FRACTURE, TRIBOLOGY, AND CONDUCTIVITY OF ELECTRIC FIELD-ALIGNED CNF/EPOXY NANOCOMPOSITES

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OCTOBER 2022

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By

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Submitted

in fulfillment of the requirements for the degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2022

CERTIFICATE

This is to certify that the thesis entitled '**Fracture, Tribology, and Conductivity of Electric Field-Aligned CNF/Epoxy Nanocomposites**' being submitted by **Amit Chanda** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**, is a bonafide record of original research work carried out by him under our supervision in conformity with rules and regulations of the 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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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and thanks to my supervisors, Prof. Naresh Varma Datla and Prof. Sujeet Kumar Sinha, for providing me the opportunity to pursue my doctoral dissertation and for their consistent support, guidance and encouragement throughout the journey.

I would like to express my gratitude to my student research committee (SRC) members Prof. Satinder P Singh, Prof. Raj K Pandey, and Prof. Jayashree Bijwe for their beneficial feedback and valuable suggestions.

I am grateful for the financial and research support from IIT Delhi. I would like to thank Mr. Navnath, Mr. Sreejath, Mr. Tauheed, Mr. Panda, Mr. Yaswant Pydi, Mr. Jaswant, Mr. Akash, Mr. Tesfaye, Mr. Sunil, Mr. VB Sathpathy and Mr. Ashish Verma for their continuous support and motivation during the course of the degree.

I am indebted to my parents, Arun Kumar Chanda and Bela Rani Chanda, my brother Swadhin Chanda, and my fiancé Ms. Anwesha Paul for their continuous mental support and aspiration. I want to dedicate my thesis to my family.

Amit Chanda

ABSTRACT

Epoxy resins have become one of the most used polymeric materials in several engineering applications such as structural composites, adhesives, and tribological coatings. This is due to their superior adhesive properties, mechanical strength, chemical resistance, and their ability to be modified. Despite these benefits, there are few limitations that restrict the greater use of epoxies. The highly cross-linked structure and brittleness of pure epoxy result in poor friction and wear performance that restricts its use in tribological applications. Moreover, the low fracture toughness of epoxy leads to rapid crack propagation, which limits its use as a structural adhesive. The low conductivity also restricts its use in different applications such as sensors, coatings, and adhesives where electrical and thermal conductivity might be beneficial.

The use of carbon nanofillers showed possibilities of improving the performance of epoxy to some extent, however, there is a necessity for better design and development of epoxy nanocomposites for enhanced performance. Tailoring the performance of nanocomposites was found to be largely dependent on the dispersion as well as the directional orientation of nanofillers in the matrix.

From the above perspective, aligned carbon nanofiber (CNF)/epoxy nanocomposite was fabricated, and the fracture, tribological, conductivity as well as other multi-functionalities was investigated. Initially, the alignment of CNFs inside epoxy was carried out using an AC electric field, followed by the investigation of their dispersion and orientation.

The analysis of the tensile, compressive, and thermomechanical properties of random and aligned nanocomposites revealed that the mechanical properties improved with CNF addition and their longitudinal alignment. The nonlinear tensile responses of nanocomposites were accurately captured by the finite element analysis of a three-dimensional representative volume element (3D-RVE) model, which considered fiber structure, alignment, concentration, and loading condition.

The DC electrical conductivity and thermal conductivity of nanocomposites increased with CNF addition and alignment. Electrical conductivity of 0.6 wt% aligned nanocomposites enhanced by 7 and 2 orders of magnitude, while the thermal conductivity improved by 77% and 44% compared to pure epoxy and random nanocomposites, respectively, for the same filler content. Simple analytical models, micromechanics and fiber-fiber contact-based, were developed for the electrical conductivity prediction of polymer composites, which was validated with our experimental results as well as with the literature data.

The effect of CNF alignment on tribological behavior of epoxy nanocomposites was studied by carrying out friction and wear tests keeping the sliding direction normal to nanofiber orientation. At 1wt% CNF content, the aligned nanocomposites exhibited 25 and 7 times improvement in wear resistance compared to pure epoxy and random composites, while the friction coefficient reduced from 0.6 for pure epoxy to 0.44 and 0.24 for random and aligned composites, respectively.

The effect of through-thickness CNF alignment was also investigated further on the enhancement of mode-I, mixed mode, and mode-II fracture toughness of CNF/epoxy adhesive joints. The CNF alignment increased the fracture toughness under all modes of fracture (increased by 195%, 20%, and 31.5% for mode-I, mixed-mode, and mode-II, respectively), however, a more profound effect was observed under mode-I. The numerically predicted load-displacement responses for all joints matched satisfactorily with experimental findings.

Finally, the electromechanical responses of bulk nanocomposites and nano-adhesive joints were investigated. The nanocomposites showed excellent strain sensing capability at all CNF concentrations, however, the highest sensing capability was observed at 0.4 wt% CNF content. Moreover, the alignment of CNF was found to enhance the crack growth sensing capability of nano-adhesive joints.

Overall, aligned epoxy nanocomposites have been designed and fabricated with excellent mechanical, electrical, tribological, and fracture behavior along with damage sensing capability. The predictive models for mechanical and electrical properties have also been presented. The fabricated nanocomposites can be used as adhesives, coatings, and other load-bearing applications with non-destructive damage sensing capability.

सार

एपॉक्सी रेजिन कई इंजीनियरिंग अनुप्रयोगों जैसे संरचनात्मक कंपोजिट, चिपकने वाले और ट्राइबोलॉजिकल कोटिंग्स में सबसे अधिक उपयोग की जाने वाली बहुलक सामग्री में से एक बन गए हैं। यह उनके बेहतर चिपकने वाले गुणों, यांत्रिक शक्ति, रासायनिक प्रतिरोध और संशोधित करने की उनकी क्षमता के कारण है। इन लाभों के बावजूद, कुछ सीमाएं हैं जो एपॉक्सी के अधिक से अधिक उपयोग को प्रतिबंधित करती हैं। अत्यधिक क्रॉस-लिंक्ड संरचना और शुद्ध एपॉक्सी की भंगुरता खराब घर्षण और पहनने के प्रदर्शन में परिणाम देती है जो आदिवासी अनुप्रयोगों में इसके उपयोग को प्रतिबंधित करती है। इसके अलावा, एपॉक्सी की कम फ्रैक्चर बेरहमी से तेजी से दरार का प्रसार होता है, जो संरचनात्मक चिपकने के रूप में इसके उपयोग को सीमित करता है। कम चालकता सेंसर, कोटिंग्स और चिपकने वाले विभिन्न अनुप्रयोगों में इसके उपयोग को प्रतिबंधित करती है जहां विद्युत और तापीय चालकता फायदेमंद हो सकती है।

कार्बन नैनोफिलर्स के उपयोग ने कुछ हद तक एपॉक्सी के प्रदर्शन में सुधार की संभावनाएं दिखाईं, हालांकि, बेहतर प्रदर्शन के लिए एपॉक्सी नैनोकम्पोजिट के बेहतर डिजाइन और विकास की आवश्यकता है। नैनोकम्पोजिट्स के प्रदर्शन को सिलाई करना काफी हद तक फैलाव के साथ-साथ मैट्रिक्स में नैनोफिलर्स के दिशात्मक अभिविन्यास पर निर्भर पाया गया।

उपरोक्त दृष्टिकोण से, संरेखित कार्बन नैनोफाइबर (CNF) / एपॉक्सी नैनोकम्पोजिट का निर्माण किया गया था, और फ्रैक्चर, ट्राइबोलॉजिकल, चालकता के साथ-साथ अन्य बहु-कार्यात्मकताओं की जांच की गई थी। प्रारंभ में, एपॉक्सी के अंदर सीएनएफ का संरेखण एक एसी विद्युत क्षेत्र का उपयोग करके किया गया था, इसके बाद उनके फैलाव और अभिविन्यास की जांच की गई।

यादृच्छिक और संरेखित नैनोकम्पोजिट के तन्य, संपीड़ित और थर्मोमेकेनिकल गुणों के विश्लेषण से पता चला कि यांत्रिक गुणों में सीएनएफ जोड़ और उनके अनुदैर्ध्य संरेखण के साथ सुधार हुआ है। नैनोकम्पोजिट्स की नॉनलाइनियर तन्यता प्रतिक्रियाओं को त्रि-आयामी प्रतिनिधि मात्रा तत्व (3D-RVE) मॉडल के परिमित तत्व विश्लेषण द्वारा सटीक रूप से कैप्चर किया गया था, जिसे फाइबर संरचना, संरेखण, एकाग्रता और लोडिंग स्थिति माना जाता था।

CNF जोड़ और संरेखण के साथ नैनोकम्पोजिट्स की DC विद्युत चालकता और तापीय चालकता में वृद्धि हुई। 0.6 wt% संरेखित नैनोकम्पोजिट की विद्युत चालकता परिमाण के 7 और 2 आदेशों से बढ़ी है, जबकि समान भराव सामग्री के लिए शुद्ध एपॉक्सी और यादृच्छिक नैनोकम्पोजिट की

तुलना में तापीय चालकता में क्रमशः 77% और 44% का सुधार हुआ है। पॉलिमर कंपोजिट की विद्युत चालकता भविष्यवाणी के लिए सरल विश्लेषणात्मक मॉडल, माइक्रोमैकेनिक्स और फाइबर-फाइबर संपर्क-आधारित विकसित किए गए थे, जिसे हमारे प्रयोगात्मक परिणामों के साथ-साथ साहित्य डेटा के साथ मान्य किया गया था।

एपॉक्सी नैनोकम्पोजिट्स के जनजातीय व्यवहार पर सीएनएफ संरेखण के प्रभाव का अध्ययन घर्षण और पहनने के परीक्षण द्वारा किया गया था, जो स्लाइडिंग दिशा को नैनोफाइबर ओरिएंटेशन के लिए सामान्य रखता है। 1wt% CNF सामग्री पर, संरेखित नैनोकम्पोजिट्स ने शुद्ध एपॉक्सी और यादृच्छिक कंपोजिट की तुलना में पहनने के प्रतिरोध में 25 और 7 गुना सुधार का प्रदर्शन किया, जबकि शुद्ध एपॉक्सी के लिए घर्षण गुणांक 0.6 से घटकर 0.44 और यादृच्छिक और संरेखित कंपोजिट के लिए क्रमशः 0.24 हो गया।

सीएनएफ/एपॉक्सी चिपकने वाले जोड़ों के मोड-I, मिश्रित मोड, और मोड-II फ्रैक्चर बेरहमी की वृद्धि पर थ्रू-थिकनेस सीएनएफ संरेखण के प्रभाव की भी जांच की गई। CNF संरेखण ने फ्रैक्चर के सभी तरीकों के तहत फ्रैक्चर की कठोरता को बढ़ा दिया (क्रमशः 195%, 20% और मोड- I, मिश्रित-मोड और मोड- II के लिए 31.5% की वृद्धि), हालांकि, एक अधिक गहरा प्रभाव देखा गया। मोड- I। सभी जोड़ों के लिए संख्यात्मक रूप से अनुमानित लोड-विस्थापन प्रतिक्रियाएं प्रयोगात्मक निष्कर्षों के साथ संतोषजनक रूप से मेल खाती हैं।

अंत में, बल्क नैनोकम्पोजिट्स और नैनो-चिपकने वाले जोड़ों की इलेक्ट्रोमैकेनिकल प्रतिक्रियाओं की जांच की गई। नैनोकम्पोजिट्स ने सभी CNF सांद्रता में उत्कृष्ट तनाव संवेदन क्षमता दिखाई, हालांकि, उच्चतम संवेदन क्षमता 0.4 wt% CNF सामग्री पर देखी गई। इसके अलावा, सीएनएफ का संरेखण नैनो-चिपकने वाले जोड़ों की दरार वृद्धि संवेदन क्षमता को बढ़ाने के लिए पाया गया था।

कुल मिलाकर, संरेखित एपॉक्सी नैनोकम्पोजिट्स को उत्कृष्ट यांत्रिक, विद्युत, ट्राइबोलॉजिकल और फ्रैक्चर व्यवहार के साथ-साथ क्षति संवेदन क्षमता के साथ डिजाइन और निर्मित किया गया है। यांत्रिक और विद्युत गुणों के लिए भविष्य कहनेवाला मॉडल भी प्रस्तुत किया गया है। गैर-विनाशकारी क्षति संवेदन क्षमता के साथ गढ़े हुए नैनोकम्पोजिट का उपयोग चिपकने वाले, कोटिंग्स और अन्य लोड-असर अनुप्रयोगों के रूप में किया जा सकता है।

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List of Abbreviations

CNF	Carbon nanofiber
AC	Alternating current
RVE	Representative volume element
DC	Direct current
CNT	Carbon nanotube
GNP	Graphene nanoplatelet
SEM	Scanning electron microscopy
ADCB	Asymmetric double cantilever beam
DCB	Double cantilever beam
ENF	End notch flexure
CZM	Cohesive zone modeling
RSA	Random sequential adsorption
SW, MW	Single-walled, Multi-walled
SWR	Specific wear rate
PTFE	Polytetrafluoroethylene
PEEK	Polyether ether ketone
SENB	Single edge notch bending
NDT	Non-destructive testing
CFRP	Carbon fiber reinforced composite
GFRP	Glass fiber reinforced composite
MD	Molecular dynamics
AR	Aspect ratio
FEM	Finite element method
PBC	Periodic boundary conditions
DMA	Dynamic mechanical analyzer
ROM	Rule of mixtures
IPD	Inter-particle distance
SCF	Short carbon fiber
GF	Gauge factor