

SHEAR THICKENING MATERIALS BASED ON BORON MODIFIED MESOPOROUS SILICA AND ITS APPLICATION IN MICROCELLULAR POLYBOROSILOXANE-THERMOPLASTIC POLYURETHANE FOAMS

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**Shear thickening materials based on boron modified mesoporous
silica and its application in microcellular polyborosiloxane-
thermoplastic polyurethane foams**

By

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Submitted

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to the



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Dedicated to the sweet memory of
*my beloved daughter “**Wafia**”*
(who is now in her heavenly abode)

CERTIFICATE

This is to certify that the thesis entitled “*Shear thickening materials based on boron modified mesoporous silica and its application in microcellular polyborosiloxane-thermoplastic polyurethane foams*” being submitted by Mr. Ehteshamul Islam 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 him. Mr. Ehteshamul Islam has worked under my guidance and supervision and has fulfilled the requirements for the submission of his thesis, which, to our knowledge, has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any University or Institute for the award of any degree or diploma.

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(EHTESHAMUL ISLAM)

ABSTRACT

Shear thickening fluids (STFs) have so far been developed by conventional methods using hard solid particles of silica of different shapes and sizes. The potential of hybrid mesoporous silica for STF preparation has remained unexplored. Similarly, the integration of polyborosiloxane (PBS) into thermoplastic polyurethane (TPU) matrices and the development of PBS/TPU composite foams via supercritical CO₂ (scCO₂) foaming have not yet been investigated. This thesis addresses these gaps by systematically designing, synthesizing, and characterizing boron-modified mesoporous silica of various particle sizes and different morphologies for the preparation of STFs. This study extends further to reorganization and transformation of those STFs into PBS/TPU-based composites and foams aiming at high-performance impact protection.

Under the present research-work, a co-condensation strategy was optimized to synthesize mesoporous and non-porous silica by controlled boron content, and variation in particle size and morphology. Rheological studies revealed that mesoporous silica significantly outperformed non-porous analogues. With its porosity and minimal boron content it synergistically enhanced shear thickening behavior. Moreover, it was observed that particle size greatly helps tune the critical shear rate and viscosity response. Mesoporous silica having relatively larger particles effectively imparts viscoelasticity and discontinuous thickening via dense frictional contact networks. Morphology was found to be equally critical. Spherical and short-rod particles enabled efficient energy dissipation, while Kevlar fabrics treated with short-rod-STF composites demonstrated superior yarn pull-out resistance and absorbed up to 91.9 J in drop impact tests, far surpassing untreated fabrics.

Based on these insightful results, PBS was melt-blended with TPU and reinforced with mesoporous silica, followed by scCO₂ foaming. The results revealed that low PBS loadings (≈ 5

wt%) substantially improved compatibility and stress transfer, while higher loadings caused phase separation. Boron-modified mesoporous silica markedly improved interfacial adhesion, dispersion, and foam nucleation, enabling stable bimodal cell structures under optimized foaming pressures, (at 180–190 bar). Mechanical testing also confirmed that low PBS blends and silica-reinforced composite achieved superior tensile strength. The TPU/PBS boron modified mesoporous silica composites have shown excellent ductility, fatigue resistance, and damping capacity, making them a promising candidate for lightweight protective and vibration-damping applications.

Overall, this thesis involves a pioneering work on the use of hybrid mesoporous silica in STF formulations and attempts to establish a scalable pathway to engineer PBS/TPU-based foams with tailored morphologies for multifunctional performance.

शोध प्रबंध सार

तनाव—बल अथवा प्रतिबल की क्रियाशीलता के फलस्वरूप गाढ़ा हो जाने वाले तरल पदार्थ (शियर थिकेनिंग फ्लूइड, संक्षेपतः एस.टी.एफ) अब तक परंपरागत पद्धति से तैयार किये जाते रहे हैं, जिस में प्रायः सिलिका या कैल्शियम कार्बोनेट के विभिन्न आकृतियों और साइजों के ठोस कणों का प्रयोग किया जाता है। लेकिन मध्यम—सरंध्र (मेसोपोरस) बौरोन—मिश्रित सिलिका की संभाव्यता को खोजने परखने का प्रयत्न अब तक नहीं किया गया। इसी प्रकार मूल पदार्थ थर्मोप्लास्टिक पॉलीयुरिथेन (टी.पी.यू) में पॉलीबौरोसाइलोकसेन (पी.बी.एस) के समावेशन से, अधिक्रांतिक (सुपरक्रिटिकल) CO_2 द्वारा फोमिंग कर, पी.बी.एस/टी.पी.यू कम्पोजिट फोम बनाने पर अब तक विचार नहीं किया गया। प्रस्तुत शोध प्रबंध का लक्ष्य उपर्युक्त अभाव—सूचक रिक्तियों (गैप्स) को भरने का एक परिणामदायक और आशाजनक प्रयास है।

यह शोध प्रबंध एस.टी.एफ बनाने के लिए विभिन्न साइजों और बहुविध आकृतियों के बौरोन—संशोधित मध्यम—सरंध्र सिलिका को सुव्यवस्थित तरीके से संश्लेषित एवं रूपायित करने तथा उन की विशेषताएं निर्धारित करने का विवरण, और इस से आगे, उत्कृष्ट निष्पादन क्षमता से परिपूर्ण आघात प्रतिरोधक निर्मित करने के उद्देश्य से पी.बी.एस/टी.पी.यू—आधृत एस.टी.एफ को कम्पोजिट एवं फोम में पुनर्गठित और रूपान्तरित करने की प्रक्रिया का विस्तारपूर्वक अध्ययन, प्रस्तुत करता है।

परिकल्पित शोध प्रयोजन के अनुसार, मध्यम—सरंध्र एवं असरंध्र सिलिका के संश्लेषण हेतु, बौरोन की नियंत्रित मात्रा और कणों के साइज एवं आकृति की विविधता द्वारा, एक सहसंघनन (को-कंडेन्सेशन) प्रणाली अनुकूलित की गई। प्रवाहिकीय (रियोलोजिकल) अध्ययनों से पता चला कि असरंध्र की अपेक्षा मध्यम—सरंध्र सिलिका में असाधारण क्षमता पाई जाती है। उक्त सिलिका अपनी छिद्रिल आकृति और बौरोन

की अल्पिष्ठ मात्रा के कारण शियर-प्रभावित सघनन (शियर थिकेनिंग) व्यवहार में सहक्रियात्मकतापूर्वक सकारात्मक बदलाव लाता है। इसके अतिरिक्त, यह भी देखा गया कि कणों का साइज क्रांतिक शियर दर (क्रिटिकल शियर रेट) और श्यानता (विस्कोसिटी) को समंजित करने में अत्यधिक सहायक है। मध्यम-सरंध्र सिलिका के सापेक्षतः बड़े कण घनीभूत एवं प्रस्पर संबद्ध घर्षणात्मक संस्पर्शतंत्रों द्वारा प्रभावी रूप से श्यानप्रत्यास्थता (विस्कोइलास्टिसिटी) एवं असंतन सघनन (डिस्कोन्टिन्यूअस थिकेनिंग) उत्पन्न करते हैं। अध्ययन में यह भी पाया गया कि कणों की आकृति उतनी ही महत्वपूर्ण है जितना कि साइज। गोलाकार एवं रौंड आकार के छोटे कणों द्वारा उर्जा विसर्जन अधिक कुशलता से निष्पादित होता है। अनुसंधान के क्रम में छोटे रौंडरूपी कणों से निर्मित एस.टी.एफ कम्पोजिटों के समावेशन वाले केवलर फैब्रिक ने बहिर्गामी धागा खिंचाव का उत्कृष्ट प्रतिरोध प्रदर्शित करते हुए पातन परिणाम प्रीक्षण (ड्राप इम्पैक्ट टेस्ट) में 91.9 J तक के आघात को अवशोषित किया।

इन्हीं संकेतपूर्ण परिणामों के आधार पर पी.बी.एस को द्रवित अवस्था में टी.पी.यू के साथ ब्लेंड करके उसे मध्यम-सरंध्र सिलिका द्वारा प्रबलित किया गया। तत्पश्चात क्रान्तिक CO_2 द्वारा फोमिंग की गई। परिणामों से पता चला कि कम मात्रा के भारण (लोडिंग) से समानुकूलता (कॉम्पैटिबिलिटी) एवं स्ट्रेस स्थानान्तरण में सार्थक परिवर्तन आता है, जब कि उच्चतर मात्रा के भारणों से प्रावस्था पृथक्कन (फेज़-सेपैरेशन) हो जाता है। परीक्षणों से प्रमाणित हुआ है कि मध्यम-सरंध्र सिलिका अन्तरापृष्ठीय आसंजन (इन्टरफेशियल ऐडहीज़न), विक्षेपन (डिस्पर्सन), तथा फोम-न्यूक्लीयन (फोम-न्यूक्लियेशन) को समुन्नत एवं समन्वित कर, अनुकूलित फोमिंग प्रेशर के अधीन, (180–190) बार पर, स्थिर द्विमोडीय सेल संरचनाएं विकसित करता है। यांत्रिक परीक्षणों से भी यह सत्यापित हुआ है कि पी.बी.एस की कम मात्रा वाले ब्लेन्ड और

सिलिका-प्रबलित कम्पोजिट उच्चतर टेन्साइल शक्ति प्राप्त करने में सफल रहे हैं। टी.पी.यू./पी.बी.एस सह बौरोन-संशोधित मध्यम-सरंध्र सिलिका द्वारा निर्मित कम्पोजिटों ने उत्कृष्ट तन्यता (डकटीलिटी), पर्याप्त फटींग प्रतिरोध, तथा उत्तम अवमंदन (डैम्पिंग) क्षमता जैसे महत्वपूर्ण एवं उपयोगी गुणों का प्रदर्शन किया है। इन्हीं सम्मिलित गुणों के कारण ये कम्पोजिट कमवजन आघात-प्रतिरोधकों के सृजन तथा कंपन-अवमंदन संबंधित अनुप्रयोगों (ऐप्लिकेशन्स) के लिए प्रत्याशित विकल्प बनने योग्य है।

कुल मिलाकर, यह शोध प्रबंध एस.टी.एफ के विभिन्न सूत्रीकरणों (फार्मूलेशन्स) में बौरोन मिश्रित मध्यम-सरंध्र सिलिका के प्रभावशाली प्रयोगों पर सब से पहला अध्ययन प्रस्तुत करता है। यह पी.बी.एस/टी.पी.यू-आधृत फोम की अनुरूपित आकृतियों एवं संरचनाओं को बहुकार्यात्मक निष्पादन योग्य बनाने के उद्देश्य से उन के अभियंत्रण और उत्पादन की एक व्यापक प्रणाली विकसित करने की दिशा में पहली खोज का परिचायक है।

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LIST OF ABBREVIATIONS

STF	Shear Thickening Fluid
PEG	Polyethylene glycol
EG	Ethylene Glycol
SANS	Small-angle neutron scattering
SALS	Small-angle light scattering
CST	Continuous shear thickening
DST	Discontinuous shear-thickening
PS	Polystyrene
MWCNT	Multi-walled carbon nanotube
GO	Graphene oxide
PMMA	Polymethylmethacrylate
SSG	Shear stiffening gel
PBS	Polyborosiloxane
UHMWPE	Ultra-high molecular weight polyethylene
PDMS	Polydimethylsiloxane
NIJ	National Institute of Justice
HMPP	High modulus polypropylene

PU	Polyurethane
EVA	Ethylene vinyl acetate
NPR	Negative Poisson's ratio
CNT	Carbon nanotube
PVC	Polyvinylchloride
STU	Shock transmission unit
TENG	Triboelectric nanogenerator
NNFQS	non-Newtonian fluid quasi-solid
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
FTIR	Fourier transform infra-red spectroscopy
FESEM	Field emission scanning electron microscopy
BET	Brunauer-Emmett-Teller surface area analysis
TEOS	Tetraethyl orthosilicate
CTAB	Cetyltrimethylammonium bromide
MSi	Mesoporous silica
Si	Non-porous silica
MSiB	Boron modified hybrid mesoporous silica
SiB	Boron modified non-porous hybrid silica

GNP	Graphene nanoplatelet
TPU	Thermoplastic polyurethane
scCO ₂	Supercritical carbon dioxide
SAOS	Small angle oscillatory shear
SiO ₂	Silicon dioxide
DTGA	Differential thermogravimetric analysis
LVER	Linear viscoelastic region
RSTe	Relative Shear Stiffening Effect
tan δ	Loss factor
Phr	Parts per hundred

LIST OF SYMBOLS

η_c	Viscosity at critical shear rate
η_{min}	Minimum viscosity
η_{max}	Maximum viscosity
ϕ	Volume fraction
η_0^{rev}	Zero-shear viscosity after shear reversal
η_{rev}^∞	Steady state viscosity before shear reversal
Γ	Aspect ratio
η_r	Relative viscosity
N	Normal stress difference
Ia	Illumination intensity
$\dot{\gamma}_c$	Critical shear rate
η_c	Viscosity at critical shear rate
$\dot{\gamma}_m$	Critical shear rate at maximum viscosity
L_C	Counter length
G'	Storage modulus
G''	Loss modulus
ω	Angular frequency

$\text{\AA}$	Angstrom
N_0	Cell density
ρ	Density of the unfoamed samples
ρ_f	Density of the foamed samples
T_g	Glass transition temperature
ΔH_m	Enthalpy of fusion
T_m	Melting temperature
τ_c	Characteristic relaxation time
η^*	Complex viscosity

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