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Review

From Neat Epoxy to Nanocomposites: Innovations in Bonding Systems for FRP-based Concrete Retrofitting: A Mini Review

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Abstract: Structural retrofitting with Fiber-Reinforced Polymer (FRP) systems has become a vital approach for enhancing the strength, ductility, and durability of deteriorating concrete structures. The efficiency of these systems largely depends on the adhesive layer, where conventional Neat Epoxy (NE) adhesives often suffer from brittleness and limited crack resistance. Recent advancements in Nanomaterial-Modified Epoxy Adhesives (NMEAs) have led to notable improvements in their mechanical, thermal, and interfacial properties. Incorporating carbon-based nanomaterials such as Carbon Nanotubes (CNTs), Carbon Nanofibers (CNFs), and graphene has been shown to enhance fracture toughness, tensile strength, and load transfer. For example, introducing 0.1 wt.% single-walled CNTs resulted in a 13% increase in fracture toughness and a 3.5% improvement in compression-after-impact strength, while 0.5 wt.% multi-walled CNTs achieved up to 7% higher elastic modulus and 10% greater tensile strength compared to NE. Similarly, silicon-based nanomaterials, including silica nanoparticles and nanoclays, enhance stiffness, minimize porosity, and improve adhesion efficiency in both Externally Bonded Reinforcement (EBR) and Near-Surface Mounted (NSM) FRP systems. Spectroscopic and microstructural analyses reveal that nanoparticles influence cross-linking and crystallinity within the epoxy matrix, leading to more stable and durable adhesive bonds. Beyond mechanical enhancement, eco-friendly nanomaterials, such as rice husk ash-derived silica and biomass-based graphene, contribute to sustainability by lowering embodied carbon and extending the structural lifespan. This mini-review synthesizes recent developments, identifies critical research gaps, and outlines future directions toward resilient, high-performance, and sustainable FRP-retrofitting systems.

***Keywords*:** epoxy nanocomposites, mechanical and thermal properties, bonding performance, concrete retrofitting, Fiber-Reinforced Polymer (FRP) composites, sustainable construction materials

1. Introduction

Structural retrofitting using Fiber-Reinforced Polymer (FRP) systems has become a prominent approach for improving the strength and durability of deteriorating concrete structures [1], [2]. A key factor in the success of these systems is the adhesive, which ensures efficient stress transfer between the FRP reinforcement and the concrete surface [1], [3]. Conventional Neat Epoxy (NE) adhesives, however, are limited by their brittleness and low crack-growth resistance, reducing their effectiveness in demanding structural applications [1], [2]. In contrast, Nanomaterial-Modified

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Epoxy Adhesives (NMEAs) present a more advanced option, offering notable enhancements in mechanical performance, thermal stability, and bonding characteristics [2], [4], [5]. Recent comprehensive reviews [6], [7] have also discussed emerging bonding agents and nanomaterial-modified adhesives for FRP strengthening systems, highlighting evolving approaches in their design and application.

Recent investigations have also emphasized the importance of durability, hybrid nanofiller systems, and sustainability in advancing NMEAs for FRP retrofitting. Durability studies have demonstrated that epoxy adhesives containing nanomaterials maintain superior bond strength and resistance to environmental degradation under thermal, cyclic, and moisture exposure conditions [8], [9]. The use of hybrid nanofillers, combining carbon-and silicon-based nanoparticles, has been shown to create synergistic effects that enhance stiffness, crack-bridging capacity, and interfacial bonding durability [10], [11]. Moreover, recent research highlights the potential of eco-friendly nanomaterials, such as nanoclay and nanosilica derived from sustainable or waste sources, to improve mechanical performance while reducing environmental impact [12]-[14]. These developments align with global efforts to create high-performance yet sustainable adhesive systems for long-lasting infrastructure rehabilitation.

Recent research has demonstrated that incorporating carbon-and silicon-based nanoparticles into epoxy matrices can significantly improve fracture toughness, tensile strength, stiffness, and thermal resistance [4], [5], [15]-[18]. Spectroscopic and microstructural analyses reveal that these nanomaterials also influence chemical reactivity and crystallinity, which are critical for optimizing adhesive performance in both Externally Bonded Reinforcement (EBR) and Near-Surface Mounted (NSM) FRP systems [5], [12], [15]. For example, studies on Carbon Nanotubes (CNTs)-and graphene-modified epoxies have shown improved load-bearing capacity and flexural performance in reinforced concrete elements [4], [15], [16]. Moreover, NMEAs have demonstrated the potential to extend the service life of retrofitted structures while supporting sustainable construction practices by reducing material waste and construction-related carbon emissions [11], [13], [19].

Recent advances have also introduced the use of eco-friendly and naturally derived nanomaterials, which further align NMEAs with sustainable construction goals. For example, nano-silica derived from rice husk ash, graphene oxide synthesized from biomass waste, and nanoclays obtained through low-energy processing have demonstrated strong reinforcement potential while minimizing environmental impact [13], [14], [19]. The adoption of such renewable or low-carbon nanofillers not only enhances the mechanical and thermal properties of epoxy adhesives but also contributes to reducing the embodied energy and carbon footprint of FRP-retrofitted systems. Integrating these sustainable nanomaterials represents a promising direction toward greener and more resilient infrastructure. Furthermore, next-generation bonding agents incorporating eco-friendly nanomaterials have been introduced to align FRP retrofitting technologies with sustainable construction goals [7].

This perspective highlights recent advances in NMEAs for FRP-retrofitted concrete structures, with a focus on their transformative potential compared to conventional systems. It examines how carbon-and silicon-based nanoparticles influence the mechanical, thermal, chemical, and microstructural properties of epoxy adhesives, and evaluates their performance in both EBR and NSM strengthening techniques. Beyond summarizing existing knowledge, the paper emphasizes the dual role of NMEAs in enhancing structural performance and promoting sustainable construction practices. By framing critical innovations alongside unresolved challenges and research gaps, this perspective aims to guide the optimization of NMEA applications in structural engineering and to stimulate future interdisciplinary progress [10], [11], [13].

This mini-review aims primarily to synthesize recent developments in NMEAs for FRP-based concrete retrofitting, emphasizing their role in enhancing mechanical, thermal, and interfacial performance compared to conventional neat epoxies. A secondary objective is to explore how advances in nanomaterial chemistry, hybrid filler systems, and sustainable material design contribute to improving long-term durability and environmental performance. By clarifying these goals, the review distinguishes between current state-of-the-art insights and forward-looking perspectives that can guide future interdisciplinary research in adhesive nanocomposites for structural engineering applications. The review focuses on carbon-and silicon-based nanomaterials (e.g., CNTs, graphene, nanosilica, and nanoclay) incorporated into epoxy matrices, and the discussion is based on synthesizing data and findings reported in recent peer-reviewed studies.

2. Enhancements in mechanical and thermal properties

Incorporating carbon-based nanomaterials, such as CNTs, Carbon Nanofibers (CNFs), and graphene, into epoxy systems has been shown to improve fracture toughness, tensile capacity, and thermal resistance. These enhancements are primarily attributed to strong interfacial bonding between the nanoparticles and the epoxy matrix, combined with efficient crack-bridging mechanisms. For example, introducing 0.1 wt.% single-walled CNTs led to a 13% increase in fracture toughness and a 3.5% improvement in compression-after-impact strength [3]. Similarly, silicon-based nanomaterials, including silica nanoparticles and Montmorillonite (MMT) nanoclay, improve epoxy performance by minimizing void formation and enhancing stiffness. Studies on epoxy/silica nanocomposites and epoxy/nano clay hybrid composites confirm these benefits, provided that uniform nanoparticle dispersion is achieved throughout the matrix [4], [5], [9], [20].

Gojny et al. [21] systematically investigated the effect of different CNT types and concentrations on the mechanical properties of epoxy nanocomposites. They reported that incorporating Single-Walled CNTs (SWCNTs) at 0.05-0.3 wt.% increased Young's modulus by 3.16-8.19% and tensile strength by 3.2-4.45% compared to neat epoxy. Similarly, the addition of 0.1 wt.% Multi-Walled CNTs (MWCNTs) enhanced the elastic modulus by approximately 7%, while 0.5 wt.% amino-functionalized Double-Walled CNTs (DWCNTs) achieved the most pronounced improvements, raising the ultimate tensile strength and stiffness by 10% and 15%, respectively, and the fracture toughness by up to 43%. These findings highlight the critical role of optimizing CNT concentration and surface functionality to balance mechanical enhancement with dispersion uniformity, as excessive loading often leads to nanoparticle agglomeration and reduced performance.

Thermal and curing behaviours of NMEAs are critical for understanding nanoparticle-matrix interactions and the resulting network structure. Studies have demonstrated that the incorporation of Fluorinated Single-Walled CNTs (FSWCNTs) into epoxy resins can increase the storage modulus by approximately 20% at 0.3 wt.% loading due to improved dispersion and the anti-plasticization effect arising from an excess of curing agent. However, this also resulted in a reduction in the glass transition temperature (T_g) by around 30 °C, attributed to the fluorine-induced non-stoichiometry within the epoxy network [22]. Conversely, the use of BOC-protected diamine-functionalized SWCNTs enhanced both T_g and storage modulus by about 10 °C and 10%, respectively, owing to strong covalent interactions between the nanoparticles and the epoxy during cross-linking [23]. Similarly, the addition of 0.3 wt.% Multi-Walled CNTs (MWCNTs) increased T_g and decomposition temperature by 2-4 °C, reflecting the bridging effect and uniform dispersion of CNTs that restricted crack propagation [24]. Further enhancement was observed with the incorporation of 0.3 wt.% polyaniline-functionalized MWCNTs, which improved T_g by 6-25 °C due to strong interfacial bonding and efficient load transfer between the nanofillers and epoxy matrix [25]. On the other hand, some studies reported a slight T_g reduction, suggesting that nanoparticle addition does not always alter crosslink density, particularly when dispersion is incomplete or when weak physical interactions dominate over chemical bonding [26].

3. Chemical and microstructural properties

Nanoparticles also alter the chemical characteristics of epoxy adhesives, as demonstrated by Fourier-Transform Infrared (FTIR) and Raman spectroscopy analyses. These techniques detect variations in functional groups and molecular configurations, offering valuable insights into the interactions between nanoparticles and the polymer matrix. For instance, the appearance of ester bonds in CNT-reinforced epoxies indicates chemical reactivity between the nanoparticles and the epoxy network [6]. FTIR spectroscopy further confirmed chemical variations among NE and nanomaterial-modified systems. The spectra showed noticeable intensity shifts in key absorption bands depending on the nanomaterial type and concentration, reflecting changes in bond strength and molecular environment. Notably, no new bonds were detected with most nanomaterials; however, when 1.0 wt.% CNFs were added, a distinct peak appeared at around 1,710 cm^{-1}, corresponding to C=O stretching, which suggests limited chemical interaction between CNFs and the epoxy matrix [15]. These findings are consistent with earlier studies, such as those of Morimune et al. [16], which also reported functional group modifications and bond rearrangements in graphene oxide-based epoxy nanocomposites.

From a microstructural standpoint, the crystallinity of nanocomposites plays a crucial role in defining their mechanical behavior. X-Ray Diffraction (XRD) analyses reveal that nanoparticles may either promote crystallinity by acting as nucleation sites or suppress it by disrupting the ordered polymer structure, depending largely on the nanoparticle type and concentration. In the study conducted by Al-Zu'bi et al. [15], nanoparticle dispersion within the epoxy matrix was achieved through a simple, cost-effective process combining manual mixing and ultrasonication. Initially, a few drops of acetone were added to the nanoparticle powder to minimize agglomeration and enhance dispersibility, followed by manual mixing with the epoxy resin. The mixture was then subjected to high-intensity ultrasonic irradiation (37 kHz for 5 min) before adding the hardener. Scanning Electron Microscopy (SEM) observations confirmed that this hybrid dispersion technique resulted in a relatively uniform distribution of nanoparticles throughout the epoxy matrix, though some localized agglomeration persisted at higher nanoparticle loadings.

Furthermore, XRD analysis indicated that both nanoparticle agglomeration and increased porosity contributed to a reduction in crystallinity across all nanocomposites compared with the Neat Epoxy (NE). The reduction in crystallinity was more pronounced when the nanoparticle content doubled (from 0.5 to 1.0 wt.%) than when it increased only moderately (from 1.0 to 1.5 wt.%).

4. Applications in FRP structural retrofitting

NMEAs have demonstrated considerable potential in both Externally Bonded Reinforcement (EBR) and Near-Surface Mounted (NSM) FRP strengthening techniques [27]. For example, CNT-enhanced epoxies have been shown to improve the flexural strength and toughness of reinforced concrete beams and columns [2], [28]. In NSM-FRP systems, epoxies modified with silica or nano clay enhanced load-bearing capacity and ductility, underscoring their effectiveness in overcoming the shortcomings of conventional neat epoxy adhesives [12], [17].

For instance, comparative studies have demonstrated how the performance of NMEAs compares with traditional NE systems. Al-Zu'bi et al. [2] reported that, relative to NE, the use of CNF-and cellulose-modified adhesives led to decreases in load-carrying capacity by approximately 37% and 9%, respectively, primarily due to nanoparticle agglomeration and increased porosity that weakened interfacial bonding. Despite this reduction, ductility improved substantially, by about 49% and 36%, indicating enhanced energy dissipation and crack-bridging capacity. Conversely, silica-, clay-, and graphite-modified epoxies produced capacity gains of roughly 17%, 5%, and 15%, respectively, over NE, with ductility increasing by 19% and 24% for the silica and clay systems, though decreasing by about 12% for graphite-filled adhesives due to their higher crystallinity. Similarly, Irshidat et al. [4] observed that incorporating CNTs into epoxy resin enhanced the ultimate load and stiffness of retrofitted Reinforced Concrete (RC) beams, with improvements strongly dependent on CNT dispersion, anchorage length, and the number of FRP layers. Their SEM characterization revealed improved adhesion at both the concrete/epoxy and carbon fiber/epoxy interfaces, leading to superior load transfer efficiency and higher ultimate capacity.

Moreover, to quantify how nanoparticle modification affects interfacial performance, recent single-lap joint studies report large improvements in shear capacity that correlate directly with microstructural changes observed by SEM. For example, Venugopal et al. [17] investigated Graphene-Nanoparticle (GNP) additions in adhesive layers for single-lap glass FRP joints and found that a 0.75 wt.% GNP content increased Single-Lap Joint (SLJ) shear strength by about 69.4% compared with the unmodified adhesive, while flexural strength improvements up to about 46.6% were recorded at 1.25 wt.% GNP. Fractography showed rougher fracture surfaces and enhanced adhesive-adherend contact, consistent with improved load transfer and crack-bridging mechanisms. These findings indicate that interfacial shear strength (assessable via standard tests such as American Society for Testing and Materials (ASTM) standard D5868 or SLJ protocols) can be substantially enhanced by controlled nanoparticle addition, provided dispersion and interfacial adhesion are maintained. In the nanocomposite adhesives reviewed here, SEM evidence of crack-bridging, pull-out, and particle-bridging features offers a microstructural explanation for the observed macroscopic gains in shear and flexural capacity [6], [10].

5. Environmental and sustainable benefits

In addition to improving mechanical properties, NMEAs support sustainable construction by enhancing the durability of retrofitted structures and reducing material consumption. Life cycle assessment studies highlight their environmental benefits compared to conventional adhesives, aligning with international goals to lower carbon emissions from the construction sector [14], [19].

6. Conclusions

The integration of nanomaterials into epoxy adhesives has demonstrated clear advantages for structural retrofitting with FRP systems. Compared to conventional neat epoxy adhesives, NMEAs exhibit superior mechanical, thermal, and bonding performance, largely due to strong interfacial interactions and effective crack-bridging mechanisms. Carbon-based nanomaterials, such as CNTs, CNFs, and graphene, significantly improve toughness and strength, while silicon-based nanoparticles and nano clays enhance stiffness and reduce voids when uniformly dispersed. Beyond property enhancement, NMEAs also alter the chemical and microstructural behavior of epoxies, as confirmed by spectroscopic and diffraction studies, further contributing to their effectiveness in EBR and NSM applications.

Importantly, NMEAs extend the service life of strengthened concrete structures and reduce material consumption, thereby supporting sustainable construction practices. Their use has been linked to lower environmental impacts in life cycle assessments, positioning them as a viable solution for reducing carbon emissions in the construction sector.

Taken together, this perspective underscores the transformative role of NMEAs in FRP-based concrete retrofitting. Beyond summarizing advancements, it highlights the dual promise of these adhesives in delivering both enhanced structural performance and sustainable construction outcomes. At the same time, unresolved challenges in dispersion control, hybrid formulation, and durability assessment remain critical frontiers. By framing these opportunities and gaps, this perspective aims to guide ongoing research and stimulate interdisciplinary progress in adhesive systems for structural retrofitting.

Finally, the author encourages continued interdisciplinary efforts to translate these laboratory-scale advances into practical, sustainable retrofitting applications.

7. Future research directions

Building on the advances summarized in this review, future research should aim to expand the understanding and application of Nanomaterial-Modified Epoxy Adhesives (NMEAs) in FRP-retrofitted systems. Priority areas include exploring the synergistic effects of carbon-and silicon-based nanomaterials to further enhance mechanical, thermal, and microstructural properties [1], [5]-[7], [14], [21]. Promising findings in NSM-FRP applications have demonstrated the potential for improved structural performance [2], but further studies are needed to optimize bonding mechanisms, hybrid filler formulations, and interfacial behavior [3].

Continued research should also evaluate the long-term durability of NMEAs through systematic fatigue and creep testing by conducting the ASTM D3479 and ASTM D2990 standard tests, respectively, considering the combined effects of environmental exposure, sustained loading, and thermal cycling on bond strength and adhesive integrity. Such investigations would provide deeper insight into time-dependent deformation and damage accumulation mechanisms, enabling the development of predictive models for service-life assessment of FRP-retrofitted systems [8], [10], [11], [13], [17], [28].

Future research should also explore the long-term durability of NMEAs through controlled accelerated aging protocols, such as UV exposure (ASTM G154) and freeze-thaw cycling (ASTM C672), to complement natural weathering studies like those conducted by Cruz et al. [8]. Further investigations should also explore hybrid nanofiller systems that combine carbon-based nanoparticles (e.g., CNTs) with silicon-based nanoparticles (e.g., silica) to achieve optimized balances between toughness, stiffness, and bonding performance. Experimental programs incorporating mechanical testing, dispersion characterization (e.g., SEM, Transmission Electron Microscopy (TEM)), and interfacial behavior analyses are recommended to evaluate potential synergistic effects and establish structure-property relationships for these hybrid NMEAs [10].

In addition, the standardized testing protocols and evaluation methods proposed for NMEAs can be extended to other emerging materials, such as poly(lactic acid) (PLA)-based bio-composites and Hollow Glass Microsphere-Polyvinyl Alcohol (HGM)-(PVA) cementitious composites, to enable consistent benchmarking and comparative assessment across different sustainable strengthening systems.

Implementing these standardized tests would provide valuable insight into degradation mechanisms under combined mechanical and environmental stresses, enabling more reliable predictions of service life and performance retention in FRP-retrofitted structures. Future studies should also extend Life Cycle Assessments (LCAs) of NMEAs to encompass the entire production and application chain, including energy consumption during nanomaterial synthesis, adhesive formulation, and structural application. Building on the methodological recommendations outlined by Cabeza et al. [14], such expanded LCAs would enable more accurate quantification of embodied energy and carbon footprint reductions, thereby clarifying the overall environmental benefits of using nanomodified adhesives in sustainable FRP retrofitting systems.

Conflict of interest

The author declares no competing interests.

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