

PERFORMANCE AUGMENTATION OF POLYMER COMPOSITES WITH THE APPROPRIATE SELECTION OF NANOPARTICLES AND FIBERS

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by

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CERTIFICATE

This is to certify that the thesis entitled **“Performance augmentation of polymer composites with the appropriate selection of nanoparticles and fibers”** being submitted by **Ms. MEGHASHREE PADHAN** 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. **Ms. MEGHASHREE PADHAN** has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis.

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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ABSTRACT

High-performance polymer composites have become integral parts of various sectors such as automobiles, aerospace, ballistics, medical implants, space, sports, tribo-components (gears, bushes, bearings), etc. Researchers are striving to attain higher performance from the existing system of the matrices by appropriate selection of constituents to tailor the composites and their filler-matrix interfaces equipped with the right processing technology. The major themes focused on developing high-performance composites for the current work are as follows.

- To develop erosion and abrasion-resistant composites based on Ultra-high molecular weight polyethylene (UHMWPE) using nanoparticles (NPs) and microparticles (MPs) of carbides.
- To critically assess the potential of two solid lubricants viz. graphite and PTFE (Polytetrafluoroethylene) in varying PAEK (Polyaryletherketone) composite combinations to understand which property of a lubricant is more important for superior tribo-performance.
- To explore the potential of spherical NPs of alumina and siloxane functionalized version to improve performance properties of PAEK composites for adhesive wear performance.
- To develop novel composites using Zylon fibers in PEEK (Polyetheretherketone) for superior strength and tribo-performance.
- To explore in-situ grown Ag NPs on carbon fabric for improvement in Epoxy composite

The developed composites were evaluated for physical, thermal, mechanical, and tribological performance. Microstructural analysis was done by X-ray micro-computed tomography. The characterization of worn surfaces and interfaces was done with various techniques such as field emission scanning electron microscopy (FE-SEM), Atomic force microscopy (AFM), Energy dispersive spectroscopy (EDS), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The thesis is divided into nine chapters. Each chapter starts with a literature survey, the theme of work, experimentation, results, analysis, and conclusions.

Chapter 1 introduces concepts of tribology, polymers, and composites as tribo-materials, their applications, and their performance in various wear modes. It further discusses the literature on the specific themes for UHMWPE, PAEK, PEEK, and Epoxy-based composites. It leads to research gaps, implementation strategies, and objectives.

Chapter 2 deals with the general experimental characterization techniques and methods for evaluating performance.

Chapter 3 aims at two main themes – to compare various hard carbide particles (WC, TiC, ZrC, SiC) in UHMWPE for strength and tribo-performance for a constant amount (0.5 vol.%) and

varying sizes (micro and nano). The order of potential was; WC > TiC > ZrC > SiC. NPs proved superior by a wide margin.

Chapter 4 explores the simultaneous inclusion of two efficient solid lubricants – Graphite (20 – 0 wt.%) and PTFE (0 – 20 wt.%) in short glass fiber reinforced (30 wt.%) PAEK composites for possible synergism. Graphite proved superior compared to its combinations with PTFE.

Chapter 5 focuses on modifying a composite with short glass fiber (35 wt.%) reinforced PAEK and graphite (15%) by two strategies. First by incorporating spherical alumina NPs (2 wt.%) and second, its siloxane functionalized version. The performance in adhesive wear mode improved due to treated NPs compared to untreated ones and those without NPs.

Chapter 6 focuses on exploring Zylon fibers (50 wt.%) in PEEK by developing novel bi-directional composites by braiding technique followed by compression molding. The developed composites were characterized for mechanical strength and adhesive, abrasive, and erosive wear modes and showed significant improvement in all wear modes.

Chapter 7 explores the braided fiber-based Zylon (50 wt.%) -PEEK composites in both unidirectional (UD) and bi-directional (BD) forms to compare its performance with neat PEEK. The major theme was to compare the performance of UD and BD composites. UD composite proved superior in all properties.

Chapter 8 discusses the effect of Silver NPs decorated carbon fabric (55 %) on the performance enhancement of Epoxy composite. The decorated fibers and the developed composites were characterized for various properties, followed by tribo-evaluation in adhesive wear mode, leading to substantial improvement in all performance properties.

Chapter 9 concludes the overall work with comments on key findings for each objective. It also discusses the scope for future work.

Keywords- High-performance composites, PEEK, PAEK, braiding, Zylon, UHMWPE, Epoxy

सार

हाई-परफॉर्मेंस पॉलीमर कंपोजिट ऑटोमोबाइल, एयरोस्पेस, बैलिस्टिक्स, मेडिकल इम्प्लांट्स, स्पेस, स्पोर्ट्स, ट्राइबो-कंपोनेंट्स (गियर, बुश, बियरिंग्स) आदि जैसे विभिन्न क्षेत्रों के अभिन्न अंग बन गए हैं। शोधकर्ता मौजूदा से उच्च प्रदर्शन प्राप्त करने का प्रयास कर रहे हैं। सही प्रसंस्करण प्रौद्योगिकी से लैस कंपोजिट और उनके फिलर-मैट्रिक्स इंटरफेस को तैयार करने के लिए घटकों के उचित चयन द्वारा मैट्रिसेस की प्रणाली। वर्तमान कार्य के लिए उच्च-प्रदर्शन कंपोजिट विकसित करने पर केंद्रित प्रमुख विषय इस प्रकार हैं।

- कार्बाइड के नैनोकणों (एनपी) और माइक्रोपार्टिकल्स (एमपी) का उपयोग करके अल्ट्रा-उच्च आणविक भार पॉलीथीन (यूएचएमडब्ल्यूपीई) पर आधारित क्षरण और घर्षण-प्रतिरोधी कंपोजिट विकसित करना।

- दो ठोस स्नेहक की क्षमता का गंभीर रूप से आकलन करने के लिए अर्थात् ग्रेफाइट और PTFE (Polytetrafluoroethylene) को अलग-अलग PAEK (Polyaryletherketone) मिश्रित संयोजनों में यह समझने के लिए कि बेहतर ट्राइबो-प्रदर्शन के लिए स्नेहक की कौन सी संपत्ति अधिक महत्वपूर्ण है।

- चिपकने वाले पहनने के प्रदर्शन के लिए PAEK कंपोजिट के प्रदर्शन गुणों में सुधार के लिए एल्यूमिना और सिलोक्सेन कार्यात्मक संस्करण के गोलाकार एनपी की क्षमता का पता लगाने के लिए।

- बेहतर शक्ति और ट्राइबो-प्रदर्शन के लिए PEEK (Polyetheretherketone) में Zylon फाइबर का उपयोग करके उपन्यास कंपोजिट विकसित करना।

- एपॉक्सी कंपोजिट में सुधार के लिए कार्बन फ़ैब्रिक पर इन-सीटू उगाए गए एजी एनपी का पता लगाने के लिए विकसित कंपोजिट का मूल्यांकन भौतिक, थर्मल, मैकेनिकल और जनजातीय प्रदर्शन के लिए किया गया था। माइक्रोस्ट्रक्चरल विश्लेषण एक्स-रे माइक्रो-कंप्यूटेड टोमोग्राफी द्वारा किया गया था। पहना सतहों और इंटरफेस का लक्षण वर्णन विभिन्न तकनीकों जैसे क्षेत्र उत्सर्जन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एफई-एसईएम), परमाणु बल माइक्रोस्कोपी (एएफएम), ऊर्जा फैलाव स्पेक्ट्रोस्कोपी (ईडीएस), रमन स्पेक्ट्रोस्कोपी, और एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (एक्सपीएस) के साथ किया गया था।) थीसिस नौ अध्यायों में विभाजित है। प्रत्येक अध्याय एक साहित्य सर्वेक्षण, कार्य का विषय, प्रयोग, परिणाम, विश्लेषण और निष्कर्ष के साथ शुरू होता है।

अध्याय 1 ट्राइबोलॉजी, पॉलिमर और कंपोजिट की अवधारणाओं को ट्राइबो-सामग्री, उनके अनुप्रयोगों और विभिन्न पहनने के तरीकों में उनके प्रदर्शन के रूप में पेश करता है। यह आगे UHMWPE, PAEK, PEEK, और एपॉक्सी-आधारित कंपोजिट के लिए विशिष्ट विषयों पर साहित्य पर चर्चा करता है। यह अनुसंधान अंतराल, कार्यान्वयन रणनीतियों और उद्देश्यों की ओर जाता है।

अध्याय 2 प्रदर्शन के मूल्यांकन के लिए सामान्य प्रयोगात्मक लक्षण वर्णन तकनीकों और विधियों से संबंधित है।

अध्याय 3 का उद्देश्य दो मुख्य विषयों पर है - स्थिर मात्रा (0.5 वोल्ट%) के लिए ताकत और ट्राइबो-प्रदर्शन के लिए UHMWPE में विभिन्न हाई कार्बाइड कणों (WC, TiC, ZrC, SiC) की तुलना करना और अलग-अलग आकार (सूक्ष्म और नैनो)। क्षमता का क्रम था; डब्ल्यूसी > टीआईसी > जेडआरसी > सीआईसी। एनपी व्यापक अंतर से बेहतर साबित हुए।

अध्याय 4 संभावित तालमेल के लिए दो कुशल ठोस स्नेहक - ग्रेफाइट (20 - 0 wt.%) और PTFE (0 - 20 wt.%) को शॉर्ट ग्लास फाइबर प्रबलित (30 wt.%) PAEK कंपोजिट में एक साथ शामिल करने की पड़ताल करता है। PTFE के साथ इसके संयोजन की तुलना में ग्रेफाइट बेहतर साबित हुआ।

अध्याय 5 दो रणनीतियों द्वारा लघु ग्लास फाइबर (35 wt.%) प्रबलित PAEK और ग्रेफाइट (15%) के साथ एक समग्र को संशोधित करने पर केंद्रित है। पहला गोलाकार एल्यूमिना एनपी (2 wt.%) और दूसरा, इसके

सिलोक्सेन कार्यात्मक संस्करण को शामिल करके। एडहेसिव वियर मोड में उपचारित एनपी के कारण अनुपचारित और बिना एनपी वाले लोगों की तुलना में प्रदर्शन में सुधार हुआ।

अध्याय 6 में ज़ाइलॉन फाइबर (50 wt.%) की खोज पर ध्यान केंद्रित किया गया है, जिसमें ब्रेडिंग तकनीक के बाद संपीडन मोल्डिंग द्वारा उपन्यास द्वि-दिशात्मक कंपोजिट विकसित किए गए हैं। विकसित कंपोजिट को यांत्रिक शक्ति और चिपकने वाले, अपघर्षक, और क्षरणकारी पहनने के तरीके के लिए चित्रित किया गया था और सभी पहनने के तरीकों में महत्वपूर्ण सुधार दिखाया गया था।

अध्याय 7 यूनिडायरेक्शनल (UD) और द्वि-दिशात्मक (BD) दोनों रूपों में ब्रेडेड फाइबर-आधारित Zylon (50 wt.%) -PEEK कंपोजिट की पड़ताल करता है, ताकि इसके प्रदर्शन की तुलना नीट PEEK से की जा सके। प्रमुख विषय यूडी और बीडी कंपोजिट के प्रदर्शन की तुलना करना था। यूडी कंपोजिट सभी संपत्तियों में श्रेष्ठ साबित हुआ। अध्याय 8 एपॉक्सी कंपोजिट के प्रदर्शन में वृद्धि पर सिल्वर एनपी से सजाए गए कार्बन फ़ैब्रिक (55%) के प्रभाव पर चर्चा करता है। सजाए गए फाइबर और विकसित कंपोजिट को विभिन्न गुणों के लिए चित्रित किया गया था, इसके बाद चिपकने वाले पहनने के तरीके में ट्राइबो-मूल्यांकन किया गया, जिससे सभी प्रदर्शन गुणों में पर्याप्त सुधार हुआ।

अध्याय 9 प्रत्येक उद्देश्य के लिए प्रमुख निष्कर्षों पर टिप्पणियों के साथ समग्र कार्य का समापन करता है। यह भविष्य के काम की गुंजाइश पर भी चर्चा करता है।

कीवर्ड- उच्च प्रदर्शन वाले कंपोजिट, PEEK, PAEK, ब्रेडिंग, Zylon, UHMWPE, एपॉक्सी

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ABBREVIATIONS

PTFE: Polytetrafluoroethylene
UHMWPE: Ultra-high molecular weight polyethylene
PEEK: Polyetheretherketone
PAEK: Polyaryletherketone
PBO: Poly p-phenylene bis-benzoxazole
 μ : Coefficient of friction
 K_0 : Specific wear rate
WC: Tungsten carbide
TiC: Titanium carbide
SiC: Silicon carbide
ZrC: Zirconium carbide
Ag: Silver
 Al_2O_3 : Alumina
DSC: Differential Scanning Calorimetry
TGA: Thermogravimetric Analysis
DMA: Dynamic Mechanical Analysis
SEM: Scanning electron microscopy
EDS: Energy Dispersive Spectroscopy
XPS: X-ray photoelectron Spectroscopy
XRD: X-ray diffraction
LSS: Lap Shear Strength
 μ CT: Micro-computed X-ray tomography