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Dispersion and Functionalization: Carbon nanotubes in polymer-based Nanocomposites

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ABSTRACT

The potential for extraordinary mechanical qualities and multifunctional traits in carbon nanotubes (CNTs) is exciting. The increased demand for CNT applications has prompted researchers to work tirelessly on dispersal and functionalization methods. For carbon nanotubes (CNTs) to be used as an efficient reinforcement in polymer nanocomposites, their dispersion and interfacial adherence to the polymer matrix must be ensured. Specifically, this study discusses (i) the concepts and methodologies for CNT dispersion and functionalization, and (ii) the impacts of CNT dispersion and functionalization on the characteristics of CNT/polymer nanocomposites, reviewing the present state of knowledge on CNTs and CNT/polymer nanocomposites. CNT/polymer nanocomposites, including their production methods and prospective uses, are also discussed. **Keywords: CNT, nanotubes, polymer, nanocomposite, carbon nanotubes**

I. INTRODUCTION TO CNTs

When compared to other carbon materials like graphite, diamond, and fullerenes (C60, C70, etc.), CNTs are unique because they are onedimensional carbon compounds with an aspect ratio larger than 1000. They have nanometer-scale dimensions and may be visualised as cylinders made of rolled-up graphite planes. A fullerene hemisphere caps off at least one end of the cylinder-shaped nanotube.

Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [2-5] exist because of differences in CNT synthesis methods. While a single graphene sheet is rolled up into a seamless cylinder to form a single-walled carbon nanotube (SWCNT) (Fig. 1A), multi-walled carbon nanotubes (MWNTs) consist of two or more concentric cylindrical shells of graphene sheets (Fig. 1B) coaxially arranged around a central hollow core and held together by van der Waals forces between neighboring layers.

CNTs may be armchair, zigzag, or chiral, depending on the rolling angle of the graphene sheet. The chiral vector Ch = na1 + ma2 (Fig. 2) defines the chirality of a tube, where n and m are integers representing the number of steps along the a1 and a2 unit vectors of the hexagonal lattice, respectively [3,4]. The three possible arrangements of carbon

atoms around the nanotube's circumference are designated by the (n, m) notation. "Armchair" nanotubes are what you get if you set n = m. Nanotubes are referred to be 'zigzags" if m equals zero. If not, we refer to them as "chiral." The characteristics of nanotubes electrical are profoundly affected by their chirality. To determine if a given (n, m) nanotube is metallic or semiconductor, we check to see whether (2n + m) is a multiple of 3. Predicting the physical properties of MWCNTs is more difficult than those of SWCNTs since each MWCNT comprises many layers of graphene, each of which might have a distinct chirality.

Properties of CNT, all the chemical bonds in CNTs are sp2 carbon-carbon bonds. CNTs' extraordinary mechanical qualities are the result of their bonding structure, which is stronger than the sp3 bonds found in diamond. It is well-established that CNTs have unrivalled mechanical properties [5-7].

There is currently no agreement on the precise mechanical characteristics of CNTs; nonetheless, both theory and experiment have shown their extraordinary strength and elasticity, with Young's modulus values as high as 1.2 TPa and tensile strengths in the range of 50-200 GPa [6]. Because of these properties, CNTs are the stiffest and strongest materials known to man.



Figure No. 1: TEM images of different CNTs (A: SWCNTs; B: MWCNTs with different layers of 5, 2 and 7).



Figure No. 2: Schematic diagram showing how a hexagonal sheet of graphene is rolled to form a CNT with different chirality's (A: armchair; B: zigzag; C: chiral).

II. Dispersion of CNTs

There has been a lot of work put into developing CNT/polymer composites for use in functional and structural applications [4,9,10]. Despite a decade of study, the full potential of using CNTs as reinforcements has not been realized due to issues with dispersal of entangled CNT during processing and inadequate interfacial contact between CNTs and polymer matrix. Because of their nanometer-scale tiny diameter and high aspect ratio (>1000), CNTs provide a unique dispersion challenge compared to more traditional fillers like spherical particles and carbon fibres. In addition, commercial CNTs are often provided in highly tangled bundles, which has inherent distribution challenges.

| | Description | | | |
|--|--|---------------------------------|-------------------|--------------------------|
| Filler | Average dimension of filler | Density (g/cm ³) | N ^a | Sp |
| Al ₂ O ₃ particle | 100 μ m in diameter (d) | 4.0 | 1.9 | $S = \pi d^2$ |
| Carbon fiber | 5 μ m in diameter (d) × 200 μ m in length (l) | 2.25 | 255 | S = πdl + πd²/2 |
| GNP | 45 μm in length (square, l), 7.5 nm in thickness (t) | 2.2 | $6.58 	imes 10^4$ | $S = 4l^2 + 2lt$ |
| CNT | 12 nm in diameter (d) \times 20 μ m in length (l) | 1.8 | 4.42×10^8 | $S = \pi dl + \pi d^2/2$ |

^a N: number of particles in 1.0 mm³ with 0.1 vol.% filler content.

^b S: surface area of individual particles.

Table No. 1: Dimension and corresponding number of particles in composites for different fillers

size and quantity of particles corresponding to a homogeneous filler volume fraction of 0.1% in a 1.0mm3 cube composite of frequently used fillers, including Al2O3 particles, carbon fibers, graphite nanoplatelets (GNPs), and CNTs, are compared. The number of fillers included for a particular filler volume percent will vary widely because to the vast variances in size and geometry between these four reinforcements. For comparison, there are only around two Al2O3 particles in the composite, but the number jumps to over two hundred when carbon fibre is added at the same filler volume %. This finding would explain why carbon nanotubes (CNTs) are so much harder to disperse in polymer matrices than other fillers.

In Fig. 3, we see a simplified representation of the three-dimensional distribution of micro- and nano-scale fillers in a polymer matrix, which conveys a clear picture of the variable distribution behavior of particles in the matrix because of size and geometry effects. Particles in a matrix may be clearly distinguished from one another, and the distribution of micro-scale fillers (A and B in Fig. 3) is consistent throughout. However, it is challenging to scatter individual particles equally when GNPs and CNTs are placed into the same volume of matrix (C and D in Fig. 3). Because of particle agglomeration caused by electrostatic contact and van der Waals force, the true distribution of nanoscale fillers is likely to be more intricate than shown here.

As a result of the high particle count and the size effect, the nano-scale fillers in the composite will have an extremely large surface area. Assuming that fillers are distributed equally throughout the composite, their theoretical surface area as a function of volume percent is depicted in Fig. 4. Table 2 displays the bulk density and formula for determining filler surface area. Surface areas are far greater for fillers with dimensions less than 100 nm, such as CNT and GNP, than for their micrometerscale counterparts, such as Al2O3 particles and carbon fibre. There is a difference of roughly 500 times in surface area between Al2O3 and CNT particles; for instance, the total surface areas of Al2O3 and CNT particles of the same 0.1 vol.% in a cube of 1.0 mm3 are 6.0 108 and 2.8 105 m2, respectively. Fillers with a high surface area have a sizable region of interface or interphase between them and the matrix. The 'interface" in composites is traditionally defined as the surface created by the common border of reinforcing fillers and matrix that is in contact and maintains the link between for load transmission [11]. In contrast, the 'interphase' is characterized by properties that are distinct from either the filler or the matrix, such as changed chemistry, altered polymer chain mobility, altered degree of cure, and altered crystallinity. It is well established [12,13] that the interphase thickness of typical fibre composites made from carbon or glass fibres is on the order of microns. Meanwhile, it has been observed that, depending on the filler size and dimension, CNT/polymer-matrix composites may have an interphase size of up to roughly 500 nm [4]. CNTs provide significant challenges to uniform dispersion even if the interfacial area is just a few nanometers thick.



Figure No. 3 : Total surface area of fillers in composites with varying filler contents.

Fillers' physical properties, such as particle shape and size, also have a significant impact in how well they mix with the polymer matrix. Van der Waals force holds 50–a few hundred CNTs together in bundles or entanglements as created. CNT bundles [14] and entanglements are shown in Fig. 5 from the perspective of an electronic microscope. It has been shown that the mechanical and electrical characteristics of composites are reduced due to the presence of these bundles and agglomerates, in comparison to theoretical expectations linked to individual CNTs [4,10,11]. How to insert single CNTs, or thin CNT bundles or disentangled CNTs, into a polymer matrix, is therefore difficult. Thus, dispersion of CNTs is not only a geometrical problem about the length and size of the CNTs, but also a procedure concerning the separation of individual CNTs from CNT agglomerates and the stabilization of these CNTs in a polymer matrix so as to prevent subsequent agglomeration.



Figure No. 4: Electronic microscope images of different CNTs: (A) TEM image of SWCNT bundle; (B) SEM image of entangled MWCNT agglomerates.

III. Mechanical Dispersion of CNTs

As we have already shown, there are challenges associated with the uniform dispersion of CNTs inside a polymer matrix because of the huge number of particles and high surface area of fillers produced by their integration. CNT dispersion in polymer matrices has been the subject of a substantial body of published research [15–20]. However, very little is known about the fundamentals and characteristics of these dissemination methods. Therefore, this article introduces the fundamentals of CNT dispersion methods, examples of typical outcomes from using these approaches to disperse CNTs in polymers, and

an overarching framework for identifying appropriate strategies for CNT dispersion.

3.1: Ultrasonication

The use of ultrasonic energy to agitate particles in a solution is known as ultrasonication. In the lab, this is often accomplished with the use of an ultrasonic bath or sonicator (A and B in Fig. 6). It's the gold standard for dispersing nanoparticles. The idea behind this method is that the medium's molecules will absorb less of the ultrasound as it travels through a sequence of compressions. A consequence of the generation of these shock waves is the 'peeling off' of individual nanoparticles positioned at the outer portion of the nanoparticle bundles, or agglomerates, and the subsequent separation of these nanoparticles from the bundles [2].

In low-viscosity liquids like water, acetone, and ethanol, ultrasonication is an efficient approach for dispersing CNTs. To disperse CNTs, however, the polymer must first be dissolved or diluted with a solvent to lessen its viscosity since most polymers exist only in a solid or viscous liquid form.



Figure No.57: Sonicators with different modes for CNT dispersion (A: water bath sonicator; B: probe/horn sonicator), and the effect of sonication on the structure of CNTs (C: Raman spectra of CNTs before and after sonication.

Typical laboratory sonicators (submerged in water) operate at 20–23 kHz and generate less than 100 W of power. The amplitude of commercial probe sonicators is adjustable from 20% to 70%, and their power ranges from 100-1500 W. The probe is often crafted from a nonreactive material like titanium. Most probes have a base unit with a diameter of 1.6-12.7 mm [21], and then a tapering tip. This suggests

that the probe's high intensity comes from the concentration of energy from the broad base at its tip. Because of this set-up, sonication may fast produce a lot of heat. Samples containing CNTs dispersed in volatile solvents like ethanol or acetone should be kept cold (in an ice bath, for example) and sonicated in brief bursts to prevent the solvents from evaporating.



Figure No. 6: Calendaring (or three roll mills) machine used for particle dispersion into a polymer matrix (A) and corresponding schematic showing the general configuration and its working mechanism.

CNTs are quickly and severely destroyed if the sonication treatment is too strong and/or too lengthy, particularly when a probe sonicator is used. Ultrasonicating CNTs for an extended period increases the intensity of the D band (indicating disordered sp3 carbon on CNTs) in Raman spectra (Fig. 6C), which suggests the development of defects on the CNT surface [2]. In the worst-case scenario, carbon nanotubes (CNTs) lose all of their graphene layers and transform into amorphous The CNT/ polymer carbon nanofibers [3]. composites' electrical and mechanical characteristics degrade due to localized degradation.

IV. Functionalization of CNTs

Α CNT/polymer nanocomposite's effectiveness is determined by interfacial interactions between CNTs and the polymer and CNT distribution in the matrix. The carbon atoms, however, on the aromatic characteristic of CNTs makes their walls chemically stable. about the link. So, the reinforcing CNTs don't react to their environment and can't van der Waals interactions with the ambient matrix. Waals interactions, which are inefficient in transferring loads, between carbon nanotubes and a matrix. As a result, a lot of work has focused on creating surface-altering techniques, characteristics of CNTs. Multiple indepth review articles are available. that explains how CNTs react with functional groups and how functional groups are attached to CNTs chemically. Based on the nature of the interactions between the active molecules and the carbon atoms on the CNTs, these techniques may be neatly classified as either chemical functionalization or physical procedures.

Key elements of these approaches and their accompanying Table 4 summarizes the benefits and

drawbacks. While Numerous research has been launched so far to alter the CNT surface properties using the following methods: techniques and materials that have not been fine-tuned to their maximum potential. Furthermore, there are worries that structural changes may avoid the harmful effects of ultrasonication and other dispersing and mixing operations and the chemical functionalization of CNTs continue to exist because of unavoidable consequences.

4.1: Chemical Functionalization

attachment of functional Covalent elements to the CNT carbon scaffold is the basis for chemical functionalization. It may be done on the tubes themselves, or on their ends or walls. Changes in hybridization from sp2 to sp3 and the disappearance of the p-conjugation system on the graphene layer are seen after direct covalent sidewall functionalization (Fig. 12A). Some highly reactive compounds, including fluorine, may be used in this procedure. It was shown that pure SWCNTs were fluorinated at temperatures up to 325 C, and that the fluorine could be removed using anhydrous hydrazine [4]. The C-F linkages in fluorinated CNTs are weaker than those in alkyl fluorides [4, 5], making them amenable to replacement for further functionalization [6, 7]. Fluorine atoms have been successfully swapped out for amino, alkyl, and hydroxyl groups [7]. Similar approaches to sidewall fluorination of CNTs have been used effectively in recent years. These include cycloaddition, such as the Diels-Alder reaction, carbene and nitrene addition [9], chlorination, bromination, hydrogenation, and azomethine ylides [4, 5]. All of these techniques may be seen as an offshoot of sidewall functionalization.



Figure No. 7: Strategies for covalent functionalization of CNTs (A: direct sidewall functionalization; B: defect functionalization).

4.2: Physical Functionalization

Covalent functionalization of CNTs may introduce desirable functional groups to the CNT surface. There are two fundamental downsides to these approaches, however. First, a substantial number of defects are generated on the CNT sidewalls during the functionalization reaction, particularly when combined with the harmful ultrasonication procedure. The mechanical characteristics of CNTs are severely degraded, and the p electron system in the nanotubes is disrupted, because of these harmful impacts. Because defect sites scatter electrons and phonons important for the electrical and thermal conductions of CNTs, the disruption of p electrons has a negative impact on the transport characteristics of CNTs. Second, CNT functionalization often employs the usage of ecologically harmful concentrated acids or strong oxidants. As a result, a lot of work has gone into creating techniques that aren't just cheap and easy to use, but also gentler on CNT structures.



Figure No. 8: Schematics of CNT functionalization using non-covalent methods (A: polymer wrapping; B: surfactant adsorption; C: endohedral method).

Another strategy for controlling nanotube interface characteristics is by non-covalent functionalization. When CNTs are suspended in a

polymer solvent like poly (phenylene vinylene) [6] or polystyrene, the polymer molecules wrap around the CNTs, creating CNT-polymer supermolecular

complexes. This is an example of CNTs being functionalized in a non-covalent manner. To accomplish the polymer wrapping process, aromatic ring-containing polymer chains engage with CNTs through van der Waals interactions and p-p stacking.

CNTs have been functionalized with both polymers and surfactants. Numerous research have helped to understand how surfactant influences CNTs' dispensability and other properties [7]. Polyoxymethylene 8 lauryl (CH3(CH2)11(OCH2-CH2)7OCH2CH3) [6, 8], nonvlphenol ethoxylate (Tergitol NP-7) [69, 70], and polyoxyethylene octylphenylether (Triton X-100) [69, 70] are examples of non-ionic surfactants; whereas sodium dodecylsulfate (SDS), sodium do In particular, the reasons underpinning CNTs' enhanced dispersibility are reviewed in depth in a recent work [7]. To avoid aggregation formation, CNTs had their surface tension reduced by physical adsorption of surfactant. Also, the electrostatic/steric repulsion between CNTs treated with a surfactant is stronger than the van der Waals attraction. This technique relied heavily on the characteristics of the surfactants. medium chemistry, and polymer matrix to achieve its goals. It was determined that cationic surfactants had some benefits in water-soluble polymers like polyethylene glycol, whereas non-ionic surfactants aided in CNT dispersion in water-insoluble polymers like polypropylene [7]. The hydrophobic interaction between the solid surface and the surfactant tail group is the basis for the treatment of non-ionic surfactants. Above a critical micelle concentration (CMC), surfactant molecules selfassemble into micelles after being adsorbed onto the filler surface.

V. CNT/Polymer Nanocomposites

Polymer composites, which are made up of various additives and polymer matrices (such as thermoplastics, thermosets, and elastomers), are widely recognized as a useful class of low-cost materials for a wide variety of engineering tasks. When two or more materials are joined, composites are created that have characteristics that are not possible with just one of the starting materials. Reinforced polymer composites, such as those made by incorporating high-modulus carbon fibers or silica particles into a polymer, display dramatically improved mechanical qualities including strength, modulus, and fracture toughness. Traditional micron-scale fillers provide challenges when trying to optimize the characteristics of polymer composites. Traditional polymer composites have filler contents between 10 and 70 weight percent, leading to a dense, expensive composite. High fracture toughness [9] is typically sacrificed along with composites' modulus and strength.

When nanoscale CNTs are included into a polymer system, the distance between the fillers is drastically reduced, allowing for significant modification of the composite's properties at a very low filler concentration, in contrast to standard polymer composites having micron-scale fillers. CNT/epoxy nanocomposites, for instance, may have their electrical conductivity improved by many orders of magnitude with as little as 0.5 wt.% of CNTs [3]. CNTs, as was previously mentioned, are very strong and rigid fibers. CNT/polymer nanocomposites have tremendous potential applications because of their superior mechanical capabilities and other CNT physical features. Exciting discoveries have come from ongoing experimental studies in this field, but the commercial success that has been predicted for years has yet to materialize. Furthermore, CNT/polymer nanocomposites are one of the most studied systems due to the potential advantage of reduced cost for mass production of nanocomposites, as the polymer matrix can be easily fabricated without damaging CNTs based on conventional manufacturing techniques.



Figure No. 9: Number of published papers related to CNT and CNT/polymer nanocomposites as a function of academic year.

As can be seen in Fig. 14 [8], many studies have been conducted since the first report on the preparation of a CNT/polymer nanocomposite was published in 1994 [80]. These studies aim to better understand the structure-property relationship of CNTs and to identify areas in which they can be useful. CNT/polymer nanocomposites may be categorized as either structural or functional composites [2] depending on their intended use. By investigating the classic mechanical features of CNTs, such high modulus, tensile strength, and strain to fracture, structural composites may be developed with significantly enhanced mechanical qualities. In addition to their excellent mechanical properties, carbon nanotubes (CNTs) are exploited for their electrical, thermal, optical, and damping properties to create multi-functional composites with uses as diverse as heat resistance, chemical sensing, electrical and thermal management, photoemission, electromagnetic absorption, and energy storage, among many others.

VI. CONCLUSION

CNT/polymer nanocomposites have great promise for structural and functional applications because to their superior mechanical properties, unique transport capabilities, and other multifunctional characteristics. CNT/polymer nanocomposites have been the focus of a great deal of research, but their implementation into practical products is only getting started. Before this new class of material can be widely applied in real products and systems, two major, interrelated issues must be resolved: (i) poor solubility and dispersion when mixed with polymer resins, and (ii) poor interfacial adhesion between CNTs and various polymers.

In this overview, we discuss the current state of knowledge about carbon nanotube (CNT)/polymer nanocomposites, focusing on the fundamentals of CNT dispersion and functionalization, as well as the implications of these processes on the characteristics of CNT/polymer nanocomposites. It is shown that these two issues are often problematic at various stages of nanocomposite fabrication, and that controlling them among the many material and processing parameters is of utmost importance as they govern the resulting properties of CNT/ polymer nanocomposites. Mechanical processes such as ultrasonication, shear mixing, calendaring, ball milling, stirring, and extrusion may all be used to distribute ingredients evenly throughout a product. Because the employment of various techniques produces, to completely varied degrees, mechanical damage to CNTs and their shattering into smaller pieces, the selection of a good method or a combination of many ways, as well as their processing conditions, needs to be based on the desired attributes of end products.

To get a somewhat uniform CNT dispersion in nanocomposites, techniques based on pre-dispersion of CNTs in a solvent have been shown to be successful. However, owing to the lack of transparency even at a very low CNT concentration and the absence of recognized techniques to estimate the dispersion quality, assessing a CNT dispersion in a solvent is not a simple affair. Several material parameters, such as particle size or aspect ratio, CNT surface functionalities, and surface energies, can be directly

correlated with the degree of dispersion or agglomeration in a solvent or a polymer, making it necessary to develop tools and techniques for quantitative analysis of these phenomena.

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