



Evolution of Carbon Nanotubes, Their Methods, and Application as Reinforcements in Polymer Nanocomposites: A Review

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Abstract: The demand for increased performance in structural materials has drawn attention to the use of fiber materials as a means of reinforcement to provide structural integrity. Carbon nanotube (CNT) reinforced polymer nanocomposites have become the go-to materials due to their superior properties. CNTs possess a strength 10-100 times higher than steel yet are lighter in weight. Additionally, CNTs have a remarkable thermal stability of up to 2800°C in a vacuum, and an electrical conductivity of 10³ S/cm. It also has an electric-current-carrying capacity 1000 times higher than other materials and a thermal conductivity of around 1900 W m⁻¹ K⁻¹, which is almost double that of diamond. This article explores the potential of Carbon Nanotubes (CNTs) to reinforce structural composite materials, improve sensing, and enhance responsiveness. It also examines its structure and classification as single and multi-walled, its synthesis, including laser ablation methods, arc discharge methods, chemical vapor deposition methods, and spray pyrolysis. Additionally, it discusses the applications, structural benefits, and challenges of composite materials.

Keywords: Carbon nanotubes, multi-walled carbon nanotubes, single-walled carbon nanotubes, polymer composite

1. Introduction

A carbon nanotube, or CNT, is a cylindrical tube made from rolled-up 2D-graphene sheets. They are also known as 1D nanomaterials because they are a transitional material between 0-dimension fullerene and 2-dimension graphite [1]. In addition to being one-dimensional structures, CNTs have nanoscale diameters and lengths of up to 1mm, which explains the high aspect ratio of nanomaterials [2]. Due to their remarkable tensile strength, electrical conductivity, and thermal properties as a result of their high aspect ratio, large surface area, and strong carbon atom bonds [3], carbon nanotubes have enabled remarkable progress in composite fabrication as fillers and reinforcements. This progress was made possible by advances in nanotechnology. Known for their dimensional scale, carbon nanotubes (CNTs) have attracted much research attention within nanotechnology [4]. As previously stated, carbon nanotubes have an extremely high aspect ratio, which can range from 1000:1 to a record high of 2,500,000:1. They also have typical high strength, elasticity, and modulus, which makes them an extremely efficient addition to composite materials for the construction of higher strength materials with multifunctional properties [5, 6].

With all these compelling properties of carbon nanotubes, such as excellent mechanical, electrical, and physical properties, wear resistance, and surface finish, it's easy to identify them as a reinforcing phase for composite materials [7]. This interaction has greatly benefited composites with polymeric matrixes, resulting in better, more advanced materials. CNTs are also finding applications in cementitious composites, where they actively contribute to the strength of cement composites. Garg et al. [8] discussed the challenges traditional composite sandwich structures face, such as delamination, debonding, matrix-fiber failure, stress channeling effects, and inter-laminar surfaces, and the importance of nanomaterials in overcoming these challenges. Carbon nanomaterials provide promising solutions such as increased stiffness and strength due to their shorter bond length, limited grain boundary defects due to their small size, and strong C-C bonds that reduce the possibility of creep formation [9].

In this review, the structure and forms of carbon nanotubes, their synthesis, and common challenges in composite fabrication, such as dispersion in the matrix phase, as well as CNT applications and benefits as reinforcement and fillers in composite materials, are discussed.

2. History of Carbon Nanotubes (CNTs)

Carbon nanotubes have a long history, dating back to 1991, when they first appeared in the research and scientific community. Sumio Iijima, a renowned physicist, has been officially recognized as the first to clearly define the formation of carbon nanotubes, as well as their resulting potential and applications. Iijima [10] reported on the synthesis of carbon nanotubes using an arc-evaporation synthesis of fullerenes, which sparked a revolution in the science and application of nanometer-sized materials.

Given the accomplishments and recognition of the founder of carbon nanotubes, there is a great deal of interest in learning that reports on carbon nanotubes were published well before 1991. It is only right that we recognize some of these remarkable research scientists for their outstanding contributions to the body of science in the field of nanotechnology. Radushkevich and Lukyanovich conducted a study in 1952 that suggested the discovery of carbon nanotubes with diameters of 50 nm [11, 12]. A few years later, Roger Bacon developed the electric arc method of making carbon filaments. This could have already produced carbon nanotubes [13]. Morinobu Endo and colleagues, as well as John Abrahamson, made significant contributions to proving the existence of carbon nanotubes using vapor growth and arc discharge methods, respectively [14, 15].

Kroto, Smalley, and Curl accidentally discovered fullerenes in the years leading up to the 1990s, which helped them win the Nobel Prize in 1996 [16]. This resulted in the discovery of a plethora of carbon allotropes, which were previously dominated by graphite, diamond, and amorphous carbon. This was the pivotal discovery that led to Iijima's observation of needle-like materials during the arc-discharge synthesis of fullerenes [10]. And these needle-like materials evolved into what we now call carbon nanotubes (CNTs), marking a watershed moment in the evolution of carbon nanotube technology. The question of who discovered the nanotubes and when they were discovered is a contentious one. Nonetheless, many believe that Iijima's report on carbon nanotubes was critical in bringing the entire scientific community's attention to the possibility of carbon nanotubes in the future [17].

Following this period, there has been intense research and study conducted, which has enabled us to gain a better understanding of carbon nanotube structure, properties, synthesis, and applications in a wide variety of fields, such as microelectronics, composite materials, biomedical applications, and self-cleaning surfaces.

3. Structure of CNTs

Carbon is the precursor element for the synthesis of CNTs. Carbon is the chemical basis for life on Earth, according to [18]. The description was bolstered by scientific evidence, which revealed that carbon is the fourth most abundant element after hydrogen, helium, and oxygen. Carbon, it was also stated, forms the most organic compounds of any other element, with up to 10 million organic compounds, due to its unique diversity and polymer-forming ability. Carbon can be crystalline diamond films, nanoparticles or tubes, amorphous carbons, or any combination of the above [19].

Carbon nanotubes, like graphite, diamond, and fullerenes, are crystalline allotropes of carbon [20]. They are drawn on an infinite cylindrical surface with a regular hexagonal lattice structure, with the vertices representing the positions of

the carbon atoms. A relatively fixed carbon-carbon bond length creates rigidity around the carbon atom arrangement and cylinder diameter [19]. The bonding structure of a CNT is similar to that of graphite rather than diamond, which has sp^3 hybridization in the bonding structure, which accounts for their high strength because sp^2 strength is greater than sp^3 strength. Nanotube linking allows the formation of strong, infinite-length wires under high pressure or load by exchanging some sp^2 bonds for sp^3 bonds [21].

3.1 Classification of Carbon Nanotubes

In essence, carbon nanotubes are broadly classified into two categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).

3.2 Single-Walled Carbon Nanotubes (SWCNTs)

Single-walled carbon nanotubes (see Fig. 1) are cylindrical tubes made of seamless rolled-up graphene sheets that have been thinned to a single atom thickness on the walls. SWCNTs, like graphene, have properties that are significantly different from those of bulk carbon (e.g., graphite) [22, 23].

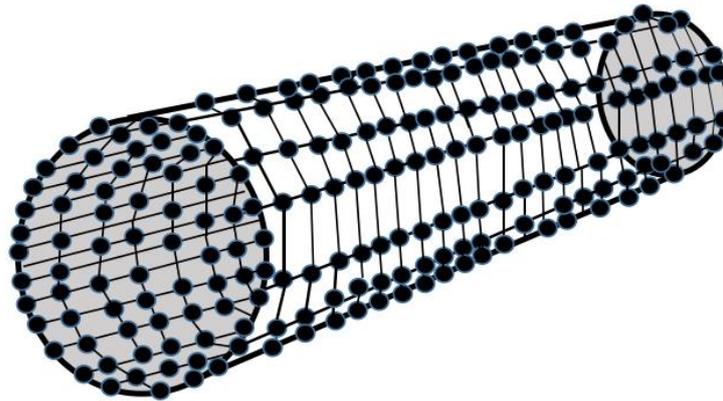


Fig. 1 - Single-walled carbon nanotubes. Figure adapted from [24]

Because of their carbon-carbon covalent bonds, small diameter, and high aspect ratio, they have unusual properties such as high tensile strength, resilience, and thermal conductivity. The mechanical properties of nanotubes vary greatly depending on their measurement axis (see Fig. 2), with the longitudinal axes producing extremely high Young's moduli (up to 1 TPa) and tensile strengths (up to 100 GPa). These values decrease by several orders of magnitude as you move along the radial axis.

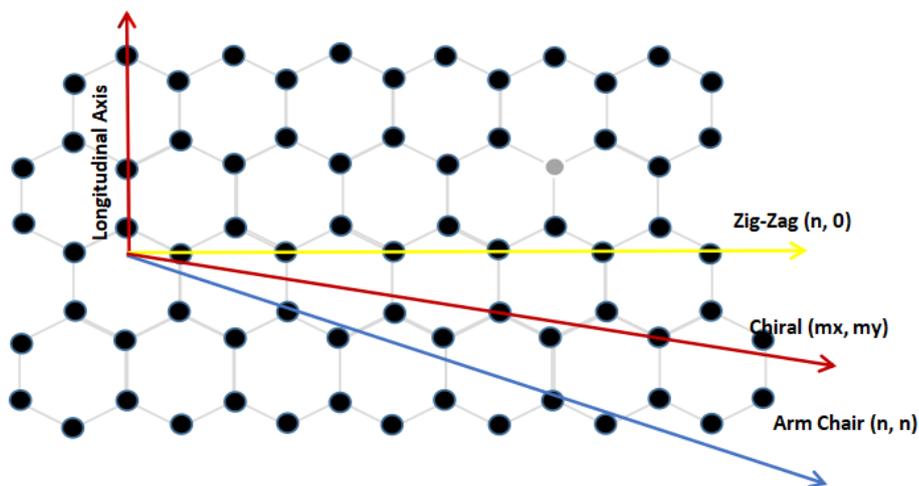


Fig. 2 - Single-walled carbon nanotubes configurations. Figure adapted from [24]

Single-walled carbon nanotubes come in three shapes: zigzag, armchair, and chiral. By following the pattern across the diameter of the tubes and analyzing their cross-sectional structure, zigzag, armchair, and chiral nanotubes can be identified [24].

3.3 Multi-Walled Carbon Nanotubes (MWCNTs)

As the name implies, multiwalled carbon nanotubes (see Fig. 3) are graphene sheets rolled into successive concentric layers with increasing diameters. While SWCNTs have a single layer of rolled graphene sheets, MWCNTs can have as many as two layers, up to an infinite number [25].

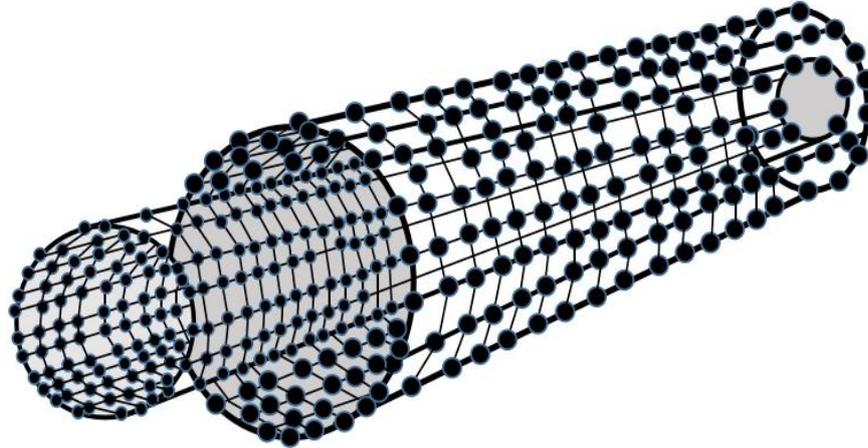


Fig. 3 - Multi-walled carbon nanotubes. Figure adapted from [26]

Typical MWNCT diameters range between 30 and 100 nm, significantly greater than those of single-walled nanotubes, which range between 0.5 and 2.0 nm. As the diameter increases, so does the size, which aids in the processing of MWCNTs as they progress into the micrometer scale. Although the large diameter reduces the aspect ratio, which can have a significant impact on mechanical properties, MWCNTs can be produced in large quantities using simpler processing techniques at a lower cost, which explains their growing commercial acceptance [26]. See Table 1 for a summary of the properties of SWCNTs and MWCNTs.

Table 1 - Summary of SWCNTs and MWCNTs

SWCNTs	MWCNTs	References
Contains a single layer of graphene sheets.	Multiple layers of graphene sheets.	[24]
It is easily twisted, tweak-able, and malleable.	Because of the bulk structure containing multiple graphene layers, it cannot be easily twisted.	[27]
Catalyst is often required for synthesis.	Can be produce without catalyst.	[28]
Simple structure.	Structure is complex and rigid.	[27]
Structural models: Zigzag, Chiral, and Armchair.	Structural models: Russian Doll and Parchment.	[29]
Diameter ranges from 0.5 - 2.0 nm.	Diameter is in the range of 30 - 100 nm.	[26]
Bulk synthesis is difficult.	Bulk synthesis is easy.	[30]
High aspect ratio.	Lower aspect ratio to SWCNTs.	[25]

4. Synthesis of Carbon Nanotubes

This distinct class of materials is an excellent example of novel nanostructures produced by bottom-chemical synthesis methods [31]. Arc discharge, laser ablation, chemical vapor deposition, and the fast-emerging synthesis method for commercial-scale production via spray pyrolysis are the most fundamental nanotube formation techniques.

4.1 Laser Ablation Method

Laser ablation (as depicted in Fig. 4) gained popularity when it was first used to synthesize clustered fullerenes in the gas phase [16]. This method of CNT synthesis focuses on the vaporization of a metal graphite target in an inert atmosphere using a laser as the energy source [1, 12, 16]. CNTs are recovered after vaporization via a condensation process in a carrier gas stream. Because vaporization occurs at extremely high temperatures, up to thousands of degrees Celsius, a significant amount of energy is required [31, 32]. This method produces nearly pristine nanotubes. According to Wikipedia contributors [21], the synthesis process is energy-intensive and results in the formation of by-product impurities, which is a major drawback considering the requirement for high-purity CNTs.

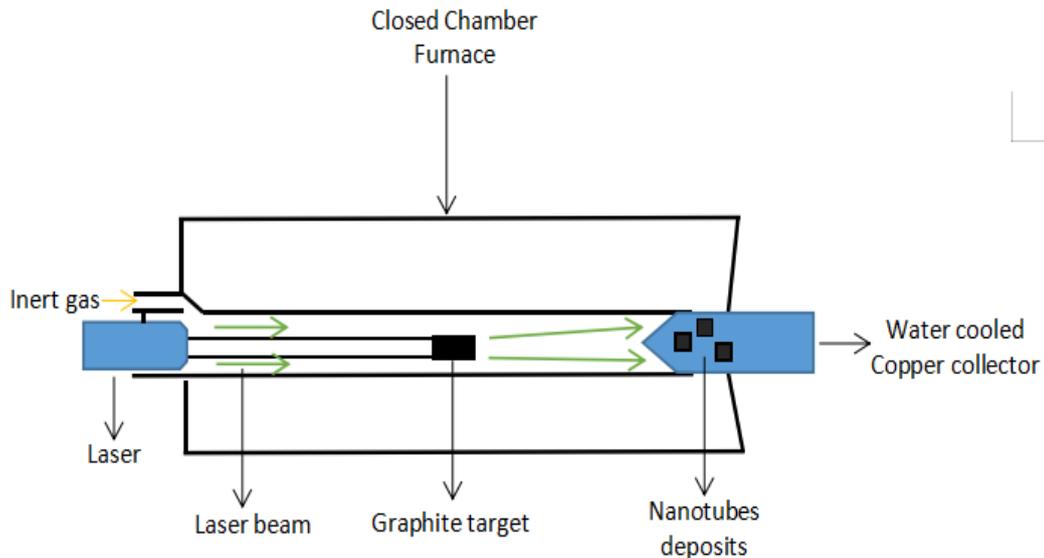


Fig. 4 - Oven laser-vaporization apparatus. Figure adapted from [33]

Early experiments revealed that laser beam vaporization of graphite primarily produces MWCNTs. Using temperature as a yield and quality indicator, all nanotubes were discovered to be defect-free at temperatures as high as 1200 degrees Celsius [33]. SWCNTs can also be made by adding a small amount of transition metal to graphite targets, but this results in low-yield SWCNTs and impure nanotubes because the graphite target becomes metallic-rich. At high oven temperatures, however, two targets can be used for high-yield SWCNTs: graphite and metallic alloy targets placed front-facing each other and irradiated simultaneously [28]. Furthermore, the yield varies greatly between SWCNTs depending on the metal catalyst used. Large amounts of SWCNTs have been reported to be obtained using a Co- and Ni-based mixture, such as Ni/Co [33].

4.2 Arc Discharge Method

The arc discharge method (as depicted in Fig. 5), like the laser beam method, vaporizes solid-state carbon in the form of graphene at high temperatures. This synthesis method can also produce high-quality nanotubes. The main difference is that instead of a laser beam, direct electric current (DC) is used [34]. Iijima used the arc technique to investigate fullerene molecules during the discovery of carbon nanotubes in 1991, so it is a widely used technique [32]. Two graphite electrodes are used in a high-pressure inert gas atmosphere at temperatures exceeding 3000 degrees Celsius. This condition allows an electric arc to form between two closely spaced graphite particles. Because of the high temperature and charged environment, the graphite electrode sublimates or vaporizes [35].

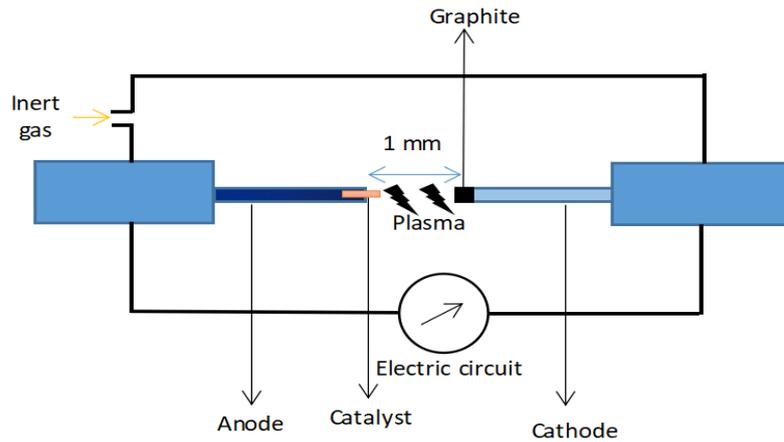


Fig. 5 - Electric arc discharge synthesis of Carbon Nanotubes. Figure adapted from [34, 35]

The anode, which contains metal catalysts such as Fe, Co, and Pt, and the cathode, which bears pure graphite, are separated by approximately 1 mm [36]. Direct current vaporizes the graphite target, leaving a deposit on the cathode identified as CNTs. The arc technique has been used to produce both SWCNTs and MWCNTs in the presence of hydrogen and helium gases, respectively. According to Iijima [37] and Ribeiro et al. [38], the latter produces MWCNTs with high crystallinity and inter-layer spacing of 0.34 nm. In addition to CNTs, this process produces carbon soot that contains fullerene molecules, amorphous carbon nanoparticles, and amorphous nanofibers, which reduces yield. However, in comparison to laser ablation, this method is less expensive, albeit with a lower yield [39]. Entangled nanotubes and associated byproducts are reportedly produced by arc discharge and laser beam methods, limiting their use in electronic product applications [40]. Generally, both methods experience drawbacks in terms of large-scale production, which hinders their application for commercial purposes.

4.3 Chemical Vapor Deposition Method

The "CVD" method, as it is also known, differs significantly from laser beam or arc discharge synthesis in that the carbon source is derived from hydrocarbon gases such as methane, ethane, acetylene, or benzene [41]. The synthesis occurs in a reaction chamber with a metal catalyst acting as "seeds" to promote growth at specific sites or locations with desirable orientation on substrate surfaces under mild conditions of temperature and pressure as low as 700–900 degrees Celsius and one atmosphere, respectively [34, 42].

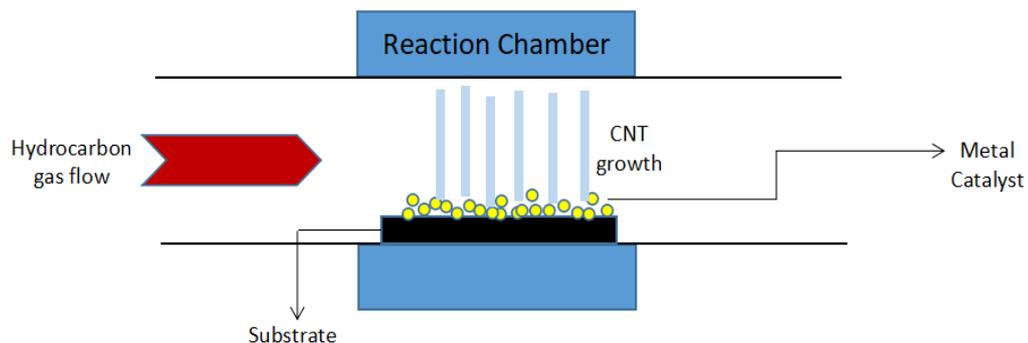


Fig. 6 - Chemical vapor deposition synthesis of Carbon Nanotubes. Figure adapted from [41]

This method addresses issues raised by the previous methods, such as large-scale production [30], a high degree of orientation (i.e., untangled vertically aligned CNTs), and controllable site selectivity on catalytic substrates [31]. As a result, this is a low-cost, high-yielding, and simple-to-control method that provides the potential for upscaling to achieve large-scale production.

4.4 Spray Pyrolysis Method

The spray pyrolysis method is similar to CVD synthesis (see Table 2 for other CNT synthesis methods and their corresponding methods), but the main difference is the simultaneous pyrolysis reaction and deposition of carbon

nanotubes on the substrate [43]. Garzon-Roman et al. [44] used ultrasonic spray pyrolysis with a solution of toluene as the carbon precursor and ferrocene as the metal catalyst to synthesize MWCNTs on porous silicon as a substrate to form a hybrid structure. Casanova et al. [45] reported the spray pyrolysis of ferrocene/benzene using argon to produce carbon/Fe nanoparticles, as a result of inert gas flow into the reaction chamber. Furthermore, the Fe displacement inside the carbon structure was said to straighten the carbon chains by correcting misalignment in the carbon walls. As a result, CNTs produced by spray pyrolysis have a high degree of alignment on a variety of substrates in addition to having a high aspect ratio and crystallinity. These substrates include conventional steel, ceramics, and other materials.

Furthermore, one of the many advantages of this method is not only its low cost when compared to other synthesis methods but also its ability to scale up to meet large commercial productions. Welch [46], for example, investigated the growth of carbon nanotube farms, also known as "CNF," and discovered that carbon atoms from the precursor carbon source were attached to the catalyst on the substrate surface, producing either single-walled or multi-walled nanotubes. Furthermore, when the catalysts are tightly packed on the substrate, CNTs can grow indefinitely to form a forest of carbon nanotubes. Other advantages include a 10-minute synthesis time, simple technical apparatus, and high efficiency and yields [45].

Precursor concentration, catalyst interaction, injection rate and duration, carrier gas flow rate, substrate surface, growth temperature, and the composition of gases inside the reactor are all factors that influence CNT growth. SWCNTs benefit from small catalyst particle diameters, whereas MWCNTs benefit from large catalyst particle diameters [47, 48].

Table 2 - Summary of CNT synthesis/methods

Synthesis	Method	Conditions	Catalyst	Product Quality	References
Laser Ablation	Laser beam vaporization	T=1200°C P ~ 1atm	Co, Ni, Pt	> 75 % Relatively high purity	[12, 49]
Electric Arc Discharge	Electrical discharge/Plasma formation	T=3000°C P=1-2atm I=100-200A Volt=20-30V	Fe, Co, Pt	>70 % Relatively high purity	[35, 50]
Chemical Vapor Deposition	Vapor Deposition	T=700-900°C P=1atm	Fe, Co	>80% High purity	[34, 42]
Spray Pyrolysis	Pyrolysis and Vapour Deposition	T=780°C P=1atm	Ferrocene	>80% High purity	[44]

5. Applications of Carbon Nanotubes: Reinforcement

Carbon nanotubes have found expression in their diverse utilization in a variety of applications, some of the notable mentions include hydrogen storage, solar (photovoltaic) cells, biomedicine (drug delivery, tissue engineering, and scaffold engineering), semiconductors, reinforced nanocomposites, polymers, and so on [51]. The scope of this work shall be limited to carbon nanotubes and their application as reinforcements in polymer nanocomposites.

5.1 Fiber-Reinforced Composite Theory

Fiber-reinforced composites, or FRCs, are the most common composite materials, according to [52]. These fiber materials can provide stiffness and strength to soft polymer matrices due to their small cross-sectional area. These materials' improved properties can match those of steel and metals while weighing only one-third as much, making them ideal for lightweight structural applications.

As a composite material, FRC is composed of two distinct and dissimilar materials: fiber and a polymer matrix. FRC consists of two phases: the polymer matrix, a continuous phase that binds the composites together, shields them, and transfers stress to the other phase; and the fiber, a dispersion phase that gives the composite structural support.

To adequately utilize FRC, engineers must know its physical and structural properties due to its structural and physical variety. Matrix and fiber volume, fiber length, length, orientation, morphology, and cross-section are physical and structural considerations to take into account. Any modification in these parameters can have a significant impact on both the material's mechanical and behavioral characteristics. According to Hsissou [53] and Vassilopoulos [52], the type of polymer matrix and the type of fiber or class have an impact on the matrix and fiber constituents.

5.2 Polymer Nanocomposites

Polymer nanocomposite materials, like bulk composite materials at the macro level, are composed of a matrix-supporting polymer phase, but the reinforcement or fillers are nanometers in size. Researchers and scientists have been intrigued by the number of varieties nanomaterials can bring to composite materials. As a result, their small size led to a lightweight material, high surface-to-volume ratio, high stiffness and strength, and being less brittle and susceptible to abrasion, wear, and tear, and general failure since their emergence [54]. Based on the available matrix classifications, this study will be limited to polymer matrix-based nanocomposites, with a focus on polymer/CNT nanocomposites.

5.3 Carbon Nanotubes as Reinforcement in Polymer Nanocomposites

CNT structure reveals Van der Waals forces between carbon atoms and weak inter-planar interactions of graphene sheets, indicating how closely packed CNTs are [55]. This is visible in the tightly packed nature and aggregation of CNTs, which is responsible for their size, shape, and surface area. Although they have become an essential building block in the formation of high-performance polymer nanocomposites [56], aggregation must be overcome to achieve and exploit this potential [57].

Furthermore, using a high proportion of CNTs as fillers in nanocomposites should improve their mechanical properties. Zhang [58], on the other hand, argues that this is not the case. In contrast to increased nanomaterial addition to achieve increased mechanical properties, it has been reported that a small weight percentage addition can significantly increase mechanical properties [59]. Agglomeration occurs with high CNT loading, interfering with filler matrix dispersion and distribution. It also creates defect sites, which reduce the ability of the reinforcing phase to transfer load, implying a decrease in mechanical properties. As a result, determining the microstructure and properties that will facilitate CNT controlled-particle distribution and dispersion within the matrix requires careful consideration of the processing route and fabrication technique used [60].

5.4 Nanocomposites Processing and Fabrication

To achieve a homogeneous matrix, and to eliminate the possibilities of agglomeration formation and insufficient interfacial adhesion of CNTs to the polymer matrix, modification of the CNTs needs to be carried out. Because the modification of CNTs (see Fig. 7) results in the creation of additional functionality, this process is also known as "CNT functionalization" (see Table 3). Before composite fabrication, functionalization is frequently used to ensure smooth, untangled [61], highly oriented nanotubes with proper distribution, alignment, and dispersion within the polymer matrix. This increases compatibility and solubility within the host material [62, 63]. CNTs can be covalently or non-covalently functionalized to improve their compatibility and solubility.

Covalent functionalization, also known as chemical treatment, modifies CNTs by adding a functional group to a defect site or the side wall of the nanotubes. It entails the purification of carboxylic groups via oxidation [64], while simultaneously opening the CNT endcaps, allowing direct bonding, and increasing functionality such as adhesion and dispersion within the matrix [65]. On the other hand, the π - π bond attracts and binds external guest molecules to the side walls of CNTs, resulting in non-covalent functionalization [64]. It can also be referred to as the physical or mechanical treatment of CNT. This ability to form an extended π -system takes advantage of the adsorption of adsorbates on the CNT surface without necessarily disturbing the π structure, hence, preservation of the properties of the CNT. The mechanism is characterized by the interaction between the hydrophobic parts of the adsorbate with the side walls of the CNT as a result of the Van der Waals force [66]. The presence of a van der Waals interaction poses a drawback in terms of the binding forces of the bound/grafted molecule and the side wall, which are identified as weak forces [67]. Fig. 7 gives a vivid description of functionalization and the different methods to achieve it.

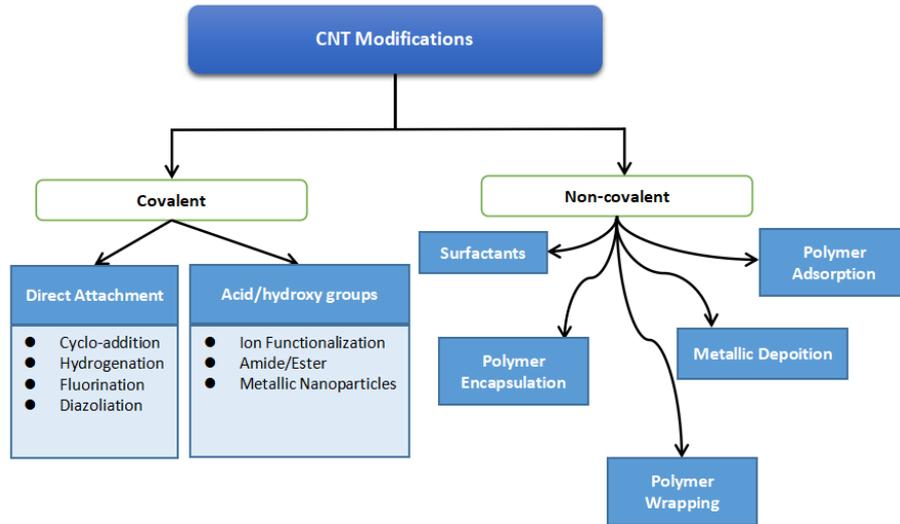


Fig. 7 - Approaches to CNT modification via functionalization. Figure adapted from [61-63]

Table 3 - Summary of CNT functionalization

S/N	Method	Conditions	Additives	Properties	References
1	Covalent/Chemical	T=140°C P=1atm Time=15mins	Sulfuric Acid, Nitric Acid	30% increase in tensile and flexural strength, 300% increase in Young’s modulus (at 60 wt% CNT)	[68, 69]
2	Non-covalent/ Physical/ Mechanical	Inert atmosphere Sonication (60% amplitude (~60W, cycles of 5s and 3s))	Surfactants (eg. sodium dodecyl sulphate (SDS), cationic cetyl trimethyl ammonium bromide (CTAB))	48% increase in tensile strength, 40% increase in storage modulus, elongation at break increase by 53%	[70-72]

5.5 CNT/Polymer Composite Fabrication

The three primary processing techniques to achieve efficient dispersion are dispersion, de-agglomeration, and solubility. These processing techniques include melt mixing, solution processing, and in-situ polymerization [73], as mentioned below.

5.5.1 Melt Mixing

This alternative method for insoluble polymers is frequently used to create thermoplastic polymer blends and composites. It also offers a relatively simple CNT/polymer composite fabrication method that is highly compatible with existing polymer processing methods such as injection, extrusion, and compression molding, opening up new opportunities for large-scale production [74]. The thermoplastic polymer pellets used in this process can melt (see Fig. 8) when heated to high temperatures. Shear stress blending and elevated temperatures in the compounding process achieve high dispersion of the CNT fillers as well as agglomeration breakup. In general, this is regarded as a preferred method for composite fabrication in a variety of scenarios due to the reduction of agglomeration formation as a result of shearing [75].

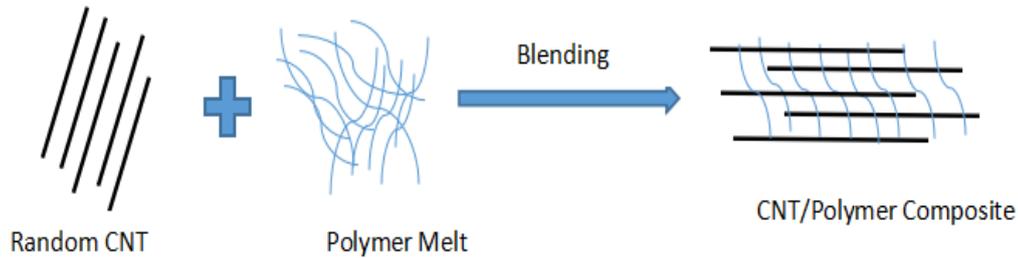


Fig. 8 - Steps in Melt mixing of CNT/Polymer Composite. Figure adapted from [74]

One significant challenge that could be encountered is the possibility of nanotube damage caused by high shear mixing or ultrasonication at high frequency and rotating speed [76]. Despite this, reports of MWCNTs-Poly (methyl methacrylate) (PMMA) composites have demonstrated that they are well dispersed, have no visible or apparent breakage, and have a high storage modulus as a result of melt mixing [77].

5.5.2 In Solution Processing

As the name implies, processing occurs in a solution of a soluble polymer solvent, such as toluene, dimethyl formamide (DMF), tetrahydrofuran (THF), sodium dodecyl sulfate, and others [78]. The main difference between melt mixing and dispersion is the dispersion of the CNT in a suitable solvent, which results in three major steps: CNT dispersion in solvent, insertion and mixing with polymer melt/solution, and finally recovery of the CNT/polymer composite by evaporating a large amount of the solvent. The loss of solvent and the energy used to achieve this will limit its mass production and adoption. This processing method, however, is effective in the production of composites with homogeneous CNT distribution and is widely used in the production of composite films [75]. Thermosetting polymer materials are utilized in solution processing, with reports from Mani and Sharma [79] on the use of epoxy resin via this method to produce CNT/epoxy composites.

5.5.3 In-Situ Polymerization

It can be otherwise seen as reaction processing, which is simply the polymerization reaction between a CNT and a monomer under specified controlled conditions [58]. This has proven to be an efficient method for the uniform dispersion of CNTs in thermosetting polymers and the formation of strong interfacial bonds as a result of covalent bonding that enhances mechanical properties [80]. Primarily, for thermosetting polymers, such as epoxy, an initiator is added to facilitate curing, leading to faster polymerization, whereas for thermoplastics, initiators may or may not be added, but a simple increase in temperature can suffice to facilitate the polymerization reaction. An impressive result in tensile strength and ultimate strain from in-situ polymerization processing was seen in the preparation of surfactant-coated CNT/epoxy resin with polyamide as the curing agent [81]. Generally, thermally unstable and insoluble polymers that are not easily processed by either melt mixing or in-solution processing are processed efficiently using in-situ polymerization.

5.6 Mechanical Properties of CNT/Polymer Nanocomposites

An overview of CNTs as reinforcement in several polymer nanocomposites and their fabrication methods and mechanical properties are summarized in Table 4 below.

Table 4 - CNT/Polymer Nanocomposites, fabrication, and mechanical properties

Composite	Filler Content	Fabrication Technique	Strength (MPa)	Modulus (GPa)	References
CNT/Polypropylene	14-16 wt%	Melt mixing + extrusion	45-50	0.4	[82, 83]
CNT/Epoxy	0.4 wt%	Melt mixing + sonication	46	2.0	[84]
CNT/PMMA	4-6 wt%	Solution mixing	29-31	1.2-1.4	[83, 85]
CNT/PE-UHMW	10 wt%	Solution mixing + sintering	20-24	0.3	[86, 83]

5.7 CNT/Polymer Composites: Current State of Development

In Kirmani et al. [87], shear mixing was used to investigate CNT dispersion in polypropylene. It was reported that there was a significant change in properties, which led to advancements in thermal, electrical, and mechanical properties.

Furthermore, at low CNT loadings, the elastic modulus increased slightly and the tensile strength decreased slightly. However, as the concentration/loading increased, the stiffness and strength properties of the CNT/polypropylene composite also improved.

Neptun et al. [88] investigated an impressive new route for nanocomposites processing using a powder-based processing route. It was reported to be effective in the production of thermosetting nanocomposites with CNT filler loading concentrations of up to 20 wt% and 13.6 vol%. Shear mixing was also used to ensure a uniform filler distribution in the polymer matrix, even at the highest loading. It was also stated that the flow distance was reduced during consolidation to minimize agglomeration, allowing for a well-percolated CNT network, which was responsible for the increased electrical and conductive properties. Although the porosity increased by 2%, the modulus and strength increased, yielding mechanical properties of 5.4 GPa Young's Modulus, 90 MPa, and 2.5 yield strength and strain. Filler quality, of which longer, straighter, and higher quality CNTs should be used for optimum output, was one of the limitations encountered. Furthermore, powder particle size was found to be critical in achieving proper consolidation, which impacts composite properties and performance; thus, reducing and narrowing the distribution of powder particle size was recommended.

Because of these exceptional properties, the structural capacity of polymer nanocomposites was tested in a variety of applications, including high-impact velocity bulletproof tests for defense applications. Bullet-proof applications commonly use para-aramid and UHMWPE fibers, but nanomaterials are being extensively explored as nanofillers in polymer and fiber-based polymer nanocomposites for improved mechanical properties, energy absorption capacity, and/or impact resistance, according to Wu et al. [2]. A significant increase in performance-to-weight ratio and a decrease in trauma could be achieved by incorporating nanomaterials into ballistic materials.

Njuguna and Pieliowski [89] used advanced microscopic and spectroscopic techniques to characterize CNT/polymer nanocomposites at the microscale level, including Atomic Force Microscopy (AFM), Raman spectroscopy, Scanning Electron Microscopy (SEM), X-ray diffraction, and others. It was concluded that proper modeling at the micro and nanoscale levels allows engineers, scientists, and manufacturers to tailor polymer nanocomposites' requirements and behaviors, as well as provide insight into knowledge at the molecular level, providing a better chance for future developments, which would, in turn, improve fabrication procedures, modeling, and properties for various applications such as aerospace.

6. Conclusion and Future Perspectives

An outlook on carbon nanotube evolution and entry into the spotlight of innovative science and engineering, particularly in polymer composite modification and enhancement, calls for even more research into seemingly limitless applications. Researchers are inadvertently reducing the cost of conventional synthesis methods by generating carbon nanotubes (CNTs) from recycled plastic waste and agrowaste. Furthermore, carbon nanotubes are being used as reinforcement fillers in sensor and detection materials, whether through thermal or electrical means, and as self-healing materials that can be used for biomaterial applications. Polymer nanocomposite membranes are also used in filtration, denture formation, bone repair, and other applications. Carbon nanotubes, in fact, have altered the landscape of materials science, opening up a curiously endless potential in engineering and materials.

The use of carbon nanotubes in polymer matrices has shown that they have great potential for modifying matrix properties. Dispersion, defect density, chirality, aspect ratio, interfacial adhesion, and purity are all determinants that influence the incorporation of CNTs into nanocomposites. Researchers have done in-depth studies to enhance the characteristics of carbon nanotubes and their production techniques. The primary hurdle in utilizing carbon nanotubes to their fullest capacity is achieving even dispersion to optimize the surface area available for loading and transferring between the filler and matrix. The use of functionalization in nanotubes can increase dispersion and stress transfer, but further studies are necessary in order to keep the intrinsic characteristics of carbon nanotubes intact. Three key techniques are used in the production procedure to disperse the carbon nanotubes in the polymer matrix: solution processing, in-situ polymerization, and melt mixing. Producing higher-grade composites can be achieved through solution processing, while melt compounding is simpler and allows for greater production capacity. In-situ polymerization has also been successful in creating mixtures of polymers and CNT nanocomposites. The effectiveness of the processing approach has a direct influence on the efficiency of the composite. The incorporation of in-situ polymerization, which creates covalent bonds between the CNT and the polymer matrix, has seen the greatest enhancements in the mechanical properties of the polymer matrix. Despite the fact that polymer and CNT nanocomposites offer a notable advantage of increased electrical conductivity of the polymer material when CNTs are present, even at low carbon nanotube loading, this does have an adverse effect on the electrical properties of the composite. These composites are frequently employed as a low-cost shield against electrostatic discharge and electromagnetic interference due to their lightweight nature. Carbon nanotubes can also modify the thermal attributes of a polymer matrix, including the melting, thermal decomposition, and glass transition temperatures, as well as the percentage crystallinity and crystallization rate, when used as a nucleating agent. As the crystallization rate and amount of crystallinity increase, the mechanical and processing characteristics of carbon nanotubes in polymer composites improve significantly. Therefore, carbon nanotubes make an ideal filler for polymer composites, yet there are still obstacles that must be surmounted in order to take advantage of the remarkable properties of polymer nanocomposites with carbon nanotubes.

Conflict of Interests

The authors confirm not having any affiliations or involvements with any organization or entity that is financially or non-financially interested in the subject matter or materials discussed.

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