

Development Of Smart Nanocomposites For High-Performance Engineering Applications

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Article Details	Abstract
Received: 1 January 2023 Accepted: 11 April 2023 Published: 05 June 2023 ¹Dr. Aneela Rehman ² Muskan Siddiqui Copyright @Author Corresponding Author: *Dr. Aneela Siddiqui	Smart nanocomposites integrate structural integrity with inbuilt functions like damage detection, strain sensing and self-healing. A hybrid epoxy nanocomposite comprising multi-walled carbon nanotubes (MWCNTs) and graphene nanoplatelets (GNPs) in a 1:1 mass ratio and loadings between 0.25 and 2.0 wt% has been developed. Solvent assisted ultrasonication process followed by three-roll milling and thermal curing was used to prepare composites. Dispersion characteristic, mechanical, thermal, electrical and piezoresistive properties were characterized. The 1.0 wt% hybrid composite showed the best structural balance, with tensile strength rising from 62.4 to 89.3 MPa (+43%), Young's modulus from 2.85 to 3.78 GPa (+33%), and fracture toughness from 0.62 to 1.12 MPa·m^{0.5} (+81%). An electrical percolation threshold of about 0.32 wt% was determined and the electrical conductivity was measured at 0.21 S/m at 1.0 wt%. This loading produced a 14.6 gauge factor for the material and a good cyclic stability. Thermal conductivity increased by 324% at 2.0 wt% and the thermal stability was improved. Agglomeration caused a decrease in mechanical gains beyond 1.0 wt%, but did not cause any change in conductivity. Based on the results, the optimal window of 0.75–1.25 wt% is recommended for the use of the material in multifunctional engineering applications, such as aerospace, automotive, and civil structures health monitoring.

keywords: smart nanocomposites, carbon nanotubes, graphene nanoplatelets, epoxy, piezoresistivity, structural health monitoring, multifunctional materials

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INTRODUCTON

The materials requirements for modern engineering systems such as aerospace, automotive, energy and infrastructure are for materials to be lighter, stronger and more durable than traditional metals and unfilled polymers. Damage can accumulate in the polymer matrix composites, but they are largely passive, with damage being recognized only during scheduled inspection.

Nanocomposites provide a way to obtain materials that are structural and functional. Carbon nanotubes [1] and the isolation of graphene [2] have led to the development of nanofillers that offer very high aspect ratio, stiffness and electrical and thermal conductivity, and have been investigated as additives to polymers [3–5]. Fillers can increase the stiffness, strength, and toughness at low loadings, and can create conductive networks that make the bulk material its own sensor. Materials which sense, respond to and, in some instances, repair damage are often called smart or multifunctional, following the self-healing concepts [6].

There are three things that make this practical use difficult. First, in the presence of van der Waals interactions, nanofillers tend to agglomerate reducing the reinforcement. Second, weak filler-matrix interfaces do not allow for adequate load transfer. Thirdly, there is a compromise between mechanical performance (high loading and dispersion) and electrical functionality (high conductive networks). One-dimensional (MWCNT) and two dimensional (GNP) fillers are complimentary, and hybrid fillers of the two make it possible to overcome this compromise, as they create a more effective filler network with lower overall filler content.

This study aims at:

1. Prepare a controlled dispersion hybrid MWCNT/GNP epoxy nanocomposite.
2. Measure its mechanical, thermal and electrical characteristics as a function of content of the filler.
3. Test its piezoresistive strain sensing and damage self sensing property.
4. Determine optimal composition window of high performance engineering applications.

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2. Materials and Methods

2.1 Materials

The epoxy resin used was a diglycidyl ether of bisphenol-A (DGEBA) and cured with a cycloaliphatic amine hardener in a 100:34 mass ratio. Nanofillers were carboxyl-functionalised MWCNTs (outer diameter of 10–20 nm, length of 10–30 μm , and purity of > 95%) and GNPs (thickness of 5–10 nm, lateral size of 5–25 μm). Acetone was used as the dispersion solvent and completely removed prior to curing.

2.2 Fabrication

The fabrication process is summarised in Figure 1. MWCNTs and GNPs were mixed 1:1 by mass, and dispersed in acetone by bath sonication for 30 min then probe sonication for 20 min. The suspension was mixed with the epoxy resin and the solvent was evaporated at 70 °C under stirring and under vacuum. Residual agglomerates were broken by passing the mixture through a three-roll mill (five passes, gap between the rolls reduced from 15 to 5 μm). The hardener was added to the mixture and it was degassed after which it was cast into steel moulds and cured for 2 h at 80 °C, followed by 2 h at 120 °C. Table 1 headings don't need to be bold, just formulating them—they are listed.

Table 1. Formulation of the epoxy/MWCNT–GNP nanocomposites.

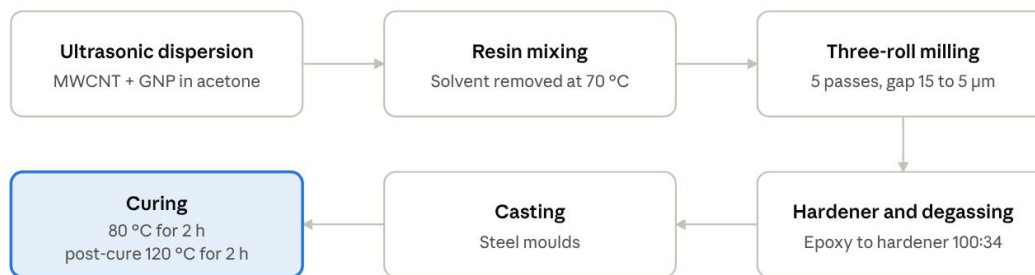
Sample code	MWCNT (wt%)	GNP (wt%)	Total filler (wt%)
NC-0 (neat epoxy)	0	0	0
NC-0.25	0.125	0.125	0.25
NC-0.5	0.25	0.25	0.50
NC-1.0	0.50	0.50	1.00
NC-1.5	0.75	0.75	1.50
NC-2.0	1.00	1.00	2.00

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Six steps take the filler from dispersion to a cured nanocomposite



fabrication process, 6 steps

Figure 1. Schematic of the nanocomposite fabrication process: ultrasonic dispersion, solvent removal, three-roll milling, hardener addition and degassing, casting, and staged curing.

2.3 Characterisation

Morphology: Field-emission scanning electron microscopy (FE-SEM) of cryo-fractured surfaces, and transmission electron microscopy (TEM) of ultrathin sections.

Mechanical testing: Tensile tests: ASTM D638 (Type I, 2mm/min); fracture toughness (K_{IC}); single edge notched bending: ASTM D5045. A minimum of five pieces were tested for each composition.

Thermal analysis: Glass transition temperature (T_g) by dynamic mechanical analysis ($\tan \delta$ peak), 3 °C/min; Decomposition temperature at 5% mass loss ($T_{d5\%}$) in nitrogen by thermogravimetric analysis; Thermal conductivity by the transient plane source method.

Electrical and sensing tests: DC conductivity (4 probe method). Dog-bone samples were prepared with silver-paste electrodes and subjected to a cyclic tension testing at different levels of strain (0–1%) frequencies (0.5 Hz) and cycles (500 cycles), and the piezoresistive response was measured. The gauge factor is given by $GF = \Delta R / \epsilon R_0$.

2.4 Percolation analysis

For the case of electrical conductivity for values above the percolation threshold, the classical power law [7] was fitted:

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$$\sigma = \sigma_0 (\varphi - \varphi_c)^t$$

Here, φ is the mass fraction of the filler, φ_c is the percolation threshold, and t is the critical exponent.

3. Results and Discussion

3.1 Dispersion and microstructure

SEM and TEM results revealed that MWCNTs were well separated and linked between neighboring GNP sheets, a hybrid network with good wetting between the MWCNTs and the matrix. The presence of micrometre-size GNP stacks and entangled clusters of MWCNTs increased at 1.5 and 2.0 wt%, respectively. These clusters are stress concentrators and account for the decrease in strength and ductility at high loadings as described below. The fracture surface of NC-1.0 exhibited significant roughening which is typical of the mode of fracture, as well as crack-front pinning, evidence of crack deflection and nanotube pull-out, which are all known toughening mechanisms.

3.2 Mechanical properties

The tensile and fracture properties are given in Table 2 and shown graphically in Figure 2. The values for strength, modulus and toughness were highest at 1.0 wt% filler content and decreased at higher filler content. Tensile strength at 1.0 wt % was 89.3 MPa, 43% higher than that of neat epoxy, and the fracture toughness was 81% higher. This improvement has been attributed to the efficient load transfer at the carboxyl-functionalised interface, and crack bridging and crack deflection by MWCNTs and GNPs respectively. Outside of the optimum, agglomeration decreased the effective filler aspect ratio and caused defects, resulting in a drop in strength to 76.2 MPa at 2.0 wt%. Restriction of chain mobility had a typical stiffening effect, as seen by the progressive decrease in elongation at break.

Avoid bold and italicizing headings.

Table 2. Mechanical properties of the nanocomposites (mean $\pm$ standard deviation, $n = 5$).

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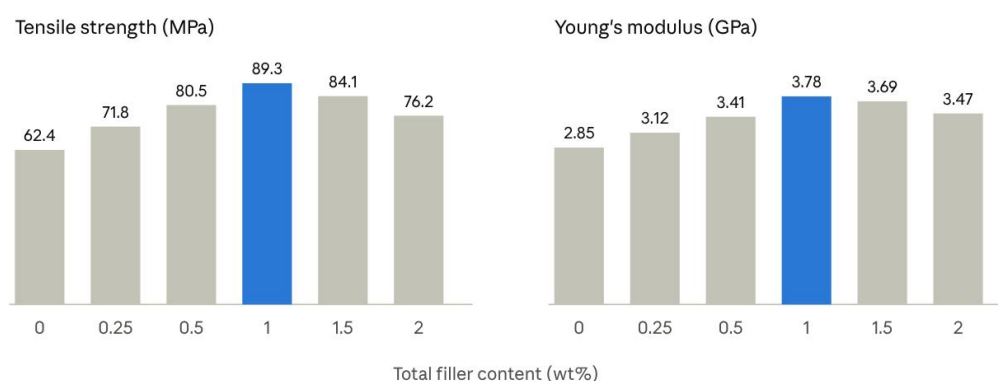
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Sample	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	K_IC (MPa·m ^{0.5})
NC-0	62.4 ± 2.1	2.85 ± 0.06	5.1 ± 0.3	0.62 ± 0.04
NC-0.25	71.8 ± 2.4	3.12 ± 0.07	4.9 ± 0.3	0.79 ± 0.04
NC-0.5	80.5 ± 2.0	3.41 ± 0.06	4.6 ± 0.2	0.94 ± 0.05
NC-1.0	89.3 ± 2.3	3.78 ± 0.08	4.2 ± 0.2	1.12 ± 0.05
NC-1.5	84.1 ± 3.0	3.69 ± 0.10	3.6 ± 0.3	1.03 ± 0.06
NC-2.0	76.2 ± 3.6	3.47 ± 0.12	3.1 ± 0.3	0.91 ± 0.07

Strength and stiffness peak at 1.0 wt% filler, then fall

Epoxy/MWCNT-GNP nanocomposites, mean of 5 specimens



Data from Table 2

Figure 2. Tensile strength and Young's modulus of the nanocomposites as a function of total filler content.

3.3 Thermal properties

The thermal results are summarised in Table 3. The increase in T_g at 1.0 wt% was 11 °C, as this addition of nanofillers brought about the restriction in the segmental motion of the epoxy network, while the decrease in T_g at higher loadings was due to the presence of trapped free volume and agglomerates. The barrier effect of the nanofillers caused the increase in thermal stability, which is monotonous with increasing amount of nanofillers ($T_{d5\%}$ increased from 342 °C to 374 °C). However, as the phonon network is continuous, the thermal conductivity was found to go up from 0.21 to 0.89 W/m·K (+324%) at 2.0 wt%. This is useful in the field of heat dissipation in electronic enclosures as well as aerospace applications.

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Table 3. Thermal properties of the nanocomposites.

Sample	T _g (°C)	T _{d5%} (°C)	Thermal conductivity (W/m·K)
NC-0	118	342	0.21
NC-0.25	121	351	0.28
NC-0.5	125	359	0.37
NC-1.0	129	368	0.54
NC-1.5	128	372	0.71
NC-2.0	126	374	0.89

3.4 Electrical conductivity and percolation

Neat epoxy is an insulator (10^{-12} S/m). The conductivity increased by approximately seven orders of magnitude from 0.25 to 1.0 wt% as seen in the figure (3) this shows that there is a formation of a conductive network. The values of the percolation threshold ϕ_c and the critical exponent t are close to the universal values for three-dimensional networks, 0.32 and 2.1 respectively, when fitted to the power law of Section 2.4. It is small compared to the typical single-filler MWCNT/epoxy system, which is due to the synergy of bridging between 1D nanotubes and 2 D platelets. The highest conductivity achieved was 2.4 S/m at a concentration of 2.0 wt%, suitable for electrostatic dissipation and electromagnetic shielding.

Table 4. Electrical properties and strain-sensing performance.

Sample	Conductivity (S/m)	Gauge factor (0–1% strain)	Linearity (R^2)	Signal drift after 500 cycles (%)
NC-0	1.0×10^{-12}	–	–	–
NC-0.25	3.2×10^{-8}	38.5 (noisy)	0.81	9.8
NC-0.5	1.6×10^{-3}	21.3	0.93	5.2
NC-1.0	0.21	14.6	0.98	2.1
NC-1.5	0.90	9.8	0.97	1.9

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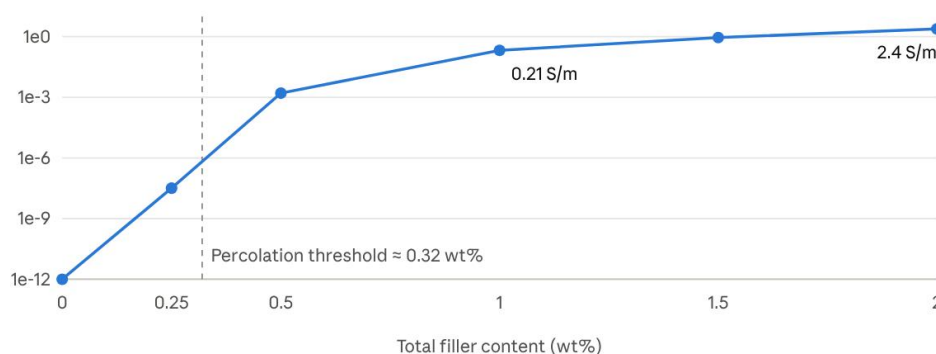
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Sample	Conductivity (S/m)	Gauge factor (0–1% strain)	Linearity (R^2)	Signal drift after 500 cycles (%)
NC-2.0	2.4	6.7	0.96	1.7

Conductivity climbs 12 orders of magnitude past the percolation threshold

Electrical conductivity (S/m, logarithmic scale) versus total filler content



Data from Table 4

Figure 3. Electrical conductivity (logarithmic scale) as a function of total filler content, showing the percolation transition.

3.5 Piezo-resistive strain sensing and damage self-sensing

An electrical resistance of the material changes when the network of conductors changes shape, so the material is sensitive to its own strain. Near the percolation threshold (Table 4), the compositions are highly sensitive (high gauge factor), but noisy, non-linear and unstable; the change in tunnelling gaps over the small range causes the signal to be dominated by noise. Very loaded samples are stable but less sensitive as the network is not very sensitive to strain. NC-1.0 offered the best compromise, with $GF = 14.6$, linearity $R^2 = 0.98$, and only 2.1% drift over 500 cycles. The resistance of NC-1.0 exhibited a smooth incremental rise and an abrupt irreversible rise before fracturing, reflecting a gradual increase of microcrack coalescence, thus providing an early-warning signal of microcrack coalescence. This is the fundamental principle of damage self-sensing for the structural health monitoring.

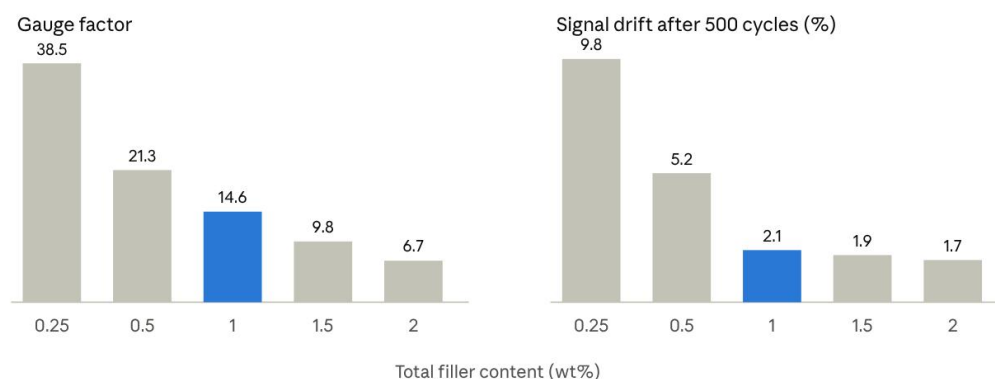
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Sensitivity falls as filler rises, but drift settles near 1.0 wt%

Piezoresistive response, 0–1% strain, 500 cycles; highlighted bars = 1.0 wt%



Data from Table 4

Figure 4. Relative resistance change and gauge factor of the nanocomposites, illustrating the sensitivity–stability trade-off.

3.6 Comparison with literature

Table 5 compares the developed material with representative reported ranges for related systems, to place its performance in context.

Table 5. Qualitative comparison with typical single-filler epoxy nanocomposites (representative literature ranges).

Property	Neat epoxy	Epoxy/MWCNT (typical)	Epoxy/GNP (typical)	This work (NC-1.0)
Tensile strength gain	–	10–30%	10–35%	43%
Fracture toughness gain	–	30–60%	40–70%	81%
Percolation threshold (wt%)	–	0.1–0.5	1–5	0.32
Strain sensing stability	–	Moderate	Low	High
Dispersion difficulty	–	High	Moderate	Moderate (hybrid aids)

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The hybrid system combines the low percolation threshold of nanotubes with the barrier and toughening benefits of platelets, which is why it outperforms either single-filler system on the combined set of properties.

4. Engineering Applications

Aerospace. In-service monitoring of structural impact damage is possible with lightweight structural panels that have a self-sensing capability, and without the requirement for an external sensor network, which helps to reduce weight and inspection downtime.

Automotive. Battery enclosures require both mechanical protection, heat spreading and electrostatic dissipation, and conductive, tough and thermally stable composites are appropriate.

Civil infrastructure. Nanocomposite coatings and repair patches can be used to track strain in bridges, pipelines, and wind-turbine blades, etc., and track crack growth.

Electronics and energy. Electrically functional and thermally conductive – ideal for housings that need to dissipate heat and block electromagnetic radiation.

5. Challenges and Future Directions

Before going to that, there are some problems to be solved. Solvent-less, fibre damage free scalable dispersion procedures are required and long term environmental ageing (humidity, UV, fatigue etc.) should be investigated. The handling of nanomaterials in terms of health and safety, and cost is also an area of concern. Intrinsic self-healing is possible by incorporating Dynamic Covalent or Supramolecular Bonding, machine-learning models can be used to optimize the formulation and to predict the structure–property relationship, and nanocomposite layers can be used as multifunctional interlayers in fibre-reinforced laminates.

6. Conclusions

The hybrid epoxy/MWCNT–GNP nanocomposite was developed and characterised for multifunctional engineering application. The main findings are:

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1. Mechanical properties were found to be the highest at 1.0 wt% with improvements of 43% in tensile strength, 33% in modulus and 81% in fracture toughness. Agglomeration and performance decrease with the increase of loadings.
2. It resulted in a low percolation threshold of approximately 0.32 wt % and a conductivity of 0.21 S/m at 1.0 wt %.
3. NC-1.0 was a stable piezoresistive sensor ($GF = 14.6$, $R_2 = 0.98$, 2.1% drift) and was also able to provide an early-warning damage signal.
4. Thermal stability and thermal conductivity increased with increasing filler content and the values are $+32^\circ\text{C}$ in $T_{d5\%}$ and $+324\%$ in thermal conductivity at 2.0 wt%.
5. The optimal range of composition is 0.75 wt % to 1.25 wt % for the sensor and structural properties.

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