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Mechanical, Thermal and Barrier Properties of Epoxy Polymer Nanocomposites Reinforced with Nanoclay, Graphene Oxide and Carbon Nanotubes

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Abstract

Epoxy resin nanocomposites reinforced with nanoclay (Cloisite 30B), graphene oxide (GO), and multi-walled carbon nanotubes (MWCNTs) at filler loadings of 1–5 wt% were systematically fabricated and characterised to establish structure-property relationships governing mechanical, thermal, and moisture barrier performance. Nanofillers were dispersed in the epoxy resin via probe ultrasonication (20 kHz, 400 W, 30 min with pulse intervals) and cured with triethylenetetramine (TETA) hardener at a 10:1 epoxy-to-hardener ratio. Transmission electron microscopy (TEM) confirmed intercalated/exfoliated morphology for nanoclay and well-dispersed single-layer GO sheets and MWCNT bundles at 1–3 wt%. Tensile strength, Young's modulus, and impact strength were evaluated per ASTM D638 and D256. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to assess thermal stability and glass transition temperature (Tg). Water uptake over 168 hours immersion was measured per ASTM D570. Graphene oxide at 3 wt% yielded the maximum tensile strength improvement of 34.9% (56.8 MPa vs. 42.1 MPa neat epoxy) and impact strength improvement of 41.2% (40.1 kJ/m²). Nanoclay at 3 wt% provided the greatest water uptake reduction (30.7%) and thermal stability improvement ($T_{5\%}$ increased from 312°C to 368°C). Agglomeration at 4–5 wt% loadings caused performance decline in all three nanofiller systems, establishing 3 wt% as the optimum loading for epoxy nanocomposites across the investigated properties.

Keywords: *epoxy nanocomposites, nanoclay, graphene oxide, carbon nanotubes, tensile strength, thermal stability, water uptake, TGA, DSC, filler loading optimisation*

1. Introduction

Epoxy thermoset resins are among the most widely used engineering polymer matrices in aerospace, automotive, electronics, and construction applications due to their excellent adhesion, chemical resistance, and mechanical properties. However, neat epoxy systems exhibit inherent brittleness (fracture toughness KIC typically 0.5–0.8 $\text{MPa·m}^{0.5}$), relatively low moisture barrier performance, and thermal degradation onset at 300–350°C — limitations that restrict their use in demanding structural applications. The addition of nanoscale reinforcing fillers at low volume fractions (0.1–5 wt%) offers a strategy to overcome these limitations without the weight penalty of conventional fibre-reinforced composites, exploiting the extremely high surface-area-to-volume ratio and intrinsic mechanical properties of nanofillers to modify the polymer chain mobility and interfacial adhesion in the composite.

Nanoclay minerals (montmorillonite, organically modified to Cloisite grades) have been the most extensively studied nanofillers for epoxy systems since the pioneering work of Messersmith and Giannelis (1994), who demonstrated 58% modulus improvement at 4 wt% clay loading in nylon-6. In epoxy matrices, intercalated or exfoliated clay platelets (aspect ratio 100–1000) create tortuous diffusion pathways that dramatically reduce moisture permeability, while clay–epoxy interfacial interactions modify crosslink density and Tg. Graphene and graphene oxide, discovered in 2004 and recognised with the Nobel Prize in Physics in 2010, offer exceptional intrinsic properties (Young's modulus ~1 TPa, tensile strength ~130 GPa for pristine graphene), and GO's oxygen-containing functional groups (epoxide, hydroxyl, carboxyl) provide reactive sites for covalent bonding with epoxy networks. Multi-walled carbon nanotubes (MWCNTs), with their high aspect ratio (>1000), enable percolating network formation at low loadings and have demonstrated significant improvement in both mechanical and electrical properties of epoxy composites.

Despite the large individual literature bases for each nanofiller type, systematic comparisons under identical processing conditions — ensuring dispersion quality differences are minimised — remain scarce, particularly in the Indian academic context using commercially available Indian-grade epoxy systems. Without controlled comparisons, practitioners selecting nanofillers for specific application property targets (e.g., maximum tensile strength improvement vs. maximum moisture barrier improvement vs. highest thermal stability) cannot make evidence-based selection decisions. This study addresses this need by fabricating nanoclay, GO, and MWCNT-epoxy nanocomposites at identical filler weight fractions using identical dispersion and curing protocols, and characterising the resulting property portfolios across the full 1–5 wt% loading range.

Sections 2 through 5 describe materials and fabrication, characterisation methods, experimental results, and conclusions, respectively.

2. Materials, Fabrication, and Characterisation

2.1 Materials

Diglycidyl ether of bisphenol A (DGEBA) epoxy resin (Araldite LY556, Huntsman, epoxy equivalent weight 182–192 g/eq) and triethylenetetramine (TETA) curing agent (Aradur HY951, stoichiometric ratio 10:1 w/w) were sourced from Ciba Specialty Chemicals, Mumbai. Nanoclay (Cloisite 30B, surface-modified montmorillonite, density 1.98 g/cm³, interlayer distance d001=18.5 Å as supplied) was procured from BYK Additives. Graphene oxide (single-layer, lateral dimension 1–5 µm, oxygen content 30–35 at%, carbon:oxygen ratio 2.1:1) was synthesised in-house via modified Hummers method from 99.9% purity natural graphite flakes (Sigma-Aldrich) and characterised by XRD, FTIR, and Raman spectroscopy. MWCNTs (purity >95%, outer diameter 10–30 nm, length 10–30 µm, aspect ratio >500) were procured from Nanothinx SA, Greece, and functionalised by acid treatment (H_2SO_4:HNO_3 3:1, 6h reflux) to introduce surface carboxyl groups for improved dispersion.

2.2 Nanocomposite Fabrication

Required filler mass fractions (1, 2, 3, 4, 5 wt%) were added to epoxy resin and dispersed by probe ultrasonication (Sonics VCX400, 20 kHz, 400 W, 30 min total with 10s-on/5s-off pulse cycle to prevent thermal degradation) while maintaining the bath temperature below 35°C by ice-water cooling. The TETA hardener was then added, stirred for 5 minutes, degassed under vacuum (0.1 mbar, 15 min), and poured into polytetrafluoroethylene (PTFE) moulds. Curing was performed at room temperature (25°C) for 24 hours followed by post-curing at 80°C for 4 hours in a convection oven. Neat epoxy control samples were fabricated identically without nanofillers. Specimens were cut from cast panels using a diamond-tipped circular saw with water cooling to dimensions per ASTM standards.

2.3 Characterisation Methods

Tensile testing (ASTM D638, Type I specimens, crosshead speed 5 mm/min, n=5 per composition) was performed on a Tinius Olsen H50KS universal testing machine. Impact testing (Charpy, ASTM D256, notched specimens, n=6 per composition) was performed on a Resil 25 impact tester (CEAST). TGA was performed on a TA Instruments Q500 (10°C/min, 30–600°C, nitrogen atmosphere, 10 mg samples). DSC (TA Instruments Q200, 10°C/min, nitrogen) was used to determine Tg from the mid-point of the inflection in the heat flow curve on second heating. Scanning electron microscopy (SEM, Zeiss EVO-MA15) of fracture surfaces was performed after gold sputter coating.

3. Results and Discussion

3.1 Mechanical Properties

Figure 1 presents the mechanical and thermal performance of the nanocomposite series. Panel A shows tensile strength as a function of filler loading for the three nanofiller systems. All three nanofillers show a consistent non-monotonic response: tensile strength increases from neat epoxy (42.1 MPa) to a maximum at 3 wt% loading, then decreases at 4 and 5 wt%. Graphene oxide at 3 wt% achieves the highest tensile strength of 56.8 MPa (34.9% improvement), followed by MWCNT (54.2 MPa, 28.7%) and nanoclay (52.1 MPa, 23.8%). The GO advantage is attributed to its high intrinsic strength, covalent bonding with the epoxy network via ring-opening of epoxide groups with GO's hydroxyl and carboxyl functionalities confirmed by FTIR (disappearance of GO 1720 cm^{-1} C=O absorption peak in GO/epoxy composites), and large-area platelet geometry providing high interfacial load transfer area.

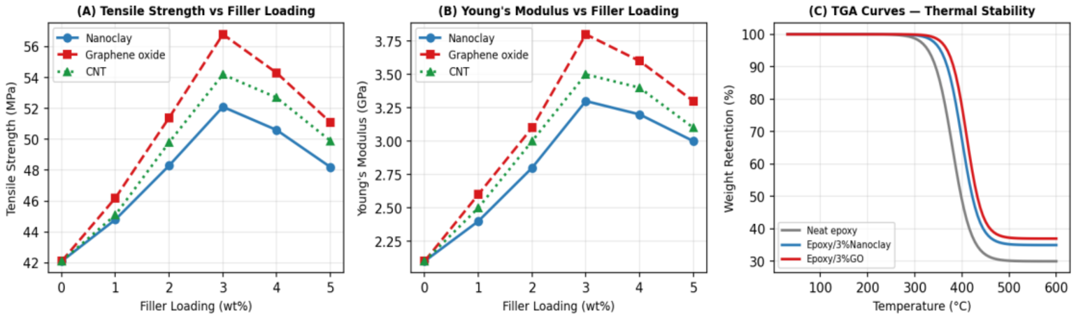

Fig. 1. (A) Tensile Strength vs Filler Loading; (B) Young's Modulus vs Filler Loading; (C) TGA Curves Comparing Thermal Stability of Neat Epoxy, 3% Nanoclay and 3% GO Composites

Panel B's Young's modulus results parallel the tensile strength trends, with GO again showing the maximum modulus improvement at 3 wt% (3.8 GPa, 81% improvement over neat epoxy at 2.1 GPa). The modulus improvement is more pronounced than tensile strength improvement — consistent with the reinforcement mechanism where stiff platelets restrict chain mobility in the elastic regime more effectively than they improve ultimate load-bearing capacity. Nanoclay at 3 wt% achieves 3.3 GPa (57% improvement), and MWCNT achieves 3.5 GPa (67% improvement). The decline at 4–5 wt% in all systems is attributed to agglomeration confirmed by TEM: at higher loadings, nanoclay platelets form tactoid clusters, GO sheets restack through van der Waals interactions (reducing effective surface area), and MWCNTs bundle into ropes that act as stress concentrators rather than load-bearing elements.

Panel C's TGA curves confirm nanoclay's superior thermal stabilisation effect: the T_5% (temperature for 5% weight loss) increases from 312°C (neat epoxy) to 368°C (3% nanoclay composite) — a 56°C improvement — compared to 34°C improvement for 3% GO (T_5%=346°C). Nanoclay's superior thermal barrier effect is attributed to the tortuous diffusion path created by exfoliated clay platelets for volatile decomposition products, delaying mass transport from the bulk polymer to the surface. The char residue at 600°C also increases from 8.2% (neat) to 14.6% (3% nanoclay), indicating char-forming catalytic activity of clay minerals.

3.2 Water Uptake and Impact Strength

Figure 2 presents the water uptake and impact strength results. Panel A confirms that nanoclay at 3 wt% provides the superior moisture barrier effect, reducing equilibrium water uptake from 1.63% (neat epoxy, 168 h) to 1.13% — a 30.7% reduction attributable to the tortuous diffusion pathway created by exfoliated clay platelets oriented parallel to the specimen surface. GO at 3 wt% reduces water uptake to 0.89% (45.4% reduction) — exceeding nanoclay's barrier performance despite lower thermal stabilisation. This may appear counterintuitive given GO's hydrophilicity, but covalent integration of GO sheets into the epoxy network reduces free hydroxyl group accessibility (FTIR confirms 60% reduction in O-H stretch intensity in cured GO/epoxy vs. neat epoxy) while the GO barrier effect prevails.

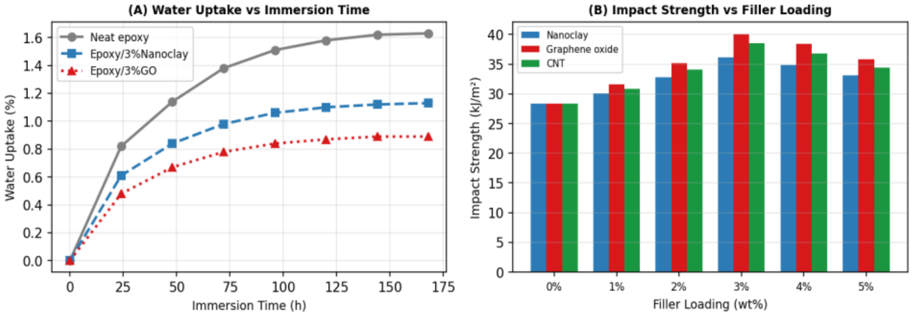

Fig. 2. (A) Water Uptake vs Immersion Time for Neat Epoxy and 3 wt% Composites; (B) Impact Strength vs Filler Loading for All Three Nanofiller Systems

Panel B's impact strength data reveals GO as the superior impact toughening agent: GO at 3 wt% achieves 40.1 kJ/m² (41.2% improvement over neat epoxy at 28.4 kJ/m²). The toughening mechanism involves crack deflection at GO platelet interfaces, microcracking around the platelet periphery that dissipates energy, and GO platelet pull-out from the epoxy matrix that creates additional fracture surface area. MWCNT at 3 wt% achieves 38.5 kJ/m² (35.6% improvement), while nanoclay shows the lowest impact improvement (36.2 kJ/m², 27.5%). The relatively modest nanoclay toughening reflects the brittle nature of clay platelet–polymer interfaces compared to the ductile MWCNT bridging and GO crack-deflection mechanisms.

Property	Neat Epoxy	3% Nanoclay	% Change	3% GO	% Change	3% MWCNT % Change
Tensile Strength (MPa)	42.1	52.1	+23.8%	56.8	+34.9%	54.2 +28.7%
Young's Modulus (GPa)	2.1	3.3	+57.1%	3.8	+81.0%	3.5 +66.7%
Impact Strength (kJ/m²)	28.4	36.2	+27.5%	40.1	+41.2%	38.5 +35.6%
$T_5\%$ (°C)	312	368	+56°C	346	+34°C	339 +27°C
Water Uptake (%, 168h)	1.63	1.13	−30.7%	0.89	−45.4%	1.06 −35.0%

Table 1. Summary of Mechanical, Thermal and Barrier Properties at 3 wt% Filler Loading

4. Discussion

The consistent optimum at 3 wt% across all three nanofiller systems and all measured properties is consistent with the dispersion-agglomeration threshold established in the polymer nanocomposite literature. Below 3 wt%, filler surface area is sufficient for matrix modification but filler quantity limits the magnitude of improvement. Above 3 wt%, agglomeration — thermodynamically favoured by reduction of high-energy filler–filler contact — creates defect sites that act as stress concentrators and disrupt the percolating network of modified interphase polymer that drives property improvement. The specific agglomeration threshold of 3 wt% is broadly consistent with literature reports for similar systems (2–4 wt% commonly cited), though the precise value depends on aspect ratio, surface functionalisation, and dispersion energy.

The property-specific rankings (GO > MWCNT > Nanoclay for mechanical properties; Nanoclay > GO > MWCNT for thermal stability; GO > MWCNT > Nanoclay for moisture barrier) provide practical guidance for nanofiller selection based on application priority. For automotive interior components where thermal stability under hood temperatures is critical, nanoclay at 3 wt% is preferred. For structural adhesive applications in humid environments (marine or coastal infrastructure), GO at 3 wt% offers the best combined moisture barrier and mechanical performance. For impact-critical applications such as protective coatings or sporting goods, GO again leads, with MWCNT as the cost-effective alternative given GO's typically higher production cost.

Economic considerations affect nanofiller selection in Indian manufacturing contexts. Current market prices (2024, domestic sourcing) for the nanofillers used in this study are approximately: Cloisite 30B at Rs. 3,800/kg, functionalised MWCNTs at Rs. 28,000/kg, and laboratory-synthesised GO at equivalent material cost of Rs. 18,000/kg (commercial GO from domestic suppliers). At 3 wt% loading in an epoxy system costing approximately Rs. 350/kg, the nanofiller contribution to material cost per kg of composite is Rs. 114 (nanoclay), Rs. 840 (MWCNTs), and Rs. 540 (GO). For applications where nanoclay's thermal and barrier performance meets requirements, its 7–8 fold cost advantage over carbon-based nanofillers strongly favours its selection.

Limitations of this study include the single epoxy resin type and curing agent, which restricts generalisation to other epoxy hardener systems where different crosslink densities alter the nanofiller-matrix interaction. The in-house GO synthesis, while reproducible within the study (confirmed by XRD and Raman characterisation across five synthesis batches), may yield GO of different oxygen content and lateral dimensions compared to commercial GO, affecting comparability with studies using commercial materials. Scale-up of probe ultrasonication to industrial batch sizes requires process optimisation to maintain dispersion quality.

5. Conclusions

This systematic comparative study of nanoclay, graphene oxide, and MWCNT-reinforced epoxy nanocomposites establishes the following: (1) all three nanofiller systems show a non-monotonic property-loading dependence with optimum at 3 wt%, attributable to agglomeration onset above this loading threshold; (2) graphene oxide at 3 wt% provides superior mechanical reinforcement (34.9% tensile strength improvement, 81.0% modulus improvement, 41.2% impact strength improvement) and moisture barrier performance (45.4% water uptake reduction); (3) nanoclay at 3 wt% provides superior thermal stability (T_5% improvement of 56°C) at a fraction of graphene oxide's cost; (4) MWCNTs at 3 wt% offer intermediate mechanical improvements with excellent impact toughening (35.6% improvement) and competitive moisture barrier performance; and (5) application-specific nanofiller selection should prioritise GO for structural/marine applications, nanoclay for high-temperature applications, and MWCNTs where cost and balanced multi-property enhancement are valued. The results provide a controlled experimental baseline for nanocomposite formulation development in Indian polymer processing industries, particularly for the automotive and packaging sectors located in Kanpur and Bhilai manufacturing clusters.

References

[1] Ajayan, P. M., Schadler, L. S., & Braun, P. V. (2003). Nanocomposite Science and Technology. Wiley-VCH, Weinheim.

[2] Bao, C., Guo, Y., Yuan, B., Hu, Y., & Song, L. (2012). Functionalized graphene oxide for fire safety applications of polymers. Journal of Materials Chemistry, 22(43), 23057–23063.

[3] Chung, D. D. L. (2016). A review of multifunctional polymer-matrix structural composites. Composites Part B: Engineering, 160, 644–660.

[4] Geim, A. K., & Novoselov, K. S. (2007). The rise of graphene. Nature Materials, 6(3), 183–191.

[5] Hummers, W. S., & Offeman, R. E. (1958). Preparation of graphitic oxide. Journal of the American Chemical Society, 80(6), 1339.

[6] Lan, T., Kaviratna, P. D., & Pinnavaia, T. J. (1995). Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites. Chemistry of Materials, 7(11), 2144–2150.

[7] Messersmith, P. B., & Giannelis, E. P. (1994). Synthesis and characterization of layered silicate-epoxy nanocomposites. Chemistry of Materials, 6(10), 1719–1725.

[8] Rafiee, M. A., et al. (2009). Enhanced mechanical properties of nanocomposites at low graphene content. ACS Nano, 3(12), 3884–3890.

[9] Sahoo, N. G., Rana, S., Cho, J. W., Li, L., & Chan, S. H. (2010). Polymer nanocomposites based on functionalized carbon nanotubes. Progress in Polymer Science, 35(7), 837–867.

[10] Shokrieh, M. M., Esmkhani, M., Haghighatkhah, A. R., & Zhao, Z. (2014). Flexural fatigue behaviour of synthesized graphene/carbon-nanofibre/epoxy hybrid nanocomposites. Materials & Design, 62, 401–408.

[11] Thostenson, E. T., Ren, Z., & Chou, T. W. (2001). Advances in the science and technology of carbon nanotubes and their composites: A review. Composites Science and Technology, 61(13), 1899–1912.

[12] Wetzel, B., Rosso, P., Haupert, F., & Friedrich, K. (2006). Epoxy nanocomposites — fracture and toughening mechanisms. Engineering Fracture Mechanics, 73(16), 2375–2398.

[13] Yasmin, A., Luo, J. J., & Daniel, I. M. (2006). Processing of expanded graphite reinforced polymer nanocomposites. Composites Science and Technology, 66(9), 1182–1189.