Role of Nanofillers in Improving Delamination Resistance of Laminated Composites

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Abstract: Laminated composites, widely used in aerospace, automotive, and marine applications, are susceptible to delamination, a primary failure mode that compromises structural integrity. Nanofillers such as carbon nanotubes (CNTs), graphene nanoplatelets (GNPs), carbon nanofibers (CNFs), and nanoclays have been extensively investigated for enhancing interlaminar properties and delamination resistance. This review synthesizes recent studies on the incorporation of nanofillers into epoxy-based fiber-reinforced polymers (FRPs), focusing on mechanisms like crack bridging, pull-out, and deflection. Experimental and modeling approaches reveal improvements in mode I and II fracture toughness (G_Ic and G_IIc) by 30-140%, fatigue life extensions up to fivefold, and reductions in delamination areas by 20-50%. Functionalization and optimal loadings (0.1-4 wt.%) are critical to avoid agglomeration. Hybrid multi-scale reinforcements show synergistic effects, particularly in carbon fiber/epoxy systems. Challenges include dispersion uniformity and rate-dependent behavior, with future directions emphasizing multiscale modeling and environmental durability assessments. This paper provides insights for designing damage-tolerant composites.

Keywords: Material Science, Polymers, Composites, Biomaterials, Metallurgy

Introduction

Laminated composites, consisting of stacked plies of fiber reinforcements (e.g., carbon, glass, or aramid) embedded in a polymer matrix like epoxy, offer high strength-to-weight ratios and design flexibility. However, their layered architecture makes them vulnerable to interlaminar stresses, leading to delamination—a separation between plies that initiates from manufacturing defects, impact events, or cyclic loading. Delamination reduces compressive strength, promotes crack propagation, and can cause catastrophic failure, limiting applications in high-load environments.

To mitigate delamination, strategies such as through-thickness reinforcements (e.g., z-pinning, stitching) have been employed, but they often compromise in-plane properties. Nanofillers, with dimensions below 100 nm, emerge as a promising alternative due to their exceptional mechanical properties (e.g., CNTs with tensile strength >100 GPa) and ability to reinforce at the nanoscale without significantly altering macrostructure. Nanofillers enhance matrix toughness, improve fiber-matrix interfacial adhesion, and create tortuous crack paths, thereby boosting delamination resistance.

Key nanofillers include CNTs, GNPs, CNFs, nanoclays, and silica nanoparticles. Studies demonstrate that low loadings (0.1-2 wt.%) can increase interlaminar fracture toughness by 50-100% through mechanisms like bridging and energy dissipation. For instance, graphene variants have shown up to 67% G_Ic improvement in CFRPs. Multi-scale approaches combining nano- and micro-fillers yield synergistic enhancements in impact tolerance.mdpi.com

This review examines the role of nanofillers in improving delamination resistance, drawing from experimental, numerical, and stochastic modeling studies. It covers materials, mechanisms, quantitative improvements, and challenges, aiming to guide optimized composite design for enhanced durability.

Literature Review

The literature underscores nanofillers' efficacy in addressing delamination in FRPs. Carbon-based nanofillers dominate due to their conductivity and strength, while inorganic ones like nanoclays provide cost-effective toughening.

CNTs reinforce epoxy matrices by bridging cracks and deflecting paths, as seen in glass fiber/epoxy laminates where CNT additions improved mode I toughness considerably. Stochastic multi-scale modeling accounts for CNT agglomeration and waviness, predicting toughness enhancements aligned with experiments (e.g., 48-143% in prior mode I/II studies). Functionalized CNTs in glass/epoxy interlayers achieved 95% mode I and 109% mode II fracture toughness gains via the interlayer approach, outperforming matrix dispersion.sciencedirect.cometda.libraries.psu.edu

Graphene nanofillers, such as reduced graphene oxide (rGO) and carboxyl-functionalized GNPs (HDPlas), enhance static and fatigue delamination resistance in CFRPs. At 0.5 wt.%, rGO increased G_Ic by 36% and fatigue threshold by 24%, while HDPlas yielded 67% for both, extending fatigue life fivefold through pull-out and bifurcation. GNPs in epoxy showed 53% mode I toughness and reduced crack growth rates by two orders.pmc.ncbi.nlm.nih.govmdpi.com

Nanoclays at 4 wt.% in titanium-Kevlar/jute fiber metal laminates improved fatigue life by 37.5% and reduced crack growth by suppressing propagation via energy dissipation. Electrospun nano-interlayers (e.g., polycarbonate nanofibers) raised microcracking and delamination stresses by 8-10% in [30/−30/90] laminates.4spepublications.onlinelibrary.wiley.comsciencedirect.com

Multi-scale toughening with CNFs and short carbon fibers (SCFs) in CFRPs synergistically boosted mode II toughness and reduced impact damage areas by 24%, with CAI strength up 29%. Electrophoretic deposition of CNTs on carbon fibers enhanced flexural strength and ILSS, improving delamination resistance under impact.sciencedirect.comresearchgate.net

Reviews highlight consistent ILSS gains (20-61%) with functionalized MWCNTs and GNPs, fatigue life extensions (3-1200x), and delamination reductions (up to 50%) via interleaves. However, high graphene in nanofibers may not always enhance toughness due to agglomeration.mdpi.comdoi.org

Materials and Methods

This section outlines a synthesized framework from reviewed studies for investigating nanofiller effects on delamination resistance.

Materials

- Matrix: Epoxy resins (e.g., DGEBA with amine hardeners).
- Fibers: Unidirectional carbon (T300) or glass fibers (E-glass) at 50-70 vol.%.
- Nanofillers: MWCNTs (10-50 nm diameter, functionalized with COOH or NH2), GNPs (5-50 nm thick), CNFs (70-300 nm), nanoclays (montmorillonite), at 0.1-4 wt.%.
- Functionalization: Silane coupling (APTES) or plasma treatment for dispersion.

Sample Preparation

- Dispersion: Three-roll milling or ultrasonication (500 W, 30 min) for nanofillers in epoxy, followed by degassing.

- Laminates: Vacuum-assisted resin transfer molding (VARTM) or hand lay-up with 16-24 plies; interleaves via spraying or electrophoretic deposition.
- Curing: 120-180°C under 1-7 bar pressure for 2-4 hours.

Testing Procedures

- Interlaminar Fracture: DCB (ASTM D5528) for mode I G_Ic; end-notched flexure (ENF) for mode II G_IIc; loading rates 1-5 mm/min.
- Fatigue: Cyclic DCB tests (ASTM D6115) at R=0.1, 5 Hz; Paris law for da/dN vs. ΔG.
- Impact and CAI: Drop-weight impact (ASTM D7136) at 10-50 J; compression after impact (ASTM D7137).
- Characterization: SEM/TEM for fractography; DIC for strain; FTIR/XPS for interfaces.
- Modeling: Stochastic multi-scale FEA (Abaqus) with cohesive zones; random variables for CNT morphology.

Data analysis includes modified beam theory for G, Weibull statistics for failure, and statistical convergence (80-170 samples).

Results and Discussion

Enhancements in Fracture Toughness

Nanofillers significantly boost interlaminar fracture toughness. In CNT-reinforced glass/epoxy, mode I toughness increased considerably, with modeling showing 50-100% gains via bridging. Graphene in CFRPs: HDPlas at 0.5 wt.% raised G_Ic from 0.42 to 0.70 kJ/m² (67%), with rGO at 36%. Interlayer CNTs in glass/epoxy yielded 95% mode I and 109% mode II improvements.sciencedirect.com

Table 1: Fracture Toughness Improvements

Nanofiller	System	Mode I Improvement (%)	Mode II Improvement (%)	Reference
CNTs	Glass/Epoxy	95	109	[22]
HDPlas GNP	CFRP	67	-	[21]
CNFs + SCFs	CFRP	Synergistic (steady-state)	Greater-than-additive	[25]
Nanoclay	FML	-	-	[9]
Electrospun	Laminate	8.4 (microcracking)	8.1 (delamination)	[23]

Fatigue and Delamination Resistance

Fatigue threshold G_Ith rose 67% with HDPlas, extending life fivefold. Nanoclay (4 wt.%) improved fatigue life 37.5% in FMLs. Multi-scale fillers reduced delamination areas by 24% and CAI by 29%.pmc.ncbi.nlm.nih.gov

Mechanisms

Crack bridging and pull-out dominate; HDPlas shows extensive pull-out, creating tortuous paths. Stochastic variations in CNT properties affect energy absorption. Functionalization enhances adhesion, shifting failure to cohesive.pmc.ncbi.nlm.nih.gov

Challenges

Agglomeration at high loadings reduces benefits; e.g., excessive graphene in nanofibers may hinder toughness. Rate effects and environmental factors need further study.doi.org

Conclusion

Nanofillers play a pivotal role in enhancing delamination resistance in laminated composites through toughening mechanisms and interfacial improvements. CNTs, GNPs, and hybrids offer

30-140% fracture toughness gains and substantial fatigue life extensions, with optimal designs involving functionalization and low loadings. Multi-scale modeling aids prediction, but dispersion challenges persist. Future research should focus on scalable fabrication and long-term performance for advanced applications.

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