RHEOLOGY OF SHEAR THICKENING FLUIDS AND THEIR EFFECT ON ENERGY DISSIPATION OF IMPREGNATED FABRICS

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MARCH 2019

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by

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Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

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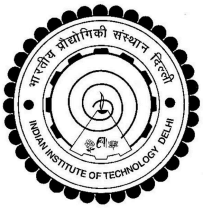

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MARCH 2019

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Certificate

This is to certify that the thesis entitled "**Rheology of shear thickening fluids and their effect on energy dissipation of impregnated fabrics"** being submitted by **Ms. Swarna** to the Indian Institute of Technology Delhi, for the fulfillment of award of the degree **"Doctor of Philosophy"** is a record of bonafide research work carried by her under our supervision. This thesis has been prepared in conformity with the rules and regulations of the Indian Institute of Technology Delhi, New Delhi. We further certify that the thesis has attained a standard required for the Ph.D degree of the institute. The research reported and results presented in the thesis have not been submitted in part or full to any other institution or university for the award of any other degree or diploma.

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Acknowledgements

This thesis finds its existence today to be a gift of ceaseless efforts, constant guidance and countless prayers by many individuals. With great humility, love and benevolence I express my deepest gratitude to all of them for having made my stay and doctoral studies at IIT Delhi a memorable one.

I express my sincere regards and respects to my supervisors, Prof. Anup K. Ghosh and Prof. Sudip K. Pattanayek for their able and timely guidance all throughout my PhD tenure. Their constant inspiration and encouragement have been invigorating and has doubtlessly played the most uplifting part in the fortification of this work. I heartily appreciate their patience and perseverance with me which helped propel through difficult situations.

I am grateful to Terminal Ballistics Research Laboratory, Defence Research and Development Organisation, for funding the project and allowing me to utilise facilities.

I am indebted to my student research committee members Prof. S.N Maiti, Dr. Bhabani K. Satapathy, and Prof. Ashwini Agarwal who have monitored my work and provided me with their valuable feedback. I am also warmly obliged to Prof. Veena Choudhary, Prof. Jacob Josemon, Dr. Leena Nebhani, Dr. Sampa Saha and Dr. Bijay Tripathi who inspite of their busy schedule have always made themselves available for valuable discussions and versatile support.

I revere the laboratory staffs Mr. Ashok Kapoor, Mr. Surender Sharma, Mr. Shiv Kant, Mr. Ehteshamul Islam and Mr. Gajraj Singh for their timely help and suggestions. I also honour and praise Mr. Narender Kumar, Ms. Shalini Arora, Mr. Sudhir Kumar Pandey and Pramod Kale for they were true catalysts in my work.

I extend my appreciation to my research colleagues both in project as well as at department. We have shared a fulfilling friendship that has nurtured integral parts of my doctorate studying experience. Mr. Anindya Dutta, Mr. Sabapathy S, Ms. Aronya Ghosh and Ms. Sanchi Arora are not just names but my beacons of strength.

A big hat tip to my friends Dr. Neha Bhardwaj, Pragati, Banpreet, Debanga Konwar, Srijita Purkayastha, Abhilasha, and Dr. Bhavana Sharma who have made my life cohesive, cheerful and charged.

A special thanks to Dr. Jutika Goswami, Dr. Priyanka Singh, Rashmi Torgalmath and Shobitha Shetty for encouraging me and keeping me agile while I ran from pillar to post.

My parents and family have been a part of me always. I don't think words would be enough to thank them.

Above all while I offer my work to the Scientific fraternity in particular and to the world at large I offer myself to Lord God Almighty. I urge Him to make me a worthy instrument in his Divine masterplan.

Swarna

Abstract

Shear thickening fluids (STFs) are amongst the new class of smart materials developed over a decade to explore its exceptional energy dissipating property associated with a rise in fluids' viscosity. This unique characteristics is a result of particles' rearrangements under shear in presence of a Newtonian liquids. These smart fluids thus give a synergistic impact characteristics when impregnated with fabrics which are applicable in ballistic resistant clothing and protective gears. Though STFs comprise of simple raw materials (particles of different size and a Newtonian liquid) and much simpler preparation methods (vortex mixing, sonication, homogenization), achieving a shear thickening flow is a challenge in itself. This is due to interplay of various forces between particles and suspending medium. A detailed comprehension of the change in the flow induced microstructures and the associated transition behaviour is thus vital and can be accomplished with various rheological measurements.

In the current study, non-colloidal and colloidal particles in a Newtonian fluid are considered for comparative studies correlating with their linear and non-linear rheological properties. The research presents the occurrence of shear thickening as well as shear thinning in colloidal particle suspensions using rheological fingerprints. The steady rheology shows a continuous shear thickening for 50 wt% of cornstarch in water suspensions. However, a shear thinning behaviour with high yield stress was exhibited with the addition of polyethylene glycol (PEG) to water at the same cornstarch concentration. Similar phenomenon was also identified for fumed silica in PEG 400 at 20 wt% particle concentration and surface functionalized silica in PEG 400 at 62 wt% particle concentration. The particle concentration enhanced the thickening phenomenon however, unlike fumed silica-PEG and cornstrach-water suspensions, shear thinning and discontinuous shear thickening behaviour were not recorded in spherical silica-PEG based STFs. Such discrepancy lead to further investigations of suspensions in non-linear region, to individually determine the elastic and viscous domain contributions.

Extending the investigations to non-linear region, analysis of non-sinusoidal waveforms was acquired through the large amplitude oscillatory shear (LAOS) characterization for fumed silica-PEG STFs. Through the leading order description of moduli, the suspensions were found to increase in modulus at critical strain (due to strong secondary bonding effects like the formation of shear-induced network) which initiates early with increase in frequency. Combination of four types of amplitude-dependent leading order LAOS behaviour indicated complex microstructural changes with increasing strain. It was found that with increasing particle concentration, the suspensions tend towards elastic response. At a given particle concentration, on the other hand, increasing frequency and strain amplitude resulted in a liquid response. Further, the nonlinear response of the suspensions was visualised graphically from the corresponding elastic and viscous Lissajous-Bowditch plots. The calculated energy dissipation per cycle for 20 wt% particle concentration was found to have the highest dissipation energy. Thus, though a shear thinning behaviour was observed in steady rheology with increasing particle concentration, the analysis of nonlinear response resulted in strength as well as better energy dissipation: the two significant traits of a STF to be used in protective ballistic armours.

Additionally, studies on alteration of surface silanols on silica nanoparticles with different end functional groups and their interaction with PEG influencing the thickening phenomenon were explored. The steady rheology showed prominent enhanced thickening for Octyl triethoxy silane [TE(O)S]-silane and 3-(Aminopropyl)trimethoxysilane [APTMS]-silane STFs however, 3-(Glycidoxypropyl)trimethoxysilane [GPTMS]-silica suspensions showed shear thinning behaviour (similar to fumed silica-PEG suspensions) with increasing silane concentration. The elastic and viscous nonlinearity parameters was found to vary with increasing frequency for a given silane concentration. This was found to be in agreement with the leading order moduli. The highest energy dissipation values were observed for GPTMS-silica suspensions followed

by APTMS-silica suspensions. Due to synergistic effect of both strength and energy dispersion of APTMS-silica suspensions, 100 nm size spherical silica was further modified with 5% APTMS.

In conjunction with LAOS, the effect of silicas' shape polydispersity on the structural deformation and regeneration characteristics of silica-PEG suspensions was demonstrated by the three-interval thixotropic test (3ITT). Due to induced greater particle agglomeration (increase in viscosity) after disruption of its microstructure at higher shears, the calculated viscous energy dissipation after each disruption phase carried out 3 times in succession was observed to be greater than the previous phase. This can be assumed as a novel testing technique considering the fact that this being the first attempt for the analyses of structural deformations and recovery in shear thickening fluids which are applicable in protective gears and military applications.

The optimized ten suspensions from various categories were impregnated with Kevlar fabric to investigate the impact energy dissipation characteristics which was corelated with the energy dissipation obtained from non-linear rheology. The energy absorption of the fabrics enhanced after treating with STF (spherical SiO_2 suspensions). However, yarn slippage caused the reduction in energy absorption in fumed silica treated fabrics due to higher PEG content. Two suspensions out of eleven (polydispered silica suspensions and APTMS-silica 100 nm suspensions) showed resistance to the impact of 20 kg indenter without any penetration. Amongst them, polydispersed silica suspension resulted in higher energy dissipation during repeat impact indicating a potential candidate for ballistic protection. Thus, this thesis presents a wide range of linear and non-linear rheological fingerprints for various types of STFs. The energy dissipation of STFs and STFs impregnated fabrics was correlated for their application in ballistic protective systems.

सार

शियर थिकेनिंग फ्लुइड्स एक नए वर्ग के स्मार्ट पदार्थ हैं जिन्हे एक दशक से खोजा जा रहा है उनकी अनोखी एनर्जी डीसिपेसन की काबिलियत पर जो इन फ्लुइड्स की चिपचिपापन के बढ़ने या घटने से सम्बन्ध रखता है। ये अनोखे लक्षण तब दीखते हैं जब हम इनपर अपरूपण बल का प्रयोग किसी न्यूटोनियन फ्लूइड की मौजूदगी में करते हैं। ये स्मार्ट फ्लुइड्स एक सिनर्जिस्टिक विशेस्ता तब दिखाते हैं जब इनमे किसी फैब्रिक को इम्प्रेग्नेट किया जाए और ये बैलिस्टिक रेसिस्टेंट कपडे और अन्य बचाव सामग्री में काम आते हैं। ऐस टी ऍफ़ वैसे तो बहुत ही सरल मूल सामग्री (अनेक आकारों के पदार्थ और एक न्यूटोनियन फ्लूइड) और आसान बनाने के तरीके (वोर्टेक्स मिक्सिंग, सोनिकेसन, होमोजेनाइजेसन) से बन जाने हैं किन्तु शियर थिकेनिंग फ्लो प्राप्त कर पाना अत्यंत कठिन काम है। यह इसलिए की इन पदार्थों और सस्पेन्डिंग मीडियम के बीच में अनेक पकड़ के बालों का आदान प्रदान होता है। अतः फ्लो एंड्यूस्ड माइक्रो स्ट्रक्चर में बदलाव और उनसे जुड़ी ट्रांसिसन व्यवहार का विस्तार से समझना अलग अलग किसम के रियोलॉजी के माप से संभव है।

इस अध्ययन में नॉन कोलॉइडल और कोलॉइडल कणों का न्यूटोनियन फ्लूइड में होकर उनके लीनियर एवं नॉन लीनियर विषेशताओं का तुलनात्मक विश्लेषण किया गया है। यह अनुसन्धान , कोलॉइडल पार्टिकल सस्पेंशन के शियर थिकेनिंग एवं शियर थिन्निंग की घटना के होने का अध्ययन रियोलोग्य फिंगरप्रिंट्स के माध्यम से करता है। एक नियमित रियोलॉजी 50 wt% के कॉर्न स्टार्च का पानी में सस्पेंशन का कॉन्टिनोस शियर थिकेनिंग दिखाती है। किन्तु पोलीएथीलेने ग्लाइकोल (PEG) का पानी के सस्पेंशन में उसी कॉर्न स्टार्च की मात्रा के साथ शियर थिन्निंग का प्रभाव देखा गया है हाई यील्ड स्ट्रेस के साथ। कुछ ऐसी ही घटना फ्यूम्ड सिलिका PEG 400 में 20 wt% पार्टिकल कंसंट्रेशन पर और सरफेस फंक्शनलिज़्ड सिलिका PEG 400 में 62 wt% पार्टिकल कंसंट्रेशन पर देखि गयी है। पार्टिकल कंसंट्रेशन से थिकेनिंग में वृद्धि हुई किन्तु फ्यूम्ड सिलिका -PEG और कॉर्नस्टार्च पानी सस्पेंशन के सामान स्पेरिकल सिलिका PEG ऐस टी ऍफ़ में शियर थिन्निंग और विच्छिन शियर थिकेनिंग के गुणों को अभिलिखित नहीं पाया जा सका। ऐसे अंतर इन सस्पेंसन की नॉन लीनियर रीजीएन में इलास्टिक एवं विस्कोस डोमेन योगदान में और खोज की ओर ले गए।

नॉन लीनियर रिजियन में इस खोज को जारी रखते हुए फ्यूम्ड सिलिका -PEG के इस टी ऍफ़ पर LAOS लक्षण वर्णन नॉन साइनोसोडल वेव्स के विस्लेषण से किया गया। लीडिंग आर्डर मॉड्युलाई के जरिये ये पाया गया की क्रिटिकल स्ट्रेन के दौरान इन सस्पेंसन की मॉड्युलस में बढ़ौती देखि गयी जो की फ्रीक्वेंसी के बढ़ाते ही पहले दौर में आ जाती है। चार प्रकार के एम्पलीटूड डिपेंडेंट लीडिंग आर्डर LAOS ने स्ट्रेन के बढ़ते ही जटिल सूक्ष्म संरचनात्मक बदलाव की ओर इंकित किया। ये पाया गया की कण की संकेन्द्रण की वृद्धि से सस्पेंसन और इलास्टिक बनता चला गया। लेकिन एक नियमित कण की संकेन्द्रण पर फ्रेक्वेंसी के बढ़ाने और स्ट्रेन एम्पलीटूड से वापस तरल पदार्थ जैसा व्यवहार पाया गया। इनके तत्स्थानी इलास्टिक एवं विस्कोस लिस्साजोस -बौडित्च प्लॉट्स के जरिये इनके नॉन लीनियर रिस्पांस की भी ग्राफ द्वारा कल्पनातमक पुष्टि की गयी।20 wt% पार्टिकल कंसंट्रेशन पर एनर्जी दिसिपेशन प्रति साइकिल का आकलन सबसे अधिक पाया गया। इसलिए जब नियमित रियोलॉजी में पार्टिकल कंसंट्रेशन के बढ़ते शियर थिनिंग को देखा गया वहीँ नॉन लीनियर रिस्पांस के अध्ययन ने अधिक ऊर्जा अपव्यय एवं मजबूती की पुष्टि की है। यही दो महत्वपूर्ण जरूरतें हैं किसी इस टी ऍफ़ के रक्षात्मक बैलिस्टिक कवचों में।

इसके साथ ही सिलिका नैनो पार्टिकल्स के साथ अलग एन्ड फंक्शनल ग्रुप पर सरफेस सिलेनोल्स के अल्टरेशन का PEG से प्रभाव और इसका थिकेनिंग पर असर के बारे में भी छान बिन की गयी। नियमित रियोलॉजी से ये साबित हुआ की Octyl triethoxy silane [TE(O)S]-silane और 3-(Aminopropyl)trimethoxysilane [APTMS]-silane ऐस टी ऍफ़ में थिकेनिंग की महत्वपूर्ण वृद्धि हुई किन्तु 3-(Glycidoxypropyl)trimethoxysilane [GPTMS]-silica के सस्पेंशन में शियर थिन्निंग सिलने की संकेंद्रता बढ़ते साथ ही घटता नज़र आया। एक दिए गए सिलेन संकेंद्रता पर फ्रीक्वेंसी के बढ़ते ही इलास्टिक और विस्कोस नॉन लिनियरिटी की मात्राओं का बदल जाना पाया गया। यह लीडिंग आर्डर मॉडुलाई के सूत्रों के अनुबंध था। GPTMS-silica suspensions और उससे कम APTMS-silica suspensions में सबसे ज्यादा ऊर्जा अपव्यय

के मूल्य पाए गए। APTMS-silica suspensions के बल और ऊर्जा अपव्यय के सिनर्जिस्टिक व्यवहार के चलते 100nm स्फेरिकल सिलिका को 5 % APTMS से फिरसे रूपांतरित किया गया।

LAOS के संयोजन के साथ सिलिका के आकर पॉलीडिस्पेर्सिटी उसके संरचनात्मक विकृति एवं उत्थान के लक्षण को सिलिका- PEG सस्पेंशन में थ्री इंटरवल थ्रिसोट्रॉपिक टेस्ट (3ITT) के जरिये प्रदर्शित किया गया। उच्च अनु ढेर के प्रेरित करने से उसके सुक्ष्म संरचना के उच्च अपरूपण बल के विघटन के बाद ऐसे ही ३ प्रक्रियाएं एक के बाद एक की गयी और ये पाया गया की वह मूल्य पिछले फेज से जयदा था। इसको एक नयी परिक्षण तकनीक भी कहा जा सकता है क्योंकि ये पहला ऐसा प्रयास है संरचनात्मक विकृति और ऐस टी ऍफ़ की आरोग्य प्राप्ति जिनके सीधा उपयोग रक्षात्मक उपकरण और सैन्य प्रयोग के हैं।

अलग अलग वर्ग से अनुकूलित दस सस्पेंसन में केवलर फैब्रिक को इम्प्रेगनटे किया गया। इससे हमे प्रभाव ऊर्जा अपव्यय लक्षण पर खोज और इसकी तुलना नॉन लीनियर रियोलॉजी से मिली ऊर्जा अपव्यय से की गयी। इन फैब्रिक्स की अबशोषण ऊर्जा में ऐस टी ऍफ़ द्वारा उपचार किये जाने पर वृद्धि हुई। किन्तु फ्यूम्ड सिलिका जड़ित फैब्रिक में अधिक PEG की मात्रा हेतु सूत फिसलन के प्रभाव से ऊर्जा अवशोषण में कमी पायी गयी। इन ग्यारह सस्पेंसनो में केवल दो (polydispered silica suspensions और APTMS-silica 100 nm suspensions) ने 20 Kg इंडेंटेर के प्रवेश का प्रतिरोध किया और उसे आर पार न जाने दिया। इनमे पॉलीडिस्पेर्सेड सिलिका सस्पेंशन ने पुनः संघात पर अधिक मात्रा में ऊर्जा अपव्यय की ये साबित करते हुए की ये पदार्थ बैलिस्टिक रक्षा हेतु एक उपयुक्त एवं संभावित पदार्थ है। इस प्रकार यह थीसिस कई भिन्न प्रकार के इस टी ऍफ़ के विस्तृत श्रृंखला से लीनियर और नॉन लीनियर रियोलॉजी फिंगरप्रिंट्स का उल्लेख करता है। इन एस टी ऍफ़ की और फैब्रिक जड़ित ऐस टी ऍफ़ की ऊर्जा अपव्यय के बीच पारस्परिक सम्बन्ध की गयी है जिनसे इनका बैलिस्टिक रक्षात्मक प्रणाली में उपयोगिता नज़र आये।

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List of Schemes

List of Abbreviations

PEG	Polyethylene glycol
STFs	Shear thickening fluids
LAOS	Large amplitude oscillatory shear
SAOS	Small amplitude oscillatory shear
LVR	Linear viscoelastic region
GPTMS	3-(Glycidoxypropyl)trimethoxysilane
TE(O)S	Octyl triethoxy silane
APTMS	3-(Aminopropyl)trimethoxysilane
CST	Continuous shear thickening
DST	Discontinuous shear thickening
SEM	Scanning electron microscope
ESEM	Environmental scanning electron microscope
FTIR	Fourier transform infrared spectroscopy
EDX/S	Energy-dispersive X-ray spectroscopy
FSi	Fumed silica nanoparticles
UnM	Unmodified silica nanoparticles-PEG suspensions
3ITT	Three interval thixotropic tests
CSi	Colloidal silica nanoparticles-based suspension
RSi	Irregular silica nanoparticles-based suspension
MSi	Mixed silica nanoparticles-based suspension

List of Symbols

wt%	Weight fraction
η	Viscosity
γ	Shear strain
$\dot{\gamma}$	Shear rate
τ	Shear stress
G’	Storage modulus
G”	Loss modulus
tan δ	Loss factor
γo	Strain amplitude
ω	Frequency
t	Time
δ	Phase lag
σ′	Elastic stress
σ′′	Viscous stress
G'_M	Minimum-strain dynamic moduli
G'_L	Large-strain dynamic moduli
η'_M	Minimum strain-rate dynamic viscosity
η'_L	Large strain-rate dynamic viscosity
S	Stiffening ratio
T	Thickening ratio
J	Damping constant
n	Damping exponent
E_d	Energy dissipation
G_i	Average storage modulus at interval 1 in 3ITT
G_{30}	Storage modulus within the first 30 seconds after interval 2
G_o	G’ value immediately after the end of interval 2 in 3ITT
G_r	Equilibrium G’ values at 3^{rd} interval in 3ITT
D_i	Percentage deformation
D_r	Total deformation in percentage
W_i	Weight of fabric before impregnation
W_t	Weight of fabric after impregnation

Preamble

Background and Motivation:

The basic concept of a body armor is to protect the body by stopping the speeding weapons or projectiles and diffuses the weapons' energy by dispersing into maximum area thus causing less damage to the body. However, a body can be only be protected from serious injuries and death by the right body armor specific to the weapon. With increasing sophisticated weapons, the need for a stronger body armour with advanced technology has also been in great demand. Currently, the available body armors are capable of protecting personnel (especially military troops, police, special force) from stab and low velocity bullets (180 m/s of 0.38 special, rifles to 335 m/s of shotgun). A few armors (multilayered Kevlar fabrics with hard panels) also protect from high velocity bullets and explosives however they dissipate impact energy into the body causing blunt force trauma. Further to it, they are heavy (2-4 kgs), bulky and rigid which cause discomfort during combat with terrorists. One approach to overcome these challenges is to use a smart liquids (STFs) having an ability to resist the impact force. These liquids when incorporated in fabric would result in synergistic impact properties. Various parameters influence the flow behavior of these STFs which calls for a detailed fundamental as well as molecular level structure-property perceptions. It is therefore important to study the rheological behavior of STFs encompassing linear and nonlinear viscoelastic responses. This motivated the current research to investigate the flow behavior of STF and its role in the energy dissipation property of impregnated fabrics. It is expected that a thorough rheological understating of the suspensions would enable to design the STF-high tenacity fiber system, which would overcome a challenging task of reducing the overall weight of a body armor without compromising its bullet resisting property.

Therefore, the thesis format was formulated which comprises of six chapters:

Chapter 1: Introduction and literature survey – This chapter deals with fundamentals of the concept and comprehensive review of the most recent literature relevant to the research project.

Chapter 2: Materials and experimentations - The chapter describes the particulars of raw materials procured, process of suspension preparation and various experimental techniques utilised throughout the research-work.

Chapter 3: Steady and dynamic rheological studies of shear thickening fluids - This chapter discusses the preparation of shear thickening fluids from three different particles and correlate their steady-dynamic rheological characterizations.

Chapter 4: Nonlinear viscoelastic studies through large amplitude oscillatory shear (LAOS) of fumed silica-PEG suspensions - The chapter commences with a detailed overview of nonlinear oscillatory shear tests. It reviews and compares several quantitative methods which have been proposed for analyzing nonlinear stress responses to deformation-controlled oscillatory shear.

Chapter 5: Modification of silica nanoparticles using i) GPTMS, ii) TE(O)S, and iii) APTMS and their rheological studies in PEG medium - This chapter presents the modification of silica nanoparticles with three different silane coupling agents for the purpose of investigating the effects of functional groups and their interactions in a suspension.

Chapter 6: Energy dissipation studies on fabrics impregnated with silica-PEG suspensions - This chapter emphasises, for the first time in literature, the three interval thixotropic (3ITT) to investigate the particles' microstructural regeneration in shear thickening fluids.

Chapter 7: Conclusions and future scope - This chapter summarizes the key results of major findings, possible explanations to the gaps found in literature and future recommendations of the research work.