime of PEG400 + OX50, PPG400 + OX50, PEG400 + A90 and PPG400 + A90 as both functions to visualise when the thickening effect will occur. Albeit with several modelling inaccuracies, these models simply serve as a guide to future researchers who would like to select an ideal STF that would become active for their specific application.

### 3.4. Relating material variables with rheology of STFs

Barnes initially stated “All suspensions of solid particles will show the phenomenon [shear thickening effect]” [30]. This can be interpreted that material properties such as particle size, particle shape, weight fraction and surface chemistry have an effect on the resultant rheology when mixed with a fluid. It is also crucial to account for the reaction between carrier fluid and particles when attempting to account for the relationship between material properties and the resultant rheological behaviour. The aim is to develop a relationship that can quantify the effect of differing particle and carrier fluid material properties on the thickening performance of STFs.

#### 3.4.1. Weight fraction

During STF fabrication, the end-groups of the polymer chains that make up the carrier fluid react with the surface hydroxyl groups (silanol groups) of the hydrophilic fumed silica via hydrogen bonding. The resulting reaction between polymer and fumed silica surface results in the formation of a layer of polymer chains surrounding the silica called a “solvation layer” [36, 50, 57, 75]. This solvation layer theory, as previously mentioned in the review, was initially proposed by Raghavan et al. in which they stated “In strongly hydrogen-bonding liquids, a solvation layer is envisioned to form on the silica surface through hydrogen bonding between liquid molecules and surface silanol groups.” [36]. The solvation layer was also used to explain the results found by He et al. when combining porous nano-silica particles in ethylene glycol [51]. This hypothetical solvation layer around silica would increase interparticle distancing resulting in increased deflocculation and interparticle repulsion forces.
By increasing the weight fraction in STFs, the available silanol surface area. As shown in Figures 3.3-3.7, there exists an optimum weight fraction of silica, regardless of size, in which the thickening performance is at its maximum. The author suggest that unreacted carrier fluid that has not bonded with the silanol surface of silica, is in abundance and acts as lubrication between adjacent fumed silica particles in the STF allowing for increased particle distancing and mobility to rearrange whilst under shear stress. Thus the conclusion can be made that a STF with a particle weight fraction below that of its optimum value will result in increased $\dot{y}_c$ and decreased STR. This could be due to the larger interparticle distancing due to the abundance of unreacted liquid polymer chains present, requiring larger external forces to overcome this separation distance and the interparticle repulsion forces simultaneously. Inversely, by increasing the weight fraction beyond the optimum weight fraction, the STF is deprived of lubrication from unreacted polymer chains which results in creation of entanglement of particle clusters, leading to complete disappearance of the shear thickening effect. A diagrammatic representation of what this may look like can be seen below in Figure 3.15.

Figure 3.15 Diagrammatic representation of the possible STF composition at optimum weight fraction (a), below the optimum weight fraction (b) and above the optimum weight fraction (c). Blue circles represent fumed silica aggregates within the STF carrier fluid.
This optimum weight fraction was more dependent on the size of the fumed silica and less on the chemistry of the carrier fluid. A graphical example of this proposed theory can be seen below in Figure 3.16 where $\dot{\gamma}_c$ and $\eta_{\text{max}}/\eta_c$ were plotted as a function of weight fraction.

![Graphical example](image)

**Figure 3.16** Thickening performance (a) and critical shear rate (b) measured as a function of weight fraction mixed with A90 fumed silica under steady shear conditions.

It is apparent that the critical shear rate of STFs containing PEG400 at varying weight fractions was significantly larger than STFs containing PPG400 and PPG725. It is noticeable that PPG has an additional methyl group in placement of a hydrogen atom which increases the volume occupied by PPG (Figure 3.17).

![Monomer units](image)

**Figure 3.17** Monomer unit for (a) PEG and (b) PPG.

When an external shear force is applied to the STFₚₑ₉₉, the PEG carrier fluid can respond relatively faster due to increased flexibility and spacing, leading to more packed silica within the fluid when compared to PPG carrier fluid. In PPG, the size of
3.4.2. Primary particle size

From Table 3.1, the BET-surface area of fumed silica is inversely proportional to its primary particle size which can be interpreted as the smaller fumed silica particles will attain a higher effective surface area for hydrogen bonding to occur between carrier fluid and silanol groups. Comparing the material properties of A90 and OX50 fumed silica variants, the optimum weight fraction for STFs containing A90 was found to be relatively lower than that for STFs containing the larger OX50 variant. A relationship exists in which a combination of particle size and weight fraction will exhibit maximum performance during the thickening stage and any given carrier fluid; An ‘Effective surface area’ exists in which the interparticle distancing and lubrication are at its most efficient. In different terms, interparticle distancing is minimised without resulting in permanent clustering and allowing to flow into hydroclusters with increasing applied shear force.

This relationship is supported when comparing the optimum weight fraction of OX50 and A90 (Figure 3.18).

![Figure 3.18](image)

**Figure 3.18** Thickening performance (a) and critical shear rate (b) measured as a function of weight fraction mixed in PEG400 carrier fluid under steady conditions.
The optimum weight fraction of PEG400 mixed with OX50 is almost twice that of A90, and almost three times that of A130 which also coincides with the surface area of OX50 almost halving that of A90 and a third of A130.

By increasing particle size, the author was able to increase the weight fraction before attaining this ‘effective surface area’, allowing him to maximise weight fraction of fumed silica within the STF, and to reduce interparticle distancing whilst allowing for sufficient space for particle rearrangement under shear stress. This would result in increased thickening performance and lower $\dot{\gamma}_c$ due to the reduced shear forces required to overcome particle repulsion forces.

In terms of potential applications, using larger particles will amplify the shear thickening effect $\dot{\gamma}_c$ at the compromise of using larger amounts of particles. By analysing the requirements of the STF in mechanical applications, a suitable STF mixture can be fabricated that satisfy the application’s thickening requirements and the shear force range at which it occurs.

### 3.4.3. Carrier fluid chemistry

Comparing the differing thickening behaviours of differing carrier fluid chemistry with equal molecular weight (PEG400 vs. PPG400) was done experimentally. With STFs containing PPG400, the thickening effect began at lower shear rates and with larger degrees of thickening when compared with STFs containing PEG400. It was also observed that there was infinitesimal change in $\dot{\gamma}_c$ with varying weight fraction in STFs containing PPG400 (Figure 3.19).
Figure 3.19 Thickening performance (a) and critical shear rate (b) measured as a function of weight fraction mixed with OX50 fumed silica under steady shear conditions.

A proposed theory as to why STFs with PPG are more sensitive to thickening at lower shear rates is the relatively smaller Degree of Polymerization (DP) which can affect the thickness of the solvation layer formed around the particles in the STF. This can attribute to smaller interparticle distancing and weaker interparticle repulsion forces which result in less external force required for initiating shear thickening. Another possible theory is the compositional difference between PEG and PPG. As mentioned previously, the PPG monomer has an additional methyl branch in place of a hydrogen atom, resulting in more rigid behaviour under flow. This increased rigidity can typically lead to increased distance between adjacent chains and reduced entanglement which allows for easier rearrangement whist under shear flow. Therefore, ease of polymer flow will result in easier particle rearrangement to attain the shear thickening at low $\dot{\gamma}_c$.

Comparing both STF mixtures with differing carrier fluids as shown in Figure 3.19, a similar trend is observed in which the rheological response of STFs containing PPG400 shows low $\dot{\gamma}_c$ but higher thickening performance and vice versa for STFs containing PEG400. Another interesting observation is the similar optimum weight fractions observed in both PEG400 and PPG400. The difference in rigidity of the carrier fluid chemical composition has little effect on the ‘effective surface area’ at which the same amount of particles added to both PEG400 and PPG400 will exhibit the maximum thickening performance and critical shear rate of both STFs.
Comparing carrier fluids with similar chemical composition but with varying molecular weights (PPG400 vs. PPG725) in Figure 3.16 showed that STFs with higher molecular weight carrier fluid resulted in significantly lower thickening performance and lower optimum weight fraction. These findings are consistent with those reported by Xu et al. [16]. Ethylene glycol (EG) and PEG are commonly used in STF research and their mixtures with silica particles usually exhibit shear thickening when mixed [1, 5, 9, 16, 40, 54, 57, 58]. The main differentiation between PEG and EG is that PEG is a polymer of EG with a much higher DP which could affect fluid viscosity. The molecular weight of a polymer is proportional to the DP which could result in heavier polymer chains to form larger solvation layers and the particles, increasing interparticle distancing and repulsion forces. Another possible explanation is the increased DP resulted in polymer entanglement, which hindered the formation of hydroclusters under shear stress. However, by observing Figure 3.22, the $\dot{\gamma}_c$ of both PPG400 and PPG725 show minute changes. One could infer the effect of decreasing the molecular weight of the carrier fluid would increase the thickening effect while $\dot{\gamma}_c$ remains relatively stable.

3.5. Validity with the Modified Cox-Merz Rule

As mentioned in the literature review, several previous investigations have attempted to relate the rheological behaviour of STFs under steady shear conditions to those under dynamic (oscillatory) shear conditions using the Modified Cox-Merz theory (MCM) (Equation 3.9):

$$\eta(\dot{\gamma}) = \eta^*(\omega\gamma_0)$$  \hspace{1cm} (3.9)

The significance of relating STF mixtures containing fumed silica using the MCM theory is to verify that these rheological and thickening behaviours are relatable to previously known STFs [75, 89]. It is also useful in relating and extrapolating steady and dynamic shear conditions for further potential application experimentation.

Both STF_{PEG} and STF_{PPG} were tested under dynamic testing conditions with increasing angular frequency $\omega$. The results of these dynamic testing conditions are displayed below in Figure 3.20.
Figure 3.20 Dynamic frequency tests conducted on STF$_{\text{PEG}}$ (a) and STF$_{\text{PPG}}$ (b). Each data series represents the strain amplitude ($\gamma_0$).

The measured viscosity under these conditions, Complex viscosity ($\eta^*$), is the frequency-dependent viscosity function under oscillatory conditions. Li et al. [90] expressed $\eta^*$ as in Equation 3.10:

$$\eta^* = \frac{1}{\omega}(G'' - iG')$$  \hspace{1cm} (3.10)

where $G'$ and $G''$ are storage modulus and loss modulus respectively. Both moduli are indicative of both elastic-like behaviour and liquid-like behaviour respectively under dynamic shear conditions.

From first impressions, both STF mixtures also show differing stiffening behaviours as they did under steady shear conditions. STF$_{\text{PEG}}$ begins to show signs of shear stiffening when $\gamma_0 \geq 500\%$ whereas in STF$_{\text{PPG}}$ the stiffening effect is apparent at $\gamma_0 \geq 100\%$ which also shows a relative increase in the stiffening ratio ($\eta^*_{\text{max}}/\eta^*_c$). As observed previously, STF$_{\text{PPG}}$ was observed to exhibit shear thickening at lower shear rates and greater degrees of thickening than STF$_{\text{PEG}}$. This also appears evidently under oscillatory conditions. Further analysis was completed by calculating the dynamic shear rate, $\omega \gamma_0$, and comparing with steady shear results to observe the validity of the MCM rule (Figure 3.21).
Figure 3.21 Correlation of steady and dynamic shear test data of STF$_{\text{PEG}}$ (a) and STF$_{\text{PPG}}$ (b) using MCM rule. Each data series represents the strain amplitude ($\gamma_0$) when applicable.

The MCM model applied to a limited extent in both STFs but only a higher strain amplitudes ($\gamma_0 \geq 500\%$). The dynamic shear data fits relatively well with the shear data as the deviation of $\dot{\gamma}_c$ with $\omega \gamma_0$ is relatively minor.

The significance of these findings can allow for future research to extrapolate findings from steady shear tests to estimate the STF’s shear stiffening performance under dynamic testing.

3.6. Chapter Summary

The effect of varying particle and carrier fluid parameters on the resultant shear thickening effect was quantified. For each STF, there existed an optimum weight fraction that depended on the size of the fumed silica and larger particles resulted in the increased thickening performance and $\dot{\gamma}_c$. The chemical properties of carrier fluids had a significant effect on the thickening properties by adjusting $\dot{\gamma}_c$ and thickening performance. It was proposed that the mentioned variables affect the formation of solvation layer around the particles and interparticle distancing via polymer lubrication. Two STFs were selected for further testing based on their improved rheological behaviour to observe whether they conform to the Modified Cox-Merz rule and relate steady shear and dynamic shear conditions. Both STF’s conformed to the rule which
showed a relationship between shear thickening and shear stiffening at high strain amplitudes ($\gamma_0 \geq 500\%$). These theories and suggestions into the effect of varying material properties on rheology aim at providing the ability to ‘tailor’ STFs for potential applications and future testing will be planned to observe the effect of differing $\dot{\gamma}_c$ and thickening performance on current and potential real world situations.
4. THE EFFECTS OF ADDITIVES ON SHEAR THICKENING FLUIDS

As part of the overall aim of this project, we need to comprehend the effects of using various carrier fluids and particles and the resultant rheological properties to fit the applications where the STFs will be used in. One example is the effect of increasing temperature on the shear thickening performance of STFs as shown in Chapter 3. Increasing the temperature of any solution would result in decreasing viscosity and interparticle activity changes which may affect the shear thickening behaviour negatively. One possible method of increasing temperature stability is to add different extra particles, as a heat sink, in small weight fraction to the STF to enhance the STF’s thermal conductivity.

Boron nitride (BN) is a compound frequently used in high temperature applications such as furnace refractories due to its significantly increased thermal conductivity, chemical inertness, low thermal expansion and thermal shock. Depending on the method of synthesis, it can also exist in plates, ribbons or rods on the nanoscale. Titanium dioxide (TD) is another material that, like BN, exhibits very good thermal and chemical stability.

In the present work, various forms of BN particles and TD were added to STFs in different weight fractions. The rheological properties of each mixture were recorded with increasing temperature in order to observe any noticeable difference in behaviour as a function of temperature.

4.1. Materials

4.1.1. STFs

The carrier fluid used in the STFs was PEG400 with a density of 1.13 g/mL at 20°C, supplied by Sigma-Aldrich and used ‘as is’ prior to fabrication.

The primary particles consisted of hydrophilic fumed silica sourced from Evonik Industries. The fumed silica, named AEROSIL® OX 50 (OX50), had primary particle
size of 40 nm and BET-surface area of $50 \pm 15 \text{ m}^2/\text{g}$. Prior to fabrication, OX50 was measured and placed into an oven at 110°C for 24 hours under very low pressure to eliminate any moisture form the silica.

4.1.2. Boron nitride (BN) particles, BN2.0

Two variants of BN particles, each consisting of varying morphology, size and sensitivity to moisture were tested: BN2.0 and TubularBN. Both BN variants were chemically synthesised by the Intelligent Polymer Research Institute in Innovation Campus at the University of Wollongong.

BN2.0 was named as so due to the failed synthesis of the first batch of BN (Named BN1.0) resulting in contamination of remaining reactants and large particle size distribution. After modifying and correcting these errors, the second batch showed minimal contamination of reactants and a narrower particle size distribution. X-ray diffraction (XRD) was completed on BN2.0 for characterisation purposes and is displayed in Figure 4.1.
Figure 4.1 XRD pattern of BN2.0 samples received. X-axis represents 2-theta ($2\theta$) and y-axis is the Counts per second.

Albeit the significant amount of distortion due to the non-metallic nature of boron nitride, the two featured peaks present at approximately 26° and 42° are indicative of boron nitride presence. This essentially validates that BN2.0 has been successfully synthesised.

Further characterisation was completed via Infrared Spectroscopy on BN2.0 as shown below in Figure 4.2.
Figure 4.2 FTIR spectrum analysis of BN2.0. X-axis represents the inverse of wavelength (cm$^{-1}$) and y-axis as Transmittance (%).

The FTIR spectrum analysis of BN2.0 showed two featured bands at both 1400 and 790 cm$^{-1}$, both associated with boron-nitrogen stretching and banding modes respectively [91]. This provides further evidence of successfully synthesised boron nitride in BN2.0. Another band was observed at 3200 cm$^{-1}$ which arouses from the hydroxyl (-OH) stretching mode. This qualifies the presence of hydroxyl groups on the surface of BN, therefore making BN2.0 hydrophilic in nature.

Transmission electron microscopic (TEM) images were recorded for BN2.0 to verify its morphology and the results can be seen in Figure 4.3.
BN2.0 appears to consist of nanoplaelets of varying sizes but average to hundreds of nanometres.

4.1.3. Boron nitride (BN) particles, TubularBN

For comparison, a different variant of boron nitride (TubularBN) was added to the STF. This variant consisted of tubular BN particles with a hydrophobic surface chemistry, completely opposite to that of BN2.0. XRD was completed on the TubularBN to determine the crystallinity of the sample (Figure 4.4).
There were clear peaks of crystalline BN which generally confirm the successful synthesis of BN particles.

Infrared Spectroscopy was completed to characterise the material properties of TubularBN and are displayed in Figure 4.5.

![FTIR spectrum analysis of TubularBN. X-axis represents the inverse of wavelength (1/cm) and y-axis as Transmittance (%).](image)

Some similarities in peaks are found in both TubularBN and BN2.0: 3200 cm\(^{-1}\) and 1400 cm\(^{-1}\) which show that both variants have O-H stretching modes and B-N stretching modes, respectively. However, a different peak has emerged, 1200 cm\(^{-1}\) which is indicative of B-N stretching deformation vibration mode [92] and minor peaks at 2900-3000 cm\(^{-1}\) which indicate the potential presence of C-H\(_x\) stretching modes [93]. From preliminary observations, TubularBN appears to have both hydroxyl and hydrocarbon surface groups on the surface which may result in the presence of a neutral surface behaviour, neither hydrophilic nor hydrophobic, due to the presence of both. Further examination was conducted to determine the surface composition of TubularBN.

TEM images were recorded of TubularBN and are shown in Figure 4.6.
At first glance, the TubularBN consists of a relatively constant diameter tubes but with varying lengths which may alter the aspect ratio of each nanoparticle. The TubularBN particles were used ‘as is’ prior to STF+ADDITIVE fabrication.

4.1.4. Titanium dioxide (TD) particles

The TD particles used in this experiment were hydrophilic fumed titanium dioxide labelled as AEROXIDE® TiO₂ P 25 which was sourced from EVONIK Industries AG. The TD particles have a stated BET-specific surface area of between 35-65 m²/g and a tamped density of 100-180 g/L. The stated properties mentioned in the product information sheet state [94]: high purity, very good thermal and chemical stability. The average primary particle size recorded is 21 nm. The TD particles were used ‘as is’ prior to fabrication. A representative TEM photograph can be seen in Figure 4.7.
Figure 4.7 Representative TEM image of the TD particles used.

The morphology of the TD consisted of aggregates of partially spherical titanium dioxide particles of varying particle size.

4.2. Method

*STF + ADDITIVE* fabrication and characterisation

The initial weight fraction of OX50 into both PEG400 carrier fluids was predetermined from previous experiments in Chapter 3. It was found that at 45 wt%, the STF exhibited optimum shear thickening performance and critical shear rate $\dot{\gamma}_c$. The OX50 and PEG400 were then manually mixed to ensure efficient homogeneity and mixing in the carrier fluid. Once completed, the BN or TD particles were added at various weight fractions (0.5%, 1.0% and 3.0%) to the STF and mixed mechanically again. Once completed, each STF+ADDITIVE mixture was inserted into the vacuum chamber at room temperature under low pressure for 1-2 hours to ensure all air bubbles trapped in the mixture are evacuated.
Testing was completed with a parallel-plate Rheometer (MCR 301, Anton Paar, Germany) under steady shear conditions. A 20 mm diameter testing geometry (PP-20) was used with a gap of 0.8–1.0 mm to ensure adequate filling of the STF over the testing disk. Viscosity was measured as a function of shear rate within the range of 0.1–1000 s\(^{-1}\) at 20°C, 40°C, 60°C and 80°C. Various temperatures were attained via a water-cooled temperature control device (Viscotherm VT2, Anton Paar, Germany) integrated with the rheometer. Once the stated temperature was attained and kept steady, the steady shear tests were then conducted.

4.3. Results

4.3.1. Characterisation of STF with increasing temperature

Initially, the STF without any additive was tested by measuring viscosity as a function of increasing shear rate. The STF was determined in Chapter 3 as attaining the best thickening performance and increased \(\dot{\gamma}_c\) (PEG400 + 45 wt% OX50). The rheology of the STF at differing temperatures can be viewed below in Figure 4.8.

![Figure 4.8 Viscosity measured as a function of shear rate under steady shear conditions of PEG400 + 45 wt% OX50. Each series denotes the testing stage temperature during testing.](image)

As stated previously, the overall viscosity of the STF decreases due to the increased excitation of both liquid molecules and fumed silica allowing for relatively easier
particle flow. It is also observed that with increasing temperature the critical shear rate at which shear thickening begins, $\dot{\gamma}_C$, decreases exponentially. One possible explanation is the increased excitation of carrier fluid and particle motion would result in increased external shear force required to overcome the interparticle distancing and particle-particle repulsion forces between fumed silica particles and form hydroclusters and therefore thickening would occur. It is also observable that the thickening performance also decreases gradually with increasing temperature. One possible explanation is that the increased viscosity of the carrier fluid molecules in combination with the increased shear forces required to initiate hydrocluster formation could result in premature shear thinning effect due to hydrocluster motion within the solution essentially becoming part of viscous flow.

For easier comparison, critical shear rate $\dot{\gamma}_C$ and the thickening performance ($\eta_{max}/\eta_C$) was extracted from each test under differing testing temperatures and plotted as a function of temperature, which can be viewed in Figure 4.9.

![Figure 4.9 Thickening performance (a) and $\dot{\gamma}_C$ (b) measured as a function of testing temperature of PEG400 + 45 wt% OX50 control sample. Lines denote trend line with equation and regression adjacent.](image)

It is apparent that there is an exponential decrease in thickening performance and inversely an exponential increase in $\dot{\gamma}_C$ with increasing temperature. These findings will be used in comparison with STF samples mixed with BN particles to observe differences in performance and rheological behaviours with increasing testing temperature.
4.3.2. *STF + BN2.0*

**BN2.0** particles were mixed into the STF in weight fractions of 0.5, 1 and 3 wt%.

The rheological behaviours of the above STFs with **BN2.0** at varying testing temperatures can be seen below in Figure 4.10.

![Figure 4.10 Viscosity measured as a function of shear rate under steady conditions under varying temperatures for STFs containing 0.5 wt% BN2.0 (a), 1 wt% BN2.0 (b) and 3 wt% BN2.0 (c)](image)

From first appearance, the addition of **BN2.0** to the STF resulted in significant changes to the rheology with increasing temperature. At 0.5 wt%, the $\dot{\gamma}_c$ remains relatively...
stable when $T \geq 40^\circ C$ showing that even a small addition of BN2.0 has a significant effect in temperature stability of the STF in retaining a portion of its original thickening behaviour at room temperature.

When the weight fraction of BN2.0 is increased to 1 wt%, the effects of BN2.0 are more noticeable. With increasing temperature, the behaviour exhibited changes significantly as the thickening curve is reduced and $\dot{\gamma}_c$ initially increases and then decreases. The type of behaviour is gradually trending to that of a gel as the overall viscosity begins to decrease with increasing shear rate. This transition is more apparent when compared to 3 wt% as the thickening effect diminishes and eventually behaves as a gel material where viscosity constantly decreases.

From these results, it becomes apparent that to effectively utilize the thermal stability and heat sink features of BN2.0, only a small amount is needed (0.5 wt%) to manipulate STF’s properties to preserve the thickening effect and critical shear rate of the STF at higher temperatures. Any higher than 0.5 wt% will induce gel-like behaviour and decrease or diminishment of the thickening effect.

One possible explanation is that the BN2.0 acts as a heat sink which helps the applied temperature to be flushed out of the STF+BN2.0 sample during testing, reducing the relative temperature of the sample. An additional factor to be considered is the morphology of the BN2.0 sample consisting of nanoplatelets. The addition of a separate phase in the STF consisting of long rods alongside the predominate fumed silica suspension, consisting of spherical silica aggregates, can provide an additional mechanism of interparticle clustering between BN/silica particles, resulting in relatively less external shear forces required to form hydroclusters and eventually exhibit the shear thickening effect. A final postulation is that with increasing temperature, the BN2.0 becomes more active within the STF, becoming more influential in the formation of hydroclusters within the STF by dominating the motion and behaviour of the fumed silica. Beyond a combination of increased temperature and increased weight fraction of BN2.0, the thickening effect has diminished and a gel-like rheology is observed. The BN2.0 has potentially become ‘too active’ that it dominated viscous flow of fumed silica particles and formed a network of interconnected BN/fumed silica particles resulting in no flow.
A more comparative analysis of the important thickening parameters for each mixture was extracted and plotted against the testing temperature. These can be viewed below in Figure 4.11.

![Figure 4.11](image)

**Figure 4.11** Thickening performance (a) and $\dot{\gamma}_c$ (b) measured as a function of testing temperature of STF+BN2.0. Each series denote the weight fraction of BN2.0 added to the STF.

Comparing the relative thickening performance of STF+BN2.0, it appears that adding any amount of BN2.0 will somewhat decrease the thickening performance, proportional to the weight fraction, at room temperature. However, by increasing the testing temperature, the thickening performance greatly varies with changing weight fraction. For 0.5 wt% BN2.0, the decay in thickening performance is much slower and even is improved when $T \geq 40^\circ$C. The $\dot{\gamma}_c$ with increasing temperature also changes behaviour significantly as the $\dot{\gamma}_c$ begins to plateau and stabilise with increasing temperature. For increasing weight fraction of BN2.0, at 1 wt% the sample loses almost half of its thickening performance but attains similar thickening behaviour with increasing temperature when compared to the STF without BN2.0. More so, the $\dot{\gamma}_c$ does not vary much with increasing temperature even begins to decrease at high temperatures. The thickening effect is almost diminished at 3 wt% with increasing temperature when past $T > 20^\circ$C the STF mixture behaved like a gel.

For STF + BN2.0, the optimal weight fraction was determined as 0.5 wt% due to the boron nitride’s ability to relatively stabilise and somewhat improve the thickening
performance at elevated temperatures as well as stabilise $\dot{\gamma}_c$. Both of these benefits were at the offset of decreased thickening performance and a small decrease in $\dot{\gamma}_c$ at room temperature.

It is possible that there is a relationship between the temperature applied to the STF+BN2.0 and the weight fraction of BN2.0 that ultimately affects the thickening behaviour of the mixture and a certain combination of the two variables will exhibit favorable thickening performance.

4.3.3. STF + TubularBN

TubularBN additives were added to PEG400 + 45 wt% OX50 STF in various weight fractions of 0.5, 1 and 2 wt%. The mixtures were then tested under similar testing temperatures to those with BN2.0 as 20°C to 80°C. The rheological results from these tests under steady shear conditions are displayed in Figure 4.12.
Figure 4.12 Viscosity measured as a function of shear rate under steady conditions under varying temperatures for STFs containing 0.5 wt% TubularBN (a), 1 wt% TubularBN (b) and 3 wt% TubularBN (c).

The rheological behaviours of STFs with TubularBN show significantly difference to those of STF+BN2.0. At all additions, the TubularBN appears to cause some outlier results with increasing shear rate. This may be due to the hydrophobic nature of the TubularBN. As it is resistant to bonding with both carrier fluid chains and fumed silica alike, TubularBN essentially behaves as a separate phase whilst under steady shear stresses and may result in randomly affecting the readings measured by the rheometer. This could potentially be a negative effect as this would result in the STF+additive to become more unpredictable with random ‘jumps’ in viscosity.
Another overall trend is the increased distortion of the rheological behaviour with increasing weight fraction of TubularBN. For STF with 1 wt% TubularBN, the $\dot{\gamma}_c$ becomes unclear and less defined with increasing temperature while at 2 wt%, $\dot{\gamma}_c$ is significantly undefined and convoluted, making TubularBN unfavorable as a potential additive for use as a temperature stabilising agent in STFs. For a more comparable analysis of the thickening behaviour with the varying weight fractions and STFs without any additives, the various thickening parameters are extracted from the previous graphs and displayed in Figure 4.13.

An overall observation is that the addition of TubularBN generally decreases the thickening performance by at least 40% when temperature increases. Both STF with 0.5 wt% TubularBN and STF with 1 wt% TubularBN added STFs performed similarly with consistently lessened thickening performance whilst at 2 wt%, the thickening performance is relatively constant with increasing temperature. It could be noted that with maximum weight fraction, the TubularBN becomes active with increasing temperature and stabilises the thickening performance with all temperatures. One could say the critical combination of TubularBN particles and temperature significantly affects the hydrocluster formation of fumed silica at increased shear rates.

Figure 4.13 Thickening performance (a) and $\dot{\gamma}_c$ (b) measured as a function of testing temperature of STF+TubularBN. Each series denote the weight fraction of TubularBN added to the STF.
The critical shear rate $\dot{\gamma}_c$ of STF was only affected by minimal additions of TubularBN. Uniquely at 0.5 wt%, $\dot{\gamma}_c$ increased significantly with increased temperature when compared to the control STF. This implies that increased temperature resulted in the STF requiring substantially larger shear force to form hydroclusters that, in turn, result in increased viscosity. One possible explanation would be that the relatively neutral surface chemistry of TubularBN becomes more active with increased temperature, resulting in increased separation of adjacent fumed silica resulting in more energy required to overcome these additional interparticle repulsive forces. At higher weight fractions 0.5 wt%, this behaviour diminishes and is similar to that of STFs without TubularBN.

Overall, the addition of TubularBN has a negative impact on the thickening performance and onset value of thickening and should not be considered as a potential candidate.

### 4.3.4. STF+TD

The TD additive was added to the PEG400 + 45 wt% OX50 in weight fractions of 0.5, 1 and 3 wt%. The resultant rheological behaviours were recorded at 20, 40, 60 and 80°C. The results are displayed below in Figure 4.14.
Figure 4.14 Viscosity measured as a function of shear rate under steady conditions under varying temperatures for STFs containing 0.5 wt% TD (a), 1 wt% TD (b) and 3 wt% TD (c)

For STF with 0.5 wt% TD, the rheological performance with increasing temperature shows decreased $\dot{\gamma}_c$, which is the only difference. Like BN variants, the use of additives with increased thermal conductivity tends to reduce the required external shear stresses to initiate shear thickening. This trend is also apparent in STF with 1 wt% TD.

At 3 wt%, other additives are considered to be saturating the STF, but STF+TD still shows shear thickening at lower temperatures. However, this quickly diminishes at 80°C. A more comparative view of the thickening parameters of STF+TD is shown below in Figure 4.15.
The thickening performance of STF+TD shows unique behaviours with different weight fractions and various temperatures. For STF with 0.5 wt% TD, the thickening performance is relatively less than the STF without TD. However, the $\dot{\gamma}_c$ with increasing temperature shows a differing behaviour as it increases with a decreasing rate as a function of temperature as opposed to the control STF which increases $\dot{\gamma}_c$ exponentially. This is similar to STF with 3 wt% TD, where the thickening performance is almost half of that without additives over all temperatures whereas the $\dot{\gamma}_c$ plateaus when $T \geq 40^\circ C$. Only when $T = 80^\circ C$, the sample behaves like a gel and the thickening effect has diminished. In practical terms, both STF with 0.5 wt% TD and STF with 3 wt% TD mixtures showed unfavourable benefits to the thickening effect of PEG400 + 45 wt% OX50.

STF + 1 wt% TD showed differing performance compared to the others. At room temperature, the thickening performance was increased over the STFs without additives and with increasing temperature, which was quite similar to the control STF. Another noticeable departure in behaviour was the impact on $\dot{\gamma}_c$. The parameter increases with decreasing rate. Although it is not stabilised like as observed in STF+BN2.0 mixtures, it is a departure to the exponentially increasing $\dot{\gamma}_c$ with increasing temperature which is a considerable improvement. Due to the relatively smaller particle size of TD (21 nm), it is possible that TD particles are able to penetrate deeply within the STF mixture, and to insert themselves in between OX50 aggregates without directly interfering with OX50.

**Figure 4.15** Thickening performance (a) and $\dot{\gamma}_c$ (b) measured as a function of testing temperature of STF+TD. Each series denote the weight fraction of TD added to the STF.
movement and hydrocluster formation which is opposite to that of BN2.0 and TubularBN. Explanations and postulations will be considered based on experimental results in the following sub-section.

Compared to all of the other additives tested, STF+1 wt% TD was the only mixture that displayed an improvement to the thickening performance albeit with a less significant impact to temperature stabilisation of the critical shear rate in which it begins.

4.4. Discussion

Effect of material properties of additives on the thickening performance

As seen in the results section, the morphology and the surface chemistry of each additive varied and showed differing rheological modifications to the thickening effect of PEG400 + 45 wt% OX50. Liu et al. [57] stated that “With temperature increasing, the hydrogen bond between particles and solvents is weakened with the temperature further increasing, the solvation layer covered the particles gradually disappear and the particles gradually get rid of the interactions between particles and solvents”. This is applicable to the STF results without additives as \( \dot{\gamma}_c \) increases exponentially whilst the thickening performance decreases rapidly with increasing temperature. Liu et al. [57] further stated that “With enhanced Brownian motion opportunity to collide, the particles form hydrogen bonds owing to the abundant silanol groups on their surface…form a network structure, that is, gel.” This can translate with our results since with increasing temperature the shear stresses required to corral fumed silica to form hydroclusters are significantly higher due to increased Brownian motion of both carrier fluid and fumed silica. However, the combination of fumed silica and temperature is not sufficient to result in the formation of a network structure. It is only with the addition of certain additives that becomes apparent. In summary, it is believed with increasing temperature, the solvation layer surrounding the fumed silica deteriorates and beyond a critical point, the particles would preferably bond with each other.

A significant trend found here was that the two better performing additives for STFs, BN2.0 and TD, were both hydrophilic in nature. When analysing the rheological results of adding BN2.0 or TD to the STF, \( \dot{\gamma}_c \) was somewhat stabilised with increasing
temperature. This can be attributed to the previous theory that with increasing temperature, the solvation layer surrounding the OX50 particles decays, leading to possible increased exposure of reactive silanol surface groups of the OX50 as well as free-flowing PEG400 polymer chains separating OX50 particles. The addition of relatively larger BN2.0 and TD particles may potentially behave as an alternative bonding opportunity between OX50 and BN2.0 or TD, resulting in the formation of OX50 particles surrounding BN2.0 or TD particles into clusters. This can be further supported due to the superior thermal conductive properties of BN2.0 and TD allowing for hydrogen bonding to occur on its surface due to its behaviour as a ‘heat sink’. A diagrammatic representation of this suggestion is displayed in Figure 4.16.

![Diagrammatic representation of the possible changes in STF+BN2.0/TD with increasing temperature. Blue circles represent fumed silica aggregates, red ovals represent BN2.0 particles and black lines are PEG400 polymer chains.](image)

This could be potentially explained as to why \( \dot{\gamma}_c \) remains relatively stable as the microstructure of the STF+BN2.0/TD at 0.5 wt% would not change if \( \dot{\gamma}_c \) is the same. The impact of BN2.0 and TD additions in small weight fractions appears to positively impact the hydrocluster formation of OX50 and BN2.0 or TD with increasing temperature.

This theory only applies to additives with a hydrophilic surface which allows for hydrogen bonding between the surface and other particles (Carrier fluid polymer chains, adjacent additive particles or OX50) as both the BN2.0 and TD performed positively in terms of stabilising \( \dot{\gamma}_c \). The differing performance associated with each additive:
• **BN2.0**: $\dot{\gamma}_c$ stabilised with increasing temperature, thickening performance reduces at 0.5 wt%

• **TD**: $\dot{\gamma}_c$ somewhat stabilised with increasing temperature, thickening performance increased or stabilised at 1 wt%

It could be related to the degree of hydrophilicity separating **BN2.0** and **TD**. As **TD** requires relatively larger weight fraction to enable optimum thickening modification, it does so at the expense of reduced temperature stabilisation but increasing thickening performance. At lower weight fraction, **BN2.0** becomes effective at modifying the thickening effect. One could infer that **TD** is relatively less hydrophilic than **BN2.0** as more particles are required to effectively modify the rheological behaviour at increased temperature.

When observing **STF+TubularBN**, the rheological results were significantly different to that of **STF+BN2.0** and thus cannot assume that the previous explanation of particle interactions will be the same. The minimal addition of **TubularBN** resulted in a significant increase in $\dot{\gamma}_c$ which may be contributed to the absence of a hydrophilic nature of the additives, essentially repelling nearby particles from contact or bonding. The additional repulsive forces of **TubularBN** within the OX50 substrate would increase separation distance and thus would require larger external shear stresses to overcome and form hydroclusters and begin thickening. As to why this behaviour is not observed in **STF+TubularBN** at 1 wt% and 2 wt% mixtures is not clear or explainable using the previous suggestion. Maybe the increased presence of **TubularBN** particles would essentially ‘cage’ in groups of OX50 particles.

Although this is mostly speculation, it would be informative to future research to consider the potentially positive impact of using additives with STF’s in order to augments some of the additive’s superior material properties to the STF.
4.5. Chapter Summary

The effect of adding different additives to STFs in order to modify the rheological response of STFs and potentially augment the additive’s favourable material properties into said STF was explored in this chapter. The addition of very small weight fractions of the hydrophilic boron nitride (BN2.0), the ‘neutral surface chemistry’ boron nitride (TubularBN) and titanium dioxide (TD) were added to STF with varying effects to the thickening effect. Adding 0.5 wt% BN2.0 resulted in critical shear rate becoming stabilised with increased temperature at the compensation of decreased thickening performance. However adding 1 wt% TD resulted in somewhat increased thickening performance but less stabilised critical shear rate with increasing temperature. The addition of TubularBN showed little to negative effects on both the thickening performance and the onset point. It was speculated that a combination of superior thermal conductivity and hydrophilic surface chemistry of both TD and BN2.0 particles have positively altered the hydrocluster formation of the STF leading to thickening. Another possible factor affecting the additive’s impact on the thickening effect is the morphology of the additive in use. The proposed suggestions were not limited to those made in this chapter and further research should be undertaken to further explore the mechanism behind the relationship between increasing temperature and the addition of additives.

The potential of augmenting additives with STFs is attractive as it increases the potential applications of STFs in varying scenarios such as in the use of STFs in elevated temperature environments or scenarios in which friction from use may induce an increased temperature.
5. CONCLUSION

The aims of this dissertation are to deeply understand the mechanisms behind the shear thickening in STFs, such as how and when the thickening will occur and in what magnitudes as well as develop a possible model for mechanical engineers to select an STF for their specific application.

From reviewing the literature, several research strengths and gaps were quantified. The explanation behind the mechanism of shear thickening is still undefined and is mostly considered to be the effect of clustering particles in solution which increases viscosity past a critical shear rate (Hydroclusters). Considerable effort was exerted on utilising the mechanical applications of STFs, particularly impregnation with Kevlar® fabric to increase penetration resistance of projectiles using similar STF mixtures examined previously in other journal articles. The limitation was the gap between understanding the material properties of constituting STFs and the resulting effect on mechanical properties for potential applications. The experiments conducted in this project aimed to bridge this gap.

Several STFs were fabricated with various carrier fluid chemistry, primary particle size and particle weight fraction in order to quantify each variable’s effect on the thickening parameters. The results showed the possible presence of an optimal weight fraction of particles, dependent on size that exhibited efficient thickening performance. Mathematical models were developed for several rheological parameters as a function of both temperature and weight fraction in order to display the active thickening region of shear stresses and shear rates.

The effects of introducing additives into STFs were also explored in a bid to improve the STFs’ thickening performance and stability. Several additives were tested; varying in chemical composition, surface chemistry morphology and particle size. Two additive variants appeared to affect the thickening effect with varying temperature positively: BN2.0 and TD. Both showed relative temperature stability of critical shear rate, at weight fractions as 0.5 and 1 %, compared to STFs without additives. However BN2.0 differentiated from TD as the temperature stabilisation effect was more profound in BN2.0 at the compromise of decreased thickening performance and TD vice versa. Two
postulations were given in an attempt to quantify the different material properties of the additives with the resulting rheological behaviours when applied temperature increases.

From the results gathered and presented, the understanding of fumed silica based STFs, and STFs in general, should be relatively clearer to understand the effects of certain variables such as weight fraction, carrier fluid chemistry and particle size. It is a step closer in bridging the gap between materials and mechanical engineering in effectively utilising STFs for future mechanical applications and exploiting the thickening properties appropriate for the applications mentioned above. Applications such as impact-resistant uses from sharp or blunt objects at various velocities for both personal and larger-scale protective scenarios, vibrational dampening in various forms such as acoustic or mechanical vibrations or augmented into other applications to provide a passive force-adsorbing property with other intelligent materials. The additional potential applications of STFs in combination with properly understanding thickening mechanism can almost certainly make the future use of STFs limitless in engineering applications.
6. REFERENCES


84. Ding, J., et al., *Smart multifunctional fluids for lithium ion batteries: Enhanced rate performance and intrinsic mechanical protection.* Scientific Reports, 2013. 3.

85. *Basic characteristics of AEROSIL® fumed silica.* Technical Bulletin Fine Particles 11 [pdg] [cited 2016 12/1/2016]; 11th:


7. APPENDIX A

(a) Shear stress, (b) viscosity and (c) shear rate thickening parameters as a function of weight fraction of PEG400 + OX50 mixtures.
8. APPENDIX B

Varying thickening parameters as a function of weight fraction of PPG400 + OX50 mixtures, shear stress (a), viscosity (b) and shear rate (c)
9. APPENDIX C

Varying thickening parameters as a function of weight fraction of PEG400 + A90 (left column) and PPG400 + A90 (right column) mixtures, shear stress (a), viscosity (b) and shear rate (c).
### 10. APPENDIX D

<table>
<thead>
<tr>
<th>STF composition</th>
<th>Proposed models</th>
<th>Regression</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG400 + OX50</td>
<td>$\dot{\gamma}_c = 288.33e^{-0.069\phi}$</td>
<td>0.5365</td>
</tr>
<tr>
<td></td>
<td>$\dot{\gamma}_\text{max} = 87698\phi^{-2.015}$</td>
<td>0.4749</td>
</tr>
<tr>
<td></td>
<td>$\eta_c = 0.0131e^{0.1399\phi}$</td>
<td>0.5854</td>
</tr>
<tr>
<td></td>
<td>$\eta_{\text{max}} = (3 \times 10^{-12})\phi^{8.5525}$</td>
<td>0.9736</td>
</tr>
<tr>
<td></td>
<td>$\tau_c = 3.8041e^{0.0707\phi}$</td>
<td>0.4990</td>
</tr>
<tr>
<td></td>
<td>$\tau_{\text{max}} = (3 \times 10^{-7})\phi^{6.5423}$</td>
<td>0.9746</td>
</tr>
<tr>
<td>PPG400 + OX50</td>
<td>$\dot{\gamma}_c = 165.06e^{-0.094\phi}$</td>
<td>0.7391</td>
</tr>
<tr>
<td></td>
<td>$\dot{\gamma}_\text{max} = (1 \times 10^8)\phi^{-4.244}$</td>
<td>0.8071</td>
</tr>
<tr>
<td></td>
<td>$\eta_c = (1 \times 10^{-5})e^{0.3309\phi}$</td>
<td>0.7525</td>
</tr>
<tr>
<td></td>
<td>$\eta_{\text{max}} = (6 \times 10^{-13})\phi^{9.3097}$</td>
<td>0.9861</td>
</tr>
<tr>
<td></td>
<td>$\tau_c = 0.0018e^{0.2367\phi}$</td>
<td>0.5593</td>
</tr>
<tr>
<td></td>
<td>$\tau_{\text{max}} = (7 \times 10^{-5})\phi^{5.0627}$</td>
<td>0.9591</td>
</tr>
<tr>
<td>PEG400 + A90</td>
<td>$\dot{\gamma}_c = 0.9954e^{0.0607\phi}$</td>
<td>0.2829</td>
</tr>
<tr>
<td></td>
<td>$\dot{\gamma}_\text{max} = (832.08)\phi^{-1.172}$</td>
<td>0.4808</td>
</tr>
<tr>
<td></td>
<td>$\eta_c = (0.0186)e^{0.2768\phi}$</td>
<td>0.6640</td>
</tr>
<tr>
<td></td>
<td>$\eta_{\text{max}} = (1 \times 10^{-6})\phi^{6.0347}$</td>
<td>0.9653</td>
</tr>
<tr>
<td></td>
<td>$\tau_c = 0.0185e^{0.3376\phi}$</td>
<td>0.8335</td>
</tr>
<tr>
<td></td>
<td>$\tau_{\text{max}} = (0.0012)\phi^{4.8651}$</td>
<td>0.9848</td>
</tr>
<tr>
<td>PPG400 + A90</td>
<td>$\dot{\gamma}_c = 39.707e^{-0.123\phi}$</td>
<td>0.8569</td>
</tr>
<tr>
<td></td>
<td>$\dot{\gamma}_\text{max} = (14943)\phi^{-2.256}$</td>
<td>0.8514</td>
</tr>
<tr>
<td></td>
<td>$\eta_c = (0.0244)e^{0.2252\phi}$</td>
<td>0.7860</td>
</tr>
<tr>
<td></td>
<td>$\eta_{\text{max}} = (3 \times 10^{-7})\phi^{6.6468}$</td>
<td>0.9598</td>
</tr>
<tr>
<td></td>
<td>$\tau_c = 0.9675e^{0.1022\phi}$</td>
<td>0.5045</td>
</tr>
<tr>
<td></td>
<td>$\tau_{\text{max}} = (0.0046)\phi^{4.3943}$</td>
<td>0.9500</td>
</tr>
</tbody>
</table>

Table of the proposed models of the four STF mixtures as a function of weight fraction. Rightmost column details the regression of each model compared to the raw experimental data.