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REVIEWS

Structural Composites Hybridized with Nanofillers: An Overview

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Abstract | Structural composites find extensive applications in virtually every sector of engineering due to several advantages associated with them such as high specific strength and stiffness, tailorability, corrosion resistance etc. Their hybridization with nanofillers for further enhancement of properties is comparatively a recent enterprise. This review surveys the recent research efforts in the field of hybridization of structural composite materials with nanofillers.

Keywords: *structural composites, carbon nanotubes, carbon nanofibers, nanosilica, nanoclay*

1 Introduction

Nanoparticles are the most fundamental components in the fabrication of nanostructures, with sizes in nanometer (1 nm = 10^{-9} m) range. They are far smaller than the world of everyday objects that are described by Newton's laws of motion, but bigger than an atom or a simple molecule that are governed by quantum mechanics. In principle the size of a nanoparticle spans in the range of 1 and 100 nm. While nanoparticles, like proteins, are common in nature, engineered nanoparticles are intentionally designed and created with physical properties tailored to meet the needs of specific applications. They can be end products in themselves, as in the case of quantum dots or pharmaceutical drugs, or they can be components later incorporated into separate end products, such as carbon nanotubes in polymers. Either way, physical properties of a particle are extremely important to their performance, and the performance of any product into which they are ultimately incorporated.

Nanoparticles continue to receive widespread acclaim for their potential to reinforce polymers. Their high aspect ratio and large surface area improve the mechanical and thermal properties of polymer nanocomposites in comparison to conventional composites at considerably low loading fractions owing to their greater interaction with the matrix. The properties are reported to be influenced by the shape and size of nanofiller, volume fraction, quality of dispersion, and interaction between the filler and matrix. The ground breaking discovery of carbon nanotubes (CNTs) in 1991,[1] followed by the realization of their amazing mechanical, thermal and electrical properties led materials scientists all over the world to focus their research efforts on advanced nanocomposites incorporated with these fascinating structures. Carbon nanotubes (also known as bucky tubes) are long thin cylinders of carbon that are unique for their size, shape, and remarkable physical and electrical properties.[2–5]

For over the past two decades, carbon nanotubes reinforced polymer composites[6,7] have spurred considerable attention in the materials research community, in part due to their potential to provide orders of magnitude increase in strength and stiffness when compared to typical fiber reinforced polymer composites. Their mechanical properties, coupled with their relatively low density, make these materials ideal candidates for weight-efficient structures, and have been heavily scrutinized for the same. For the same reason, CNTs are considered to be the ultimate reinforcement in polymeric composites.[8–10] Carbon nanotubes-polymer composites were initially reported by Ajayan et al.[11] They mechanically mixed purified multiwalled carbon nanotubes (MWCNTs) with epoxy resin, a most widely studied non-conjugated polymer-based composite system. Later Sandler et al. also reported the electrical percolation threshold at 0.0025 wt% nanotube loading and conductivity of 2 S/m at 1.0 wt% nanotubes in epoxy matrices.[12] Biercuk et al. observed a monotonic increase of resistance to indentation by up to 3.5 times on adding 2 wt% single-walled carbon nanotubes (SWCNTs) in epoxy resin.[13]

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There are many other reports in literature regarding the preparation and characterization of nanotube-epoxy nanocomposites.[14–18] In short, the potential of nanofillers to significantly improve properties of polymer composites and allied problems such as dispersion of these nanofillers has been the focus of researchers once the potential of CNTs became evident.

After nearly two decades of research, the potential of carbon nanotubes as reinforcement for polymers has not been fully realized; the mechanical properties of at least some of the derived composites have fallen short of predicted values. Few mechanisms about adhesion, load transfer and deformation were investigated, which make it difficult to accurately predict behaviors of nanotube-polymer composites and fabricate 'ideal' nanocomposites. Even though carbon nanotubes possess excellent mechanical characteristics, significant improvement in the composites' properties is possible only when the CNT's unique attributes exhibited at the nanoscale are transferred to the macroscale. This essentially defines the fundamental challenge for applied CNT-polymer composites research.[19] A better understanding of the relationships between processing, interfacial optimization, and composite properties is a major goal of this area of research, which may lead to optimal reinforcement of polymer matrices with CNTs.

Characteristics of some of the inorganic nanofillers such as nanosilica, nanoclay or layered silicates as a reinforcement, and their interactions with organic matrices are also worth noticing. Inorganic particulate fillers have shown significant improvement in thermal, mechanical, and impact properties.[20] Considerable effort has been devoted to studies on nanosilica-reinforced epoxy nanocomposites.[21–26] In a 2013 article by Conradi, a concise summary of nanosilica-reinforced polymer composites is presented.[27]

Although large numbers of polymers have been reinforced with nanofillers to realize nanocomposites, their structural applications are limited, considering their inadequate load bearing capacity. However, with the use of continuous fiber reinforcement, polymer composites are widely commercialized for load bearing structural applications. The use of composite materials in structures of all kinds is accelerating rapidly with the major impact being felt in aerospace industry, where the use of composites has directly enhanced the capability of fuel efficient aircrafts in commercial as well as new generation arena of the military sphere. In subsequent sections, research on nanoparticles filled polymer composites for structural applications is reviewed.

2 Carbon Nanotubes in Structural Composites

Structural composites are at times referred to be the result of embedding high-strength, high-stiffness fibers of one material in a surrounding matrix of another material with a distinct interface between them. In general, the fibers are the principal load carrying members, whereas the surrounding matrix keeps them in desired location and orientation, act as a load transfer medium between them, and protect them from environmental damages due to elevated temperature or humidity. Many fiber-reinforced polymers offer a combination of strength and modulus that are either comparable, or better than several traditional metallic materials. Because of their low density, strength to weight ratios and modulus to weight ratios, these composites are markedly superior to those of metallic materials. In addition, fatigue strength as well as fatigue damage tolerance of many composite laminates are excellent. For these reasons, fiber reinforced polymers have emerged as a major class of structural materials, and are either used or being considered for use as a substituent for metals in many weight-critical components in aerospace, automotive, and other industries.

Commercial and industrial applications of fiber-reinforced polymer composites are so varied that it is next to impossible to list them all. Fiber-reinforced polymer composites are used in aerospace (aircraft structures), naval (ship hull), automotive, electronics (e.g. printed circuit boards), building construction (e.g. floor beams), power industry (e.g. transformer housing), oil industry (e.g. offshore oil platforms), medical industry (e.g. bone plates for fracture fixation, implants, and prosthetics), and in many industrial products, such as step ladders, oxygen tanks, and power transmission shafts. Potential use of fiber-reinforced composites exist in many other engineering fields as well. Putting them to actual use requires careful design practice and appropriate process development based on the understanding of their unique mechanical, physical, and thermal characteristics.

Even though structural composites have excellent properties, there are still demands for improvement in tensile and compressive strength in the fiber direction, interlaminar strength and toughness. Use of nanofillers as additional reinforcement to realize 'hybrid composites' is expected to resolve the limitations of laminated composites with regard to compressive and interlaminar strength. CNTs as potential nanofillers are known to not only have excellent mechanical properties,[28–32] but also outstanding electrical[33] and thermal conductivities.[34–36] One of the properties of the composite that is expected to be an improvement is the compressive strength in the fiber direction, because shear modulus and shear strength of a matrix resin would be enhanced by CNTs, preventing fiber buckling. The other expected property improvement is the interlaminar fracture toughness, because of the bridging effect by CNTs, which prevents crack propagation. In addition, electrical and thermal conductivities are expected to be increased by creating electrical and thermal paths, between carbon fibers (CF) by CNTs.

2.1 *Hybrid composites through matrix modification*

In this section, a concise summary of attempts to realize CNTs-modified hybrid composites by the incorporation of CNTs in polymer resin matrix is presented; several researchers have reported such attempts. Lee et al.[37] reported that 1 wt% silane modified CNTs improved tensile strength and modulus of carbon/CNTs/epoxy three-phase composites. Kim et al.[38] also showed that addition of 2 wt% silane-modified MWCNTs improved flexural properties of carbon/epoxy composites. Rahman et al.[39] reported an improvement in flexural properties of fiber reinforced composites with addition of 0.3 wt% amine modified MWCNTs fabricated through hand layup and compression molding processes. In a recent report, Soliman et al.[40] showed that addition of 1.5 wt% acid functionalized MWCNTs enhanced low-velocity impact of glass/epoxy composites designed through hand layup method. Mode II fracture behavior of the laminates was examined by Karapappas et al.[41] and an increase was reported in fracture energy of the carbon fiber reinforced plastic (CFRP) doped with 0.5 and 1% CNTs (about 45 and 75%, respectively). Gojny et al.[42] made glass fiber/CNT/epoxy composites and reported an increase in interlaminar shear strength (ILSS) by 20%. Fan et al. studied ILSS of glass fiber reinforced epoxy composites enhanced with multi-walled CNTs.[43] Tsantzalis et al.[44,45] doped carbon fiber-reinforced epoxy laminates with carbon nanofibers and titanate piezo electric particles, and reported a 100% increase in fracture energy of laminates with the addition of 1 wt% CNFs. Wichmann et al.[46] developed fumed silica/glass fiber/epoxy, carbon black/glass fiber/epoxy, and CNT/glass fiber/epoxy micro-nanocomposites by resin transfer moulding (RTM) method, and reported a 16% increase in ILSS and superior electrical properties with 0.3 wt% CNTs.

Two critical factors that influence mechanical properties of such hybrid composites with CNTs are their dispersion within the matrix, and adhesion with the matrix. Both these have been challenges to the realization of hybrid-CNT composites. Most of the research with CNT filled hybrid composites has been focused on dispersing CNTs in polymeric matrices to reinforce the matrix. For example, the dispersion of SWCNTs treated by dispersing agents in glass fiber reinforced polymer composites was investigated by Zhao Yan et al.[47] Gong et al. also reported that using surfactants as wetting agents might improve the dispersion and thermo mechanical properties of carbon nanotubes-epoxy composites, but even with the addition of surfactant, complete homogeneous dispersion of the nanotubes was not obtained.[48] Dispersion is important because CNTs tend to agglomerate when dispersed in a polymeric resin. The formation of agglomerates reduces the effective contact area between the nanotubes and the polymer, hence reducing the adhesion between the two materials. These can also act as stress concentrators, reducing the final performance of the composite.[49] CNT agglomerates also reduce aspect ratio of the reinforcement, lowering the reinforcing effect, and can further act as dry inclusions that reduce the strength of the reinforced polymer. One of the most commonly used methods to disperse CNTs into a polymer matrix is sonication. Nevertheless, beyond a certain weight fraction (usually around 3%), no significant improvements in the composite mechanical properties are achieved using sonication.

Reinforcement of carbon/epoxy composites with MWCNTs has been reported by Cho and Daniel.[50] The epoxy matrix of the composite was modified with MWCNTs, and their dispersion within the matrix was enhanced by the use of a commercial block copolymer. A pronounced improvement in matrix dominated properties was achieved. Glass transition temperature of the composite was increased by 39°C, and the compressive and interlaminar shear strengths were increased by 39% and 15%, respectively. The epoxy matrix of a carbon fiber/epoxy composite was modified with MWCNTs to improve the matrix dominated thermomechanical properties of the composite by Cho et al.[51] They have experimentally investigated the effects of improved dispersion and nanotube length on reinforcement of the composite. The dispersion of CNTs was enhanced with the use of a block copolymer. Two different CNT lengths, 1 and 10 μm on average, were considered in this study. Irrespective of the length, a pronounced improvement of the composite properties was achieved with 0.5 wt% of MWCNTs with the use of block copolymer. Without the block copolymer, it was found that a higher enhancement of composite properties was achieved with longer nanotubes.

The potential of advanced carbon/glass hybrid reinforced composites with secondary carbon nanotube reinforcement for wind energy applications was investigated with the use of computational experiments by Gaoming Dai et al.[52] They simulated fatigue behavior of composites with and without secondary CNT reinforcement using multiscale 3D unit cells. The materials behaviors under both mechanical cyclic loading as well as combined mechanical and environmental loading (with phase properties degraded due to the moisture effects) were studied. 3D computational studies of environment and fatigue analyses of multiscale composites with secondary nano-scale reinforcement in different material phases and different CNT arrangements have demonstrated that composites with the secondary CNT reinforcements (especially, aligned tubes) present superior fatigue performances than those without reinforcements.

Based on overview of literature, it is also known that the interaction between pristine nanotubes and polymers is dependent on the choice of the matrix polymer and also polymer conformation, thus the molecular structure may play a critical role in the interaction. Even with 'best polymer', pristine nanotube may not form strong interfaces. It has been proposed that functionalizing nanotubes or chemical bonding might increase the interaction with polymer matrix, but it was found that some mechanical properties decrease after covalent chemical modification, and the structure of nanotubes would be destroyed partially.[53] It seems that MWCNTs are more suitable for chemical treatment because their inner graphene layers can remain unreacted, thus the essential electronic structure can be retained, but less excellent properties than SWCNTs and weak interaction between layers make them not attractive for a lot of applications.

2.2 *Large scale manufacturing of hybrid structural composites*

Manufacturing processes for advanced composites include methods such as hand lay-up, resin transfer molding (RTM), compression molding, filament winding, autoclave curing, vacuum-assisted resin transfer molding (VARTM), etc.[54] Some of these advanced fabrication techniques enable structural composites to be manufactured with better compaction and low void fractions, and in turn superior mechanical properties. Nevertheless, manufacture of high performance composites using prepregs with autoclave curing has been the gold standard established by aerospace industry. Adopting these processes to realize nanomaterials, e.g. CNTs-filled hybrid composites, require an additional processing of dispersing of nanofiller in the matrix resin, prior to component fabrication. Although this method shows some positive results, significant viscosity increase due to CNTs causing imperfect impregnation and voids have been reported. It also becomes difficult to avoid the agglomeration of CNTs because of increasing resin viscosity during mixing.

One of the applications of CNT reinforced polymer for filament wound carbon fiber-reinforced composites was demonstrated by Spindler-Ranta and Bakis.[55] 1 wt% SWCNTs were added to the polymer matrix. However, this study concluded that SWCNTs did not produce any noticeable effect in the CNT reinforced composites and filament wound CFRP rings.

An interlaminar reinforcement using aligned carbon nanotubes was demonstrated for prepreg unidirectional carbon tape composites by Garcia et al.[56] They grew aligned CNTs at high temperature and then transfer-printed to prepreg at room temperature, maintaining CNT alignment in the through-thickness direction. In initial testing, the CNT-modified interface was observed to increase fracture toughness by 1.5–2.5 times in mode I, and 3 times in mode II. Both compliant interlayer and bridging are considered as mechanisms of toughening, with evidence of CNT bridging observed in fracture micrographs. Their fabrication methods were compatible with existing manufacturing processes, and had the potential to enhance the structural and multifunctional properties of composites.

Composites manufacturing through liquid molding techniques using polymer resins that are premodified with nanofillers remains as a major concern. The process is even more challenging with the use of fabric of unidirectional (UD) architecture, because of its low permeability. Dispersed nanoparticles will filter away while moving from the resin reservoir toward the vacuum line. Also, increased viscosity of the resin even at low concentrations of nanofillers will have a considerable effect on composite processing.

Photograph of a glass/epoxy laminate fabricated through VARTM with E-glass fabric of unidirectional architecture is shown in Figure 1 (unpublished data). MWCNTs were dispersed in epoxy using a probe sonicator, to result in

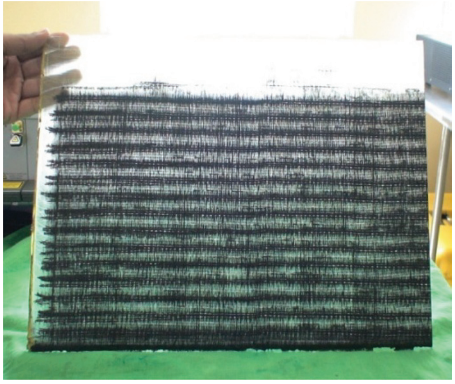


Figure 1: Photograph of a 1 mm thick GFRP laminate fabricated through vacuum assisted resin transfer molding using CNTs-dispersed epoxy.

stable dispersion with no sedimentation for at least 6 weeks after its preparation. Top end of the laminate in the photograph is the vacuum side, and it is evident that the nanoparticles did not travel through the thickness of the laminate. However, upper surface of the laminate was filled with nanoparticles as the permeable mesh on the laminate aids them to infuse through the upper surface, and only nanoparticles-free epoxy get infused in the area after the mesh.

With the use of fabric of woven architecture, use of VARTM seemed apparently working. For example, Kim et al. reported the processing, characterization, and modeling of carbon nanotube-reinforced multiscale composites.[57] They have used high-energy sonication to disperse CNTs in the resin, followed by infiltration of fiber preform with the resin/CNT mixture. The effects of sonication time on the mechanical properties of multiscale composites, which contain reinforcements at varying scales, were studied. A low CNT loading of 0.3 wt% in resin had little influence on tensile properties, while it improved the flexural modulus, strength, and percent strain to break by 11.6%, 18.0%, and 11.4%, respectively, as compared to the control carbon fiber/epoxy composite.

Resin Film Infusion (RFI), one of the most promising methods for composites in aerospace, automotive and military applications, is the best solution to alleviate the aforesaid issues. It is a cost-effective technique for the fabrication of complex shaped parts resolving several critical concerns of conventional liquid composite molding methods. RFI also ensures near zero void fractions because of better compaction and local flow of the polymer resin. In a recent investigation, an attempt was made using resin film infusion, to improve the matrix dominated properties of epoxy composites reinforced with unidirectional E-glass using MWCNTs, dispersed in the matrix component.[58] Attempts to develop effective methods to de-bundle and discretely disperse CNTs (which are agglomerated in their as-prepared form) are mostly done using surfactants.[59,60] In general, a medium for the dispersion of CNTs should be capable of both wetting the hydrophobic tube surfaces, and then modifying these surfaces to decrease the interaction between tubes. Polymers are appealing candidates for this, since, given an appropriate structure, they can wrap themselves around CNTs. Indeed, such cases have been reported in literature.[61,62]

Thermoplastics, such as polyethylene terephthalate, polycarbonate and a commercial block copolymer were found to effectively disperse MWCNTs in solution; their mixing and subsequent solvent removal resulted in reinforced epoxy resin.[58] This modification of the matrix component with low weight fractions of CNTs is found to have negligible effect on the processing parameters of composites. CNTs also improved the glass transition temperature of matrix epoxy resin. Laminates were fabricated through RFI process. In this method, epoxy resin is cast to film forms. They are then transferred to fabric layers (over a metallic mold plate), ensuring that the film just sticks to the fabric. The process is repeated to yield sandwiches of resin films with two fabric layers on both sides. Such sandwiches are cut to the desired dimension and placed on one another to build desired thickness. The sandwich stack over the mold is then cured by vacuum bagging technique inside an oven (Figure 2). Heated molds can replace the use of ovens for large structures. Pristine composites and composites using nanofillers-modified epoxy are fabricated under identical conditions. Local flow of resin through the sandwiched fabric layers in RFI process ensures proper nanofiller distribution in hybrid composites, which is correlated with their consistently improved mechanical properties. When subjected to tensile and compressive loads, the composites showed a more pronounced enhancement in compression

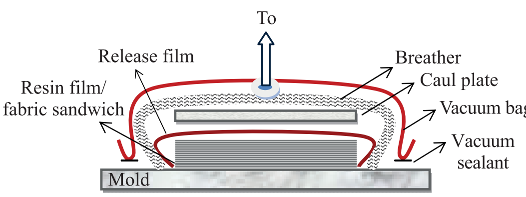


Figure 2: Schematic of the resin film Infusion process.

properties, as would be expected, considering the fiber dominated nature of tensile properties.[63] While tensile strength and modulus of composites remain unaffected, compressive strength of hybrid composites was improved by up to 25% at low loading fractions of MWCNTs.

2.3 *Carbon nanotubes at the interface of composites*

Several researchers have attempted to develop CNT containing carbon fiber reinforced polymer composites as well. However, acquisition of substantial improvement and implementation of real manufacturing are still challenging. Therefore, several alternative processes are proposed.[64–68] One of them is the use of CNT grown carbon fibers (CFs), which usually consist of the following two steps. In the first step, CNTs are grown on carbon fibers with metal catalysts by chemical vapor deposition (CVD) method or by an electrophoresis method. In the second step, an array of CNT grown CFs are impregnated with a matrix resin. The other method is the use of a CNT array, which is grown on a substrate such as a silicon wafer by CVD with metal catalysts. The CNT array is then transferred onto the CF array. Subsequently the CF array and the CNT array are impregnated with a matrix resin. These processes may enable one to overcome existing problems, for example, the agglomeration of CNTs. However, significant technical challenges that impact manufacturing still remain in these processes. The CVD of CNTs in large scale is difficult due to the limitation in size of the furnace for the process. The electrophoresis method of CNTs in large size is also difficult because the method is basically based on batch process. Also, in the case of CVD with metal catalysts, it is difficult to remove the metal catalysts that can have adverse effects on CFRP properties.

Carbon nanotubes were grafted on carbon fibers using chemical vapour deposition method by Hui Qian et al.[69] CNTs-graftings have resulted in a threefold increase of the BET surface area of carbon fibers compared to their pristine counterparts. At the same time, there was a degradation of fiber tensile strength by around 15%, due to the dissolution of iron catalyst into carbon; the modulus was not significantly affected. The wetting behaviour between fibers and matrix was directly quantified using contact angle measurements and indicated good wettability. Single fiber fragmentation tests were conducted on model composites, demonstrating a 26% improvement in the apparent interfacial shear strength (IFSS) over the baseline composites. The result is associated with improved stress transfer between the carbon fibers and the surrounding matrix, through the grafted CNT layer. The improved IFSS was found to correlate directly with a reduced contact angle between fiber and matrix.

In another attempt, Kepple et al. functionalized woven carbon fiber with carbon nanotubes, in situ, to evaluate the enhancement of properties of epoxy-carbon composites.[70] The CNT as-grown on the woven CF were shown to improve the fracture toughness of the composite by 50%. This was accompanied by no loss in structural stiffness of the final composite structure. In fact, the flexural modulus increased by approximately 5%. The significant increase in the fracture toughness indicated that the damage tolerance of a composite structure would benefit from the CNT material applied in this manner.

Effect of carbon nanotubes on the interfacial shear strength of carbon fiber in an epoxy matrix has also been studied by Sager et al.[71] Carbon fibers were coated with carbon nanotubes on the fiber surface using thermal chemical vapor deposition. The CVD process was adjusted to produce two CNT morphologies for the study: radially aligned and randomly oriented. Results of single-fiber fragmentation tests indicated an improvement in interfacial shear strength with the addition of a nanotube coating. Randomly oriented MWCNT and aligned MWCNT coated fibers demonstrated a 71% and 11% increase in interfacial shear strength over untreated, unsized fibers. This increase was attributed to an increase in both the adhesion of the matrix to the fiber, and the interphase shear yield strength due to the presence of nanotubes.

Growth of carbon nanotubes on carbon fiber substrates to produce hybrid composites with matrices other than epoxy has also been attempted. For example, Mathur et al. reported on CNTs on CF substrates to realize phenolic composites.[72] Chemical vapor deposition has been used to grow CNTs on unidirectional carbon fiber tows, bi-directional carbon fiber cloth and three dimensional carbon fiber felt. These substrates were further used as the reinforcement in phenolic resin matrix to develop hybrid CF–CNT composites. Mechanical properties of hybrid composites were found to increase with the increasing amount of deposited carbon nanotubes. The flexural strength improved by 20% for UD, 75% for 2D, and 66% for 3D hybrid composites as compared to those prepared by neat reinforcements (without CNT growth) under identical conditions. Flexural modulus of these composites was also found to be improved by 28%, 54% and 46%, respectively.

In one of their recent publications, Kamae and Drzal reported property enhancement of carbon fiber/epoxy composite through incorporation of carbon nanotubes at the fiber-matrix interface.[73] They developed a process to realize uniform coating of CNTs on CFs simply by dipping CFs into a CNT/water suspension, which enables a scalable fabrication of CNT containing CFRPs. The advantage of this process is that making of the CNT coated CFs is quite easy since it requires only dipping CFs into a CNT/water suspension after a conventional CF manufacturing process. Once CNTs are coated on CFs, it is possible to fabricate CNTs containing CFRP by any conventional molding method such as hand lay-up, resin transfer molding, filament winding, pultrusion, prepreg/autoclave process etc. Uniform coating of MWCNTs to CFs was achieved by the use of attractive force between the positive charge of a cationic polymer treated MWCNTs and the negative charge of surface oxidized CFs. The combination of epoxy resin sizing and the cationic polymer treated MWCNTs coating resulted in good adhesion to an epoxy resin matrix. The use of cationic polymer resulted in high IFSS due to the formation of strong interaction between its amine groups with the epoxy groups of the sizing and matrix resin. The incorporation of MWCNTs at the CF/epoxy matrix interface enhances shear modulus and strength, and thereby increases the stress transfer, resulting in increasing IFSS of composites.

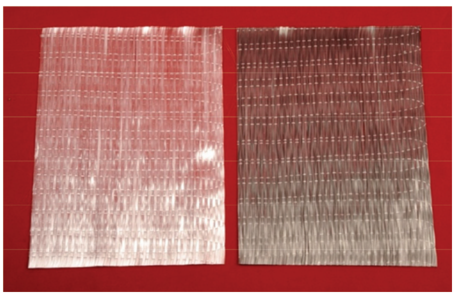


Figure 3: Photographs of pristine and CNT-coated E-glass fabric.

A similar methodology has been adopted in our group for GFRP composites with functionalized multiwalled carbon nanotubes, (unpublished data). In this attempt, unidirectional E-glass fabric was dipped in an aqueous solution of functionalized multiwalled carbon nanotubes, to result MWCNTs-grafted E-glass. Figure 3 shows the photograph of CNT-coated fabric in comparison to pristine glass fabric. SEM images (Figure 4) of the same depict a uniform thin deposition of CNTs, which remained adhered even after washing. Wettability of modified fibers to epoxy resin is improved, which was proved by contact angle measurements. Composites could be manufactured by any conventional fabrication processes.

Photograph of a 2 mm thick laminate with CNT-coated unidirectional E-glass fabric, made by vacuum assisted resin transfer molding is shown in Figure 5. Compressive strength of composite laminates, with CNTs at the interface, increased by over 15% as compared to their baseline (control) specimens that are manufactured from glass fabric treated under identical conditions used for coating CNTs, except for CNTs in solution. Nevertheless, because of the strong affinity of glass toward water, mechanical properties of both control composites and composites made with CNT-coated glass, degrade. The substantial reduction of compressive strength of control GFRP specimens (which was fabricated using glass fabric treated under identical conditions used for CNTs coating) as compared to pristine E-glass/epoxy composites and effect of CNTs in interface of the composites is depicted in Figure 5. Hence, the concept of use of an aqueous

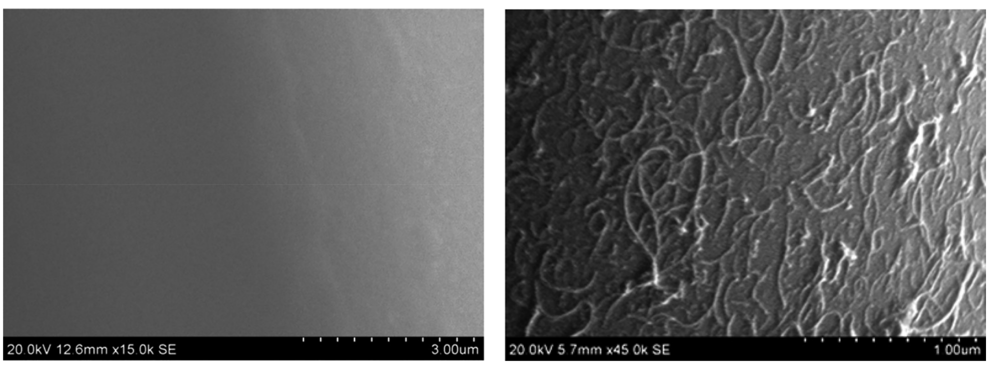
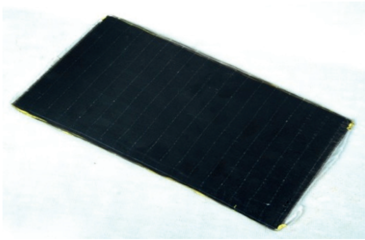


Figure 4: SEM images of pristine and CNT-coated E-glass fabric.



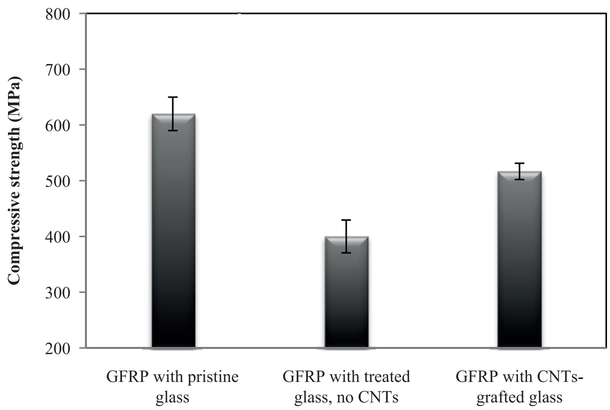


Figure 5: Left: Photograph of a GFRP laminate with glass fibers coated with CNTs. Right: Compressive strength of laminates with CNTs-coated glass fabric in comparison to that of a pristine GFRP and control specimens.

medium to transfer CNTs onto glass fabric has been discarded.

Studies have also shown that carbon nanotubes on the surfaces of fibers grown by CVD methods[74] significantly increase the surface area (e.g., from 1.77 to 17.2 m^2/g after growing 500-nm-long CNTs on the surface of the fibers[75]), yielding an increase in interfacial shear strength. Other mechanisms for the increase in strength might be mechanical interlocking of the CNTs with the polymer and/or the neighboring fibers and a reduction in stress gradients in which the CNTs may be seen as an interlayer of intermediate modulus between the stiff fiber and the compliant matrix. Although mechanistically interesting, the CNT lengths obtained to date vary from 200 nm to 1–2 μm,[76] and due to the limited length of the CNTs, the reinforcement of the matrix is limited only to the vicinity of the fiber.

3 Carbon Nanofiber Reinforced Hybrid Structural Composites

Compared to carbon nanotubes, carbon nanofibers (CNFs) have received less research attention, though they can be excellent alternatives for CNTs, and are available at relatively low price. Thermoplastics such as polyethylene terephthalate,[77] polypropylene,[78] polycarbonate,[79] poly (ether etherketone)[80] etc., have been reported reinforced with CNFs. Results indicate that the addition of small amounts of CNFs (<3 wt%) to a matrix system can increase thermal and mechanical properties of nanocomposites without compromising their processability. They derive their improved properties at low filler volume fractions, because of their high aspect ratio and surface area to volume ratio. Studies related to the enhancement of mechanical properties of epoxy matrix by the introduction of CNFs have also been reported.[81–85] To achieve maximum utilization of the properties of nanofibers, their uniform dispersion and good wetting within the host matrix must be ensured. It has been reported that dry nanofibers often agglomerate, and thereby greatly reduce their ability to bond with the matrix; the local interfacial properties drastically affect the macro level material behavior.[86] General review of properties of CNF-based composites is available in literature.[87] However, the use of CNFs in fiber-reinforced composites is limited to reports with academic interests. For example, Morales et al.[88] presented CNF-filled glass reinforced composites made by resin transfer molding; these glass reinforced plastics showed improved mechanical properties with low weight fractions of CNFs in the matrix.

Investigations on improvement in mechanical properties of carbon fabric–epoxy composite using carbon nanofibers were carried out by Yuanxin Zhou et al.[89,90] They used a high-intensity ultrasonic liquid processor to obtain a homogeneous mixture of epoxy resin and carbon nanofibers. The epoxy filled with 2 wt% CNF was used with satin weave carbon fabric in a vacuum assisted resin transfer molding set up, to fabricate composite panels. The tensile and flexural strengths showed 11 and 22.3% improvement respectively, compared to the composite without CNF. The fatigue strength was also improved significantly.

Iwahori et al. also pursued the concept of matrix modification by dispersing CNFs into the matrix of carbon fiber/polymer composites.[91] They envisioned improvements in elastic modulus and resistance to crack propagation of the matrix phase and, consequently, its compressive strength and interlaminar strength. It was observed that the properties of carbon fiber woven fabric reinforced epoxy resin showed improved matrix properties, albeit at loading levels of CNFs as high as 5 and 10 wt%.

In a recent article from this group, hybrid composites of continuous unidirectional E-glass and epoxy modified with carbon nanofibers, fabricated through resin film infusion have been reported.[92] Amine functionalized CNFs had diameter of 80–100 nm, ~200 mm length and >95% purity. Ultrasonication assisted dispersion route has been used to generate epoxy mix with properly dispersed CNFs. Modifying the matrix component with low weight fractions of CNFs is found to have negligible effect on the processing parameters of composites. Glass transition temperature of epoxy is found to have considerably improved with CNFs. While the tensile strength and modulus remained unaffected, matrix dominated properties, such as compressive strength, of the hybrid composite was improved by 40% at a weight fraction of nanofibers as low as 0.5 wt%. CNFs also improved the interlaminar shear strength (ILSS) of hybrid composites by 33%.

4 Inorganic Nanofillers in Structural Composites

During the last decade, numerous attempts have been reported on the use of inorganic nanofillers in hybrid composites. For example, Chowdhury et al.[93] investigated the effects of nanoclay on the mechanical and thermal properties of woven carbon fiber-reinforced epoxy, and reported an 18 and 9% improvement in flexural strength and modulus, respectively, with the addition of 3 wt% nanoclay. Xu and Hoa[94] observed that carbon fiber-reinforced epoxy/clay nano composites manufactured through hot melt layup, plus autoclave process improved flexural and inter laminar shear strength of glass/epoxy composites with the addition of 2–4% of nanoclay. Water absorption characteristics of epoxy/glass fiber/organo-montmorillonite nanocomposites were investigated by Chow.[95] Ye et al.[96] found that the addition of halloysite nanotubes up to 5 wt% also enhanced ILSS and mode I and mode II fracture resistance of carbon/epoxy laminates. Mechanical and thermal behaviors of glass/epoxy hybrid composites containing organo-montmorillonite clay have also been reported by Zulfli et al.[97] According to Haque et al., improvement of fracture toughness in fiber reinforced nanocomposites is due to the strong interfacial bonding of epoxy-clay system.[98] Khan et al. also reported that the enhancement of fiber-matrix interfacial bonding in the presence of nanoclay can maximize stress transfer between matrix and fiber.[99] Influence of nanoclay dispersion methods on the mechanical behavior of E-glass/epoxy composites was studied by Agubra et al.,[100] while, the nanoclay influence on impact response of laminated plates was reported by Avila et al.[101] Dispersion of nanoclay clusters during resin transfer molding of nanoclay/glass/epoxy composites was studied by Aktas et al.[102]

A recent study from our group toward developing hybrid GFRP and CFRP composites with epoxy compatible nanoclay at a loading fraction of 5 wt% with respect to epoxy have also revealed that there is a 15–20% increase in the compressive strength of hybrid composites in comparison to their respective baseline specimens. NanomerI.30E from Nanocor Inc., a montmorillonite based layered clay mineral, was used in this research. Their individual platelet thicknesses are 1 nm, but surface dimensions are generally 300 to >600 nm, and hence have a high aspect ratio. The filler was surface modified and designed to easily disperse to amine-cured epoxy resins. However, 5 wt% seemed to be a higher loading fraction considering the subsequent film casting and composite manufacturing through resin film infusion technique. The increase in compressive strength of nanoclay incorporated hybrid composites is reported in Table 1. Lower weight fractions of the nanofiller was also attempted, but resulted in no remarkable improvement in mechanical properties. Several other studies have also reported on properties enrichment due to addition of inorganic nanofillers in composite matrices.[103,104] The incorporation of filler particles also resulted in higher fracture toughness by improving significantly the toughness of the matrix and crack deviation.

Karaki et al.[105] incorporated layered clay, alumina, and titanium dioxide into an epoxy matrix and fabricated continuous carbon fiber-reinforced polynanomeric matrices to study tension–tension fatigue behavior. They found

Table 1: Compressive strength of nanoclay incorporated hybrid composites in comparison to their respective control composites.

Specimen	Compressive strength, MPa
Glass/epoxy	619.7 ± 61.2
Glass/epoxy/nanoclay	714.4 ± 33.5
Carbon/epoxy	702.2 ± 67.6
Carbon/epoxy/nanoclay	850.4 ± 27.3

that the number of microcracks in each layer depended on the type of particles and their concentration. Wang et al.[106] demonstrated that the exfoliated clay with only 2.5 wt% in epoxy showed a significant improvement in fracture toughness, and concluded that an increase of the microcracks and the fractured surface due to crack deflection resulted in increase in toughness. Siddiqui et al.[107] investigated the mechanical properties of nanoclay-dispersed CFRP, and showed that the interlaminar fracture toughness of nanoclay dispersed CFRP is higher than that of the conventional CFRP. Subramaniyan and Sun[108] also reported that compressive strength of unidirectional GFRP with nanoclays increased in comparison to conventional GFRP.

Layered clays were used as nanoparticle fillers infiber-reinforced polymeric materials by Timmerman et al.[109] also; they reported that transverse cracking in symmetric carbon fiber/epoxy laminates as a response to cryogenic cycling was significantly reduced when nanoparticle fillers were used at concentrations much lower than those used for traditional fillers. The mechanical properties and processing characteristics of the laminates were not adversely influenced by the presence of nanoparticles and thermal expansion characteristics were improved. Flexural and morphological properties of epoxy/glass fiber/silane-treated organo-montmorillonite composites have also been studied by Zulfli and Shyang.[110]

Hackman and Hollaway[111] studied the potential applications of clay nanocomposite materials to civil engineering structures. They concluded that the materials ability to increase service life of materials subjected to aggressive environments could be utilized to increase the durability of glass and carbon fiber composites. In an appealing development, Miyagawa et al.[112] studied the influence of biobased epoxy organomontmorillonite clay and PAN-based carbon fiber composites. A sonication technique was utilized to process the organically modified clay into glassy biobased epoxy networks. This process resulted in clay nanoplatelets being homogeneously dispersed and completely exfoliated in the matrix. Carbon fiber reinforced composites were processed by compression moulding, using the biobased epoxy/clay nanocomposites as the matrices. The study found that the flexural strength and modulus did not change with the use of nanoclay. It was, however, observed that the interlaminar shear strength of CFRP improved by adding 5 wt% intercalated clay nanoplatelets. Dynamic mechanical analysis depicted an increase of 0.9 GPa for the storage modulus of biobased epoxy at 30°C with the addition of 5 wt% exfoliated clay nanoplatelets. The glass transition temperature, however, decreased with addition of the organo-clay nanoplatelets.

Epoxy modified with 10 wt% nanosilica used to fabricate glass fiber reinforced composite laminates by resin infusion under flexible tooling (RIFT) technique improved fatigue life by about three to four times, as reported by Manjunatha et al.[113] and Boger et al.[114] In an earlier publication, Kornmann et al.[115] reported that the addition of about 10 wt% fluorohectorite enhanced the flexural strength and flexural modulus of glass/epoxy composites fabricated through hand layup, vacuum bagging, and hot pressing techniques. Transmission electron microscopy indicated that silicate layers dispersed in the epoxy matrix present/enable a long-range order with an interlamellar spacing of about 9 nm. X-ray diffraction analysis confirmed this nanostructure both in the nanocomposites and in the fiber-reinforced composite based on the same matrix. Flexural testing of the laminates showed that the nanolayers improved the modulus and the strength, respectively, by 6% and 27%. Dynamic mechanical analyses of the epoxy and nanocomposite plates and their corresponding laminates showed a systematic glass transition temperature decrease of the nanocomposite based materials. This, the researchers suggested, explained the larger water uptake observed at 50°C in the plate and the laminate based on a nanocomposite matrix as compared with those based on pristine epoxy.

In a 2014 article, epoxy-based hybrid structural composites reinforced with 14 nm spherical silica particles have been reported.[116] Hydrophobic fumed nanosilica AEROSIL R 202 with an average particle size of 14 nm, >99.8% SiO_2 content, specific surface area (BET) of 100 m^2/g and an approximate density of 60 g/L, from Degussa, has been used in this research. Composites were fabricated using continuous glass or carbon fiber of unidirectional architecture and nanosilica dispersed epoxy, through resin film infusion process (Figure 6). Uniform dispersion of nanoparticles in resin matrix was ensured by an optimized ultrasound-assisted process. Although resin viscosity marginally reduces in the presence of nanosilica enabling a better control in composite manufacturing process, glass transition temperature of epoxy remained unaffected at low weight fractions. Compressive strength of hybrid glass or carbon fiber/epoxy composites showed more than 30–35% increase with nanosilica at a concentration as low as 0.2 wt%. Tensile and

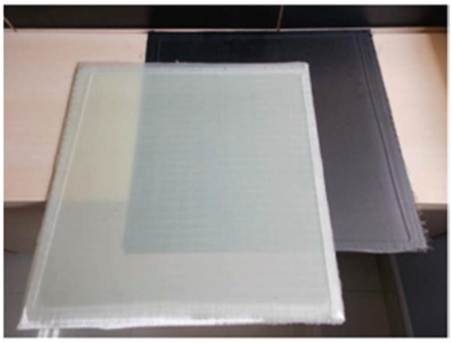


Figure 6: Hybrid GFRP and CFRP laminates with 0.2 wt% nanosilica, fabricated through RFI process.

compressive properties of hybrid composites in transverse direction to the reinforcement remained unaffected.

5 Conclusions

Large numbers of polymers have been modified with nanofillers for either reinforcing them or for introducing multifunctionality. Use of such modified polymers for structural composites with fiber reinforcement has been a challenge considering their altered process characteristics. Rheological changes of the modified matrix will impede the stringent process requirements, and in turn large scale manufacturing of composites may not be feasible. While liquid composite molding techniques have limitations to process nanofillers-modified polymer resins, processes such as resin film infusion can pave ways towards reinforced and multifunctional hybrid composites. This article has been an attempt to review the recent developments in realizing nanofillers incorporated hybrid composites. As a final remark, it can be concluded that the vigorous progress in this field during the last two decades are leading to new exciting developments dealing with both fundamental aspects and applications of such materials.

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