TUNING OF RHEOLOGICAL RESPONSE OF SHEAR THICKENING FLUIDS FOR IMPROVING THE IMPACT ENERGY ABSORPTION OF PARA-ARAMID FABRICS

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by

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Dedicated to my family

CERTIFICATE

This is to certify that the thesis titled **'Tuning of Rheological Response of Shear Thickening Fluids for Improving the Impact Energy Absorption of Para-Aramid Fabrics'**, being submitted by **Ms. Aranya Ghosh** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. She has worked under my guidance and supervision and fulfilled the requirements for submission of the thesis which has attained the standard required for a Ph.D. degree of this Institute.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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Aranya Ghosh

ABSTRACT

In the last few decades, shear thickening fluid (STF) impregnated fabrics have generated huge interest amongst the researchers attempting to engineer light-weighing and flexible body armour. The non-Newtonian STF undergoes unique liquid to solid transition under stressed condition, thereby augmenting the impact energy absorption of the fabric treated with it. Both the constituents of STF, i.e., dispersion medium and dispersed phase, significantly influence the nature and extent of shear thickening. Thus, this research focuses on understanding the role of chemical interactions between these constituents in determining the rheology of silica particle and polyethylene glycol (PEG) based STFs, as well as the impact resistance behaviour of high-performance fabrics treated with such STFs.

The first part of this research involved studying the effect of micro and nano fibrous additives on the rheological performance of prepared multi-phase STFs. Cellulose nanofibres (CelNF) and Kevlar microfibres (KMF) were extracted by a novel grinding technique and subsequently added to the silica-PEG 200 STF system. A miniscule amount (0.1 to 0.3 wt. %) of CelNF significantly increased the peak viscosity and decreased the critical shear rate owing to the presence of a large number of surface -OH groups, consequently helping in better H-bond formation among STF constituents. The maximum increase of 278% in peak viscosity with respect to neat STF was observed for 0.2% CelNF based STF. It was also attempted to establish the role of surface chemistry of additives using surface modified (hydrophobic) CelNF i.e., M-CelNF reinforced STFs which showed decreased peak viscosity due to their relatively inert surface. The rheological response of both the variants of CelNF reinforced STF was translated to impact energy absorption of the fabrics treated with them. The KMF reinforced STFs showed diminishing rheological response owing to inert surface chemistry and micron size (thickness) of KMF. However, this reduction in rheological performance was not reflected in the impact resistance performance of the fabrics treated with KMF reinforced STFs.

The effect of molecular weight of carrier fluid on the rheological performance of an STF was explored in the second part of this research. Different high molecular weight PEGs (HMW-PEG: 1000, 3000 and 6000 g mol^{-1}) were individually added to a mixture of PEG 200 and PEG 600 to prepare ternary mixtures of carrier fluids. Increase in

average molecular weight of the carrier fluid via addition of HMW-PEG 1000 and 3000 enhanced the peak viscosity values by 88% and 832%, respectively with respect to neat STF. On the other hand, addition of HMW-PEG 6000 led to a rheological response inferior to that obtained via addition of HMW-PEG 3000 owing to solidification of the former at room temperature, subsequently resulting in fusion of silica particles. However, an inverse correlation was observed between the rheological behaviour of HMW-PEG based STFs and impact resistance performance of fabrics treated with them. The possible reason is lubrication caused by long polymer chains of HMW-PEG, which was confirmed from yarn pull-out results.

An attempt was made in the third part of this research to study the effect of chemical modification of carrier fluid on the rheological performance of STFs. STF prepared using citric acid modified PEG 200, i.e., M-STF, exhibited 76 times increase in peak viscosity owing to alterations in both chemical structure (hydrophilic functional groups) and molecular chain length. Besides, the impact energy absorption by M-STF treated fabric was also 35% higher than that of fabric treated with neat STF.

In the last part of the research, an attempt was made to understand the role of particle surface chemistry in tailoring the rheological behaviour of STFs. Silica particles were functionalised by hydrophilic and hydrophobic silane coupling agents (two each) at three different concentrations (3, 6 and 9 % on the wt. of silica particles). The hydrophilic particles based STF showed better rheological properties than neat STF because of stronger inter-particle interaction forces (more H-bonds) in the former. On the contrary, STF prepared using hydrophobic particles exhibited inferior rheological properties due to weaker inter-particle interactions. Interestingly, it was found that along with rheological behaviour of STFs, the pattern of their distribution over the fabric surface (governed by STF-fabric interactions) also played an important role in determining the impact resistance performance of fabrics treated with these STFs. The deposition of STF in the inter filament or inter yarn gaps was found to favour the enhancement in impact resistance performance rather than its uniform distribution over the fabric surface.

सार

पिछले कुछ दशकों में, शियर थिकिनंग फ्लूईड (एसटीएफ) संसेचन वाले कपड़ों ने हल्के वजन वाले नरम और लचीले रक्षा कवच बनाने के लिए शोधकर्ताओं के बीच रुचि पैदा की है। गैर-न्यूटोनियन एसटीएफ तनावग्रस्त स्थिति में, ठोस अवस्था से तरल अवस्था में परिवर्तन की एक अद्वितीय प्रक्रिया से गुजरता है, जिससे उससे उपचारित कपड़े की आघात ऊर्जा अवशोषण में वृद्धि होती है । एसटीएफ के दोनों घटक यानी डिस्पर्स माध्यम और डिस्पर्सड फेज, शियर थिकिनंग फ्लूईड की प्रकृति और सीमा को काफी प्रभावित करत है। इस प्रकार, यह शोध सिलिका कणों और पॉलीथीन ग्लाइकोल (पीईजी) आधारित एसटीएफ की रियोलॉजी का निर्धारण करने में, इन घटकों के बीच रासायनिक संबद्ध की भूमिका एवं एसटीएफ के साथ संसेचित किए गए अत्यधिक मजबूत कपड़ों के आघात प्रतिरोध व्यवहार को समझने पर केंद्रित है।

इस शोध के पहले भाग में तैयार मल्टी फेज एसटीएफ के रियोलॉजिकल प्रदर्शन पर माइक्रो और नैनो रेशेदार एडिटिव्स के प्रभाव का अध्ययन करना शामिल था । सेल्यूलोज नैनोफाइबर्स (CelNF) और केवलार माइक्रोफाइबर (KMF) एक विशेष पीसने वाली तकनीक द्वारा बनाये गए और बाद में सिलिका- पीईजी २०० एसटीएफ में मिलाये गये। एक अल्प मात्रा (0.१ से 0.३ wt. %) CelNF के मिलाने पर एक बड़ी संख्या मे सतह पर -OH समूह होने तथा हाइड्रोजन बॉन्ड के प्रभावी होने से चरम विस्कोसिटी में वृद्धि और शियर रेट में कमी पाई गई। सादे एसटीएफ के संबंध में चरम विस्कोसिटी में अधिकतम २७८ प्रतिशत की वृद्धि 0.२ % CelNF आधारित एसटीएफ के लिए देखी गई। सतह-रसायन विज्ञान की भूमिका स्थापित करने लिए , सतह संशोधित (हाइड्रोफोबिक) CelNF यानी, एम-CelNF प्रबलित एसटीएफ का उपयोग किया गया तथा अपेक्षाकृत निष्क्रिय सतह के कारण चरम विस्कोसिटी में कमी दर्ज की गई । CelNF प्रबलित एसटीएफ के दोनों वेरिएंट की रियोलॉजिकल प्रतिक्रिया को उनके साथ उपचारित कपड़े की ऊर्जा अवशोषण क्षमता के साथ सम्बन्धित किया गया। केएमएफ प्रबलित एसटीएफ ने केएमएफ के निष्क्रिय सतह रसायन विज्ञान और माइक्रोन आकार (मोटाई) के कारण रियोलॉजिकल प्रतिक्रिया को कम दिखाया। हालांकि, रियोलॉजिकल प्रदर्शन में यह कमी केएमएफ प्रबलित एसटीएफ के साथ उपचारित किए गए कपड़ों के आघात प्रतिरोध प्रदर्शन में परिलक्षित नहीं हुई।

इस शोध के दूसरे भाग में एसटीएफ के रियोलॉजिकल परफॉर्मेंस पर कैरियर फ्लूइड (तरल वाहक) के आणविक वजन के प्रभाव का पता लगाया गया । विभिन्न उच्च आणविक वजन वाले पीईजी (एचएमडब्ल्यू - पीईजी : १०००, ३००० और ६००० ग्राम मोल$^{-1}$) को पीईजी २०० और पीईजी ६०० के मिश्रण में मिलाकर टर्नरी मिश्रण वाले तरल वाहक तैयार किये गए । एचएमडब्ल्यू- पीईजी १००० और ३००० के अलावा तरल वाहक पदार्थ के औसत आणविक वजन में वृद्धि ने सादे एसटीएफ के संबंध में क्रमशः ८८% और ८३२% तक पीक विस्कोसिटी को बढ़ाया। दूसरी ओर, एचएमडब्ल्यू - पीईजी ६००० मिलाने पर एचएमडब्ल्यू- पीईजी ३००० की तुलना मे रियोलॉजिकल प्रतिक्रिया मे कमी दर्ज की गयी क्योंकि एचएमडब्ल्यू - पीईजी ६००० को कमरे के तापमान पर मिलाने से ठोसीकरण हो गया। हालांकि, एचएमडब्ल्यू- पीईजी आधारित एसटीएफ के

रियोलॉजिकल व्यवहार और उनके साथ उपचारित किए गए कपड़ों के आघात प्रतिरोध प्रदर्शन के बीच एक व्युत्क्रम संबंध देखा गया। संभावित कारण एचएमडब्ल्यू- पीईजी की लंबी बहुलक श्रृंखलाओं का स्नेहन है, जिसकी पुष्टि यार्न पुल-आउट परिणामों से की गई थी।

इस शोध के तीसरे भाग में एसटीएफ के रियोलॉजिकल प्रदर्शन पर वाहक तरल पदार्थ के रासायनिक संशोधन के प्रभाव का अध्ययन करने का प्रयास किया गया। एसटीएफ बनाने मे साइट्रिक एसिड संशोधित पीईजी २०० यानी एम-एसटीएफ का उपयोग किया गया, रासायनिक संरचना (हाइड्रोफिलिक कार्यात्मक समूह) और आणविक श्रृंखला लंबाई, दोनों में परिवर्तन के कारण चरम विस्कोसिटी में ७६ गुना वृद्धि का प्रदर्शन किया गया। इसके अलावा, एम-एसटीएफ द्वारा ऊर्जा अवशोषण का प्रभाव, सादे एसटीएफ के साथ उपचारित कपड़े की तुलना में ३५% अधिक था।

शोध के अंतिम भाग में एसटीएफ के रियोलॉजिकल व्यवहार को अध्ययन करने में पार्टिकल सतह केमिस्ट्री की भूमिका को समझने का प्रयास किया गया। सिलिका कणों को हाइड्रोफिलिक और हाइड्रोफोबिक सिलेन कपलिंग एजेंटों (दो प्रत्येक) द्वारा तीन अलग-अलग सांद्रता (सिलिका कणों के wt. ३ , ६ और ९ %) पर कार्यात्मक किया गया। हाइड्रोफिलिक कणों आधारित एसटीएफ ने मजबूत अंतर-कण बल (अधिक एच-बांड) के कारण सादा एसटीएफ की तुलना में बेहतर रीलॉजिकल गुण दिखाए। सिलिका कणों को हाइड्रोफिलिक और हाइड्रोफोबिक सिलेन कपलिंग एजेंटों (दो प्रत्येक) द्वारा तीन अलग-अलग सांद्रता (सिलिका कणों के wt. ३ , ६ और ९ %) पर कार्यात्मक किया गया था। हाइड्रोफिलिक कणों आधारित एसटीएफ ने पूर्व में मजबूत अंतर-कण बल (अधिक एच-बांड) के कारण सादे एसटीएफ की तुलना में बेहतर रीलॉजिकल गुण दिखाए। इसके विपरीत, हाइड्रोफोबिक सतह वाले कणों का उपयोग करके तैयार किये गए एसटीएफ द्वारा कमजोर अंतर-कण बल के कारण निम्न रीलॉजिकल गुणों का प्रदर्शन किया गया। दिलचस्प बात यह है कि एसटीएफ के रियोलॉजिकल व्यवहार के साथ-साथ फैब्रिक की सतह पर उनके वितरण के पैटर्न (एसटीएफ-फैब्रिक इंटरैक्शन) ने भी इन एसटीएफ के साथ उपचारित किए गए कपड़ों के आघात प्रतिरोध प्रदर्शन का निर्धारण करने में महत्वपूर्ण भूमिका निभाई। इंटर फिलामेंट या इंटर यार्न अंतराल में एसटीएफ का इकट्ठा होना, कपड़े के पृष्ठ पर समान वितरण के बजाय आघात प्रतिरोध प्रदर्शन में वृद्धि के पक्ष में पाया गया।

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