

# EFFECTS OF NANOMATERIALS ON POLYMER COMPOSITES - AN EXPATIAATE VIEW

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**Abstract.** This paper portrays the various combinations of nanomaterials and matrix materials which were used to fabricate the nanocomposite laminates with and without fiber. An in-depth analysis was made on the various ways of preparing the nano influenced matrix and composite panels. In addition to this, an effort has been made to afford an outline of the impact of nanofillers within the matrix from the results of numerous tests made with the laminated composites. Conjointly, a distinctive estimation has been made to elaborate the material details, processing steps and also the impact of the inclusion of nanofillers.

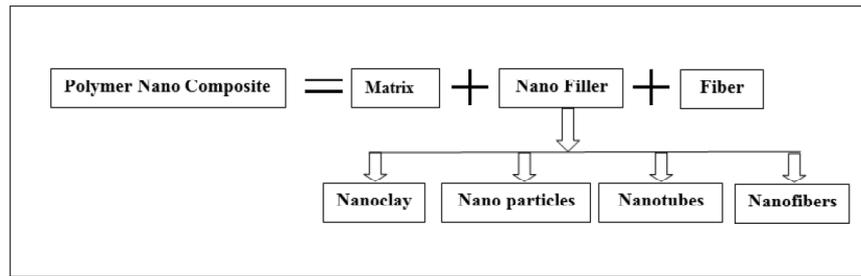
## 1. INTRODUCTION

Nowadays, polymer nanocomposite materials are coming up with the incorporation of nano fillers like nano clays, nano particles, nano tubes, nano fibers, etc., additionally, this incorporation of nano reinforcements into elastomers, which considerably enhances their mechanical and thermal barrier properties in conjunction with noticeable improvements in adhesion, rheological and processing behavior. Furthermore, better dispersion of these fillers within the matrix provides high performance nano composites and also the properties of the nano scale filler are significantly higher than those of the base matrix [1-2]. Owing to this fact, a very important parameter for characterizing the effectiveness of reinforcement is the ratio of surface area (A) of rein-

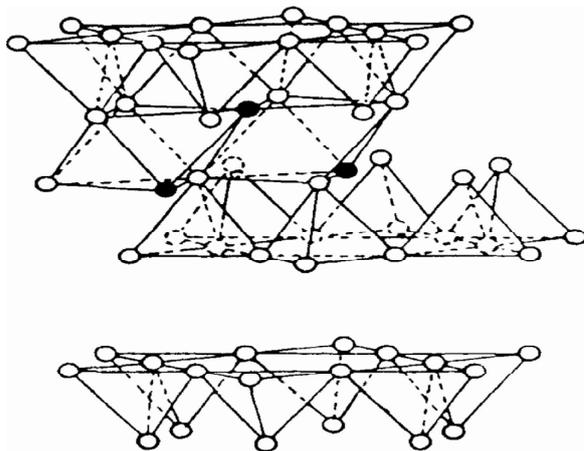
forcement to volume of reinforcement (V) as suggested by McCrum et al. [3].

Among varied nanoclays, Montmorillonite (MMT) is a naturally occurring 2:1 phyllosilicate, which has a similar layered and crystalline structure as talc and mica but a different layer charge as noted by Giese and Van Oss [4]. Recently, the behavior of nano materials in epoxy adhesive for the aim of enhancing the interfacial properties of composites was investigated. During this state of affairs, nanoparticles with higher active surface composition will act as stress concentrators and a binding bridge at the interphase. In addition to this, these nanoparticles as a new material have been extensively used to improve the strength, stiffness and toughness of resin composites [5]. Moreover, the discovery of

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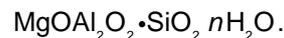
carbon nanotubes (CNTs) and their subsequent use to fabricate composites exhibiting some of the distinctive CNT related mechanical, thermal and electrical properties superimposed a new and interesting dimension to this area. The likelihood of spinning CNTs into composite products and textiles made further inroads for the process and applications of CNT containing nanomaterials [6-10]. Pavia and Curtin [11] suggested that the development of nanofiber and nano/micro hybrid CMCs ought to be steered by an accurate understanding of the underlying toughening/strengthening mechanisms imparted by the nanofibers because these properties rely upon several system and material parameters. To the author's knowledge, the polymer nanocomposites could be devised as shown in the following flow chart. From the above facts, an effort has been made to elaborate the effects of polymer reinforced nano composites.



**Fig. 1.** Idealized structure of 2:1 layered silicates showing two tetrahedral-site sheets fused to an octahedral-site sheet. Open circles represent oxygen's shaded circles are hydroxyls. The galleries in the pristine silicates are usually occupied by hydrated alkali metal cations. Reprinted with permission from E. P. Giannelis // *Adv. Mater.* 8 (1996) 1, (c) 1996 Wiley.

## 2. NANO COMPOSITES WITH NANOCLAYS

Table 1 clearly picturizes several processing steps carried out by some of the researchers in reinforcing nano clay within the nano composite system. As stated earlier, many of the studies had been conducted with Montmorillonite, whereas very few concentrated on organic rectorite clay and nanomer. Montmorillonite (MMT) is a colloidal layered silicate mineral generally formed by the deposit of volcanic ash in lakes. It is a member of the Smectite family, stacks of plate like structures or platelets with octahedral sheet covered by tetrahedral sheets on both sides like sandwich (Fig. 1) and its basic structure is:



From Table 1 one could clearly understand the promising results achieved by researchers in adding nanoclay within the matrix system.

## 3. NANOCOMPOSITES WITH NANOPARTICLES

The rapid advances of chemistry in the development of nanoparticles over the recent years have verified tremendous improvements in the field. The notion of using nanoparticles as fillers in polymer materials have conveyed the attention of researchers due to their exclusive mechanical, electrical, optical, and thermal properties [19-24]. Variety of nanoparticles such as alumina [25], Micro and nanosized silicon carbide [26], Silica [27], Zinc [28], calcium carbonate [29], carbon black nanoparticles [30], etc., were used as fillers to enhance the material properties for polymer nanocomposites. In general, nanoparticle and matrix are mixed together by solvent casting method, melt mixing method and in-situ polymerization. Fig. 2 shows the common processing steps of nano particles-polymer composites and Table 2 exemplifies the step-by-step procedure implicated by various researchers to fabricate the nano composite panels.

**Table 1.** Various processing steps and inferences made on nanoclays.

Ref.		
[12]	<p>Nano Clay Samples</p> <p>Processing Steps</p> <p>Inferences</p>	<p><i>Cloisite 20A and Nanomer I.30P</i> with SILRES BS1701 Silane Cloisite 20A – 1 wt.%, 3 wt.%, and 5 wt.% Nanomer I.30P– 1 wt.%, 3 wt.%, and 5 wt.%</p> <p>1. MMT was mixed with silane and ultra sonicated (70 W, 42 KHz) for 3h. 2. The mixture was applied as coating on concrete surface and cured at room temperature for 7 days. 3. With and without coating was examined by using FEM (Finite element method) software.</p> <ul style="list-style-type: none"> <li>· Lower viscosity (0.02 Pa's) of 5 wt.% Nanomer I.30P was more suitable for coating.</li> <li>· Lower contact angle of droplet (42.6°) of 5 wt.% Nanomer I.30P gave better adhesion and wettability for coating.</li> <li>· Moisture barrier performance of 5 wt.% Nanomer I.30P was slightly greater than neat silane, but 5 wt.% Cloisite 20A was almost twice better than the neat silane.</li> <li>· Chloride content was reduced to an average of 92% for neat silane, but it reduced by about 69% for nano composite coatings.</li> </ul>
[13]	<p>Nano Clay Samples /Loading</p> <p>Processing Steps</p> <p>Inferences</p>	<p><i>MMT nano clay</i> with DDM curing agent and SCA (Silane types: APS, GPS, MPS).</p> <p>1. Na-MMT (Non-treated MMT), 2. as-received (MMT after ion exchange), 3. AP-MMT (APS - treated MMT), 4. GP-MMT (GPS - treated MMT), and 5. MP-MMT (MPS - treated MMT).</p> <ul style="list-style-type: none"> <li>· All above samples were 5wt.% loading with epoxy.</li> </ul> <p>1. SCA was dispersed in a solvent of 90% methanol and 10% distilled water. 2. SCA was then hydrolyzed at 4.0 pH for 1 h. 3. MMT was dipped in a hydrolyzed solution for 1h and then dried at 120 °C. 4. Modified MMT was dispersed in epoxy at 80 °C for 30 min and then ultra sonicated for 30 min. 5. Mixtures were degassed at 50 °C for 2h and subsequently poured into the mold. 6. Finally, cured at 120 °C for 2h.</p> <ul style="list-style-type: none"> <li>· <math>K_{IC}</math> and ILSS improved for all treated MMT/epoxy composites; highest <math>K_{IC}</math> (3.55 MPa m<sup>1/2</sup>) and ILSS (13.8 MPa) value yield for AP-MMT.</li> <li>· Inclusion of SCA improved the interfacial adhesion between MMT and epoxy matrix.</li> </ul>
[14]	<p>Nano Clay</p> <p>Loading</p> <p>Processing Steps</p> <p>Inferences</p>	<p><i>Cloisite 30B</i> with EPON 815C epoxy, carbon fiber, ternary ammonium salt and aromaticdiamine curing agent.</p> <p>2 wt.%, 4 wt.%, and 6 wt.%; with and without reinforcement of fiber.</p> <p>1. 10 grams of epoxy was added with silicate; using a mechanical stirrer this mixture was mixed for 20 min. 2. Additionally two grams of curing agent was added with the mixture and then mixed for 5 min. 3. Mixture was then infused into carbon fiber by VARIM and allowed through hydraulic press for 4 h at 150 °C. 4. Finally, degassed in vacuum for 4 h at 150 °C.</p> <ul style="list-style-type: none"> <li>· ILSS for FRC with 2% loading drop by 11%, but for 4% and 6% loading, a drop by 18% and 14% was evident.</li> <li>· Flexural modulus and flexural strength increased for Fiber Reinforced Polymer (FRP) by 31% and 24%, respectively.</li> <li>· Flexural modulus for silicate nano composites drop by 8% for 2% loading, but increased by 12% and 18%, respectively for 4% and 6% loading.</li> <li>· <math>T_g</math> increased to 136 °C for 2% loading, whereas an increase in 131 °C for 4% loading and 130 °C for 6% loading was apparent.</li> </ul>
[15]	<p>Nano Clay</p>	<p><i>Nanomer 1.28E</i> with SC-15 epoxy and carbon fiber.</p>

	Samples /Loading	1. B45 (Biaxial ( $\pm 45^\circ$ )), 2. T45 (Triaxial ( $\pm 45^\circ$ )) and 3. T60 (Triaxial ( $\pm 60^\circ$ )) with 1 wt.% and 2 wt.% clay loading.
	Processing Steps	1. The clay was heated up to 100 °C for 2 h in order to remove moisture. 2. Heated clay was mixed with epoxy and magnetically stirred for 4 h at 40-50 °C. 3. Clay mixture was then added with hardener and magnetically stirred for 5 min. 4. Composite panels were fabricated by VARIM process at room temperature and allowed to post cure at 100 °C for 5 h.
	Inferences	<ul style="list-style-type: none"> <li>• Flexural strength and flexural modulus for 1 wt.% B45 panels were improved by 11% and 33%, respectively. Similarly for 1 wt.% T45 panels as 6.6% and 15.3%, respectively, and for 1 wt.% T60 panels as 20% and 12.4%, respectively.</li> <li>• Absolute energy and impact energy also improved for 1 wt.% loading than 2 wt.%.</li> </ul>
[16]	Nano Clay	<i>Organically modified MMT nano clay</i> with DGEBA epoxy, aliphatic amine (triethylenetetramine) hardener and S2 glass fiber.
	Samples	1 wt.%, 2 wt.%, 5 wt.%, and 10 wt.%.
	Processing Steps	1. Nano clay was dispersed in acetone and then mixed with hardener. 2. Acetone / nano clay / hardener foaming solution was degassed for 1 h. 3. After that the mixture was mixed with resin. 4. Composite laminates were stacked with vacuum assistance and then cured for 24 h at room temperature.
	Inferences	<ul style="list-style-type: none"> <li>• Impact energy absorption improved by 48% for 20J, 15% for 60J, and 4% for 80J.</li> <li>• Stiffness increased by 11.63% for 3.5% nano clay loading.</li> <li>• 5% loading showed better damping performance.</li> <li>• Nano clay inclusion increased stiffness, impact resistance and fracture toughness.</li> </ul>
[17]	Nano Clay	<i>Nanocer nano clay</i> with SC-15 epoxy and carbon fiber.
	Samples /Loading	1 wt.%, 2 wt.%, and 3 wt.% at room temperature curing and thermally post cured samples.
	Processing Steps	1. Epoxy was added with nano clay and then stirred for 30 min in sonicator. 2. Nano clay mixture was heated up to 100 °C for 2 h. 3. Epoxy mixture was heated to 40-50 °C and then cooled down to room temperature. 4. The epoxy mixture was added with hardener and then degassed by using vacuum oven. 5. Laminates were fabricated by VARIM process.
	Inferences	<ul style="list-style-type: none"> <li>• Flexural strength and modulus enhanced greatly for 2 wt.% loading composites cured at room temperature by about 25% and 14%. Similarly for 2 wt.% thermally post cured panels by about 14% and 9%, respectively.</li> <li>• <math>T_g</math> improved by 9 °C for 2 wt.% room temperature cured panels and 13 °C for thermally cured panels.</li> <li>• Better storage modulus and loss modulus attained for 2 wt.% room temperature cured panels by about 14% and 9%. Likewise, for 2 wt.% thermally cured panels improved by 52% and 47%, respectively.</li> </ul>
[18]	Nano Clay	<i>RXG7000 and Cloisite 30B nano clay</i> with DGEBA based EC157 epoxy, amine (W131) hardener and glass fiber
	Samples /Loading	RXG7000 – 1 wt.%, 3 wt.%, and 5 wt.% with and without sonication. Cloisite 30B – 1 wt.%, 3 wt.%, and 5 wt.% with and without sonication.
	Processing Steps	1. Nano clay dispersed in resin through shear mixing at 3500 rpm for 1 h. 2. Ultrasonic mixture was made for 40 min. 3. Next hardener was added with the mixture and shear mixed for 10 min. 4. During entire process resin was cooled by external path. 5. Degassed by for 30 min and then poured into silicone mould. 6. Panels were made by VARIM with post cure for 12 h at 60 °C.

- Inferences
- Fracture toughness improved by 40% for 1 wt.% Cloisite 30B clay modified epoxy.
  - Fatigue property increased by 35% for 1 wt.% Cloisite 30B.

MMT - Montmorillonite, SCA - Silane Coupling Agent, DDM - Diamino diphenyl methane,  $K_{Ic}$  - Critical stress intensity factor, APS-  $\gamma$ -amino propyl triethoxy silane, GPS -  $\gamma$ -glycidoxy propyl methoxy silane, MPS -  $\gamma$ -methacryloxy propyl trimethoxy silane, ILSS - Interlaminar shear stress, FRC – Fiber reinforced composites,  $T_g$  – Glass transition temperature, SC-15 epoxy contains cycloaliphatic amine 70-90% and poly oxylalkylamine 10-30% hardener.

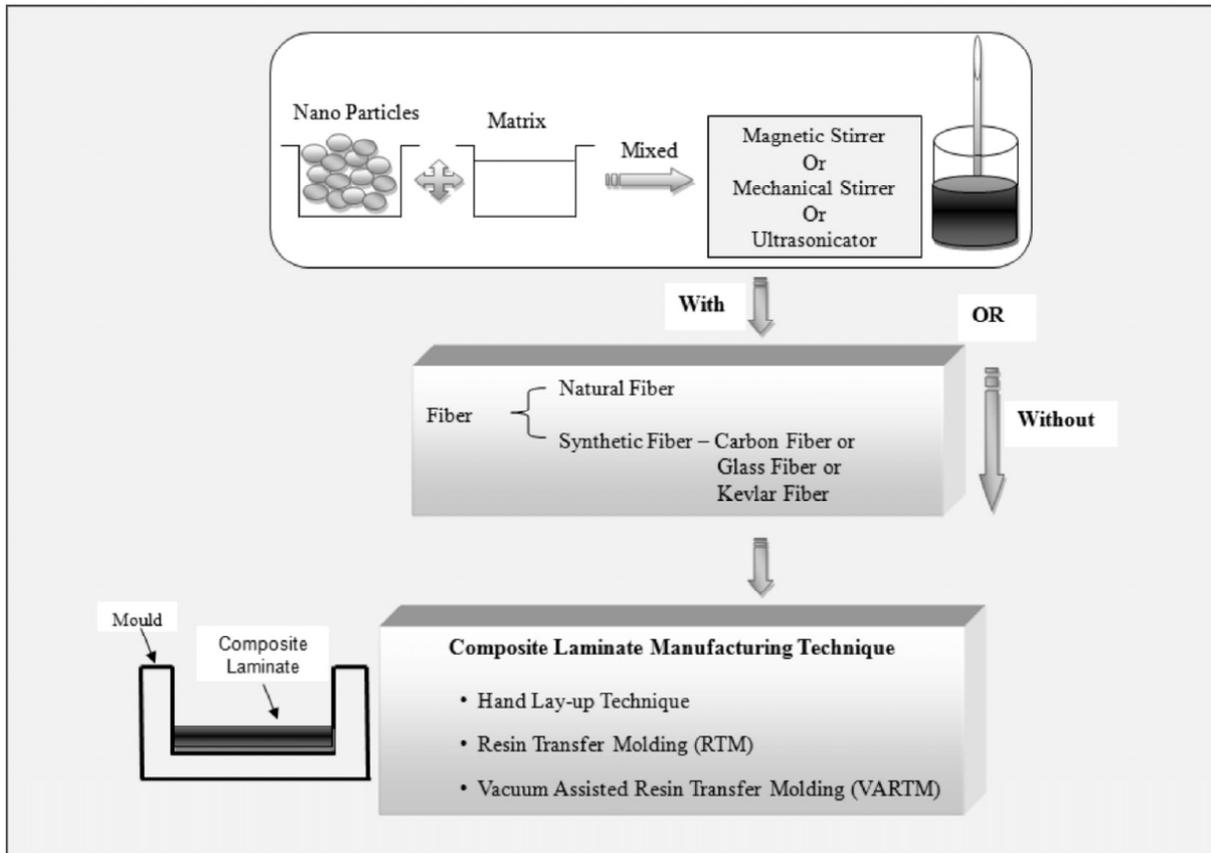


Fig. 2. Processing steps of nanoparticle reinforced composite.

Table 2. Various processing steps and inferences made on nanoparticles.

Ref.		
[31]	Nano Particles	<i>Silica nano particles</i> with CTBN and CSR rubber particles, DGEBA epoxy and H-100 curing agent.
	Samples /Loading	1. Pure, 2. Epoxy + 10 wt.% Silica, 3. Epoxy + 20 wt.% Silica, 4. Epoxy + 10 wt.% CTBN, 5. Epoxy + 10 wt.% Silica + 10 wt.% CTBN, 6. Epoxy + 10 wt.% CSR and 7. Epoxy + 10 wt.% Silica + 10 wt.% CSR.
	Processing Steps	1. Synthesized silica particles were uniformly dispersed in DGEBA resin. 2. Modified epoxy was mixed with curing agent 3. Laminates were prepared by vacuum assisted hand-lay-up process with 14 layers.
	Inferences	· Fracture toughness improved by 82% for silica nanoparticles added with CSR, but merely 48% for silica nanoparticles added with CTBN.
[32]	Nano Particles	<i>Carbon black nanoparticles</i> with Cloisite 93A nanoclay, DGEBA based YD - 114E epoxy and polyetheramine (JEFFAMINA D-230) hardener.

	Samples/Loading	Carbon black – 0.5 wt.%, 1 wt.%, 1.5 wt.%, 2 wt.%, 2.5 wt.%, and 3 wt.%. Cloisite 93A – 0.5 wt.%, 1 wt.%, 1.5 wt.%, 2 wt.%, 2.5 wt.%, and 3 wt.%.
	Processing Steps	1. Nanoparticles manually mixed with epoxy resin followed by a magnetic stirrer for 60 min at 60 °C. 2. 0.15 kg of the mixture was added batch wise to the three roll mill for high shear mixing. 3. Hardener mixing in vacuum at a magnetic stirrer for 30min. 4. Finally mixture was cured for 2 h at 125 °C.
	Inferences	<ul style="list-style-type: none"> <li>• Fracture toughness increased by 18% for 2 wt.% carbon black loading and 23% increased for 3 wt.% loading.</li> <li>• For clay loading, the fracture toughness enhanced by 20% for 0.5 wt.%, and <math>K_{IC}</math> improved by 46% for lesser than 1.5 wt.% and 50% greater than epoxy for 3 wt.%.</li> <li>• At the cryogenic temperature (-150 °C), modulus and strength improved by 160% and 90%, correspondingly, for nano particle loading. Similarly, fracture toughness was 2.3 times higher than the room temperature (25 °C).</li> </ul>
[33]	NanoParticles	<i>Silica nanoparticles</i> with DGEBA based LY556 epoxy, methylhexa hydrophthalic acid anhydride curing agent and E glass fiber.
	Samples/Loading	Bulk epoxy - 1. Neat epoxy and 2. 10 wt.% - modified epoxy. Glass Fiber Reinforced Polymer (GFRP) - 1. Neat matrix and 2. 10 wt.% - modified matrix.
	Processing Steps	1. Resin mixture was poured into release-coated steel moulds. 2. Filler moulds were placed in a circulating air oven with temperature 100 °C and allowed to cure for 2 h. 3. The temperature was then revised to 150 °C for post curing for 10 h.
	Inferences	<ul style="list-style-type: none"> <li>• Fatigue strength coefficient (FSC) and Fatigue strength exponent (FSE) increased by 34% and 16%, correspondingly, for 10 wt.%-modified epoxy and fatigue life improved by 3 to 4 times than neat epoxy.</li> <li>• FSC increased by 13% for 10 wt.%-modified matrix GFRP.</li> </ul>
[34]	NanoParticles	<i>Fullerene (Carbon 60) nanoparticles</i> with Epichlorohydrin and DGEBA based DOWDER 331 epoxy and cycloaliphatic polyamine (DOW HY 2954) hardener.
	Samples	0 wt.%, 1 wt.%, 2 wt.%, and 3 wt.%.
	Processing Steps	1. Fullerene was disposed into the epoxy resin with the aid of pure ethanol. 2. Mixture was ultra sonicated to avoid agglomeration. 3. In order to remove the solvent before curing agent, the mixture was stirred by high speed dissolver under vacuum. 4. Finally the mixture was poured into mould for casting.
	Inferences	<ul style="list-style-type: none"> <li>• For 3 wt.% loading transverse fiber bundle tension (TFBT) strength improved by 42%, <math>K_{IC}</math> improved by 31%, and the young's modulus, tensile strength and elongation were increased slightly by 6%.</li> <li>• Tensile strength improved by 26% for 2 wt.% loading.</li> <li>• Good interfacial bonding was made between fibers and matrix with 3 wt.% (TFBT specimen) and 2 wt.% (GFRP laminate).</li> </ul>
[35]	NanoParticles	<i>TiO<sub>2</sub> nanoparticles</i> with graphite flake, Polyetherimide (PEI) resin, and SCF.
	Samples/Loading	1. Pure Polyetherimide (PEI), 2. Graphite + SCF / PEI, and 3. Nano-TiO <sub>2</sub> + Graphite + SCF / PEI.
	Processing Steps	1. PEI composites with different fillers were achieved by a twin screw extruder. 2. Wear specimen was produced using injection molding machine. 3. Two PEI filled composites were prepared with (i) 5% graphite and 15% SCF, and (ii) 5% graphite, 15% SCF, and 5% TiO <sub>2</sub> nanoparticles.
	Inferences	• Wear rate of PEI was decreased by 800 times more than that of neat matrix.
[36]	Nano Particles	<i>Carbon black nano particles</i> and <i>DWCNT</i> with DGEBA based L135i epoxy and amine (H137i) hardener.
	Samples/Loading	Carbon Black – 0.1 wt.% and 0.3 wt.%. DWCNT - 0.1 wt.% and 0.3 wt.%.

Processing Steps	1. Nano particles were added within the epoxy resin and then batch wise shear mixing were performed. 2. The Dwell time of each batch of suspension rolls was 2 min. 3. Suspension was collected and mixed with hardener for 10 min by intense stirring. 5. Curing was made for 24 h at room temperature followed by post curing at 60 °C for 24 h.
Inferences	· ILSS improved by 9% and 20% for both 0.3 wt.% loading (Carbon black and DWCNT).
[37] NanoParticles	<i>Silica nanoparticles</i> with teraglycidylidiamino diphenylmethane (Ag-80) epoxy, DDS curing agent and $\gamma$ (Methylacryloxy) propyltrimethoxyl silane (KH-570) coupling agent
Samples /Loading	1. Un-sized composites, 2. Nano-SiO <sub>2</sub> modified sizing, and 3. Un-modified sizing.
Processing Steps	1. SiO <sub>2</sub> particles were pretreated by the SCA and then added to acetone solution 2. Then SiO <sub>2</sub> particles were added to the epoxy resin. 3. Nano particles / Epoxy mixture was placed in ultrasonic wave for homogeneous dispersion and then the mixture were placed in vacuum oven at 80 °C for 30 min. 3. Emulsification was carried out by adding deionizer with acute stirring at ambient temperature.
Inferences	· ILSS enhanced by 14% and 9% for Nano-SiO <sub>2</sub> modified sizing and Un-modified sizing composite panels. · Interfacial adhesion improved through sizing.

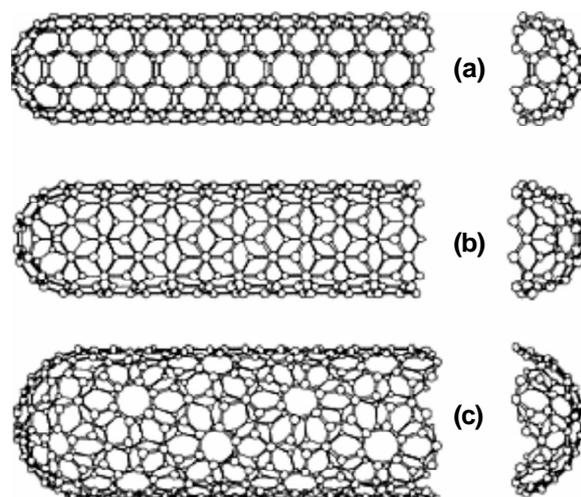
DDS - diaminodiphenyl sulfone, DWCNT - Double Walled Carbon Nano Tube, SCF - Short Carbon Fiber.

#### 4. NANOCOMPOSITES WITH NANOTUBES

CNT is considered the most promising source among the classes of nanofillers and applied as the modifiers of the traditional polymers in order to add multifunctional properties to the material matrix system [38-45]. CNTs are allotropes of carbon with a fullerene-related cylindrical nano structure which consist of graphene cylinders closed at either end with caps containing pentagonal rings. Figs. 3a-3c clearly show the types of CNT. Apart from types, the CNTs can be categorized as single-walled carbon nano tube (SWNT), double-walled carbon nano tube (DWNT), multi-walled carbon nano tube (MWNT), etc.

Recently, many of the studies had been carried out to focus mainly on the strength and stiffness of CNT reinforced composites [46,47], whereas only few dealt with the fracture behavior of CNT composite systems [48,49]. Based on the above facts, an overview of the CNT reinforced composite systems has been discussed in the subsequent paragraphs.

Davis et al. [50], analyzed the mechanical properties of a fiber reinforced epoxy composites using amine functionalized single wall carbon nano tubes (a-SWCNTs). It was evident from the study that the average strength and stiffness increased by 10% and 19%, respectively, for the carbon fiber epoxy composite laminate reinforced with 0.5 wt.% a-SWCNT. On the other hand, the average value of strength and stiffness were found to be 7% and 13%



**Fig. 3.** Types of Carbon Nanotube (CNT): (a) arm-chair nanotube, (b) zigzag nanotube and (c) chiral nanotube, [92].

over the neat material for 0.2 wt.% a-SWCNT reinforcement. Further, tension-tension cycling tests proved ductile type fracture for 0.2 wt.% and 0.5 wt.% a-SWCNT materials, whereas the fracture surface of neat material showed brittle-like fracture mode. Thus the improved fiber-matrix interfacial strength, due to functionalized carbon nano tubes reinforcements was found to be the primary reason for the improved durability of the composite laminate. A characteristic study on the compressibility of carbon woven fabrics with CNT/CNF material

matrix system was carried out by Lomov et al. [51]. Their test results showed poor compressibility of CNT/CNF grown on fibers and the researchers suggested a need for an optimization method over the current FRC- processing technologies. In continuity to the above work, Lomov et al. [52] conducted another study on compression resistance and hysteresis of carbon fiber tows with grown carbon nano tubes/nano fibers. The test results conformed substantial increase of the compression resistance of the yarns after the growth of CNT/CNF, associated with the addition of catalyst and thermal treatment were the promising reasons for an increase in the compression resistance of yarns. Jeffery Baur et al. [53] synthesized carbon nanotubes grown on high performance carbon fibers to test the tensile properties of the fibers. For the study, higher density multi-wall carbon nano tubes were grown on T650 and IM-7 carbon fibers by thermal chemical vapour deposition (CVD) process. Promising tensile properties were seen under thermally stable unsized fiber at appropriate growth conditions.

In an experimental study, an exploration of the inherent sensing and interfacial properties of carbon nano fiber and nano tube/epoxy composites was made by Joung-Man Park et al. [54]. Their investigation was carried out with filler content using electrical micro-mechanical tests. Inherent sensing of carbon nanotube/epoxy composite was found to be better than carbon nanofiber/epoxy composite. The mechanical properties and apparent modulus were also found to be significant for carbon nano tube/epoxy composite among three carbon nanomaterials chosen for study. The interlaminar properties of halloysite nanotubes filled carbon fiber-reinforced epoxy was studied by Jingshen Wu et al. [55], which revealed improvements in the interlaminar shear strength of around 25% obtained with 5% of halloysite nanotubes, significant improvements in the fracture toughness under mode-I and mode-II loadings were also noted by the addition of halloysite nanotubes. Furthermore, examination of the hybrid composite under SEM revealed non-uniform dispersion of halloysite nanotubes in the epoxy matrix.

Koziol et al. [56] synthesized the aligned carbon nanotube-polystyrene composites, which is prepared by in situ polymerization of stacked layers. In their study, styrene and benzoyl peroxide were used for the synthesis of polystyrene. Furthermore, the authors had employed an in-house CVD process to synthesis the multi-walled carbon nano tubes (MWNTs), in which ferrocene in toluene solution (6 wt.%) was used as a precursor of carbon and iron. The CNTs were grown on quartz substrate

in an argon atmosphere and finally the aligned MWNTs carpets exhibited the dimensions of ~60 nm (outer diameter) and ~10 nm (inner diameter) with the thickness of 0.4 nm. These aligned carbon nano tube-polystyrene composites possessed characteristic anisotropic electrical and thermal properties.

An analytical pullout model for inclined carbon nanotube was developed by Xiaodong He et al. [57] to assess the mechanical properties of CNTs reinforced composites. Their study revealed that the matrix compression effects mainly contribute to the de-bonding displacement and the maximum pullout increased with an original angle of inclination. On the other hand, the friction coefficient and the compression stress possessed to have a greater effect on the maximum pullout. Experimentation with Basalt fiber-epoxy laminates by functionalized MWCNTs was carried out by Wei et al., 2009. It was evident from their study that the dispersion of MWCNTs within the epoxy was improved by surface modification, resulted in significant improvements in composite mechanical properties as well as increased elastic modulus and strength, albeit lower than of the theoretical predictions due to the partial agglomeration and natural waviness of CNT.

Kevin L White and Hung-Jue Sue [59] had presented a simple, out-of-autoclave approach to enhance the delamination toughness of fiber-reinforced composites using epoxy thin film interlayer containing polyimide-12 (PA) particles and MWCNTs. Their study exhibited high fracture toughness for epoxy/PA interlayers due to the plastic deformation and crack bridging of spherical PA particles. Nevertheless additional phase attributed to facilitate MWCNT network stress redistribution within the resin-rich region. An attempt was made by Myung-Gon Kim et al. [60] to enhance the crack resistance of a carbon/epoxy composite by reinforcing CNTs into the resin formulation. In their study, the interfacial bonding between CNTs and epoxy resin were enhanced by conducting chemical surface treatment and amino-functionalization, which attributed to good interfacial bonding quality. The authors had noted improvements in interlaminar fracture toughness and transverse crack resistance at the cryogenic temperature (-150 °C) for the carbon/epoxy composite containing functionalized CNTs.

Cho et al. [61] studied the effects of epoxy matrix of carbon fiber/epoxy composites modified with MWCNTs to enhance the matrix dominated thermo mechanical properties of the composite. The authors had experimented that a pronounced improvement of composite properties was achieved with 0.5

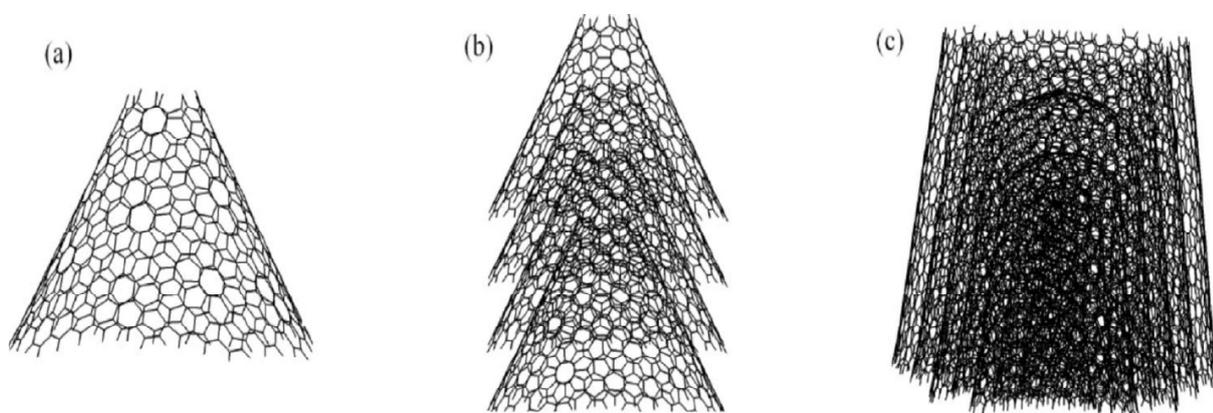
wt.% of MWCNTs irrespective of its length using block copolymer. In contrast, longer nanotubes had exhibited a higher enhancement of composites properties without using block copolymer. The tensile and the fracture characteristics of MWCNTs after surface modification, and moisture absorption of MWCNT/epoxy nanocomposites were investigated by Ji Hoom Lee et al. [62]. Their study had revealed that the moisture absorption phenomenon of epoxy could cause a decrease in mechanical properties, changes in internal stress conditions, and de-bonding due to the volume expansion between MWCNTs and the epoxy matrix. The effects of silane functionalization on the properties of carbon nanotube/ epoxy nanocomposites were studied by Peng Cheng Ma et al. [63]. Their results proved that the better dispersion of CNTs in epoxy could be achieved by grafting silane molecules on to the CNT surface, which extensively enhanced the mechanical and thermal properties as well as fracture resistance of nanocomposites with reduced electrical conductivity due to wrapping of CNTs with non-conductive silane molecules. An experimental investigation by Kim et al. [64] on the effects of silane modified carbon nanotubes on flexural and fracture behavior of modified CNT/epoxy/basalt composites showed ~10% and ~14% improvements in flexural modulus and strength, respectively. This may be due to enhanced dispersion and interfacial interaction between the silane modified CNTs and epoxy. An improvement in mechanical properties of CNTs deposited onto the carbon-fiber fabric using electrophoretic deposition had been noticed by Qi An et al. [65]. The authors had adopted recirculation, ultrasonicated, and ozonolysis system to efficiently prepare large volumes of stable MWCNT dispersions

that were well suited for electrophoretic deposition onto carbon fiber fabrics.

Grimmer and Dharan [66] had examined the delamination crack propagation phenomenon in glass-fiber composites with and without the addition of CNTs. Their tests revealed that the cyclic delamination crack propagation rates significantly reduced by the small fraction addition of MWCNTs, with an associated increase in both critical and sub-critical inter-laminar fracture toughness due to the shift in the fracture behavior of CNTs. Myung-Gon Kim et al. [67] had attempted to enhance the crack growth resistance of carbon/epoxy composites by reinforcing MWCNTs at cryogenic temperature. The authors had noticed promising results with fracture toughness and crack density at the cryogenic temperature by the addition of 0.2 wt.% and 0.7 wt.% of MWCNTs to the material matrix system. By using a digital speckle correlation method, an experimental study was conducted on the mechanical properties of CNT film by Ma et al. [68]. The researchers had found that the measured accuracy of the mechanical properties of thin film material is more reliable. An in-depth study of CNT growth on a commercially available woven alumina fiber was proposed by Yamamoto et al. [69]. Their study exemplified that by using a low cost and scalable catalyst deposition process, a uniform CNT growth can be achieved, which can be effectively used in integral armors with enhanced impact resistance.

## 5. NANOCOMPOSITES WITH NANOFIBERS

Carbon nanofibers (CNFs)/vapour grown carbon nanofibers (VGCNFs) are cylindrical nanostructures



**Fig. 4.** Three structural types of carbon nanofiber: (a) A single-shell nano cone with  $u = 30^\circ$ ; (b) A four nano cone-stacked CNF with each individual shell the same as in (a) and (c) A seven-shell CNF, with  $u = 10^\circ$ . Reprinted with permission from C. Wei and D. Srivastava // *Appl. Phys. Lett.* **85** (2004) 2208, (c) 2004 American Institute of Physics.

**Table 3.** % Decrease of fracture toughness.

Nano Clay	Wt.%	0.5%	1%	1%	1.5%	3%
	Name	Cloisite 93A	Cloisite 30B	RXG 70001	Cloisite 93A	Cloisite 93A
	% Increase	20%	40%	30%	46%	50%
	Ref.	[32]	[18]	[18]	[32]	[32]
Nano Particle	Wt.%	2%	3%	3%	10%	10%
	Name	Carbon Black	Carbon Black	Fullerene (Carbon 60)	CTBN Rubber particles	CSR Rubber particles
	% Increase	18%	23%	31%	48%	82%
	Ref.	[32]	[32]	[34]	[31]	[31]
Nano Tube	Wt.%	1%		2%	3% to 5%	5%
	Name	Silane treated CNT		HNT	HNT	CSCNT
	% Increase	40%		37%	50%	300%
	Ref.	[60]		[55]	[55]	[48]
Nano Fiber	Wt.%	1%	1%	1%	1%	2%
	Name	Polyester / GNF	CNF	VGCF	CNF	CNF
	% Increase	100%	35%	50%	100%	23%
	Ref.	[79]	[81]	[83]	[85]	[78]

CSCNT – Cup Stacked Carbon Nano Tube, HNT – Hallosite Nano Tube, CNF – Carbon Nano Fiber, GNF – Glass Nano Fiber, VGCF – Vapour Grown Carbon Fiber

**Table 4.** % Increase or decrease of ILSS.

Nano Clay	Wt.%	2%	4%	6%		
	Name	Cloisite 30B	Cloisite 30B	Cloisite 30B		
	% Decrease	11%	18%	14%		
	Ref.	[14]	[14]	[14]		
Nano Particle	Wt.%	0.3%				
	Name	Carbon Black				
	% Increase	9%				
	Ref.	[36]				
Nano Tube	Wt.%	0.3%	0.5%	1%	0.5% & 1%	5%
	Name	DWCNT	Short CNT	Short CNT	Long CNT	HNT
	% Increase	20%	11%	6%	13%	25%
	Ref.	[36]	[61]	[61]	[61]	[55]
Nano Fiber	Wt.%	0.69%	0.69%	1%	2.5%	2.5%
	Name	Unidirectional CNF	Quasi Isotropic CNF	A-CNF Sized	GMF	EGNF
	% Increase	15%	22%	10.01%	29.5%	35.3%
	Ref.	[87]	[87]	[82]	[77]	[77]

DWCNT – Double Walled CNT, GMF – Glass Microfiber Fabrics, EGNF – Electrospun Glass Nano Fiber, A-CNF – Amine functionalized CNF

with graphene levels organized as cone stacked, cups or plates. Interestingly, CNFs have the unassuming electrochemical properties and furthermore its incorporation into polymers is simpler because of its bigger fiber dimensions [70]. The qualitative pictures of three structural nanofibers are depicted in Figs. 4a-4c. The variation of functional properties

of CNF reinforced composites undertaken by various investigators are considerably elaborated in the following sections.

Bortz et al. [71] conducted an experimental study on an augmented fatigue performance and analyzed the cyclic loading conditions of all-carbon hierarchical fiber architecture. It had been evident from the

study that the modest stiffness and strength increased by 6-8% between the neat and CNF reinforced laminates. Furthermore, an increase in stiffness of CNFs was found due to the better matrix-bonding, which may be able to accept the strain energy transfer during elastic deformation. The fatigue tests disclosed that the mean fatigue life enhancement of 150-670% under fully compressive, tensile and tensile dominated loadings for CNF-reinforced composites. Further, outcomes from the constant life diagram proved that the mean power law fits of tension to be moderately additional damaging than the compression in neat laminates. Sohel Rana et al. [72] developed three-phase carbon/epoxy/CNF composites by dispersing vapour-grown carbon nano fibers in the carbon fabric reinforced epoxy matrix. The dispersion was cured with 15 phr of triethylene tetramine hardener at room temperature for 12 h followed by 80 °C for 2h as post curing. It was also observed that the uniform dispersion with few CNF cluster for 0.1% CNF and good CNF dispersion for 0.2% nonionic surfactant. However, surfactant concentration more than 0.2% showed deterioration of the epoxy matrix properties. Furthermore, a combination of ultrasonification and high-speed string was adapted for dispersing 0.5% CNF. Overall, the experimental results proved improved young's modulus, tensile strength, compressive modulus and strength by 37%, 50%, and 18%, respectively, for 0.5% CNF dispersion.

Paul Akangah et al. [73] investigated the effects of Nylon-66 nanofiber interleaving on the impact resistance of epoxy/carbon fiber composite laminates. Their study displayed increased laminate thickness and threshold impact force for polymer nanofabric interleaving of about 2.0% and 60%, respectively. On the other hand, the rate of impact damage growth rate reduced. Wee-Eong Teo and Seeram Ramakrishna [74], discussed succinctly the construction of nano composite system with five distinct levels using electrospun fibers. The five distinct levels are nano fiber composite core, nanofiber with a core and a shell layer, nanofiber surface modification, organization of nanofibers and finally incorporation of nanofibers composite in matrix. Their work extends to interpret the promise applications encompassing Health-tissue scaffold, environmental-water remedy, in defense-detection and detoxification.

An experimental investigation was carried out by Tong Lin et al. [75] to improve the toughness of carbon/epoxy composites by using interlayers of electrospun polyetherketone cardo (PEK-C) nano

fiber. The nanofibers with an average diameter of 450 nm, 750 nm, and 950 nm were electrospun. Test results demonstrated that the nanofiber with an average diameter of 950 nm offered an increased nanofiber interlayer thickness as a result enhanced mode I delamination fracture toughness and reduced flexure strength were noted. Hossain et al. [76] analyzed the mechanical properties of polyester matrix with infused carbon nanofiber. Analysis under SEM proved excellent dispersion for CNF-filled polyester, due to strong attractive fiber vander walls force. Results from flexural test, Quasi-static compression test and fracture analysis showed better strength and modulus. Hao Fong et al. [77] evolved hybrid multi-scale composites from glass microfiber fabrics and nanoepoxy resins containing electrospun glass nanofibers. Vacuum assisted was adapted to fabricate the composites. Mechanical properties such as interlaminar shear strength, flexural properties, impact absorption energy, and tensile properties were analyzed in the study. It was noted that up to 0.25 wt.% of Electrospun glass nanofibers (EGNs) or chopped Glass Micro fibers (GMFs) increased interlaminar shear strength and their values are noted to be 29.5% and 35.3%, respectively, whereas for epoxy resin that contained 0.5 wt.% of the above said fibers, the values of interlaminar shear strength degraded. The flexural properties, impact absorption energy and tensile properties too proved improvements in the respective properties up to 0.25 wt.% of EGNs or GMFs.

An enhancement in the mechanical properties of carbon nanofibers fixed epoxy and carbon fabric epoxy composites was noted by Yuanxin Zou et al. [78]. In their study the homogeneous mixture of the composites was produced by high-intensity ultrasonic liquid processor. The results proved significant improvements in the tensile and flexural strength and were noted to be 11% and 22.3%, respectively, for 2.0 wt.% carbon nanofiber filled epoxy composite. Kuang-Ting siao et al. [79] manufactured carbon nanofibers toughened polyester/glass fiber composites to study the interlaminar fracture properties. The dispersion and infusion of composites were done by vacuum assisted resin transfer molding. The experimental results proved enhanced mode-I delamination resistance for 1 wt.% carbon nanofiber toughened composites. El-Hajjar et al. [80], studied the effects of cellulose nanofiber and bio-based epoxy composite. Results from swelling of carbon nanofiber in water and epoxy showed reduction in porosity and permeability. Further an increased porosity led to lower the anticipated me-

chanical properties with higher reinforcement volumes. An experimental study of hierarchical carbon nanofibers/continuous carbon fiber reinforced composite [81] displayed significant improvements in tensile stiffness, strength, and toughness. Through the addition of 1 wt.% carbon nanofiber proved increase in the modest tensile stiffness and strength by 5% and 8%, respectively. However, the short beam shear strength did not see any improvement with carbon nanofiber addition. Bob Minaie et al. [82] characterized the mechanical properties of hierarchical polymer composites by multi scale reinforcement fabrics, which proved a significant increase in interlaminar shear strength and compressive strength by the addition of carbon nanofiber followed by difficulties such as an increase in viscosity and void formation. An analysis [83] was made for mode-I and mode-II interlaminar fracture toughness of carbon fiber reinforced plastic laminates and fiber reinforced plastic laminates, toughened by carbon nanofiber interlayer. In this study, the double cantilever beam test and end notch flexure tests were applied to evaluate the mode-I and mode-II fracture toughness, in which mode-I test failed 50% greater fracture toughness and mode-II confirms 2-3 times greater interlaminar fracture toughness for hybrid laminate than the base laminates.

Bond et al. [84] investigated the different interleave layer of damage suppression and control within glass fiber reinforced plastic composites. The thermoplastic film, thermoplastic particles chopped E-glass and aramid fibers, E-glass/epoxy pre-preg orthogonally aligned, thermostat adhesive particles and thermo sat adhesive film were different interleave layers used in their study. The interleaved inserts inclusion increased the interlaminar fracture toughness under mode-I loading. The interlaminar mode-I fracture behavior of doped carbon fiber reinforced polymer laminates was investigated by Kostopoulos et al. [85]. The carbon nanofibers and piezoelectric particles were used as dopants. The study revealed that 1% addition of carbon nano fiber as dopant resulted in 100% fracture energy, on the other hand, the addition of piezoelectric particles led to a reduction in fracture energy. In addition to this, the fracture process of the laminates was monitored by acoustic emission technique. Hannah Harel et al. [86] assessed the inherent properties of carbon fiber reinforced composites based on thermoplastic Polyimide composites, in which the reinforcement of vapour grown carbon fibers compensated the toughness loss of high crystallinity degree Brinson et al. [87] studied the multi scale rein-

forcement of carbon fiber reinforced plastics using carbon nano fibers. The enhancement of interfacial adhesion between the matrix and carbon fibers were noted for both triblock copolymer and carbon nanofibers. The modulus and strength were also found to be enhanced in the study.

An experimental study to advance the toughness of fiber reinforced polymer laminates doped with carbon nanofibers and piezoelectric particles was done by Kostopoulos et al. [88], in which the carbon nanofiber as dopants proved a tremendous increase in the fracture energy, whereas the reduced fracture toughness due to poor interfacial properties was noted for piezoelectric addition. Chun H. Wang et al., [89] had studied the phase morphology of electrospun poly (E-capolactones), polyvinylidene fluoride (PVF) and polyacrylonitrile (PAN) as an interlayer modifier to toughness carbon fibers/epoxy laminates. Among three nanofiber interlayer chosen for study, only poly E-capolactone showed better polymerization-induced phase separation with epoxy and proved better properties. Jinsong Li and Ruying Luo [90] had deliberated the consequences on mechanical properties of Carbon/Carbon (C/C) composites strengthened by carbon nanofiber. Experiments were conducted with plain carbon cloth of type HS of 3 K PAN based carbon fiber on C/C composites. The preforms were densified by utilizing the technique of isothermal chemical vapor infiltration (ICVI) by a flowing mixture with 13:1 of propane and nitrogen within the ICVI furnace at the temperature of 1100 °C. Outcomes verified vital enhancements in flexural strength, modulus and interlaminar shear strength by nearly 21.5%, 33.5%, and 40.7%, respectively, for 5 wt.% carbon nano fiber reinforcement, whereas on the other hand, reinforcement up to 20 wt.% of CNF proved degradation of structural properties of composite matrix laminates due to the cavities and holes inside the composite panels.

The tensile properties, flexural properties, fracture toughness, interlaminar shear strength (ILSS), glass transition properties, microstructure, etc., of various nanoclay, nanoparticle, nanotube, and nanofiber reinforced nanocomposites have been discussed. Among these properties, toughness and ILSS properties were consolidated in Tables 3 and 4, respectively. Both tables exhibited that the properties hold good for nano tube and nano fiber in comparison with the other two nano fillers. This trend might be due to the amazing thermal conductivity, electrical, and mechanical properties, and highest strength to weight ratio of any known material.

## 6. CONCLUDING REMARKS AND RECOMMENDATION

In this article, an endeavor has been made to present a review of representative journal publications covering trials conducted with the inclusion of nanoclays, nanoparticles, nanotubes, and nanofibers within the material matrix in the preceding few decades. Albeit the development of nano materials have afforded materials with superior properties, still there is an obligation to conduct more analysis to find out feasible, viable and dominant category of composite systems, that might inherently contribute to a wide range of industry and society as well. Based on the review conducted, it had been clearly found out that there may be a chance for agglomeration of nanomaterials inside matrix material due to improper dispersion that may result in stress concentration, which could be eluded by proper mixing through ultrasonic mixture, shear mixture, and mechanical mixture. In addition to these, three major conclusions have been drawn.

The first and foremost conclusion proved that the addition of nanofillers reduced the brittleness property of composite laminates. Moreover, much of the experimental studies had been targeted to enhance the tensile, flexural, compression, Inter-Intra laminar fracture toughness, impact strength, shear strength, stiffness, electrical, and thermal properties, chemical and corrosion resistance, etc., seldom few concentration on applications by using biodegradable natural resin.

The second conclusion to be drawn is that the analytical and simulation models for the experimental study should be developed so as to interpret the experimental results, which is adept to be useful to settle on the foremost acceptable applications.

The last and the third major conclusion emphasizes the need to develop composite systems with improved tribological properties, study on fatigue and creep resistance, study on degradation due to fire, hot/cold cycles. Since the presence of unavoidable micro/macro voids in the composite laminates throughout the fabricating process, which can magnificently result in the propagation of crack subjected to the continual loading process. Hence, an in depth evaluation of non destructive test methods is suggested. Apart from this, use of vacuum assisted technique to fabricate laminates could eliminate void issues to a greater extent.

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