

Experimental and Numerical Investigations of Carbon-based Nanoparticle Reinforcement on Microstructure and Mechanical Properties of Epoxy Coatings

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Abstract The addition of nanoparticles serves as an effective reinforcement strategy for polymeric coatings, utilizing their unique characteristics as well as extraordinary mechanical, thermal, and electrical properties. The exceptionally high surface-to-volume ratio of nanoparticles imparts remarkable reinforcing potentials, yet it simultaneously gives rise to a prevalent tendency for nanoparticles to agglomerate into clusters within nanocomposites. The agglomeration behavior of the nanoparticles is predominantly influenced by their distinct microstructures and varied weight concentrations. This study investigated the synergistic effects of nanoparticle geometric shape and weight concentration on the dispersion characteristics of nanoparticles and the physical-mechanical performances of nano-reinforced epoxy coatings. Three carbon-based nanoparticles, nanodiamonds (NDs), carbon nanotubes (CNTs), and graphenes (GNPs), were incorporated into epoxy coatings at three weight concentrations (0.5%, 1.0%, and 2.0%). The experimental findings reveal that epoxy coatings reinforced with NDs demonstrated the most homogenous dispersion characteristics, lowest viscosity, and reduced porosity among all the nanoparticles, which could be attributed to the spherical geometry shape. Due to the superior physical properties, ND-reinforced nanocomposites displayed the highest abrasion resistance and tensile properties. Specifically, the 1.0wt% ND-reinforced nanocomposites exhibited 60%, 52%, and 97% improvements in mass lost, tensile strength, and failure strain, respectively, compared to pure epoxy. Furthermore, the representative volume element (RVE) modeling was employed to validate the experimental results, while highlighting the critical role of nanoparticle agglomeration, orientation, and the presence of voids on the mechanical properties of the nanocomposites. Nano-reinforced epoxy coatings with enhanced mechanical properties are well-suited for application in protective coatings for pipelines, industrial equipment, and automotive parts, where high wear resistance is essential.

Keywords Nano-reinforced composite; Geometric shape; Weight concentration; Experimental characterization; Finite element analysis (FEA); Representative volume element (RVE) modeling

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INTRODUCTION

Epoxy-based polymeric coatings play a pivotal role in shielding metal substrates from corrosion, abrasion, chemical exposure, and other forms of degradation, thereby extending their service life and maintaining operational efficiency.^[1] However, despite these advantages, epoxy coatings are susceptible to inherent porosity, resulting in the formation of numerous microcracks and voids during the curing process.^[2,3] Due to thermal expansion and mechanical stress, these structural imperfections may subsequently develop over time, which compromises the adhesion of the coating on the metal substrate, undermines coating uniformity, and potentially leads to other detrimental issues like coating cracking and delamination.^[4,5] Thus, the development of epoxy coatings with enhanced durability and mechanical

performance is essential to ensure long-term protection and preserve the metal substrate integrity in real-world applications.

The incorporation of nano-reinforcements has attracted significant attention in the development of advanced materials.^[6–9] Numerous recent studies have been dedicated to exploring the impact of nanomaterials on enhancing the mechanical, electrical, and thermal properties of polymer composites. Among the array of nanomaterials, nanocarbons, including graphenes (GNPs), carbon nanotubes (CNTs), and nanodiamonds (NDs) possessing different dimensionalities have emerged as particularly promising candidates.^[10,11] This enhancement can primarily be attributed to their high surface area, high strength and rigidity, low density, and strong bonding capabilities with polymeric matrices.^[12,13] Specifically, NDs are spherical carbon nanoparticles with a highly crystalline structure. Their small size and large surface area contribute to significant improvements in the mechanical strength, hardness, and wear resistance of coatings.^[14] CNTs, with their cylindrical carbon structures, are renowned for their

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exceptional tensile strength, electrical conductivity, and thermal properties.^[15] GNPs, two-dimensional nanomaterials composed of stacked graphene layers, are widely recognized for their outstanding mechanical strength, thermal conductivity, and barrier properties.^[16]

The uniform distribution of nanoparticles is essential for achieving superior properties in composite materials.^[17,18] Notably, the homogeneous dispersion of CNTs and GNPs within the polymer matrix can serve as nucleation sites, regulating the performance of the proposed nanocomposite.^[19] However, ensuring a homogeneous and consistent dispersion of nanocarbons within the polymer matrix poses a significant challenge.^[20] During the mixing process, nanoparticles tend to agglomerate due to two competing factors: (i) strong self-attractions driven by van der Waals forces and (ii) low interfacial interaction with the surrounding polymers.^[21–23] Extensive research has underscored the critical role of functionalization, dispersion methods, particle geometry, and concentration in determining the dispersion quality of carbon-based nanoparticles.^[24–26] In addition to these well-discussed factors, the dimensional characteristics of carbon-based nanoparticles may also affect their dispersion in epoxy coatings, yet this aspect remains to be systematically investigated. Among the carbon-based nanoparticles, ND exhibits a spherical geometric shape, with carbon atoms arranged in a tetrahedral structure through sp^3 hybridization, where each carbon atom forms covalent bonds with four adjacent atoms.^[27] In contrast, CNT and GNP are composed of carbon atoms arranged in a sp^2 hybridization pattern.^[28] CNTs are characterized by tubular structures with diameters typically in the nanometer range.^[29] While GNP consists of a single layer of carbon atoms forming a 2D hexagonal lattice structure, with a thickness of approximately 0.142 nm between adjacent carbon atoms.^[30] Thus, ND, CNT, and GNP are classified as zero-dimensional (0-D), one-dimensional (1-D), and two-dimensional (2-D) material, respectively, based on their dimensions exceeding 100 nanometers in 0, 1, or 2 dimensions. The majority of previous studies have primarily concentrated on exploring the enhanced performance of epoxy-based nanocomposites reinforced with individual nanoparticles. There has been very limited research investigating the influence of various geometric shapes of carbon-based nanoparticles on the overall performance of these nanocomposites. In addition, numerous investigations have demonstrated that the weight concentration of carbon-based nanoparticles has been identified as a significant factor influencing the mechanical performance of nanocomposites. Furthermore, there is a severe lack of literature investigating the synergistic effects of nanoparticle geometric shapes and weight concentrations.

Computational methodologies, such as finite element analysis (FEA), are broadly employed as indispensable tools in simulating the mechanical behaviors of nanocomposites, due to its ability to model heterogeneous materials with complex geometries and offer insights in stress distribution, failure mechanism, and other detailed data that is difficult to obtain through experimental method alone.^[31,32] However, it is challenging for macro-scale computational models to assess microscopic features and interactions of nanocomposites due to the vast differences in scale and complexity between

nanoparticles and macro composites.^[33,34] Multiscale modeling has been widely used to address these challenges by bridging the wide range of length and time scales in various material phenomena.^[35,36] Representative volume element (RVE), as the smallest volume to represent the whole material domain, is an efficient approach to simulate the microstructural features of composites from micro- to macroscales.^[37,38] Conducting both experimental and RVE simulation in studying nanocomposites leverages the respective strengths of each method and achieves a comprehensive understanding that neither method could achieve alone.

To date, the influence of nanoparticle geometries on the performance of carbon-based nanoparticle-reinforced epoxy coatings remains inconclusive, as does the impact of geometric shapes at different nanoparticle weight concentrations. To bridge this research gap, this study aimed to investigate the synergistic effects of nanoparticle geometric shape and weight concentration on epoxy nanocomposite coatings, using both experimental investigation and numerical simulation approaches. Nanoparticles with three different geometric shapes (0D ND, 1D CNT, and 2D GNP) and three different weight concentrations (0.5%, 1.0%, and 2.0%) were incorporated into the epoxy coatings. transmission electron microscopy (TEM), scanning electron microscopy (SEM), and dynamic light scattering (DLS) were employed to distinguish the unique geometric shapes of these three carbon-based nanoparticles and characterize their dispersion qualities. Rotational viscosity tests, micro-computed tomography (micro-CT), and contact angle tests were conducted to evaluate the porosity, viscosity, and wettability of the nanocomposites, respectively. The mechanical properties of the nanocomposites were examined by Taber abrasion and dog-bone tensile tests. Finite element analyses (FEA) using multiscale Representative Volume Element (RVE) modeling were also performed to validate the mechanical property results and further explore the effects of nanoparticle orientation and agglomeration on the mechanical properties of the nanocomposites. Although the findings in this study on carbon-based nanoparticles may not be universally valid for other nanoparticle with different chemical compositions, this study may still provide valuable insights into the effect of nanoparticle geometries on the performance of polymer nanocomposites.

EXPERIMENTAL

Materials

A commercially commonly used epoxy, EPONTM Resin 828, obtained from Hexion Inc. (Columbus, OH, USA), was utilized as the polymer matrix material. The undiluted clear difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin was crosslinked with a modified polyamide curing agent, EPIKURETM 3175. Three carbon-based nanoparticles, namely 0D NDs, 1D CNTs, and 2D GNPs, were selected aimed to explore the impact of the geometric morphology on nanofiller-reinforced nanocomposites. Additionally, their carbon-based nature facilitates the absence of chemical reactions between the nanofillers and the polymers^[39], allowing a focused examination on the effects of nanoparticles' geometric morphology. The nanoparticles were procured from Skyspring Nanomaterials Inc., and their specifications are detailed in Table 1. Regarding the particle di-

Table 1 Specifications of the carbon-based nanoparticles.

Specifications	Nanoparticles		
	ND	GNP	CNT
Appearance	Grey powder	Black powder	Black powder
Purity	>95%	>95%	>95%
Morphology	Spherical	Platelets	Fibrous
Dimension (nm)	Diameter: 3–4	Average diameter: 1.5×10^4 Thickness: 6–8	Outside diameter: 50–100 Inside diameter: 5–10 Length: 5×10^3 – 2×10^4
Surface area (m^2/g)	~282	120–150	>60
True density (g/cm^3)	3.05–3.30	~2.27	~2.10

mensions of each nanoparticle, the most commonly used dimensions were selected to align with their practical applications as nanofillers in polymer nanocomposites. Even though the three carbon-based nanoparticles showed some variations in size, the modification effects remained valid and comparable when the weight additions of all the nanoparticles were kept the same.

Fabrication Process of Nanocomposites

The dispersion of nanoparticles has a significant impact on defining the microstructure and properties of coatings, as agglomeration can lead to uneven particle distribution, reduced surface area, and compromised performance. Various dispersion techniques are employed to achieve uniform nanoparticle distribution within coatings. Among these methods, the use of surfactant is relatively simple and cost-effective; however, surfactant residues may adversely affect the final properties of the coatings. Surface functionalization of nanoparticles, by forming strong covalent bonding with the coating matrix, improves particle-matrix interaction, though it requires additional chemical processing, which can be time-consuming and costly. In contrast, ultrasonication offers a more efficient approach without the need for chemical additives, thereby preserving the inherent properties of the nanoparticles. Furthermore, it is highly effective at breaking down agglomerates, particularly in high-concentration nanoparticle dispersions. Thus, this study employed mechanical dispersion techniques, including ultrasonication, high shear dispersion and stirring, without the use of additional chemicals, such as solvents or surface modification agents. This approach ensured that the performance of the fabricated nanocomposites was solely dependent on the geometric morphology of the nanoparticles. The identical dispersion and fabrication procedures were applied to all selected nanoparticles (NDs, GNPs, and CNTs), as illustrated in Fig. 1. Initially, nanoparticles were introduced into the epoxy resin and pre-dispersed through 1-min hand-stirring with a spatula in a fume hood. Subsequently, a combination of high-shear dispersion and high-power ultrasonication methods was employed. A 30-min high-shear mixing at a controlled speed of 4000 r/min

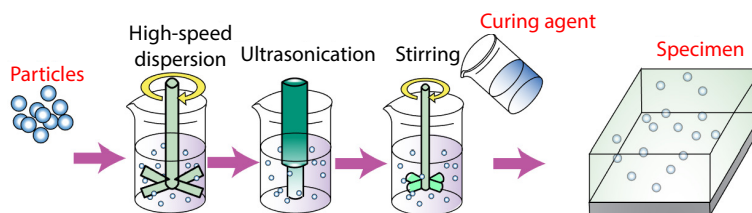
broke down large particles in the mixture, followed by transferred to a probe ultrasonic system for further dispersion. The ultrasonication involved a 15-s “on/off” cycle with 100% amplitude over 30 min. Water baths were utilized during both dispersion techniques to prevent overheating, with water renewal every 10 min. After the dispersion, the curing agent was added at a 1:1 molar ratio to the epoxy and mixed by mechanical stirring at 600 r/min for 10 min. Three different concentrations (0.5%, 1.0%, and 2.0% by weight) were used for all nanoparticles, alongside neat epoxy samples as the control group. All prepared samples were stored at room temperature for a minimum of seven days before subsequent experiments were conducted.

Physical Characterization

The JEM-2100 high-resolution analytical TEM device was utilized to scrutinize the morphologies and microstructures of the nanofillers. To ensure clear imaging, nanofillers were dispersed into ethanol at an appropriate weight ratio prior to TEM observation. Dynamic light scattering (DLS) was performed by using a submicron particle sizing instrument (Nicomp 380) to measure the particle size distributions of each nanofiller. The Brookfield DV-II viscometer was used to measure the rheological properties of the epoxy nanocomposites. The GE v|tome|x microfocus X-ray computed tomography system was used to nondestructively detect and quantify the porosity and voids within nanocomposite coatings. The water contact angle tests were conducted by using the DSA100S Drop Shape Analyzer equipped with a software-controlled dosing system and a tilt stage. The JSM-7600F Schottky field-emission scanning electron microscope (FE-SEM) was employed to examine fracture surfaces after mechanical tests.

Mechanical Properties

The wear resistance of nano-reinforced composite coatings was measured using the Taber abrasive method specified in ASTM D4060. The surface of each sample underwent abrasion by two CS-10 wheels rotating at a speed of 72 r/min, with a load of 1000 g applied to each wheel during the test. The abrasion resistance was determined by quantifying the mass loss before and after

**Fig. 1** Schematic of the fabrication process of nanoparticle reinforced epoxy composites.

abrasion. A more robust abrasion-resistant nanocomposite coating is anticipated to exhibit a lower mass loss, indicating enhanced protective property against damage induced by abrasive motions. To evaluate the tensile properties of polymeric nanocomposites reinforced with nanofillers, dog-bone coupon tensile tests were conducted in accordance with ASTM D638 standards. The tests were carried out using Shimadzu's EZ-X tester (Columbia, MD, USA) at a controlled loading rate of 1.0 mm/min until the sample broke at the narrow section, while recording the real-time applied load and corresponding displacement.

RVE MODELING

Material Properties

The FEA was performed through SIMULIA/ABAQUS 2023 to simulate the tensile properties of epoxy nanocomposites reinforced with different nanoparticles (0D ND, 1D CNT, and 2D GNP) ranging from 0% to 2% weight concentrations. FEA with RVE is effective for simulating material properties such as stress-strain curves and failure patterns in composite materials. It allows for the application of real-world loading conditions, such as tensile or compressive forces, and translates microscopic results into macroscopic homogeneous material properties. To predict the mechanical properties of filler-reinforced polymer composites, FEA is widely used to analyze the failure of composites.^[40,41] The material properties of these three nanoparticles are obtained from references and materials providers,^[42–45] which are implemented in the simulation. The epoxy matrix properties were experimentally measured in the dog-bone tensile test, with the ultimate stress as 34.15 MPa, ultimate strain as 2.95%, and Young's modulus as 1216.93 MPa. The following Table 2 shows the material information implemented for ND, MWNT, and GNP.

Table 2 Physical and mechanical properties of nanodiamonds, multi-walled carbon nanotubes and graphene nanoplatelets.

Nanofiber	Young's modulus (GPa)	Ultimate stress (GPa)	Poisson's ratio
ND	880	95	0.2
MWNT	450	27	0.2
GNP	800	85	0.2

Multiscale Approach with RVE Modeling

The finite element models were constructed by preserving the dog bone sample in tensile tests. RVE modeling approach was utilized to precisely capture the microstructural behaviors and faithfully reproduce the mechanical performance of the nanocomposites in macro-scale mechanical tests. RVE models are constructed as a standard microstructural unit cube cell, incorporating various types of fibers. The quadratic nodes and linear solid elements C3D20R are used. This study adopted a scale bridging method called 'volume-averaged stress', which emphasizes the use of mean fields as an efficient means to construct this link without sacrificing accuracy. It allows the volume-averaged (mean) stress at the microscale to serve as a continuously varying function of coordinates at the next larger length scale.^[46] Mathematical Eqs. (1) and (2) show the average stress principle:

$$\bar{\sigma}_{\mu+1} = \bar{\sigma}_{\mu} + \sum_{j=1}^{\infty} \frac{1}{V_{\mu} |\bar{x}|^j} \int_{V_{\mu}} (\bar{\sigma}_{\mu} - \bar{\sigma}) |\bar{x}|^j dV \quad (1)$$

$$\bar{\sigma}_{\mu} = \frac{1}{V_{\mu}} \int_{V_{\mu}} \bar{\sigma}_{\mu} dV \quad (2)$$

where $\bar{\sigma}_{\mu}$ represents the volume average stress at the microscale which is a continuously varying function of coordinates $\bar{x}_{\mu+1}$. The next larger length scale is $\mu + 1$. The RVE requires the object to exhibit statistical homogeneity at the microscale. This implies the microscale volume needs to have a statistically uniform distribution in terms of both their placement and orientation. Thus, implementing the initial boundary condition that preserves linear momentum on the RVE is a crucial requirement for the suggested multiscale approach to yield reasonably precise prediction at greater length scales.^[46]

$$\bar{\nabla} \cdot \bar{\sigma}_{\mu} + \rho \bar{f} = 0, \forall \bar{x}_{\mu} \in V_{\mu} \quad (3)$$

$$\bar{\sigma}_{\mu} = \frac{1}{V_{\mu}} \int_{V_{\mu}} \bar{\sigma}_{\mu} dV \quad (4)$$

where $\bar{\sigma}_{\mu}$ represents the Cauchy stress tensor defined on the length scale μ , ρ is the mass density, and $\bar{f}$ represents the body force vector per unit mass.

RVE Geometry

The effective response of the RVE model was calculated as the field-averaged value, which was then considered as the equivalent homogenized UD lamina at a global scale.^[47] For simplicity purposes in modeling, numerous micromechanical approaches adopt the assumption of a periodic distribution of fillers, facilitating the isolation of an RVE or unit cell on a local scale. This RVE is characterized by equivalent elastic constants and filler volume fraction as observed in the composite material. Additionally, the unidirectional filler composite models were used in this study, which can be a square or hexagonal localized filler array packing representing the global behavior of fiber-reinforced composite.^[48–50] A periodical distribution RVE provides a streamlined representation of the microstructure of fiber-reinforced composites, which significantly reduces the complexity of simulations. The unidirectional or uniformly distributed RVE models have been validated by experimental data in references.^[40,51–56] Using this approach allows for easier comparison and validation with experimental studies, making it a common choice in the field of composite materials. Based on the given geometry of nanoparticles and weight concentrations, the RVE model for ND, CNT, and GNP-reinforced epoxy composites are generated accordingly. A representative ND model showcasing the nanoparticle geometry is shown in Fig. 2(a), while another example of GNP model demonstrating the nanoparticle arrangement and distribution is illustrated in Figs. 2(b)–2(d).

Boundary Conditions of RVE Model

Boundary conditions are essential to define the constraints or loading factors, which significantly affect the overall behaviors of the RVE system. Displacement control mode was selected in the simulation. Here, direction 1 corresponds to the x-direction, aligning parallel to the fillers when they were oriented in the same direction as the load. The microscopic stress σ_{μ} at any point in the RVE domain Ω should also satisfy the following Eq. (8):

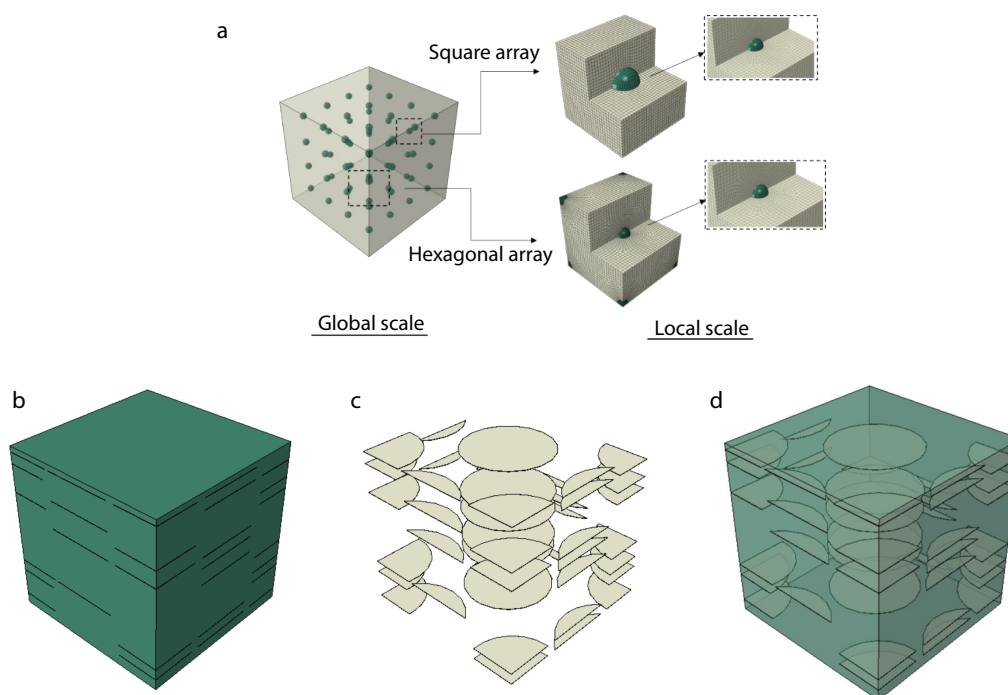


Fig. 2 Visual illustration of RVE models: (a) square or hexagonal array packing from ND-reinforced nanocomposite; Aligned platelets of GNPs; (b) model configurations; (c) distribution of GNP platelets; (d) transparent view.

$$u_z(u_x, u_y, l) - u_z(x_x, x_y, -l) = 2l\varepsilon_{zz}^a \quad (5)$$

$$-m < x_y \leq m \text{ and } -n \leq x_x \leq n, \text{ while } \varepsilon_{xz}^a = 1$$

$$u_y(u_x, m, u_z) - u_y(x_x, -m, u_z) = 0 \quad (6)$$

$$-l < x_z \leq l \text{ and } -n \leq x_x \leq n$$

$$u_x(n, u_y, u_z) - u_x(-n, u_y, u_z) = 0 \quad (7)$$

$$-m < x_y \leq m \text{ and } -l < x_z \leq l$$

$$\nabla_x \cdot \sigma_\mu(x) = 0; x \in \Omega \quad (8)$$

where $2l\varepsilon_{ij}^a$ is the displacements of the RVE model, 1, n , m are the RVE sizes in each direction.

EXPERIMENTAL

Morphology and Dispersion Characteristics

TEM analysis

High-resolution TEM images provide crucial insights into the individual characteristics of nanoparticles revealing accurate size measurements and detailed morphological features. The microstructures and morphologies of ND, CNT, and GNP were visualized at atomic and nanoscale levels through TEM analysis, as depicted in Figs. 3(a)–3(c). NDs exhibited consistent spherical shapes with diameters at the nanometer scale; CNTs displayed varied diameters ranging from several to tens of nanometers, with their lengths reaching micrometer levels; GNPs appeared as extremely thin, stacked single-layer sheets with lateral dimensions in the micrometer range and thickness in nanometers. These observations aligned with the category of carbon-based nanoparticles, with NDs, CNTs, and GNPs as 0D, 1D, and 2D nanomaterials. Notably, due to their various geometry shapes,

NDs, CNTs, and GNPs exhibited distinct agglomeration behaviors, impacting the physical and mechanical performance of the nanocomposites. Specifically, NDs tended to form agglomerates due to high surface energy and strong interparticle attractions. NDs also provided a small surface area for interaction; however, their isotropic nature facilitated a more uniform distribution within the matrix. In contrast, CNTs tended to bundle or form ropes owing to their tubular structure and strong van der Waals interactions, leading to more constrained regions within the polymer network that might limit chain mobility and enhance stiffness. GNPs stacked together, predisposed by π - π stacking interactions between graphene layers. Their large surface area enabled extensive contact with the epoxy, promoting stronger interfacial adhesion. Despite their particle size variations, agglomeration analysis remained crucial for understanding the microstructural and dispersion characteristics of these nanoparticles, compensating for size differences by maintaining consistent weight additions.

Particle size distribution

Particle size distribution is a critical characteristic for assessing the efficacy of dispersion techniques, including high-shear dispersion and ultrasonication, which could be measured by DLS. Figs. 4(a)–4(b) show the particle size distributions of ND, GNP, and CNT. In Fig. 4, it is noteworthy that all the nanoparticles display typical unimodal particle size distributions. To quantitatively compare the agglomeration sizes among the different nanoparticles, the particle size distribution parameters, including mean (D_{mean}), standard deviation (STD, σ), and mode (M), are presented in Table 3. It is evident that NDs exhibited the smallest agglomeration size compared to GNPs and CNTs. This significant discrepancy in agglomeration size was attributed to their distinct geometric shapes, which profoundly affect their

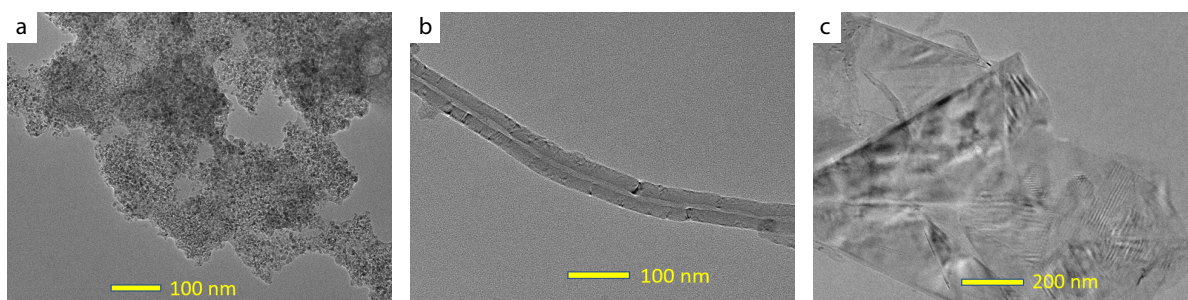


Fig. 3 TEM images of (a) ND, (b) GNP, and (c) CNT.

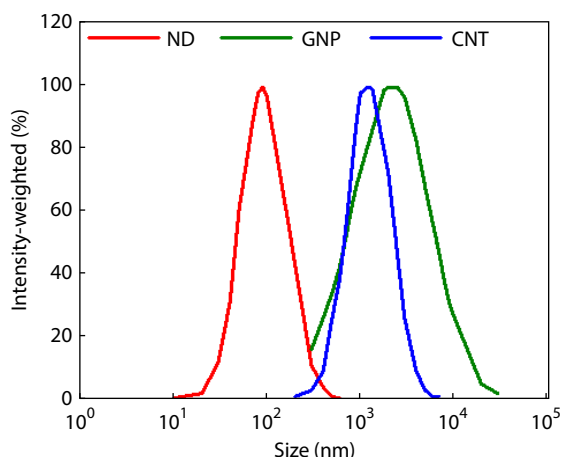


Fig. 4 Particle size distributions of three nanoparticles.

mutual interaction and agglomeration inclination. The spherical NDs displayed a more uniform mass distribution, enhancing mobility and reducing interparticle contact, mitigating larger agglomerate formation. Conversely, due to lower molecular mobility and greater intermolecular attractions, cylindrical CNTs and planar GNPs were more inclined to aggregate and form larger agglomerates.

$$D_{\text{mean}} = \sum_{i=1}^n (P_i \cdot D_i) \quad (9)$$

$$\sigma = \sqrt{\sum_{i=1}^n (D_i - D_{\text{mean}})^2 \times P_i} \quad (10)$$

Where n is the number of particle size classes, P_i is the frequency of particle sizes in various classes i , and M is defined as the particle size with the highest frequency.

Physical Properties

Viscosity

Rheological behavior, especially viscosity, enables to assess the quality, properties, and performance of nano-reinforced epoxy composites. Elevated viscosity of nanocomposites often indicates non-uniform dispersion or severe agglomeration, negatively impacting the properties of nanocomposites. Fig. 5 shows

Table 3 Particle size distribution parameters of three nanoparticles pre- and post-dispersion.

Nanoparticle	D_{mean} (nm)	σ (nm)	M (nm)
ND	5.59×10^2	1.08×10^3	9.00×10^1
GNP	3.52×10^4	1.08×10^5	2.25×10^3
CNT	9.74×10^4	2.41×10^4	1.24×10^3

the viscosity comparison between nano-reinforced epoxy composites at three different weight concentrations (0.5 wt%, 1.0 wt% and 2.0 wt%), with the viscosity of pure epoxy serves as a reference. Adding nanoparticles evidently modified the viscosity of the epoxy composites, and both the geometric shapes and concentrations of the nanoparticles had a considerable impact on the viscosity increments. The most significant viscosity increments were observed in CNT-reinforced epoxy nanocomposites, due to substantial agglomeration of CNTs resulting from their cylindrical geometry and strong mutual attraction. Moreover, GNP-reinforced epoxy nanocomposites displayed an approximately linear relationship between viscosity increments and GNP concentration, reaching a peak at 2.0% with a 45% increment compared to pure epoxy. On the other hand, the addition of NDs slightly reduced the viscosity of the nanocomposites. The reduction was attributed to the lubrication effect of spherical ND nanoparticles, which minimized the friction between the polymer chains of epoxy.^[57]

Micro-CT

In this study, micro-CT was employed to examine the size, quantity, and distribution of voids and defects within the nanocomposites. As depicted in Fig. 6(a), the reconstructed 3D image and vertical view obtained via micro-CT provide a comprehensive visualization of the epoxy composite's internal structure, illustrating the extensive presence of randomly distributed voids within the pure epoxy matrix. Figs. 6(b)–6(j) present vertical views of the CNT-, GNP-, and ND-reinforced epoxy nanocomposites. Compared to pure epoxy, a notable reduction in both quantity and size of voids was observed for all the nanocomposites, indicating lower porosity and improved structural integrity. This was

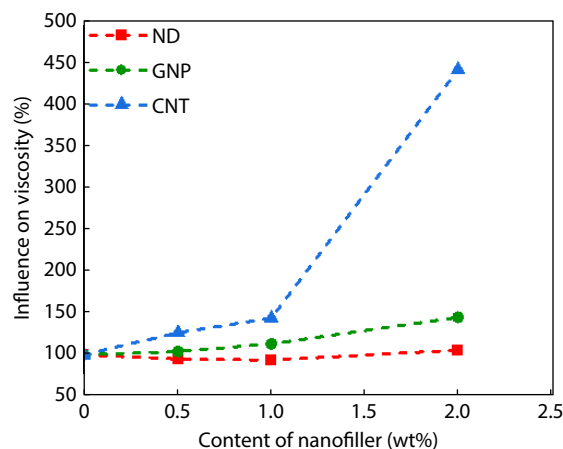


Fig. 5 Viscosity comparison between nano-reinforced epoxy composites and pure epoxy.

because nanoparticles could act as effective fillers, bridging and filling gaps within the epoxy composite. Specifically, for CNT-reinforced nanocomposites, a larger percentage of voids was observed at high concentrations, which was attributed to the tubular shape of CNTs. CNTs may exhibit a greater tendency to agglomerate at elevated concentrations, forming clusters or bundles within the epoxy matrix. These clusters increased the density of some certain localized regions, resulting in voids and porosity in adjacent areas where the epoxy may not fully penetrate or surround the CNT clusters.^[58] Compared to CNTs, GNPs demonstrated remarkable effectiveness in reducing voids, especially at higher concentrations. This can be attributed to the large surface area and excellent dispersibility of GNPs within the epoxy matrix, facilitating the formation of a more uniform and densely packed network structure.^[59] Spherical NDs consistently contributed to the reduction of void size and percentage across all the concentrations, owing to their compact shape and small size. The spherical geometry of NDs enabled them to efficiently fill interstitial spaces between epoxy molecules, minimizing void formation and enhancing structural integrity.^[60] Fur-

thermore, the geometry of nanoparticles influences their interaction with the epoxy matrix, impacting the distribution of free volume within the composite. Specifically, cylindrical CNTs and planar GNPs created more constrained regions within the matrix, leading to a reduction in free volume, while spherical NDs promoted a more uniform free volume distribution and a more uniform particle size distribution after dispersion.

Water Contact Angle of Developed Nanocomposites

The contact angle test was used to determine the wetting behavior of the nanocomposite surface in accordance with ASTM D7334. A camera was used to capture the image, while the angle θ between the water droplet and the coated substrate was calculated by a computer from the image, as shown in Fig. 7(a). Water contact angle measurements of epoxy nanocomposite coatings reinforced with NDs, GNPs, and CNTs are presented in Fig. 7(b). Surprisingly, the addition of these nanoparticles, irrespective of their concentration, did not make substantial changes in the water contact angle. Specifically, while pure epoxy coating exhibited a water contact angle of around 55°,

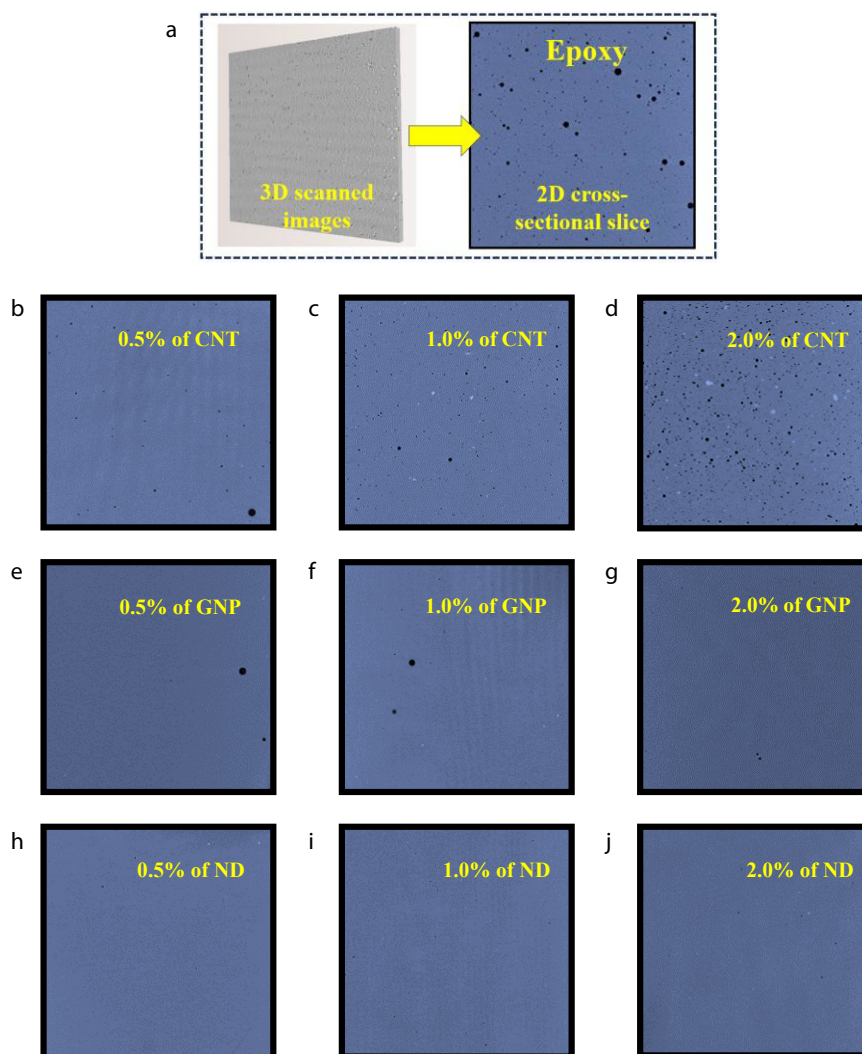


Fig. 6 Vertical view micro-CT images of nanocomposites reinforced with different nanoparticles at various weight concentrations: (a) 3D scanned image of pure epoxy; (b) 0.5% of CNT; (c) 1% of CNT; (d) 2% of CNT; (e) 0.5% of GNP; (f) 1% of GNP; (g) 2% of GNP; (h) 0.5% of ND; (i) 1% of ND; (j) 2% of ND.

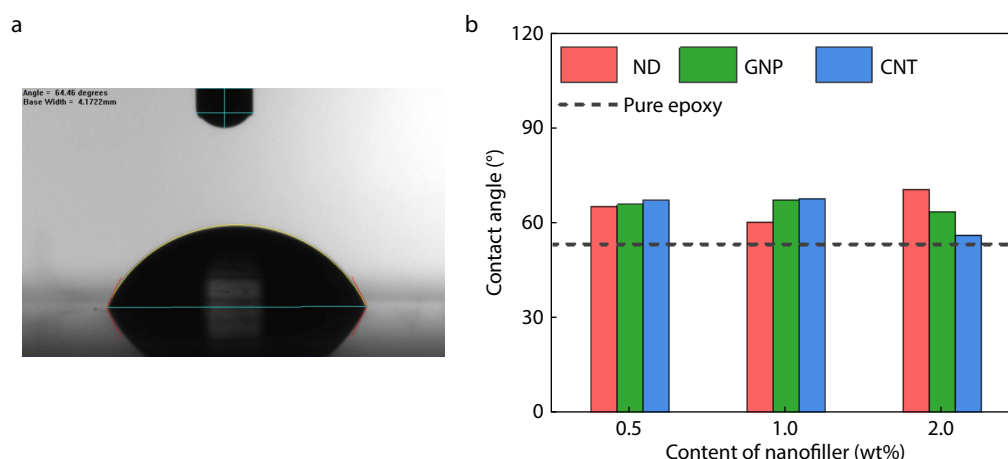


Fig. 7 (a) Image captured and (b) test results of water contact angle test.

nanocomposite coating displayed slightly higher values around 60°. Thus, it can be inferred from the results that the incorporation of nanoparticles fails to significantly alter neither the surface tension of the materials themselves nor the texture of the surface. Thus, this experimental observation can be attributed to the effective dispersion of nanoparticles within the epoxy matrix, excusing that all nanoparticles were covered by epoxy, thereby maintaining the overall surface properties of the epoxy material.

Abrasion Resistance of Developed Nanocomposites

The wear resistance of nanocomposites, influenced by different weight concentrations of ND, GNP, and CNT, was assessed through the Taber abrasion test, as depicted in Fig. 8. Among the nanocomposites reinforced by the three different nanoparticles, NDs exhibited superior wear resistance compared to GNP and CNT at all concentrations. This exceptional performance can be attributed to the inherent characteristics of NDs, such as exceptional hardness, chemical inertness, and high surface area, which enhanced the hardness and damage tolerance of the composite.^[61] Similarly, CNT-reinforced epoxy nanocomposites exhibited improved wear resistance as the increase of CNT concentrations, although the improvements were less significant than ND-reinforced epoxy nanocomposites. In contrast, although 1% and 2% GNP-reinforced epoxy nanocomposites still achieved 18% and 53% higher wear resistance, respectively, 0.5% GNP addition increased the mass loss and deteriorated the wear resistance. The variations of wear resistance could be interpreted by agglomeration at higher, nanoparticle-polymer interactions, nanocomposite defects, and nanoparticle load transferability.^[62] Specifically, as indicated by the particle size distribution measured by DLS in Fig. 4, the significant agglomeration of CNTs resulted in the formation of weak spots within the coating matrix, thereby reducing the effectiveness of the nanoparticles in reinforcement and leading to the lowest observed abrasion resistance.

The SEM images on the abraded surfaces further elucidated the wear resistance differences between pure epoxy and epoxy nanocomposites, as presented in Fig. 9. Pure epoxy showed noticeable material loss and worn surface textures, suggesting its vulnerability to plastic deformation and low wear resistance. Conversely, nano-reinforced composite sur-

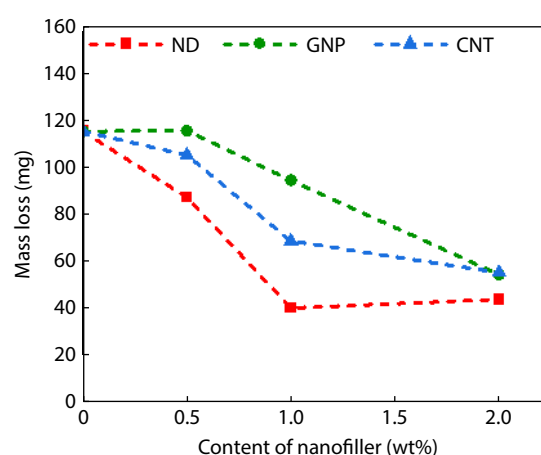


Fig. 8 Abrasion resistance in terms of mass loss for three nano-reinforced epoxy composites.

faces displayed smoother finishes with fewer and smaller cracks, indicating better wear resistance and improved load transferability of wear forces due to strong nanoparticle-epoxy interactions. Generally speaking, the preservation of the original abrasion surface appearance is the direct feature for enhanced wear performance. The spherical shape and smoother surface of NDs reduced the frictional forces, resulting in ND-reinforced epoxy nanocomposites with exceptional surface integrity and superior wear resistance.^[63]

Tensile Properties of Developed Nanocomposites

The tensile properties of nanocomposites play a pivotal role in assessing nanoparticle reinforcement and composite performance. Fig. 10 compares the impact of differently shaped nanoparticles (ND, GNP, and CNT) and their weight concentrations on the tensile strength and failure strain of nano-reinforced epoxy composites. All the nanocomposites exhibited improved tensile properties over pure epoxy because the high surface area of these nanoparticles helped form robust bonds within the surrounding epoxy, enhancing both strength and toughness of the composites. For ND-reinforced epoxy nanocomposites, the peak tensile properties were achieved at 1.0% addition, with 52% and 100% improvements in tensile strength and fail-

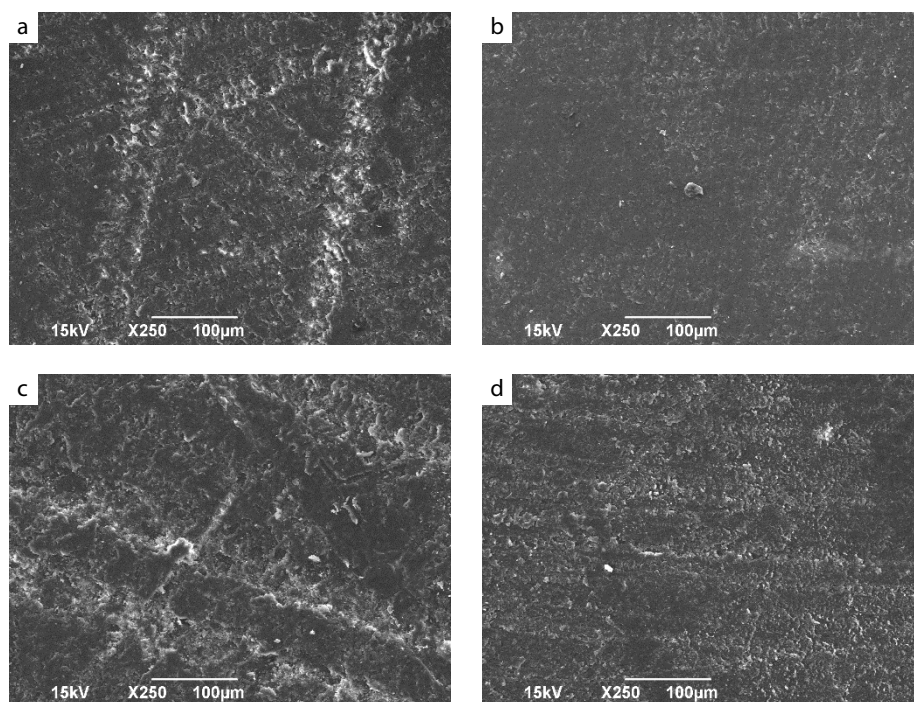


Fig. 9 Abraded surfaces of 1.0 wt% nano-reinforced epoxy nanocomposites: (a) pure epoxy; (b) ND; (c) GNP; (d) CNT.

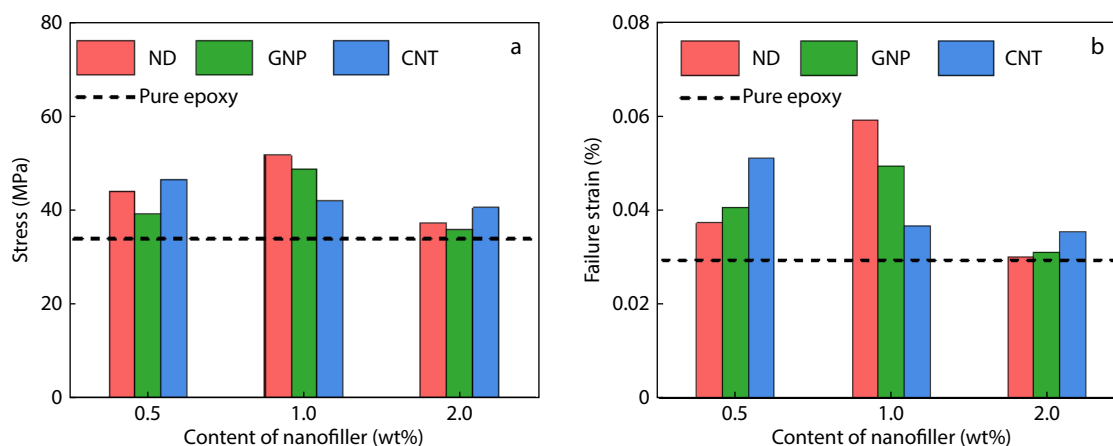


Fig. 10 Tensile properties of nano-reinforced epoxy composites: (a) tensile stress; (b) failure strain.

ure strain, respectively. The spherical shape of NDs and lower concentration contributed to better dispersion, fostering improved interaction with the epoxy matrix. Moreover, increasing the weight concentration of NDs typically resulted in a greater number of interface regions between the matrix and the nanoparticles, which reduced free volume by filling voids and constraining polymer chain mobility. This reduction in free volume contributed to enhanced tensile properties. However, the tensile properties of the composites exhibited a decline when further adding ND to 2.0% due to increased agglomeration, which potentially created stress concentration or defects, and diminished overall strength and ductility. A similar changing trend was observed for GNP-reinforced epoxy nanocomposites. In contrast, the incorporation of CNTs in epoxy nanocomposites exhibited a significant increase in tensile strength and failure strain up to 0.5% CNT concentration, followed by a decline at

higher loadings (1.0% and 2.0%). It is noteworthy that the negative effect of CNT agglomeration was observed at lower concentrations compared to NDs and GNPs. Yet, higher weight concentrations led to significantly more severe agglomeration, introducing more defects and negatively affecting tensile properties.

The fracture surfaces of pure epoxy and nanocomposite samples were also characterized by the SEM images, revealing distinct features as illustrated in Fig. 11. Pure epoxy exhibited large fracture textures with a relatively smooth and uniform appearance, indicating a dominant failure mode of brittle failure. Conversely, nano-reinforced composite displayed rougher surfaces with compacted cracking cleavages. The rougher surface and compacter cleavages were observed as the indication of improved nanoparticle-epoxy matrix interactions, which facilitated more effective load transfer and energy dissipation during the tensile testing.

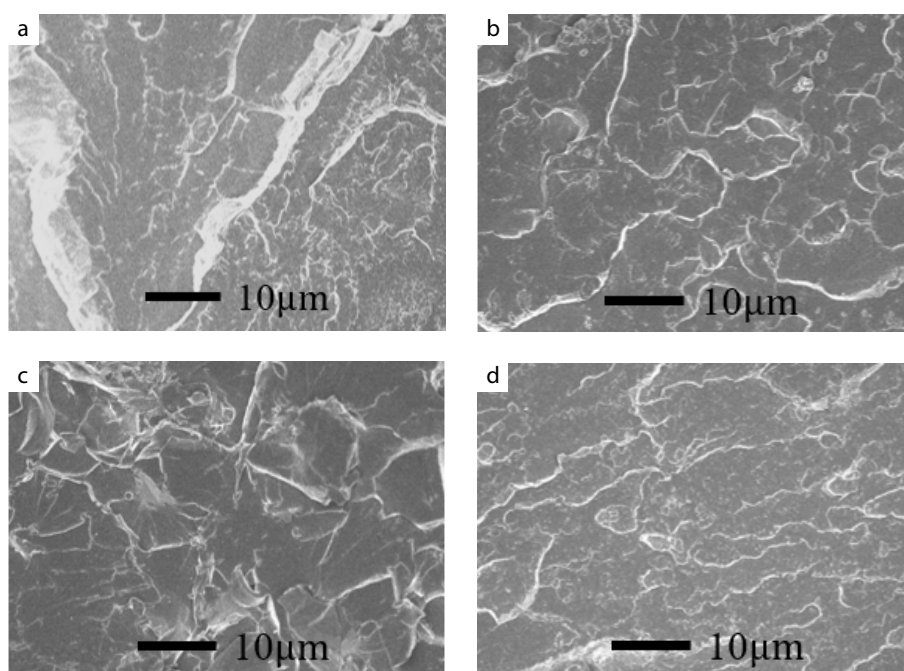


Fig. 11 Fracture surfaces of 1.0 wt% nano-reinforced epoxy nanocomposites: (a) pure epoxy; (b) ND; (c) GNP; (d) CNT.

RVE SIMULATION RESULTS

Fig. 12 presents a visualization from the RVE simulations results under tensile load for 0D nanodiamond composites, showing the distribution of plastic strain throughout the composites and highlighting the areas of maximum principal stress within the nanoparticles. Due to the ND geometry shape, the nanoparticles in the corner and center had little impact or contribution for load transmission, as indicated by a very small plastic deformation.

The stress-strain results obtained from the RVEs are presented in **Fig. 13**, which summarizes the ultimate stress across various weight fractions. Nanocomposite with 0% weight fraction of nanoparticles, considered as pure epoxy, serves as a reference. In **Fig. 13(a)** for ND-reinforced composites, the variation of weight concentration from 0.5% to 2.0% did not substantially affect the plastic region but had a minimal impact on the material's ultimate strength, indicating that ND spherical geometry had almost no contribution to plastic

stress on current RVE models. A similar trend was observed in CNT-reinforced composite at the 90° orientation, shown in **Fig. 13(b)**. By varying different weight concentrations, the tensile strength remained nearly unchanged in the 0° loading direction, demonstrating the non-isostrain condition in both reinforcements and surrounding matrix materials. In **Fig. 13(c)** for GNP-reinforced composites, a generally constant stress was observed with different weight concentrations under axial loading. While the radial simulation suggested that increasing the weight concentration enhanced the ultimate stress.

Fig. 14 displays the ultimate strength outcomes of nanocomposites reinforced with different nanoparticles at different weight concentrations. Regarding NDs in **Fig. 14(a)**, when the weight concentration increased from 0% to 2%, the tensile strength only increased around 5%, which was attributed to non-isostrain condition as discussed in the previous section. Regarding CNTs in **Fig. 14(b)**, a similar trend was observed for CNTs with 90° orientation, while 0° oriented CNTs achieved the highest tensile strength than all other

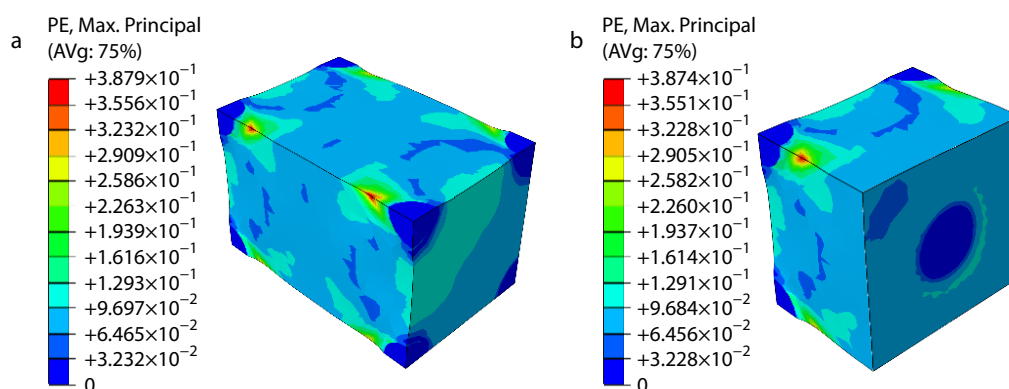
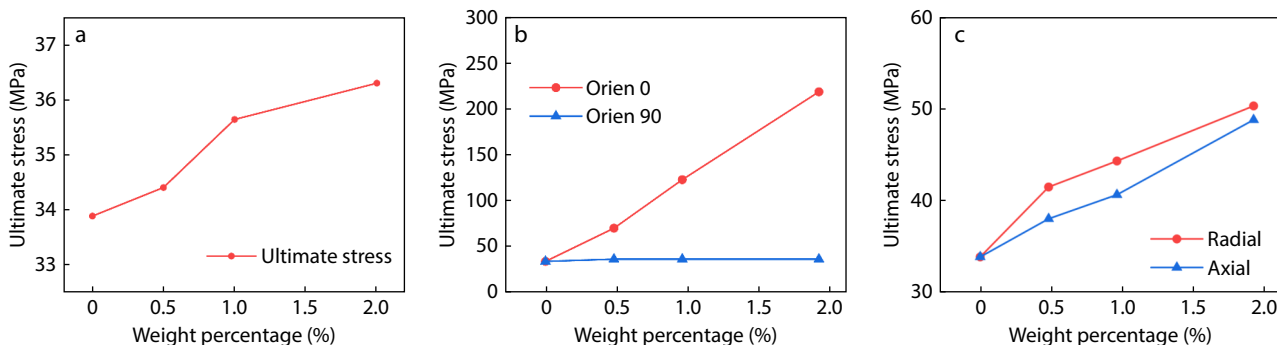
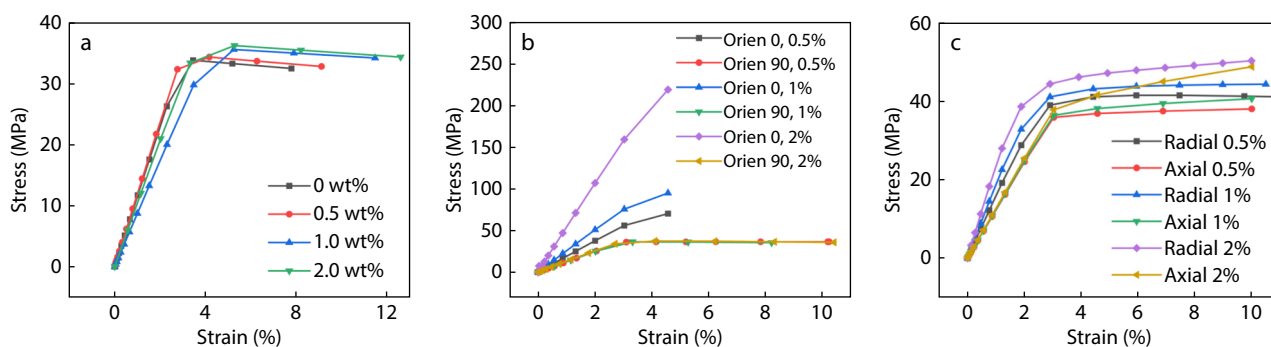


Fig. 12 Simulation visualization results with 2.0% weight fraction of ND diamond additive: (a) external view, (b) internal view.



nanocomposite, suggesting that the mechanical properties of nanocomposites were significantly affected by the nanofillers orientation. However, the orientation effect did not produce a highly sensitive influence in GNP-reinforced nanocomposites, as shown in Fig. 14(c). As the weight concentration of GNPs increased from 0.5% to 2%, the ultimate stress under radial loading direction also improved considerably. The increasing tendency of GNPs was attributed to the alignment of nanoplatelets with the loading direction, facilitating optimal load transfer through the shear lag mechanism. The results were consistent with another reference where an increase in weight volume fraction of aligned graphene oxide resulted in a gradual rise in ultimate stress of composite material. The findings above not only clearly indicate the remarkable influence of nanoparticle weight concentration on the mechanical performance of nanocomposites, but also highlighted the critical role of nanoparticle geometric shape and morphology in determining the effectiveness of load transmission and stress transfer. Essentially, the geometrical configuration of nanoparticles can alter the mechanical pathways and the overall mechanical performance of the nanocomposite, emphasizing the importance of considering nanoparticle geometric shape in the design and application of advanced composite materials.

UNDERSTANDING THE DISCREPANCIES BETWEEN NUMERICAL AND EXPERIMENTAL RESULTS

The numerical results were validated against the experimental results. ND, as the OD nanoparticle, eliminates the influence of

nanoparticle orientation. By comparing the mechanical properties of ND-reinforced composites experimentally and numerically, it was found that tensile strengths measured in dog-bone tests were non-negligible higher than numerically predicted tensile strengths. The improvements in simulation output were mainly attributed to changes in microstructure within the ND-reinforced nanocomposite. Micro-CT images confirmed the presence of voids in the epoxy matrix, which were significantly reduced by the addition of ND, leading to substantial strength enhancement.

For CNT-reinforced nanocomposites, experimental strengths were slightly lower than those predicted by simulations with 90° orientation, but tremendously lower than simulation strengths with 0° orientation. The reasons behind the discrepancies lie in the importance of nanoparticle orientation. When all the cylindrical CNTs are aligned along the loading direction, the entire length of an individual CNTs can contribute to the load-bearing capacity, and the tensile load is evenly distributed along the length of the CNTs. In this case, the extraordinary mechanical properties of CNTs are fully utilized, maximizing their effectiveness in reinforcing the nanocomposites. On the contrast, the reinforcing efficiency of 90° oriented CNTs are rather limited. The differences in radially and axially distributed GNP-reinforced nanocomposites can be interpreted by the effect of nanoparticle orientation.

In addition to nanoparticle orientation, nanoparticle agglomeration can also contribute to the lower experimental strengths compared to simulation outputs in CNT- and GNP-reinforced nanocomposites. The results of nanoparticle dispersion characteristics revealed the severe agglomeration of CNTs and GNPs in the epoxy matrix, especially at relatively

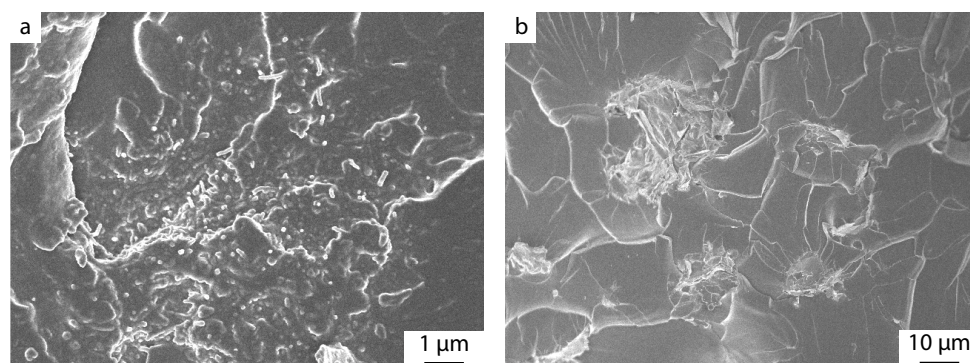


Fig. 15 SEM images at high magnifications: (a) agglomeration of CNTs at 2%; (b) agglomeration of GNPs at 2%.

higher weight concentrations as shown in Fig. 15. Fig. 15 displays the SEM images at high magnifications revealing the agglomeration of nanoparticles in the epoxy coating. It can be observed in Fig. 15(a) that all the visible CNTs stayed tightly and closely with each other in the form of a huge CNT clusters. No individual CNT can be detected beyond this cluster. A similar agglomeration phenomenon is found in the Fig. 15(b) for GNPs. Severe agglomerated nanoparticles acted as defects and imperfections inducing stress concentration and reducing the interfacial bonding between nanofillers and polymer materials, which eventually diminished the mechanical performance of nanocomposites. However, agglomeration was not considered in the RVE modeling. All the nanoparticles were separately distributed in the matrix materials, resulting in better mechanical properties than experimental values.

It should be noted that although the RVE modeling and simulation were performed under idealized conditions without considering nanoparticle orientation and agglomeration, the largest differences between experimental and numerical tensile strengths were less than 18%, except 0° oriented CNTs which are difficult to achieve in the experiments. The reasonable consistency between numerical and experimental results proved the validation of the FEA results. The RVE modeling successfully reproduced the mechanical behaviors of the nanocomposites. Regarding the discrepancies between numerical and experimental results, identifying the influencing factors such as nanoparticle orientation and agglomeration, may provide valuable insights into understanding the potential performance of nanocomposites, paving the way for more accurate simulations and design framework for functional nanomaterials.

CONCLUSIONS

This study systematically investigated the influence of different nanoparticles, including 0D NDs, 2D GNPs, and 1D CNTs, on the performance of epoxy nanocomposites. The effects of weight concentrations (0.5%, 1.0%, and 2.0%) of these nanoparticles were also assessed, providing valuable insights into the correlation between nanoparticle shape, concentration, and resulting properties in the nanocomposites. Experimental results showed that NDs with spherical geometry shape achieved the most homogeneous dispersion and smallest agglomeration, which further led to lower porosity and viscosity, compared to GNPs and CNTs. While the addition of nanoparticles failed to produce ob-

vious variations in water contact angles regardless of their geometric shapes and concentrations. Regarding mechanical properties, the spherical shape and smooth surfaces of NDs also facilitated enhanced nanofiller-epoxy interactions, efficient load transfer and energy dissipation, resulting in the superior wear resistance and tensile strength of ND-reinforced epoxy nanocomposites. The experimental results were further validated by FEA using RVE modeling approach. The RVE model faithfully predicted the tensile properties of nanoparticles to a reasonable approximation. The discrepancies between experimental and numerical results highlighted the effects of influencing factors, such as porosity, nanoparticle agglomeration and orientation, on the mechanical performance of nanocomposites in practical applications.

In future work, a more comprehensive investigation will be undertaken to explore a broader range of nanoparticles, including graphene oxide, boron nitride nanotubes, silicon carbide nanoparticles, or others, to evaluate their comparative effects on the mechanical, thermal, and chemical resistance properties of epoxy coatings. In addition, the long-term durability of epoxy coatings under various environmental conditions, such as UV exposure, humidity, and temperature variations, will be examined to provide a more comprehensive evaluation of coating performance over time.

Conflict of Interests

The authors declare no interest conflict.

Data Availability Statement

Data that should not be shared: The related data of this paper is data that should not be shared, and can be obtained from the author for reasonable reasons. The authors' contact information: luyang.xu@nds.edu and dawei.zhang.1@nds.edu.

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REFERENCES

- Hassan, N.; Sun, J.; Shen, Z.; Xiao, Q. Synthesis of polymeric superhydrophobic coatings of nickel stearate for excellent corrosion resistance, self-cleaning, and photodegradation. *Surf. Interfaces* **2024**, *51*, 104648.
- Akçay, S. B.; Kocaman, M.; Çelebi, M.; Güler, O.; Varol, T. Surface modification for improving interfacial, mechanical and thermal performance characteristics in epoxy composites, Electroless nickel enhancement of dendritic copper particle-reinforced epoxy. *Surf. Coat. Technol.* **2024**, *478*, 130417.
- Wei, H.; Xia, J.; Zhou, W. Adhesion and cohesion of epoxy-based industrial composite coatings. *Compos. Part B Eng.* **2020**, *193*, 108035.
- Dorado, F.; Toledo, L.; de la Osa, A. R. Adhesion enhancement and protection of concrete against aggressive environment using graphite-Fe₂O₃ modified epoxy coating. *Constr. Build. Mater.* **2023**, *379*, 131179.
- Su, X.; Wang, R.; Li, X. A comparative study of polymer nanocomposites containing multi-walled carbon nanotubes and graphene nanoplatelets. *Nano Mater. Sci.* **2022**, *4*, 185–204.
- Li, X.; Warzywoda, J.; McKenna, G. B. Mechanical responses of a polymer graphene-sheet nano-sandwich. *Polymer* **2014**, *55*, 4976–4982.
- Srividhya, D.; Manjunathan, S.; Nithyanandan, S.; Balamurugan, S.; Senthil, S. Synthesis and characterization of triazole containing liquid crystalline polymers through 1,3-dipolar cycloaddition polymerization. *Chinese J. Polym. Sci.* **2009**, *27*, 761–770.
- Nishi, T.; Nukaga, H.; Fujinami, S.; Nakajima, K. Nanomechanical mapping of carbon black reinforced natural rubber by atomic force microscopy. *Chinese J. Polym. Sci.* **2007**, *25*, 35–41.
- Peng, Y.; Du, R.; Fu, Q.; Wang, Y. Reinforcement of polydimethylsiloxane networks by nano-calcium carbonate. *Chinese J. Polym. Sci.* **2005**, *23*, 411–416.
- Jabeen, S.; Kausar, A.; Muhammad, B.; Gul, S.; Farooq, M. A review on polymeric nanocomposites of nanodiamond: carbon nanotube, and nanobifiller, structure, preparation and properties. *Polym. Plast. Technol. Eng.* **2015**, *54*, 1379–1409.
- Speranza, G. The role of functionalization in the applications of carbon materials: an overview. *C* **2019**, *5*, 84.
- Kordi, A.; Adibnazari, S.; Imam, A.; Najafi, M. Effects of two- and three-dimensional graphene-based nanomaterials on the fatigue behavior of epoxy nanocomposites. *Mater. Today Commun.* **2020**, *24*, 101194.
- Kumar, A.; Sharma, K.; Dixit, A. R. A review of the mechanical and thermal properties of graphene and its hybrid polymer nanocomposites for structural applications. *J. Mater. Sci.* **2019**, *54*, 5992–6026.
- Singh, B.; Mohanty, A. Nano-mechanical approach to study the behavior of annealed nanodiamond reinforced epoxy nanocomposites. *Polym. Compos.* **2023**, *44*, 2997–3006.
- Singh, N. P.; Gupta, V. K.; Singh, A. P. Graphene and carbon nanotube reinforced epoxy nanocomposites: A review. *Polymer* **2019**, *180*, 121724.
- Liu, S.; Gu, L.; Zhao, H.; Chen, J.; Yu, H. Corrosion resistance of graphene-reinforced waterborne epoxy coatings. *J. Mater. Sci. Technol.* **2016**, *32*, 425–431.
- Lazutin, A. A.; Vasilevska, V. V. Matrix free polymer nanocomposites from amphiphilic hairy nanoparticles: Solvent selectivity and mechanical properties. *Polymer* **2022**, *255*, 125172.
- Cui, W.; Liu, J.; You, W.; Yu, W. Mechanical reinforcement by bridging chains in polymer nanocomposites. *Polymer* **2024**, *306*, 127208.
- Cao, M.; Wang, S.; Zang, J. Experimental and simulation analysis of the effect of GNPs on the mechanical and interfacial properties of CF/PEEK-Ti fiber metal laminates. *Compos. Sci. Technol.* **2024**, *246*, 110387.
- Zhang, D.; Huang, Y.; Xu, L. Synergistic effects of nanoparticle geometric shape and post curing on carbon-based nanoparticle reinforced epoxy coatings: Characterization, microstructure, and adhesion properties. *Prog. Org. Coat.* **2023**, *185*, 107929.
- de Oliveira T. C.; Ferreira F. V.; de Menezes, B. R. C. Engineering the surface of carbon-based nanomaterials for dispersion control in organic solvents or polymer matrices. *Surf. Interfaces* **2021**, *24*, 101121.
- Wang, J.; Sun, Y.; Yu, M. Emulsions stabilized by highly hydrophilic TiO₂ nanoparticles via van der Waals attraction. *J. Colloid Interface Sci.* **2021**, *589*, 378–387.
- Ferreira, F. V.; Francisco, W.; de Menezes, B. R. C. Carbon nanotube functionalized with dodecylamine for the effective dispersion in solvents. *Appl. Surf. Sci.* **2015**, *357*, 2154–2159.
- Zhang, D.; Huang, Y.; Chia, L. Effects of carbon nanotube (CNT) geometries on the dispersion characterizations and adhesion properties of CNT reinforced epoxy composites. *Compos. Struct.* **2022**, *296*, 115942.
- Mozaffarinasab, H.; Jamshidi, M. Surface modification of carbon nanotubes by a bifunctional amine silane; effects on physical/mechanical/thermal properties of epoxy nanocomposite. *Prog. Org. Coat.* **2023**, *179*, 107521.
- Shokrian MD, Shelesh-Nezhad K, Najjar R. Effect of CNT dispersion methods on the strength and fracture mechanism of interface in epoxy adhesive/Al joints. *J Adhes Sci Technol* **2019**, *33*, 1394–1409.
- Nunn, N.; Torelli, M.; McGuire, G.; Shenderova, O. Nanodiamond: a high impact nanomaterial. *Curr. Opin. Solid State Mater. Sci.* **2017**, *21*, 1–9.
- Veeman, D.; Shree, M.V.; Sureshkumar P. Sustainable development of carbon nanocomposites: synthesis and classification for environmental remediation. *J. Nanomater.* **2021**, *2021*, e5840645.
- Rathinavel, S.; Priyadarshini, K.; Panda, D. A review on carbon nanotube: an overview of synthesis, properties, functionalization, characterization, and the application. *Mater. Sci. Eng. B* **2021**, *268*, 115095.
- Liu, X. M.; Huang, Z.; Oh, S. Carbon nanotube (CNT)-based composites as electrode material for rechargeable Li-ion batteries, a review. *Compos. Sci. Technol.* **2012**, *72*, 121–144.
- Uthale, S. A.; Dhamal, N. A.; Shinde, D. K.; Kelkar A. D. Polymeric hybrid nanocomposites processing and finite element modelling: an overview. *Sci. Prog.* **2021**, *104*, 00368504211029471.
- Najafi, M.; Salami-Kalajahi, M.; Haddadi-Asl, V. Quantitative evaluation of arrangement of monomers in linear binary copolymers using a Monte Carlo simulation method. *Chinese J. Polym. Sci.* **2009**, *27*, 195–208.
- Li, Y.; Tang, S.; Abberton, B. C. A predictive multiscale computational framework for viscoelastic properties of linear polymers. *Polymer* **2012**, *53*, 5935–5952.
- Burgos-Mármol, J. J.; Patti A. Unveiling the impact of nanoparticle size dispersity on the behavior of polymer nanocomposites. *Polymer* **2017**, *113*, 92–104.
- Bishara, D.; Xie, Y.; Liu, W. K.; Li, S. A state-of-the-art review on machine learning-based multiscale modeling, simulation, homogenization and design of materials. *Arch. Comput. Methods Eng.* **2023**, *30*, 191–222.
- Hu, J.; Wang, L.; Wang, X. Non-probabilistic uncertainty quantification of fiber-reinforced composite laminate based on micro-and macro-mechanical analysis. *Appl. Sci.* **2022**, *12*, 11739.
- El Moumen, A.; Kanit, T.; Imad, A. Numerical evaluation of the representative volume element for random composites. *Eur. J.*

- Mech-A Solids* **2021**, 86, 104181.
- 38 Li, G.; Sharifpour, F.; Bahmani, A.; Montesano, J. A new approach to rapidly generate random periodic representative volume elements for microstructural assessment of high volume fraction composites. *Mater. Des.* **2018**, 150, 124–138.
 - 39 Kausar, A. Nanocarbon and macrocarbonaceous filler-reinforced epoxy/polyamide: a review. *J. Thermoplast Compos Mater* **2022**, 35, 2620–2640.
 - 40 Sharma, A.; Munde, Y.; Kushvaha, V. Representative volume element based micromechanical modelling of rod shaped glass filled epoxy composites. *SN Appl. Sci.* **2021**, 3, 232.
 - 41 Mohammadpour, E.; Awang, M.; Kakooei, S.; Akil, H. M. Modeling the tensile stress-strain response of carbon nanotube/polypropylene nanocomposites using nonlinear representative volume element. *Mater. Des.* **2014**, 58, 36–42.
 - 42 Chanda, S.; Bajwa, D. S. A review of current physical techniques for dispersion of cellulose nanomaterials in polymer matrices. *Rev. Adv. Mater. Sci.* **2021**, 60, 325–341.
 - 43 Wang, X.; Tang, F.; Cao, Q. Comparative study of three carbon additives: carbon nanotubes, graphene, and fullerene-C60, for synthesizing enhanced polymer nanocomposites. *Nanomaterials* **2020**, 10, 838.
 - 44 Popov, V. Carbon nanotubes: properties and applications. *Mater. Sci. Eng. R-Rep.* **2018**, 43, 61–102.
 - 45 Kukovec, Á.; Kozma, G.; Kónya, Z., in Multi-Walled Carbon Nanotubes, Vajtai, R. ed, *Springer Handbook of Nanomaterials*. Berlin, Heidelberg, **2013**, 147–188.
 - 46 Shen, M. Y.; Chang, T. Y.; Hsieh, T. H. Mechanical properties and tensile fatigue of graphene nanoplatelets reinforced polymer nanocomposites. *J. Nanomater.* **2013**, 2013, 565401.
 - 47 Gavallas, P.; Savvas, D.; Stefanou, G. Mechanical properties of graphene nanoplatelets containing random structural defects. *Mech. Mater.* **2023**, 180, 104611.
 - 48 Fish, J., in Multiscale Modeling and Simulation of Composite Materials and Structures, de Borst, R.; Ramm, E., ed, *Multiscale Methods in Computational Mechanics*, Dordrecht, **2010**, 55.
 - 49 Devireddy, S. B. R.; Biswas, S. Effect of fiber geometry and representative volume element on elastic and thermal properties of unidirectional fiber-reinforced composites. *J. Compos.* **2014**, 2014, 629175.
 - 50 Balasubramani, N. K.; Zhang, B.; Chowdhury, N.T. Micro-mechanical analysis on random RVE size and shape in multiscale finite element modelling of unidirectional FRP composites. *Compos. Struct.* **2022**, 282, 115081.
 - 51 Devireddy, S. B. R.; Biswas, S. Effect of fiber geometry and representative volume element on elastic and thermal properties of unidirectional fiber-reinforced composites. *J. Compos.* **2014**, 2014, e629175.
 - 52 Hussein, A.; Ramasundaram, S.; Kim, B. A novel method for fabricating bioinspired layered nanocomposites using aligned graphene oxide/PVDF and their micromechanical modeling. *Mater. Today Commun.* **2020**, 24, 101050.
 - 53 Sun, C. T.; Vaidya, R. S. Prediction of composite properties from a representative volume element. *Compos. Sci. Technol.* **1996**, 56, 171–179.
 - 54 Romanov, V.; Lomov, S. V.; Swolfs, Y. Statistical analysis of real and simulated fibre arrangements in unidirectional composites. *Compos. Sci. Technol.* **2013**, 87, 126–134.
 - 55 Tian, W.; Qi, L.; Zhou, J.; Guan, J. Effects of the fiber orientation and fiber aspect ratio on the tensile strength of Csf/Mg composites. *Comput. Mater. Sci.* **2014**, 89, 6–11.
 - 56 Turaka, S.; Chintalapudi, R.; Kannaiyan Geetha, N.; Pappula, B.; Makgato, S. Experimental and numerical analysis of the Microstructure and mechanical properties of unidirectional glass fiber reinforced epoxy composites. *Compos. Struct.* **2024**, 331, 117887.
 - 57 Li, W.; Suzuki, T.; Minami, H. The interface adsorption behavior in a Pickering emulsion stabilized by cylindrical polystyrene particles. *J. Colloid. Interface Sci.* **2019**, 552, 230–235.
 - 58 Chen, H.; Lian, Q.; Xu, W. Insights into the synergistic mechanism of reactive aliphatic soft chains and nano-silica on toughening epoxy resins with improved mechanical properties and low viscosity. *J. Appl. Polym. Sci.* **2021**, 138, 50484.
 - 59 Bisht, A.; Dasgupta, K.; Lahiri, D. Effect of graphene and CNT reinforcement on mechanical and thermomechanical behavior of epoxy—a comparative study. *J. Appl. Polym. Sci.* **2018**, 135, 46101.
 - 60 Wetzel, B.; Hauptert, F.; Zhang, M. Epoxy nanocomposites with high mechanical and tribological performance. *Compos. Sci. Technol.* **2003**, 63, 2055–2067.
 - 61 Alexopoulos, N. D.; Paragkamian, Z.; Poulin, P.; Kourkoulis, S. K. Fracture related mechanical properties of low and high graphene reinforcement of epoxy nanocomposites. *Compos. Sci. Technol.* **2017**, 150, 194–204.
 - 62 Abedi, M.; Gulisano F.; Han, B.; Fanguero, R.; Correia, A. G. The pioneer of intelligent and sustainable construction in tunnel shotcrete applications: a comprehensive experimental and numerical study on a self-sensing and self-heating green cement-based composite. *Meas. Sci. Technol.* **2024**, 35, 065601.
 - 63 Shekar, K. C.; Priya, M. S.; Subramanian, P. K. Processing, structure and flexural strength of CNT and carbon fibre reinforced, epoxy-matrix hybrid composite. *Bull. Mater. Sci.* **2014**, 37, 597–602.