

**DESIGN AND DEVELOPMENT OF GRAPHITE FABRIC-  
PAEK TRIBO-COMPOSITES AND NANO-ADHESIVES  
FOR PERFORMANCE AUGMENTATION**

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by

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Submitted

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## **CERTIFICATE**

This is to certify that the thesis entitled “**Design and development of graphite fabric- PAEK tribo-composites and nano-adhesives for performance augmentation**” being submitted by **Mr. UMESH NIVRUTTI MARATHE** 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. UMESH NIVRUTTI MARATHE** 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

Composites have penetrated every aspect of our life to the extent that we hardly use pure metals, polymers, or ceramics for fulfilling ever-increasing demands for better and better performance of the materials as a consequence of advancement in technology in various sectors such as automobiles, aircraft, space, sports, tribo-machine elements such as gears, bushes, bearings, etc. High-performance polymer composites are growing expeditious due to their versatile properties such as highest specific strength, resistance to corrosion, wear and impact, self-lubricity, absorption of noise and vibration, ease of manufacturing, and eco-viability. The performance of composites depends mainly on the type and amount of matrix and reinforcement, a form of reinforcement (if nano-particles, then their size, shape, de-agglomeration, etc.), fiber-matrix interface, processing technology, etc. Each aspect has a significant weightage on the final performance.

Specialty polymers such as Polyaryletherketone (PAEK), Polyetheretherketone (PEEK), Polyetherketoneketone (PEKK), Polyetherimide (PEI), polyethersulfone (PES), etc. are at the forefront of the design and development of high-performance super-composites. The higher the aspect ratio of fibers, the higher the performance, and hence fabric is more reliable than short fibers for performance augmentation.

Graphite fabric having very high strength with additional advantages of self-lubricity and high thermal conductivity was selected as reinforcement for PAEK matrix. Series of composites were developed keeping in view the following objectives.

- Influence of fiber-matrix adhesion by treating fibers with a novel technique
- Influence of novel sizing agent and its concentration to get most performing composite
- Influence of processing techniques on performance leading to a selection of a correct technique

The composites were evaluated for physical, mechanical, and tribological performance. The characterization of worn surfaces and interfaces was done with various techniques such as field emission scanning electron microscopy (FE-SEM), interlaminar shear strength (ILSS), etc.

Another research module was on the design and development of nano-adhesives and nano-composites based on matrices such as Polyetheretherketone (PEEK), Polyaryletherketone (PAEK), Polyetherketoneketone (PEKK), and epoxy using various nano-particles (NPs) such as carbides (TiC, SiC, ZrC, and WC), MWCNTs (Multi-walled carbon nanotubes), and Titanium

nitride (TiN) in varying concentrations. The adhesives showed excellent performance, nano-adhesive with 0.3 wt. % MWCNTs showed improvement by 150 %, proving to be the best choice.

The thesis is divided into nine chapters. Each chapter (barring the first two and last) starts with a pertinent literature survey, the theme of work, experimentation, results, analysis, and conclusions.

**Chapter 1** The chapter starts with the introduction to tribology and tribo-materials, in particular to the polymers and composites. It further explores the processing techniques for fabric-reinforced high-performance polymer composites, more explicitly for polyetheretherketone (PEEK), polyaryletherketone (PAEK), and polyetherketoneketone (PEKK) as matrices and related literature review. The chapter further explores the utility of tribology in the adhesive application, including a literature review. Moreover, the chapter ends up with research gaps, strategies, and objectives.

**Chapter 2** This chapter deals with the details of materials selected, broad methodology to develop composites and adhesives followed by characterization techniques used.

**Chapter 3** focuses on two main aspects. The first was to remove the existing sizing agent on the graphite fibers to be treated further for enhanced surface properties and compatibility with the selected thermoplastic PAEK (Polyaryletherketone) polymer. The second was on applying a simple but novel treatment to the fabric to physically, chemically, and mechanically change its surface. Furthermore, the composites were developed with desized and treated fabric. The developed composites were characterized for various performance properties.

**Chapter 4** commenced with an introduction to processing techniques of high-performance composites and limitations, followed by the processing of the same composite with two different techniques and their comparative aspects, especially the superiority of one over the other.

**Chapter 5** is on a maiden effort to size the graphite fibers with a solution of PEI with various concentrations to optimize to render the best performing composite using PAEK as a matrix. It describes the process of composite development, followed by characterization, performance analysis, and conclusions.

**Chapter 6** focuses on the exploration of MWCNTs, for enhancing the performance of PEK-based adhesive. It starts with a literature status followed by a brief methodology of development of nano-adhesives and their characterization. It ends with salient conclusions.

**Chapter 7** starts with a small introduction to high-performance adhesives, especially thermoplastics filled with hard nanoparticles (NPs). It then presents the development,

characterization, and performance analysis of nanocomposites and nano-adhesives based on NPs of Titanium carbide (TiC), Silicon carbide (SiC), Zirconium carbide (ZrC), and Tungsten carbide (WC) in Polyaryletherketone (PAEK) matrix. It is divided into two parts; part A deals with various % of NPs of TiC in PAEK-based adhesives, while Part B deals with various types of carbides in a fixed % (0.5 vol. %) in PAEK-based adhesives.

**Chapter 8** starts with an introductory literature survey of epoxy-based adhesives reinforced with hard NPs, particularly those of nitrides, followed by material selection, methodology of developing adhesives, their characterization results, and discussions. Finally, it ends with brief conclusions.

**Chapter 9** is the concluding chapter, with conclusions on the whole work and overall comments with scopes of future work.

*Keywords: Graphite fabric, PAEK composites, Nano- adhesives, Nanocomposites*

## सार

कंपोजिट ने हमारे जीवन के हर पहलू में इस हद तक प्रवेश किया है कि हम ऑटोमोबाइल जैसे विभिन्न क्षेत्रों में प्रौद्योगिकी में प्रगति के परिणामस्वरूप सामग्री के बेहतर और बेहतर प्रदर्शन की बढ़ती मांगों को पूरा करने के लिए शुद्ध धातुओं, पॉलिमर या सिरेमिक का शायद ही उपयोग करते हैं। विमान, अंतरिक्ष, खेल, ट्राइबो-मशीन तत्व जैसे गियर, झाड़ियों, बियरिंग्स, आदि। उच्च-प्रदर्शन बहुलक कंपोजिट अपने बहुमुखी गुणों जैसे उच्चतम विशिष्ट शक्ति, जंग के प्रतिरोध, पहनने और प्रभाव, आत्म-चिकनाई के कारण तेजी से बढ़ रहे हैं। , शोर और कंपन का अवशोषण, निर्माण में आसानी और पर्यावरण-व्यवहार्यता। कंपोजिट का प्रदर्शन मुख्य रूप से मैट्रिक्स और सुदृढीकरण के प्रकार और मात्रा पर निर्भर करता है, सुदृढीकरण का एक रूप (यदि नैनो-कण, तो उनका आकार, आकार, डी-एंग्लोमरेशन, आदि), फाइबर-मैट्रिक्स इंटरफ़ेस, प्रसंस्करण प्रौद्योगिकी, आदि। अंतिम प्रदर्शन पर प्रत्येक पहलू का महत्वपूर्ण महत्व है।

Polyaryletherketone (PAEK), Polyetheretherketone (PEEK), Polyetherketoneketone (PEKK), Polyetherimide (PEI), पॉलीएथरसल्फोन (PES), आदि जैसे विशेष पॉलिमर उच्च प्रदर्शन वाले सुपर-कंपोजिट के डिजाइन और विकास में सबसे आगे हैं। फाइबर का पहलू अनुपात जितना अधिक होगा, प्रदर्शन उतना ही अधिक होगा, और इसलिए प्रदर्शन वृद्धि के लिए छोटे फाइबर की तुलना में कपड़े अधिक विश्वसनीय होते हैं।

स्व-चिकनाई और उच्च तापीय चालकता के अतिरिक्त लाभों के साथ बहुत अधिक ताकत वाले ग्रेफाइट कपड़े को PAEK मैट्रिक्स के लिए सुदृढीकरण के रूप में चुना गया था। निम्नलिखित उद्देश्यों को ध्यान में रखते हुए कंपोजिट की श्रृंखला विकसित की गई थी।

- नई तकनीक से रेशों का उपचार करके फाइबर-मैट्रिक्स आसंजन का प्रभाव
- सबसे अधिक प्रदर्शन करने वाले समग्र प्राप्त करने के लिए उपन्यास आकार देने वाले एजेंट और इसकी एकाग्रता का प्रभाव

- निष्पादन पर प्रसंस्करण तकनीकों के प्रभाव से एक सही तकनीक का चयन होता है

भौतिक, यांत्रिक और जनजातीय प्रदर्शन के लिए कंपोजिट का मूल्यांकन किया गया था। घिसी हुई सतहों और इंटरफेस का लक्षण वर्णन विभिन्न तकनीकों जैसे कि फील्ड एमिशन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (FE-SEM), इंटरलामिनर शीयर स्ट्रेंथ (ILSS), आदि के साथ किया गया था।

एक अन्य शोध मॉड्यूल नैनो- एडहेसिव्स और नैनो-कंपोजिट्स के डिजाइन और विकास पर था, जो मैट्रिसेस जैसे पॉलीएथरेथरकेटोन (पीईईके), पॉलीरीलेथरकेटोन (पीईईके), पॉलीथरकेटोनकेटोन (पीईकेके), और विभिन्न नैनो-कणों (एनपी) जैसे धातु का उपयोग करके एपॉक्सी पर आधारित था। अलग-अलग सांद्रता में कार्बाइड (TiC, SiC, ZrC, और WC), MWCNTs (बहु-दीवार वाले कार्बन नैनोट्यूब), और टाइटेनियम नाइट्राइड (TiN)। चिपकने वाले ने उत्कृष्ट प्रदर्शन दिखाया, 0.3 wt के साथ नैनो- एडहेसिव्स । % MWCNTs ने 150% सुधार दिखाया, जो सबसे अच्छा विकल्प साबित हुआ।

यह थीसिस नौ अध्यायों में विभाजित है। प्रत्येक अध्याय (पहले दो और अंतिम को छोड़कर) एक प्रासंगिक साहित्य सर्वेक्षण, कार्य का विषय, प्रयोग, परिणाम, विश्लेषण और निष्कर्ष के साथ शुरू होता है।

**अध्याय 1** अध्याय ट्राइबोलॉजी और ट्राइबो-सामग्री के परिचय के साथ शुरू होता है, विशेष रूप से पॉलिमर और कंपोजिट के लिए। यह आगे मैट्रिसेस और संबंधित साहित्य समीक्षा के रूप में फैब्रिक-प्रबलित उच्च-प्रदर्शन बहुलक कंपोजिट के लिए प्रसंस्करण तकनीकों की पड़ताल करता है, पॉलीएथरेथरकेटोन (पीईईके), पॉलीरीलेथरकेटोन (पीईईके), और पॉलीएथरकेटोनकेटोन (पीईकेके) के लिए अधिक स्पष्ट रूप से। अध्याय आगे एक साहित्य समीक्षा सहित चिपकने वाले अनुप्रयोग में ट्राइबोलॉजी की उपयोगिता की पड़ताल करता है। इसके अलावा, अध्याय अनुसंधान अंतराल, रणनीतियों और उद्देश्यों के साथ समाप्त होता है।

**अध्याय 2** यह अध्याय चयनित सामग्री के विवरण, मिश्रित और चिपकने वाले विकसित करने के लिए व्यापक कार्यप्रणाली के बाद उपयोग की जाने वाली विशेषता तकनीकों से संबंधित है।

**अध्याय 3** दो मुख्य पहलुओं पर केंद्रित है। पहला यह था कि ग्रेफाइट फाइबर पर मौजूदा साइजिंग एजेंट को हटा दिया जाए ताकि सतह के गुणों को बढ़ाया जा सके और चयनित थर्मोप्लास्टिक PAEK (Polyaryletherketone) पॉलीमर के साथ संगतता बनाई जा सके। दूसरा भौतिक, रासायनिक और यांत्रिक रूप से इसकी सतह को बदलने के लिए कपड़े के लिए एक सरल लेकिन उपन्यास उपचार लागू करने पर था। इसके अलावा, कंपोजिट को डिसाइज्ड और ट्रीटेड फैब्रिक के साथ विकसित किया गया था। विकसित कंपोजिट विभिन्न प्रदर्शन गुणों के लिए विशेषता थे।

**अध्याय 4** उच्च-प्रदर्शन वाले कंपोजिट और सीमाओं की प्रसंस्करण तकनीकों के परिचय के साथ शुरू हुआ, इसके बाद दो अलग-अलग तकनीकों और उनके तुलनात्मक पहलुओं के साथ एक ही कंपोजिट का प्रसंस्करण, विशेष रूप से एक की दूसरे पर श्रेष्ठता।

**अध्याय 5** विभिन्न सांद्रता वाले पीईआई के समाधान के साथ ग्रेफाइट फाइबर को आकार देने के पहले प्रयास पर है ताकि मैट्रिक्स के रूप में पीईके का उपयोग करके सर्वश्रेष्ठ प्रदर्शन करने वाले समग्र को प्रस्तुत किया जा सके। यह समग्र विकास की प्रक्रिया का वर्णन करता है, उसके बाद लक्षण वर्णन, प्रदर्शन विश्लेषण और निष्कर्ष।

**अध्याय 6** पीईके-आधारित एडहेसिव के प्रदर्शन को बढ़ाने के लिए एमडब्ल्यूसीएनटी की खोज पर केंद्रित है। यह एक साहित्य की स्थिति के साथ शुरू होता है जिसके बाद नैनो- एडहेसिव्स और उनके लक्षण वर्णन के विकास की एक संक्षिप्त पद्धति होती है। यह प्रमुख निष्कर्षों के साथ समाप्त होता है।

**अध्याय 7** उच्च-प्रदर्शन चिपकने वाले, विशेष रूप से कठोर नैनोकणों (एनपी) से भरे थर्मोप्लास्टिक्स के एक छोटे से परिचय के साथ शुरू होता है। इसके बाद यह टाइटेनियम कार्बाइड (TiC), सिलिकॉन कार्बाइड (SiC), ज़िरकोनियम कार्बाइड (ZrC), और टंगस्टन कार्बाइड (WC) के एनपी के आधार पर Polyaryletherketone (PAEK) में नैनोकम्पोजिट्स और नैनो-एडहेसिव्स वाले विकास, लक्षण वर्णन और प्रदर्शन विश्लेषण प्रस्तुत करता है। आव्यूह। इसे दो भागों में बांटा गया है; भाग A, PAEK-आधारित एडहेसिव में TiC के विभिन्न% NPs से संबंधित है, जबकि भाग B PAEK-आधारित एडहेसिव्स में एक निश्चित% (0.5 vol.%) में विभिन्न प्रकार के कार्बाइड से संबंधित है।

**अध्याय 8** हार्ड एनपी, विशेष रूप से नाइट्राइड के साथ प्रबलित एपॉक्सी-आधारित एडहेसिव्स के एक परिचयात्मक साहित्य सर्वेक्षण के साथ शुरू होता है, इसके बाद सामग्री चयन, विकासशील एडहेसिव्स कार्यप्रणाली, उनके लक्षण वर्णन परिणाम और चर्चाएं होती हैं। अंत में, यह संक्षिप्त निष्कर्ष के साथ समाप्त होता है।

**अध्याय 9** समापन अध्याय है, जिसमें संपूर्ण कार्य पर निष्कर्ष और भविष्य के कार्य के दायरे के साथ समग्र टिप्पणियां शामिल हैं।

कीवर्ड: ग्रेफाइट फैब्रिक, PAEK कंपोजिट, नैनो- एडहेसिव्स, नैनोकम्पोजिट्स

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