Industry Science and Engineering Vol. 3 No. 2, 2026

Interfacial Optimization of Functionalized Graphene/Epoxy Nanocomposites for Concrete Repair: A Review

Junxi Liu[1], Yanzhe Wang[2], Yu'ao Li[2]
[1]*School of Materials and Energy, Yunnan University, Kunming, Yunnan, China*
[2]*School of Architecture and Planning, Yunnan University, Kunming, Yunnan, China*
[*]*Corresponding Author*

Abstract: Functionalized graphene oxide (GO) and graphene (FG), as nanofillers embedded in epoxy resin matrix, can be utilized for concrete protection and reinforcement. Key techniques such as TiO_2 modification and silane coupling covalent functionalization were employed to enhance graphene dispersion and compatibility with the epoxy matrix. The 3D graphene network construction technology was utilized to assemble the composite into a dense mass transfer barrier network with efficient thermal conduction channels. Experimental results demonstrate that this method achieves 46% and 33% increases in maximum flexural strength and interlayer shear strength, respectively, while reducing capillary water absorption and chloride ion diffusion coefficient by over 50%. The thermal conductivity coefficient improves by 1388%, realizing dual functional enhancements of mechanical reinforcement and impermeable protection. Additionally, functionalized graphene significantly improves composite performance through diversified interface strengthening mechanisms including physical barriers, chemical bonding, and 3D network interlocking. However, challenges such as process optimization, cost control, and long-term durability remain to be addressed.

Keywords: Graphene Functionalization; Nanocomposites; Concrete Repair; Interfacial Design

1. Introduction

In modern construction, protective materials are required to possess excellent protective performance. Traditional epoxy resin, owing to its strong adhesion, good chemical stability, and high mechanical strength, has become one of the most common matrix materials for building protection [1]. For the protection of building concrete, it is essential to ensure comprehensive properties such as good impermeability, corrosion resistance, and mechanical durability [2]. However, epoxy resin also has drawbacks like brittleness and poor thermal conductivity. When subjected to harsh environments such as alternating humidity and heat or salt spray erosion, it is prone to interfacial debonding and the initiation and propagation of microcracks [3,4], thereby affecting the durability of the repaired protective layer.

To overcome these limitations, researchers have recently attempted to incorporate nanomaterials into epoxy resin, aiming to collectively enhance the mechanical properties, durability, and smart characteristics of composites by improving the performance of the interfaces among the nanofiller, resin, and concrete. Graphene, renowned as the "king of new materials" with its unique two-dimensional structure of single-layer carbon atoms, is considered one of the optimal choices for reinforcement fillers due to its high strength, thermal conductivity, and enormous specific surface area [5]. Utilizing graphene's effects of inducing crack deflection and stress bridging can significantly improve the mechanical and durability properties of composites. However, its immense specific surface area makes it highly susceptible to agglomeration, and it exhibits poor compatibility with polymer matrices. Therefore, to facilitate its application in epoxy resins, external additives are often required for functionalization (e.g., via oxidation or fluorination). While this can improve its dispersibility and interfacial interactions to some extent, universally applicable additives that efficiently ensure the dispersion and stability of functionalized graphene in various epoxy resin composites have not yet been developed, leading to certain limitations in practical engineering applications.

This article reviews research on constructing and optimizing the "nanofiller-resin-concrete"

interface in functionalized graphene/epoxy nanocomposites through functionalization strategies to synergistically enhance the composite's mechanical properties and durability. It provides a theoretical basis for developing high-performance, long-lasting novel concrete repair materials.

2. Graphene Functionalization Strategies

Functionalization strategies refer to the chemical modification of GO and FG to improve the dispersion of graphene in epoxy resin and the interfacial bonding strength, thereby preventing agglomeration and enhancing composite performance. Current research primarily focuses on covalent functionalization, including hydroxylation, carboxylation, among others. Beyond these, there are methods such as inorganic nanoparticle functionalization, organic molecule functionalization, and self-healing functionalization.

2.1 Hydroxylation Modification

Hydroxylation primarily involves introducing hydroxyl (-OH) functional groups onto the graphene surface through oxidation reactions. GO is the most typical hydroxylation product, containing a large number of oxygen-containing groups such as hydroxyl and epoxide groups [5]. These highly polar groups significantly enhance the hydrophilicity of graphene, thereby greatly improving its dispersibility in aqueous systems (e.g., cement-based systems) [6]. For instance, Yu et al. [6] added only a trace amount (0.0078 wt%) of industrial GO along with fly ash (FA) to cemented waste rock backfill. Observations via metal injection and backscattered electron (BSE) imaging revealed that after GO addition, the porosity of the cement matrix significantly decreased (maximum reduction of 24.4%), with pore refinement (equivalent diameter reduction ranging from 19.1% to 26.7%). GO increased the tensile strength by up to 25.7%, compressive strength by up to 53.6%, and the fractal dimension of the strain field at failure by up to 19.6%. The hydrophilic functional groups of GO disperse uniformly in water, acting as effective and uniform hydration nucleation sites in cement, leading to increased and denser hydration products, thus reducing porosity and improving pore structure. The uniform dispersion of GO also produces a uniform nano-enhancement effect, resulting in cement-based materials with good mechanical properties and impermeability, demonstrating the effectiveness of GO's good dispersibility for improving the macroscopic properties of cement-based materials. However, upon heat treatment, the oxygen-containing functional groups in GO decompose, causing spontaneous reduction and stacking of GO, which further reduces its interfacial activity [7]. This is one of the challenges faced by this type of functionalization method.

2.2 Carboxylation Modification

This carboxylation modification typically involves treating graphene with strong oxidants to introduce carboxyl (-COOH) groups at the edges or defect sites of graphene. Graphene acid (G-COOH) is a typical representative. Its carboxyl groups can undergo esterification/amidation reactions with the epoxy/amino groups of epoxy resin, forming covalent bonds [8]. Studies have found that phosphate-functionalized graphene, due to its numerous phosphate groups with high active terminal groups, can enhance the interaction with geopolymer matrices while improving the hydrophilicity and dispersibility of graphene in aqueous systems, thereby enhancing material formability [6]. However, excessive oxidation during carboxylation can introduce significant structural defects into graphene, degrading its intrinsic electrical properties. Mukesh Kumar Thakur et al. [9] grew monolayer graphene using ^{12}C and ^{13}C isotopes, respectively. By tracking the positional shifts of characteristic peaks in Raman spectra (mass effect), they non-destructively detected and monitored the Raman signals of top and bottom graphene layers. This demonstrates that covalent functionalization is a "double-edged sword": while it enables strong interfacial bonding and property modulation, it may also disrupt the perfect lattice of graphene, introducing defects that degrade electrical performance. Their proposed method constructed a "sandwich" structure (F-BLG), which can maintain functionalized edge interactions (via shared and stabilized F) while passivating defects and restoring electrical performance.

2.3 Inorganic Nanoparticle Functionalization

Decorating graphene with inorganic nanoparticles (e.g., TiO_2) can enhance the interfacial compatibility between them and the epoxy resin. For example, Tang et al. [10] prepared TiO_2-graphene nanocomposites via a

sol-gel method and applied the resulting coating onto ordinary Portland cement (OPC) concrete surfaces using spin coating. SEM characterization showed that TiO_2 particles were uniformly embedded between graphene sheets, forming a rough surface structure that improved the hydrophobic properties of the coating. Electrochemical test results indicated that when the content of the added TiO_2-graphene was 0.5 wt%, the chloride ion penetration coefficient of the coated concrete decreased to 1.74×10^{-12} m²/s, a reduction of 77.4%. The enhanced anti-corrosion performance at the interface is primarily attributed to the combined barrier effects: the UV scattering effect of TiO_2 shielding corrosive media and the isolation barrier formed by graphene. Additionally, Shen et al. [11] used fly ash as a carrier to support graphene, forming GO-FA hybrid materials that filled the pores of the cement matrix. However, the low activity of fly ash may lead to less than ideal interfacial durability.

2.4 Organic Molecule Functionalization

Organic molecules, particularly ILs, can improve the dispersion of graphene in epoxy resin through chemical bonding. Dhongde et al. [12] studied triethylsulfonium bis(trifluoromethylsulfonyl) imide ILs-functionalized GO. XPS characterization of the GO surface indicated that sulfonic acid groups can undergo amidation reactions with -COOH groups on GO, forming amide bonds and reducing graphene agglomeration. It also demonstrated that the long alkyl chains in the IL can enhance the hydrophobicity of the epoxy resin matrix. Although ILs can improve the dispersion of graphene in epoxy composites, their high cost may hinder large-scale application. Therefore, compared to TiO_2 modification, which primarily provides a physical barrier effect, IL modification is more aimed at achieving better chemical interfacial optimization, offering good complementary effects in blocking corrosion paths.

2.5 Other Functionalization Methods

Self-healing capabilities of coatings can be achieved by leveraging inherent reversible chemical bonds or supramolecular interactions within the material. Banerjee et al. [13] grafted bismaleimide (BMI) onto carbon fiber surfaces using a Diels-Alder reaction and composited them with GO-modified epoxy resin,yielding two GO-modified resin formulations: 0.2 wt% GO and 0.5 wt% GO. When the coating is damaged, the ILSS sample with the damage is heated at 60℃ for 24 hours (triggering the Diels-Alder thermal reversible bond cleavage-recombination), followed by slow cooling to room temperature, which facilitates the interlayer cross-linking, recovering the interlaminar shear strength (ILSS) by up to 70%. SEM analysis showed that the crack width at the interface decreased by approximately 50% after healing.

3. Interfacial Structure Design

Functionalizing nanofillers and employing interfacial modification methods to improve their dispersion and compatibility in the polymer matrix is fundamental to addressing issues of poor dispersion, compatibility, and difficult interfacial heat/mass transfer in polymer matrix composites. Building on this, utilizing interfacial structure design methods to form efficient multifunctional networks can achieve good thermal conduction and enhance mechanical properties.

3.1 Three-Dimensional Network Design

Constructing interconnected pore channel structures (e.g., aerogels) using porous skeletons ensures continuous mass transfer paths at the interface, improving thermal conductivity, electrical conductivity, or mechanical properties. Cui et al. [1] modified graphene with a titanate coupling agent and prepared a three-dimensional aerogel structure via a hydrothermal method. The aerogel had a porosity of approximately 54.54% and a specific surface area of 299 m²/g. Compounding it with epoxy resin yielded a lightweight reinforcement. The three-dimensional network skeleton built by the aerogel provides the potential for constructing continuous thermal conduction pathways. The EMT model fitting revealed that the interfacial thermal resistance (R_b) of 3DGA/EP was 7.8×10^{-7} m² W K, while that of F-3DGA/EP decreased to 1.8×10^{-8} m² W K (a reduction exceeding 97%). This confirms that the long-chain alkyl group in NDZ-201 enhances the compatibility between the aerogel and EP, significantly lowering the interfacial thermal resistance. The graphene sheets in the aerogel are connected by covalent bonds (Ti-O-C) to form a stable skeleton structure, while the epoxy resin fills the aerogel's pore space, enhancing

interfacial bonding strength. At a 2.5 wt% loading, the F-3DGA/EP exhibits a tensile strength of 128 MPa, marginally exceeding that of 3DGA/EP (125 MPa) and pure EP. This performance enhancement is attributed to the stress transfer capability and lubrication effect of the long-chain NDZ-201, which significantly improves both the processability and mechanical properties of the material.

3.2 Layered Structure Design

Layered structure design achieves interfacial stress dispersion and functional integration by alternately stacking different functional layers. Poulami Banerjee et al. [13] first modified carbon fiber surfaces with ZnO nanorods to increase roughness, and then prepared a multi-layered structure by alternately stacking bismaleimide-functionalized carbon fibers and GO-modified epoxy resin. Subsequently, the ZnO-modified carbon fibers were alternately stacked with two layers, ultimately allowing the GO-modified epoxy resin to fill the interlayer spaces. The layered structure facilitates interlocking, with ZnO nanorods providing mechanical anchoring points at the interface. The introduction of Diels-Alder bonds in the BMI layer enables self-healing. Upon interfacial damage, bonding can be re-established upon heating, recovering the ILSS up to 70%. In simulated concrete repair scenarios, the resulting laminate structure exhibited greater durability, with fatigue life extended by approximately 50%.

3.3 Self-Compositing Design

A recycling strategy is self-compositing, where waste from crushed composites is reused as filler, optimizing interfacial orientation through shear-induced alignment. As reported by Qiu et al. [14], 10 wt% GN/EP composite was first mechanically crushed into micron-sized powder (average particle size ~378 μm), then mixed with fresh graphene powder and epoxy resin, and formed into a self-composite via vacuum-assisted molding. During crushing, shear forces cause graphene to align on the powder surface, forming a dense barrier. Upon recomposition, the crushed powder acts as "seeds" to induce the reconstruction of the graphene network, reducing agglomeration and thus improving the continuity of electrical conduction paths. This approach enabled the electrical conductivity of this self-composite to increase by 1280% compared to the original composite. Meanwhile, the mechanical properties remained relatively good, with the tensile strength of this self-composite decreasing by only 9.8%.

4. Conclusion

Interfacial optimization of functionalized graphene/epoxy nanocomposites can significantly enhance the performance of concrete repair.

(1) Interfacial enhancement mechanism: Functionalization (e.g., with ILs) promotes graphene dispersion, constructing a dense barrier that prevents the penetration of corrosive media.

(2) Performance improvement: Enhances mechanical strength, increases impermeability, and provides efficient self-healing capability.

(3) Value of structural design: Strategies like 3D network, layered structure, and self-compositing design help shorten mass transfer paths at the interface.

However, the difficulty in achieving uniform dispersion of graphene or its derivatives within the epoxy matrix still hinders the application of these new materials in concrete. Although functionalization modifications (e.g., covalent bonding with hyperbranched epoxy resin) can improve the compatibility of GO to some extent, nanoscale fillers are prone to agglomeration, increasing interfacial defects and affecting the overall composite performance. Furthermore, predictive models for the long-term durability of functionalized graphene/epoxy nanocomposites after application in concrete repair are still underdeveloped. Future research needs to develop multi-component synergistic functionalization methods, select nanomaterials with multiple functional groups to modify the composite's nano-interface, thereby laying the foundation for the development of low-cost industrial dispersion technologies.

References

[1] CUI S, WU W, LIU C, et al. Modification of the three-dimensional graphene aerogel self-assembled network using a titanate coupling agent and its thermal conductivity mechanism with epoxy composites.[J]. Nanoscale, 2021, 13(43): 18247-18255.

[2] KRYSTEK M, PAKULSKI D, GORSKI M, et al. Electrochemically Exfoliated Graphene for High-Durability Cement

Composites.[J]. ACS applied materials & interfaces, 2021, 13(19): 23000-23010.
[3] YUSUF J, SAPUAN S M, RASHID U, et al. Water immersion behavior of CNF/GNP reinforced green epoxy hybrid nanocomposites.[J]. International journal of biological macromolecules, 2025, 317(Pt 1): 144790.
[4] LIANG X, LI X, TANG Y, et al. Hyperbranched epoxy resin-grafted graphene oxide for efficient and all-purpose epoxy resin modification.[J]. Journal of colloid and interface science, 2022, 611: 105-117.
[5] RATHEE M, SURENDRAN H K, THAKUR A, et al. Tailoring Functional Graphene-Derived Geopolymer Nanocomposites: Interfacial Interactions and Mechanical Strength Enhancement[J]. ACS Materials Au, 2025, 5(4): 698-708.
[6] YU Z, JING H, GAO Y, et al. Performance enhancement and environmental impact of graphene oxide-fly ash hybrid on cemented waste rock backfill[J]. Environmental Research, 2025, 282: 122055.
[7] ORTIZ-ANAYA I, OBATA S, NISHINA Y. Tunable interlayer distance in graphene oxide through alkylamine surface coverage and chain length.[J]. Journal of colloid and interface science, 2025, 695: 137727.
[8] PADINJAREVEETIL A K K, PYKAL M, BAKANDRITSOS A, et al. Real Time Tracking of Nanoconfined Water-Assisted Ion Transfer in Functionalized Graphene Derivatives Supercapacitor Electrodes[J]. Advanced Science, 2024, 11(39): 2307583.
[9] THAKUR M K, HAIDER G, SONIA F J, et al. Isotope Engineered Fluorinated Single and Bilayer Graphene: Insights into Fluorination Selectivity, Stability, and Defect Passivation[J]. Small, 2023, 19(12): 2205575.
[10] TANG Q, LI Y, LIU J, et al. Constructing High-Performance Composite Epoxy Resins: Interfacial π-π Stacking Interactions-Driven Physical Rolling Behavior of Silica Microspheres[J]. Advanced Materials, 2025, 37(6): 2415485.
[11] SHEN B, SHENG Y, ABDULAKEEM A, et al. An experimental characterization of the properties of graphene oxide—Waterborne epoxy resin coating of concrete after chloride erosion[J]. Construction and Building Materials, 2024, 428: 136207.
[12] DHONGDE N R, ADHIKARI S, RAJARAMAN P V. Anticorrosion properties of ionic liquid functionalized graphene oxide epoxy composite coating on the carbon steel for CCUS environment[J]. Environmental Science and Pollution Research, 2025, 32(8): 4511-4522.
[13] BANERJEE P, PARASURAM S, KUMAR S, et al. Graphene oxide-mediated thermo-reversible bonds and in situ grown nano-rods trigger ‘self-healable’ interfaces in carbon fiber laminates[J]. Nanoscale, 2022, 14(25): 9004-9020.
[14] QIU X, LIN Z, ZHAO Y, et al. Self-Compositing: A Efficient Method of Improving the Electrical Conductivity of Graphene Nanoplatelet/Thermosetting Resin Composites[J]. Small, 2023, 19(33): 2300931.