Effect of Carbon Nanotubes on Electrical Properties of Polymer Nanocomposites: A Review

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ABSTRACT- The carbon nanotube (CNT) is the folded structure of single sheet of the Graphite having novel properties of high thermal, mechanical & electrical properties. In present review the dispersion of CNT's with polymer matrix is studied. CNTs are required to functionalize for better compatibility along with higher interfacial adsorption with surface of polymer matrix. Polymer/CNT nanocomposites are prepared by different techniques such as solution technique, in-situ polymerization and melt mixing. Prepared nanocomposites are characterized by Fourier-transformed infrared (FTIR) and X-ray diffraction (XRD) study. The morphology of polymer/CNT nanocomposites can be studied by Scanning electron microscope (SEM) and Transmission electron microscope (TEM). The conducting properties of nanocomposites of different polymer matrix are summarized. The effects of f-CNT are predicted by in order to establish the interfacial adhesion between polymer matrix and CNTs.

I. INTRODUCTION

In 1980's only three forms of carbon are known to all and these are graphite, diamond and amorphous carbon. Today there are a whole family of new carbon structures known, first of them is buckminster fullerene (C_{60}), named after Richard Buckminister Fuller. More than thirty forms of fullerenes [1] with its extended family are now under the roof of advanced research. Carbon, the sixth element of the periodic table with its unique catenation property makes the basis of organic chemistry and of life and also serves to the mankind from earlier (fuel purpose, jewelry purpose, conducting material purpose and also some basic application) with its older allotropes and stepped in to the modern civilization by the hand of Iijima and his co-workers[2] with the discovery of carbon nanotube(CNT) . CNTs are elongated fullerene or in other word hexagonal networks formed by the sp^2 hybridized carbon atoms (like grapheme sheet) ,arranged in a tube shape[3]. CNTs are of two types, one is single-walled carbon nanotubes (SWCNTs) and other is multi-walled carbon nanotubes (MWCNTs). The SWCNT is formed by rolling a sheet of graphene co-axially into a cylinder and capped by hemispherical ends, might be result from the pentagon inclusion in the hexagonal sp^2 hybridized carbon network of the CNTs during the growth process. On the other hand stack of graphene sheets rolled up in a concentric cylinder results in the formation of MWCNTs with a diameter ranges from 2 -25nm and inter layer spacing of about 0.34nm[4].The diameter of SWCNT is around 0.4-3nm and several micro-meter in length[5], Figure 2 shows the defect free SWCNTs with open ends (A,B,C) and bundles of SWCNTs strong pi-bond interactions(D).Due to the reduction of size in nanometer range(high aspect ratio-1000 or more than this) CNT shows some unique properties such as high mechanical strength, high electrical and thermal conductivity .Due to such extraordinary properties CNT has wide application in the field of conducting device, field emitter, Industrial packaging material and opto-electronics, photovoltaic cell[7]. Among all properties, electrical conductivity of CNT grabs more attention as because of the electrical conductivity of metallic SWCNT which is 1000 times larger than silver or copper. Because of the symmetry and unique electronic structure of graphene (schematic representation of hexagonal grapheme sheet with different vectors is shown in **Figure 1**), the structure of a nanotube strongly affects it's electrical properties .Depending on the helicity and diameter it could be metallic or semiconducting [9-10]. The armchair nanotubes are always metallic, where as the zigzag and chiral tubes can be either metallic or semiconducting. As the electrons in nanotube are confined in the singular plane of graphene sheet in radial direction, electronic conduction is quantum confined. In case of armchair conduction occurs through gapless mode due to the crossing of valence band and conduction band at Fermi energy for a certain special wave vector (K point in Brillouin zone)[11]. On the other hand for semiconducting nanotube, there is a band gap revealing between the valence band and conduction band. Due to this quantum confined nature of conduction process the MWCNT shows semi-metallic behavior. There have been some reports in support of intrinsic

superconductivity in CNT. Many other experiments, however found no evidence of superconductivity and validity of these claims of intrinsic superconductivity remains a subject of debate. Whatever may be the case of superconductivity, there is no doubt that CNT is a good conductor of electricity and that's why it is efficiently used as conducting filler into the nonconducting polymer matrix and thereby forming a conducting nanocomposite for a wide range of application like electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding etc with a very low CNT content [12]. However the distribution of CNTs throughout the polymer matrix plays an important role in governing the affectivity of the outcome properties. So in order to get the desired level electrical conductivity CNTs should be well dispersed into the polymer matrix.
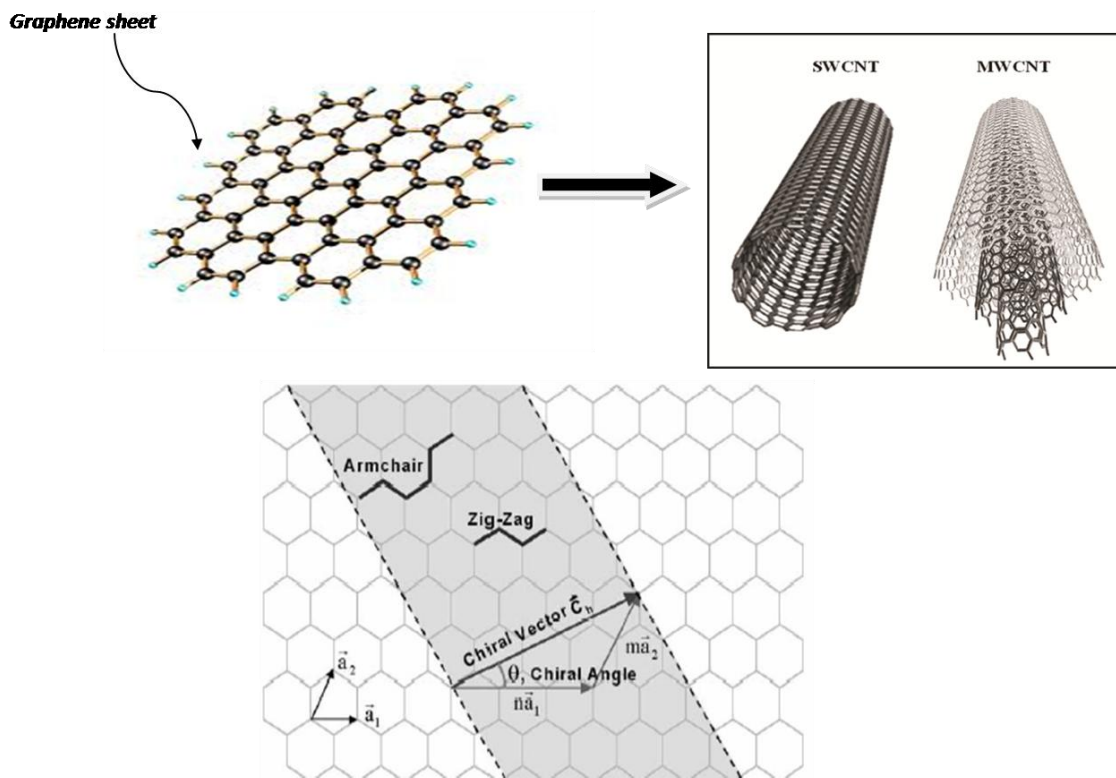
Figure 1:Schematic diagram of open hexagonal graphene sheet with different vectors **[8].**
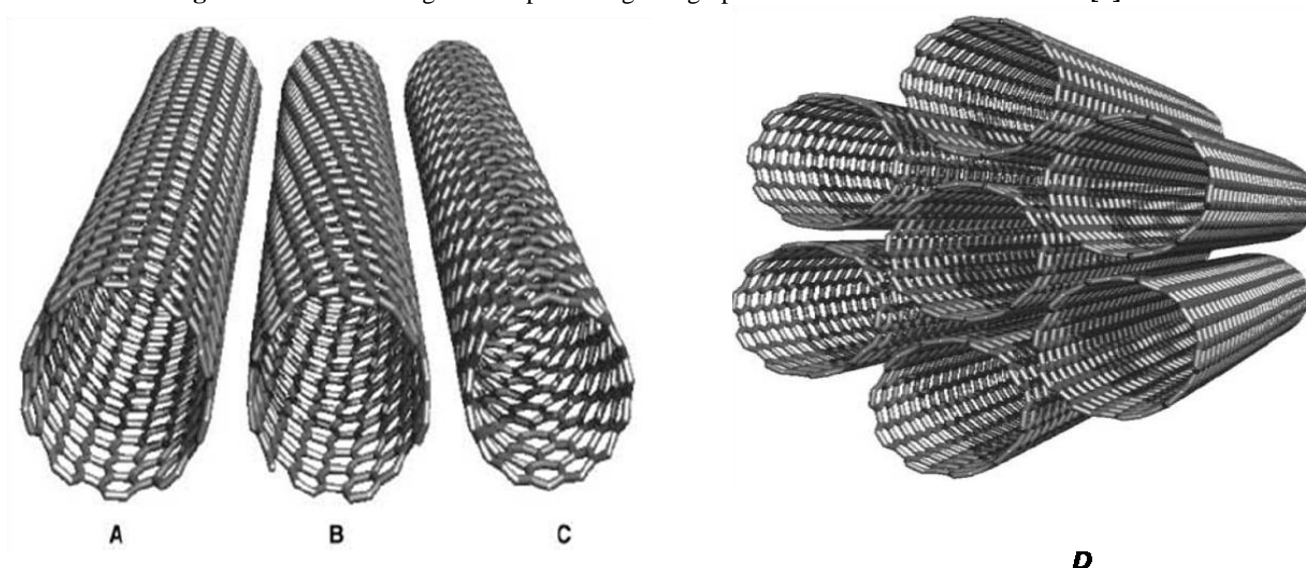

Figure 2: (A) Defect free (n, m) SWCNT with open ends, (A) metallic conducting (10, 10) tube (arm chair), (B) chiral semi conducting tube (12, 7), (C) a conducting (15, 0) tube (zig zag) and (D) bundle of (10, 10) SWCNT nanotubes held with strong π-π stacking interactions **[6]**

II. DISPERSION OF CNTs INTO THE POLYMER MATRIX

To achieve better results for the nanocomposites, filler should be well dispersed within the hosting polymer matrix and dispersed form should be stabilized. Otherwise   reaggregation of the nanofiller within the polymer matrix will be occurred .The reason behind the reaggregation to form agglomerates is their large surface area. The SWCNT tend to aggregate into crystalline ropes due to strong Vander Waal's forces of attraction among   CNTs. These ropes are composed of 100 to 500 tubes together in a triangular lattice form with a lattice constant of valued 1.7 nm [13]. The MWCNT also form highly entangled carbon network. Due to local non-uniformity along a CNT with varying diameter and kinks at places result in the micro-mechanical interlocking with the polymer matrix [14]. Sometimes the interaction mode between polymer/CNT is weak Vander Waal's bonding and sometimes chemical bonding (where functionalization of CNT is performed by chemical treatment).For the first two type, interaction possibility is very little compared to the last one. So the dispersed phase, achieved by the ultrasonication or mechanical mixing [15-17] can be stabilized by chemical functionalization of CNTs which allows coupling with a polymeric matrix and co-operated by the defect in the SWCNT shown in the **Figure 3.** .Functionalization can be accomplished through insitu polymerization via radical reaction or Diels-Alder reaction [18, 19]. Much more common chemical modification of CNT is the direct oxidation with strongly oxidizing reagent such as nitric acid or $KMnO_4/H_2SO_4$ [20-22] .On direct oxidation disentangling of CNT is occurred. Liu et al used 3:1 mixture of concentrated sulfuric acid and nitric acid to cut the CNT bundles into 150 nm in length. The short CNTs are then treated by 4:1 mixture of concentrated sulfuric acid and 30% aqueous hydrogen peroxide. Different types of functionalization of SWCNT has been done such as Defect group functionalization, Co-valent side wall functionalization, Non-co-valent exohedral functionalization with surfactant, Non exohedral functionalization with polymer, Endohedral functionalization, shown in Figure 4. Covalent functionalization by direct oxidation deteriorates the electrical property of CNTs. There another way known as Third component assisted dispersion is accepted .According to this approach   CNTs are mixed with a third component chemical in solution. Through sonication CNTs are exfoliated and stabilized by third component a chemical which provides a solvophobic barrier to inhibit CNT agglomeration. Many chemicals have been used as third component, such as Small molecule surfactants [23, 24], polymer-electrolytes [25-27], proteins [28-31], DNA [29,30,32], conjugated polymers [33-36], block copolymers [37,27,38-41] etc. It is a non destructive, non covalent interactive process and thereby no hamper of electrical property   of the modified CNTs. In polymer/CNT nanocomposite, dispersed CNTs have a tendency to align themselves which is shown in Fig 5.
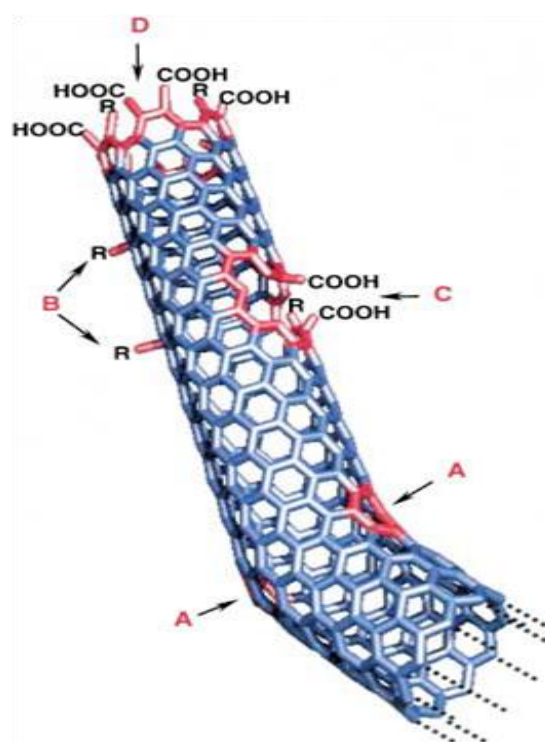
Figure 3: Defects in a SWCNT: (A) five or seven membered ring in the ring surface can bend the ring, (B) sp^2 hybridized defects(R= H and OH),(C) CNT surface damaged by oxidation terminated with COOH group, and (D) open end of SWCNT   with –COOH group [6].
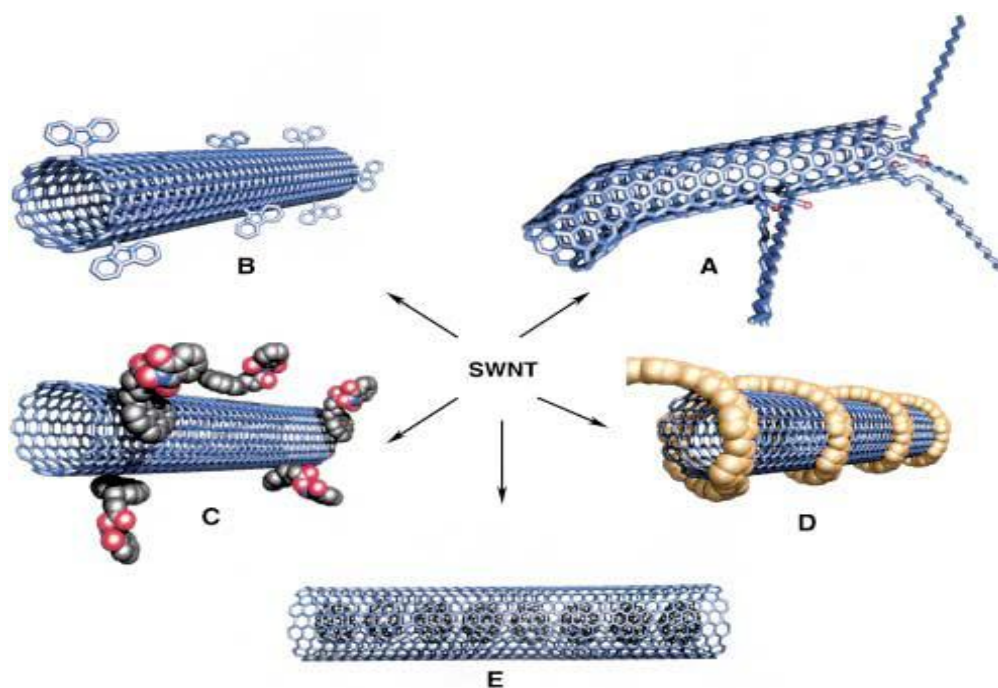
Figure 4: Different types of functionalization of SWCNT: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent exohedral functionalization with surfactant, D) noncovalent exohedral functionalization with polymers, E) endohedral functionalization **[6]**
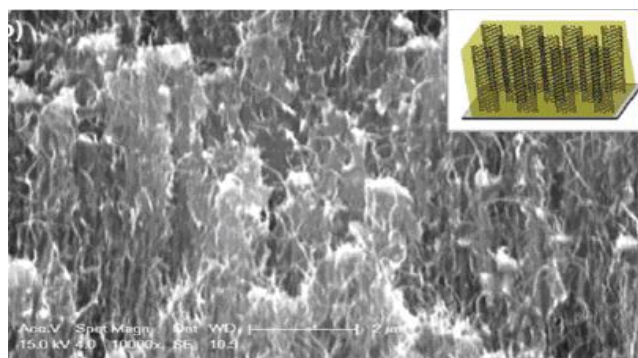
Figure 5: SEM image of aligned-CNT polymer nanocomposite with epoxy matrix **[42].**

III. ACTIVATION TREATMENT ON CNT

Due to the introduction of functional groups such as carboxylic acid and hydroxyl group on CNT by oxidation treatment it becomes chemically active. To further activate the carboxylic acid group on the surface of CNT, it is treated with thionyl chloride in order to convert the carboxylic acid group into acyl chloride. On treatment with formaldehyde -OH groups on the surface of CNTs are converted into hydroxymethyl groups ($-CH_2OH$) **[43]**. Zhou**[44]** converted hydroxyl and carboxylic acid groups on the surface of CNTs into vinyl groups on treatment with 3-isopropenyl-α,α-dimethylbenzyl isocyanate so that vinyl monomers could be grafted on the surface of CNTs. Introduction of aldehyde (-CHO) and amino($-NH_2$) groups have been done by plasma modification**[45]**. Bahr et al **[46]** functionalized SWCNTs with electrochemical reduction of aryl diazonium compounds, resulting a free radical attached to the surface of CNTs. Anhydrides, quinine and ester can also be introduced to the CNT surface by ozone oxidation**[47]**.Treatment of fluorine at elevated temperature is also useful for the functionalization of SWCNT**[48]**.

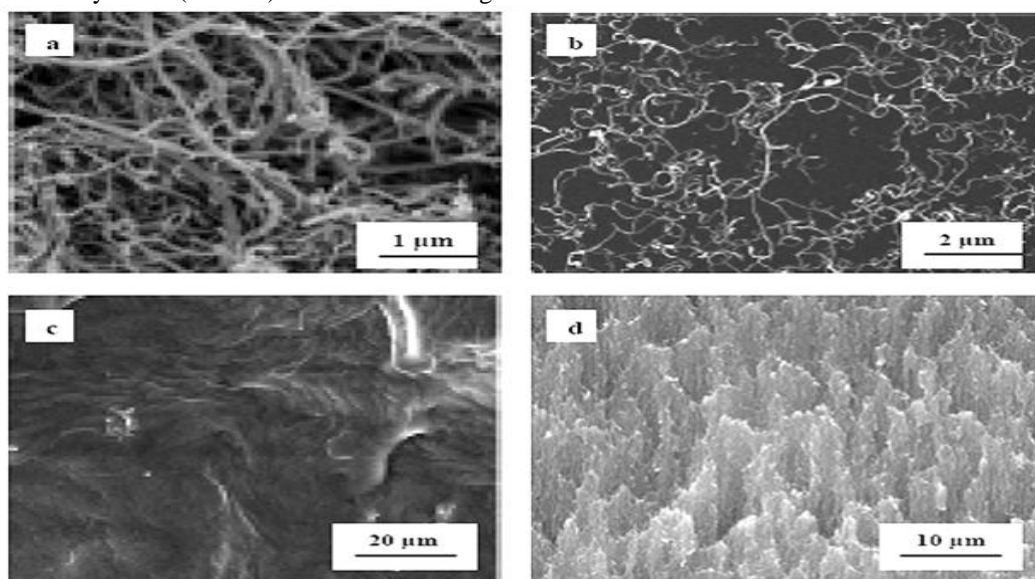## IV. PREPERATION OF POLYMER/CNT NANOCOMPOSITE

After functionalization and activation of the functionalized group (if necessary) it is the time to go through the procedures which are accepted worldwide for the preparation of polymer/CNT nanocomposite and these are a) Solution casting method, b) Insitu

polymerization and c) Melt mixing. a) Solution casting method: This method involves 3 major steps. The first step is to make dispersion of CNTs in solution phase using a suitable solvent (organic or aqueous solvent) through proper mechanical stirring and sonication .Obviously before that surface modification of CNTs is necessary to achieve metastable dispersion. The second step is to blend with desired polymer (at room temperature or some elevated temperature) so that intercalation between polymer and CNTs can occur. The last step involves recovery of the nanocomposite by precipitating or film casting. This technique has been adopted to synthesize PVC/CNT and Poly (9-vinylcarbazole)/CNT nanocomposites (aqueous phase synthesis) [49]. It is also used to synthesize Polystyrene (PS)/MWCNT with Gemini surfactant [50] and Polymethylmethacrylate (PMMA)/SWCNT with DMF surfactant [51]. b) Insitu polymerization: In this method polymer/CNT nanocomposites was prepared by dispersing nanotubes in monomers followed by polymerization (low polymerization temperature 0°-80°) of monomers ,resulting in a covalent bonding between CNTs and polymer matrix .It requires the addition of initiator and terminator to get the desired nanocomposite. Zhu et al [52] prepared epoxy nanocomposite with functionalized SWCNT and observed improved conductivity with a very low wt% of CNT loading. Tang and Xu [53] synthesized poly (phenyl acetylene) PPA/CNT which are soluble in organic solvents(THF, toluene, chloroform etc) . Fan et al [54] synthesized conducting polypyrrole coated CNT nanocomposites. Cochet et.al [55] synthesized polyaniline (PANI)/MWCNT, where site selective interaction between quinoid ring of PANI and MWCNT opening a way of charge transfer process and showed improved electrical conductivity. Polymethylmethacrylate (PMMA)/MWCNT having high electrical conductivity,was prepared by Zhang and his co-workers [56]. c) Melt mixing: This involves high temperature and high shear forces to disperse the CNTs into the polymer matrix. This is a enthalpy favorable industrial process. Some examples are MWCNT/Nylon 6[57], MWCNT/polycarbonate [58] and SWCNT/Polypropylene [59]. Besides above 3 process Vigolo et al [60] developed coagulation spinning method to form polymer/CNT nanocomposites.

V. CHARACTERIZATION OF POLYMER/CNT NANOCOMPOSITE

Better dispersion of nanofiller into the polymer matrix always leads to the improvement in some specific properties of the nanocomposite .Thereby it is very important to examine the location of nanofillers within the polymer matrix with the help of some advanced instruments such as Transmission electron microscope (TEM), Scanning electron microscope(SEM),High resolution transmission electron microscope (HRTEM). Among these three instruments SEM gives the surface picture of the nanocomposite while other two give the inner picture of filler distribution within the polymer network.SEM images of raw MWCNT, f-MWCNT, PAN/MWCNT nanocomposite, vertical alignment of f-MWCNT are shown in Fig 6[61].In both the cases high velocity electrons serve the purpose of light as in the case in the case of ordinary microscope to get the surface image. There are also some other instrumental facility like X-ray electron diffractometer (XRD), Fourier transformed infrared (FTIR) spectrometer, UV-visible spectrometer to give a intense understanding regarding the presence of nanofiller and polymer matrix together.


Figure 6. SEM image of (a) raw MWCNT (b) functionalized MWCNT (c) PAN/MWCNT nanocomposites (d) vertical alignment of functionalized MWCNT [61]

VI. ELECTRICAL PROPERTIES OF POLYMER/CNT NANOCOMPOSITES

The commercial application of CNTs is their use as conducting filler in multifunctional polymers to make the insulating polymer become conductive. But regarding this filler content must exceeds some critical value, known as percolation threshold. This is characterized with a sharp rise in conductivity. It is reported that, GE plastic used CNTs in poly(phenylene oxide)/polyamide blend for automotive mirror housing for Ford to replace micron sized conductive filler(required loading 15 wt%).With 8% loading of CNTs into poly(p-phenylenevinylene-co-2,5-dioctoxy-m-phenylenevinylene)PMPV showed a dramatically increase in the electrical conductivity up to ten order of magnitude with an indication of percolating behavior [62].The polymer/CNT composites exhibit very low percolation threshold because of the fact that CNT has large aspect ratio with nanoscale dimension. Percolation threshold of polymer/CNT composites depends on the dispersion and alignment of CNTs throughout the polymer network. Better the dispersion of CNTs low will be the percolation threshold due to the fact that with better dispersion a conductive network through the polymer matrix will be formed easily. Hence, with increase in CNT content in polymer/CNT nanocomposite electrical percolation threshold increases, shown in Figure 7 [63]. On the other hand alignment of CNTs in polymer matrix reduces the electrical properties of polymer/CNT nanocomposites due to the decrement in number of CNTs that are in contact with each other. For polymer/SWCNT composites, the electrical percolation threshold ranges from 0.005 volume % to several volume% .The lower percolation threshold 0.002 volume% for long flexible ropes of MWCNT in polymer was reported[64]. Du et al[65]studied that in case of PMMA/SWCNT nanocomposite, where the alignment of CNTs can be controlled, the electrical conductivity of the composite increases with decrease in alignment .In epoxy/MWCNT nanocomposites with MWCNTs aligned under a 25T magnetic field leads to a 35% increase in electrical conductivity compared to those similar composites without magnetic aligned CNTs. Sometimes chemical functionalization of CNTs influences the electrical properties of polymer/CNT nanocomposites. Electrical conductivity of silane f-MWCNT/epoxy composite was observed much more compared to the untreated f-MWCNT/epoxy composite, shown in Figure 8 [66]. Addition of 0.33 wt% of MWCNT in Polyacrylonitrile (PAN) matrix increases the electrical conductivity of the nanocomposite and becomes double at 1.32 wt% of MWCNTs, shown in Figure 9 [61].
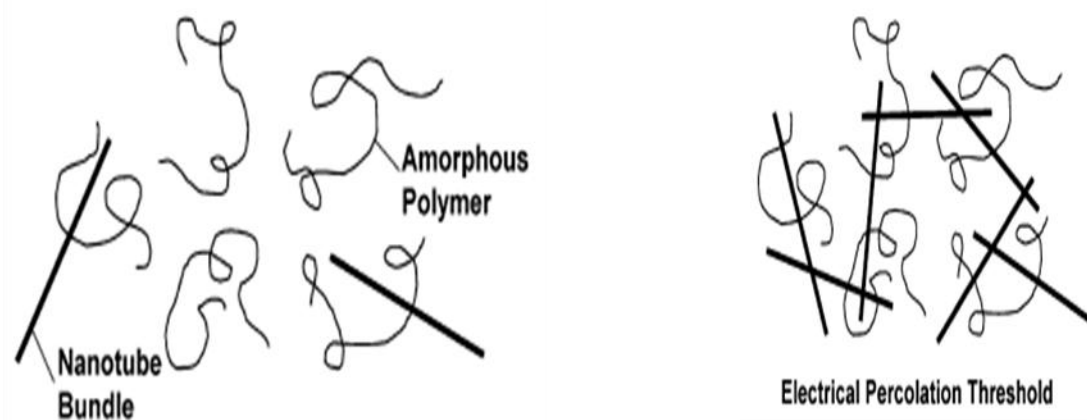

Figure 7: Electrical percolation threshold of polymer/SWCNT composites [63]
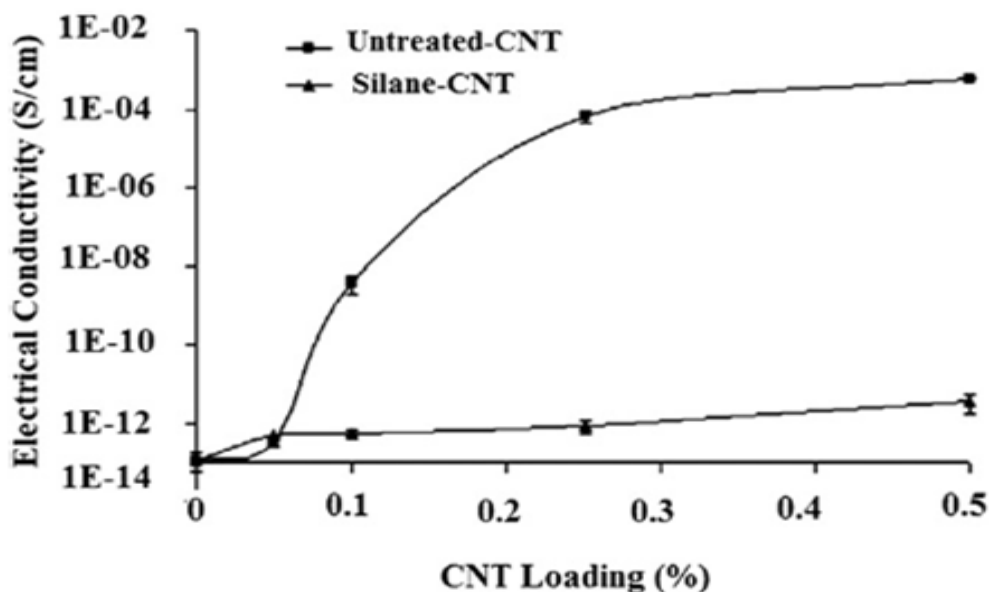
Figure 8: Electrical conductivity of untreated and silane f-MWCNT/epoxy composites **[66]**.

We have reported the dispersion of functionalized CNT with different polymer/biopolymer matrixes [67-69] in order to prepare the conducting nanocomposites. Multiwalled carbon nanotubes (MWCNTs)/poly(methyl methacrylate) (PMMA) nanocomposites were prepared by ultrasonic assisted emulsifier free emulsion polymerization technique with variable concentration of functionalized carbon nanotubes. MWCNTs were functionalized with H2SO$_4$ and HNO$_3$ with continuing sonication and polished by H$_2$O$_2$. The appearance of Fourier transform infrared absorption bands in the PMMA/MWCNT nanocomposites showed that the functionalized MWCNT interacted chemically with PMMA macromolecules. The surface morphology of functionalized MWCNT and PMMA/MWCNT nanocomposites were studied by scanning electron microscopy. The dispersion of MWCNT in PMMA matrix was evidenced by high resolution transmission electron microscopy. The oxygen permeability of PMMA/MWCNT nanocomposites gradually decreased with increasing MWCNT concentrations.
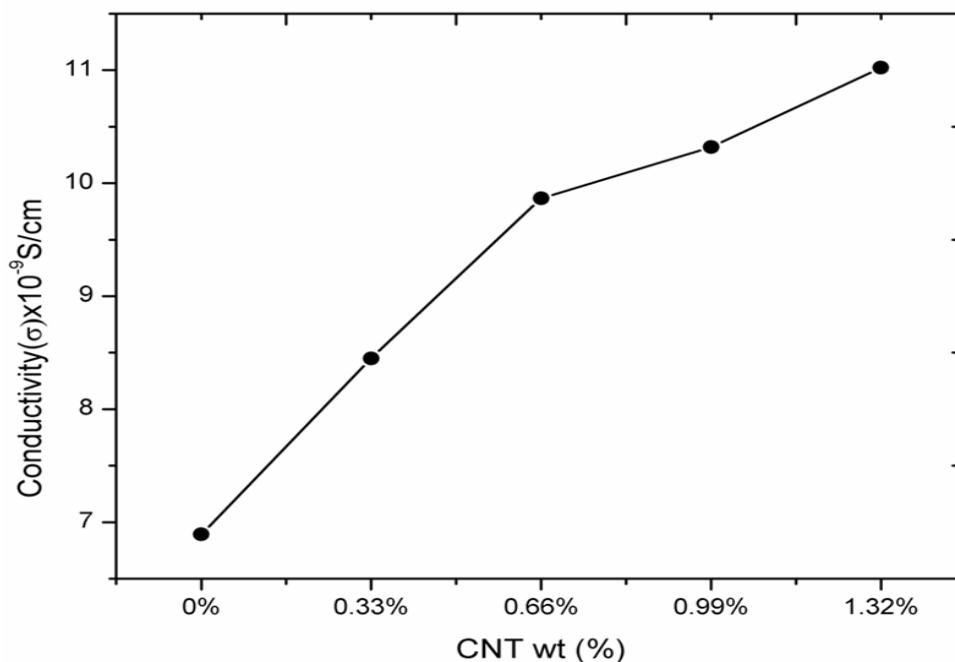
Figure 9: Electrical conductivity of PAN/MWCNT composites at different wt% of MWCNT **[61]**

In another study [61], PAN/MWCNT nanocomposites were characterized by ultraviolet-visible (UV-visible) spectroscopy and Fourier transforms infrared (FTIR) spectroscopy. The result from UV-visible suggested that the functionalized MWCNT had interfacial interaction with PAN matrices. The surface morphology of functionalized MWCNT and PAN/MWCNT nanocomposites were studied by scanning electron microscopy (SEM). Electrical properties of PAN/MWCNT nanocomposites were measured and the result indicated that the conductivity increased with increasing concentration of MWCNTs. The oxygen permeability of PAN/MWCNT nanocomposites gradually increased with increase of MWCNT concentration, the result which was in agreement with the vertical alignment of MWCNT in SEM (Figure 6). Further, the conducting properties of starch were investigated with reinforcement of functionalized CNT which was prepared by solution casting technique [69].

VII. CONCLUSION

The uniform distribution of CNTs can be achieved with manipulating the interfacial adhesion of f-CNTs with polymer matrix. The conducting properties of polymer/CNT nanocomposites are governed by the continuous connectivity of CNTs. Recently, polymers are extensively used for industrial purpose due to their light weight, high strength and nature to easily biodegradable .But they are non conductor of electricity. This drawback can easily be defeated by introducing a little amount of conducting CNTs in to the polymer matrix which enables the nanocomposite materials for electronic application.

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