FATIGUE AND FRACTURE ANALYSIS OF GRAPHENE AND CNT EPOXY NANOCOMPOSITES

Thesis submitted in partial fulfilment for

the award of degree

Doctor of Philosophy

by

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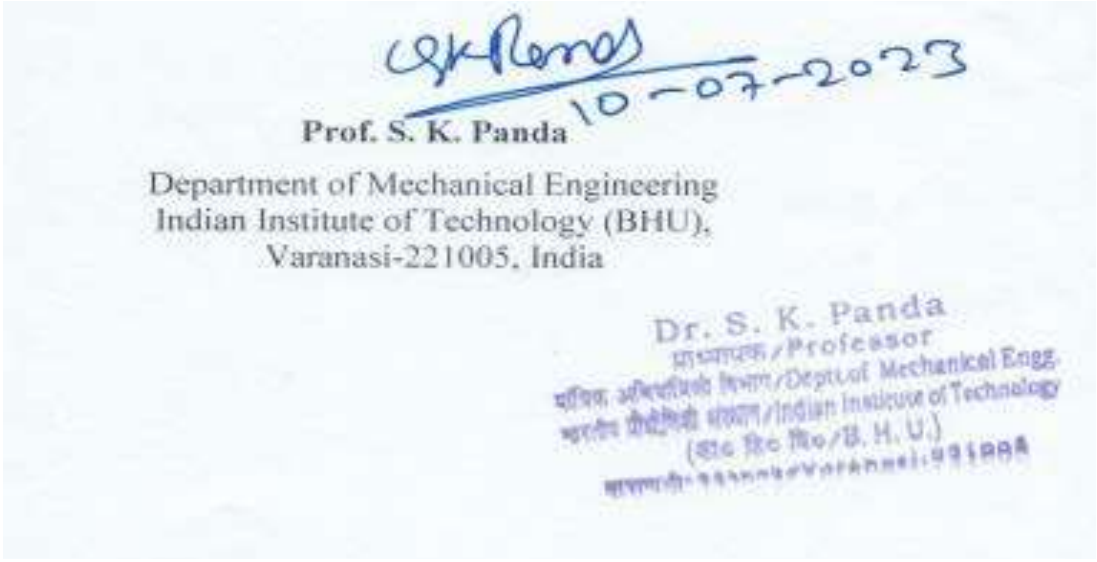

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ABSTRACT

Epoxy has been extensively studied for structural composites in industries such as aerospace, automotive, marine, construction, shipbuilding, and electronics. Its cross-linked structure imparts desirable properties like high glass transition temperature, stiffness, creep resistance, dimensional stability, and chemical resistance. However, uncured epoxy exhibits poor mechanical, chemical, and thermal properties. Curing with suitable agents forms a strong 3-D cross-linked structure but diminishes strength, fracture toughness, and fatigue resistance. Researchers have explored various nanoparticles and microparticles for reinforcement, with graphene nanoplatelets (GNP) emerging as superior nanofillers. Yet, challenges in exfoliation, dispersion, orientation, and interfacial bonding hinder graphene's full potential, thus limiting the structural applications of graphene-reinforced epoxy.

This study aimed to overcome challenges associated with the dispersion and spatial orientation of GNP to enhance the benefits of GNP epoxy nanocomposites. A mathematical model is developed to optimize the alignment parameters of GNP and magnetite ferric oxide (Fe_3O_4)-GNP applying a weak DC magnetic field (0.05T), considering rotation, translation, migration, and slackening mechanisms of the nanoparticle in the epoxy. Optimisation of magnetic field, epoxy viscosity, and time required to complete all mechanisms before gelation of epoxy has been carried out to fabricate a highly aligned GNP nanocomposite.

The characteristic magnetic, viscosity, and hydrodynamic parameters required by the mathematic model are determined experimentally. The Fe_3O_4 synthesized by solve-thermal and attaching them to the GNP surface to increase its magnetic susceptibility in order to utilize the model's suggested optimized magnetic parameters. The Morphology, microstructure, and magnetic properties of GNP, Fe_3O_4, and Fe_3O_4-GNP nanoparticles have been characterized by

XRD, FTIR, Raman spectroscopy, TGA, AFM, XPS, BET, TEM, SEM, EDXMA, and VSM. A highly aligned Fe_3O_4-GNP nanocomposite is fabricated at 0.05T magnetic field and 40Pa-s dynamic viscosity of epoxy, as evident from the aforementioned characterization methods, DSC, optical microscopy, and studying the fracture surface morphology confirmed the highly aligned alignment Fe_3O_4-GNP epoxy nanocomposite.

Furthermore, our investigation focuses the influence and comparative impact of alignment, as well as wt% loading, of both nanoparticles GNP and Fe_3O_4-GNP on various mechanical properties, such as tensile and compressive strength, K_{IC}, G_{IC}, $CTOD_c$, crack propagation, and fracture mechanisms. This study utilizes AFM analysis to examine the roughness parameters of fractured surfaces. The conclusion asserts that nanoparticle alignment increases the likelihood of primary crack fronts interaction and results in a change in a stress state, deflection, branching, and bifurcation, ultimately leading to increased crack growth resistance.

Moreover, being a leading cause of catastrophic failure in structural materials, fatigue is the primary focus of this present study, which aims to investigate the fatigue thresholds (ΔK_{th} and ΔG_{th}) fatigue crack growth rate (FCGR) resistance, and the contribution of toughening mechanisms under cyclic fatigue loading in the nanocomposites. The investigation concludes that increasing the weight percentage (wt%) leads to higherΔK_{th}, ΔG_{th} and FCGR resistance, with alignment having a more significant impact. Moreover, the Paris law constants (C, C', and m) exhibit a decrease. Through fractography and roughness analysis, it has been determined that alignment enhances the probability of interaction among primary crack fronts, leading to tip shielding, crack bifurcation, deflection, local mixed mode, striation marks, shear yielding, crack twisting and tilting, micro-crazing, void nucleation, nanoparticle debonding, pullout, and cavitation. Consequently, the alignment significantly enhances resistance to FCGR.

As part of this Ph.D. study, we also investigated the fracture energy of CNT/epoxy nanocomposites using a mathematical model. The characteristics of the debonding process zone

involving macro-scale, micro-scale and nano-scale mechanisms along CNT interface influence the fracture behaviour of nanocomposites and their structural integrity. In current study, a multi-scale and multi-mechanism modelling approach with a cylindrical RVE comprising CNT, interphase and matrix is developed to assess such damage progression and energy dissipation occurring at the nano-scale. The model considers the dominant damaging phenomena emerging in CNT/epoxy nanocomposites, i.e., CNT debonding with an interphase zone around nanoparticles, cavitation, and plastic deformation of nanovoids. Enhancement of fracture toughness with the weight fraction of CNT is investigated with a qualitative variation of geometric and mechanical properties of the interphase, cavitation and plastic yielding adopting strain energy release rate procedures. The fracture energy is shown to be critically influenced by the stiffness ratio of interphase to the matrix, interphase thickness, and hardening exponent. The Model is validated using experimental and analytical data.

DEDICATION

I dedicate this thesis to **Shri Vishwanath Temple (VT), BHU,** the eternal source of inspiration and wisdom, guiding my academic journey beyond earthly bounds. Its cosmic presence symbolizes knowledge's eternal cycle, providing unwavering strength and insight for my quest.

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Anupam Tiwari

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List of Abbreviations

Abbreviation	Definition
AC	Alternating Current
AFM	Atomic Force Microscopy
ASTM	American Society for Testing and Materials
BADGE	Bisphenol A Diglycidyl Ether
BET	Brunauer–Emmett–Teller
CNF	Carbon Nanofibres
CNT	Carbon Nanotubes
CO	Carbon Monooxide
COD	Crack Opening Displacement
CODc	Critical Crack Opening Displacement
CQD	Carbon Quantum Dots
CT	Compact Tension
CTOD	Crack Tip Opening Displacement
CTODc	Critical Crack Tip Opening Displacement
CVD	Chemical Vapor Deposition
DC	Direct Current
DD	Double Distilled
DGEBA	Diglycidyl Ether Bisphenol A
DGEBF	Diglycidyl Ether Of Bisphenol F
DPZ	Debonding Process Zone
DSC	Differential Scanning Calorimetry
EDM	Electrical Discharge Machining
EDS	Energy Dispersion Spectroscopy
EDXMA	Energy-Dispersive X-Ray Microanalysis
FCGR	Fatigue Crack Growth Rate
FRP	Fibre-Reinforced Polymer
FTIR	Fourier-Transform Infrared Spectroscopy
GNP	Graphene Nanoplatelets
GNS	Graphene Nanosheets
HRVM	High-Resolution Video Monitoring
MAP	Magnetophoretic
MWCNT	Multi-Walled Carbon Nanotubes
PE	Polyethylene
PECVD	Plasma-Enhanced Chemical Vapor Deposition
PMMA	Poly Methyl Methacrylate
PVA	Polyvinyl Alcohol
RMS	Root-Mean-Square
RTV	Room Temperature Vulcanization
RVE	Representative Volume Elements
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscopy

SPM	Scanning Probe Microscopy
SWCNT	Single-Walled Carbon Nanotubes
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TGIC	Triglycidyl Isocyanurate
TGMDA	Tetraglycidyl Methylene Dianiline
THF	Tetrahydrofuran
UTM	Universal Testing Machine
VSM	Vibrating Sample Magnetometry
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

List of Nomenclature

Symbol	Definition
$\overline{m}_{eff}$	*effective dipole magnetic moment*
F_m	*attracting magnetic force*
Ω	*sub-domain $\Omega \rightarrow$ n (=CNT), i (=interphase), m (=matrix)*
a, b	*use as subscript and superscript, a→ after, b→ before CNT debonding*
Δa	*change in crack length*
C_x, C_y, C_z	*magnetic field components' direction cosines*
$A_\Omega, B_\Omega,$	*coefficients*
$\lambda_\Omega, \mu_\Omega$	*Lame constants, shear modulus*
v_Ω	*Poisson's ratio*
v_{nc}	*Poisson's ratio of nanocomposite*
v_m	*migration velocity of the nanoparticles*
$u, u_{rr,\Omega}$	*radial displacements*
μ_m, μ_0	*magnetic permeability of epoxy and air*
$\xi_a, \zeta_a,$ ξ_b, ζ_b	*an assumed factor*
$r, r_n, r_i,$ r_m, r_c, r_p	*radii of RVE element, CNT, interphase, matrix, cavity and plastic zone*
L_{xx}, L_{yy}, L_{zz}	*depolarization factor along the respective axis of the ellipsoidal*
l_n	*length of CNT*
V	*volume of RVE*
V_f	*volume fraction of CNT in the RVE*
$\hat{V}$	*volume of single nanoparticles*
P	*applied load at the outer lateral area of RVE*
H	*global stress concentration tensor (gsct)*
$\overline{H}_0$	*applied DC magnetic field*
$\overline{H}^-$	*induced magnetic intensity within the Fe_3O_4-GNP*
$\hat{\sigma}, \hat{\varepsilon}$	*stress and strain Field*
σ, ε	*average stress and strain applied at the macro-scale in RVE*
$\sigma_{rr}, \varepsilon_{rr}$	*mean radial stress and strain*
$\sigma_{\theta\theta}, \varepsilon_{\theta\theta}$	*mean angular stress and strain*
$\bar{\sigma}_P, \bar{\varepsilon}_P$	*equivalent plastic stress and strain*
$S_{ij}^p, \varepsilon_{ij}^p$	*deviatoric stress component of the plastic stress and strain tensor where$(i, j = r, \theta, z)$*
λ	*stiffness ratio of interphase and matrix material*
t	*interphase thickness*
t_r	*rotating time*
t_c	*Chaining time*
t_m	*migration time*

t_{s-r}	*slacken rotation time*
t_{s-t}	*slacken translation time*
$\overline{T}^{m}$	*magnetic alignment torque*
$\bar{T}^{H}$	*hydrodynamic torque*
λ_p	*von Mises yield criterion constant*
δ_{ij}	*Kronecker delta*
σ_{kk}	*hydrostatic stress component*
n, n_{Ω}	*hardening exponents*
σ_Y, ε_Y	*yield stress and strain*
C_{Ω}, D_{Ω}	*constant*
$*$	*superscript → elastic region*
σ_{cr}	*critical stress around CNT*
$\sigma_{11}, \sigma_{22}, \sigma_{33}$	*principal stresses*
ξ_1, ξ_2, ξ_3	*assume constant*
γ_i	*interface fracture energy*
$K_{I,nc}$	*Mode I stress intensity factor of nanocomposite*
K_{IC}, ΔK_{IC}	*stress intensity factor and range*
ΔK_{th}, ΔG_{th}	*Fatigue thresholds*
k_r	*rotational friction coefficient of the particle's geometry*
k_t	*translational friction coefficient*
k_B	*Boltzmann constant*
K_s	*ellipsoidal form factor*
σ_n	*average stress at the nano-scale*
$\bar{\sigma}_{rr}$	*effective radial stress distribution in the DPZ*
$G_{Ic,nc}, G_{Ic,m},$ ΔG_i	*Mode I critical energy release rate of nanocomposite, neat epoxy and contribution of individual toughening mechanism, respectively.*
G_{IC}, ΔG_{IC}	*strain energy release rate and range*
$\Delta G_{cd}, \Delta G_{db},$ $\Delta G_{pull}, \Delta G_{cv},$ $\Delta G_{SB}, \Delta G_{py}$	*Mode I critical energy release rate contribution by crack deflection, interfacial debonding, CNT pull-out, cavitation, shear band formation and plastic deformation (or yielding) of nanovoids, respectively.*
ϕ	*angle with the direction of crack front*
θ_i, θ_f	*initial and final angular position of the easy axis*
θ_{s-r}	*slacken angle*
ρ	*radial distance from the crack tip*
ρ^*	*radius of DPZ at* $\phi = {}^{\pi}/_{2}$
η	*dynamic viscosity of the epoxy*
$\Delta U_i, \Delta U_{db},$ $\Delta U_{cv}, \Delta U_{py}$	*Strain energy of individual mechanism, debonding, cavitation and plastic deformation*
U_m	*magnetophoretic mobility of nanoparticles*
$w_i, w_{db},$	*Strain energy density of individual mechanism, debonding, cavitation and plastic deformation*

$w_c,\ w_{py}$	
Ψ	*a constant factor*
$\bar{\chi}_V, \bar{\chi}_{V,yy}, \bar{\chi}_{V,zz}$	*tensor magnetic effective volume susceptibility, along x and y axis*
$\bar{\chi}_{V,II}\ , \bar{\chi}_{V,\perp\perp}$	*tensor magnetic effective volume susceptibility parallel and perpendicular to the particle's easy axis*
$\bar{\chi}_{V,a}$	*volume anisotropic susceptibility*
x,y,z	*Axis*
Θ	*an assumed factor*

Preface

Researchers are exploring emerging materials to enhance engineering systems by improving performance, reducing components, minimizing maintenance, achieving weight reduction, enhancing corrosion resistance, increasing design flexibility, improving fatigue resistance, leveraging thermal and electrical properties, enhancing impact resistance, achieving cost-effectiveness, ensuring biocompatibility, and enhancing reliability. Composites combine distinct phases to retain individual qualities while exhibiting superior properties. Nanocomposites are a specific focus in this thesis on materials.

Chapter 1 lays the groundwork for GNP epoxy nanocomposites research. It explores the basics of nanocomposites, their applications, and the objective of developing a GNP epoxy nanocomposite. The chapter outlines the research aims, such as characterizing mechanical properties and exploring potential applications. It also emphasizes that this study serves as a basis for future research, providing a starting point for advancements in nanocomposites and expanding scientific knowledge.

Chapter 2 provides a detailed analysis of carbon nanomaterials epoxy composites. It includes an overview of epoxy, its classification, and structure. The chapter explores various studies on the use of nanomaterials for nonreinforcement purposes, with a focus on GNP and carbon nanotubes (CNT). The properties, applications, fabrication process, and real-world implementation of nanocomposites are extensively examined in this chapter.

Chapter 3 focuses on developing a mathematical model to understand the alignment mechanisms of GNP and Fe_3O_4-GNP in an epoxy matrix under a magnetic field. The model considers rotational, translational, chaining, migration, and slackening motions. Key alignment parameters, such as magnetic field strength and epoxy viscosity, are optimized to achieve a fully

cured nanocomposite with aligned Fe_3O_4-GNP particles. Surprisingly, a weaker magnetic field is found to be sufficient for aligning Fe_3O_4-GNP, unlike GNP, revealing interesting alignment requirements.

Chapter 4 focuses on the synthesis of Fe_3O_4-GNP nanoparticles by attaching Fe_3O_4 to GNP surfaces. The nanoparticles are extensively characterized using techniques such as XRD, FTIR, Raman spectroscopy, TGA, DSC, AFM, XPS, BET, TEM, SEM, EDXMA, and VSM. Aligned Fe_3O_4-GNP nanocomposites are successfully fabricated by optimizing parameters, and their alignment within the epoxy matrix is confirmed through characterization methods, optical microscopy, and fracture surface analysis. The investigation validates the suitability of these nanocomposites for various applications.

Chapter 5 focuses on evaluating the implications of incorporating aligned Fe_3O_4-GNP epoxy nanocomposites. The study analyzes key parameters such as crack growth resistance, K_{IC}, G_{IC}, $CTOD_c$, and fracture mechanisms, comparing them with GNP nanocomposites. Through optical and AFM imaging techniques, the investigation provides valuable insights into fracture toughness mechanisms, showcasing the significant potential of aligned Fe_3O_4-GNP reinforced nanocomposites in various engineering applications.

Chapter 6 extensively investigates the fatigue thresholds (ΔK_{th} and ΔG_{th}) and fatigue crack growth rate (FCGR) resistance of GNP and aligned Fe_3O_4-GNP nanocomposites. The incorporation of these additives has shown remarkable improvements in mitigating fatigue crack growth and enhancing overall fatigue lifespan of the epoxy material. Aligned Fe_3O_4-GNP nanoparticles exhibit exceptional fatigue properties, surpassing those of GNP nanocomposites. This finding underscores the significant potential of aligned Fe_3O_4-GNP nanocomposites in applications requiring superior fatigue resistance.

In Chapter 7, a comprehensive multi-scale and multi-mechanism mathematical framework for CNT/epoxy nanocomposites' fracture characteristics is presented. The model incorporates multiple scales and mechanisms, including debonding, cavitation, and plastic deformation of nanovoids. It predicts enhanced fracture energy and shows good agreement with experimental and analytical results. The model's performance is encouraging, demonstrating qualitative agreement with existing literature data.

Chapter 8 concludes the research with a comprehensive summary of the findings and recommendations for future work. It consolidates the key conclusions and proposes avenues for further exploration and advancement in the field, serving as a guide for future investigations.

The chapters enhance the understanding and optimization of nanocomposites, emphasizing aligned Fe_3O_4-GNP reinforced materials for advanced engineering applications. The exploration of fracture characteristics, including a mathematical model for CNT/epoxy nanocomposites, provides valuable insights and accurate predictions for fracture behavior.