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Review

Multiscale Polymer Composites: A Review of the Interlaminar Fracture Toughness Improvement

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Abstract: Composite materials are prone to delamination as they are weaker in the thickness direction. Carbon nanotubes (CNTs) are introduced as a multiscale reinforcement into the fiber reinforced polymer composites to suppress the delamination phenomenon. This review paper presents the detailed progress made by the scientific and research community to-date in improving the Mode I and Mode II interlaminar fracture toughness (ILFT) by various methodologies including the effect of multiscale reinforcement. Methods of measuring the Mode I and Mode II fracture toughness of the composites along with the solutions to improve them are presented. The use of different methodologies and approaches along with their performance in enhancing the fracture toughness of the composites is summarized. The current state of polymer-fiber-nanotube composites and their future perspective are also deliberated.

Keywords: interlaminar fracture toughness; CNTs; carbon fiber reinforced plastic (CFRP) laminates; delamination

1. Introduction

Composites laminates of carbon fiber reinforced plastic (CFRP) are generally created by aligning several sheets of CFRP or prepregs followed by curing and consolidation at the same time. Therefore, the layers stick together and have extraordinary mechanical properties in the in-plane direction but still they are weaker in the transverse direction, which causes separation of plies under many different loading scenarios. These defects are caused by either inter-ply defects due to overloads, intra-ply cracks, areas with high porosities, and poor adhesion at the ply interface. The inter-ply behaviour of a composite may have a direct say on the interlaminar fracture toughness (ILFT) and interlaminar shear stress distribution within the material. Therefore, in designing the laminated composite structures, one of the limiting factors is the poor interlaminar strength. Hence it is important to improve resistance to interlaminar fracture, which essentially means improved ILFT and researchers have given utmost attention in procuring ways to suppress or minimise the initiation and growth of delamination in laminated composites [1–8].

Failure analysis is essential to determine the nature of loading a composite structure that can be endured without damage. There are three types of failure commonly observed in composites, viz; interlaminar, intralaminar, and translaminar, amongst which the interlaminar is the most common. The interlaminar stresses cause plies or groups of plies in a laminate to separate from each other, leading to a phenomenon called, delamination. This initiates and propagates in the matrix layers intervening the reinforcement plies of the composite system, limiting their life and performance.

As the layers are stuck together by resin, the resulting bond provides the fracture path with low energy. Catastrophic damage without any external signs may also result from the undetected sub-surface interlaminar fracture. There is a tremendous loss of strength and stiffness due to interlaminar fracture which raises serious concerns about the safety and reliability of the composite structure. This is a dominant obstacle in attaining the light weight potential of a composite material [9–11].

The loading conditions are also different for all the three types of composite failures, viz. tensile loading (Mode I), shearing load (Mode II), and the tearing load scenario (Mode III) as schematically seen in Figure 1, or a combination of the three. Previous research pertaining to interlaminar fracture in composite materials has been reported by Garg et al. [10], Pagano et al. and Schoeppner et al. [12], and Tay et al. [13].

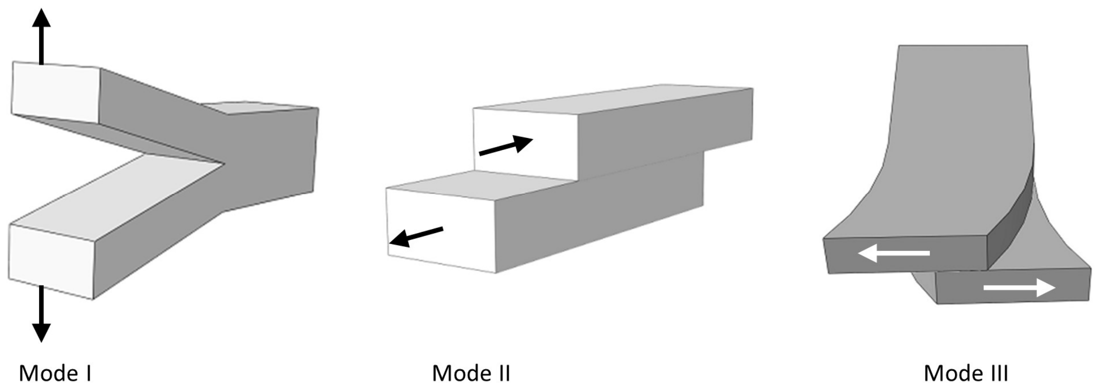


Figure 1. Schematic diagrams of various types of loading for crack induction.

2. Mode I, Mode II, and Mode III ILFT Measurement

As composite laminates are prone to massive delamination phenomenon, they should be carefully examined as part of safety evaluation. Delamination can occur when the applied load reaches the optimum and critical limit. Different loading scenarios lead to opening, sliding, and tearing modes as far as fracture mechanics is concerned. The parameter which is used to calculate the delamination resistance is the critical strain energy release rate (G_c) which is generally termed as interlaminar fracture toughness. The crack growth can be either a pure or mixed mode or even a combination of the both, but the delamination resistance requires the measurement of the critical energy release rate. So, all the above-mentioned modes are required to be investigated to understand and predict the overall impact of delamination in the composites.

The above mentioned interlaminar fracture (ILF) features generated from different loading scenarios can be characterized effectively by carefully fabricating the composite laminates and applying the desired loading in a stable and controlled manner. As the crack direction is known for a particular loading, the fracture features can then be well documented.

Many test methods have been developed which are suitable for measuring the ILFT of the composite laminates. The Japanese Industry Standards (JIS), American Society for Testing and Materials (ASTM), and the European Structural Integrity Society (ESIS) are the main standard organisations evaluating the proposed methods of measuring and quantifying ILFT properties. Recent findings leading to the developments of new standards of testing of interlaminar toughness were reviewed by Brunner et al. [14], complementing and updating earlier reviews [10,13,15]. In general, most standards are applicable for the unidirectional composites to predict and understand the fracture toughness under different modes of fracture.

As per the literature [16,17], double cantilever beam (DCB) and end notched flexure (ENF) specimens are more popular for quantifying Mode I and II delamination behaviour and these are highly effective procedures to evaluate the delamination resistance of these composite materials. Standards for testing DCB and ENF specimens have been produced by ASTM [18,19] but are limited for testing unidirectional laminates. Many researchers have carried out a detailed study to propose the test method for a Mode III ILFT test, however, none of the testing standards has been widely accepted, so still, there is a lot of debate in recommending an efficient Mode III testing approach [15,20–28]. Although, Split Cantilever Beam (SCB) and edge crack torsion are the two prioritized methods which are widely used to compute the tearing mode details. As, the first two modes are the critical modes of delamination, the current review paper is limited to the DCB and ENF test results in the context of ILFT improvement.

3. Factors Influencing the ILFT and Methods for Improving ILFT

The growing demand for lighter and superior performance materials, especially in the area of aerospace, automobile, and defence applications has attracted the interest of many towards woven and unidirectional CFRP composites. However, in spite of very good in-plane strength, they have poor resistance to interlaminar fracture under different loading conditions. A lot of experimental and analytical research has gone into enhancing fracture toughness of laminated composite structures [29–33]. Many factors can affect the ILFT value; the factors influencing the ILFT as found in the literature are material system, lamina stacking and laid up configurations [34–37], fabrication quality and fabrication procedure [38–40], specimen thickness [41], and environmental effects [42,43]. Among all, lamina stacking, laid up configurations, and fabrication procedure are the main parts of composite manufacturing and hence are the most important parameters to understand properly and to be discussed in detail here (Refer Figure 2).

Considering the improvement of the ILFT, various hierarchical progression approaches adopted by researchers to impede the interlaminar fracture in composites as depicted as a flow diagram in Figure 2. Figure 2 shows that the first attempts were made to modify the matrix system with different fillers with an aim to improve the resin toughness. This technique was followed with the changes in the fiber architecture as well as the surface modification so as to improve the thickness direction properties. Interleaving and interlayer additions in between the fiber layers are also used as an interlaminar improvement mechanism. But the latest in the hierarchical progression is the multiscale composite approach where various kind of micro/nano fillers is added in the composite system. The methodologies used for enhancing the fracture toughness of composites are detailed in the following sub-sections.

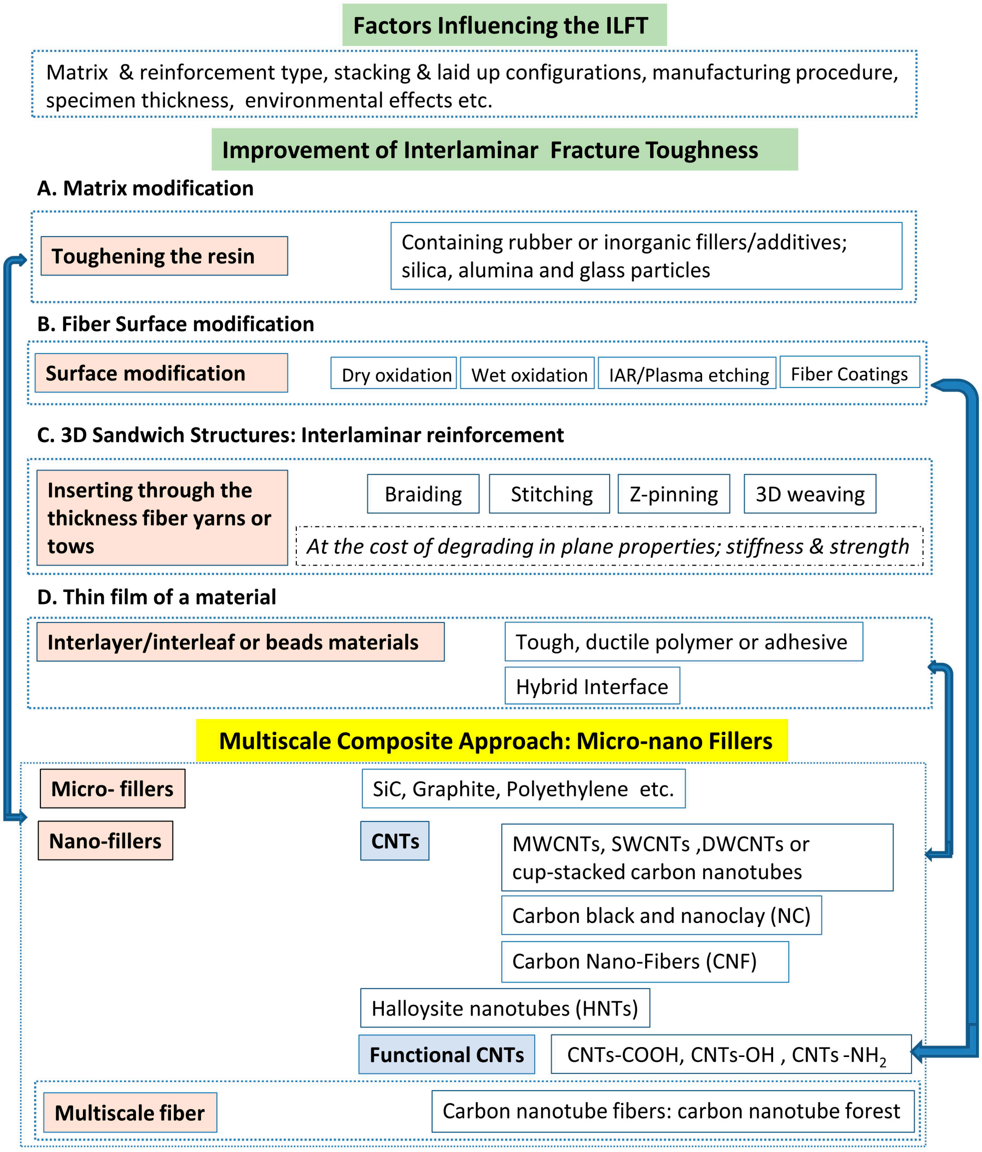


Figure 2. Various approaches to obtain improved interlaminar fracture toughness (ILFT).

3.1. Lamina Stacking and Laid-Up Configurations

Interlaminar fracture can either be suppressed or delayed. This is achieved by altering the laminate stacking sequence under usual loading, which in turn changes the intralaminar and/or interlaminar stresses from tensile to compressive. However, with the load reversal, the advantage provided by the stacking sequence vanishes, as there is simultaneous stress reversal [36,44]. There are also other possibilities of different weaves using cloth fabric reinforcement and ply lay-up configurations, with these laminates. Twills and 5HS weave types have been considered for models of different laminate stacking by S. W. Yurgartis et al. and J. P. Maurer et al. [45].

In plain weave in the context of CFRP, there are three types of laid-up configurations available, out-of-phase/folded configuration, iso-phase/stacked configuration, and random phase configuration [46–48]. Also, the placement of the end of the crack-starter Polytetrafluoroethylene (PTFE) film may vary with respect to the position of the transverse or fill yarn and this can affect the crack propagation results [49]. Figure 3 shows the out-of-phase/folded configuration used to produce laminates for the current experimental investigation. As regards stacking configuration, they reported significant effect due to weaving offset and also highlighted that the folded configuration results in unexpected results and that no improvement was shown by using the mixed weave. Results of Kim et al. [44] also showed similar observations.

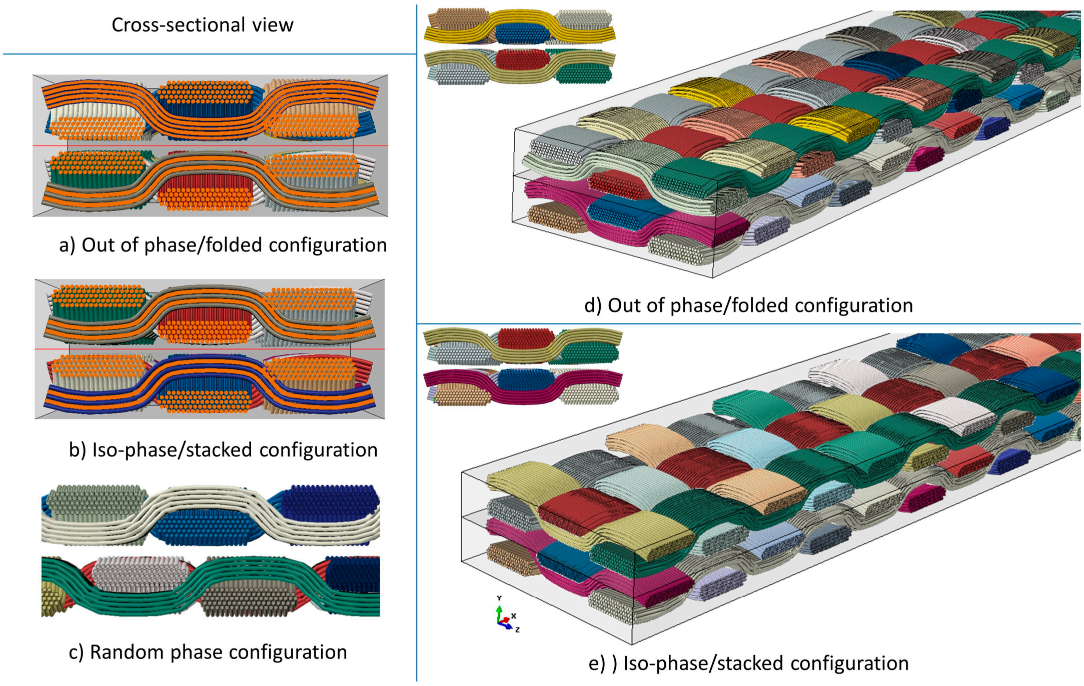


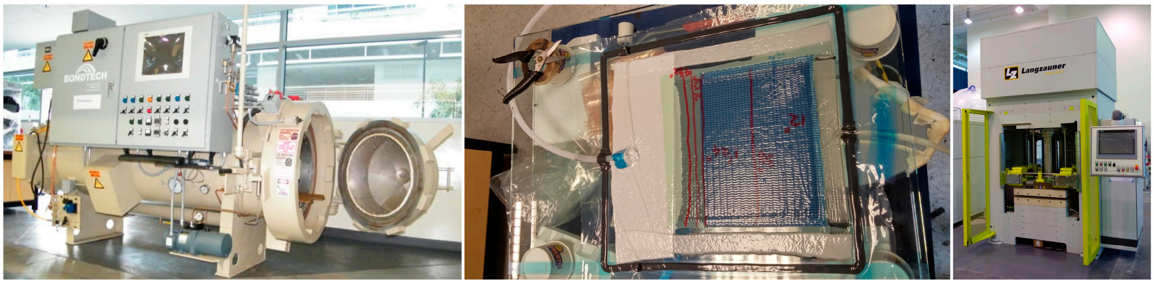
Figure 3. Lamina laid up configurations.

This is also known as a laminate construction approach in the context of delayed delamination. This concept is taken with the idea of reducing the magnitude of either interlaminar stresses or crack opening. Consequently, it was observed that the rate of energy was reduced, which is the detrimental source of energy available for damage growth. For arresting delamination, multiple innovative designs have been created like "Lamina stacking and laid up configurations" which include (1) Inter ply Hybridization, (2) Ply Termination, and (3) Edge Modification.

3.2. Influence of the Manufacturing Procedure

A composite laminate is widely fabricated by (1) autoclave, (2) vacuum infusion, and (3) hot press techniques as shown in Figure 4. These processes have an influence over the ILFT of these laminates. The specimens fabricated by autoclave and the 'Quickstep' process showed much higher fracture toughness than for specimens produced by the hot press [39,40,50–54]. In addition, it was noted that there was more fiber bridging during the Mode I test for the Quickstep specimens. Quickstep specimens had enhanced fiber/matrix adhesion [39,40,50].

Zhang et al. and Fox et al. reported fracture toughness G_{Ic} values of 564 and 527 J/m^2 for the laminates prepared by autoclave and Quickstep. The average fracture toughness (G_{Ic}) for the specimens fabricated by the hot press was 783 J/m^2, which is 2.6 times higher compared to the specimens fabricated by autoclave [50].



(a) Autoclave (b) Vacuum Infusion Process (c) Hot press

Figure 4. Composite laminate fabrication process.

3.3. Toughening of Epoxy Resins (with Additives/Modifiers) and the Thermoplastic Matrices

The unique characteristics of epoxies such as superior adhesive strength, hardness, and resistance to chemicals and heat make them popular in the engineering field. However, most of the cured epoxy systems display lower fracture toughness, inadequate resistance to cracks, and lower impact strength [55–57]. For instance, delamination and inferior impact resistance caused by low delamination resistance of the epoxy resin. The toughness of epoxy resin enhances its ILFT. However, the relative enhancement in ILFT is not as much as that of the resin itself. Due to the brittleness and limited resistance of epoxy resin to cracks, impact modifiers are used to enhance the toughness and flexibility [58] but this also has degrading effects on the mechanical properties. Further, to improve matrix toughness, modifiers such as thermoplastics and rubber particles have been tested with success, but they also result in degradation of the matrix [59].

Elastomers (e.g., Carboxyl-terminated butadiene-acrylonitrile (CTBN)) improves the fracture toughness of an epoxy resin as the cross linking density is reduced along with the increased mobility between the cross-links [60]. By adding rigid thermoplastic resins, fracture toughness is improved. In addition to this, use of thermoplastic matrix constituting of Polyether ether ketone (PEEK), Polyphenylene sulfide (PPS), Polyamide-imide (PAI) etc. also results in improvement. The fracture toughness of these materials is up to 1000 J/m^2, which is ten times more than that of general epoxy resins. In pure epoxy based composites, a fracture toughness G_{Ic} value of 600 J/m^2 has been reported, whereas in modified resin composites the value was found to be approximately 750 J/m^2. Fiber pull-out test investigations showed that fiber–matrix interface adhesion is very poor in modified epoxies. An improvement of fracture toughness value up to 1400 J/m^2 has been achieved due to the addition of the amine. Similarly, hyperbranched polymer (HBP) is also used to improve the toughness in the pure epoxy resin. Curing kinetics were altered slightly but remained suitable for RTM (Resin Transfer Molding) processing. By adding HBP modifiers, fracture toughness shows an improvement of 130% compared to the pure resin [61]. DeCarli et al. [62] proved that epoxy HBP can be used to achieve high toughening in epoxy anhydride composites. The Mode I and Mode II ILFT values of the laminates increased to 224% and 265% respectively, when subjected to an addition of 10 wt% of HBP additives.

Another alternate modifier which can be used to toughen epoxy resins is epoxidized soybean oil (ESO). By using 10 wt% ESO content, reported results of critical stress intensity factor and the flexural strength showed improvement [63]. Although such modifiers have been proved effective, they cause deleterious effects on other properties like strength, modulus, and glass transition temperature (T_g), a detailed discussion and reviews are presented in a number of papers [64–66].

Thermoplastic composites possess comparatively higher interlaminar fracture toughness, G_{1C}, with at least one order higher than thermoset composites [67]. Friedrich et al. investigated the comparative fracture toughness Mode I and Mode II performance of carbon fiber-epoxy and thermoplastic polyether ether ketone (PEEK), and it was highlighted that G_{1C} and G_{2C} were around ten times higher in the case of CF/PEEK [68]. Mode I and Mode II performance of reactive poly (ethermide)/carbon laminates was studied by Bullions et al. in the class of reactive polymer composites [3]. The role of matrix toughness, as well as fiber/matrix adhesion in improving the fracture toughness, is also to be found in the detailed literature [69,70].

3.4. Fiber Surface Treatments

The purpose of treating the surface of fibers is wettability improvisation with the resin system and to induce a strong adhesion at the fiber/matrix interface [71] Generally, the functional group of an organic polymer reacting with the resin is used to coat the fiber surface. Some of the surface coatings are copolymers based on methyl acrylate–acrylonitrile, styrene–maleic anhydride, and polyamides [72–74]. Two commonly employed methods of surface treatments are an oxidative method and a non-oxidative method. The techniques and processes for enhancing the adhesion of the interface in fibre-reinforced composites are available in the literature [75,76].

These methods also have a varied effect on the fiber surface. Hence, an optimization is necessary to choose an appropriate treatment method for a particular application with the required properties [71]. Excessive oxidation leads to pitting on the surface of the fiber and adversely affects the tensile strength. Non-oxidative technique showcases improved ILFT properties, however, the cost is a major issue. Oxidation technique is widely used for treating commercial fibers as the process is fast, uniform, and applicable for mass production [77,78].

Albertsen et al. [79] investigated four different types of carbon fibers with varying levels of wet oxidative surface treatment. The fibers embedded in a particular type of thermoset resin, thermoplastic systems, were subjected to interlaminar fracture testing. Results showed an improvement in the crack initiation with an increased level of surface treatment. However, when the surface treatment levels are intermediate, the propagation reaches its maximum due to fiber bridging effects.

Varelidis et al. [74] demonstrated the results of coatings based on polyamide 6,6 on the delamination resistance of unidirectional carbon/epoxy composites. They showcased the presence of fiber bridging due to an interfacial coating. Due to this, values of propagation and ΔG_{Ic} also increased.

3.5. 3D Sandwich Structures

Skin and the core comprise generic composite sandwich structure. When transverse fibers are used to join the skins, the resulting composite structure is termed a 3-D sandwich structure. These structures possess excellent delamination resistance and peeling properties due to the fibers in the transverse direction [32].

There are several manufacturing techniques available for making reinforcement preforms for composite laminates and these include (1) Braiding [80,81], (2) Stitching [82–88], (3) 3D Z-Pinning [89–91], and (4) 3D weaving [92]. The schematic of different types of 3D sandwich structure is depicted in Figure 5. The primary objective of all the techniques is to develop processes to manufacture 3D complex near-net shaped preform with fiber architecture, which leads to enhanced component performance, through an automated and in a cost effective manner [32].

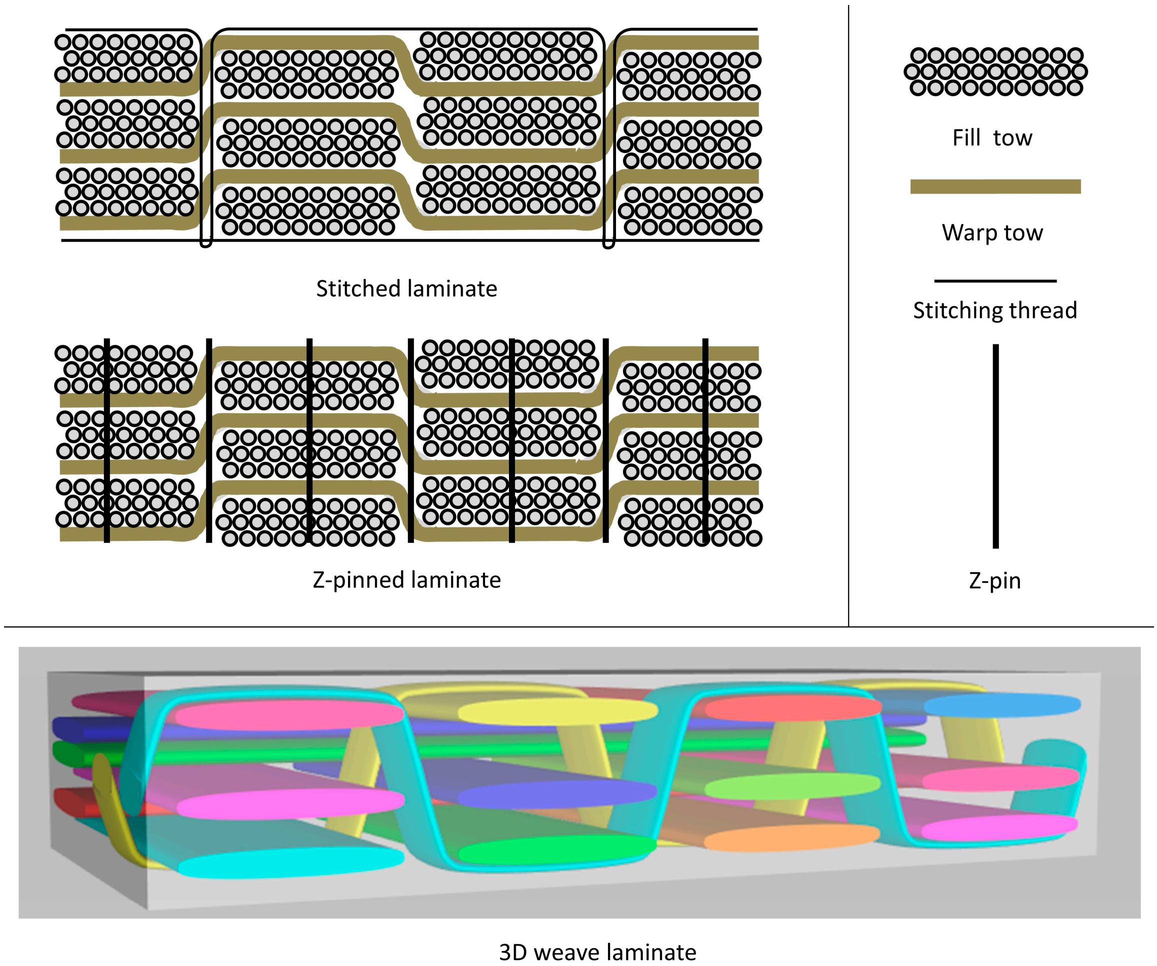


Figure 5. Schematic showing various 3D Sandwich Structures.

Braiding eliminates weak ply interfaces of the laminates. Therefore, braided laminates gave static strength comparable to that of conventional laminates but a shorter life [81]. Braiding, which requires a complicated manufacturing process, may involve the loss of flexibility in laminate construction. ILFT can be substantially increased by adding the reinforcement in the thickness direction like non crimp fabrics with stitches, z-pinning, and metallic wire usage as well as 3-D structural composites [2,4,32,83,84,93–97]. It was reported [4] that extensive crack branching caused toughening in the textile composites as the interlaminar crack followed a meandrous crack path inside a complex fiber architecture. The G_{Ic} values were found to be greater for the through thickness reinforced composites by a factor of two to three than the composites without thickness reinforcement. The dominant mechanism of toughening is the bridging of cracks in the through-thickness direction [4].

Even though 3D composites possess many properties superior to 2D laminates, they have failed in replacing 2D laminates for structural applications [93]. The high cost of producing 3D woven preforms [98], damage in the reinforcing fibers during the weaving process, and reduction of in-plane properties by Z-pinning [99] are the causes attributed to this failure.

R. Velmurugan et al. and S. Solaimurugan et al. also reported that stitching could arrest ILFT effectively and significantly G_I increased by 20 times as opposed to unstitched laminate [100]. On the other hand, stitching the laminates could reduce the strength and stiffness of the composite specimens [101,102]. With the introduction of stitching, it would cause little change in the interlaminar normal stresses but would reduce delamination crack opening.

Significant research has taken place to investigate the effect of fiber architecture in improving delamination properties [1,4,95,97,103]. Structurally stitched composites are an area of great interest as they offer tremendous property improvement in the out of plane direction being z-direction reinforcement. Structurally stitched composites with polyester (PES) yarn can increase the initial fracture toughness by nearly 100% relying upon the diameter and density of the stitch material [96], while the use of high strength glass, carbon, Kevlar, and even some hybrid yarns can dramatically increase the fracture toughness by a factor of 10–15 [94].

3.6. Interleaving or Interleafing

The idea of interleaved composites was first proposed by Cyanamid et al. [104]. Interleaving is a method of introducing tough, ductile polymers or adhesive at the fiber interfaces, as an additional layer. To improve the ILFT, composite strips and/or tough adhesives are interleaved between ply interfaces to arrest delamination [105–107]. It was also reported that high strain rate and failure strains must be characterized by the interleaf layers [108,109]. However, resin-rich interleaves, which enhance the ILFT, also decrease fiber-dominated properties (modulus and tensile strength) as the fiber volume fraction is comparatively reduced [107].

Several other studies have shown that the incorporation of particles as fillers in the regions of interlayers can enhance Mode I ILFT of a composite system. Moloney et al. [110] found that (1) toughness and modulus of the composite depends on the volume fraction of the fillers used; (2) laminate strength is inversely proportional to the particle size; (3) laminate strength, modulus and the Mode I ILFT is directly proportional to the particle strength and modulus; (4) better particle adhesion to the matrix does not signal improved fracture toughness.

The process of achieving higher ILFT involves placing a thin, high elongation resin interleaf between each fiber ply. For high hot-wet performance, each ply has its own fibers in an epoxy matrix. As the resins during curing remain discrete, matrix hot-wet compression strength is not observed in interleaf toughness [111].

The effect of the thickness of the film interleaved with the matrix on the fracture toughness performance of unidirectional carbon (IMS)/epoxy (Fiberdux 927) is also reported in the literature [112]. It was highlighted that the values of G_{Ic} and G_{IIc} showed an increase with the thickness (50 and 200 μm) of the used film by 70% and 200%, respectively, over the baseline comparison material.

Jiang et al. [113] studied the fracture toughness attributes of unidirectional carbon-epoxy composites containing interleaving polyethene terephthalate (PET) films with and without plasma surface treatment. They found that, with different modes of fracture, the interleaves have completely reverse effects on ILFT. Interleaf reduces G_{Ic} up to 70% and its toughness reduction is effectively mitigated through plasma treatment. However, in Mode II, the interleaves improve the corresponding toughness, with the impact of plasma treatment on G_{IIc} being negligible.

Hojo et al. [114] conducted studies on ILFT and fatigue crack growth studies on carbon fiber/epoxy composite with an epoxy interleaf made of the same polymer (thickness approximately 50 μm). They compared the in the Mode I and Mode II properties of these CFRP specimens where the matrix was interleaved. The Mode I properties remain unchanged. Whereas, the initial and propagation Mode II ILFT values for modified laminates was 1.6 and 3.4 times superior in comparison to the unmodified laminates. Furthermore, the epoxy-interleaved laminates had 2 to 2.3 time's higher Mode II delamination fatigue threshold than base CFRP laminates.

Wong et al. [115] added phenoxy fibers in carbon epoxy composite in the interlaminar region. They observed that with the addition of around 10% phenoxy fibers, the average G_{Ic} increased tenfold. Moreover, poorly distributed phenoxy fiber led to property variations within the interlaminar region.

The effect of adding Nylon-6 powder (N6P) with short kevlar fiber (SKF) was investigated by Park et al. [116] to investigate the ILFT of the new CFRP composites. They concluded that the volume of SKF and its orientation are important factors that play a major role in fiber bridging. Presence of an equal proportion of N6P and SKF resulted in reduced fracture toughness values as opposed to composites with only SKF, within experimental deviations. The G_{Ic} values measured using only N6P as reinforcement, showed no improvement owing to their incompatibility with the matrix. With SKF addition of up to 25.5 g/m^2 starting from 4 g/m^2, G_{IIc} reached the highest value of 3.7 kJ/m^2. In composites with both the constituents of 17 g/m^2, fiber bridging contributes to the reduction of G_{IIC} values to 3.1 kJ/m^2. With further addition of 4.0–25.5 g/m^2 of either of the constituents, the G_{IIc} values further decrease to 1.7 and 1.0 kJ/m^2 respectively and did not exhibit any fiber bridging. Lee et al. [117,118] fabricated several non-woven tissue (NWT) based hybrid composite materials and reported an increase in Mode II ILFT by interleaving the non-woven carbon tissue, without any prominent effect on the Mode I ILFT.

Over the last decade, multiscale composites have evolved as a solution for improving the mechanical and interlaminar fracture toughness performance of the composites. So, it is essential to understand in detail, how these kinds of composites are manufactured and the improvement they offer in the delamination resistance of the composites. The section below discusses in detail the evolution, the manufacturing, and the advantages offered by these class of composites.

4. Multiscale Composites

Previous studies reported improved mechanical performance of conventional composites with the addition of nano fillers [119–124]. Researchers also verified that the toughness of the composite improves because of nano fillers [125,126]. A nanocomposite phase could be produced by using them on the composite interface as shown in Figure 6a–d. This improves interlaminar fracture property and gives an advantage for nanocomposite over the pure matrix. The methodology to improve the toughness of composites using nanofillers is shown in Figure 6e by a schematic diagram. The primary objective here is to explore the use of nano-fillers in the polymer (particularly because the nanocomposite has improved properties than pure polymers) as matrix material on the interlaminar site (or interleaved material) to form traditional carbon fiber based composites. The field of multiscale composite has been revolutionized by adding nanocomposites with traditional composites. Since it is a primarily emerging field, further work on framing of this multiscale/nano-filled/nano-interfaced fiber reinforced plastic is called for. Details of different types of nanofillers and nanocomposites are elaborated in Section 4.1.

Moreover, the benefits of increasing delamination resistance in fiber reinforced composites have been proven using multiscale reinforcement, using fibers and CNTs together on the resin system or on the surface of the fibers [5,119–124,127–149]. The ILFT of the multiscale composite is of further interest. As the name suggests, "multiscale" composites comprise reinforcements at varying scales, such as continuous or discontinuous fibers of the order of mm, along with microscale fibers and/or nanoscale fillers or tubes. They are manufactured by merging nanoscale-sized fillers (e.g., CNTs) with traditional fiber reinforcements like glass and carbon [150,151]. The fiber resists in-plane load whereas the nanoscale reinforcement improves the performance of the through-thickness direction. Many techniques have been used by researchers to produce multiscale composites:

1. Nanofillers in the polymer
2. Dry CNTs transferred to the composite interface
3. Interleaving by CNTs/epoxy film
4. Multiscale fibers

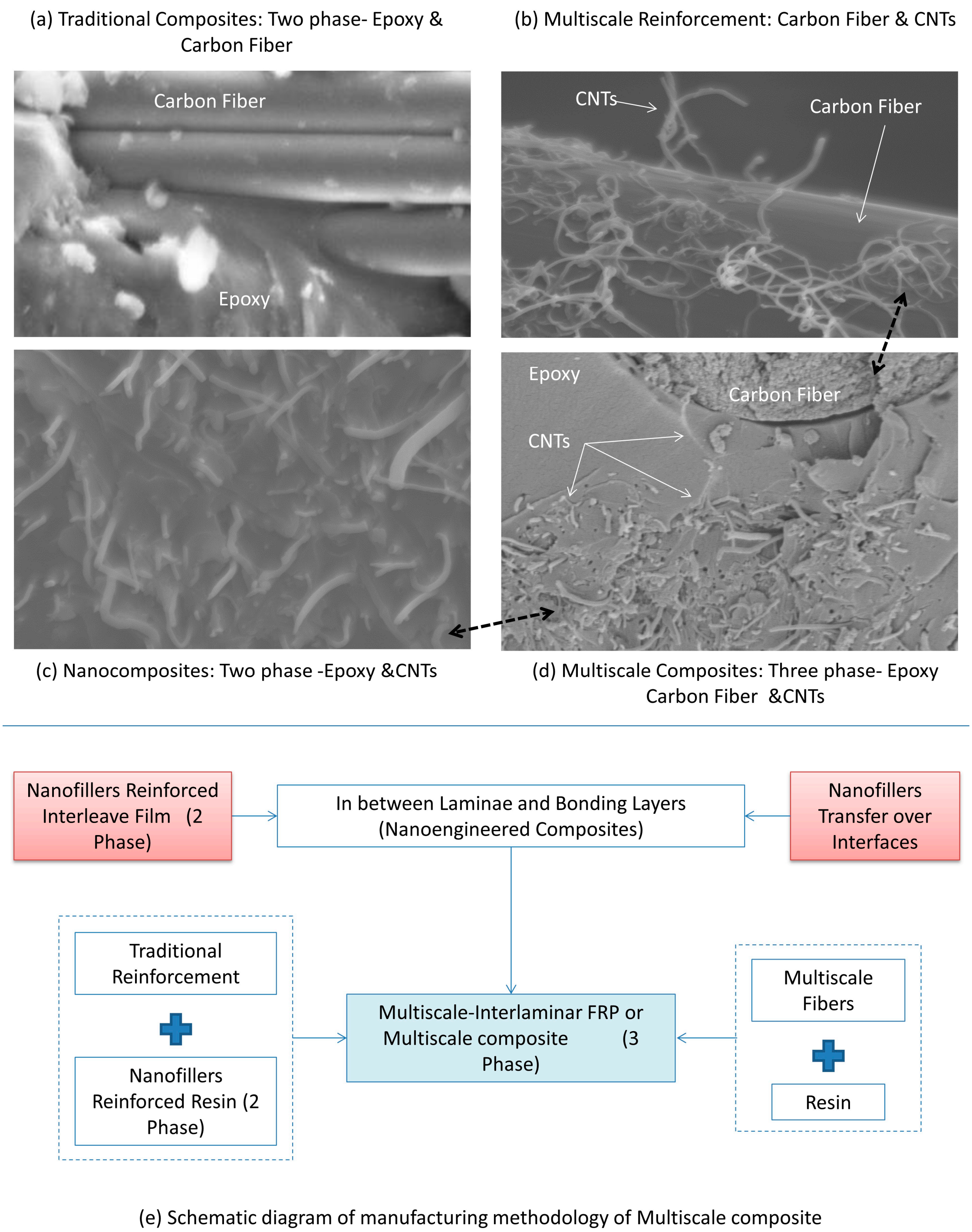


Figure 6. Nanofillers in traditional composite: multiscale composite.

4.1. Nanofillers in Polymer

Many classes of resin systems such as including metals, ceramics, and polymers are used in fabricating CNTs-based composites (i.e., nanocomposites) and their mechanical response has been studied [134,136,137,152,153]. The schematic diagram of nanofillers in polymers is shown in Figure 7. Different categories of nanofillers are available which can to be used in conjunction with the resin to form nanocomposites like nano silica, nano-aluminum oxide (Al_2O_3), nano-titanium oxide (TiO_2), polyhedral oligomeric silsesquioxane (POSS®), layered silicate (nano clay), Halloysite nanotubes (HNTs), montmorillonite (MMT), graphite, carbon nanofibers (CNFs), and CNTs. Nanoparticles are further sub grouped into particulates, layered, and fibrous materials. So, multiple types of nanofillers are available today. Carbon nanotubes are mainly mentioned, according to the scope of this research study. CNTs are extensively used owing to high strength and low density. They also have superior electrical and thermal conductivity performance. CNTs have a tremendous impact on the overall material properties even if they are mixed in low quantities of weight fractions [125,147,154]. CNTs are suitable for nanoscale reinforcement and provide versatility to fiber-reinforced composites. CNTs tend to agglomerate to form bundles. Dispersing the CNTs uniformly in the resin system is tedious owing to the presence of the van der Waals force effect. Here comes the role of functionalization of CNTs. The addition of functionalized groups onto the molecules by chemical methods is called functionalization and there are many approaches to the functionalization of CNTs [155]. Some of them include defect, noncovalent, and covalent functionalization. This prevents the nanotubes from agglomerating and helps in achieving stabilization and good dispersion of CNT within the base matrix. This engagement between the particles and the resin system improves the final properties of the CNTs/polymer composites [156–165]. The carboxyl (-COOH) or hydroxyl (-OH) groups present on the CNTs' surface provide a conducive environment for the various chemical reactions to take place [166–168]. Ma et al. [169] reported an exhibition of better wettability and high surface energy with epoxy matrix by amino-functionalized CNTs in comparison to pristine CNTs. The CNTs with amino functional groups improved interfacial adhesion, thereby resulting in better flexural and thermo-mechanical properties. Traditional composite fibers are chemically modified to increase the adhesion between resin and fibers. The idea that the interaction between CNTs and polymer matrix can be a sum of Van der Waals bonds and first order chemical bonds strongly supports the fact that the CNTs/polymer results are comparable with those of strongly bonded composite system supports.

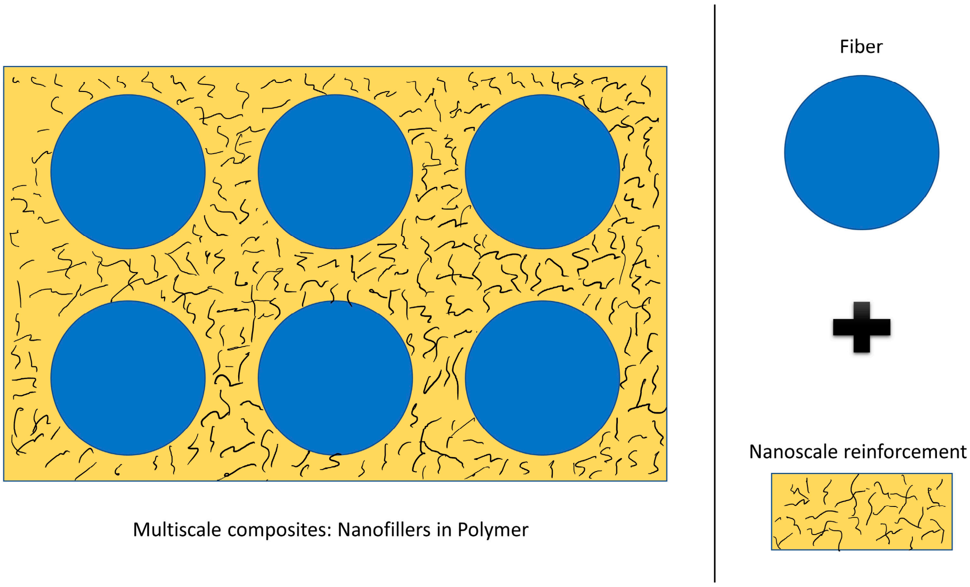


Figure 7. Schematic diagram of nanofillers in polymers.

The characteristics of traditional polymer matrix composites are changed by introducing nano based particles such as clay nanoparticles, nanotubes, and CNFs, etc. Nanotubes improve many functional properties such as toughness, stiffness, and thermal performance of pure polymers and their composites, unlike macroscopic fillers that decrease the impact resistance and strength of the pure polymers and composites. The major benefit of using nanotubes is the capability to remarkably increase the delamination resistance properties of the composites. Gojny et al. [170] studied the effect of the addition of nanoparticles on toughness properties of epoxy resins using double-wall CNTs and carbon black. They found that, in comparison to neat epoxy, nanocomposites had significantly higher fracture toughness. The dominating mechanism for dispersion of energy as reported by them was nanotube bridging cracks and deflection at small clusters. Enhancement of toughness is affected by the propagation of cracks and reduces the growth of nanopores. While CNTs and other nanoparticles can improve a few of the properties of composites, others investigations [171–173] indicated that it also resulted in reduction of some of the mechanical properties.

Chisholm et al. [173] utilized 1.5 to 3.5 wt% SiC (silicon carbide) dispersed in the epoxy polymer and carbon fiber (satin weave) for manufacturing multiscale composites by a resin infusion process. The composites reinforced with 1.5 wt% SiC displayed an enhancement in tensile strength (up to 16%) and tensile modulus (up to 45%) of the composites.

Gojny et al. [174] via resin transfer moulding manufactured nano-particle reinforced FRP composites, with CNTs and carbon black. The measured flexural and interlaminar shear strength of the matrix showed a significant increase of 20% with the addition of only 0.3 wt% CNTs (double wall) whereas the tensile properties did not show improvement and remained fiber-dominated. CNT influenced the fracture toughness behaviour also. The addition of carbon black in a similar proportion was found to be less effective in improving the mechanical properties of pure polymer material.

Tsantzalis et al. [175] used CNF and lead zirconate titanate (PZT) particles to modify the CFRP laminates. They reported fracture toughness increase of 100% in G_I (Mode I) with an addition of 1% CNF in the matrix. Yokozeki et al. [176] found similar improvement of tensile and shear ILFT modes (97% and 29% respectively) for 5 wt% cup stacked carbon nanotubes (CSCNTs)-laminates.

Kim et al. [177] investigated the delamination resistance characteristics of CFRP composite by mixing multi-walled carbon nanotubes (MWCNTs) into the matrix. Composites with 0.2 and 0.7 wt% of MWNTs enhanced theMode I ILFT at the cryogenic temperature. It was also concluded that a lower improvement of critical energy release rate of the modified resin was observed at very low and cryogenic temperatures compared to room temperature. Chen et al. [178] manufactured laminates using functionalized MWCNTs with varied surface synthesis as reinforcements. MWCNTs were dispersed efficiently on the epoxy by modifying the surfaces and subsequently resulted in better mechanical properties of the composite. The micrographs revealed that CNTs tend to realign during processing. They also noticed that the well oriented and positioned CNTs as reinforcements influenced those properties that were attributed to the fiber.

Green et al. [179] produced fiber reinforced multiscale composites which consisted of dispersed CNFs in an epoxy resin. By adding 0.1 and 1 wt% CNF, the flexural strength increased by 16% and 20% while the modulus also improved by 23% and 26% respectively. The shear strength (ILSS) was also enhanced by 6% and 25% for the 0.1 and 1 wt% CNFs, respectively when compared to fiber reinforced composites without CNFs dispersion.

Several groups of researchers investigated the effect of toughening the brittle matrix system as an effective way to reduce delamination onset [180–182]. Hunston et al. carried out a detailed investigation and showed that 3 J/m^2 higher toughened resins in general increases the composite interlaminar fracture toughness by 1 J/m^2 compared to neat resin composite laminates [183]. Recently Ozdemir et al. also studied the toughening attributes of rubber nano particles in carbon fiber polymer composites and 250% increase in delamination resistance was reported with the addition of 20 parts per hundred of rubber particles in the epoxy matrix [184]. Although certainly, the research in this direction has reached greater heights, there are still problems like particle dispersion during ex-situ processes using dry fabrics with liquid resin injection and the associated cost of the filler particles.

4.2. Dry CNTs Transfer to the Composite Interface

Research on dry CNT transfer on the composite interface has also gained significant attention and a schematic is depicted in Figure 8. Techniques like spraying [185], sprinkling [186], buckypaper (dry CNTs) [124,138,187], electrophoresis [139] etc. are used to improve the properties of composite specimens with nanofillers as localized reinforcements.

Thakre et al. [188] manufactured the nanotube composites with a spray of nanotube–ethanol solution sonicated (for an hour at 40 kHz) on the carbon fabric lamina using vacuum assisted resin transfer moulding (VARTM). Both the functionalized and non-functionalized single-walled carbon nanotubes (SWCNTs) were added and the mechanical performance was compared to laminates without any nanotubes. The ILSS showed an improvement of 4.4% with functionalized nanotubes whereas no improvement was seen for the case of the pristine or non-functionalized nanotubes.

The electrophoresis method was implemented by Bekyarova et al. [139] for the deposition of the fillers (MWCNTs and SWCNTs) on woven carbon preform and composite manufactured by transfer moulding using epoxy resin. The carbon fabric/epoxy composites with CNTs incorporation exhibited 30% improvement of ILSS as opposed to baseline composites with no CNTs and demonstrated considerable improvement in electrical conductivity in the transverse direction.

Arai et al. [189] fabricated a CFRP/CNF hybrid laminates by inserting CNFs with a small quantity of ethanol (solvent) between prepregs. Then the solvent with an areal density between 10 g/m^2 and 30 g/m^2 was allowed to volatilize from the prepreg sheets. For hybrid laminates, they found the Mode I ILFT shows improvement of half a factor compared to unmodified composites. The Mode II ILFT was also improved about three times compared to unmodified laminates but the in-plane rigidity decreases by 12% relative to the unmodified CFRP laminate.

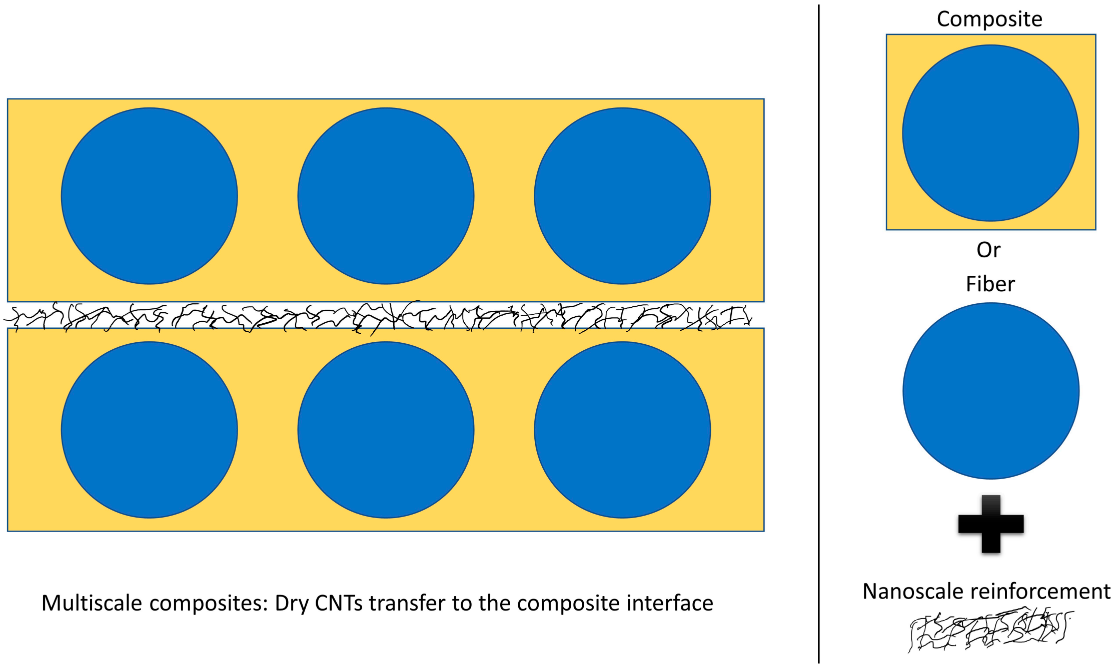


Figure 8. Schematic diagram showing dry CNTs transfer to the composite interface.

4.3. Nanofillers in Interleave

The approach of using nanofillers in interleave with an aim to toughen the composite system is widely used by researchers and a simplified schematic is shown in Figure 9. Well dispersed CNTs are formed as thin interleave film [5,130,132,190–193]. The nanocomposites thin film can also be manufactured using electrospinning [194–197] and electrospun [198–200] processes. These methods have gained popularity and are found to be an effective technique to also produce the electrospinning/electrospun nano-interlayers [201–205] which toughen the composite laminate. Klein et al. [206] reported the ILFT of specimens (satin woven CFRPs) with carbon nanotube/epoxy films. They noted that the interleaving films with the inclusion of carbon nanotubes was diminished. They observed this consequence as a thick epoxy layer was created in the mid-plane due to the film.

Warren et al. [207] also prepared and examined B-staged epoxy/SWCNT nano-composite thin films toughened laminate by nylon particles. The epoxy nanocomposites had well-dispersed SWCNTs and nylon particles that were made into films by controlling the curing and viscosity of the epoxy resin. They noticed that the surface functionalization of SWCNT and the inclusion of preformed nylon particles enhanced the mechanical performance of the nano-composites. The thin films seamlessly integrate into a laminated composite system upon heating and serve as interleaves for improving the mechanical properties and conductivity.

Davis et al. [208] fabricated nano composite (carbon fiber/epoxy) laminates by spraying fluorine functionalized carbon nano tubes (0.2, 0.3 and 0.5 wt%) on either side of 4 hardness satin carbon fabric and through a resin infusion process. The fabricated nano composites showed improved mechanical properties and durability under both tension-compression (with R ratio of −0.1) and tension-tension (with R ratio of +0.1) cyclic loadings. The CNTs incorporation toughened the fiber matrix interfaces and deflected the interfacial crack development and delamination both under cyclic and static loading.

Yokozeki et al. [186] utilized the combination of three different techniques to improve the ILFT of unidirectional CFRP laminates; namely, (1) Sprinkling of CSCNTs between the prepreg layers during stacking of plies, (2) Incorporation of resin films with CSCNT dispersed in matrix films, and (3) Dispersion of CSCNTs into the epoxy resin using the epoxy to produce prepregs. Two types of CSCNTs were used; aspect ratio of about 10 and 100 (designated as AR 10 and AR 100 respectively). They found that the incorporation of CSCNT (AR 10) films with CSCNT-dispersed resin was the most effective in enhancing Mode I (up to 300%) and Mode II (up to 160%) fracture resistance.

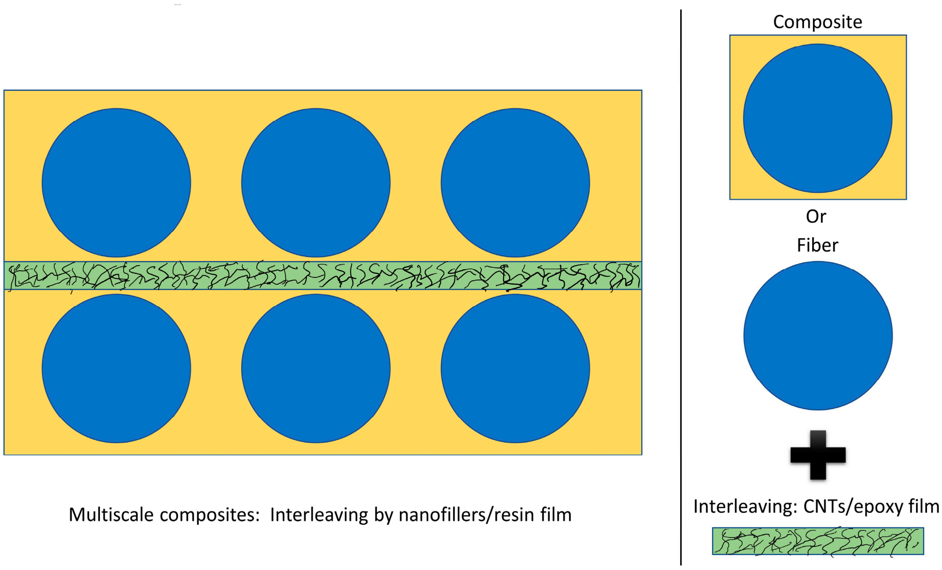


Figure 9. Schematic diagram showing interleaving by CNTs/epoxy film.

4.4. Multiscale Reinforcement

One of the techniques used to produce multiscale composites is by growing carbon nanotubes on the fiber surface and is termed as multiscale fiber approach [209]. The schematic of multiscale reinforcement approach is shown in Figure 10.

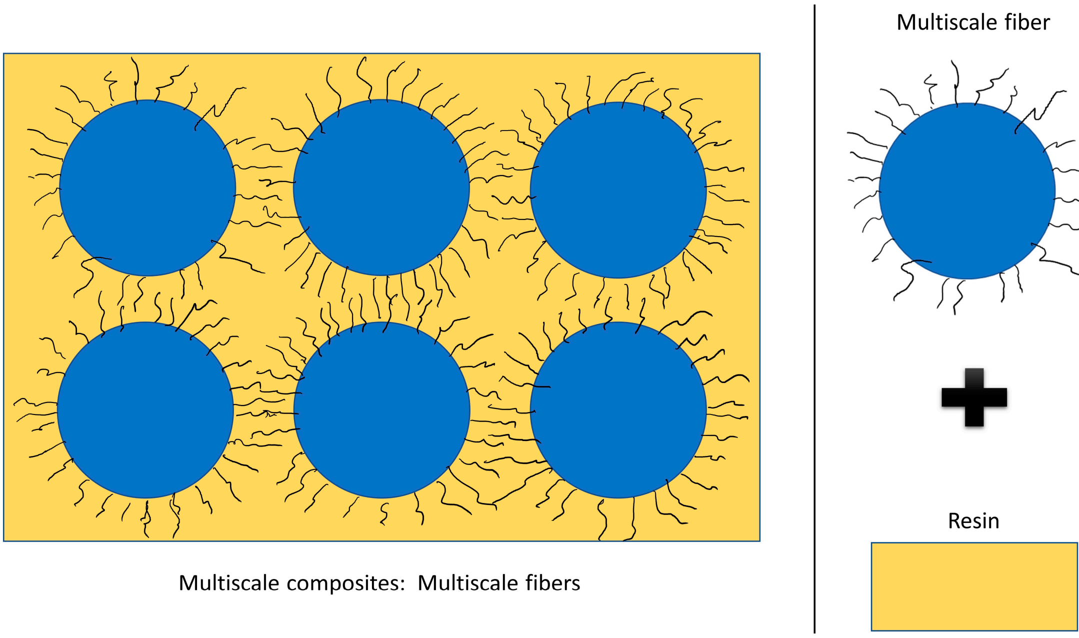


Figure 10. Schematic diagram of the multiscale composite using multiscale fiber approach.

CNTs were grown on the fibre surface by the chemical vapour deposition method in a study by Thostenson et al. [128] which resulted in a multi scale reinforced material. The localized effect of adding nano-reinforcements on transferring the load at the fiber matrix interface was studied by manufacturing the single-fiber composites. It demonstrated that the interlaminar shear (ILS) of the composite was increased with the addition of nanotubes at the interfacial region.

Woven carbon fiber laminate was prepared in situ with CNTs by Kepple et al. [210] to investigate the influence of growing nanotubes on carbon fiber. They noticed that the carbon fibers with grown nanotubes improve the delamination resistance of the laminates by up to 50%. Also, it was reported that the structural integrity of the final part was unaffected. Even 5% increase in the flexural modulus was reported. This work also demonstrated that CNTs on the flexible substrate even after functionalization remain as such, and most CNTs are rigid enough to tolerate the high temperatures higher than 800 °C undergone during the synthesis [210].

Mathur et al. [211] also grew CNTs on different carbon fiber substrates by chemical vapour deposition to produce hybrid/phenolic composites. They manufactured uni-directional cafron fibers tows, bi-directional (2D) CF cloth, and 3D CF felt. For unidirectional, 2D and 3D composites, the flexural strength was enhanced by 20%, 75%, and 66% respectively as opposed to the one without nanotubes under similar test scenarios.

5. Conclusions and Future Directions

CNTs are the perfect fillers for multiscale reinforcement in laminated composites owing to their dimensions of nanoscale and exceptional properties. The delamination resistance of the matrix resin can be dramatically enhanced by the proper use of the CNTs. CNTs have large surface area and are very flexible, thus having an ability to dissipate energy during the fracture event. In addition to the improvement of toughness, CNTs have also the potential to enhance the thermal, mechanical, and delamination performance of the resulting composite materials. Multiscale fiber approach yields significant increases in the delamination resistance properties, but there is an associated complicated manufacturing process as well as the cost.

Although, substantial research has been done in the area of using CNTs in polymers and FRP composites, the manufacturing of CNT/FRP multiscale composites is still gathering considerable pace and remains an area requiring continued investigation. In addition, it is still not known how both the flow of resin during curing and the curing parameters help in further dispersion and in the pore-filling process during composites manufacturing. This is especially important when one uses the CNT-engineered prepregs in making such laminates. The in-situ and ex-situ manufacturing of dry non-crimp fabrics with CNTs also requires detailed investigation as non-crimp composites have huge potential in aerospace, automotive, and many other industrial applications. Also, the literature lacks detailed investigation on composites manufactured with reactively processed thermoplastic matrices, toughened with CNTs.

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