Embedding carbon nanotubes (CNTs) in load-bearing composite laminate hosts to turn them into nano-laminates is a rapidly emerging field and has tremendous potential in enhancing the mechanical performance of the host laminates. This state-of-the-art review intends to provide a physical insight into the understanding of the enhancing mechanisms of the processed and controlled CNTs in the nano-laminates. It focuses on four aspects: (1) physical characteristics of CNTs, including CNT length, diameter, weight percentage and surface functionalization; (2) processing and control techniques of CNTs in the fabrication of nano-laminates, including distribution, dispersion and orientation controls of CNTs; (3) mechanical properties along with their testing methods, including tension, in-plane compression, in-plane and interlaminar shear (ILS), flexure, mode I and mode II fracture toughness as well as compression-after-impact (CAI), ballistic protection and fatigue; and (4) CNT–matrix load transfer and enhancing mechanisms along with a few major governing factors. The selective and uniform production of CNTs with specific dimensions and physical properties has yet to be achieved on a consistent basis. Moreover, the processing details of CNTs vary very significantly among different researchers so that the processed CNTs share little common characteristics. There is little control over the CNT orientations in most fabrication processes of the nano-laminates except for some cases associated with chemical vapor deposition (CVD). There are only two reports on in-plane compression and there is only one on in-plane shear. For reinforcement-dominated mechanical properties such as longitudinal tension and flexure, there was little enhancement reported. However, the substantial enhancement in in-plane compression strength was also reported. For matrix-dominated mechanical properties, such as transverse tension, in-plane shear, ILS strength and mode I and mode II fracture toughness, a significant enhancement, albeit with substantially varying degrees, was reported for ILS strength and mode I and mode II fracture toughness values. Meanwhile, the lack of consistent characterization of those properties was also noticeable. There is little established understanding of the enhancing mechanisms in nano-laminates.

Keywords: carbon nanotube (CNT); nano-laminate; mechanical properties

1. Introduction

Fiber-reinforced composite laminates have been used extensively in various sectors of industry, including aerospace, land and marine transport, to name just a few. The majority of the composite laminates in use lack reinforcement in the through-the-thickness direction. As a result, a damage mechanism such as delamination could occur at a relatively early stage...
of loading when the induced local interlaminar shear (ILS) stress within the laminate reaches a critical level, thereby affecting their structural performance. Delamination is thus one of the most detrimental damage mechanisms and causes considerable problems for structure designers and stress and maintenance engineers. At present, load-bearing composite laminates are designed such that the occurrence of delamination is minimized. This practice often leads to composite laminates being over-weight, less cost-effective and less efficient in terms of performance. Over the years, various solutions such as resin-toughening, stitching, interleaving and z-pinning have been attempted but with limited success. Some of these techniques could improve the delamination resistance of the composite laminates to some extent but at the expense of substantial reduction of their basic mechanical properties. The recent advent of carbon nanotubes (CNTs) provides many exciting possibilities for engineering exploitations. One particular area of innovation is to introduce CNTs into the composite laminates to enhance their resin-dominated mechanical properties so that their delamination resistance can be substantially improved, while ensuring that their reinforcement-dominated mechanical properties do not degrade.

CNTs can be both single-walled (SWNTs) and multi-walled (MWNTs). They have a nominal diameter between 2 and 100 nm and a length between tens and hundreds of a micron, depending on their manufacturing techniques and their surface functionalization. These dimensions typically result in aspect ratios of at least two orders of magnitude. They have a Young’s modulus of around 1 TPa (or five times that of steel) and a strength of around 20 GPa (or one hundred times that of steel). Their elastic and failure strains are greater than 5% and 12%, respectively. These physical features along with their mechanical properties make the CNTs easily embeddable in the host laminate without imposing any substantial intrusion and ideal for enhancing the mechanical properties of the resins. They are capable of playing a vital role in creating new-generation (nano-) laminates with enhanced mechanical performance. To achieve the stiffening and strengthening of the resin, the CNTs have to bond well with the matrix so that the load transfer from the matrix to individual CNTs can be effective. Because this field is very much emerging, there is little information in the public domain on the link between the enhancing mechanisms via mechanical performance and associated processing details of the CNTs. In particular, the research works reviewed here reflect on many occasions results of their preliminary trials. Therefore, it is essential to have an in-depth and comprehensive overview of this field in this embryonic state such that the key and critical issues in CNT processing and control, nano-laminate manufacturing and enhancing mechanisms in their mechanical performance are highlighted. As a result, research efforts worldwide, especially from newcomers entering this emerging field, could be focused more on these issues and thereby channeled into making greater progress rather than reinventing the wheel.

This paper intends to provide a state-of-the-art review of the published literature in this field [1–25] with exclusive attention being paid to experimental work, except for Section 5, which discusses load transfer and enhancing mechanisms. It aims ultimately at the establishment of an understanding of how and via what deformation mechanisms the purposely processed and controlled CNTs influence the mechanical performance of the laminate host. It has four specific focuses. The first one is to identify manufacturing methods for nano-laminates along with the techniques of incorporating CNTs. The second one is to ascertain processing and control techniques that CNTs are subjected to before/during the manufacture of nano-laminates. At this stage, attention will be exclusively paid to the dispersion and orientation controls of CNTs, the in-plane and through-the-thickness locations of CNTs in the nano-laminates and the role played by the length, weight fraction and surface functionalization of CNTs. The third one examines types of mechanical properties
and testing methods used. For the former, mechanical properties reviewed include tension, in-plane compression, in-plane shear and ILS, flexure, mode I and mode II fracture toughness as well as compression-after-impact (CAI) strength property plus fatigue strength. For the latter, critical discussion will be carried out as for whether or not the used testing methods are suited and/or adequate to the evaluation of the mechanical performance of the nano-laminates. It is conceivable that the testing methods that have already been established for conventional composite laminates are not necessarily adequate to evaluate the mechanical performance of the nano-laminates. The final focus includes discussion on the effects of factors that influence the load transfer and thus the enhancing mechanisms in the mechanical performance of the nano-laminates.

To this end, it is essential to clearly define a scope of involvement of nanomaterials along with conventional host materials in this review, as numerous definitions and phrases have already appeared in the open literature. A definition of nanomaterials generally includes CNTs and nanoparticles, each of which can be used as filler, reinforcement or functional material in the host material. Typical host materials are usually either polymers or fiber-reinforced composite laminates, though metals and ceramics are also used on some occasions. A broad definition of nanocomposites has been used extensively as one of three combinations, namely, (a) nanoparticles with a conventional polymer, (b) nanoparticles with a fiber-reinforced composite laminate and (c) CNTs with a conventional polymer. The reason that the mixture of nanoparticles with the conventional fiber-reinforced composite laminates is also included under the nanocomposites is because the nanoparticles with small aspect ratio are unable to provide any substantial improvement of the mechanical properties of the laminate host. In particular, the nanocomposites, except for case (b), are generally considered as being homogeneous and isotropic, even on a microscopic scale, so that their mechanical testing methods follow those standards of metals and plastics. Here, a nanolaminate is defined as a mixture of the conventional fiber-reinforced composite laminate as a host and CNTs as a nanomaterial. Since in the nano-laminate, continuous reinforcement, say carbon or E-glass fibers, is already present, extremely short CNTs are no longer considered as the reinforcement in the same sense as carbon or E-glass fibers and therefore will always be identified as CNTs. Thus, the terms fibers, reinforcement and matrix hereafter refer to those conventionally used in the host composite laminates. Moreover, the mechanical testing standards of the nano-laminates follow those that have already been established for the conventional composite laminates. The present review covers the mechanical behavior of nano-laminates only, whereas the mechanical behavior of nanocomposites has been comprehensively reviewed in [26–30], though some significant results regarding interfacial strength and load transfer in the nanocomposites will be included and discussed in Section 5. It must be stressed that this is the first time that the mechanical behavior of the nano-laminates embedded with CNTs has been reviewed.

2. Manufacturing methods of nano-laminates

The manufacture of nano-laminates is a very complex process due primarily to the fact that it is generally difficult to disperse CNTs and control their orientations and is even more difficult to introduce the so-processed CNTs into the conventional laminate host and keep them in such a state successfully during cure. As a result, in addition to different manufacturing methods, there are a significant number of material and processing parameters, as indicated in Table 1, which could influence the quality and thus the mechanical performance of the nano-laminates.
Table 1. Physical characteristics of laminate hosts and carbon nanotubes (CNTs) in nano-laminates.

| Ref. | Manufacture technique | Host laminate and lay-up | No of plies/thickness in mm (t ply thickness) | CNT type | Product. method | Functional group | Length (l) in μm and diameter (d) in nm | Location within nano-laminate |
|------|----------------------|--------------------------|---------------------------------------------|----------|-----------------|-----------------|----------------------------------------|-------------------------------|
| [1]  | Autoclave            | A: IM7/Ep T700/Ep UD B: AS4/Ep UD | 24/3                                         | MWNT     | CVD             | –               | l = 60, 120, 150                          | CNTs in 12th and 13th plies  |
| [2]  | CM                   | PW T300/Ep                | 8/3.5                                        | MWNT     | CVD             | –               | l = 50                                  | CNTs in 4th or 5th ply       |
| [3]  | A: VARTM B: IDVART   | PW E-glass/Ep             | 8/4.4 (B) & 6.8 (A)                         | MWNT     | CVD             | –               | l = 15                                  | CNTs in resin                |
| [4]  | VARTM                | ?HSW Carbon/Ep            | 4/2 (t = 0.23 mm)                           | MWNT     | –               | –               | d = 30–60, l = 3–10                       | CNTs in resin                |
| [5]  | Hand lay-up          | ?HSW Al/Ep                | 4/2,1                                        | MWNT     | CVD             | –               | l = 30                                  | CNTs in resin                |
| [6]  | VARTM                | IM7/Ep UD                 | 8/1                                          | SWNT     | EAD             | -COOH           | l = 0.75, d = 2–6                         | CNTs in resin                |
| [7]  | Hand lay-up          | PW T300/Ep                | 4/2                                          | MWNT     | CVD             | –               | –                                       | CNTs on both sides of each ply|
| [8]  | VARTM                | PW IM7/Ep                 | 4/1.2                                        | SWNT, MWNT | CVD           | -COOH           | l = 2–6                                 | CNTs on both sides of each ply|
| [9]  | VARTM                | PW E-glass/VE             | 10/5.7–6.0                                  | SWNT     | CVD             | F, Br, Ally, Sila d = 1.1                  | CNTs in 2 plies at the mid-plane|
| [10] | Autoclave            | T700/Ep UD                | 8/2                                          | CSCNT    | CVD             | –               | d = 70–80                                | CNTs in resin                |
| [11] | Autoclave            | T700/Ep UD                | 36/4 (t = 0.12 mm)                          | CSCNT    | CVD             | –               | d = 70–80                                | CNTs in resin & at 18th–19th ply interface |
| [12] | Autoclave            | 5HSW AS4/VE               | 48/–                                         | MWNT     | CVD             | –               | A: l = 1, B: l = 10, both d = 20–50        | CNTs in resin                |
| [13] | VARTM                | E-glass/Po QI             | 8/–                                          | MWNT     | –               | -NH₂            | –                                       | CNTs in resin                |
| [14] | CM                   | PW E-glass/Ep             | A, B, C and E: 6 plies D: 5 plies, (t = 0.16 mm) | MWNT     | –               | -COOH           | A, D & E: d = 10–30, l = 5–15 B & C: d = 40–60, l = 1–2 | A, B C and E: CNTs in resin C: additional CNTs at the mid-plane D: one CNT epoxy film at interfaces |
Table 1. (Continued).

| Ref. | Manufacture technique | Host laminate and lay-up | No of plies/thickness in mm (i ply thickness) | CNT type | Product, method | Functional group | Length ($l$) in μm and diameter ($d$) in nm | Location within nano-laminate |
|------|-----------------------|--------------------------|-----------------------------------------------|-----------|----------------|-----------------|------------------------------------------|-----------------------------|
| [15] | Autoclave             | T700/Ep UD & QI          | 16/2 & 36/4, 24/3 for QI                      | CSCNT     | CVD            | –               | $d = 70–80$                | CNTs in resin               |
| [16] | RTM                   | E-glass/Ep UD & QI       | 4/- for QI                                    | DWNT      | –              | -NH$_2$          | $d = 2.8$                  | CNTs in resin               |
| [17] | VARTM                 | 4HSW IM7/Ep              | 4/1                                           | SWNT, MWNT| –              | –               | $d = 10–30$                | CNTs in resin               |
| [18] | CM                    | Basalt/Ep CP             | 4.0/5                                         | MWNT      | CVD            | -COOH, PGE      | $d = 20–60$, $l = 5–15$    | CNTs in resin               |
| [19] | Autoclave             | Carbon/Ep UD             | 8/2–2.5                                      | MWNT, DWNT| –              | -NH$_2$          | A: $d = 9.5$, B: $d = 8–9$, C: $d = 3.5$ | CNTs in resin               |
| [20] | Hand lay-up           | E-glass/Ep UD            | -/0.5                                        | MWNT      | CVD            | –               | $d = 10–20$, $l = 10–50$  | CNTs in resin               |
| [21] | Autoclave             | T700/Ep UD               | A: 14/3.3–3.4, B: 16/3.8–4.0                  | MWNT      | CVD            | –               | $l = 10–20$, A: $d = 150$, B: $d = 80$ | CNTs at the mid-plane      |
| [22] | CM                    | PW E-glass/PA6           | 10/2.5                                       | MWNT      | –              | –               | –                         | CNT on the surfaces and at interfaces |
| [23] | Autoclave             | Carbon/Ep UD             | 16/-                                         | MWNT      | CVD            | –               | $d = 10–15$, $l = 500$    | CNTs in resin               |
| [24] | VARTM                 | E-glass/PEVE             | A: 2/12.8                                    | MWNT      | –              | PmPV-DOctOPV     | $l = 100$                 | A: nano film at interface, B: CNTs in resin |
| [25] | CM                    | PW E-glass/Ep            | 8 plies (t = 0.28 mm)                        | MWNT      | –              | –               | –                         | CNTs in resin               |

Notes: UD, CP, AP and QI denote unidirectional, crossply, angle-ply and quasi-isotropic lay-up, respectively. PW and xHSW denote plain and x harness satin weave, respectively. Al denotes alumina fibers. Ep, Po, VE, PA6 and PVEE denote epoxy, polyester vinyl ester, nylon 6 and poly-vinyl-ester-epoxy, respectively. SWNT, DWNT, MWNT and CSCNT denote single-walled, double-walled, multi-walled and cup-stacked carbon nanotubes, respectively. CVD and EAD denote chemical vapor deposition and electric arch discharge, respectively. CM denotes compression molding.
2.1. Material characteristics of laminate hosts and CNTs

Laminate hosts that have been used in nano-laminates so far are composed of either carbon or E-glass fibers (except in [5,18]) and polymeric matrix such as epoxy, polyester, or vinyl ester (except in [22]). Whereas epoxy is the most dominant matrix material, both carbon and E-glass fibers are equally popular. Their weave patterns in the host laminates seem to be influenced by the manufacturing method of the nano-laminates with unidirectional (UD) being generally used with autoclave and fabric preforms being popular with vacuum-assisted resin transfer molding (VARTM); see Table 1.

The physical characteristics of the CNTs used (Table 1) vary significantly, depending on their production methods and on whether they are SWNTs or MWNTs. SWNTs with better mechanical properties are usually smaller in diameter and shorter in length than MWNTs. Three major production methods for CNTs are electric arch discharge [6], laser ablation of metal-doped carbon rods and chemical vapor deposition (CVD) [1–3,5,8,10,12,15]. Whereas the first two methods produce high-quality CNTs in general, they are neither able to produce only SWNTs nor able to control CNT length. In addition, they have low yield. CVD and its variants seem most popular because of their ability of overcoming these limitations as specifically stated in the following. Firstly, CVD could be set up to synthesize SWNTs only via HiPco (variant of CVD with high temperature and high pressure) [9]. Secondly, it is capable of controlling CNT length and growth direction. For instance, vertically aligned CNTs, called CNT forests, can be grown. Finally, CNTs can be grown in situ directly from the surface of fabric preforms. The other additional useful features include its relatively low cost and versatility, say, growing CNTs as stacked truncated cups (CSCNTs) [10,11,15]. It is unsurprising that CVD-produced CNTs have dominated applications in nano-laminates. However, there are published reports [31] that suggest that the quality of CVD-produced CNTs were not as good as those produced by the other two methods. Nevertheless, it still seems challenging to produce a particular type of CNTs, say SWNTs, with the uniform dimensions and physical properties. In addition, as the natural sidewall surface of CNTs is atomically smooth, they may not bond well with the resin matrix of the laminate host. It is thus desirable to attach functional groups to the CNTs so that a good interfacial bonding with the matrix can be developed. Moreover, the surface functionalization of the CNTs could also improve the uniformity of their dispersion [32–34].

2.2. Manufacturing methods for laminate hosts

Typical manufacturing methods that have been used to fabricate flat laminate hosts are VARTM, autoclave molding, compression molding (including hot pressing) and hand lay-up. Autoclave molding, a well-established predominant method in the aerospace industry, usually uses prepregs as starting materials in a double-sided mold. With a precise control over time, temperature and pressure, laminates of high quality are produced routinely. Naturally, it has also been used to fabricate nano-laminates [1,10–12,15,19,21,23]. VARTM has been equally popular due to the possibility of using dry fabric preforms and liquid resins as starting materials, low tooling requirement and low cost [3,4,6,8,9,13,16,17,24]. As a single-sided mold is usually used under atmospheric pressure in VARTM, it has limited ability to consolidate laminates and thereby control the thickness of the laminates. Thus, a uniform infiltration of the resin doped with CNTs could be difficult, especially when the amount of CNTs is significant, due to the relatively high viscosity of the resin at room temperature and relatively high surface area of CNTs. This could be compounded by relatively long CNTs, if used, as they could reduce the flow rate of the resin and increase the resin viscosity and thereby
processing difficulty. However, this process could be improved by using double vacuums and was renamed as IDVARTM [3]. As a result, up to 2 wt% concentration of CNTs was successfully incorporated into the laminate host.

Compression molding is another low-cost method for fabricating host laminates [2,14,18,22,25]. It usually involved a pair of heated pressing platens for applying pressure but with no vacuum environment. Starting materials can be either dry fabric preforms with liquid resin or prepregs. Pressure is applied to the laminate stack either directly or via an additional molding tool. Hand lay-up is the simplest method of all, using usually dry fabric preforms and liquid resin as starting materials along with a single-sided mold [5,7,20]. As resin is brushed/sprayed onto the fabrics layer after layer or the fiber tows are pulled through a doped resin bath, there is little control over the quality of the laminates without consolidation pressure.

2.3. Processing techniques for introduction of CNTs into laminate hosts

Whereas autoclave molding is still the most predominant method for fabricating high quality laminates, VARTM has become the most effective non-autoclave low-cost method. Nevertheless, the merits of the methods as techniques for fabricating nano-laminates ultimately rest on their effectiveness in controlling or maintaining the uniform distribution and especially orientation of the CNTs within the host. Three techniques that have been used to introduce CNTs into a host laminate are based on doping, growth and transplanting or insertion, respectively.

2.3.1. Doping technique

The doping technique so far seems the most straightforward and popular for introducing CNTs into a host laminate as it can be used along with any one of the aforementioned laminate assembly and curing methods, such as VARTM, autoclave and compression molding. CNTs are first dispersed in a liquid resin via a simple mixing or three-roll milling. The surface functionalization of the CNTs was reported to improve their dispersion uniformity [32–34]. Then the doped resin is drawn through fabric preforms stacked in a mold to allow its infiltration just as in usual operation of VARTM [3,4,6,13,16,17,24]. As a result, during the infiltration there was little control over the preservation of the original uniformity of the dispersed CNTs, let alone the control over their orientations. The other way of making use of VARTM was to either soak fabric preforms in a solution dispersed with CNTs [8] or spray CNT-dispersed liquid onto fabric preforms [9]. The fabric preforms then had CNTs stuck on their surfaces once suspension liquid dried up. A final usual operation of the resin infiltration was carried out to produce a nano-laminate. The advantage of the fabric doping techniques is that not all fabric layers need to be doped so that they could be used cost-effectively for wherever the enhancement of mechanical performance is desired. Alternatively, the doped resin could be poured onto individual dry fabric preforms and then all the individual preforms stacked up to be cured using an autoclave [10–12,15,19–23]. The advantage of this process was that it also allowed the additional CNTs to be either sprinkled or inserted in the form of film at selected through-the-thickness locations. Another alternative to autoclave was to cure nano-laminates via compression molding [14,18,22,25].

2.3.2. Growth technique

The growth technique starts by either soaking individual fabric preforms in a solution [5] or spraying liquid catalyst onto the two surfaces of individual fabric preforms [7]. Under high
temperature (up to 1000°C), CNTs grew from the catalyst precursor deposited on the preform surface with the aid of blended gases within a furnace as part of the CVD process. The direction of the growth was controlled by application of strong electron field. The fabric preforms with grown CNTs on their surfaces were soaked in resin, then stacked up individually and finally cured either in a vacuum bag [5] or at room temperature [7].

2.3.3. Transplanting or insertion technique

The transplanting or insertion technique starts by either planting/growing CNTs on a silicon wafer via the CVD process [1,2] or fabrication of nanocomposite films [11,14]. For the former, the grown CNTs arrays or forest were then mechanically transplanted individually onto the surface of conventional preplreg [1,2]. Finally, those individual prepregs were stacked up and were cured either using an autoclave [1] or with compression molding [2]. Since the grown CNT arrays were parallel to one another, the transplanted CNTs were supposed to be in theory perpendicular to the prepreg surface. If so-oriented CNTs survived the lamination process and pressure during cure, they could be effective barriers to the occurrence and propagation of delaminations. For the latter, nanocomposite films were prepared with semi-cured resins. These films were then inserted at the selected through-the-thickness locations during the conventional lamination. Finally, the nano-laminate stacks were cured either using an autoclave [11] or with compression molding [14]. It is unclear whether the CNTs in the film were random or orientation-controlled. The advantage of this transplanting/insertion technique was that it allowed the CNTs to be inserted at selected through-the-thickness locations.

Throughout all three techniques, the weight percentage (indicated by wt%), length, uniformity of dispersion, orientation and surface functionalization of CNTs, CNT–matrix interfacial bonding as well as the load transfer from the matrix to the CNTs will all affect the mechanical behavior of the nano-laminates. Being too long is not necessarily helpful to the enhancement of the mechanical performance of the host [1]. Detailed microscopic physical characterization for the uniformity of dispersion and orientation of CNTs at specific locations is extremely important but often not available.

3. Fundamental mechanical properties of nano-laminates

The mechanical behavior of the nano-laminates can generally be characterized by both modulus and strength properties in tension, in-plane compression, flexure, in-plane shear and ILS. The fracture toughness performance of the nano-laminates can be represented by mode I and mode II critical strain energy release rates. All mechanical property results of the reviewed publications in terms of average values are summarized in Tables 2–7, including the baseline values of the host laminates for the specific properties. The corresponding details for the physical characteristics of the CNTs and the host laminates in addition to the manufacturing methods can be looked up in Table 1 for the same reference numbers. The respective mechanical testing standards, which were indicated in those tables, largely followed ASTM standards. Tables 2a, 3 and 4 cover the mechanical property results for longitudinal tension, in-plane compression and flexure, which are generally considered to be dominated by the reinforcement of the host laminates. Tables 2b, 5, 6 and 7 cover the mechanical property results for the transverse tension of UD nano-laminates, in-plane shear, ILS, mode I and mode II fracture toughness, which are generally considered to be dominated by the matrix of the host laminates. For clarity and ease of comparison, most of the original numerical results are also presented with bar charts in Figures 1–23, in which the average baseline values are plotted.
Table 2. Tension mechanical properties of (a) nano-laminates in the fiber direction and (b) UD nano-laminates in the transverse direction.

| Ref. | Tensile modulus (GPa) | Tensile strength in (MPa) | Test method  |
|------|-----------------------|---------------------------|--------------|
| (a)  |                       |                           |              |
| [8]  | Baseline (CP): 67.5   | Baseline (CP): 600        | ASTM D3039   |
|      | Nano-laminate at 0.25 wt%: 70 | Nano-laminate at 0.25 wt%: 580 |              |
| [10] | Baseline (UD): 131    |                           | ASTM D3039   |
|      | Nano-laminate at 5 wt%: 129 |                          |              |
|      | Nano-laminate at 12 wt%: 131 |                          |              |
| [15] | Baseline (QI): 46.5   |                           | ASTM D3039   |
|      | Nano-laminate at 5 wt%: 47.9 |                          |              |
|      | Nano-laminate at 10 wt%: 48.3 |                         |              |
| [16] | Baseline (QI): 25.5   |                           | DIN EN 52 7.1/2 Tension |
|      | Nano-laminate at 0.1 wt%: 26.4 |                      |              |
| [17] | Baseline (CP): 60.2   |                           | ASTM D3039   |
|      | Nano-laminate at 0.3 wt%: 59.4 (P2), 59.9 (P3) |                          |              |
| [18] | Baseline (CP): 27.7   | Baseline (CP): 585        | ASTM D3039   |
|      | Nano-laminate at 0.2 wt% pristine CNT: 27.4 | Nano-laminate at 0.2 wt% pristine CNT: 564 |              |
|      | Nano-laminate at 0.6 wt% pristine CNT: 28.5 | Nano-laminate at 0.2 wt% pristine CNT: 504 |              |
|      | Nano-laminate at 0.2 wt% -COOH: 30.4 | Nano-laminate at 0.2 wt% -COOH: 636 |              |
|      | Nano-laminate at 0.6 wt% -COOH: 36.4 | Nano-laminate at 0.6 wt% -COOH: 628 |              |
|      | Nano-laminate at 0.2 wt% PGE-CNT: 29.9 | Nano-laminate at 0.2 wt% PGE-CNT: 609 |              |
|      | Nano-laminate at 0.6 wt% PGE-CNT: 34.9 | Nano-laminate at 0.6 wt% PGE-CNT: 615 |              |
| [19] | Baseline (UD): 140    |                           | ASTM D3039   |
|      | A: Nano-laminates at 0.5 wt%: 140 |                          |              |
|      | B: Nano-laminates at 0.5 wt%: 136 |                          |              |
|      | C: Nano-laminates at 0.5 wt%: 144 |                          |              |
| [20] | Baseline (UD): 844    |                           | Tension      |
|      | A: Nano-laminates at 0.5 wt%: 1668 |                          |              |
|      | B: Nano-laminates at 0.5 wt%: 1668 |                          |              |
|      | C: Nano-laminates at 0.5 wt%: 1500 |                          |              |
| [23] | Baseline (UD): 122    |                           | Tension      |
|      | Nano-laminate at 0.1 wt%: 121 |                          |              |
|      | Nano-laminate at 0.5 wt%: 128 |                          |              |
|      | Nano-laminate at 1 wt%: 129 |                          |              |

(Continued)
| Ref. | Tensile modulus (GPa) | Tensile strength (MPa) | Test method |
|------|-----------------------|------------------------|-------------|
| [10] | Baseline (90°): 8.61  | Baseline (90°): 51.2   | ASTM D3039  |
|      | Nano-laminate at 5 wt%: 9.11 | Nano-laminate at 5 wt%: 57.9 |             |
|      | Nano-laminate at 12 wt%: 9.08 | Nano-laminate at 12 wt%: 55.1 |             |
| [16] | Baseline (90°): 12.3   | –                      | DIN EN 527.1/2 Tension |
|      | Nano-laminate at 0.1 wt%: 13.2 |                        |             |
| [19] | Baseline (90°): 7.4    | Baseline (90°): 51     | ASTM D3039  |
|      | A: Nano-laminate at 0.5 wt%: 6.6 | A: Nano-laminate at 0.5 wt%: 54 |             |
|      | B: Nano-laminate at 0.5 wt%: 7.3 | B: Nano-laminate at 0.5 wt%: 50 |             |
|      | C: Nano-laminate at 0.5 wt%: 6.9 | C: Nano-laminate at 0.5 wt%: 54 |             |
|      | D: Nano-laminates at 0.5 wt%: 6.6 | D: Nano-laminates at 0.5 wt%: 54 |             |

Note: P2 and P3 and denote panel 2 and panel 3 in [17], respectively.
against the average mechanical properties of the nano-laminates with major contributing factors such as CNT weight percentage, length, diameter and functional groups of CNTs and the presence of dispersants used during the CNT processing being identified.

3.1. Tension
3.1.1. Longitudinal tension
Table 2a summarizes the tension results of both baseline laminates and nano-laminates with some of the comparable results being presented graphically in Figures 1–3. The majority of the host laminates [8,10,15,17,19,23] used carbon/epoxy as the host material, whereas one [18] used basalt fiber/epoxy and the remaining two [16,20] used E-glass/epoxy. Moreover, the majority of the host laminates [8,10,16,17,18,20] were constructed with no more than eight plies. The host laminates were in a lay-up of UD [10,19,20,23], cross ply (CP) [8,17,18] and quasi-isotropic (QI) [15,16]. The majority (two thirds) of them [8,10,15,17–19] followed the ASTM standard D3039 [35] and one [16] used the DIN EN 527.1/2 standard, whereas the remaining two did not follow any standard in their specimen preparation and test set-up. The results shown in Table 2a and Figures 1–3 show that neither tensile modulus nor tensile strength was substantially enhanced even when the amount of CNTs was increased up to 10 wt% [15] or 12 wt% [10] except for one case in [18] where the tensile moduli of basalt fiber/epoxy laminates with 0.6 wt% functionalized MWNTs were increased by over 26%. Generally, the amounts of the increase and decrease in both modulus and strength were within or similar to the respective ranges of data scatters, when compared with those of the baseline values. This was expected of the nano-laminates where the reinforcement of the host dominated their tensile behavior, irrespective of host material, lay-up and the presence of CNTs. In addition, these results also confirmed that there was no clear evidence to suggest that embedding CNTs in the host laminates would adversely affect their tensile mechanical properties.

![Figure 1](image1.png)
Figure 1. Tensile modulus results of nano-laminates with carbon/epoxy laminate hosts with various lay-ups [8,10,15].
3.1.2. Transverse tension of UD nano-laminates

Although the transverse tensile properties of UD nano-laminates are matrix-dominated, the overall test results, as summarized in Table 2b plus examples in Figures 4 and 5, show little enhancement in terms of both modulus and strength. Whereas the volume of data available is very small for any reliable judgement, the only result that is worth commenting is a 13%
increase in transverse tensile strength with 5 wt% CNTs [10], which was still in the same range of data scatter. On the whole, this seems to suggest that the CNTs in the doped resins [10,16,19] might have been oriented in the same transverse direction as the reinforcement, since that was the flow direction of the CNTs with the least resistance during the resin infiltration. Clearly more research will be needed in this area.
3.2. In-plane compression

There is a dearth of information on the in-plane compression results of nano-laminates [12,15] due probably to the well-known complexity involved in jig requirement and assembly, if using the ASTM standard D3410 [36], as well as test execution. Both groups of researchers [12,15] used their own testing methods and neither provided details of compression load introduction techniques. The only compressive modulus results in Figure 6 from the latter investigators [15] show that the compressive modulus of carbon/epoxy host in a QI lay-up was not affected by the inclusion of 10 wt% CNTs. However, the findings for compressive strength are slightly inconsistent from the two investigations. In [12], the researchers examined the respective effects of dispersant and CNT length on the compressive strength of carbon/epoxy hosts. Both nano-laminates were relatively thick with 48 plies in a lay-up of CP [12] and 24 plies in a lay-up of QI [15]. As shown in Figure 7 and in Table 3, they found that for the short CNT length of 1 μm the presence of CNTs with 1 wt% increased the compressive strength by about 13% and the inclusion of dispersants doubled the strength increase. For the long CNT length of 10 μm, the presence of CNTs with 1 wt% increased the compressive strength by about 23% and the inclusion of dispersants had little effect on the compressive strength. Although the aspect ratio of 0.67 for the gauge section of the specimens [15] was deemed to be problematic to the nano-laminates in a QI lay-up, their compressive strength results, as shown in Figure 8 and in Table 3, show little effect of CNT inclusion, with a 10% increase for 10 wt% CNTs.

3.3. Flexure

Similar to the longitudinal tensile mechanical properties, the flexural mechanical properties are reinforcement-dominated. Whereas one [22] used E-glass/PA6 in plain weave, the rest of the host laminates [4,6,15,17] used carbon/epoxy in a lay-up of CP [4,17], UD [6] and QI

![Figure 6. In-plane compression modulus results of nano-laminates with quasi-isotropic carbon/epoxy laminate host [15].](image-url)
The nano-laminates were tested with a length-to-depth ratio of 16 [4,22], 25 [17], 27 [15] and 32 [6], following broadly the three-point bending method from the ASTM standard D790 [37]. The results in Table 4 show that neither flexural modulus, also in Figure 9, nor flexural strength (except for [17]), also in Figure 10, was increased beyond their respective ranges of data scatter. Although the amount of the used CNTs was small in [4,6], it went up to 10 wt% in [15] but still little enhancement was shown. Although these

![Figure 7](image1.png)

Figure 7. In-plane compression strength results of nano-laminates with carbon/epoxy laminate host with various CNT and processing conditions [12].

![Figure 8](image2.png)

Figure 8. In-plane compression strength results of nano-laminates with quasi-isotropic carbon/epoxy laminate host [15].
Table 3. Compression mechanical properties of nano-laminates.

| Ref. | Compressive modulus (GPa) | Compressive strength (MPa) | Test method |
|------|---------------------------|-----------------------------|-------------|
| [12] | –                         | Baseline (CP): 570          | Northwestern University Compression Fixture |
|      |                           | CNT length = 1 μm           |             |
|      |                           | Without dispersant: nano-laminate at 0.5 wt%: 680 |             |
|      |                           | Without dispersant: nano-laminate at 1 wt%: 640 |             |
|      |                           | With dispersant: nano-laminate at 0.5 wt%: 790 |             |
|      |                           | With dispersant: nano-laminate at 1 wt%: 720 |             |
|      |                           | CNT length = 10 μm          |             |
|      |                           | Without dispersant: nano-laminate at 0.5 wt%: 700 |             |
|      |                           | Without dispersant: nano-laminate at 1 wt%: 700 |             |
|      |                           | With dispersant: nano-laminate at 0.5 wt%: 780 |             |
|      |                           | With dispersant: nano-laminate at 1 wt%: 710 |             |

| [15] | Baseline (QI): 42.9       | Baseline (QI): 488          | NAL-NHC-II Compression Japan |
|      | Nano-laminate at 5 wt%: 43.2 | Nano-laminate at 5 wt%: 501 |             |
|      | Nano-laminate at 10 wt%: 45.1 | Nano-laminate at 10 wt%: 539 |             |

Table 4. Flexure mechanical properties of nano-laminates.

| Ref. | Flexural modulus (GPa) | Flexural strength (MPa) | Test method |
|------|------------------------|-------------------------|-------------|
| [4]  | Baseline (CP): 63.0    | Baseline (CP): 608      | ASTM D790 L/t = 16 |
|      | Nano-laminate at 0.3 wt%: 66.1 | Nano-laminate at 0.3 wt%: 626 |             |
| [6]  | Baseline (UD): 106     | Baseline (UD): 1534     | ASTM D790 L/t = 32 |
|      | Nano-laminate at 0.2 wt%: 106 | Nano-laminate at 0.2 wt%: 1367 |             |
|      | Nano-laminate at 0.5 wt%: 109 | Nano-laminate at 0.5 wt%: 1033 |             |
| [15] | Baseline (for QI): 53.0 | Baseline (for QI): 875  | JIS K 7074* Flexure L/t = 27 |
|      | Nano-laminate at 5 wt%: 55.1 | Nano-laminate at 5 wt%: 912 |             |
|      | Nano-laminate at 10 wt%: 55.8 | Nano-laminate at 10 wt%: 888 |             |
| [17] | Baseline (CP): 39.5    | Baseline (CP): 627      | ASTM D790 L/t = 25 |
|      | Nano-laminate at 0.3 wt%: 44.1 (P2), 42.8 (P3) | Nano-laminate at 0.3 wt%: 741 (P2), 682 (P3) |             |
| [22] | Baseline (CP): 2.4     | Baseline (CP): 92       | ASTM D790 L/t = 16 |
|      | Nano-laminate at 0.5 wt%: 3.3 | Nano-laminate at 0.5 wt%: 125 |             |
|      | Nano-laminate at 1 wt%: 2.9 | Nano-laminate at 1 wt%: 121 |             |
|      | Nano-laminate at 2 wt%: 2.7 | Nano-laminate at 2 wt%: 106 |             |
|      | Nano-laminate at 4 wt%: 2.4 | Nano-laminate at 4 wt%: 105 |             |

Note: * JIS denotes Japanese Industrial Standard.
findings are in accordance with those of the earlier tensile tests, they are interesting as the nano-laminates in bending should be more likely to fail on the compressive side of the beam surfaces. As a result, some degree of enhancement should have been exhibited, providing that the limited findings from the in-plane compression were reliable. Clearly, a further investigation of this aspect will be necessary in future in order to clear up this significant discrepancy. In [17], a 28% increase in flexural strength was reported.
3.4. **In-plane shear**

In-plane shear is part of the matrix-dominated mechanical behavior. Amazingly, there is only one investigation on the in-plane shear properties of nano-laminates [19] using 45° off-axis tension. Although three different diameters of the chemically functionalized CNTs were used in the carbon/epoxy host, neither the in-plane shear modulus nor in-plane shear strength of the nano-laminates was improved with the inclusion of 0.5 wt% CNTs, as shown in Figure 11 and Table 5. Clearly this aspect of nano-laminates will need to be investigated further.

3.5. **Interlaminar shear**

The investigation of ILS behavior has so far attracted the greatest attention with a total of eleven publications [2,3,5,6,8,9,12–14,16,19]. This is not surprising as the biggest impact of embedding CNTs in conventional composite laminates is expected to be in the area of the enhanced delamination resistance and toughness performance (see Section 3.6), as the latter two are matrix-dominated due to the lack of the reinforcement in the laminate thickness direction. In particular, all the investigations [3,5,6,8,9,12–14,16,19] but one [2] focused on ILS strength. Whereas the overwhelming majority of the investigations [3,5,6,8,9,12–14,16,19] followed the short beam shear (SBS) ASTM standard D2344 [38],

![Figure 11. In-plane shear strength results of nano-laminates with carbon/epoxy laminate host [19].](image)

| Ref. | In-plane shear modulus (GPa) | In-plane shear strength (MPa) | Test method               |
|------|------------------------------|------------------------------|---------------------------|
| [19] | Baseline (UD): 12            | Baseline (UD): 180           | 45° off-axis tension       |
|      | A: Nano-laminate at 0.5 wt%: 10.2 | A: Nano-laminate at 0.5 wt%: 175 |                           |
|      | B: Nano-laminate at 0.5 wt%: 10 | B: Nano-laminate at 0.5 wt%: 200 |                           |
|      | C: Nano-laminate at 0.5 wt%: 10.5 | C: Nano-laminate at 0.5 wt%:155 |                           |
the other test methods used are the Iosipescu shear ASTM standard D5379 [39] in [2], (direct) compression shear test (CST) [40] in [3] and unsymmetrical double-notch compression (DNC) ASTM standard D3846 [41] in [6]. Moreover, whereas the carbon/epoxy host laminates used a length-to-depth ratio of 4, as recommended by SBS, the E-glass fiber reinforced plastics (GFRP) (including matrix materials of epoxy, polyester and vinyl ester) adopted a length-to-depth ratio of 5, again as recommended. The lay-up of the host laminates was dominated by CP [2,3,8,9,12,14,16], with the remaining being UD [6,19], QI [13,16] and angle-ply (AP) [5], respectively. In addition, the majority [2,5,6,8,13,14,16] of the host laminates were only around 1 mm in thickness, except for those in [3,9,12,19]. All numerical results are given in Table 6 and some of ILS strength results are also presented graphically in Figures 12–17.

For the carbon/epoxy host laminates [2,6,8,12,19], all three testing standards, Iosipescu shear, DNC and SBS, were used for the nano-laminates. The ILS strength (ILSS) results of the nano-laminates (around 3.5 mm thick) associated with the Iosipescu shear method [2] do not exhibit any enhancement, as shown in Figure 12 and as might be expected, because premature failure could always occur at one of the notch roots. However, the ILS modulus of the same nano-laminates was increased by 87%. This lack of enhancement on the ILS strength was in accordance with the results in [19]. Nevertheless, the results of the nano-laminates tested by using the DNC [6] and SBS [8] methods in the same figure show 38% and 27% improvement, respectively, even though the corresponding amount of CNTs used is no more than 0.25 wt%. In particular, the nano-laminates in [8] were only 1.2 mm thick so that the set-up and execution of the individual tests could be very difficult with the much larger diameter loader. The ILS strength results of much thicker nano-laminates (around 6 mm thick) in Figure 13 [12] that were tested by the SBS method provide only very modest enhancement. In particular, they found that for the short CNT length of 1 μm the presence of 1 wt% CNTs (the maximum amount reported) had almost no effect on the ILS strength and the inclusion of dispersants with the same amount of CNTs increased the ILS strength by around 12%, which is modest. For the long CNT length of 10 μm, they found that the results of the nano-laminates without dispersants are the same as those with the short CNT length. Once dispersants were added, the same degree of enhancement (13%), similar to the case with the short CNT length, was obtained due likely to the improved dispersion and CNT-matrix interfacial bonding. This seems to suggest that the effect of the CNT length on the ILS strength of the nano-laminates was much less when compared to the effects of the uniformity of dispersion and interfacial bonding. As the baseline ILS strength values of these carbon/epoxy host laminates are very low to begin with, these results seem to suggest that the quality of the nano-laminates manufactured without consolidation pressure might have been poor.

For the GFRP host laminates [3,9,13,14,16], the majority of the nano-laminates (except for those in [3]) were tested using the SBS method. The ILS strength results of thin nano-laminates (around 1 mm thick) exhibit from no effect [14] to modest effect of 11% [13] and 20% [16], respectively, as shown in Figures 14 and 15, even though 12 wt% and 40 wt% CNTs were used in [14]. The researchers in [14] also examined several CNT characteristics and effectiveness of CNT functionalization. As shown in Figure 14 and in Table 6, they found that the ILS strengths of the nano-laminates with 3 wt% CNTs did not seem to be affected by either the CNT configurations such as being long thin (5–15 μm in length and 10–30 nm in diameter) and short thick (1–2 μm in length and 40–60 nm in diameter) or the surface treatment.

The ILS strength results of thick nano-laminates (over 4 mm in [3] and around 5.8 mm thick in [9]) shown in Figures 16 and 17 show substantial enhancement. In [3], an 18% increase in ILS strength was obtained with 1 wt% CNTs using the SBS method, whereas a
Table 6. Interlaminar shear mechanical properties of nano-laminates.

| Ref. | ILS modulus (GPa) | ILS strength (MPa) | Test method |
|------|-------------------|--------------------|-------------|
| [2]  | Baseline: 4.5     | Baseline (CP): 25.0| ASTM D5379 Iosipescu |
|      | Nano-laminate at 0.2 wt%: 8.4 | Nano-laminate at 0.2 wt%: 25.6 | |
| [3]  | Baseline (CP) for SBS: 32.5 | Nano-laminate at 0.5 wt%: 33.5 | ASTM D2344 SBS $L/t = 4$ and CST |
|      | Baseline (CP) for CST: 25.4 | Nano-laminate at 1 wt%: 38.4 | |
| [5]  | Baseline (AP): 20.1 | Nano-laminate at 0.5 wt%: 33.5 | ASTM D2344 SBS $L/t = 4$ |
| [6]  | Baseline (UD): 48.5 | Nano-laminate at 1 wt%: 38.4 | ASTM D3846 DNC |
| [8]  | Baseline (CP): 39 | Nano-laminate at 0.5 wt%: 66.8 | ASTM D2344 SBS $L/t = 4$ |
| [9]  | Baseline (CP): 30.7 | Nano-laminate at 0.25 wt%: 49 | ASTM D2344 SBS $L/t = 5$ |
|      | Nano-laminate at 0.5 wt% SWNT: 39.2 | Nano-laminate at 0.2 wt% SWNT: 33.3 | |
|      | Nano-laminate at 0.1 wt% F-SWNT: 29.2 | Nano-laminate at 0.1 wt% All-SWNT: 35.8 | |
| [12] | Baseline (CP): 57.3 | CNT length = 1 μm | ASTM D2344 SBS $L/t = 4$ |
|      |                        | Without dispersant: nano-laminate at 0.5 wt%: 63.6 | |
|      |                        | With dispersant: nano-laminate at 1 wt%: 60.7 | |
|      |                        | With dispersant: nano-laminate at 0.5 wt%: 65.9 | |
|      |                        | With dispersant: nano-laminate at 1 wt%: 64.2 | |
|      |                        | CNT length = 10 μm | |
|      |                        | Without dispersant: nano-laminate at 0.5 wt%: 63.6 | |
|      |                        | Without dispersant: nano-laminate at 1 wt%: 60.7 | |
|      |                        | With dispersant: nano-laminate at 0.5 wt%: 64.7 | |
|      |                        | With dispersant: nano-laminate at 1 wt%: 64.7 | |
| [13] | Baseline (QI): 25.7  | Nano-laminate at 0.1 wt% SWNT: 28.6 | ASTM D2344 SBS $L/t = 5$ |
| [14] | Baseline for A, B, C and E: 24.5 | A: Nano-laminate at 3 wt%: 24.7 | ASTM D2344 SBS $L/t = 5$ |
|      |                        | B: Nano-laminate at 3 wt%: 25.8 | |
|      |                        | C: Nano-laminate at 12 wt%: 21.2 | |
|      |                        | E: Nano-laminate at 3 wt%: 26.5 | |
|      |                        | D: Nano-laminate at 40 wt%: 18.9 | |

(Continued)
21% increase in ILS strength was obtained with the same amount of CNTs using the CST method. The researchers concluded that the CST method was more reliable than the SBS method due to more consistent failure modes observed in the failed specimens. In addition, the effect of the controlled orientation of CNTs on the ILS strength was found to be small. In addition, the effect of the controlled orientation of CNTs on the ILS strength was found to be small. In [9], the ILS strengths were found to be improved by 28% and 8% with very small amounts of pristine CNTs at 0.1 wt% and 0.2 wt%, respectively. The fact that doubling the amount of pristine CNT led to a significantly lesser enhancement of the ILS strength suggests that without surface functionalization the degree of dispersion and thus the interfacial bonding might have been limited. Indeed, the researchers found that the CNTs with various functional groups enhanced the ILS strengths of their respective nano-laminates, though by modest amounts (around 20% in three out of four cases). Again, no microscopic corroborative evidence was given.

Table 6. (Continued).

| Ref. | ILS modulus (GPa) | ILS strength (MPa) | Test method |
|------|-------------------|--------------------|-------------|
| [16] | Baseline (for QI): 31.8 |
|      | Nano-laminate at 0.1 wt%: 36.8 |
|      | Nano-laminate at 0.3 wt%: 38.1 |
| [19] | Baseline (UD): 66 |
|      | A: Nano-laminate at 0.5 wt%: 60 |
|      | B: Nano-laminate at 0.5 wt%: 52 |
|      | C: Nano-laminate at 0.5 wt%: 49 |
|      | D: Nano-laminates at 0.5 wt%: 70 |

Figure 12. ILS results of nano-laminates with carbon/epoxy laminate hosts with various lay-ups tested by various test methods [2,6,8].
With the alumina fiber/epoxy host [5], the ILS strength of its nano-laminates with a thickness of around 2.1 mm was found, using the SBS method, to be enhanced by 69% with 2 wt% CNTs. No microscopic corroborative evidence was given.
The SBS method [38] used by the majority of the researchers for the determination of ILS strength contains two well known limitations. One (most significant) is that there is no pure shear region within the gauge section of the test specimen so that delamination usually occurs at one of the two beam ends where the delamination resistance could be weakest due to the existence of the three-dimensional state of stress. As a result, the location of the...
occurrence of delamination should be described to justify the validity of the ILS strength. The other is that the applied central load often creates a high local stress concentration under the loader so that a potential bending failure is possible, especially considering that the majority [2,5,6,8,13,14,16] of the host laminates tested were only around 1 mm in thickness. The sufficient details of the failure characteristics of the tested specimens are commonly not available such that it is slightly uncertain that the reported ILS data were even valid.

3.6. Mode I fracture toughness

The majority of the nano-laminates [1,11,13,15,16,19,21,23] tested for mode I fracture toughness used the double cantilever beam (DCB) method, following the ASTM standard D5528 [42], whereas one [16] used the compact tension (CT) method, following the ASTM standard D5045 [43]. Their critical strain energy release rates ($G_{IC}$) were taken as the measure of the fracture toughness performance. All the nano-laminates had some kind of epoxy matrix [1,11,15,16,19,21,23] in the host laminates except for one which used polyester [13]. All numerical results of $G_{IC}$ for the nano-laminates are given in Table 7 and some of them are also presented graphically in Figures 18–20. The $G_{IC}$ results of the UD nano-laminates with two different lengths of CNTs from [1] exhibit very significant enhancement, as shown in Figure 18. For a CNT length of 60 μm, the average $G_{IC}$ was increased by 152% for 0.4 wt% CNTs. Interestingly, the further increase of both CNT length of up to 150 μm and amount of CNTs of up to 1 wt% resulted in only a 62% enhancement for the average $G_{IC}$. This seems to suggest that incorporating the larger amount of the longer CNTs into the host laminates might have led to the difficulty of maintaining the originally achieved uniformity of dispersion and the quality of interfacial bonding. Nevertheless, the micrographs of the fracture surfaces from the failed specimens seem to show some CNT bridging that corroborated with the enhancement. In [11,15], a 98% enhancement of $G_{IC}$ from the UD nano-laminates was reported with 5 wt% CNTs. In addition, the $G_{IC}$ values were found to increase

Figure 17. ILSS results of nano-laminates with E-glass/vinyl ester laminate host with CNTs with various functional groups [9].
further in some cases when either the additional CNT resin solution was sprinkled at the mid-plane interface during lamination or the additional resin film with 10 wt% CNT was inserted at the mid-plane interface, as shown in Figure 19. The researchers reported that the fracture surfaces of the failed nano-laminate specimens were rougher than those of the baseline laminates. Although the effect of CNT aspect ratio on $G_{Ic}$ was also investigated,

### Table 7. Mode I and mode II fracture toughness properties of nano-laminates.

| Ref. | Mode I $G_{Ic}$ (kJ/m$^2$) | Test method | Mode II $G_{IIc}$ (kJ/m$^2$) | Test method |
|------|-----------------------------|-------------|-----------------------------|-------------|
| [1]  | Baseline (A in UD): 0.21    | ASTM Baseline (B in UD): 0.35 | 4ENF | Nano-laminate C (60 μm) at 0.4 wt%: 0.53 | DCB |
|      | Baseline (B in UD): 0.21    | D5528 Nano-laminate D (120 μm) at 0.1 wt%: 1.1 | DCB | Nano-laminate E (150 μm) at 1 wt%: 0.34 |
| [7]  | Baseline (CP): 0.443        | ASTM – | – | Nano-laminate (with unknown wt%): 0.645 |
|      | Baseline (A in UD): 0.086   | ASTM Baseline (A in UD): 0.568 | – | B: Nano-laminate at 5 wt%: 0.17 |
|      | Baseline (B in UD): 0.17    | D5528 B: Nano-laminate at 5 wt%: 0.732 | – | C: Nano-laminate at 5 wt%: 0.148 |
| [11] | Baseline (QI): 0.613        | ASTM C: Nano-laminate at 5 wt%: 0.816 | ENF | D: Nano-laminate at 5 wt%: 0.227 |
|      | Nano-laminate at 0.1 wt%: 0.488 | D5528 D: Nano-laminate at 5 wt%: 1.753 | – | E: Nano-laminate at 5 wt%: 0.19 |
| [13] | Baseline (QI): 0.65         | ASTM E: Nano-laminate at 5 wt%: 1.091 | – | F: Nano-laminate at 5 wt%: 0.161 |
|      | Nano-laminate at 0.1 wt%: 0.488 | D5528 F: Nano-laminate at 5 wt%: 0.751 |
| [15] | Baseline (for UD): 0.09     | ASTM Baseline (for UD): 0.61 | ENF | Nano-laminate at 5 wt%: 0.17 |
|      | Baseline (A in UD): 0.086   | D5528 Baseline (A in UD): 0.568 | DCB | DCB |
| [16] | Baseline (QI): 0.65         | ASTM Baseline (QI): 0.68 | – | B: Nano-laminate at 0.1 wt%: 0.77 |
|      | Nano-laminate at 0.1 wt%: 0.77 | D5528 B: Nano-laminate at 0.1 wt%: 0.75 | ENF | Nano-laminate at 0.3 wt%: 0.92 |
| [19] | Baseline (UD): 0.38         | ASTM C: Nano-laminate at 0.5 wt%: 0.59 | – | D: Nano-laminates at 0.5 wt%: 0.70 |
|      | Baseline (UD with carbon fiber): | ASTM D: Nano-laminates at 0.5 wt%: 0.13 | – | A: Nano-laminate at 0.5 wt%: 0.45 |
|      | 0.53                        | D5528 Nano-laminate at 0.5 wt%: 0.48 | – | B: Nano-laminate at 0.5 wt%: 0.48 |
|      | Nano-laminate at 12 vol. %: 0.51 | D5528 Nano-laminate at 0.5 wt%: 0.59 | – | C: Nano-laminate at 0.5 wt%: 0.59 |
|      | Nano-laminate at 7 vol. %: 0.65 | DCB Nano-laminate at 0.5 wt%: 0.12 | ENF | D: Nano-laminate at 0.5 wt%: 0.50 |
|      | Nano-laminate at 9 vol. %: 0.50 | DCB Baseline (UD with nano fiber): | – | D: Nano-laminates at 0.5 wt%: 0.70 |
| [21] | Baseline (UD): 0.31         | ASTM Baseline (UD with carbon fiber): | 0.13 | Baseline (UD): 0.31 |
|      | Baseline (UD with carbon fiber): | ASTM Baseline (UD): 0.31 | Baseline (UD): 0.70 | Nano-laminate at 0.1 wt%: 0.30 |
|      | 0.53                        | D5528 Nano-laminate at 0.1 wt%: 0.30 | ENF | Nano-laminate at 0.5 wt%: 0.46 |
|      | Nano-laminate at 7 vol. %: 0.65 | DCB Nano-laminate at 0.5 wt%: 1.00 | – | Nano-laminate at 1 wt%: 0.53 |
|      | Nano-laminate at 9 vol. %: 0.50 | DCB Nano-laminate at 1 wt%: 0.95 | – | Baseline (UD): 0.31 |
there was no clear trend established to suggest that the larger aspect ratio provided the greater enhancement. The $G_{Ic}$ results of the QI nano-laminates still show the significant, but less, enhancement. However, nano-laminates with polyester matrix [13] show no enhancement on $G_{Ic}$ with 0.1 wt% CNTs. The researchers attributed this to the observation that the presence of the CNTs limited the development of CNT bridging. Nevertheless, the nano-

Figure 18. Mode I fracture toughness ($G_{Ic}$) results of nano-laminates with carbon/epoxy laminate host with two CNT lengths [1].

Figure 19. Mode I fracture toughness ($G_{Ic}$) results of nano-laminates with carbon/epoxy laminate hosts with various processing conditions [11,15].
laminates with epoxy matrix [16] in Figure 20 show a 42% enhancement of $G_{IC}$ value with 0.3 wt% CNTs. The similar findings were also reported in [19,21,23] for the UD carbon/epoxy nano-laminates. The very significant enhancement on $G_{IC}$ was attributed to CNT bridging and CNT pull-out. However, in [19], this was accompanied by the steady reduction of the ILS strengths associated, respectively, with MWNTs, thin MWNT and DWNTs (Figure 21).
Although the large deflection corrections were taken into account in the calculation of $G_{IC}$ in [13,16,19,23], some of the nano-laminates were much thinner than required by the ASTM standard D5528 in [39].

### 3.7. Mode II fracture toughness

Several mode II fracture toughness testing methods such as the end notch flexure (ENF) [44] and the four-point end notch flexure (4ENF) [45] have been developed for composite laminates over the years. Although the ENF method has been adopted in Europe and Japan as an official standard, it is yet to be adopted by ASTM in USA. In particular, the 4ENF with stable crack propagation seems to be regarded as an improved method over the ENF method. Again, in both methods, critical strain energy release rate ($G_{IIc}$) is taken as the measure of fracture toughness performance. The majority [1,11,15,21,23] of the nano-laminates used epoxy matrix in their host laminates except for one [13], which used polyester. All numerical results of $G_{IIc}$ for the nano-laminates are given in Table 7 and some of them are also presented graphically in Figures 22 and 23. The nano-laminates with the UD carbon/epoxy hosts [1,11,15,21,23] exhibit the very significant enhancement in their $G_{IIc}$ as partially shown in Fig. 22 with a 214%, 29%, 30%, 115% and 43% increase for 0.8 wt%, 5 wt%, 5 wt%, 11 wt% and 1 wt% CNTs, respectively. However, the $G_{IIc}$ results of both baseline laminates and nano-laminates in [1] were derived from the averages of two test data, respectively. In addition, the $G_{IIc}$ values in [11] were found to increase further when either the additional CNT resin solution was sprinkled at the mid-plane interface during lamination or the additional resin film with 10 wt% CNT was inserted at the mid-plane interface, as shown in Figure 23. The researchers reported that the fracture surfaces of the failed nano-laminate specimens were rougher than those of the baseline laminates. Although the effect of CNT aspect ratio on $G_{IIc}$ was also investigated, there was no clear trend established to suggest that the larger aspect ratio provided the greater enhancement. On the contrary, the nano-laminates with the QI E-glass/polyester host [13] do not seem to show any

![Figure 22](image-url)  
**Figure 22.** Mode II fracture toughness ($G_{IIc}$) results of nano-laminates with carbon/epoxy [1,23], E-glass/polyester [13] and E-glass/epoxy [15] laminate hosts.
enhancement (8%) in their $G_{IIc}$ shown in the same figure for 0.1 wt% CNTs. In addition to the fact that the amount of CNTs used in [13] was low, the thickness of the nano-laminates was also thin (< 2 mm). These conditions did not form an ideal combination of the testing setup for $G_{IIc}$. Nevertheless, the researchers attributed this to the presence of the large amount of ‘hackles’ on the fracture surface rather than CNT bridging.

4. Other significant mechanical performance of nano-laminates

Impact damage resistance and damage tolerance, including fatigue, are two important areas for advanced composite laminates. Although they are structural issues in general, these phenomena have been standardized over the years because of their significance in design and certification of composite aerospace structures. For impact damage resistance and damage tolerance, the performances are characterized, respectively, by relationships between impact energy and damage area and between CAI strength and either impact energy or damage area. Clearly, among all contributing factors, the size and through-the-thickness distribution of delaminations play a key role. The onset and propagation of delaminations are largely affected by the ILS strength and fracture toughness values of the composite laminates. For fatigue, the failure process always starts with matrix cracks and delamination.

These topics so far have received little attention. The only publication that investigated the CAI strength of the nano-laminates is from reference in [15]. With up to 10 wt% CNTs, the nano-laminates with the 24 ply QI carbon/epoxy host were subjected to 20 J impact and did not show any effect when compared to the performance of their baseline laminates in terms of impact damage area. As a result, their CAI strength was not improved. In [24], the doped MWNTs were used with E-glass fiber reinforced vinyl ester for ballistic protection and the improvement on $V_{50}$ (ballistic limit) was found to be very small.
In [25], a tension–tension fatigue of E-glass/epoxy nano-laminates with 1 wt% MWNTs was investigated at a stress ratio of 0.15 (30% of static strengths) at the frequency of 3 Hz. They found that the fatigue strength of the nano-laminates was increased by 60% up to 250%, depending on the levels of the peak alternating stresses.

5. Load transfer and enhancing mechanisms

The key to the success of embedding micron-scaled CNTs within the laminate host to enhance the mechanical performance of the host lies in a thorough understanding of physical enhancing mechanisms. Many factors that could affect the enhancing mechanisms include, among others, the uniformity of CNT dispersion; CNT orientation control, aspect ratio, weight fraction and surface functionalization; CNT–matrix interfacial bonding strengths; and ultimately the load transfer from the matrix of the laminate to individual CNTs. For some mechanical properties such as ILS and mode II critical strain energy release rate, the through-the-thickness location of CNT distribution could also be very important. In addition, the surface functionalization of CNTs improves their solubility in common solvents and thereby the uniformity of dispersion. As the experimental investigation of such enhancing mechanisms is extremely challenging due to the extremely small dimensions of the CNTs, theoretical and numerical investigations have so far provided the larger part of the published literature. Moreover, since this is, at this very moment, a very active area of intensive research, in which a good understanding of the enhancing mechanisms is still very much lacking, our overview below can serve only as a focal point of discussion.

Locally the transfer mechanism of the mechanical load from the matrix of the laminate to individual CNTs is largely dependent on CNT orientation and aspect ratio in addition to interfacial shear and tensile strengths, which could, in turn, depend on the functionalization of the CNTs to a substantial extent. To achieve generally the enhancement of the strength and modulus of the host laminate, such load transfer mechanism must be very efficient and the weight fraction of the properly processed and controlled CNTs must be sufficient especially in critically stressed regions of the host laminate such that the CNTs deform and even fracture at the same time as the matrix, if not before.

5.1. CNT functionalization, aspect ratio and CNT–matrix interfacial bonding

The CNT–matrix interfacial bonding in nanocomposites has so far appeared in the following forms: (non-bonded) van der Waals interaction; covalent functionalization [32–34,46,47]; non-covalent functionalization via molecular wrapping [12,48,49] or hydrogen bonding [50]; and the hybrid of the previous two [24,51]. Moreover, the sidewall surface of the CNTs possesses much greater area than the end area and thus is the primary bonding area with the surrounding matrix. However, the surface of the CNTs naturally is atomically smooth and non-reactive with the polymer matrices. Whereas the latter three forms of bonding are considered as chemical bonding, the van der Waals interaction with the matrix co-exists with micro mechanical interlocking formed through the shrinkage of matrix molecules during cure and this combination is conventionally considered as physical ‘bonding’. It has been used in about two thirds of the investigations [1–5,7,10–12,17,19,22] plus those in [52–55], though the weak van der Waals interaction offers a limited physical bonding between pristine CNTs and the matrix. Nevertheless, theoretical and numerical studies indicated that large aspect ratios of CNTs were needed for effective load transfer not only because of the larger bonding areas but also because of the fact that the greater interfacial tensile strength could be developed [56,57]. In particular, it was found that the load transfer efficiency could improve with the
increase of aspect ratio and there was an optimum aspect ratio of around 1000, not obvious in Table 1, beyond which the enhancement of the mechanical performance could be observed. In addition, many researchers managed to align the axis of the processed CNTs with the direction of the mechanical loads.

The chemical bonding has been considered to be able not only to provide much stronger CNT–polymer interface but also to improve the uniformity of dispersion, which in turn improves the load transfer mechanism [32–34,46,48–51]. The results of experimental [32–34,47,48,50,58,59], theoretical [56,60–63] and numerical molecular mechanics simulation [46,47,41,57,64–70] studies indicated that the chemically functionalized CNTs could improve the shear load transfer by a significant amount. The experimental work showed that the chemically functionalized SWNT [32,58] or MWNTs [59] bundles were broken under mechanical load rather than being slid or pulled out.

However, it is unclear whether or not the above findings on the load transfer mechanism, largely obtained from nanocomposites using SWNTs, are directly transferable to the nanolaminates, in which MWNTs were used on the overwhelming majority of occasions. In addition, the mechanical testing methods for nanocomposites are completely different from the standards used to evaluate nano-laminates. Nevertheless, the significant enhancements of incorporating the processed CNTs in the nano-laminates have been reported in not only the matrix-dominated properties such as ILS in Table 6 and fracture toughness in Table 7 but also in the reinforcement-dominated properties such as longitudinal tension in Table 2a, compression in Table 3 and flexure in Table 4. This range of enhancement does not seem to have any correlation with the variation of their respective aspect ratios, as seen in Table 1. Furthermore, the long CNTs could be very difficult to disperse, prone to bending within the nano-laminate, more difficult to control their orientation and thus may not necessarily facilitate the enhancement [1].

### 5.2. CNT weight fraction and orientation

The effect of continuously increasing a weight percentage of CNTs in the matrix of the laminate host on the level of enhancement may depend on the type of mechanical properties in terms of strength and modulus and the surface functionalization of the CNTs, in addition to the aforementioned factors. For the reinforcement-dominated mechanical properties such as tension, compression and flexure, the majority of the investigations [15,20,23] that did not have any enhancement on either the modulus or strength of their nano-laminates did not show any further improvement, as expected, when the amount of pristine CNTs was increased further. However, there were two cases [12,22] in which the original nano-laminates exhibited the substantial enhancement on both compressive [12] and flexural [22] strengths. With the significant further increase of pristine CNTs, the original enhancement then became much less. The reason for this could be that the addition of those extra CNTs may have reduced the uniformity of dispersion and thus degraded the quality of the interfacial bonding. Nevertheless, a small degree of uncertainty over the reliability of the results exists as for why the reinforcement-dominated mechanical properties should be this sensitive, to such a substantial extent, to the addition of the CNTs in the matrix of the host laminate. This uncertainty seems to be reinforced as the further increase of the functionalized CNTs in the matrix of the host laminates has not improved the stiffness of the nano-laminates [6,19]. Although there was further report on the enhanced flexural modulus [18], on the contrary, there were two reported cases [6,19] in which their tensile and flexural strengths of the nano-laminates decreased with the further increase of the functionalized CNTs.
For the matrix-dominated mechanical properties such as transverse tension of UD nano-laminates, in-plane shear and ILS, there is generally very little information on their respective variations with different weight percentages of CNTs. Whereas there was just one investigation on transverse tension [10], there were four on ILS strength [3,9,12,16]. Between pristine [3,9,12] and functionalized [12,16] CNTs, the further increase of their respective weight percentages had the similar enhancing effect on the ILS strength of the nano-laminates.

To all the matrix-dominated mechanical properties, especially ILS, mode I and mode II fracture toughness, transverse tension of UD nano-laminates, the orientation of the CNTs should be very important to the level of the enhancement. Whereas the CNTs in the mode I and transverse tension test pieces were generally needed to be in the loading direction, those in the ILS and mode II test pieces should be perpendicular to the shearing action in order for them to act as barriers. The fact that there was little enhancement in the transverse tension of the UD nano-laminates [10,16,19] suggests that the orientation of the CNTs might have been aligned up with the reinforcements, which was perpendicular to the loading direction.

Among the three techniques used to introduce CNTs into the laminate host as discussed in Section 2.3, the doping technique, albeit being the most popular and versatile, has the least control over the orientation of the CNTs. Although the \textit{in situ} growth technique could control the direction of the orientation of the CNTs, the risk of damaging and contaminating the reinforcement when exposed to the furnace environment of the CVD process is high for the eventual lamination of the nano-laminate. The transplanting or insertion technique could also control the orientation of the CNTs. At present, this technique seems to be more compatible with the established mainstream manufacturing techniques for conventional composite laminates. However, there was no reported study for the effect of different orientations of CNTs on the matrix-dominated mechanical properties.

6. Closing remarks

Embedding CNTs in load-bearing composite laminates is an emerging field and has been proven to have tremendous potential in enhancing the mechanical performance of the composite laminates. A key driver in the development of the nano-laminates at present has been the ability not only to control a uniform distribution and dispersion of the CNTs and maintain their orientations within the laminate hosts but also to ensure that the CNTs are well bonded with the matrix of the host laminates so that the load transfer mechanism is effective. As our ability to control these processes and our understanding of the enhancing mechanisms at the microscopic scale improve, there will be greater fulfilment to realize the potential of the enhanced mechanical performance of the nano-laminates.

As this state-of-the-art review indicates, the selective and uniform production of CNTs with specific dimensions and physical properties has yet to be achieved on a consistent basis. Moreover, the processing details of CNTs varied very significantly among different researchers so that the processed CNTs shared few common characteristics. It is not yet completely clear what the key parameters are for characterizing the mechanical performance of nano-laminates since a significant number of the publications presented an incomplete description of essential information. Much of the discrepancy in the published results could be attributed to the non-uniformity of the nano-laminate test specimens used. Moreover, more research efforts seem to be focused on the mechanical properties in tension, ILS and fracture toughness. There were only two reports on in-plane compression and there was the only one on in-plane shear, which is part of the matrix-dominated mechanical behavior. As
expected, there was little enhancement found in the reinforcement-dominated mechanical properties such as tension and flexure. Further investigations will be required for the in-plane compression properties, though their primary deformation mechanisms are known to be shear-related. For the matrix-dominated mechanical properties such as transverse tension, in-plane shear, ILS strength and mode I and mode II fracture toughness, the significant enhancement, albeit with substantially varying degrees, has been reported for ILS strength and mode I and mode II fracture toughness. At the same time, the lack of consistent characterization in those properties was also visible. On some occasions, the results were noticeably contradictory to one another. There is little established understanding over the enhancing mechanisms in nano-laminates.

Throughout the review, several key challenges have been identified and will be crucial to fulfil the potential of future nano-laminates.

1. A greater degree of orientation control for CNTs will be essential, as there is little control at present in most fabrication processes of the nano-laminates except for some cases associated with the transplanting technique.

2. Further scrutiny of the suitability of mechanical testing methods/standards for some of mechanical properties such as ILS strength will be required. As a state of pure shear does not exist in the gauge section of the beam specimen in the SBS method and thus ILS failure often occurs at one of the beam ends, it is a bit of a mystery why such significant enhancement as reported in the most publications should occur.

3. A stronger emphasis must be put on the link between the local load transfer from the matrix to the CNTs and the global stiffening and strengthening as this is crucial for providing physical insights into the understanding of enhancing mechanisms in the mechanical performance of the nano-laminates.

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