

Review

Improvement of the Impact Properties of Composite Laminates by Means of Nano-Modification of the Matrix—A Review

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Abstract: This paper reviews recent works on the application of nanofibers and nanoparticle reinforcements to enhance the interlaminar fracture toughness, to reduce the impact induced damage and to improve the compression after impact performance of fiber reinforced composites with brittle thermosetting resins. The nanofibers have been mainly used as mats embedded between plies of laminated composites, whereas the nanoparticles have been used in 0D, 1D, 2D, and 3D dimensional patterns to reinforce the matrix and consequently the composite. The reinforcement mechanisms are presented, and a comparison is done between the different papers in the literature. This review shows that in order to have an efficient reinforcement effect, careful consideration is required in the manufacturing, materials selection and reinforcement content and percentage. The selection of the right parameters can provide a tough and impact resistant composite with cost effective reinforcements.

Keywords: matrix nanomodification; nanofibers; nanoparticles; composites; impact loading; delamination

1. Introduction

The usage of composite laminates has become more widespread and attracted the interest of many industries such as marine, automobile and aerospace. The higher strength-to-weight ratio in comparison with metallic alloys helps to reduce the weight of the automobile or of the aircraft, consequently improving the fuel efficiency. The usage of composite laminates can decrease the number of parts in a structure and they may have a longer life cycle compared with metallic components, which reduces the maintenance and replacement costs.

Currently, the most widely used composite materials are made of thermoset resins, such as epoxy, phenolic and polyester, which demonstrate great mechanical and good thermal properties. Despite these valuable properties, due to their low toughness, they tend to be weak, particularly in the transversal direction when subjected to impact loading [1]. The use of thermoplastic-based laminates can decrease this drawback significantly [2] as their toughness is much higher than thermoset polymers. However, the manufacturing cost is higher for thermoplastic composites and they provide lower stiffness, compared with the reinforced thermosets.

Fiber-reinforced composites are notch sensitive and lose much of their structural integrity when damaged. Damage can be caused during service and may be introduced by machining of fastener's

holes, stress concentrations near designed cutouts, or accidentally dropping tools on the composites. In-service damage of composite airframes may also result from impact by runway debris, hailstones, bird strike, ground service vehicles, ballistics, etc. In many instances, the damage caused by such impacts may be invisible or barely visible on the surface but can significantly reduce the strength of the composite component. Such damage can cause significant reduction in the compression after impact (CAI) strength, which is a typical measure of the damage tolerance of fiber-reinforced composites. Many factors determine the damage resistance and damage tolerance of fiber-reinforced composites. Among these factors, mechanical properties of fiber and matrix, interface/interphase properties and fiber configurations play important roles in determining impact damage resistance and damage tolerance of composites [3].

Up to now, various methods have been suggested to improve the interlaminar strength and the impact resistance of composite laminates. Some of these strategies are: Z-pinning [4], tufting [5], 3D weaving [6], stitching [7] and matrix toughening [8,9]. The last of these methods has attracted the researchers' attention as the others can significantly decrease the in-plane mechanical properties [10,11]. Matrix toughening can be done by adding micro- or nano-sized fillers into the matrix or by interleaving film, fibers, or particles between the composite layers. In this review paper, the focus will be on the behavior of toughened composite laminates under impact loading using nano fillers (in the form of particle or fiber).

A search on Scopus made using the keywords: Nano, impact, composite laminate, shows that at least 144 papers have been published in this field (Figure 1). As seen in this figure, about 70% of the papers have been published after 2012.

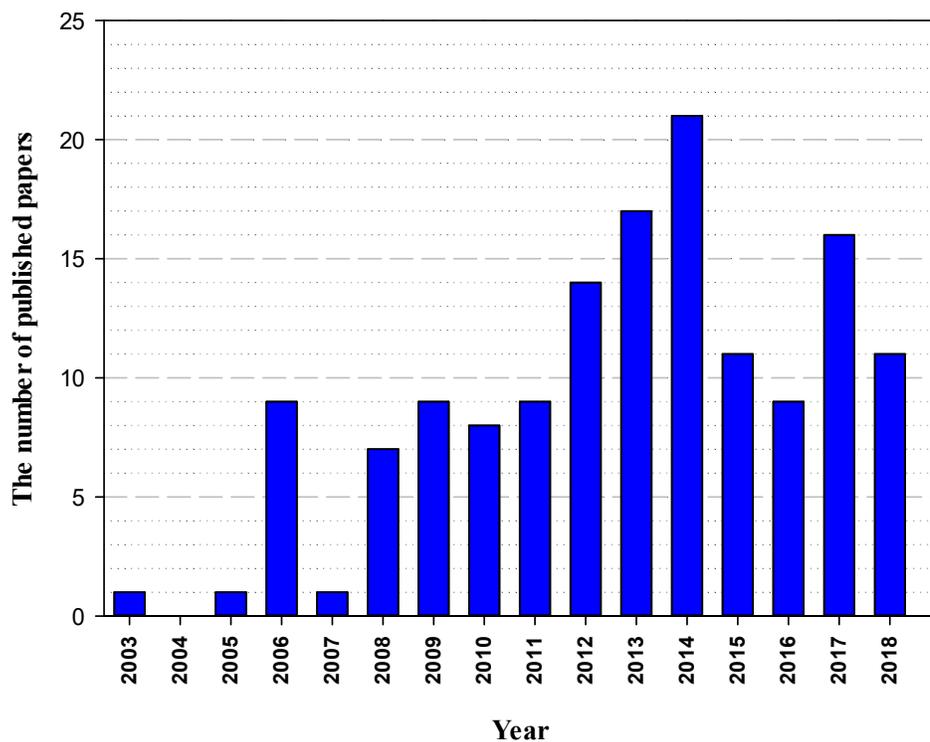


Figure 1. Indexed papers in Scopus (12 September 2018) using the keywords: nano, impact and composite laminate.

This review study is divided into two main parts. In the first part, the effect of different nanofibers types, such as Nylon66 (NY66), carbon, and Polycaprolactone (PCL) on impact response of laminated composites are presented. The effectiveness of each type of nanofiber and their toughening mechanism are also considered. In the second part, laminates toughened by

nanoparticles, such as carbon nanotubes and nano-clay, are reviewed. It is shown that some geometrical factors such as nanofibrous mat thickness and impact energies affect the efficiency of the toughening mechanism. The nanoparticles considered may have 0D, 1D, 2D, and 3D dimensional reinforcing patterns.

2. Composite Laminates Toughened by Polymeric Nanofibers

One of the most promising methods for producing nanofibers is electrospinning which uses electrical field to produce polymer fibers with diameters ranging from nanometers to micrometers. The polymers for electrospinning applications can be used in solved or melted forms, however, the solved form is more common. Generally, an electrospinning machine consists of three main parts: 1—a high voltage power supply, 2—a feeding system like injection pumps, and 3—a collector plate or a cylinder. Figure 2 shows an electrospinning machine made by SPINBOW company (Italy). Various factors affect the quality and final configuration of produced nanofibers including: solvent type, applied voltage, feed rate, distance between the needle tip and the collector, polymer concentration in the solvent, environmental temperature, humidity and etc. The identification of the best factors is very important for conducting a fast and optimized process. For instance, there are different solvent systems for producing Nylon 66 such as pure Formic Acid (FA) [12], mixture of FA/Chloroform [13–15] and mixture of FA/Trifluoroethanol (TFE) [16–19]. The use of the first two solvents results in a very slow electrospinning process (about 0.2–0.3 mL/h), while the third one allows a very fast process with about 0.8–1.2 mL/h [16,20].

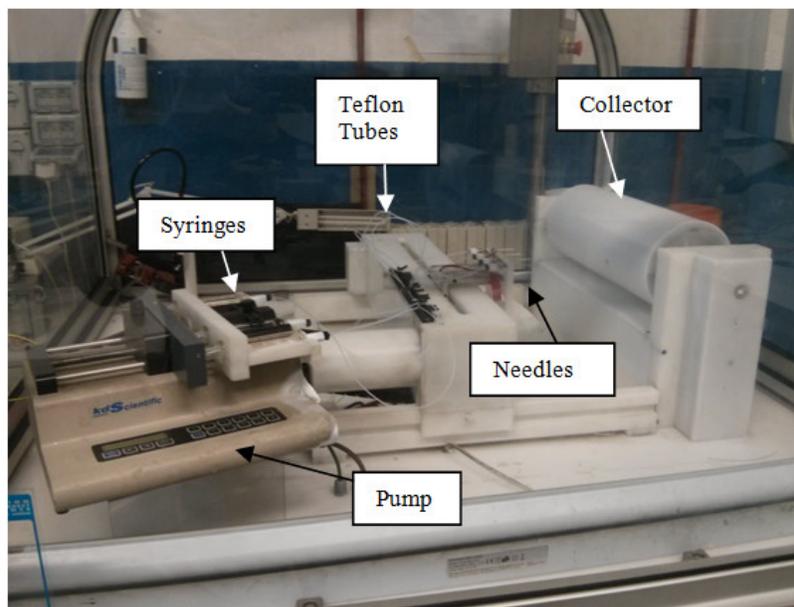


Figure 2. Electrospinning machine [21].

Up to now, 34 papers have been published regarding the effect of nanofibers on impact response of composite laminates. According to Table 1, different types of Nylon (NY) nanofibers have attracted researchers' attention more than other nanofibers (with 15 published papers). Shivakumar and his research group [22–26] applied Nylon 66 nanofibers between carbon/epoxy laminates to study their behavior under low-velocity impact loading. In the first paper [22], the diameter of the nanofibers was 65–120 nm and areal density of its mat was 0.7 g/m². The composite laminates consisted of 24 layers with stacking sequence of [−45/90/45/0]_{3s}. All composite layers were interleaved by nanofibrous mats. In addition, a layer of nanofabric was placed on the top and bottom surfaces of the laminate. The results showed that nanofibers could decrease the delaminated area significantly at lower impact energy levels, but at higher impact energies they found the opposite phenomenon. They also introduced the concept of “critical force” which corresponds to the damage initiation in the

laminates during impact. The application of nanofibers improved the critical force from an average of 4.5 to 4.7 kN, representing a 4.4% improvement. CAI tests were also conducted on impacted laminates which showed a compression strength improved by 10% in the nanomodified laminates. A similar study was conducted in [24] in which the areal density of nanofibers was 1.6–2 g/m², whereas the impact energies considered were in the range 0.46–1.8 J. The results showed that the presence of nanofibers decreased the delaminated area considerably. The authors also proved that nanofibers increased the critical force by about 60%, it reduced the rate of impact damage growth with impact height to one-half, and reduced the impact damage from 0.115 to 0.105 mm²/N. In [24,25], Shivakumar et al. used the data published in reference [24] and compared the results with commercial T800H/3900-2 composites interleaved by Polyamide particles. The results showed that the improvements obtained by applying the nanofibers were comparable to that of the commercial T800H/3900-2 composites, but with no thickness increase penalty, no loss of in-plane properties and no multiple glass transition temperatures. Ahmed and Shivakumar [26] considered the influence of the areal density of nanofibrous mat (0.5, 1.5, and 2.5 g/m²) on impact response of carbon/epoxy laminates. By applying the thickest mat, total thickness of the laminates increased by 2.5%. On the other hand, interleaving the laminates improved the critical force by 8% (using the 0.5 g/m² mat), 42% (using the 1.5 g/m² mat), and 45% (using the 2.5 g/m² mat). In addition, damage growth rates decreased by 12, 32, and 48%, respectively. The University of Bologna research group published three papers regarding the impact response of carbon/epoxy and GLARE fiber/metal laminates interleaved by NY66 [27–29]. In the first study [27], two different nanomodified configurations were investigated (Figure 3) and their responses were compared with virgin specimens. Before and after low velocity impact tests, the stiffness, the harmonic frequencies and damping of all samples were examined to consider the effect of nanofibers on these properties. Scanning electron (SEM) and optical microscopes were also used to evaluate the toughening mechanism and damages occurred during the impact. The results of the tests on non-damaged samples proved that the stiffness and the first harmonic frequency of nanomodified samples were 10% lower, but the damping ratio was 160% higher than the non-modified ones. On the other hand, the post-impact analysis of non-modified samples showed a decrease in the stiffness and harmonic frequencies, proportional to the impact energy level. Modified samples presented unexpected effects: Both the stiffness and the first harmonic frequency increased up to 14% and 12%, respectively, after 6 J impact. The outcomes also showed that Nano1 configuration (Figure 3) had better damping factor than the virgin and Nano configuration before impact test, but all these three samples had the same damping effect after impact energies of 6 and 12 J. The SEM pictures also illustrate the toughening mechanism occurred in the NY66-modified laminates. As the curing temperature of laminates is normally less than NY66 melting point, so the nanofibers were available with their initial configuration (Figure 4). Therefore, the nanofibers could make bridge between composite layers and stop the crack from propagation. In the second study, the research group focused, for the first time, on toughening fiber/metal laminates (GLARE) using NY66. No nanofibers were put between glass/epoxy layers and only two nanofibrous mats were applied between aluminum (AL) layers and composite laminate. The results showed that nanofibers could increase the adhesion strength between AL and laminate, which led to a decrease of the damaged area between 42% and 62% depending on the impact energy level (Figure 5). Anand et al. [30] used a new method for producing nanomodified laminates. In this method, the nanofibers were firstly electrospun on dry glass fibers, then cast resin film was transferred to them. The method is called RFI and more details about it can be found in [31]. They conducted impact and CAI tests, but only the results of the second test were reported. According to the outcomes, with an enhancement in the areal density of nanofibers, an increase in the residual compressive strength was obtained; for instance, about 20% increase was achieved by applying 0.4 g/m² of nanofibers. Daelemans et al. [32,33] used NY6 and 6.9 for considering their areal density on impact response (14, 28, 41, 54, 67, 79 J) of glass/epoxy laminates. The results proved that areal density did not have significant effect on impact parameters and their efficiency on damaged area was almost similar. In the lower impact energies, the modified and non-modified laminates had the same delaminated area, but nanofibers could decrease it up to 25% in higher impact energy levels. According to SEM pictures,

the toughening mechanisms of NY 6 and 6.9 is also like NY 6.6 and could increase the strength of laminate against the delamination by “Bridging” phenomena.

In addition to the experimental studies, a limited number of papers investigated the impact response of nanomodified laminates using finite element method (FEM) [18,19,34]. Giuliese et al. [34] used cohesive elements between composite layers and the effect of nanofiber configuration on delaminated area was considered. Yademellat et al. [18] conducted the first numerical and experimental studies on the virgin and NY 66-modified laminates. For the first step, cohesive parameters (K^0 , σ_{max} , and G) were obtained by conducting mode-I and mode-II fracture tests on both samples, and then by simulating them in ABAQUS commercial software. In the next step, by applying “cohesive surface” technique and introducing cohesive parameters of the reference and modified samples, the delaminated area was determined in low-velocity impact tests. By comparing the numerical and experimental results they showed that the difference was only 0.6% [18], and that the nanofibers could decrease the delaminated area by 34%. Therefore, it was shown that only by conducting fracture tests and knowing the mechanical properties of laminates, it is possible to anticipate the behavior of nanomodified laminates by FEM technique. In another study, Saghafi et al. [19] used the same numerical method to find the best interleave sequence of nanofibers mats between composite layers. Of course, the application of nanofibrous mats between all layers would be the best way to decrease the damage during impact, but since producing and manufacturing nanofibers is expensive and time consuming, it was suggested to put nanofibrous mats in one half of the composite layers’ interfaces. In this situation, various strategies were possible: Putting nanofibers between 1—the upper layers (near impact point), 2—the back layers, 3—the mid-layers and etc. (Figure 6). According to the results, interleaving between the mid-layers (G or H configuration) was the best position.

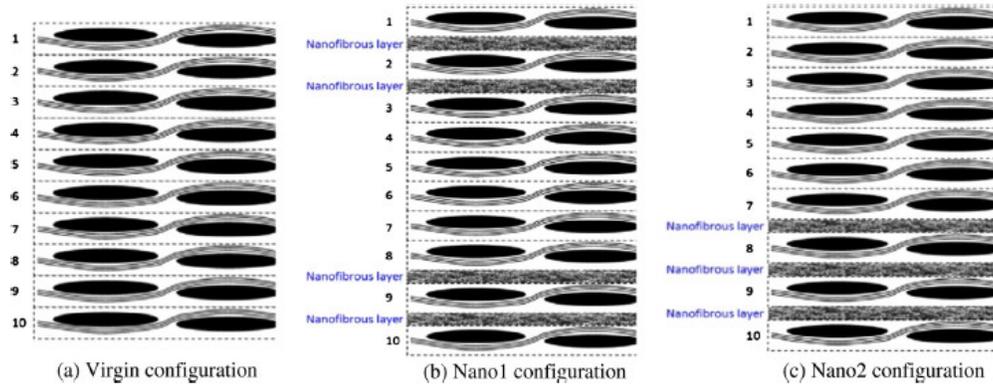


Figure 3. Two different configurations for interleaving carbon/epoxy laminates [27].

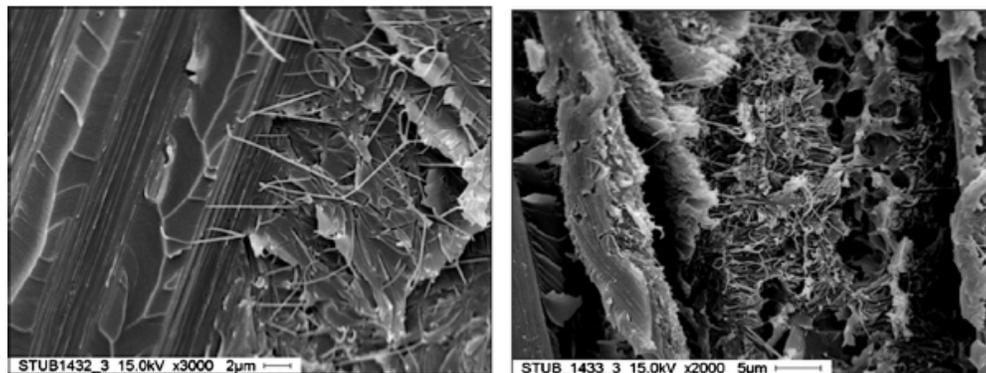


Figure 4. Toughening mechanism by NY66 [27].

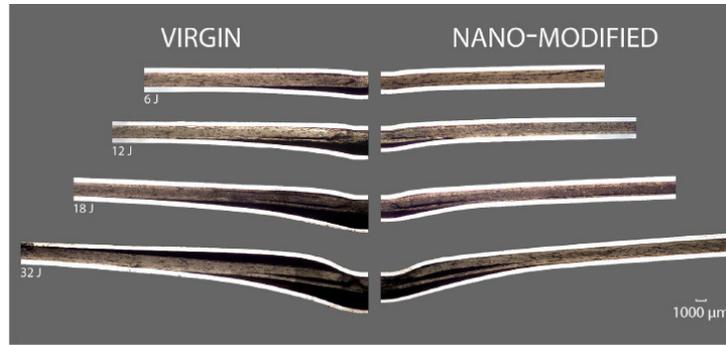


Figure 5. The effect of nanofibers on decreasing damage in GLARE [29].

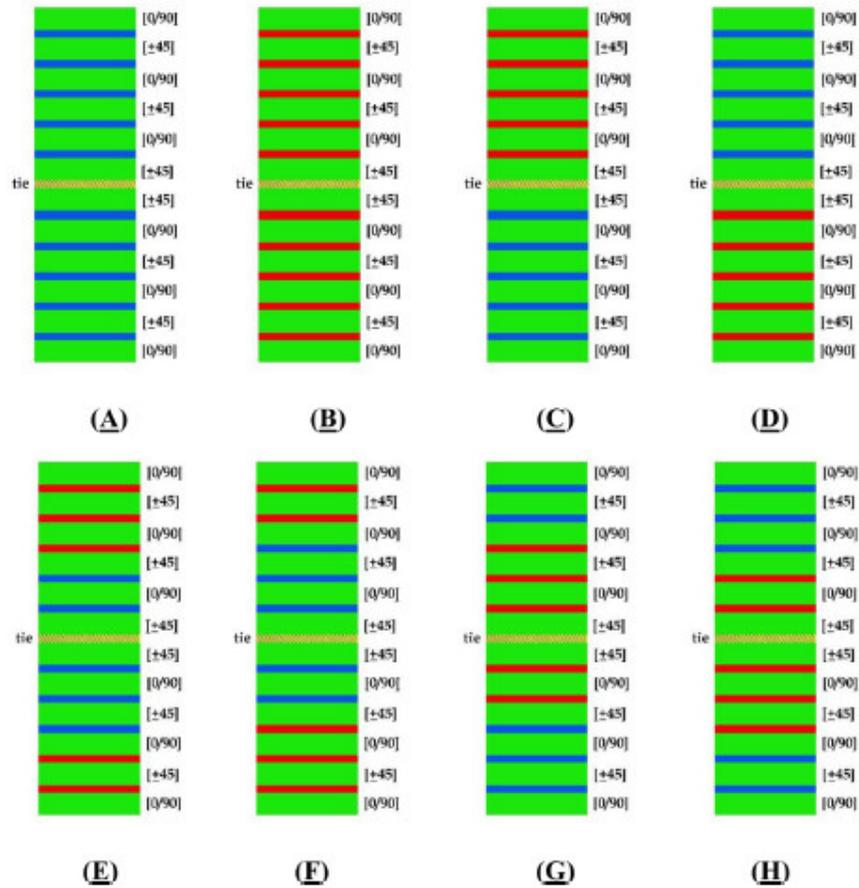


Figure 6. Different interleaved sequences used for considering their effect on delaminated area (blue areas belong to reference layer and red areas belong to nano-modified layer) [19].

Table 1. Published paper regarding the influence of nanofibers on impact response of composite laminates.

Ref.	Polymer	Composite Type	Impact Energy	Stacking Sequence	Curing Temperature
[22,23]	NY66 (0.7 g/m ²)	Carbon/epoxy (AS4/3501-6 prepreg)	2.87 J to 13.3 J	(-45/90/45/0) _{3s}	177 °C
[24]	NY66 (1.6–2 g/m ²)	Carbon/epoxy (AS4/3501-6 prepreg)	0.46 J to 1.80 J	[0/45/90/-45] _{2s}	177 °C
[24,25]	NY66 (1.6–2 g/m ²)	Carbon/epoxy (AS4/3501-6 and T800H/3900-2 prepreg)	0.46 J to 0.8 J	[0/45/90/-45] _{2s}	177 °C
[26]	NY66 (0.5, 1.5, 2.5 g/m ²)	Carbon/epoxy (AS4/3501-6)	-	-	177 °C
[27,28]	NY66 (25 µm)	Carbon/epoxy (Woven)	3, 6, 12 J	[0] ₁₀	130 °C
[29]	NY66 (40 µm)	Glass Laminate Aluminum Reinforced Epoxy (GLARE)	6, 12, 18 and 32 J	AL+[0/90] _s +AL	120 °C
[30]	NY66 (0.1, 0.2, 0.4 g/m ²)	Glass/epoxy (Bidirectional)	35 J	-	-
[32]	NY6, PCL (6 g/m ²)	Glass/epoxy (Unidirectional)	67 J	[0/90] _{2s}	24 °C (24 h)+ 80 °C (15 h)
[33]	NY6, NY69, PCL (6 and 12 g/m ²)	Glass/epoxy (Unidirectional)	14, 28, 41, 54, 67, 79 J	[0/90] _{2s}	24 °C (24 h)+ 80 °C (15 h)
[34]	NY66	Carbon/epoxy (Unidirectional)	2.1 J	[0 ³ /90 ⁶ /0 ³]	-
[18]	NY66	Glass/epoxy (Unidirectional)	30 J	[0/90] ₅	120 °C
[19]	NY66	Carbon/epoxy (plain woven)	40.5 J	[[0/90]/(+45/_45)/(0/90) /(+45/_45)/(0/90)/(+45/_45)] _s	24 °C (24 h)+ 80 °C (5 h)
[35]	PCL	Glass/epoxy (Unidirectional)	24 and 36 J	[0/90/0/90] _s	150 °C (1 h)
[36]	Carbon	biaxial braided carbon fiber/epoxy	-	-	Room Temp. (24 h)+ 100 °C (1 h)
[37]	Carbon (1.2% vol. and 1.5% vol.)	Carbon/epoxy (twill woven)	2.17, 4.34, 6.52, 8.69 J	[0/90] ₁₈	80 °C (4 h) 120 °C (2 h)
[38]	Carbon (10, 20, 30 g/m ²)	Carbon/epoxy (Unidirectional)	2.17, 4.34, 6.52 and 8.9	[0 ² /90 ⁴ /0 ²] _s [0 ² /90 ² /0 ² /90 ²] _s [0 ² /45 ² /90 ² /-45 ²] _s	-

[39]	Carbon	Glass/Polyester	-	-	Room Temp. (12 h)+ 55 °C (1.5 h) +70 °C (1.5 h)
[40]	Carbon	Carbon/epoxy (Prepreg)	10, 20 and 30	[0] ₁₆	80 °C (0.5 h) +120 °C (2.5 h)
[41–43]	TEOS (8 g/m ²)	Glass/epoxy (Woven)	7, 15, 23, 31, 39	[0] ₁₀	120 °C (2 h)
[44]	Epoxy 609 (E-03 609) and SiC	-	-	-	-
[45]	Polyvinylidene fluoride (PVDF) 39 and 64 μm	Glass/epoxy (Unidirectional)	5 J	[0/90/0/90] _s	130 °C (1 h)
[46]	Styrene Acrylonitrile (SAN) (1 g/m ²)	carbon fiber/epoxy (unidirectional)	Izod impact	[0] ₆	Room Temp. (18 h)+ 60 °C (0.5 h)
[47]	polyvinyl alcohol (PVA) (7.1 g/m ²)	carbon fiber/epoxy (unidirectional)	Charpy-impact	[0] ₄	Room Temp. + 80 °C (12 h)
[48]	polyacrylonitrile (PAN)	carbon fiber/epoxy (unidirectional and woven)	1-Charpy test (2 J) 2-drop-weight impact test (0.6 J)	Woven: [0/90] ₄ Unidirectional: [0] ₃ , [0] ₆	25 °C (6 h) +60 °C (4 h)

PCL nanofibrous mat is another possible choice for toughening composite laminates and three papers were published in this field. Daelemans et al. [32,33] used PCL nanofibers and compared their effectiveness with PA6 and PA6.9. Their results showed that PCL could decrease the delaminated area of about 50% which is significantly better than the other two nanofibers. This was due to the low adhesion between the PA6 and PA6.9 nanofibers and the epoxy matrix causing debonding of the nanofibers. On the contrary, PCL nanofibers do have a good adhesion with the epoxy matrix resulting in much better load transfer to the nanofibers. A very important point regarding toughening by PCL is that the melting point of this polymer is about 60 °C. Therefore, if the curing process temperature is lower than this critical temperature, the nanofibers will be present between the composite layers and the toughening mechanisms will be similar to the one of NY, i.e., bridging between the layers. On the other hand, if the curing temperature is higher than the melting point, a heterogeneous morphology can be observed in which spherical particles of PCL are uniformly dispersed in the continuous matrix (phase separation) [49] (Figure 7). In Daelemans's study, the maximum curing temperature (80 °C) was higher than the melting point, but toughening mechanism was "Bridging". This was due to the fact that after the first curing stage, the epoxy resin had already reacted to such extent that complete dissolution of the PCL was prevented during the second curing stage. In the third study, Saghafi et al. [50] cured the PCL-modified laminates at 150 °C. Therefore, phase separation was the toughening mechanism. Their results showed about 25% improvement, which is less than Daelemans's outcomes. Therefore, it can be concluded that the bridging mechanism is more powerful than the other mechanisms in toughening composite laminates.

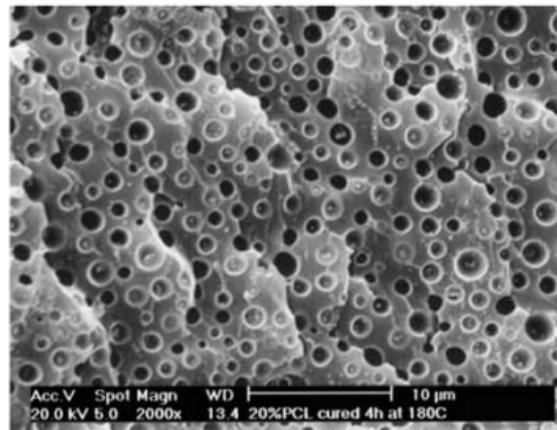


Figure 7. Phase separation in PCL/epoxy blend [49].

The effect of adding carbon nanofibers (CNF) on impact response of laminates was considered in eight papers [37–40,51,52]. In almost all these studies, the vapor grown carbon fiber (VGCF) method was used for the production of the nanofibers. The diameter was between 20 to 150 nm and length of the nanofiber was 10–200 μm and the nanofibers were mixed with the resin before manufacturing the composite sample. Parimala and Jabarajb [36] used various percentages of CNF (0.2, 0.5, and 1%) in biaxial carbon braided composites and conducted Izod impact test. CNF were in the form of nanoparticles and mixed with epoxy before producing the laminate by hand layup technique. Because of the brittle nature of the carbon fiber, the impact strength slowly increased with the increase of percentage of CNF (0.2% and 0.5%) and decreased for higher percentage of CNF (1%). Arai et al. [37] conducted almost the same study and considered the influence of volume fraction (1.2 vol % and 2.5 vol %) of CNF on absorbed energy, damaged area, CAI elastic modulus, and CAI strength. The results showed that the damaged area decreased significantly (about 50%) and CAI strength increased about 1.5 times by the addition of CNF. The same group [38] comprehensively studied this topic with different stacking sequences of laminates and various fractions of CNF (Table 1). The interesting point about this research is that CNF was interleaved between prepreg layers (not mixed with epoxy before manufacturing the samples). The most important results highlighted the

fact that CNF could decrease the delaminated area up to 90% percent and their effect were significantly better at higher impact energies. Monto et al. [39] investigated electro-mechanical characterization of CNF-modified laminates and showed that a variation in the electrical resistance of the laminate took place in correspondence with the impact induced damage. The impact tests were conducted several times and each time electrical resistance increased as function of the increase of the damaged area. The important point is that by raising the fraction of CNT from 0.5% to 1%, the authors obtained a decrease of the electrical resistance. Oxidized carbon nanofibers (O-CNF) were also applied by Rahman et al. [40] for toughening CFRP prepreg. One important point which was not considered by others is the toughening mechanism by CNF. Bridging between epoxy matrix and O-CNFs, and thus, a better adhesion between them was observed due to crosslink interaction as found by FESEM investigation of composites (Figure 8). The results showed that the damage area decreased with the incorporation of O-CNFs at all the impact energy levels (10, 20, and 30 J) and a maximum reduction of 68% in the damage area was obtained at 20 J.

Kelkar and his research group [41–43] proved that the Tetra Ethyl Orthosilicate (TEOS) chemically engineered glass nanofibers are not suitable choices for toughening laminates. Drop-weight impact tests showed that the modified laminates had about 9% larger damaged area in comparison with the unmodified ones [41]. In the second step, they used numerical modeling (by means of LSDYNA) and compared the outcomes with the experiments [42]. There was good agreement between them in lower impact energies while the simulated impact loads were smaller than the experimental impact loads which resulted in a smaller bending stiffness and a weaker laminate in higher impact energies. Finally, CAI test results were reported in reference [43]. As it is expected, compressive residual strength was decreased significantly in nanomodified laminate, for instance, a 50% reduction occurred in the specimens impacted by the higher energies.

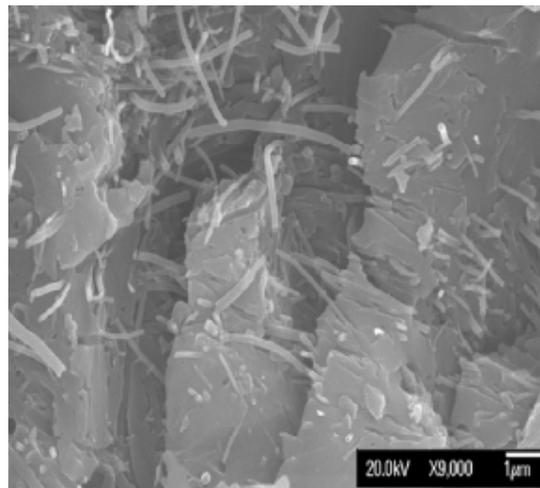


Figure 8. FESEM micrographs of fracture surfaces in 1.0 wt % O-CNFs incorporated composites showing nanofibers impregnation and bridging with epoxy [40].

There are some other types of nanofibers, such as epoxy 609 [44], Polyvinylidene fluoride (PVDF) [45], Styrene-acrylonitrile (SAN) [46], Polyvinyl alcohol (PVA) [47], Polyacrylonitrile (PAN) [48], that were reported only in one paper each. Liu et al. [44] utilized co-axial epoxy 609 and SiC nanofibers for increasing impact strength of composite laminates. Lateral impact tests were conducted, and the outcomes showed that the mechanical performances of the composite laminates do not change remarkably when the interfacial nanofibrous membranes have a proper thickness and a suitable content of SiC. PVDF nanofibers were the second choice for toughening the laminates, but according to the results it was not successful enough and could decrease the absorbed energy about 13%. As the melting point of PVDF is about 170 °C and curing temperature is 130 °C, the bridging between the composite layers is the main mechanism of toughening, similar to PA66. It is worth mentioning that recently it was proved by Saghafi et al. [21,50] that a curing temperature higher than the melting

point can increase the fracture toughness significantly. Therefore, it was suggested to study the effect of this method of providing PVDF-modified sample on damaged area under low velocity impact test. Interleaving composite laminates using SAN nanofibers and investigating its toughening effect was presented by Esmaeely Neisiany et al. [46]. These results showed that presence of the electrospun SAN nanofibers could deflect the created microcracks, leading to direct them along more tortuous paths, and consequently, increasing the resistance of resin rich area to crack propagation. Hence the microcracks broke away from the SAN nanofibers; they induced kinked fracture surfaces, which offered more strain energy to be dissipated. In this way, the absorbed energy during impact (Izod impact test) was increased by 8%. The toughening effect of PVA on composite laminates was studied by Beylergil et al. [47]. Although this nanofibrous mat had a significant effect on compressive strength, its effect during Charpy impact test was not so good and could enhance impact strength by about 11% as compared to those for the unmodified specimens. Molnar et al. [48] interleaved CFRP (Unidirectional and woven) laminates by PAN nanofibers and cured the sample at 60 °C. Therefore, the nanofibers were available with their initial configuration between composite layers. They conducted various mechanical tests, but according to topic of this review, the Charpy impact and drop-weight tests are reported. The results showed that all impact parameters were improved by incorporating nanofibers, but the effect of nanofibers was higher in unidirectional laminates in comparison with the woven one during Charpy impact test and the absorbed energy was increased by 31% in woven laminate in drop-weight impact test.

The decrease of the damaged area is one of the important parameters that can be used as a reference for finding the efficiency of a nanofiber type. Figure 9 summarizes this parameter for various nanofibers to understand which nanofibrous mat has the best effect on toughening the laminate during impact. In the figure, PCL-1 shows the laminates toughened by PCL using “Bridging” mechanism while PCL-2 presents the other toughening mechanism (Phase separation). As can be seen, the best choice is applying carbon nanofibers, which is followed by NY66 and PCL-1.

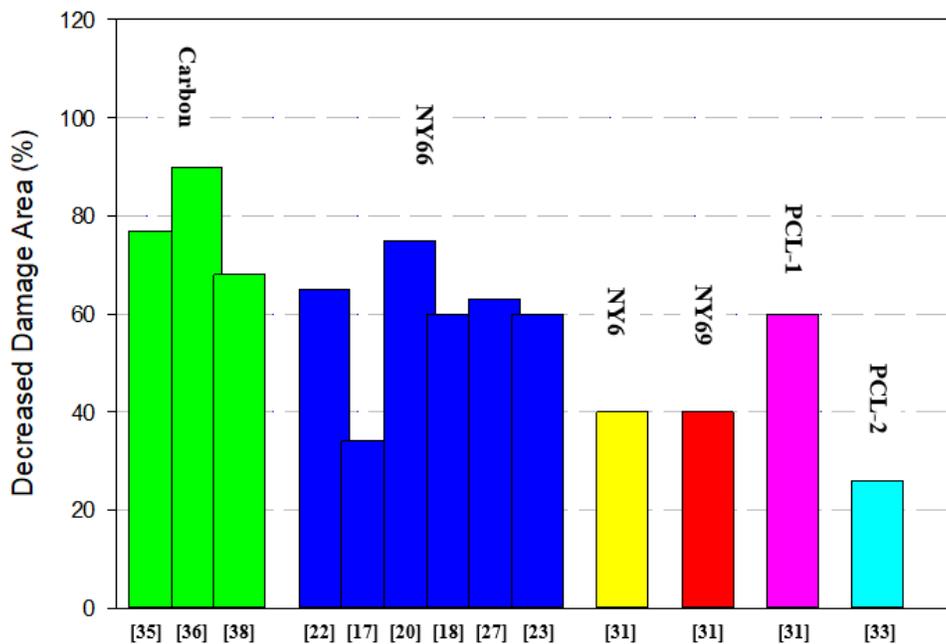


Figure 9. Decreased damage parameter caused by various nanofibers.

3. Composite Laminates Toughened by Nano-Particles

Over the past decades, considerable research efforts have been devoted to disperse nanoparticles into polymeric composites in order to enhance their toughness [53]. As illustrated in Figure 10, a

brittle polymer (G_{IC} less than 200 J/m^2) has more improvement in the fracture toughness of composite, compared with a tough polymer [54]. For the brittle polymer, the increased toughness in the composite was attributed to the fiber breakage and pullout that generally accompany composite crack growth. The low transfer efficiency of resin fracture toughness into delamination fracture toughness, for very ductile resins, is the result of the constraint on the development of a larger plastic zone in the resin-rich region between plies by the fibers in the adjacent plies [55].

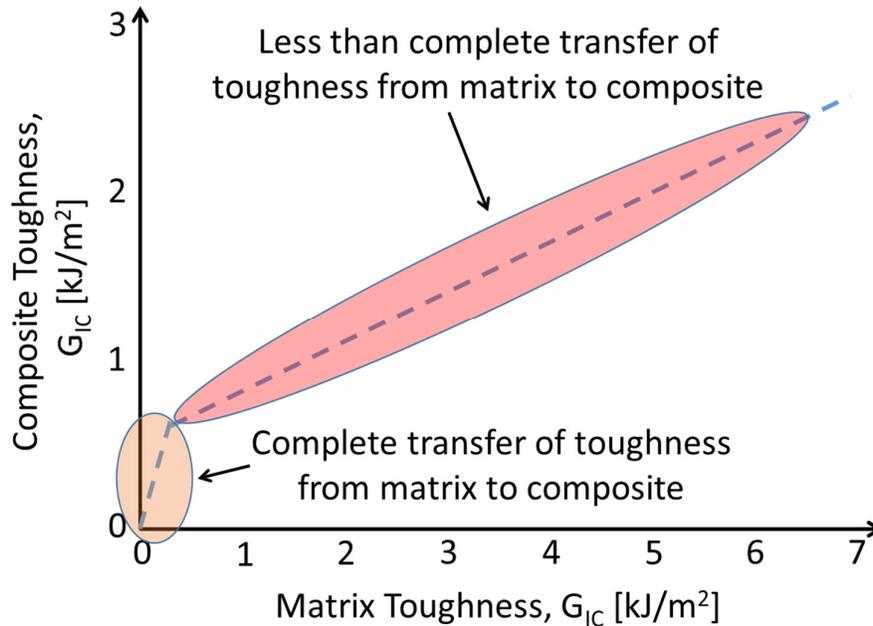


Figure 10. Mode I interlaminar fracture toughness of composites and matrix toughness [54].

A positive relationship is reported between the improvement fracture toughness, the increase of impact performance and the enhancement of the residual strength of composite materials [56], as the onset and propagation of delamination are largely affected by fracture toughness values of composite laminates.

This section reviews some recent developments in the use of nanoparticles as additional reinforcing phases in fiber-reinforced epoxy matrix composites, addressing the effects of nano-modified epoxy matrices on impact and CAI strength of fiber-reinforced laminates. The behaviors of nanoparticles strongly depend on the sizes, shapes, dimensionality and morphologies. A highlighted summary of recent works on improving the toughness and impact performance of composites is shown in Table 2. Reinforcing nanoparticles are classified into zero-, one-, two- and three-dimensional (3D) structures [57,58] as exemplified in Figure 11, and the related works are summarized in the following.

Table 2. Published paper regarding the influence of nanoparticles on fracture toughness and impact response of composite laminates.

Ref.	Particle type	Composite Type	Test Method	Improvement (%)	Content
[59]	Nanosilica	Epoxy	Compact tension ASTM Standard D5045–02	G _c value increased by more than 140%	5 vol %.
[60]	Nanosilica	Epoxy	Un-notched Charpy DIN-ISO-179-2 Compact tension ASTM Standard D5045–02	K _c value increased 78% with 14 vol % (23 wt %). Impact resistance increased 23% with 3% vol	-
[61]	Fullerene-like tungsten disulfide	Epoxy	DCB (ASTM D-3433) T-peel joints (ASTM D-1876) Charpy impact (ASTM D-950)	Impact strength improved more than 200%. G _C increased by 3 to more than 10 times compared to neat epoxy.	3 wt %
[62]	Aluminum oxide	Epoxy	Flexural testing ENISO 178	G _c increased by 120%	10 vol %
[63]	Alumina Nanofillers	Epoxy	Tensile ASTM D-638 Compact tension ASTM D5045–02	About 50% and 80% increases of K _{IC} and G _{IC}	18.4 wt %
[64]	Rubber	Carbon/epoxy	DCB (BSS 7273) ENF (BMS 8-276) Impact and CAI (BSS 7260)	G _{IC} improved about 250% G _{IC} improved about 33% Impact induced damage area decreased 82%	38%
[65]	Nanosilica and Nano-rubber	Carbon/epoxy	DCB ASTM Standard D5528	G _{IC} improved about 250% for the nano-rubber particle G _{IC} improved about 20–30% for the nano-silica	10 wt %
[66]	Nano-silica	Carbon fiber/epoxy	DCB ASTM Standard D5528 ENF	G _{IC} improved about 22% G _{IC} improved about 70%	20 wt %
[67]	Nanosilica	Epoxy	The single-edge notch bend (SENB) test ISO-13586	G _{IC} improved about 360%	13.4 vol %
[68]	Rubber and silica nanoparticles	Carbon/epoxy	DCB ASTM D5528, ENF DIN EN 6034 SENB ISO 13586	The laminate made from the rubber-only resin shows an increase in G _{IC} , a slight reduction in G _{IIc} and ILSS as well as a reduction of the delaminated area in impact testing alongside with an increase in CAI.	5–10 wt %
[69]	Nanosilica	Glass/epoxy	Charpy impact tests	Impact energy and impact toughness were improved by 38.02%, 30.86% for edgewise-notched specimens and 32.83%, 27.1% for flatwise-unnotched specimens, respectively.	1.5 wt %
[70]	Nanosilica	Carbon/epoxy	Ballistic impact	The absorbed impact energy per unit damage area increased by 90–155%.	25 wt %.
[71]	Powders of aluminum, gamma alumina, silicon carbide, colloidal silica and potato flour	Kevlar/epoxy and AA 5086-H32 aluminum hybrid	Ballistic impact NATO standards using a caliber 270 Winchester rifle	The highest impact energy absorption capacity was achieved by deposition of aluminum powder followed by colloidal silica and silicon carbide powder in that order. Addition of gamma alumina powder and potato flour has produced the least effect of enhancing the impact energy absorption capability of the laminates.	Variable

[72]	Carbon nanotubes (CNTs)	Carbon/epoxy	DCB ASTM D5528-01 Impact	23% decrease in G_{ic} 6% improvement in absorbed impact energy	0.025, 0.05, and 0.1 wt %
[73]	Functionalized SWCNT	Carbon/epoxy	Impact, CAI, DCB, ENF	5% reduction of the area of impact damage, 3.5% increase in CAI strength 13% increase in Mode I fracture toughness, 28% increase in Mode II interlaminar fracture toughness	0.1 wt %
[74]	Graphene oxide	Carbon/epoxy Glass/epoxy	Impact CAI ASTM D7137	Improved residual compressive properties, with the glass fiber laminates showing the highest improvement of 55%	0.3 and 0.5 wt %
[75]	Multi-walled carbon-nanotube (MWCNT)	E-glass/epoxy	Ballistic impact	A relatively small increase in the ballistic-protection performance	-
[76]	CNT, MOS ₂	Polyimide (PI) composites	Izod notched impact strength	The impact strength of the composites decreased by 40% when CNT reached 1%.	1 to 5 wt %
[77]	Nanoclay	Carbon/epoxy	DCB	G_{ic} improved about 85%.	4 phr nanoclay in epoxy
[78]	Nanoclay	Carbon/epoxy	Impact CAI	Smaller damage area, higher residual strength and higher threshold energy level.	3 wt %
[79]	Nanoclays	Kevlar/epoxy	Impact	The maximum load increased about 4.5% for laminates filled by cork, 10.4% for laminates filled by cork/clays and 16.1% for laminates filled by clays.	1.5 wt %
[80]	Nanoclay	Glass/epoxy	Medium velocity projectile impact	A 42% increase of ballistic limit	5 wt %
[81]	Nanoclays	Kevlar/epoxy	Impact Residual tensile strength	Impact load and the damaged area increases. Elastic recuperation and penetration threshold increases	6% wt %
[82]	Carbon aerogel	Epoxy	SENB ISO-13586	The maximum measured G_{ic} value improved 100%	0.3 wt %
[83]	Carbon aerogel	Carbon/epoxy	Impact CAI ASTM D7137	CAI improved 10% Impact force 4%	0.3 wt %

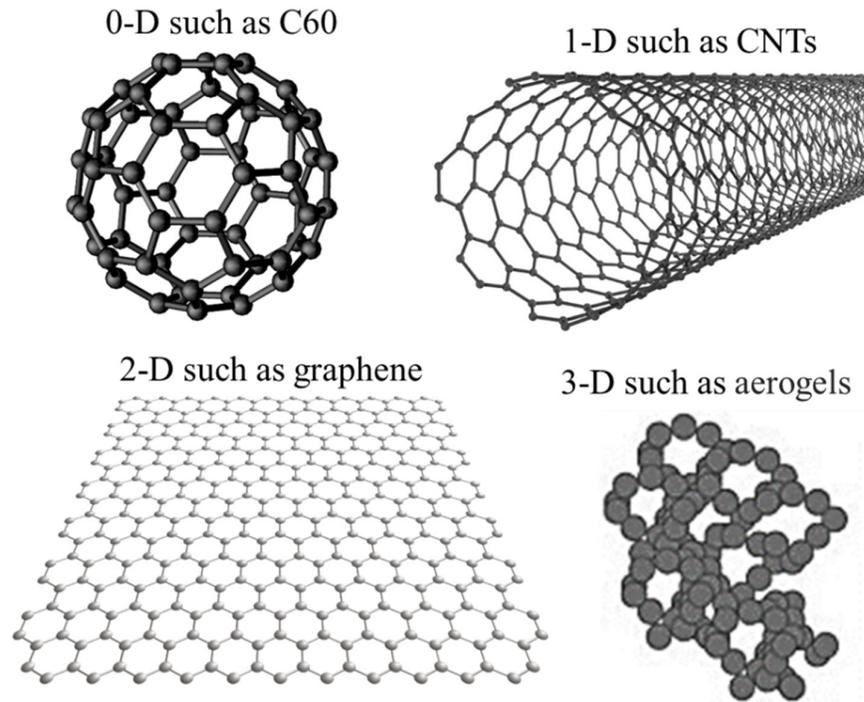


Figure 11. Schematic of 0D (C60 fullerene), 1D (CNT), 2D (graphene), and 3D (nanocarbon aerogels) nanostructures of carbon-based materials [57].

3.1. Zero-Dimensional (0D)

A rich selection of physical and chemical procedures have been developed to fabricate 0D NMSs with well-controlled dimensions, for instance by in situ sol–gel methods or by polymerization promoted directly from their surfaces [59,60,84], carbon black [85], fullerene [61], TiO₂ and alumina particles [62,63].

Positive effects of 0-D Nano particulates such as rubber [64], nanosilica [65,66,86–89], carbon black [90], fullerene [91], and alumina [67] on fracture toughness of composite laminates have been reported. A localized inelastic matrix deformation in form of shear banding between particles, void nucleation and growth as well as crack deflection at agglomerates have frequently been cited as the key mechanisms leading to the increases in fracture toughness. For nano-particulate materials, such as nanosilica, debonding and subsequent plastic void growth were most likely to be responsible for the increase in fracture toughness [92]. The nanoparticles were also found to reduce the damage area and increase the absorbed energy resulting from low velocity impact [64,68,69,90,93,94] and ballistic impact [70,71,95], with more tangible effects in the ballistic impact compared with quasi-static loading [96]. A higher residual shear strength after impact resulted by the Nano particles modification [70], however, the ultimate laminate compression strength after impact was not necessarily improved [64,68], most probably due to agglomerates of nanoparticles found in the cured resin systems. Nanoparticles were also used for multi-functionality purposes, where they improved the impact performance, and the electrical resistivity tomography was introduced as an impact damage detection method in composites, due to conductive nature of the nanoparticles [90].

For 0-D nanoparticles, the localized inelastic matrix deformation such as shear banding between particles, debonding in the particle/resin interface and subsequent void nucleation, plastic void growth, nanoparticle-induced dimples, as well as crack deflection at agglomerates (see Figure 12 as an example) were most likely to be responsible for the increase in fracture toughness [60,84,92]. For instance, as shown in Figure 13 the brittle fracture in a pure epoxy was overwhelmed by extensive plastic deformation in the nano-silica modified epoxy, when subjected to a compact tension test [84].

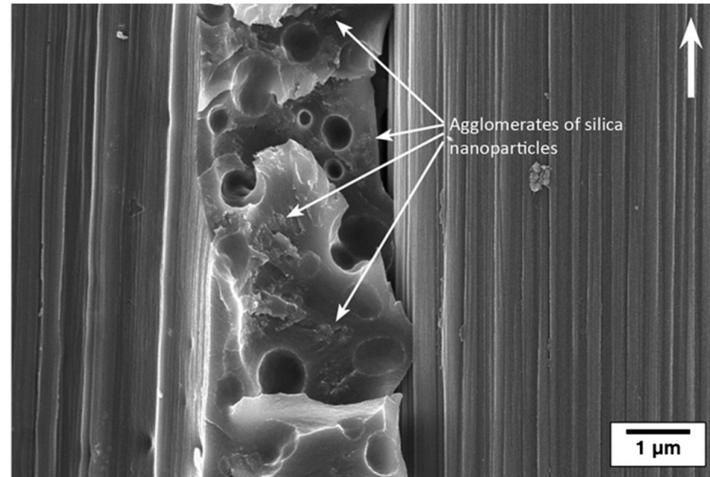


Figure 12. SEM image of carbon/epoxy laminate modified with silica/rubber nanoparticles (fracture surface of G_{IIC} test specimen). The white arrow indicates the direction of crack propagation [68].

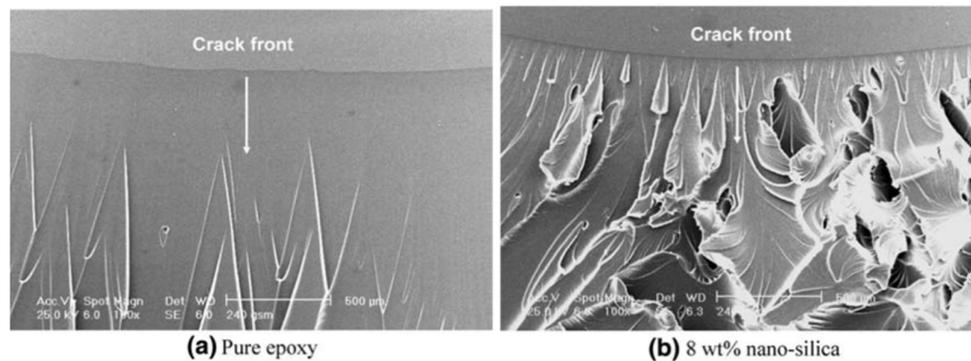


Figure 13. SEM micrographs of fracture surfaces near crack tips (a) pure epoxy, and (b) 8 wt % nano-silica [84].

3.2. One-dimensional (1D)

1D nanoparticles have stimulated an increasing interest as reinforcing nanoparticles for the research on toughening in composites. 1D nanoparticles are used in different forms of fibers or tubes such as double-walled CNTs, multi-walled CNTs [86,97–99], cup-stacked carbon nanotube (CSCNT) [100]; vertically-aligned CNT (VACNT) forest grown directly on fiber surface [101] or on Si substrate and then transfer-printed onto prepregs [102]; vapor-grown carbon nanofiber (VGCNF) [103,104]; and halloysite nanotube (HNT) [105,106].

Significant increase was reported using 1-D nanoparticles as reinforcement for matrix-dominated mechanical properties such as mode-I and mode-II fracture toughness, albeit with substantially varying degrees [72,73,107–110].

Most of the studies reported a positive effect on low-velocity impact [40,72–74,108,109,111–116] and ballistic velocity impact energies [75,117]. However, some of the researchers reported no improvements in the impact and CAI behaviors [118,119], or even a negative effect was reported by others [76]. These differences were because of the type and content of the nanoparticles and different manufacturing methodologies that were found to be very important factors in impact performance of composite materials. Aligned CNTs offer excellent mechanical toughness improvements for traditional composite laminates, and additionally enable multifunctional capabilities; i.e., to improve the impact performance (reduced damage area and better CAI) [73,120] and also as a promising damage monitoring technique of the carbon fiber laminated composites [118,120,121]. The compression strength and compression–compression fatigue after impact performance was improved [111].

The reason behind the increase in fracture toughness was linked to the extraordinary high interface area of the 1-D nanoparticles [97] and the bridging mechanism of the 1-D nanoparticles that suppresses the growth of nano-pores, as well as the propagation of cracks that contributes positively to the increase in fracture toughness [67]. Figure 14 shows SEM images of the fracture surfaces of a baseline and a nano-modified specimen at which micro-cracks and hackles, which are both related to microscale matrix failure modes are dominant toughening mechanisms involved with Mode II fracture tests [73].

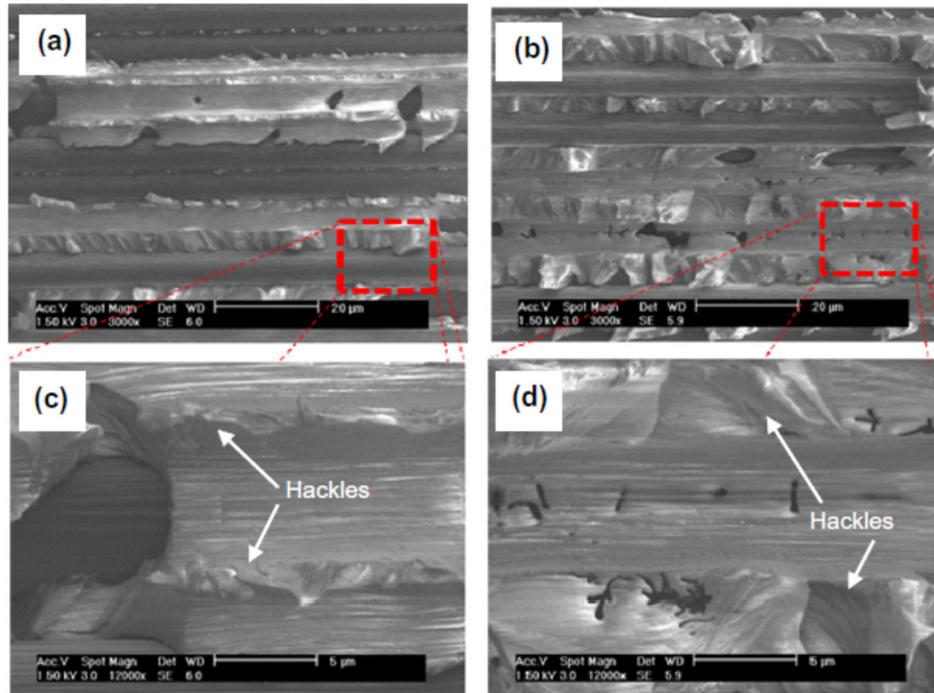


Figure 14. SEM of fractured Mode II DCB coupons at different magnifications for (a,c) baseline laminate and (b,d) SWCNT-modified laminate. The existence of larger hackles can be seen for SWCNT-modified laminate [73].

3.3. Two-Dimensional (2D)

2D nanoparticles have two dimensions outside of the nanometric size range. These layered particles are in the form of single or multiple layers of sheets such as junctions (continuous islands), branched structures, nanoprisms, nanoplates, nanosheets, nanowalls, and nanodisks [122]. Fully or partially exfoliated clays and silicates belong to this family. The effects of 2D nanoparticles on mode-I and mode-II fracture toughness of composites laminates have been studied mainly with nanoclay and occasionally by graphene [77,78,123,124].

Better low-velocity impact properties [79,125–132], CAI [74,78], residual tensile strength after impact [133], post-fire low velocity impact behavior [80,134,135] were reported using nanoclays, with more effect on low-energy levels [125]. The dispersion of clay in polymer matrix shows considerable improvement in energy absorption and ballistic limit of the composite laminates [81,133,135,136]. The fracture toughness and the threshold to crack initiation under cyclic loading were also interestingly improved for the clay modified matrix [127]. Improved toughness and impact behavior was attributed to the change in the failure mechanisms, that shifted from interlaminar failure to a mostly intralaminar failure [125] and increased the stiffness and the resistance to damage progression of the nanophased laminates [137]. The formation of massive microvoids/cracks and the increase of the fracture surface area due to crack deflection were identified as the major toughening mechanisms in highly exfoliated epoxy/clay nanocomposites [93]. Figure 15 shows the fracture morphologies after interlaminar shear tests for a carbon/epoxy laminate modified with nanoclay, indicating a strong

adhesion between the fiber and matrix by adding the nanoclay [78]. High content of nano clay causes agglomeration and leading towards limiting the improvement in impact resistance [78,138]. So there is an optimal content reported for the highest damage resistance and CAI, and the improvement was linked to the transition of failure mechanisms during the CAI test, from the brittle buckling mode to more ductile, multi-layer delamination mode [78].

Significant improvement in low-velocity impact performance was noticed for the hybrid nanoparticle-reinforced composite samples (hybrid of 1D multi-walled carbon nanotubes and 2D nanoclay Nanoparticles) compared with their individual reinforcement [139].

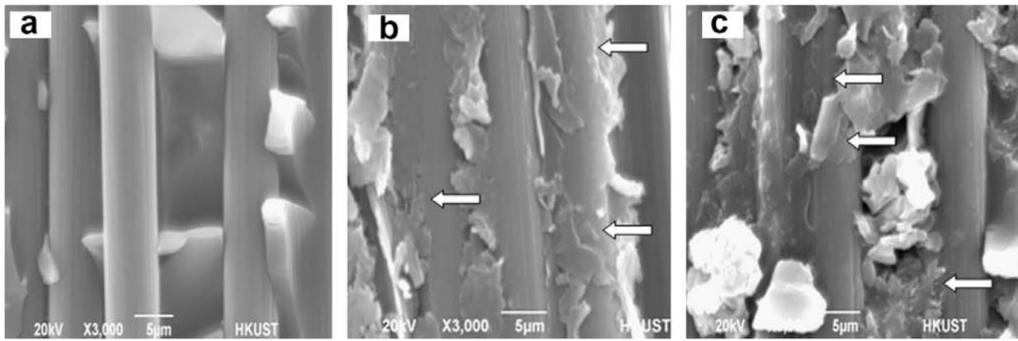


Figure 15. Photographs of fracture surfaces after an interlaminar shear test for CFRPs composites with different clay contents: (a) 0 wt %; (b) 3 wt % and (c) 5 wt % [132].

3.4. Three-Dimensional (3D)

3D nanostructures are important materials owing to the large specific surface area and other superior properties arising from quantum size effect. Nanocarbon aerogels are 3D nanoparticles with a high electrical conductivity, high porosity, controllable pore structure and high specific surface area. Nanocarbon aerogels are used to improve toughness and impact performance of composite materials. Significant improvement in the fracture toughness of the relatively low (0.3 wt %) aerogel concentration composites are reported [82,140]. The impact and CAI properties of the CFRP laminates were improved by adding the Nanocarbon aerogels and an optimum content was reported for the best performance [83].

Crack pinning, crack deflection, and plastic void growth are reported as the mechanisms for the toughness improvement of the carbon aerogel/epoxy polymers [82]. These mechanisms are caused by the obstruction of crack propagation by agglomerated carbon aerogels (see Figure 16).

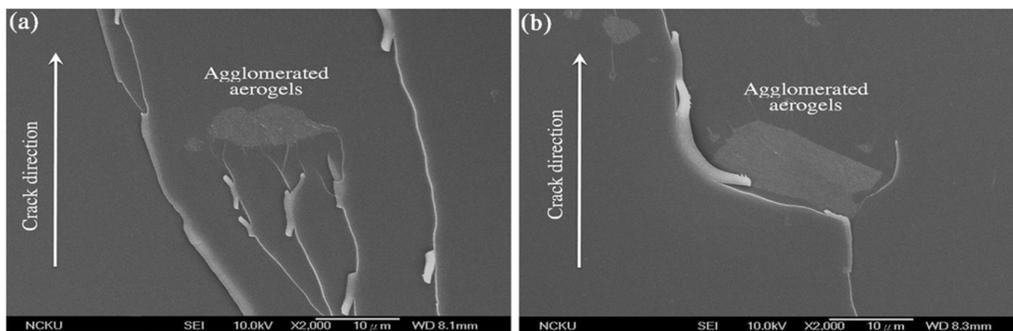


Figure 16. FEG-SEM images of the fracture surfaces of a composite with a carbon aerogel content of 0.5 wt %. The surfaces show (a) crack pinning and (b) crack deflection [82].

4. Suggested Research Directions

Although many papers have been published in the reviewed topic, there are still many unanswered questions about the use of nanofibers and nanoparticles as tougheners in composite laminates. Here it is a list of future research works that are recommended in this area:

- 1- Studying the influence of nanofiber interleaving in high-velocity impact response of laminated composites.
- 2- Some papers have shown that thermoplastic polymers like Phenoxy and Polysulfone (PSF) [141,142] are suitable choices for toughening epoxy-based laminates, but more work needs to be done on these polymers.
- 3- The effect of geometrical features of nanofibers and nanofibrous mats, such as nanofiber orientation, on the impact response of nano-modified laminates should be investigated.
- 4- To achieve practical applications of nanoparticle reinforced composites, a number of technical issues need to be solved, including the uniformity of the dispersion and the alignment of the nanoparticles, to avoid morphological changes like re-agglomeration [143], the optimal interface between nanoparticles and matrix, and the viscosity of nanoparticle-modified matrix resins for ease of fabrication of high fiber volume fraction (>60 vol %) composites.

More studies are finally needed regarding the reinforcement of composite laminates with hybrid particles (mix of micro- and nano-scales) to obtain synergetic effects in toughening, strengthening or even multi-functionality such as sensing and shielding.

5. Conclusions

In this paper, the effect of nanomaterials including nanofibers and nanoparticles on impact response of composite laminates is considered. The following conclusions can be drawn from the reviewed papers:

- Electrospun nanofibers are suitable choices for toughening thermoset based laminates. Various types of polymers have been applied for interleaving composite laminates including NY6,66,69, PVDF, PCL, Carbon.
- Each nanofiber type has its specific mechanism for toughening laminates; for instance, NY activates bridging mechanism while PCL utilizes two different mechanisms depend on curing temperature. If PCL melts during the curing process, the phase separation mechanism predominant; if not, the bridging between the composite layers is the main mechanism of toughening.
- According to the published results, Carbon, NY66, and non-melted PCL are the best choices for toughening the laminates.
- A positive effect of nanoparticles to enhance interlaminar fracture toughness, impact performance and CAI strength of composite laminates is reported, especially for brittle resin systems.
- There is a higher improvement in interlaminar shear values (G_{IC} and G_{IIC}) compared with the impact and CAI behavior. On the other hand, some authors reported a negative effect of the nanoparticles on impact and CAI, which was mainly related to insufficient solvent of the nanoparticles in the resin that led to agglomeration of the nanoparticles.
- Manufacturing methods, reinforcement content and type, material property and many other parameters are affecting the performance of nanoparticle modified composites. Therefore, careful consideration must be done when choosing these parameters to target desired properties.

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