This chapter presents a brief introduction to carbon nanotubes, conducting polymers, synthesis of CNT based TPU composites, their conducting mechanisms, properties and potential applications. A literature survey on the thermal stability of DC conductivity, thermoelectric properties, strain sensing and EMI shielding properties of CNT based polymer composites are presented. The scope and objectives of the work is also discussed.

1.1 Nano Science

The development of novel materials and methods heralds a new era of innovations in science and technology. Structures created in nanoscale possess fascinating properties with vast potential for use in a wide spectrum of applications. Richard Feynman, the great physicist who in 1959, envisioned potential of manipulation and control of individual atoms and molecules is considered the father of nanotechnology. Another scientist Norio Taniguchi coined the term Nanotechnology a decade later. The development of the Scanning Tunneling Microscope in 1981 was a major landmark in the development of this science. The scientific community has witnessed significant progress ever since.
Nanoscience and Nanotechnology deals with the study of particle sized structures in the scale 1 to 100 nanometers, which find application in almost all branches of science. At this size range, the properties of the particles are governed by the ‘quantum’ effect. A relevant example is the nanoscale gold particle, which exhibits a fascinating display of red or purple color, instead of the natural yellow. This effect is attributed to the restricted movement of gold’s electrons at nanoscale. As the dimension of a material system reduces to nanometer scale, unique physical and chemical characteristics arise. Nano-materials have been mass fabricated by novel synthetic approaches, and have attracted a great deal of interest from scientists and engineers. Carbon, in its diverse forms of compounds and allotropes, also forms one of the most extensively researched nano materials.

1.2 Carbon nanotubes

The Buckminster fullerene $C_{60}$, discovered in 1985, with 60 equivalent carbon atoms, is an unusual molecule with the highest symmetry (1). In 1991, S. Iijima discovered a tubular form of fullerene, capped at each end and connected by a straight segment of tube (2). These are called carbon nanotubes because the structure is only about a few nanometers wide and are considered to be a rolled-up graphene sheet that forms long concentric cylinders. The length of the nanotubes is significantly greater than the width, creating a large aspect ratio. Bonding in CNTs is essentially $sp^2$; the circular curvature causes $\sigma$ bonds to be slightly out of plane, the $\pi$ orbital is more delocalized outside the tube (2).

There are two main types of CNTs: Single walled carbon nanotubes (SWCNTs) which consist of a single, seamless, rolled up cylinder of a
graphene sheet. These are defined by their diameter and their chirality (Fig. 1.1). The diameter of SWCNTs varies from 0.5 to 5 nm. Multiwalled carbon nanotubes (MWCNTs) are a group of concentric SWNTs (Fig. 1.1) often capped at both ends, with diameters in the range from several nanometers up to 200 nm. The intertube spacing in MWCNT is roughly equal to the Vander Waals graphite interplane distance, 0.34 nm (3,4).

1.2.1 Structure

The structure of carbon nanotubes is described in terms of the tube chirality, which is defined by the chiral vector \( \mathbf{Ch} \) and the chiral angle \( \Theta \). The chiral vector indicates the manner in which graphene is rolled-up to form a nanotube. The tube chirality is described by the chiral vector as

\[
\mathbf{Ch} = n \mathbf{a}_1 + m \mathbf{a}_2 \]

(1.1)
where the integers \((n, m)\) indicate the number of steps along the zigzag carbon bonds of the hexagonal lattice and \(n_{a_1}\) and \(m_{a_2}\) are unit vectors (Fig.1.2) (5,6). Accordingly, three types of orientation of the carbon atoms around the nanotube circumference are specified. If \(n = m\), the nanotubes are called “armchair” and if \(m = 0\), the nanotubes are called “zigzag”. Otherwise, they are called “chiral” (Fig. 1.2). When \(n-m\) is a multiple of 3, the tube is chiral and metallic; otherwise, the tube is a semiconductor (6). The chirality of the carbon nanotubes has a huge impact on their properties, especially the electronic ones.

Each MWCNT contains a multi-layer of graphene, and each layer can have different chiralities, so the prediction of its physical properties is more complicated than that of SWCNT.

![Fig. 1.2: A sheet of graphene rolled to show formation of zigzag \((n, 0)\), armchair \((m, m)\), and chiral \((n, m)\) CNTs (5)](image)

The electron transport property of the MWCNTs is more complicated than SWCNTs. Each of its carbon shells can be metallic or semi conductive, depending on the chirality of the shell. At room temperature, the outer two
shells will interact with each other and contribute to the conductance (7). Experimentally, both metallic and semi conductive behaviour has been observed for the MWNTs. Tubes with more complex conduction behaviour have also been observed (8).

1.2.2 Synthesis

Carbon nanotubes are required in large quantities in laboratories and industry. CNTs can be produced by a variety of processes which can broadly be divided into two categories (1) high temperature evaporation using arc-discharge (8-12) or laser ablation (13,14,) and (2) various chemical vapour deposition (CVD) or catalytic growth processes (15-17). In electric arc method, direct current arc plasma between two graphitic electrodes in an inert atmosphere is generated. This creates a high temperature discharge between the two electrodes. The anode gets consumed and MWCNT deposits are formed on the cathode. Arc-discharge produces MWNTs that are almost perfectly straight and contain very few defects. Addition of a suitable catalyst such as Ni-Co, Co-Y or Ni-Y leads to the formation of SWCNT bundles on the walls of the reaction chamber (18). The yield and properties of the nanotubes depend on factors like the metal concentration, inert gas pressure, type of gas, the current and system geometry. In laser ablation process, a pulsed or continuous laser is used to vaporise a graphite target in an oven at 1200°C. The oven is filled with an inert gas like He or Ar. Though this method can produce MWCNTs, it is most often used for the production of high quality SWCNTs with minimum defects at yields higher than 70%. The graphite target contains a 1–2% metal catalyst (19).
For commercial purpose, CNT is synthesized by the CVD technique. CVD method is suitable for CNTs in composites, as large quantities at low cost and requiring no further purification can be obtained by this method. There are various CVD processes, but basically they all involve a two-step process which thermally decompose hydrocarbon gases and use metal catalyst particles (Fe,Ni,Co) to grow the nanotubes (20-22). MWNTs are mainly obtained by this method, with high purity but with limited control over structure and diameter. Generally, the experiment is carried out in a flow furnace at atmospheric pressure. The catalyst is placed in a ceramic boat which is then put into a quartz tube. Ivanov et al. (23) utilized a reaction mixture consisting of acetylene and argon which is passed over the catalyst bed kept at temperatures ranging from 500 to 1100°C. Long nanotubes with diameters ranging from 0.6 - 4 nm for SWNTs and 10 - 200 nm for MWNTs can be produced.

1.2.3 Properties of CNTs

The large aspect ratio, nanometer size, the helical structure, sp² carbon–carbon bonds and the topology of carbon nanotubes give them excellent mechanical, thermal and electrical properties. These properties have made them a potential candidate for high-tech applications such as in field effect transistor, electron field emitters, probe tips for scanning tunneling microscopy, hydrogen storage, nano tweezers, fuel cells, sensors, EMI shielding, nano-transistors (24-32).

The sp² bonding between carbon atoms confers outstanding mechanical properties on CNTs. The experimental and theoretical investigations show extraordinary mechanical properties of individual MWCNTs and
SWCNTs with Young’s modulus being over 1TPa and a tensile strength of 10 - 200 GPa (33-35). CNTs have been described as being several hundred times stronger than steel and only one-sixth as heavy.

The superior electrical properties of CNTs are due to their unique electronic structure and one dimensional characteristic (36). Structural defects as well as bends or twists are again thought to have a strong effect on the transport properties (37). Theoretical studies of the electronic properties of SWCNTs suggested that nanotube shells can be either metallic or semiconducting depending on their helicity (3). Since MWCNTs have multiple-shell structure, confinement effects disappear, and the transport properties approach that of turbostratic graphite (38). Tans et al. (39) carried out the first experimental transport measurement of individual SWCNTs and showed that there are metallic and semiconducting SWCNTs, verifying the theoretical predictions. The room temperature conductivity was about $10^5$ to $10^6$ S/m for the metallic nanotubes and about 10 S/m for semiconducting tubes. Depending on the helicities of the outermost shells and the presence of defects, conductivity of individual MWCNTs have been reported to range between 20 and $2 \times 10^7$ S/m (40). The thermal conductivity in the axial direction of individual, perfect CNTs is reported to be as high as 3000 W/m/K (41), but have very small values in the radial direction.

The characteristics mentioned above make CNTs a promising filler for the fabrication of new, advanced composite systems. Notable similarities between the conductivity behaviour of nanotube networks and conducting polymers have been pointed out by Kaiser et al. (42). In this regard, composites of π conjugated polymer and CNTs are of importance as conjugated groups of
polymers would interact strongly with the planar graphitic structure of carbon nanotubes (43–45). The excellent properties of these two materials combined, has the potential for the development of still newer materials and devices.

1.2.4 Functionalisation of CNTs

Theoretically, the integration of conducting polymers and CNT produce promising materials. But the superiority of the product is determined by the uniform dispersion of CNTs in the polymer matrix. This step is usually difficult to achieve given the poor dispersibility and insolubility of CNTs (46). Consequently, the resulting composites are of inferior quality and do not exhibit desired properties. To aid the formation of composites with improved quality, different approaches to disperse the CNTs have been reported, which includes chemical functionalisation of the nanotubes and the noncovalent adhesion of surfactant molecules (47,48). Chemical modification of CNTs ensures good dispersion of nanotubes in a medium, and enhances the interaction between the two (47). But chemical functionalisation involves harsh chemical treatments in strong acids such as sulfuric acid and nitric acid which induces defects and shortens the tubes resulting in degradation of their electronic and conducting properties (49). However, for CNTs physically dispersed in conducting polymer matrices, the interaction may not be strong enough for the ultimate transfer of CNT properties. The covalent links between CNTs and polymer matrix can be utilized provided the functionalisation of CNTs is carried out under mild reaction conditions. Baek et al. (50) reported functionalisation of MWGNT with 4-amino benzoic acid via “direct” Friedel-Crafts acylation in a mild polyphosphoric acid (PPA)/ phosphorous pentoxide (P$_2$O$_5$) medium. The reaction condition
in this approach resulted in less destructive chemical modification and the functionalised MWCNT significantly enhanced the electrical conductivity of the resultant composite (51). This kind of covalent grafting of the nanotubes improved nanotube dispersion and creates microscopic interlinking sites.

1.3 **Intrinsically Conducting Polymers**

Alan J. Heeger, Alan G. MacDiarmid and H. Shirakava discovered in 1977, that a type of conjugated polymer called ‘Polyacetylene’ could become electrically conductive after undergoing a structural modification process called doping (52). The impact of this discovery was so profound that it won them the Nobel Prize in 2000. The alternating single and double bonds in the polymer chain enabled the electrons to de-localize throughout the whole system and thus many atoms may share them (53,54). This discovery revealed previously unexploited properties in polymers resulting in a new research field namely intrinsically conducting polymers (ICPs). These ICPs combine the typical properties of organic polymers such as low density, environmental stability, resistance to corrosion and low cost of synthesis with the conductivity of metals. They are called “intrinsically conducting polymers” to distinguish them from others which acquire conductivity when loaded with conducting particles such carbon black, metal flakes or graphite.

Today we have a variety of polymers which exhibit electrical conductivity and are often called “organic semiconductors” or “synthetic metals”. The structures of a few of these ICPs such as Polyacetylene, Polyiophene, Polyyrrole, Polyphenylene, Poly(phenylene vinylene), poly(3,4-ethylenedioxythiophene) and Polyaniline are given in figure 1.3.
These ICPs are expected to find application in a variety of areas such as lighting and displays, sensors, thermoelectrics, solar cells, EMI shielding, antistatic coatings, separation membranes, lightweight batteries (55-63) etc. Due to their advantages such as easy tailoring of conductivity along with low cost, light weight, easy processability, high flexibility and large surface area, they have started to replace inorganic semiconductors and revolutionise the electronics industry. The extended π-electron systems in ICPs are highly susceptible to chemical or electrochemical oxidation or reduction. Hence the electrical properties of such polymers can be altered by
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carefully controlling the process of oxidation and reduction (64). Since these reactions are often reversible, it is possible to systematically control the afore-mentioned property with precision, changing from a highly conducting state, through semiconducting, to an insulating state (64, 65).

1.3.1 Doping

In most of the cases, these ICPs are poor semiconductors in their neutral state and they become conducting only after introduction of electron acceptors/donors by a process known as ‘doping’. Doping increases the conductivity by adding mobile charges and delocalizing the electrons along the polymer backbone (54, 66). Dopants interact with the polymer chain by oxidizing or reducing them and do not participate in the charge transport mechanism directly. The doping of conducting polymers involves (1) charge transfer by oxidation (p-type doping) or by reduction (n-type doping), (2) the associated insertion of a counter ion for the overall neutrality, and (3) the simultaneous control of chemical potential (67, 68). When doping is done through oxidation or reduction, the polymer becomes p-doped or n-doped. By oxidation, an electron is removed and the polymer becomes positively charged, which is stabilized locally by an anion. Those charges then migrate in the polymer film creating electrical current. This type of doping is preferred to reductive doping, because the n-doped polymer becomes very unstable when exposed to ambient atmosphere. It will oxidize spontaneously and revert to the neutral state (69). Conjugated polymers can also be doped by protonic acid doping. This is called non redox doping since the number of electrons associated with the conducting polymer chain does not change during doping process. But the energy
levels are rearranged. Polyaniline (PANI) is an example of the doping of an ICP to highly conducting regime by this process (70).

Charge carriers in ICPs can be formed during doping by redox reaction or protonation. The local distortion of the conducting polymer structure, followed by removal of an electron generates a radical cation. Such a radical cation which is partially delocalized over some polymer segments is called a polaron (65). It is named so as it stabilizes itself by polarizing the medium around it. When a second electron is removed from the system, it may come from either a different segment of the polymer chain creating another polaron, or from the first polaron to generate a dication which is referred to as a bipolaron. For trans-Polyacetylene, two equivalent resonance forms exist, (i.e., degenerate ground state) that differ from each other by the position of carbon–carbon single and double bonds. Consequently, when a bipolaron structure is generated, they can readily separate and is known as a soliton (65, 71). Solitons are not formed in conjugated polymers with non-degenerate ground states, such as in polypyrrole, polythiophene and polyaniline (72). Figure 1.4 gives an example of polaron and bipolaron structure for PANI. With the increase in doping level, the population of polarons, bipolarons, and/or solitons increases. At high doping levels, (foreg. 50% in PANI) the individual bipolaron states coalesce to form bipolaron bands. Application of an external electric field makes both polaron and bipolaron mobile via the rearrangement of conjugation and thus gives rise to high conductivity in ICPs. At still higher doping level, two bipolaron bands would gradually broaden producing metal like conductivity (72).
1.3.2 Conduction mechanism in ICPs

The nature of the charge transport mechanism in ICPs is still a matter of debate. Nevertheless, the transport mechanism of the charge-carriers along the polymer backbone chain is described by the Band model as in the case of metals and semiconductors. As discussed, the doping induced changes in electronic structure namely polarons, bipolarons and solitons are responsible for conduction in a single chain molecule of ICPs. But Band theory does not explain accurately the electronic conduction in polymers. Here the atoms are covalently bonded to one another forming polymeric chains that experience weak intermolecular interactions. Thus, macroscopic electronic conduction will require electron movement not only along the chains but also from one chain to another (73). Moreover, most of the ICPs are partially crystalline and partially disordered. Hence polymer matrix consisting of crystalline regions is considered as metallic grains embedded
in a poorly conducting amorphous region (74). The π bonding orbitals and quantum mechanical wave function overlap are responsible for the charge transport in ICPs. But due to inadequacy of π-bonding overlapping between the molecules of disordered organic semiconductors, the concept of quantum mechanical tunneling is appropriate to explain the charge transport in these polymers (75). The conduction between different polymer chains (charge carriers) is generally referred to as “hopping transport”. The name is attributed to its quantum mechanical tunneling nature and reliance on the probability function (76). In hopping conduction, the localized states play a major role rather than delocalized bands. The conduction in conducting polymers can be described as the hopping of charge carriers, such as polaron, bipolaron and soliton. Assuming that the electron hopping was dependent on the initial and final energy states between which hopping occurred, a Variable Range Hopping (VRH) model was proposed by Mott and coworkers (77, 78). VRH model predicts that the conductivity can be expressed by

\[
\sigma = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{\frac{1}{\eta+1}}
\]

where \( T_0 = \frac{24}{\pi r_0^3 k N(E_f)} \) and \( \sigma_0 = \frac{9}{4} \sqrt{2 \pi e^2 \gamma_0} \sqrt{\frac{r_0 N(E_f)}{kT}} \)

\( n \) is the dimensionality of the material, \( r_0 \) is the localization length, \( k \) is the Boltzmann constant, \( \gamma_0 \) is the phonon vibration frequency, \( e \) is the electron charge, \( N(E_f) \) is the density of states at the Fermi level, and \( T \) is the temperature. This model has been widely used to study conductivity/temperature correlations in conducting polymers.
Thus, electrical conduction in ICPs is due to the collective effects of intra-chain hopping, inter-chain hopping, and tunneling of charge carriers.

### 1.3.3 Polyaniline

Among all conducting polymers, Polyaniline (PANI) is unique due to its ease of synthesis, non-redox doping, high environmental stability and wide application. PANI was known since 1862, but it rose to prominence recently owing to its high electrical conductivity on treatment with protonic acids. As of now, it is the most investigated conducting polymer (79).

The general formula for the polyaniline is

\[
\left[ \left( \begin{array}{c}
H \\
N \\
\end{array} \right) \right]_{x} \left( \begin{array}{c}
H \\
N \\
\end{array} \right)_{y}
\]

The structures of each repeating unit of PANI tetramer contain benzenoid diamine and or quinoid diimine segments which are present based on the extent of reduction or oxidation. The diversity in physiochemical properties of PANI is traced to the $\text{–NH–}$ group. The difference in the composition of amine and imine segments of PANI generates several oxidation states of this material ranging from completely reduced leucoemeraldine to completely oxidized pernigraniline states (79,80). The different forms of PANI can be readily converted to one another by simple redox methods. Out of several possible oxidation states, the 50 % oxidized emeraldine salt (ES) state shows electrical conductivity.
Depending on the neutral intrinsic redox states, PANI is classified as (81).

1) Pernigraniline \((y = 0)\), which is the fully oxidized state with blue/violet color.

2) Nigraniline \((y = 0.75)\), which is the 75% intrinsically oxidized with blue/violet color.

3) Leucoemeraldine \((y = 1)\), which is the fully reduced state having white/clear & colorless appearance.

4) Emeraldine \((y = 0.5)\), which is the 50% intrinsically oxidized.

Emeraldine exist in two forms which are emeraldine base (EB) and emeraldine salt (ES). Among these, the EB is the basic form of PANI which consists of four-ring tetramer structure having two segments of amine and two of imine, and is non-conductive. The dopants can be doped into PANI or de-doped from it reversibly due to their non-redox and physical interaction. The conductive emeraldine salt is produced by the electrostatic attraction between the anions of incorporated dopants and the nitrogen on the backbone of polyaniline (Fig.1.5) (82). Hence the most common route for the synthesis of PANI involves the use of acids in the presence of oxidizing agent such as ammonium persulfate (APS) in which the polymerisation and doping occurs concurrently and may be carried out either electrochemically or chemically (83).

### 1.3.4 Protonic acid doping in Polyaniline

EB form of PANI can be doped with strong protonic acid to give the highly conducting ES form without changing the total number of electrons associated with it (Fig.1.5) (84).
Protonation of PANI is accompanied by changes in electronic structure, crystallinity, solubility and the most important one is the increase of electrical conductivity over several orders of magnitude (85,86). Inorganic mineral acids such as HCl, H$_2$SO$_4$, etc. are the most frequently used dopants but the doped PANI in most of the cases, is completely insoluble. An important aspect of the protonic acid doping is that upon doping, only the proton is chemically bonded to polymer chain, the anion stays connected to positively charged PANI chain through electrostatic interaction (85). This property of acid doping results in several types of functionalised dopants which impart additional properties to the electrical characteristics of PANI. The dopant anions such as chloride, sulphate, toluene sulphonate, naphthalene sulphonate etc. greatly influence the electrical properties of PANI.

### 1.4 MWCNT-Polymer composites

To enhance both the electrical performance of conducting polymers and CNTs, one method is to develop carbon nanotube/ICP composites. The combination of CNT with conducting polymer especially PANI, offers new electronic properties based on the morphological tuning and the electronic interaction between the two (44). CNTs have been reported to improve the electrical properties of insulating polymer matrices, besides enhancing their thermal and mechanical properties. The high surface energies on CNTs due to their nanometer size and high aspect ratio tend to their bundling in
polymer matrix (3). To achieve homogeneous dispersion, de-bundling is essential. Uniformly distributed three dimensional network is required for achieving high electrical conductivity and improved mechanical properties for composites. Introduction of PANI coated CNT into polymer matrix can be an alternative for this problem.

1.4.1 MWCNT-Polyaniline composites

As a conducting polymer PANI has many advantages and its DC conductivity has been recorded at more than 1000S/cm (86). In spite of these desirable properties, certain deficiencies in its inherent characteristics are reported. It has poor thermal stability, lacks consistency in conductivity and has low mechanical strength which will all hinder the longevity of electronic devices (87, 88). As discussed in section 1.2.3, an easy and effective solution lies in the addition of CNTs to PANI, which results in synergism in the electrical property.

The properties of CNT/PANI composites depend on the uniform dispersion of carbon nanotube in the polymer matrix. For the synthesis of CNT-PANI composites, the important approaches are (1) in-situ polymerisation, involving synthesis of PANI in the presence of CNTs (89, 90) and (2) chemical interaction or grafting of polymer chains onto the surface of CNTs by covalent bonding (91). Studies have shown that in-situ polymerisation is the most favored method for synthesizing homogeneous and high performing CNT-PANI composites. In this method, nanocomposite is synthesized by dispersing the nanotubes in the monomer or monomer solution and the resulting suspension is polymerised by standard polymerisation methods. Enhanced electrical properties were reported for the composites.
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synthesised by in-situ chemical oxidative polymerisation of aniline in the presence of CNT (92-94). According to the authors, effective site-selective interactions between the quinoid ring of PANI and MWNTs facilitated charge-transfer processes between the two components and improved conductivity was observed. In such composites, CNTs could improve the polymer properties by (i) inducing additional structural ordering of the polymer (ii) improve the compactness and conjugation or chain length (iii) higher delocalization of charges and charge carrier mobility (iii) thermal stability (94). The results of in-situ methods (95, 96) indicated that the polymerisation of aniline initiated on the CNT walls, resulting in polymer coated CNTs. Aπ-π interaction between the CNTs and the PANI is proposed by them. Gao et al. (97) synthesised nanocomposites of benzene sulfonic acid functionalised multi-walled carbon nanotubes doped polyaniline via a low-temperature in-situ polymerisation method. The benzene sulfonic acid functionality helped to disperse CNTs homogeneously in the reaction medium and the monomers were adsorbed on the surface of CNTs. This was achieved due to the hydrogen bonding between the functionalised groups and the amino groups of monomer. Many methods prevail, of which the preparation method via interfacial polymerisation demands more attention.

1.4.1.1 Interfacial polymerisation

It is well-known that polyaniline synthesised through different polymerisation process shows varied morphology, crystallinity and electrical conductivity. For the synthesis of PANI/CNT nanocomposites with good conducting properties, a method leading to formation of a thin, well-aligned and highly ordered polymer chain on nanotubes is desirable. Interfacial
polymerisation of aniline in presence of carbon nanotubes at an aqueous-organics interface is reported to be the most efficient method for meeting the above requirement (96-99). Salvatierra et al. (96) report of CNT/PANI nanocomposites obtained through interfacial polymerisation. The results indicated that the polymerisation of aniline started at the carbon nanotube walls, which resulted in a final material in which the CNTs capped by a fibrous polymer shell. With 25% CNTs, DC conductivity of 9.5 S cm\(^{-1}\) was achieved. On the basis of several characterization techniques, they provided a model for the carbon nanotube/polyaniline interactions. Jeon et al. (98) polymerised aniline through an in-situ static interfacial polymerisation to yield the mixture of PANI and PANI-FMWCNT composites. From the cyclic voltammetry and conductivity measurements, they reported that PANI-FMWCNT displayed significantly improved conductivity and capacitance over PANI homopolymer. When the same group (99) attempted a simple suspension polymerisation, better yield resulted but conductivity declined compared with that from static interfacial polymerisation.

These CNT based polymer composites are useful for developing new applications in electronic and semi-conductor devices, as the substitute of semiconducting polymer or inorganic semiconductor. PANI-MWNT composites, having synergic effect on conducting property are used in many applications like organic light-emitting diodes, energy storage devices, thermoelectrics, sensitive materials for photovoltaic devices, EMI shielding, sensors, etc.

1.4.1.2 Thermal stability of conductivity

Thermal stability of conductivity of conducting nanocomposites is important. This is because they are exposed to high temperatures during
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their fabrication process and once incorporated into functional devices they are required to withstand extremes of climatic conditions such as high temperature and strong sunlight. So, to enhance the thermal stability of conductivity and thereby improve the life span of devices, a detailed analysis of thermal ageing of conductivity is required.

Previous reports on improved thermal stability of polyaniline composites are abundant. But studies on the effect of high temperature on stability of electronic transportation of polyaniline and its composites are few. Wang and Rubner (100) synthesised polyaniline doped with hydrochloric acid, sulphuric acid, methane sulfonic acid and p-toluene sulphonic and their conductivity stability was examined at different elevated temperatures under different environments. According to them, the conductivities of all doped polymers decayed at varying temperatures, with loss in conductivity most pronounced at or higher than 150°C. Prokes et al. (101) studied the effect of addition of inorganic salts to PANI sulphate and found that it showed improved stability of the electrical properties at high temperatures. This research group has done several studies on the conductivity ageing of polyaniline at elevated temperatures and suggested the reason for conductivity degradation to deprotonation, oxidation and cross linking reactions among PANI molecules (102,103). Rannou et al. (104) suggested that the decrease in the conductivity of doped PANI appears as a result of three major degradation processes namely dedoping, oxidation/hydrolysis/ scission of the chains and cross linking. In the model put forward they proposed that the effect of ageing is to increase the width of insulating barriers between highly conducting islands, the latter being progressively nibbled by a diffusive oxidation process.
Regarding CNT-based PANI composites, Ansari et al. (105) synthesised DBSA doped PANI/MWCNT nanocomposite and studied the stability of the nanocomposites in terms of DC electrical conductivity retention. According to them, MWCNT/PANI nanocomposites showed better structural and thermal stability of DC conductivity than pure PANI. They suggested that these composites could replace PANI in various electrical and electronic applications. In another study, Cabezas et al. (106) investigated the effect of carbon nanotubes on thermal ageing and electrical conductivity of composite films containing MWCNT/ PANI nanofibres. They reported that when subjected to thermal treatment, the presence of nanotubes retarded the loss of dopants from polyaniline and enhanced the thermal stability in electrical conductivity of the composite thin films. Also there was an increase in temperature for conductivity degradation and a significant reduction in the rate of degradation of conductivity of the composite thin films.

These studies on conductivity degradation of PANI and its composites on thermal treatment, show that retention of DC conductivity at elevated temperature opens a field for further research.

1.4.1.3 Thermoelectric properties

Thermoelectric energy conversion has received great attention as heat is directly converted to electricity in these systems using a class of materials called thermoelectric materials (Fig.1.6). This type of energy conversion can be widely used as a special power source and as a novel energy harvesting system as in waste heat recovery and high efficiency solar energy conversion (107). The fundamental problem in creating efficient thermoelectric (TE) materials is that they must be very good at conducting electricity while keeping
thermal conductivity to the minimum. In most materials, increase in electrical conductivity is generally accompanied by an increase in thermal conductivity too. Hence, the main focus of the research on TE materials is to improve electrical conductivity while keeping thermal conductivity low. A measure of thermoelectric efficiency ($Z$) is often described as $Z = S^2\sigma/k$, where $S$, $\sigma$, and $k$, respectively, are Seebeck coefficient, electrical conductivity, and thermal conductivity (108). The Seebeck coefficient is defined as the voltage generated per degree of temperature difference between two points ($S = -\Delta V/\Delta T$). In general, high Seebeck coefficient and electrical conductivity and low thermal conductivity result in high performance of thermoelectric materials. But in typical thermoelectric materials, strong correlations between these parameters make $Z$ improvement extremely difficult.

**Fig. 1.6: Principle configuration of single TE couple for power generation**

Usually research in thermoelectric materials is concentrated on inorganic semiconductors such as PbTe, Bi$_2$Te$_3$ etc. But their poor processability, high cost, toxicity and high density act as barriers in their commercial use (109). In this situation we need materials that are light weight, economical, easily
processable and having good thermoelectric property. Recently, ICPs have gained a special status owing to their wide range of applications. Though ICPs have low electrical conductivity and Seebeck coefficient as compared to the state-of-the-art inorganic thermoelectric materials, their low thermal conductivity can be considered an advantage for thermoelectric applications (110-113). Polyaniline (PANI) has gained special importance among conducting polymers due to its good processability, environmental stability, economic feasibility and tunable electrical properties. Furthermore its properties can be improved by selecting the method of polymerisation, and by the dopants and fillers used. CNTs with their excellent intrinsic electrical properties and structural characteristics have been used in the fabrication of many advanced functional materials. There are reports of enhanced thermoelectric properties of CNT filled polymer composites which maintain low thermal conductivity (114-116). This extraordinary behaviour is ascribed to thermally disconnected, but electrically connected energy carrier pathways. Meng et al. (114) synthesized PANI/MWCNT nanocomposites by a two-step process using thick CNT networks as a nanocomposite template. They obtained PANI/MWCNT composites with remarkably enhanced Seebeck coefficient and Power factor with relatively low thermal conductivities. They attributed this to the size-dependent energy-filtering effect caused by the nanostructured PANI coating layer enwrapping the CNTs. Similarly Yao et al. (115) reported that incorporation of SWCNTs into polyaniline resulted in dramatic improvement in both electrical conductivity and Seebeck coefficient. At the same time thermal conductivity of the composites, even with high SWNT content showed low values thereby satisfying the so-called “phonon-glass/electron-crystal” property required for thermoelectric materials. These
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studies revealed that the preparation of PANI/MWCNT composites can be an effective way of producing relatively low density, economical and efficient TE materials. But, these research works, lack the information regarding the effect of polymerisation process on the morphology, crystallinity and thermoelectric properties of PANI/MWCNT composites. It is well-known that polyaniline synthesised through different polymerisation process shows different morphology, crystallinity and electrical conductivities. For the synthesis of PANI/CNT nanocomposites with good conducting properties, a method leading to formation of a thin, well-aligned and highly ordered polymer chain on nanotubes is desirable. This conformation of the molecular chains is expected to increase carrier mobility in composites leading to a simultaneous improvement in DC conductivity and Seebeck coefficient.

1.4.2 MWCNT/Elastomer composites

Carbon nanotubes have been reported to improve the electrical properties of insulating polymer matrices besides enhancing their thermal and mechanical properties. Elastomeric matrix composites are reported to exhibit multi functionality and are suitable for the development of conductive polymer composites for flexible strain sensing and EMI shielding applications (117,118). The majority of elastomers are thermosets, which are chemically cross linked during the process of vulcanization. In thermoplastic elastomers (TPE), instead of chemical crosslinks, the hard segments have a glass transition temperature or melting temperature below the working temperature of the polymer, and act as physical crosslinks. Thermoplastic polyurethane (TPU) which possesses rubber-like elasticity can be considered as an interesting candidate for developing CNT-filled composites for a number
of applications because of its excellent mechanical properties, resistance to chemicals and unique combination of elastomeric properties and processability which does not require vulcanization (119).

1.4.2.1 CNT/Thermoplastic polyurethane composites

Thermoplastic polyurethane is an elastomeric block copolymer consisting of a soft phase containing either polyester or polyether, reinforced by hard micro domains of an aromatic diisocyanate extended with a short-chain diol. The mechanical, physical and chemical properties of TPU can be tailored by changing the molecular chain structure and the content of soft segment and hard segment (120). TPU makes an interesting candidate for developing ICP and or CNT-filled composites for a number of applications in electrostatic imaging, sensing, electrostatic dissipation, EMI shielding etc. (121). Several studies have reported the preparation of PANI/TPU and CNT/TPU composites using various processes like solution and melt processing (122). It is reported that strong interfacial adhesion between CNTs especially, with the functionalised MWNTs and TPU matrix contribute to the improvement of the mechanical properties of TPU/MWNT composites without sacrificing the elongation at break (123).

1.4.2.2 Synthesis of conductive TPU composites through in-situ polymerisation

The poor dispersion of CNTs in elastomers hinders the utilization of high conductivity and high aspect ratio of CNTs in composites. Though functionalisation can improve the dispersion, it has a deteriorating effect on conductivity. Functionalisation under mild reaction condition can reduce this effect, but the less number of functional groups is not sufficient, for overcoming the van der Waal’s force operating among the CNTs.
In this context, various strategies are taken up researchers in order to prevent the agglomeration and achieve a homogeneous dispersion of CNTs. Hwang et al. (124) modified the MWCNTs by a polymer wrapping method using poly (3-hexylthiophene) [P3HT] to achieve a homogeneous dispersion of MWCNTs in PDMS. They report that the percolation threshold of the composites was significantly lowered by the presence of P3HT. The electrical conductivity decreased with increasing P3HT concentration on the MWCNT surface, as it disturbed electron tunneling between MWCNTs and hence lowered the electrical conduction among MWCNTs. It is clear that novel methods to the in-situ polymerisation of polyaniline in TPU attempted by following researchers is significant.

However, the approaches that involve weak interactions such as polymer wrapping around the surface of CNT may not be the best option for the ultimate transfer of CNT properties to the insulating matrix. Instead, in-situ polymerised CNT-PANI filler could serve better for the maximum enhanced properties.

Denice et al. (125) obtained conducting, free standing films of PANI. DBSA/TPU by in-situ polymerisation of aniline in TPU. The in-situ blend preparation method was able to produce PANI.DBSA/TPU blends with enhanced compatibility, resulting in a fine dispersion and fine conducting pathways. The results revealed that the extent of the conducting polymer dispersion in the isolating polymer matrix exerts a strong influence on the electrical properties. Lakshmi et al. (126) synthesised PANI/TPU composites through in-situ polymerisation of aniline in TPU. They found the composite useful for microwave absorption and can be a potential candidate for EMI shielding applications. Also the mechanical properties of the composite film...
were found to be satisfactory for normal service conditions. The interfacial adhesion between PANI and TPU improved the dispersion as well as the transport and mechanical properties. Similarly in-situ polymerisation of aniline in TPU matrix containing CNTs can be an efficient method for uniform dispersion of NTs in the matrix.

1.4.4.3 Percolation threshold

For a conductive polymer composite composed of an insulating polymer and conductive filler, electrical conduction is mainly described by three phenomena namely, percolation, hopping conduction, and fluctuation induced tunneling between the conductors. According to percolation theory (127), the continuous network of conducting filler is the only pathway for electron transporting. The transition of the composite from an insulator to a conductor, as explained by percolation theory, is depicted in the figure 1.7.

![Fig. 1.7: Formation of conductive networks with filler loading](image)
At low filler concentration the composite remains insulating as the filler particles cannot form an interconnecting network. As the filler content increases the filler particles start to form percolative network, effecting a transition from insulator to conductor. The minimum volume fraction of fillers required so as to form a continuing conductive network within the composite is called the electrical percolation threshold (127,128). Near the percolation threshold, conductivity of composites experiences a sudden rise of several orders of magnitude. According to percolation theory,

\[ \sigma = \sigma_0 (v-v_c)^t \]

for \( v > v_c \)

where \( \sigma \) is the electrical conductivity of the composite, \( \sigma_0 \) is a constant for a particular filler–polymer combination, \( v \) is the volume fraction of filler, \( v_c \) is the percolation threshold, the exponent ‘\( t \)’ is related to sample dimensionality, i.e., \( t = 1, 1.33, \) or \( 2.0 \) for one, two, or three dimensions, respectively (127,129). The equation is valid at concentrations above the percolation threshold. Percolation threshold of conductive composites depends on conductivity, geometry and aspect ratio of the filler. CNT, high aspect ratio nanofiller is reported to form a network at a lower filler loading, decreasing the percolation threshold (130). For an insulating matrix, uniform distribution of well-dispersed, individual NTs can significantly decrease the percolation threshold. In order to achieve better dispersion, the affinity of NTs to the polymer matrix has to be improved and interfacial tension between NTs and fillers has to be reduced. Other techniques such as functionalisation of NTs, non-covalent coating of NTs etc. has been attempted and yielded results, but with many shortcomings.
1.5 Applications

1.5.1 Strain Sensing

Structural health monitoring of any structure is essential be it in the field of engineering, medicine, space or ocean research. A strain sensor measures the deformation of a structure or component by experiencing the same deformation as that of the component. Usually, deformation of a strain sensor material results in change of any of its measurable properties. In an electro-mechanical strain sensor, which is a conductor or semi-conductor, the strain applied results in change of electrical properties. Sensing mechanism of the electromechanical sensors is related to change in electrical conductivity under the effect of pressure, displacement and strain and can be explained by the percolation theory (131,132).

One of the basic assumptions in percolation theory is that the filler is an infinite conductor, while the matrix is an infinite resistor, and there is no contact resistance between the fillers (127,133). But it is highly possible that barriers are present between conductive fillers and the electrons need to tunnel through these barriers by quantum mechanical tunnelling which creates tunnelling resistance. The characteristic behaviour of this tunnelling resistance is its temperature dependence. Various models such as Fluctuation Induced Tunnelling (FIT) and Variable Range Hopping (VRH) model have been developed to describe the tunnelling resistance in disordered solid. The VRH model is often used to describe the conduction mechanism of CNT composites or mats (134). Also there are reports of the charge transportation mechanism in polymer/MWNT composite regulated by the FIT model (135).
Regarding the deformation of conductive network in the composite which leads to a change in the resistivity or resistance, researchers have adopted different approaches when models were built for the strain dependent resistivity behaviour. The fundamental factors considered by them are (1) the variation of the number of conductive path; as some of the conductive pathways will be broken down with deformation that will definitely lead to an increase of the resistivity, (2) the variation of the inter-particle distance; as the electrons need to tunnel through a barrier between two conductive fillers when travelling through the conductive network of the composite. When the composite is deformed, this inter-particle distance may be increased, which leads to an increase of the resistivity (136). Knite et al. (137) proposed a model for the strain-dependent resistivity results of polyisoprene/CB composites based on these aspects. Zhang et al. (138) identified charge transport mechanism of amino-functionalised MWNT/polyurethane-urea elastomeric composite sensor material as a fluctuation induced tunneling. According to them, the prediction for the gap width modulation by this model is well supported by the resistivity-strain dependence for the 5%–80% range of strain. For strains in the range 0%–5%, the resistivity-strain dependence is dominated by the deformation of the conductive network.

1.5.1.1 CNT/Elastomer composites in Strain sensing

Conventional strain sensors such as metal-foil strain gauges, though convenient to use, suffer a number of disadvantages such as poor flexibility, low gauge factor, low dynamic range, long term stability etc. In this context, CNT/elastomer composites with their high elasticity and ability to cover...
surfaces of different shapes, large strain sensing range, and wide working range can be utilized in vast and varied environments. In an attempt to modify the strain sensitivity of CNT based elastomeric composites, Costa et al. (139) investigated the piezoresisitive properties of tri-block copolymer styrene–butadiene–styrene/CNT composites, which showed gauge factors up to 120. They reported that linearity obtained between strain and electrical resistance makes these composites interesting for large strain piezoresisitive sensors applications. Similarly, Kang et al. (140) examined the strain response of the MWCNT/ethylene–propylene–diene rubber composite and found that it was possible to measure tensile and compressive strains by using a 20 weight% MWCNT/ethylene–propylene–diene rubber composite. Recent works on TPU composites showed that they can sustain very large deformations and possess excellent thermophysical properties. MWCNT/TPU composites with their strong interfacial adhesion, stress transfer and excellent strain sensitivity have a greater potential to exhibit better piezoresistivity properties. Slobodian (141) et al. developed a highly deformable composite composed of a network of entangled carbon nanotubes embedded in polyurethane. The gauge factor of the composite increased linearly with strain from values around 4 at the start of deformation to nearly 69 at 400 % strain. This property as a strain sensor has been demonstrated in orthopedics and rehabilitation. Bautista-Quijano et al. (142) reported the enhanced piezoresistivity of MWCNT/segmented polyurethane (SPU) composites having sensing applications in prosthetics, biomedical devices, and smart textiles. For the composites at 8 weight % MWCNT, the piezoresisitive signal allowed to measure strains up to 400% before electrical depercolation did occur. Zhang et al. (143) reported the resistivity response
under cyclic loading of TPU/MWNT elastomeric nanocomposite films fabricated by a solution process with good nanotube dispersion and low percolation threshold (0.35 weight %). At 5% strain, the strain-dependent resistance showed good recoverability and reproducibility, but when larger strains were applied, only a small part of the resistance was recoverable. Bilotti et al. (144) fabricated a highly conductive TPU/CNT fibre by a continuous extrusion process. The TPU/CNT fibres were sensitive to both static and cyclic deformation, which give them potential uses in smart textiles. Lin et al. (145) demonstrated that mixed carbon fillers and functionalised carbon nanotubes were vital for preparing TPU based strain sensors with tunable sensitivity. This study provided a unique method for the preparation of high-performance conducting polymer composite (CPC) strain sensors with a large range of resistivity-strain sensitivity.

1.5.2 Electromagnetic Interference Shielding

Due to the high operating frequency and bandwidth of electronic equipments, electromagnetic interference (EMI) has attained the tag of an ‘Environmental pollutant’. EMI has negative effects on other electronic devices and also on all forms of live organisms. Electromagnetic radiation affects electrical circuits and prevents them from functioning efficiently at the receiving end. Electromagnetic Interference (EMI) is the process by which electromagnetic disturbance is transferred from one electronic equipment to another through radiation, conducted paths (or both) (146). So, commercial electronic products should meet prescribed standards of electromagnetic compatibility, i.e., the property of a device by virtue of which its emissions do not deter the device itself or others, from achieving
performing efficiency. EMI shielding denotes the reflection and/or absorption of electromagnetic radiation by a material which resists the penetration of the EM waves through the shield (147). The ability of shielding material to attenuate EM waves is called shielding effectiveness (SE).

The EMI SE of a material is expressed in terms of ratio of incoming (incident) and outgoing (transmitted) power. The EMI attenuation offered by a shield may depend on the three mechanisms: reflection and absorption of the wave as it passes through the shield’s thickness and multiple reflections of the waves at various interfaces (Fig.1.8).

Fig.1.8: The three different mechanisms of EMI shielding
Therefore, SE of EMI shielding materials is determined by three losses viz. reflection loss (SE_R), absorption loss (SE_A) and multiple reflection losses (SE_M) and can be expressed as (148)

\[ \text{SE}_{\text{TOTAL}} = \text{SE}_A + \text{SE}_R + \text{SE}_M = 10 \log_{10} \left( \frac{P_I}{P_T} \right) = 20 \log_{10} \left( \frac{E_I}{E_T} \right) \] .......(1.3)

Where \( P_I \) is the incident energy field, \( P_T \) is the transmitted energy field, and \( E \) is the root mean squares of the electric field strengths of the electromagnetic wave. When SE total > 10 dB, SE_M can be neglected (148) and it is usually assumed that

\[ \text{SE}_{\text{TOTAL}} = \text{SE}_A + \text{SE}_R \]

**1.5.2.1 CNT/Polymer composites in EMI Shielding**

Metals have excellent capability in attenuating EM waves and initially, metallic components were used for shielding purpose. But certain properties of these metal housing shields such as high density, susceptibility to corrosion, complexity and expensive processing limited their use (149). Metals also reflect radiation and cannot be used in applications where absorption is desired such as in stealth technology. Among the various materials experimented, polymer composites based on CNTs showed great promise. CNTs use both mechanisms of reflection and absorption to attenuate the incident wave. High strength and stiffness, extremely high aspect ratio and good electrical conductivity of CNT make it a filler of choice for shielding applications (31). Despite these advantages, a homogeneous dispersion of CNTs in a polymer matrix is difficult to attain. This results in low electrical conductivity of these nanocomposites. Many
groups have attempted strategies to improve the dispersion of CNTs and thereby improve electrical conductivity. Yang et al. (150) introduced MWCNTs into polystyrene and studied the EMI shielding behavior of the composites. They achieved a SE of 20 dB at 7 wt% MWCNT loading. Saini et al. (151) showed that incorporation of PANI/MWCNT in Polystyrene matrix improved the SE to the range of 23 to 46 dB depending on the chemical composition of PANI/MWCNT filler and shield thickness. Recently the same group (152) had introduced a facile, scalable and commercially viable melt blending approach involving use of twin-screw extruder with melt recirculation provision, for uniform dispersion of up to 4.6 vol% multiwall carbon nanotubes (MWCNTs) within polypropylene random copolymer (PPCP). The improved dispersion led to a very low percolation threshold (0.19 vol %) with a EMI SE value of 47 dB (>99.99% attenuation). Besides this, high tensile strength of 42 MPa and good thermal stability demonstrated its potential for making light weight, mechanically strong and thermally stable EMI shields. According to these reports, parameters such as aspect ratio, conductivity, orientation, dispersion and concentration of NTs influence percolation threshold, conductivity and EMI SE of the polymer composites. The Processing method also has a crucial influence on these parameters. Huang et al. (153) prepared functionalised-MWCNTs/poly (methyl methacrylate) (PMMA) composites by in-situ and ex-situ routes and found that in-situ formed composites give superior SE (17 dB at 12 GHz) at comparative loading than ex-situ formed composites. From the aforementioned discussion, it is evident that in-situ polymerisation is an easy method for obtaining low percolation threshold, high conductivity and high EMI SE.
Scope and objectives of the work

The unique properties of CNTs and intrinsically conducting polymers facilitate their use in organic electronics. But issues such as maintaining a strong interaction between CNTs and ICPs in the composites and retaining the thermal stability of the conductivity remain as major challenges. This thesis aims to tackle these issues. To achieve good compatibility between CNT and PANI, CNTs can be made more polar by attaching appropriate functional groups under mild conditions. Interfacial polymerisation of aniline in presence of CNT can improve interaction between CNTs and PANI. Ideal conductive filler should possess low percolation threshold, high conductivity as well as consistency in conductivity and good mechanical properties for the polymer matrix. Use of these composites in organic devices demands stable and high electrical conductivity.

The objectives of the thesis are to synthesise core-shell nanoparticles of CNT and PANI with high conductivity as well as with good thermal stability of conductivity. These PANI coated CNTs can be used as efficient fillers in polymer matrix making it a candidate material for real applications such as in thermoelectric, strain sensing and EMI shielding.

The objectives of this work are-

- To develop PANI-FMWCNT core-shell nanostructures through interfacial polymerisation process to achieve high and stable electrical conductivity.

- To understand the effect of temperature on conductivity of PANI and PANI-FMWCNT composites doped with different dopants.
To develop PANI-FMWCNT composites with good Seebeck coefficient, high electrical conductivity and low thermal conductivity.

To develop PANI-FMWCNT/TPU strain sensors with improved sensitivity, gauge factor and reversibility.

To evaluate the experimental values of strain sensitivity with theoretical values.

To develop PANI-FMWCNT/TPU composites with high electromagnetic shielding effectiveness along with low percolation threshold, good thermal stability and mechanical properties.

References


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