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INVESTIGATION OF THE EFFECT OF MIXING METHODS AND CHEMICAL TREATMENTS ON THE CONDUCTIVITY OF THE CNT/PLA BASED COMPOSITES

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Ce mémoire intitulé :

INVESTIGATION OF THE EFFECT OF MIXING METHODS AND CHEMICAL TREATMENTS ON THE CONDUCTIVITY OF THE CNT/PLA BASED COMPOSITES

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DEDICATION

“To mom, dad and baba”

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RÉSUMÉ

La popularité croissante de l'acide polylactique (PLA) est liée à sa biocompatibilité, ses bonnes propriétés mécaniques, et sa synthèse possible à partir de ressources renouvelables. Le PLA peut être mélangée avec des charges conduisant l'électricité (par exemple des nanotubes de carbone (NTC)) pour former des composites conducteurs à base de polymères (CPC). Ces charges amènent la fonction conductrice grâce à la formation de chemins de percolation. Très légers, les CPC ont le potentiel de remplacer les métaux dans l'industrie électronique s'ils atteignent des conductivités électriques similaires. Les problèmes actuels qui se posent lors du mélange de nanotubes de carbone dans une matrice de polymère sont la formation d'agrégats en raison des forces de van der Waals puissantes, et la rupture des nanotubes de carbone au cours de la dispersion. Dans cette étude, nous comparons: (1) deux méthodes de fabrication pour créer des CPC (soit le mélange de solution par ultra-sons et l'extrusion) (2) les effets des différentes techniques de fonctionnalisation NTC (c'est à dire, traitements par acide ou plasma) et (3) l'effet de l'utilisation de molécules de liaison telle que la para-phénylènediamine, qui agissent comme des ponts entre les NTC dans le CPC, et l'effet sur la conductivité des CPC. Ces matériaux composites conducteurs peuvent trouver des applications technologiques diverses qui soit nécessitent, soit peuvent bénéficier, de la capacité à réaliser des éléments avec des motifs microscopiques dans des architectures en deux dimensions (2D) et en trois dimensions (3D). Une technique de fabrication en écriture directe est utilisée pour réaliser ces motifs imprimés, en utilisant la solution de CPC comme encre.

Tout d'abord, les composites comprenant 30% massique de PLA dans du dichlorométhane (DCM) et des NTC à différentes concentrations (jusqu'à 5 %massique) sont fabriqués par une méthode en deux étapes de traitement par ultrasons (c'est à dire dissoudre le PLA dans du DCM, puis la disperser des NTC dans la solution de polymère). Deuxièmement, les CPC sont fabriqués en utilisant une micro extrudeuse à double vis fonctionnant à 180^{0}C. Pour vérifier les effets de la fonctionnalisation des nanotubes de carbone sur la conductivité des matériaux composites, les NTC sont fonctionnalisés par trois méthodes: - fonctionnalisation par l'acide HNO_3, fonctionnalisation par acide (plus fort) $HNO_3 + H_2SO_4$ avec un ratio de 3 :1, et fonctionnalisation par plasma N_2. Pour vérifier l'effet des molécules de liaison amine, les NTC fonctionnalisés par acide HNO_3 sont traités avec un mélange de para-phénylènediamine et d'aniline dans une

solution acide. Les fibres de CPC sont créées en utilisant la méthode d'impression par injection de solvant. Ces fibres sont ensuite testées pour leur conductivité électrique en utilisant le procédé de résistivité par deux sondes. La conductivité électrique maximale est observée dans les échantillons de concentration de 5%massique de NTC à 3,97 S / m et 25,16 S / m pour les fibres de CPC obtenues par le mélange de solution et le procédé d'extrusion, respectivement. En ce qui concerne les NTC fonctionnalisés, les mesures de conductivité montrent un effet négatif de la fonctionnalisation sur les propriétés électriques du CPC. Les fibres de CPC avec NTC et PLA traités par amine présentent une meilleure conductivité (4.2 S/m) que les échantillons avec CNT et PLA non traités fabriqués avec la méthode de mélange de solution.

Enfin, des structures 1D telles que les fibres et des structures 2D ou 3D d'échafaudage simples et multiples ont été fabriquées en utilisant la technique d'impression par injection de solvant avec la solution de CPC dans du di-chloro méthane (DCM) comme encre, décrite ci-dessus. Ces microstructures conductrices peuvent trouver une application dans l'industrie électronique et dans les systèmes micro-échelle telles que la détection de pollution dans les milieux naturels, l'ingénierie des tissus, les capteurs mécaniques et les appareils intelligents.

ABSTRACT

The growing popularity of Poly lactic acid (PLA) is mainly due to its biocompatibility, good mechanical properties, and its synthesis from renewable resources. PLA can be compounded with electrically conductive fillers (e.g., carbon nanotubes (CNTs)) to form conductive polymer composites (CPCs). These fillers provide conductive functionality to the composite material by forming percolation paths. Featuring very low weight densities, CPCs have the potential to replace metals in the electronic industry, if they exhibit similar electrical conductivities to that of the metals. The current challenges being faced during the mixing of CNTs in the polymer matrix are: formation of aggregates due to strong van der Waals forces and breakage of CNTs during dispersion. In this study, we compare: (1) two fabrication methods to create CPCs (i.e., solution mixing by sonication and melt extrusion) (2) effect of various CNT functionalization techniques (i.e., acid and plasma treatments) on the conductivity of CPCs and (3) effect of using binding molecules like para-phenylenediamine, that act as bridges in between the CNTs in the CPCs and its effect on the conductivity of CPCs. Such conductive composite materials find widespread technological applications which either require, or could benefit from, the ability to pattern micro-sized features in two-dimensional (2D) and three-dimensional (3D) architectures. Direct-write fabrication technique is used to realise these printed patterns, using the CPC solution as ink.

First, the composites comprising of 30% PLA by weight in Dichloromethane (DCM) and CNTs in different concentrations (up to 5wt. %) are fabricated using a two-step sonication method (i.e., dissolving PLA in DCM and then dispersing the CNTs in this polymer solution). Second, CPCs are fabricated using a twin screw micro extruder operating at 180^0C. To verify the effects of functionalization of the CNTs on the conductivity of composites, the CNTs are functionalized by three methods: HNO_3 acid functionalization, 3:1 ratio HNO_3 + H_2SO_4 acid (stronger) functionalization and N_2 plasma functionalization. To check the effect of amine binding molecules, HNO_3 acid functionalized CNTs are treated with a mixture of para-phenylenediamine and aniline in an acidic solution. These chemically treated CNTs are then mixed with PLA to form composites. CPC fibers are drawn using the solvent-cast printing method. These fibers are tested for their electrical conductivity using the two-probe resistivity measurement method. Maximum electrical conductivity was observed in the 5wt. % CNT concentration samples at 3.97 S/m and 25.16 S/m for CPC fibers obtained via the solution blend and the extrusion methods,

respectively. In the case of the functionalized CNTs, conductivity measurements show a negative effect of functionalization on the electrical properties of the CPC. While, the amine treated CNT/PLA CPC fibers show better conductivity at 4.2 S/m when compared to the untreated CNT/PLA samples manufactured using the solution mixing method.

Finally, one-dimensional (1D) structures like fibres and 2D, 3D structures like single and multi-layer scaffolds were fabricated using the solvent-cast printing technique with the above manufactured CPC solutions in DCM as inks. Such conductive microstructures find their application in the electronic industry and in micro-scale systems such as pollution detection in natural environments, tissue engineering, mechanical sensors and smart devices.

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LIST OF ACRONYMS

CNF – carbon nanofibers

CNT – carbon naotubes

CPC – conductive polymer composite

DCM – dichloromethane

DW – direct write

DWCNT – double walled carbon nanotubes

FTIR –Fourier transform infrared spectroscopy

MWCNT – multi walled carbon nanotubes

NW – nano wires

PE – polyethylene

PET – polyethylene terephthalate

PLA – poly lactide or poly lactic acid

PP – polypropylene

PS – polystyrene

SWCNT – single walled carbon nanotubes

XPS – x-ray photon spectroscopy

2D – 2 dimensional

3D – 3 dimensional

INTRODUCTION

Background and problematic

Today, a lot of interest is being expressed in the development of conductive polymer nanocomposites (CPCs), a new kind of advanced material generated by dispersing a conductive nanoparticles within an insulating polymer matrix [1-3]. After their discovery by Iijima in 1991 [4], carbon nanotubes (CNT) owing to their unique properties, lightweight and high aspect ratio that enables them to achieve the relatively low percolation threshold, have widely been investigated as filler material for CPC. CPCs also can exhibit multifunctional properties such as high mechanical stiffness and strength, along with thermal and electrical conductivity at relatively low CNT loadings, which make them suitable for a broad range of potential applications such as sensors [5], actuators [6], electromagnetic interference shielding [7], as well as energy and gas storage [8].

Most of the above mentioned applications either require, or can benefit from, the ability to pattern micro-sized features in complex three-dimensional (3D) architectures. An increasingly popular method for designing these kinds of 3D structures is the Direct-write method. Direct-write (DW) assembly is a 3D printing technique that employs a computer-controlled translation stage, which moves an ink-deposition nozzle, to create materials with prescribed 3D architecture and composition [9]. Many ink materials have been employed such as organic fugitive inks [10], concentrated polyelectrolyte complexes [11], colloidal suspensions [12-14], hydrogels [15, 16] and thermoset polymers [17]. These inks solidify through different mechanisms such as viscoelastic recoil [10], coagulation in reservoir [11], suppression of repulsive forces [12], and UV polymerization [15-17].

Polylactide (PLA) is one of the most popular bio-based thermoplastic polymer material used for the 3D printing process because it is widely available commercially, biodegradable, biocompatible and has a relative high-strength, high-modulus and good processability [18]. Several strategies and technologies using PLA to fabricate microscale 3D geometries have been developed. For the above mentioned applications and easy processability, the amount of filler loading in the CPC needs to be low (less than 5 wt. % concentration). At such low concentrations it is possible to achieve high electrical conductivity only through the formation of a conductive pathway, i.e., the CNTs need to be arranged in a way such that they are in contact with each other after their dispersion in the polymer matrix. To achieve this, method of CPC synthesis and chemical treatment and functionalization of the CNTs play a very important role. There are many ways in which the conductive fillers can be dispersed in the polymer matrix. For example, solution mixing method uses a simple sonication bath to disperse the filler in the polymer material. However this method exhibits limited precision of the desired mechanical and electrical features, and hence, the twin screw extrusion method is used, which mixes the feed material at a high shear and thus resulting in better dispersion. Also, to achieve higher conductivity values at low CNT loading we need to find a way to form the percolation pathway, for this functionalization of CNTs in tried. However, these techniques were unable to have a positive effect on the electrical properties of the CPC. Thus, new method of using amine molecules as "bridges" between two CNTs is used to develop CPC with higher electrical conductivity which would foster larger utilization of their based materials in potential applications in the electronic industry.

Thesis structure

This thesis is based on the experimental work and a peer reviewed conference article that was published and presented as ASME-IMECE 2014 conference proceeding:

Chapter 1 provides a literature survey of PLA properties, factors in the preparation of electrically conductive nanocomposites, microfabrication techniques, types and effect of functionalization of CNT on the properties of the CPC and the use of binders as bridging molecules. Research objectives and the coherence between the specific objectives and the journal article are described in Chapter 2. The main achievement of the thesis is given in the format of a peer reviewed conference article in Chapter 3. Chapter 4 deals with the additional experimental results obtained in regards to this thesis, i.e., the use of amines as binders that act as bridges in between the CNTs and their effect on the conductivity of the CPC. Also, it presents a comparison of the electrical properties of all the produced samples and gives an account on the printability of these CPCs. Finally, a general discussion of the main results is presented in Chapter 5, while conclusions and recommendations are stated towards the end of the thesis.

CHAPTER 1 LITERATURE REVIEW

Composites (sometimes referred as composite materials) are materials made from two or more constituent materials that differ significantly both in their chemical composition and physical properties [1]. The final product thus produced has different characteristics as compared to the individual components. Within the composite, each of the individual components remains distinct and separate. Today these new materials are being preferred because they tend to be stronger, lighter and less expensive when compared to the conventional materials. A few of the most common examples of composites found today are concrete, ceramics, plastic, fiber reinforced glass, etc [2,3]. The constituent materials that a composite is made of can be divided into two main categories: matrix and reinforcement. The presence of at least one portion of each type is essential. Within the composite the matrix material surrounds and supports the reinforcement materials, while the reinforcements impart their special properties to enhance the matrix properties [4]. A synergism between the mixed materials produces material properties unavailable from each of the individual constituent materials. Desired combination can be ensured due to the presence of a wide variety of matrix and reinforcement materials [5]. Many advances have been made in the manufacture, design and application of composite materials which can be quite strong and stiff, yet light in weight and possess a variety of new properties like electrical conductivity, thermal conductivity and elasticity. Such composites also exhibit toughness properties and fatigue better than most common engineering materials.

Most composites use a polymer material as the main component i.e., the matrix solution [6]. The most common polymer materials used are poly-lactic acid (PLA), polyethylene (PE), polyester, and polypropylene. Depending on the desired characteristics, there are a wide variety of reinforcement materials like metal particles and nano particles, carbon nanotubes (CNTs), carbon nanofibers (CNFs), etc [7-9]. In general, the main physical properties of the composites is mainly dependent on the kind of material chosen as the matrix material. Now-a-days composites use thermosetting or thermoplastic materials as the matrix material. Thermosets are liquid when prepared but harden on curing, the process is irreversible and they do not become soft again even on the application of high temperature, while thermoplastics are hard at low temperatures but when temperature is raise they soften [10]. Such materials are mostly recyclable, dissolve easily even in inorganic solvents, have very long shelf life and have a greater fracture toughness when compared to the thermoset materials [11]. As a summary, the two main advantages of composite materials is their strength, combined with lightness and flexibility of design and it is basing on these properties that the works have been undertaken in this project – by trying to design a conductive polymer composite (CPC) which is as conductive as the metals, light weight, and can be 3D printed has the potential to replace the metals used in the electronic and aviation industry today.

1.1 CNT-polymer nanocomposites

Electrically conductive polymer composites are of great interest because of their excellent combination of beneficial properties of polymers and electrical conductivity. The general idea behind the designing and synthesis of a CPC is the addition of conductive fillers into polymers that are usually insulators [12,13]. While polymers can be of various types depending on the type of application, among the fillers metals and carbon black are the ones traditionally used for the production of CPCs but since the discovery of CNTs by Iijima in 1991, the high aspect ratio and excellent physical as well as mechanical properties have made CNTs one of the most preferred conductive fillers for developing multi-functional CPCs. The electrical conductivity of polymers is very small compared to the electrical conductivity of CNTs [14]. Hence, small amount of CNTs when added into polymers remarkably improves the electrical conductivity without having a significant effect on intrinsic properties of the polymers [15]. Such conductive polymer composites are more desirable compared to other conductive or semi-conductive materials like silicon, ceramics and metals due to their flexibility, good chemical and biological compatibility, light weight, ease of synthesis and even printability [16,17]. These and many other properties have made CNT-polymer conductive composites one of the most promising material candidates for a large variety of applications such as conductive coatings, stretchable electronics, to design light weight electronic circuits, lightning strike protections in aircrafts, liquid and gas sensors, solar cells and electromagnetic shielding [18-20].

1.2 Electrical behaviour of CPCs

As mentioned above, small amounts of CNTs when added to a polymer significantly improve the conductivity of the composite. This has been confirmed by both experiments and simulations that electrical conductivity in any composite exhibits a percolation like behavior as shown in figure

1.1, i.e., electrical resistivity of CPCs decreases exponentially when the CNT weight percentage reaches a certain critical value, this is referred as “percolation threshold” [21]

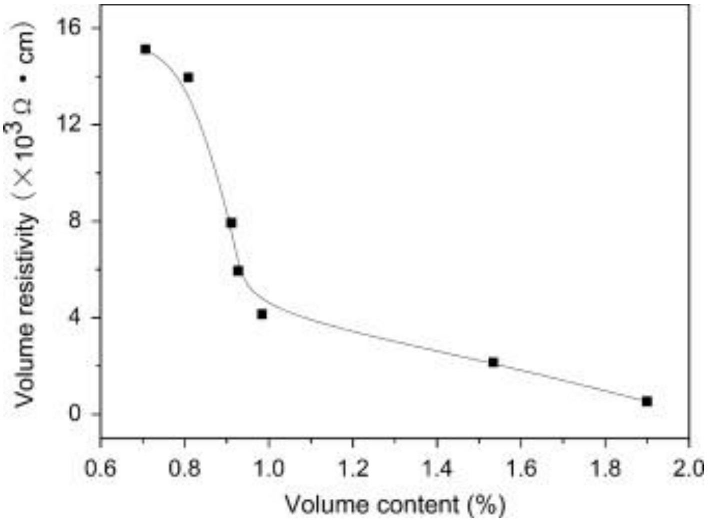


Figure 1.1 : Variation of the resistivity value of the CPC with CNT concentration [22]

This type of percolation behavior can be explained by two mechanisms: electron hopping at nanoscale and conductive networks at the micro scale [23]. The contribution of electron hopping (tunnelling) and conductive networks to electrical conductivity of composites depends on the amount of CNT in the composite. Electrons always have a probability of hopping from one CNT to the other, but this is dependent on the distance between the CNTs. When the separation distance between the CNTs is large, CNTs are electrically independent but when the concentration of CNTs in the polymer composite increases, the CNTs are more connected and thus resulting in micro scale conductive pathways. When compared to the polymer, CNTs are expensive and not easy to handle during the manufacturing process. Ideally, for their practical use, the nanocomposite manufacturing process needs to be cost effective and simple, this can be achieved by keeping the CNT concentration at a minimum (less than 5 wt.% CNT loading). Limiting the amount of the filler in the nanocomposite also keeps a check on the toxicity of the composite, which is an important parameter in many industries. In order to achieve high electrical conductivity in a nanocomposite, the reduction of the percolation threshold is important. To achieve this, a conductive network at low filler concentration is to be attained and this can be done by well dispersed and not necessarily well distributed filler. Figure 1.2 shows the various distribution and dispersion scenarios of the filler material in the polymer matrix.

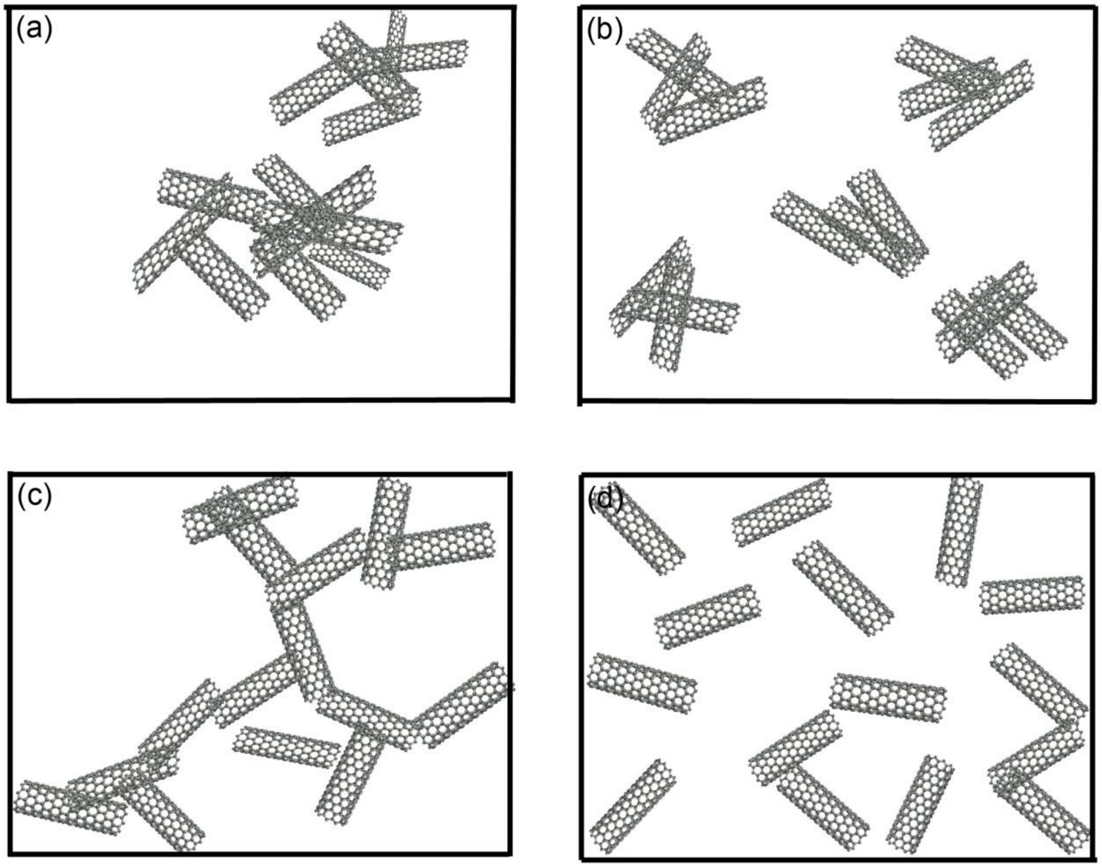


Figure 1.2 : Schematic showing the different possible dispersion and distribution scenario of filler in the polymer composite. (a) No conductivity. Bad distribution and dispersion (b) No conductivity. Good distribution and bad dispersion (c) Conductivity. Bad distribution and good dispersion (d) No conductivity. Good distribution and dispersion [24].

Apart from the dependency of electrical conductivity of composites on concentration of the CNTs and the conductivity mechanisms, the electrical performance of the CPCs also depends on the method of synthesis of the polymer composite. The type of synthesis method used has a direct effect on the dispersion of CNTs in the polymer matrix. Greater the extent of dispersion of the CNT fillers in the polymer matrix, the less probable they are to form a percolative path. This is because, greater dispersion implies that the CNT fillers are separated from each other and are not in contact which is otherwise required for the formation of a percolative path. But at the same time to ensure an ideal final nanocomposite the CNT fillers need to be thoroughly mixed to ensure their proper imbedding in the polymer [25,26].

Despite of extensive experiments and simulations being carried out regarding the electrical conductivity of composites, the experimental work on this topic is relatively less. Efforts have been made to maximise electrical conductivity by aligning the CNTs in the composite material after their synthesis by the application of an external electric field (Arguin et. al (2014)), but this makes the CPC synthesis a two-step process. For bulk manufacturing and possibility of practical application the CPCs need to be aligned to form a conductive pathway during the manufacturing step. This thesis is an investigative report on the effect of the method of synthesis and functionalization of CNT fillers on the conductivity of the manufactured composite. The project also investigates the possibility of the use of binding molecules as bridges between two CNTs within the composite thus enabling the formation of a conductive pathway.

1.3 Material selection

Material selection process is one of the most important factors for the design procedure. During the systematic selection of the material for the design process the optimization factor is taken into consideration, where the merit of a material plays an important role in the selection. In general, the parameters taken into consideration are: availability, cost, renewability, eco-friendly, density, tensile strength, resistance to corrosion and temperature and stiffness [27].

CNTs are long nano-scaled cylinders, are made of a rolled monolayer sheet of three-coordinated carbon atoms forming a hexagonal structure. This structure is similar to the structure of benzene rings. These carbon atoms are slightly pyramidalised from sp^2 hybridisation of graphene, toward the diamond like sp^3 [28]. The basic types of CNTs discovered are: single-walled CNT (SWCNT), double-walled CNT (DWCNT) and multi-walled CNT (MWCNT). A SWCNT consists of one such rolled cylinder, while DWCNT and MWCNT consist of two and several concentric cylinders whose radii differ by the inter layer spacing of graphite ~ 0.34 nm (see Figure 1.3) [29]. CNTs exhibit extraordinary mechanical properties that make it ideal for reinforced composites. They show high Young’s modulus and are stiff. The tensile strength of CNTs is also very high, it’s considered to be more than ten times that of steel, with the same weight. CNTs are found in both semiconducting and metallic forms, which contribute to the properties of their bulk materials.

SWCNTs exhibit interesting electrical properties, deriving from the quasi-one-dimensional nature, cylindrical symmetry and the sp^2 hybridization of carbon bonds. The electronic structure of SWCNTs can be described using band structure, in which grapheme is considered as a starting point and it's then wrapped to form a tube. Owing to this SWCNTs exhibit both semiconducting and metallic properties in different directions. In case of the MWCNTs, to exhibit metallic nature only one of the concentric tubes needs to have metallic character [30].

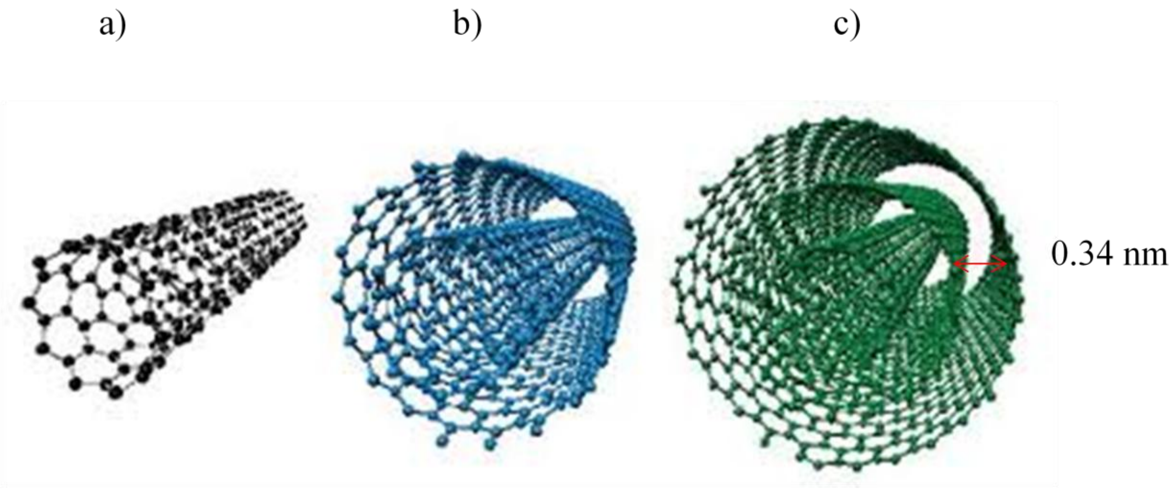


Figure 1.3 : Schematic showing the three types of CNTs:

a) Single-walled b) Double-walled and c) Multi-walled [29]

Extensive literature explains the variation of electrical conductivity of CPC with the change in weight percentage of the CNT nano filler used. Sandler et al. (1999) dispersed CNTs in an epoxy matrix and observed that, compared to carbon black, using CNTs reduces the percolation threshold and overall increases the electrical conductivity of the composite. Ramasubramaniam et al. (2005) fabricated homogeneous CNT/ polymer composites and found that CNT/polymer composite exhibits a very low percolative threshold. Quanies et al. (2004) and Gojny et al. (2009) calculated the electrical conductivity of CNT reinforced polymide composites and epoxy resins, respectively. Both demonstrated that the electrical conductivity increased with an increase of CNT concentration and the electrical property of the composite can be attributed to the formation of conductive pathways. There are other experimental works that back the same results, i.e., adding a small amount of CNTs into the polymer significantly increases electrical conductivity of the polymer composites. Hence basing on the exceptional physical and chemical properties that CNTs possess and also on the above mentioned experimental data it is inferred that in order to impart the electrical properties to the polymer composite material CNTs are one among the most ideal filler material to be used.

Another interesting property of the CNTs is the ability to modify the properties via functionalization. The functionalization process can combine unique properties of CNTs with those of other materials, required for a wide variety of applications. The carbon atoms present along the nanotube lattice can be functionalized via non-covalent (van der Waal interaction) and covalent bonding. Generally, functionalization increases the processability and solubility of the CNTs [31,32].

Because of the combination of unique properties such as nanometer sized dimensions, high aspect ratio, thermal stability, high electrical conductivity and high surface area, CNTs are considered as excellent filler materials used in the nanocomposite synthesis. Table 1.1 shows the types of common nano-fillers, i.e., SWCNTs, MWCNTs and Silver nanowires (AgNW) used and their typical properties. MWCNTs feature similar properties and lower price compared to SWCNTs and hence are more preferred as filler material in the synthesis process of composites.

Table 1.1 : Properties of commonly used conductive nanofillers [33,34]

Property	SWCNT	MWCNT	AgNW
Diameter (nm)	0.6-1.8	5-50	100-200
Aspect ratio	100-10,000	100-10,000	50-200
Density (g cm^{-3})	~1.3	~1.75	10.49
Electrical conductivity (S m^{-1})	10^5-10^6	10^5-10^6	6.30×10^7
Tensile strength (GPa)	50-500	10-60	--
Tensile modulus (GPa)	1500	1000	83

As mentioned above, composite materials are made up of two materials, one is the filler of the reinforcing phase, such as fibers, sheets, or particles while the other is the matrix material. The matrix material, generally is a high strength, low density, high strength material [35]. The common matrix materials are metals, glass, ceramics, or polymers. While ceramic materilas are mostly used for high temperature and high corrosion to resistance applications, metals and polymers are the most common matrix materials due to their high ductile nature [36,37]. But metals are heavy, expensive, require high processing conditions and are not compatiable with a large variety of filler materials, hence, polymer materials are more preferable over metals for the syntheisis of CPCs. The use of polymers as matrix material reduces cost, controls viscosity and provides good mechanical and surface properties [38].

The selection of the polymer directly depends on the type of applications. Generally, the role of the matrix is to transfer stress between the fillers and to provide a protection barrier against mechanical abrasion or adverse environment. In general the parameters taken into consideration are: [39].

- Shorter fabrication time.
- Long shelf life at room temperature.
- Ease of repair.
- Ease of handling.
- Recyclability.
- High fracture toughness.
- Delamination resistance under fatigue.

Keeping the above mentioned factors in mind, Polylactic acid (PLA) is chosen for this project. PLA is a biodegradable thermoplastic that is derived from renewable common resources such as corn starch, sugarcane [40] and is viewed as a promising material to reduce the solid waste disposal. PLA has relatively high mechanical properties when compared to other commonly used thermoplastic polymers as compared in Table 1.2 [41].

Table 1.2 : Physical properties of commonly used thermoplastic polymer materials [41]

Properties	**PLA**	**PS**	**PP**	**PET**
Density (g cm^{-3})	1.25	1.05	0.9	1.37
Young's modulus (MPa)	350-2800	3000-3500	1100-1550	2800–3100
Tensile strength (MPa)	10-60	32-60	30-38	55–75
Elastic limit (%)	1.5-380	2.8-4	200-700	50–150
Glass temperature (°C)	60-65	80-98	-10	75
Melting point (°C)	173-178	-	165	254
Thermal conductivity (W mK^{-1})	0.13	0.14-0.16	0.12-0.22	0.24
Water absorption (%)	0.5-50	0.1	0.01	0.16

PLA is formed either by direct condensation of lactic acid or via the cyclic intermediate dimer (lactide), through a ring opening process. Due to the chiral nature of lactic acid, two isomers of PLA exist: L- and D-lactic acid. PLA has a crystallinity of around 37% and is heat-resistant and can withstand temperatures of up to 110 °C. PLA also has a significantly lower maximum continuous use temperature when compared to the other common polymers. PLA is soluble in a wide variety of both polar and non-polar solvents. These properties make it the ideal feedstock material in 3D printers and can be used to design a large variety of materials including free standing structures.

1.4 Manufacturing of composites

The remarkable properties of CNT/polymer composites have motivated researchers to experimentally the mechanics of nanotube-based composites. Uniform dispersion of fillers within the polymer matrix, improved nanotube/matrix wetting and adhesion are the most critical issues in the processing of these nanocomposites. Efficient reinforcement depends on the issue of nanotube dispersion [42,43]. Slipping of the filler tubes that are not bonded to the matrix in the composite affects the stability of the final composite to a great extent. While for the synthesis of electrically conductive nano-composites, the non-uniform dispersion and the presence of aggregates might not be a big problem but the compatibility of the CNT fillers with the polymer used is an important parameter.

Mixing methods play a significant role in the filler dispersion and distribution, their orientation and even their aspect ratio. We know that, to achieve optimum quality final product we need to achieve low percolation threshold. For good electrical properties, good dispersion may not be required but uniform filler distribution is necessary to achieve good mechanical properties. The most commonly used and popular methods used for the synthesis of thermoplastic nanocomposites are solution mixing and melt mixing methods [44].

1.4.1 Solution mixing

The process of solution mixing is one of the most common methods for the preparation of thermo plastic based nanocomposites on a small scale. Generally, solution mixing involves four basic steps: [45]

1. Dissolving the polymer in an appropriate solvent.
2. Dispersing the nanofillers separately in the same solvent.
3. Mixing the nanofiller suspension with the polymer suspension.
4. Evaporating the solvent to get the composite mixture.

This method involves the use of large amount of solvents. Selection of the solvent is quite critical and affects the dissolution of the polymer and dispersion of the nanofillers. This process is ideal for manufacturing nanocomposite material as it operates at relatively low temperatures and mechanical stress thus, reducing the degradation of the mixing materials used. In general, agitation to disperse the fillers in the solvent and to mix the two suspensions of the polymer and the filler material together is provided by ultrasonication [46] (see Figure 1.4), refluxing [47], or magnetic stirring [48]. Sonication is commonly used and can be provided in two forms, mild sonication in a bath or high-power sonication using a tip or horn.

Figure 1.4 : Photograph of the ultra-sound bath used for solution mixing method. [46]

1.4.2 Melt mixing

Melt mixing is a probably the most widely used methods for synthesis of composites because of the simplicity of the process. Unlike the solution mixing method, melt mixing method does not include the use of solvents and using the mixing material in their dry state and thus in addition to the soluble polymers, this method can be used to process the polymers that are insoluble in any solvents as well. It makes use of the fact that thermoplastic polymers soften and melt on the application of heat [49]. The materials to be mixed, i.e., the polymer and the filler are fed together into the mixing chamber using the feeder, which are then mixed at a high shear and at a high temperature. The temperature ensures the melting of the polymer material and the high shear mixes the molten material and the nanofiller together thus resulting in the nanocomposite mixture formation. It is a quick, simple and is compatible with standard industrial techniques. This method of nanocomposite manufacturing is more economical and environmentally friendly as it doesn not involve the use of any solvents [50].

Traditional melt mixing methods require large amounts of materials and thus this is not suited to work with on a laboratory scale. Most twin-screw extruders, consist of a chamber into which the material is fed using the feeder and two identical conical screws that are attached to a rotor that help mixing the material together. The chamber has a nozzle at the bottom through which the composite material is extruded upon the completion of the process (Figure 1.5). Traditional melt mixing methods generally require large quantities of materials, which is expensive and is not suitable for preparing nanocomposite at the laboratory scale. Hence, a miniature twin-screw extruder has been developed to prepare thermoplastic nanocomposites from small quantities of feed material [51]. There are several manufacturers of the micro-compounder like DSM (Heerlen, Netherlands) and Haake Instruments Inc. (Paramus, NJ, USA). A typical micro-compounder as shown in Figure 1.4 inlet, consists of a conical twin-screw extruder which moves at a high speed and mix the material fed inside the mixing chamber through the feeder. The chamber is also equipped with a recirculation path, this allows the melt composite to recirculate so that the material can be mixed for a certain period of time before it is extruded through the nozzle at the bottom. Many researchers have worked with the twin screw micro compounder to produce nanocomposites. Villmov et al. (2002) investigated the effect of such mixing method on the dispersion of CNTs in PLA and concluded that the percolation threshold for the composites prepared using such a method is lower than the composites prepared using other mixing method, due to better mixing of the feed material under high shear. The high shear mixing ensures efficient dispersion of the CNT fillers compared to the other methods.

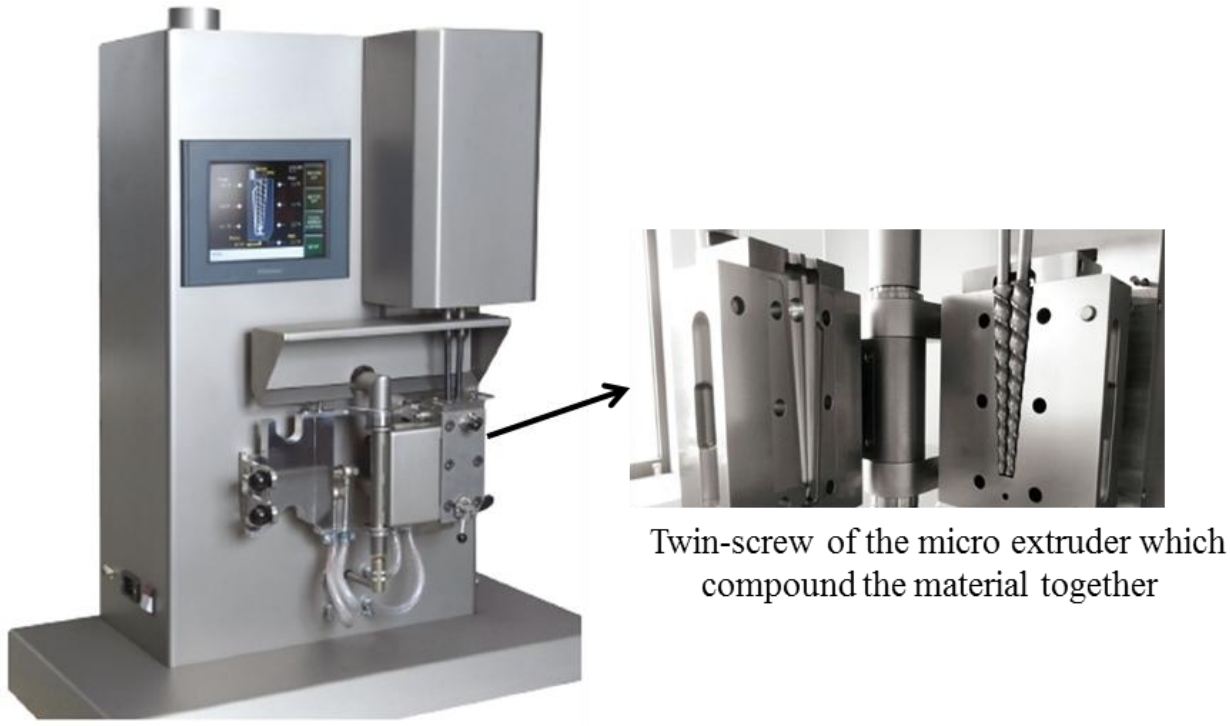


Figure 1.5 : Photograph of DSM 5 mL micro-compounder [52].

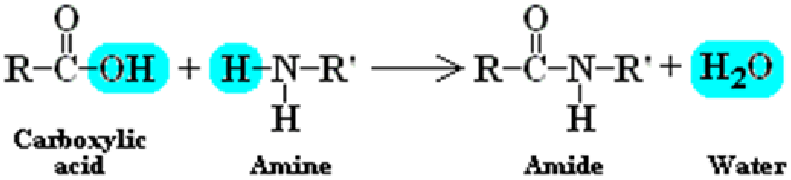
1.5 Functionalization of CNTs

CNTs possess unique electrical, mechanical and chemical property that makes their use in a variety of applications and processes. The nature of dispersion for CNTs is different from other conventional fillers, such as carbon fibers and spherical particles, because CNTs are characteristic of having a small diameter (nanometer scale) with high aspect ratio (>1000) and thus possessing large surface area [53]. In addition, the commercialized CNTs are supplied in the form of heavily entangled bundles, resulting in difficulties in dispersion [54]. The performance of a CNT/polymer nanocomposite mainly depends on the interactions between the CNT and the polymer and how well the CNT fillers are dispersed in the polymer matrix. The full potential of CNTs as reinforcements is very limited due to poor interfacial interactions between the CNTs and the polymer matrix. But the walls of the CNTs are generally chemically inert due to the presence of stable carbon atoms on their walls and interact with the surrounding polymer matrix only through van der Waals interactions. Hence, to overcome this difficulty, methods are to be developed to modify and enhance the surface properties and the reactivity of the CNTs; this can be via functionalization techniques. Functionalization technique enhances the properties of the CNT and increases their application potential [55]. There is a lot of available literature that's describes chemistry of functionalized CNTs and the mechanism between the functional groups and CNTs. Based on the interactions between the carbon atoms on the CNTs and the active molecules, functionalization of CNTs can be divided into chemical and physical methods. Most of these methods result in inevitable structural changes of the CNTs and damaging effects due to mixing processes like ultrasonication [56].

The physical methods involve phenomenon such as polymer wrapping, surfactant adsorption, etc. The chemical methods of functionalization are based on the covalent linkage of functional entities onto carbon scaffold of CNTs. This type of functionalization is generally performed at the ends or the sidewalls of the CNTs. Any defect sites present on the CNT are more likely to be effected by the functionalization step. Sidewall functionalization results in a change in the hybridization from sp^2 to sp^3 and a loss of π conjugation on graphene layer, thus making the CNTs more reactive. Besides sidewall functionalization there exists another type of method for covalent functionalization of CNTs known as defect functionalization. This phenomenon takes advantage of chemical transformation of the defect sites on CNTs. Defect sites can be of various types – open ends, irregularities in the graphene framework and/or holes on the sidewalls. Oxygenated sites that are created at the open ends and sidewalls, by an oxidative processing with strong oxidants or with strong acids like HNO_3, H_2SO_4 or a mixture of them and a reactive plasma exposure are also considered as defects. The defects caused by the oxidants are stabilized by bonding with hydroxyl (-OH) or carboxylic (-COOH) groups, present in the acid. These groups when attached to the surface of the CNTs are highly reactive and have the tendency to react with each other, through their attached reactive functional groups, or can be used as precursors for further chemical reactions. The chemically functionalized CNTs gain the ability to produce stronger interfacial bonding with a large number of polymers thus helping it attain high mechanical and functional properties. Also, this type of functionalization attaches polar groups to the tubes and renders the CNTs a hydrophilic nature thus making them soluble in many polar solvents [57,58].

1.6 Using binding molecules as bridges

In order to achieve optimum electrical conductivity for a polymer composite material, the dispersion of the CNT fillers is not an important criterion. Despite the CNTs being randomly (non-uniformly) dispersed, if they are in contact with one another, high conductivity values can be attained i.e., selective distribution contributes towards an greater electrical conductivity of the final composite material, rather than uniform dispersion. To achieve this kind of a selective dispersion, the use of bridging molecules has been discussed in this section. CNTs are generally functionalized using oxidative process such as treatment with strong acids like HNO_3 and H_2SO_4, this process is harsh and generates defects in the structure and on the side walls and tube tips of the CNTs. Such a strong treatment also introduces a large number of defects in the CNT hence, making the CNTs more fragile and leads to a reduction in their resistance against electrical conductivity of the CNTs [59]. The development of a more effective and better treatment method that has little or no structural damage to CNTs and that introduces high density and homogeneous group’s remains a major challenge. One of the most promising approach to overcome this challenge is the use binding molecules as bridges between two oxidized CNTs. During the oxidation process of the CNT, the carboxylic group (-COOH) gets attached to the surface of the CNTs. These carboxylic groups are highly reactive and among all the chemical functional groups, amines ($-NH_2$) and esters (-COO) have the most affinity to bind with the reactive carboxylic groups (Figure 1.6) [60].



$$R-\overset{O}{\overset{\|}{C}}-OH + H-\underset{H}{\underset{|}{N}}-R' \longrightarrow R-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R' + H_2O$$

Figure 1.6 : Chemical reaction explaining the bonding affinity between the carboxylic and the amine group [60]

Due to low costs, ease of availability and non-complex use in the synthesis process, amines are more preferred when compared to the ester groups. Amines are organic compounds and functional groups having a nitrogen atom and a lone pair of electrons. These are basically ammonia derivatives where one or more of the hydrogen atoms have been replaced with a substituent such as an aryl or an alkyl group. The basic types of amines generally used are aniline, amino acids and trimethylamine. Amines are generally divided into four categories; primary, secondary, tertiary and cyclic amines. Amongst these the primary amines have simple structure and need low amounts of dissipation energy for reaction to take place and thus ideal for use as bridging molecules [61].

1.7 Fabrication of 3D architectures using CPCs

Now-a-days, 3D structures made from nanocomposites are being used in a wide variety of applications like electrical, mechanical and chemical sensors [62], EMI shielding [63] and energy devices [64]. There are a wide variety of techniques that are used to fabricate 2-Dimensional and 3-Dimensional structures: direct-write method, fused deposition modeling, electro-spinning etc. Compared to the other methods the direct write technique is more used at the laboratory scale and it allows more freedom of movement, a wide variety of materials can be used as feed even in the liquid state at room temperature and thus, possibility of more complex structures [65,66].

1.7.1 Direct-write technique

This method is a way of precisely assembling periodic arrays. The set up includes a robot that is connected to and controlled by a computer, a syringe chamber, an ink-deposition nozzle that is attached to a pressure pump [67]. The composites manufactured using the above mention techniques are then made into the CPC ink by dissolved using a solvent and are fed into a syringe which is then fed into the syringe chamber and extruded using the deposition robot by applying pressure using the pressure regulator [68]. Figure 1.7 illustrates an example of a 104 layer 3D scaffold with a separation between each cylinder of 1.25 mm. This technique can be applied to a wide variety of inks like composite inks, epoxy, organic inks, etc. and a large number of structures like fibers, scaffolds and even free standing structures with varying dimension sizes can be fabricated using this technique [69].

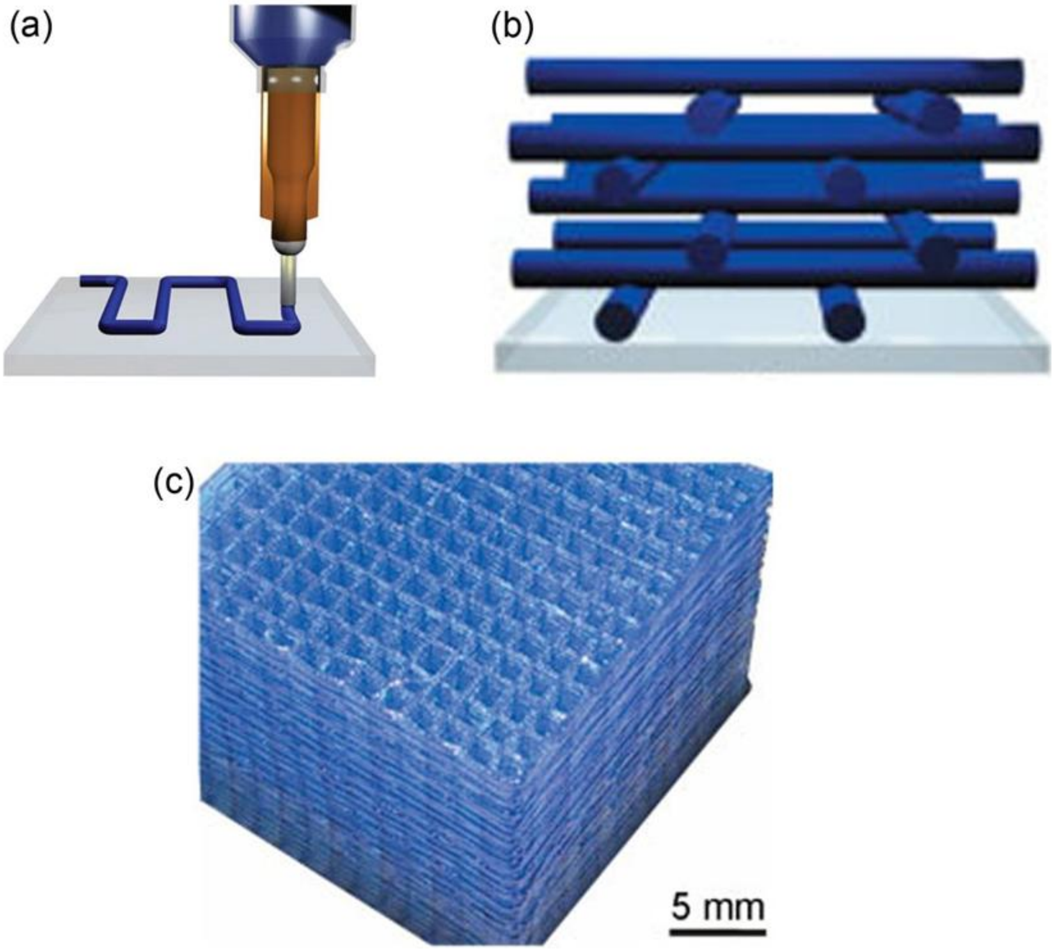


Figure 1.7 : Schematic showing the fabrication of a 3D scaffold by the direct-write method:

(a) deposition of ink from the nozzle; (b) deposited ink in a scaffold structure; (c) microscopic image of a 104-layer scaffold using organic ink deposited through a 200 μm nozzle. [68]

1.8 Resistivity measurements

The fibers designed using the direct write method is then subjected to resistivity measurements using the two-point resistance measurement method [70]. The two-point method is commonly used as it is the simplest and most straightforward method. Copper is the most recommended metal that can be used as cabling material, due it its high temperature coefficient. A test current is forced through the test leads and the resistance (R) under test. The meter then measures the voltage across the resistance through the same set of test leads and computes the resistance value accordingly [71].

The two-point resistance measurement method, gives the resistance value across the fiber. While the length and the area of cross-section of the fiber can be measured, the resistivity (Ω.m) can be obtained by the following formula [72]:

$$\boldsymbol{\rho = R.A / L}$$

Where: ρ is the resistivity (Ωm), R is the resistance (Ω), A is the area of cross-section (sq.m) and L is the length of the fiber measured.

The reciprocal of the resistivity gives the conductivity (S/m) of the CPC material. Figure 1.8 shows the apparatus used to measure the resistance of the CPC fibers [72]. Many researchers use the four-point resistance measurement method instead of the two-point method, which uses four probes (two at the ends and two at the center) to measure the resistance. In the current project we measure the resistance of printed fibers which are delicate and can easily be damaged under the force of the two center probes used in the four-point resistance measurement. Also, the four point resistance measurement method excludes the contact resistance of the material value during the resistance measurements which affects the electrical properties of composite materials [73].

Figure 1.8 : Photograph of the Keithley 6517B resistance meter. [73]

CHAPTER 2 RESEARCH OBJECTIVES AND APPROACH

2.1 Research objectives

According to the literature review presented in Chapter 1, CNT/PLA based nanocomposites are highly promising as their application as conductive composite materials in the electronic industry in designing and manufacturing circuits and electronic components via 3D printing. However, designing a composite exhibiting high electrical conductivity values at low filler (CNT) concentration (concentrations less than 5 wt.%), still remains a challenge. Thus, the principle aim objective of this work:

“is to find the most suitable composite preparation method and to design a CNT/PLA based 3D printable nanocomposite with high electrical conductivity at low filler loading”

In other words the main motive behind the project is to be able to achieve high electrical CPC conductivity (~5000 S/m) at the least possible filler loading in order to reduce the weight, ease of manufacturing (lower concentrations of CNT fillers are easy to handle and process with the polymer) and manufacturing costs that is associated with the use of more number of CNT fillers by finding an optimum combination between the mixing method and the CNT treatment so as to form a percolation path within the polymer composite and thus, high electrical conductivity.

The specific objectives of the current work are:

1. To compare and contrast between the most common composite preparations methods to see which method is the most suitable for the CPC synthesis and to verify the change in the electrical conductivity with the filler loading.
2. Explore the various types of CNT functionalization techniques and treatments and their effect on the electrical conductivity of the composite.
3. Use of binding molecules as “bridges” between the CNTs in the composite and their effect on the electrical conductivity of the composite.
4. To check the printability of such conductive PLA/CNT based nanocomposite material.

2.2 Approach

The first part of the project was to compare between the most commonly used methods of composite manufacturing i.e., solution mixing and extrusion methods have been studied. The steps in the solution mixing method included dissolving the PLA and CNTs separately in DCM and then mixing the two solutions together using the ultrasonic bath. The solution achieved is then subjected to, resulting in the formation of a dry composite. This composite is then dissolved with measured quantities of DCM to be drawn into fibres using the deposition robot for electrical analysis. While for the synthesis of composites using the twin screw micro extruder the PLA and CNTs are fed into the extruder in a dry state and then compounded together by the screws of the micro extruder at an elevated temperature, which results in grounding the CNT fillers and the polymer material together and formation of the composite material. This composite material is then extruded through the nozzle at the bottom of the chamber and is also then dissolved using measured amounts of DCM and then drawn into fibres using the deposition robot for electrical analysis. Using each of the above mentioned methods composites containing different concentrations of CNTs (0.1%, 0.2%, 0.5%, 1%, 2% and 5% by weight) were manufactured to evaluate the change in the electrical conductivity of the fibres with an increase in the filler loading and to compare the variation in the conductivity with the synthesis method for particular filler loading.

The second part of the project was to investigate the effect of the various CNT functionalization techniques on the conductivity of the final composite material. Three basic types of functionalization methods were tried – acid functionalization using HNO_3, acid functionalization using a stronger acid (3:1 mixture of HNO_3 and H_2SO_4) and plasma functionalization using the N_2 cathode ray tube plasma. From Chapter 1 we know that functionalizing the CNTs increases their reactivity and compatibility with the polymer, and so the idea behind this concept was to get the CNTs to react with each other within the polymer matrix and thus helping in the CNT-CNT linkage and the formation of a conductive pathway. The functionalized CNTs are then used for the composite preparation along with PLA using the solution mixing method as described above. This composite material is then dissolved with DCM and drawn into fibres using the deposition robot for electrical conductivity analysis.

The electrical characterizations included resistivity measurement on the composite fibres using the two point probe method, while the reciprocal of the resistivity gives the conductivity. These studies lead to a peer-reviewed conference proceeding publication at ASME, IMECE-2014 held in Montreal, Canada. (presented in Chapter 3).

As mentioned in the Chapter 1 (section 1.5) , the electrical conductivity properties of the composite material directly depend on the formation of a conductive pathway of the filler material in the polymer composite and not much on the dispersion of the fillers. Hence, selective distribution is more important compared to the uniform dispersion of the CNT fillers. To investigate the distribution, the third part of this project dealt with the use of “bridging molecules” to act as binders between the carboxylic groups attached to the CNTs after acid functionalization. For this we use phenylenediamine as the binding molecule to act as a bridge between two CNTs attached with a carboxylic group. We know that phenylenediamine has a 1:1 binding affinity with the carboxylic groups, thus helping in getting the CNTs closer together enabling a conductive pathway formation. The HNO_3 acid functionalized CNTs are then treated with phenylenediamine and these CNTs are then used for composite preparation using the solution mixing method.

Finally, the possibility of printing the above manufactured electrically conductive nanocomposite material into 2D and 3D architectures is verified. This is done by dissolving the composite material with measured quantities of DCM and extruding through the syringe pump of the deposition robot, using the solvent-cast 3D printing method to create fibres and scaffold structures.

CHAPTER 3 EXPERIMENTAL DETAILS

This chapter presents a detailed explanation of the experimental method and the process conditions, during the manufacturing, fictionalization/chemical treatments and printing step of the CPC synthesis.

3.1 Solution mixing method

Four steps are followed during the CPC synthesis using the solution mixing method of composite mixing: Figure 3.1 shows a general schematic of the steps followed during the CPC synthesis using the solution mixing method.

Apparatus used – Ultrasound bath, Model – 8891, Cole-Parmer.

Solvent used – DCM.

1. PLA is dissolved in the solvent DCM to make PLA/DCM solution with a concentration of 10 wt. % PLA in DCM and is allowed to settle for 24 hours.
2. CNTs are dispersed in DCM by sonication using an ultrasound bath for 1 hour. The amount of CNTs dispersed in the solvent is set in a way that we obtain different weight percentages of CNTs in PLA.
3. The CNT/DCM solution is added to the PLA/DCM solution and is mixed using the ultrasound bath for 2 hours.
4. This mixed solution is then subjected to drying, once again using the ultrasound bath for 3 hours. This step results in the formation of the CNT/PLA CPC by eliminating the solvent DCM.

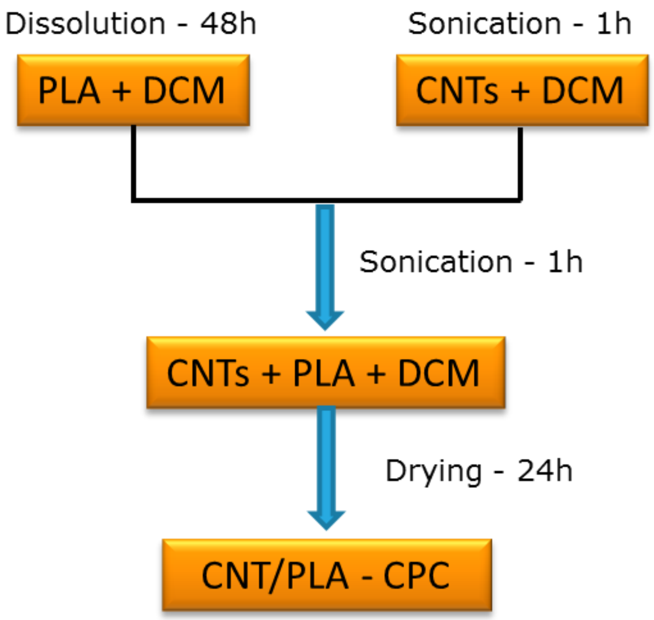


Figure 3.1 : Schematic representation of the steps involved in solution mixing method.

3.2 Twin screw extrusion method

The following procedure is used during the CPC synthesis using the twin screw extrusion method of composite mixing: Figure 3.2 shows a general schematic of the steps followed during the CPC synthesis using the extruder mixing method.

Apparatus used – DSM Xplore Twin-screw micro extruder.

No solvent used.

1. The pellets of PLA and CNTs are dried in a vacuum oven for 12 h at 50ºC before processing.
2. These dried PLA pellets and CNTs are pre mixed and then fed into the mixing chamber of the micro compounder (5 mL, capacity) at 170ºC and 100 rpm.
3. Extruding temperature and rotation speed of the twin screws is then increased to 180ºC and 300 rpm, respectively. And the material is mixed in the mixing chamber for a period of 5 minutes.
4. The CNT/PLA nanocomposite is then extruded from a nozzle at the bottom of the mixing chamber with inner diameter of 0.50 mm.

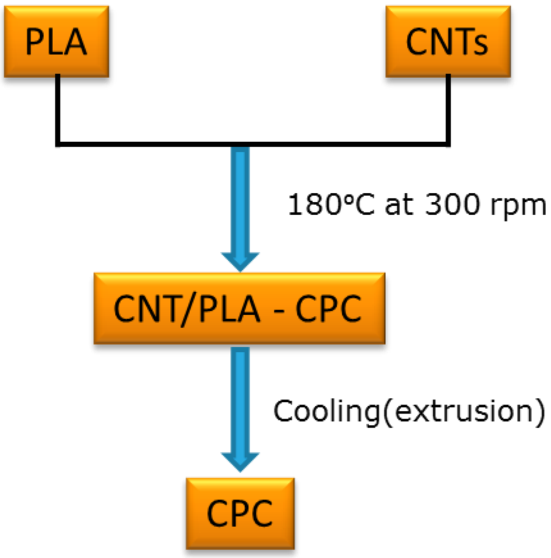


Figure 3.2 : Schematic representation of the steps involved in melt mixing method.

3.3 Functionalization of the CNT fillers

The multi-walled raw carbon nanotubes (MWCNTs, Nanocyl -7000, Nanocyl) are functionalized using three different methods as follows.

Acid treatment using Nitric acid (HNO_3): For functionalizing the CNTs using nitric acid, 1 g of CNTs were dispersed in 100 ml nitric acid (HNO_3 - 70% concentration), using an ultrasonic bath for 5 hours. The solution obtained is then diluted with water and filtered repeatedly using the 0.4 micron membrane filters (Isopore, Millipore), until CNTs are neutralized by the repetitive washes with distilled water. These CNTs are then dried in a vacuum oven for 12 h at 80 ºC.

Acid treatment using stronger acid: For functionalizing the CNTs by a stronger acid (i.e., 3:1 mix of sulfuric acid and nitric acid) 1 g of CNTs was dispersed in 100 ml of 3:1 mixture of H_2SO_4 (95% concentration) and HNO_3 (70% concentration) using a ultrasonic bath for 5 hours. The acidic solution is diluted with water and filtered repeatedly until the CNTs are neutralized. These CNTs are then dried in a vacuum oven for 12 h at 80 ºC.

Functionalization using Nitrogen (N_2) plasma: For functionalizing the CNTs using the reactive N_2 plasma, 1 g of CNTs are fed in the N_2 plasma reactor working at 600 watts and a pressure of 420 millitorr. The CNTs are subjected to a continuous nitrogen flow at 1.5 sccm for 15 minutes.

The functionalized CNTs obtained via the acid functionalization method are in the form of aggregates. These aggregates need to be separated before they can be used or processing and hence, are powdered manually or using the ball mill. These powdered CNTs are then used for the CPC synthesis via the solution mixing method as explained above. The plasma functionalized CNTs are directly used for CPC synthesis via solution mixing.

3.4 Amine treatment of the CNT fillers

Phenylenediamine, which is also known as 1, 4-Diaminobenzene is used as a bridging molecule. This is chosen compared to the other amines due to its simple structure and ease of availability and low dissipation energy. Also the benzene ring present in the molecule helps the conductivity property of the polymer synthesized [74]. Following are the steps followed during the CPC synthesis using the amine treated CNT fillers.

1. Para-phenylenediamine (0.2 M) along with 0.25 M aniline is dissolved in 0.1 M HCl and the resulting solution is then mixed with the 0.2 g of HNO_3 functionalized CNTs via constant stirring.
2. The contents are kept in an ice bath and continuously stirred, acidic aqueous solution of 0.25 M potassium persulfate was added. To ensure complete polymerization, the reaction is carried out at room temperature for 24 hours.
3. Reaction is terminated by pouring the mixture into acetone, upon which the residue precipitates out. The remaining product is thoroughly washed with deionized water to remove the unreacted monomers and other impurities.
4. The product obtained is filtered and dried in a vacuum oven for 24 hours at 50°C.

Figure 3.3 shows the schematic of the mechanism of the expected reaction that would occur on the addition of amine molecules to the acid functionalized CNTs. The amine treated CNTs obtained are then mixed with PLA and manufactured into composite via the solution mixing method described in Section 3.1.

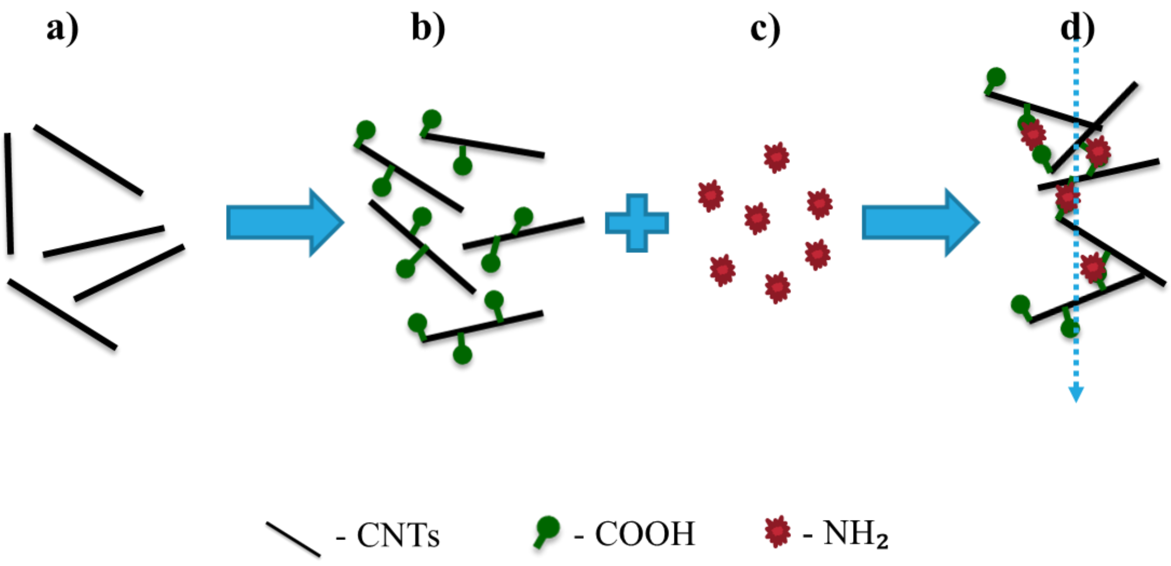


Figure 3.3 : Schematic representation of the reaction mechanism using amine binding molecules a) Un-treated CNTs; b) carboxylic groups attached to CNTs on HNO_3 functionalization; c) addition of para-phenylenediamine to the acid functionalized CNTs and d) percolation pathway formation (blue dashed arrow) due to the affinity between the carboxylic and the amine groups

3.5 Printing of the CPC material

The CPCs manufactured using the above mentioned methods is then dissolved with measured quantities of DCM, depending on the weight percentage of CNTs in them and allowed to dissolve for 24 hours. This CPC in DCM mixture is then filled into a syringe attached to a needle of varying diameter. Here, needle diameters of 0.1 mm and 0.2 mm are used. This syringe filled with CPC is then inserted in the syringe chamber of the deposition robot, which is attached to a pressure pump (Figure 3.4).

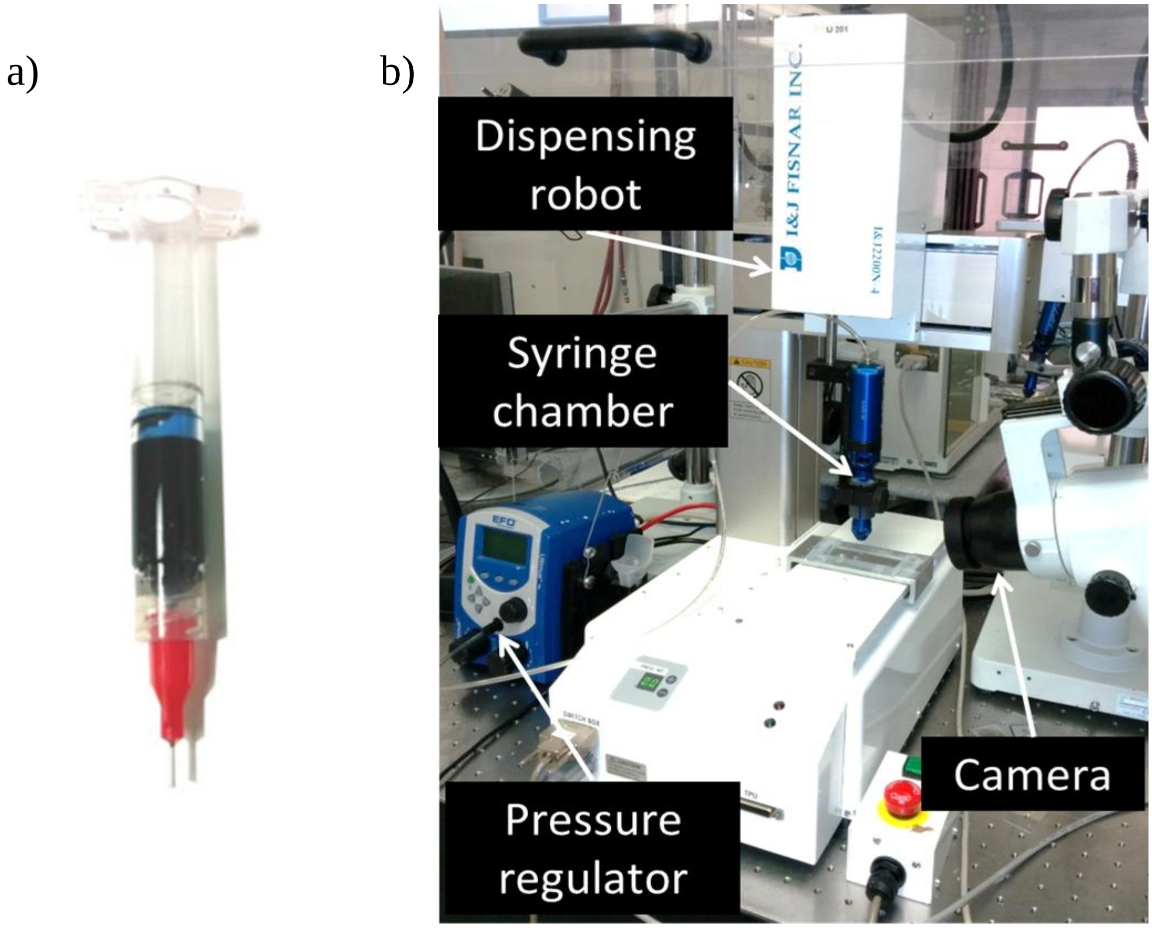


Figure 3.4 : Photograph showing a) syringe filled with the CPC ink and b) the deposition station.

The deposition robot is controlled using computer commands, in which programs can be pre-loaded. Depending on the type of the command, 2D (fibers and single layer scaffold) and 3D (multi-layer scaffold) structures can be designed. As the pressure is applied and the CPC material is extruded through the syringe needle and as the solvent evaporates on exposure to the air the CPC material solidifies and hardens into the desired structure. For optimum quality of the printed structures, the velocity at which the deposition head moves, the pressure applied to extrude the CPC material through the deposition head and the viscosity of the CPC material fed into the syringe play an important role. The printed samples are then dried in the vacuum oven at 60°C for 3 h to remove any extra solvent and strengthen the structure further.

3.6 Resistivity measurements

The CPC fibers designed using the direct-write method is subjected to resistance measurements using the two-point resistance measurement method. Figure 3.5 shows the schematic of the circuit through which the resistance across the fibers is measured using the two-point resistance measurement method.

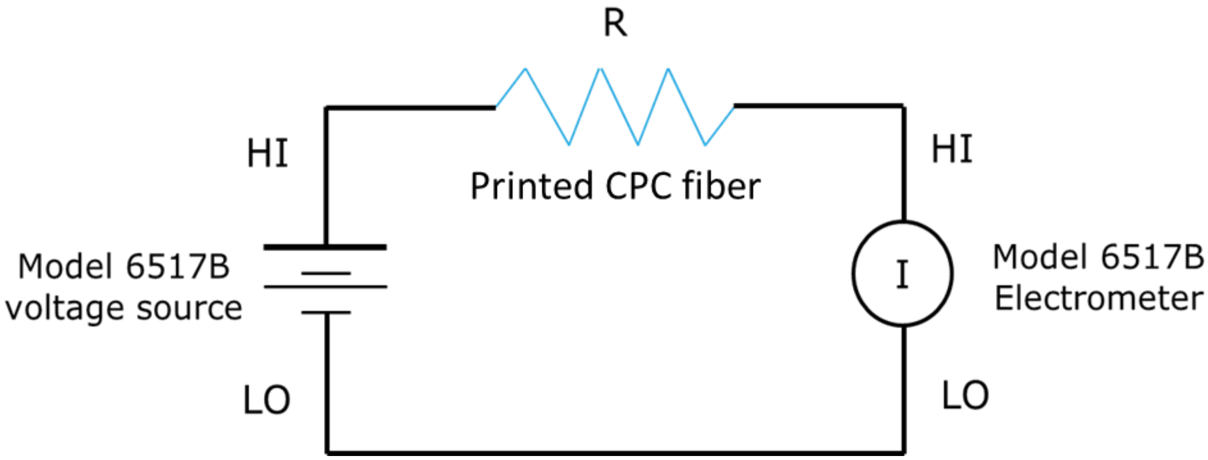


Figure 3.5 : Schematic of the circuit design used in the two point resistance mesurement.

The dried fibers are stretched between two copper pads on a glass or any non-conducting slide (see Figure 3.6). One of the pads is attached to the voltage source, while the other at the other end of the CPC fiber measures the current and directly gives the value of the resistance by the CPC material. The length and the area of cross-section of the printed fibers can be measured using the microscope. Hence, as mentioned in Chapter 1 (section 1.8), the resistivity can be attained. The reciprocal of this resistivity gives the value of the conductivity of the CPC material.

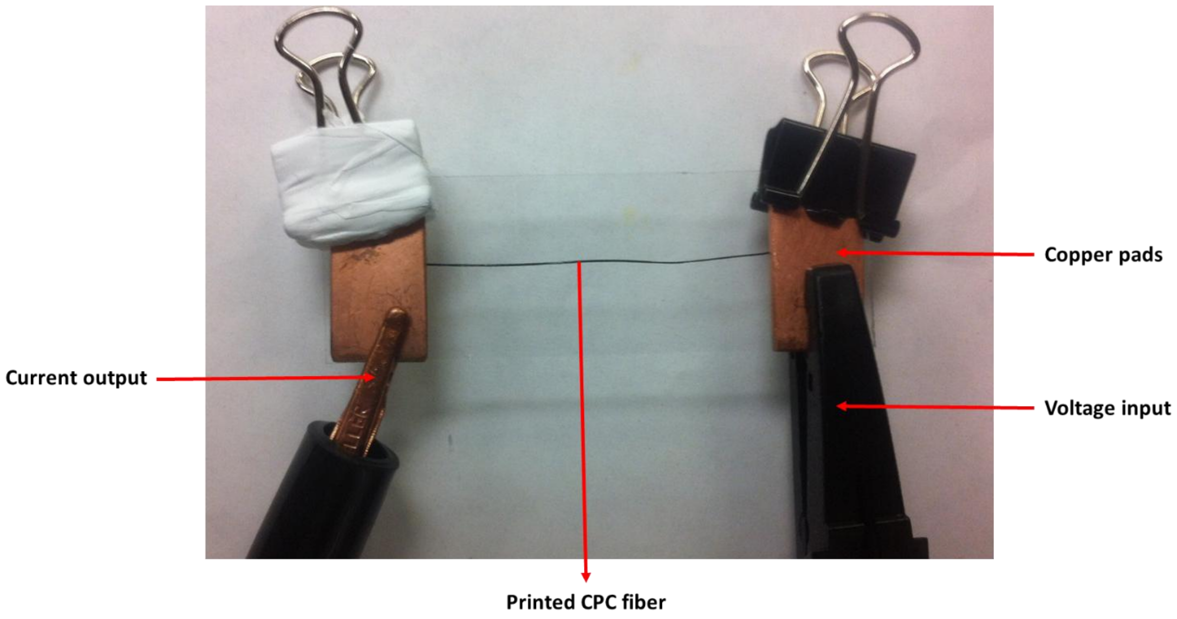


Figure 3.6 : Photograph of the set up used to measure the resistance of the CPC fibers.

CHAPTER 4 ARTICLE 1:

INVESTIGATION OF CARBON NANOTUBE MIXING METHODS AND FUNCTIONALIZATION FOR ELECTRICALLY CONDUCTIVE POLYMER COMPOSITES

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Abstract

The growing popularity of Poly lactic acid (PLA) is related to its biocompatibility, good mechanical properties, and its synthesis from renewable resources. PLA can be compounded with electrically conductive fillers (e.g., carbon nanotubes (CNTs)) to form carbon polymer composites (CPC). These fillers provide the conductive functionality by forming percolative paths. Featuring very low weight densities, CPCs have the potential to replace metals in the electronic industry if they exhibit similar electrical conductivities. The current challenges being faced during the mixing of CNTs in a polymer matrix are the formation of aggregates due to the strong van der Waals forces and the breakage of the CNTs during dispersion. In this study, we compare: (1) two fabrication methods to create CPCs (i.e., solution mixing by sonication and extrusion) and (2) effects of various CNT functionalization techniques (i.e., acid and plasma treatments) on the conductivity of the CPCs. First, the composites comprising of 30% PLA by weight in Dichloromethane (DCM) and CNTs in different concentrations (up to 5wt.%) are fabricated by two step sonication method (i.e., dissolving PLA in DCM and then dispersing the CNTs in the polymer solution). Second, CPCs are fabricated using a micro twin screw extruder operating at 180^{0}C. To verify the effects of functionalization of the CNTs on the conductivity of

composites, the CNTs are functionalized via three methods: - HNO_3 acid functionalization, 3:1 ratio HNO_3 + H_2SO_4 acid (stronger) functionalization and N_2 plasma functionalization. CPC fibers are drawn using the solvent-cast printing method. These fibers are then tested for their electrical conductivity using the two probe method. The maximum electrical conductivity is showed by the 5% CNT concentration samples at 3.97 S/m and 25.16 S/m for the CPC fibers obtained via the solution blend and the extrusion methods, respectively. Regarding the functionalized CNTs, conductivity measurements show a negative effect of the CNTs functionalization on the electrical properties of the CPC.

4.1 Introduction

Poly lactic acid (PLA) has attracted great attention over the past years [75] due to its many qualities such as biodegradability, biocompatibility, good mechanical properties, and versatile fabrication processes which make it a promising material for wide applications in the electronic industry, biomedical materials, textiles, packaging and containers [76]. It can also be used as an alternative to petroleum-based polymer [77]. However, PLA is an electrical insulator material, which limits its applications in components of electronic devices. This is because of the static charge that easily builds up on such insulator parts by contact, electrical insulator materials possibly produce an electrostatic discharge that may damage sensitive semiconductor devices and interfere with circuit operation.

To solve this problem of electrostatic discharge, an effective method is compounding PLA with electric conductive fillers to form carbon polymer composites (CPC) [78,79]. For electrical applications, conductive fillers, such as metal particles or filaments, carbon particles [81] such as carbon nanotubes or carbon fibers [80] can be used. The electrical conductivity of CPC generally increases with increasing filler concentration. However, maximum filler loading is limited because high loading filler results in the poor mechanical properties [82,83]. For materials and process cost saving and good mechanical properties, the attainment of a high electrical conductivity at low filler loading is desired. A reduction in weight of CPC is of great significance for electronic devices and the industry, since it leads to savings in materials and energy and easier manipulation of devices [84]. Compared to conventional metal particles and carbon filler, carbon nanotubes (CNTs) have remarkable structural, mechanical and electrical properties, such as smaller diameters, larger aspect ratios, higher conductivity and greater strength. With the special nanostructure, CNTs can form conductive network easily at low loading to provide the desired electrical properties [85-87].

To attain maximum conductivity, ideally the fillers need to be dispersed in the polymer in a way to form a conductive pathway, to overcome the percolation barrier. The two most commonly used methods for the CPC synthesis are solution mixing via a two-step sonication method in which the PLA is first dispersed in a solvent and then CNTs are dispersed in the polymer solution [88]. The second method most widely used method for the CPC fabrication is by extrusion using the twin screw extruder [89], in which the molten polymer and the filler (CNTs) are mixed together at high shear rates. The main challenges faced during the mixing of CNTs into the polymer are the non-uniform dispersion of the filler in the polymer matrix, formation of aggregates due to strong van der Waals forces and breakage of the fibers during the dispersion [90-92]. These challenges may be overcome by functionalizing the CNTs, as functionalization alters properties of CNTs which may improve their dispersion and enhance the adhesion of CNTs to the polymer [93].

In the present study, we compare and contrast the variation in the conductivity of the CPCs with a change in the method of synthesis and also with the functionalization of the CNT fillers. CNT/PLA fibers were extruded from a nozzle by using a dispensing robot to make filaments. The conductivity of these filaments was measured using the two probe analysis. The reason fibers were extruded from a fine nozzle is that they are considered for their application as interconnects in microelectronics and thus, extrude them into fibers supported on a substrate would be the closest to the real form.

4.2 Experimental details

4.2.1 Fabrication of CPCs (i.e., Solution Mixing and extrusion):

Solution Mixing:

2 grams of poly (lactic) acid (PLA 4032D, Natureworks LLC) was dissolved in 13.5 ml dichloromethane (DCM, Sigma-Aldrich) in order to make a PLA/DCM solution with a concentration of 10 wt.% PLA in DCM. The carbon nanotubes (Nanocyl -7000, Nanocyl) were dispersed in 15.2 ml DCM by sonication using an ultrasound bath for 1 h. The amount of CNTs dispersed in DCM was set in the way that we could obtain different weight percentages of CNTs

in PLA (i.e. 0.1%, 0.2%, 0.5%, 1%, 2%, 3% and 5%). PLA/DCM and CNTs/DCM solutions were mixed and sonicated for 1 h to make the PLA-CNT/DCM solution. This solution was dried at room temperature to obtain CNT/PLA composite.

Extrusion:

The pellets of polylactic acid (PLA 4032D, Natureworks LLC) and CNTs (MWCNTs, Nanocyl -7000, Nanocyl) were dried in a vacuum oven (G05053-10, Cole-Parmer Instrument Company) for 12 h at 50 ºC before processing. The PLA pellets and the MWCNTs were pre mixed and then fed into a micro compounder (5 mL, DSM Xplore) at 170 ºC and 100 rpm. Then the extruding temperature and rotation speed of the twin screws increased to 180 ºC and 300 rpm, respectively. The CNT/PLA nanocomposite was extruded from a nozzle with inner diameter of 0.50 mm.

The CNTs/PLA nanocomposites were diluted in DCM with the 30 wt.% of PLA to DCM in order to make an ink that can be extruded from a nozzle with an inner diameter of 200 µm by a dispensing robot (I&J2200-4, I&J Fisnar). The nanocomposite solution inks were housed in syringes (3 mL barrel, EFD), which were attached by Luer-Lock to a micronozzle. The 1D straight line is fabricated with the different concentrations of CNTs using a micronozzle with a 200 µm inner diameter (5130-0.25-B, EFD) under an applied pressure of 1.75 MPa and 0.1 mm/s robot velocity. The length of the straight line was 5 mm and the average diameter of the filament was ~ 250 µm. The fibers obtained are then dried in a vacuum oven (G05053-10, Cole-Parmer Instrument Company) for 12 h at 60 ºC. The electrical conductivity of these filaments was measured using two point probe method by the Keithley 6517B Electrometer/high resistance meter.

4.2.2 Functionalization of CNTs:

Pristine multi-walled carbon nanotubes (MWCNTs, Nanocyl -7000, Nanocyl) are functionalized using three different methods as follows.

Acid treatment using Nitric acid (HNO_3): For functionalizing the CNTs using nitric acid, 1 g of CNTs were dispersed in 100 ml nitric acid (HNO_3, ACS grade, Sigma-Aldrich) using an ultrasonic bath for 5 hours. Solution is then diluted with water and filtered repeatedly until CNTs were neutralized. These CNTs are then dried in a vacuum oven (G05053-10, Cole-Parmer Instrument Company) for 12 h at 80 ºC.

Acid treatment using stronger acid: For functionalizing the CNTs by a stronger acid (i.e., 3:1 mix of sulfuric acid and nitric acid) 1 g of CNTs was dispersed in 100 ml of 3:1 mixture of H_2SO_4 and HNO_3 (ACS grade, Sigma-Aldrich) using a ultrasonic bath for 5 hours. The solution is then diluted with water and filtered repeatedly until the CNTs are neutralized. These CNTs are then dried in a vacuum oven (G05053-10, Cole-Parmer Instrument Company) for 12 h at 80 ºC.

Functionalization using Nitrogen (N_2) plasma: For functionalizing the CNTs using the N_2 plasma, 1 g of CNTs was fed in the N_2 plasma reactor working at 600 watts and a pressure of 420 millitorr. The CNTs are subjected to a continuous nitrogen flow at 1.5 sccm for 15 minutes.

The functionalized CNTs obtained via the acid functionalization method are powdered manually as well as using the ball mill (ATS scientific 8000M mixer mill) and then used for the CPC synthesis via the solution mixing method as explained above. While the plasma functionalized CNTs are directly used for CPC synthesis via solution mixing.

4.3 Results and discussions

The CPC fibers made using the dispensing robot were viewed under a microscope, to see the structure and the cross sectional diameter of the fibers. Fig 3.1 shows the longitudinal and cross section view of the fibers produced from CPCs made by solution mixing (a & b) and extrusion (c & d) methods. The average diameter of the extruded filaments is ~ 250 µm. The flat surface on one end of the fibers is due to their extrusion from the robot nozzle on a glass substrate. The differences in the forms of the fibers cross sections shown in Fig 4.1 (b) And (d) is mainly related to the distance of the needle of the dispensing robot to the substrate. The closer the needle gets to the substrate the flatter gets the extruded filament.

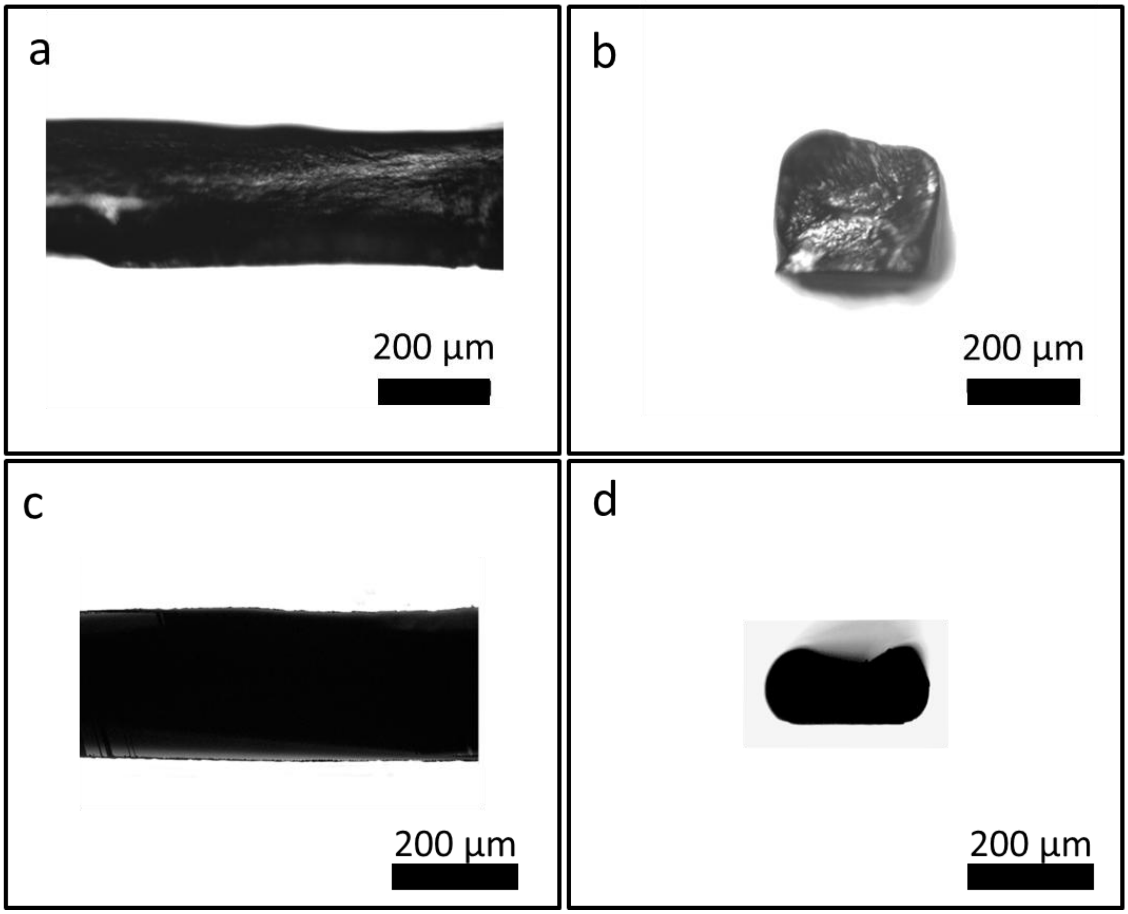

Figure 4.1 : Microscopic images of the 5 wt.% CNT/PLA fibers. (a,b) Longitudinal and cross sectional view of a fiber prepared by solution mixing, (c,d) Longitudinal and cross sectional view of a fiber prepared by extrusion.

To compare the variation of CPC conductivity with the synthesis process and the effect of functionalization, resistivity measurements were performed on the CPC fibers using the two probe resistivity measurement. Around 6 fibers in each of the cases were produced and tested. The conductivity values are an average of the measured results.

4.3.1 Solution mixing vs extrusion method of CPC synthesis:

The CPC fibers obtained via the two methods of synthesis i.e. solution mixing and extrusion were subjected to resistivity measurements using the two probe analysis. The results show less electrical resistivity in case of the fibers obtained via the extrusion method compared to the ones from the solution mixing method. The higher conductivity obtained for the CPCs made by extrusion method might be related to the better dispersion of the nanofillers that can be obtained using extruder compared to solution mixing. Fig. 4.2. Shows a comparison between the dispersion of CNTs in CNT/PLA composites made via extrusion and solution mixing methods. Sample with 0.2% CNT loading shows a difference in the extent of dispersion; the CNTs appear to be more evenly dispersed in the sample prepared via extrusion (Fig 4.2 (b)) compared to the sample prepared via solution mixing method as shown in Fig 4.2 (a). The samples with 0.5% CNT loading also showed a clear difference in the dispersion between the two methods while the comparison of nanofillers dispersion for the samples with higher CNTs concentrations was difficult as they appeared dark under the microscope. The dark and clear spots in the composite made via solution mixing shows the agglomeration of the nanoparticles (Fig 4.2 (a)). Better dispersion of CNTs in the composite made via extrusion method is obvious as the fiber appears dark through the whole body of the fiber Fig 4.2 (b).

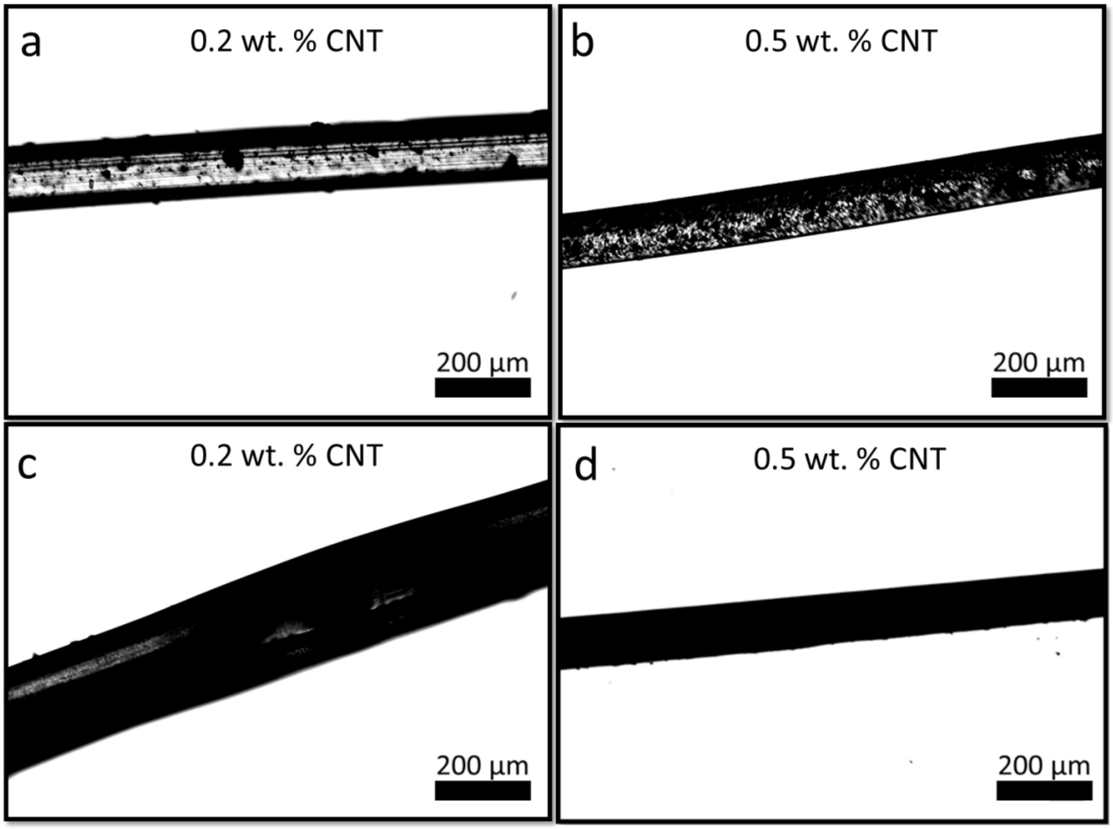

Figure 4.2 : Microscopic images of CNT/PLA fibers showing the CNT dispersion. (a,b) 0.2 wt.% and 0.5 wt.% CNT/PLA fibers prepared via solution mixing method and (c,d) 0.2 wt.% and 0.5 wt.% fibers prepared using the extruder.

The resistance was found to be least in case of the 5wt.% CNT loading samples. In case of the 5wt.% CNT/PLA mix sample prepared by solution mixing the conductivity was found to be 3.97 S/m and for the 5wt.% CNT/PLA mix sample prepared by extrusion the conductivity was found to be at 25.16 S/m. The results of conductivity measurements are shown in Fig. 4.3.

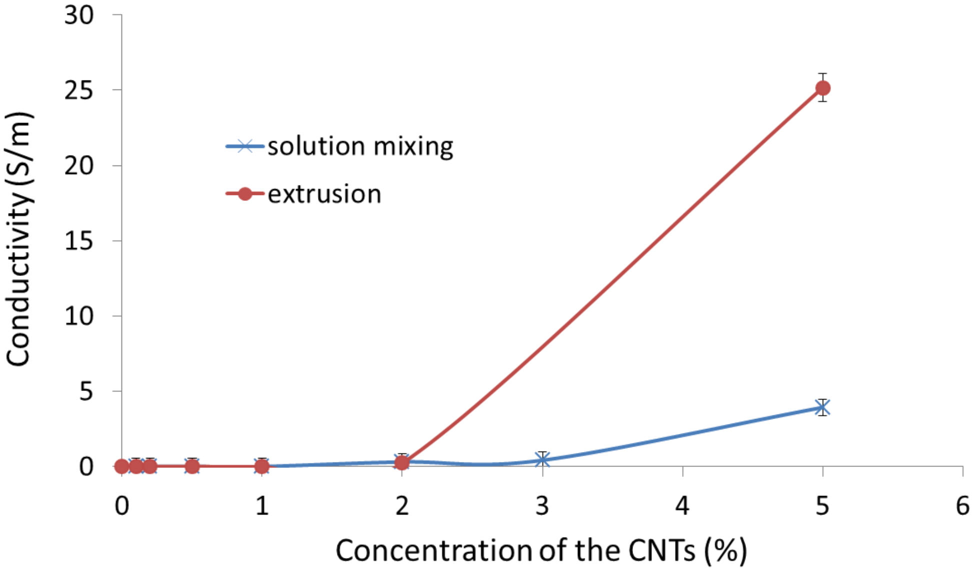

Figure 4.3 : Variation in the conductivity curve of the CPCs with the concentration of CNTs for Solution mixing and extrusion methods.

4.3.2 The effect of CNT functionalization on the electrical conductivity of the CPCs:

The resistivity analysis for the CPCs of the functionalized CNTs dispersed in PLA via solution mixing method show that functionalization of CNTs had negative effect on the conductivity of the CNT nanocomposites as; all the three functionalization methods increase the resistivity of the CPCs. The N_2 plasma functionalized CNT/PLA composite gives better conductivity results compared to both acid functionalized CNT/PLA composites. The composites synthesized from the HNO_3 acid functionalized CNT and H_2SO_4 and HNO_3 acid functionalized CNT were found not to be conductive. The comparison between the plasma functionalized and untreated CNT/PLA composite is as shown in Fig. 4.4.

The lower conductivity of the treated CNTs might be related to lower dispersion and agglomeration of functionalized CNTs in the PLA matrix due to van der Waals bonding between the individual CNTs. The conductivity of the individual carbon nanotubes also decreases after acid or plasma treatments as these treatments can introduce defects in their structure.

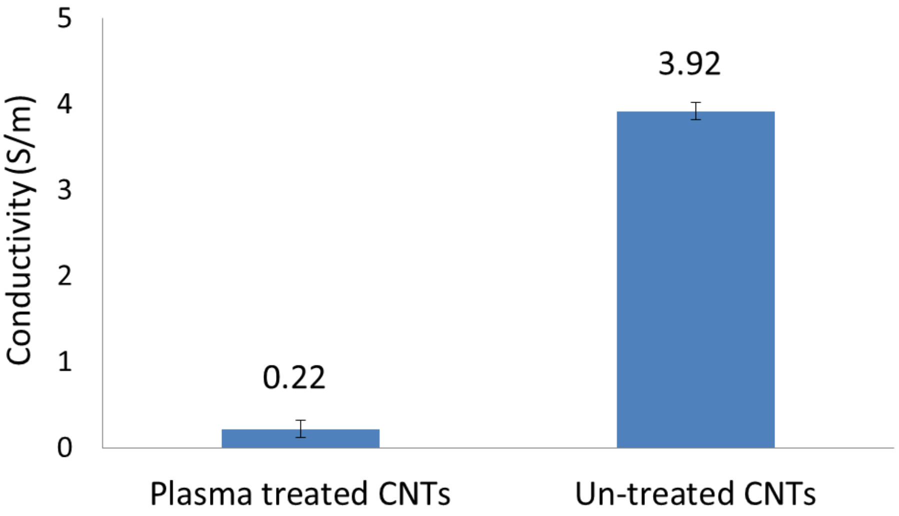

Figure 4.4 : Comparison of the conductivities of the 5 wt.% concentration of the functionalized CNT/PLA composites and un-treated CNT processed via solution mixing.

The effect of the different types of functionalization can be clearly seen on the dispersion of the CNTs in the CPCs with 1 wt.% of CNT concentration as seen in Fig. 4.5. At 1 wt.% CNT loading the acid functionalized CNTs (i.e., HNO_3 and HNO_3/ H_2SO_4 treated CNTs) in the CPC show bad dispersion as seen by the dark and clear spots shown in (Fig 4.5 (a & b)) showing an uneven dispersion, while the plasma treated CNTs in the CPC exhibit better dispersion compared to the acid treated ones as shown by less clear spots seen in Fig 4.5 (c). The untreated CNTs in the CPC show the highest dispersion when compared to the treated CNT samples showing no clear spots as seen in Fig 4 (d). The bad dispersion of treated CNTs in PLA can also be attributed to the fact that PLA and CNTs are hydrophobic and when the CNTs are subjected to acid treatments they are oxidized and this gives the CNTs a partial hydrophilic nature which reduces its compatibility with the hydrophobic PLA worsening the dispersion of CNTs in PLA.

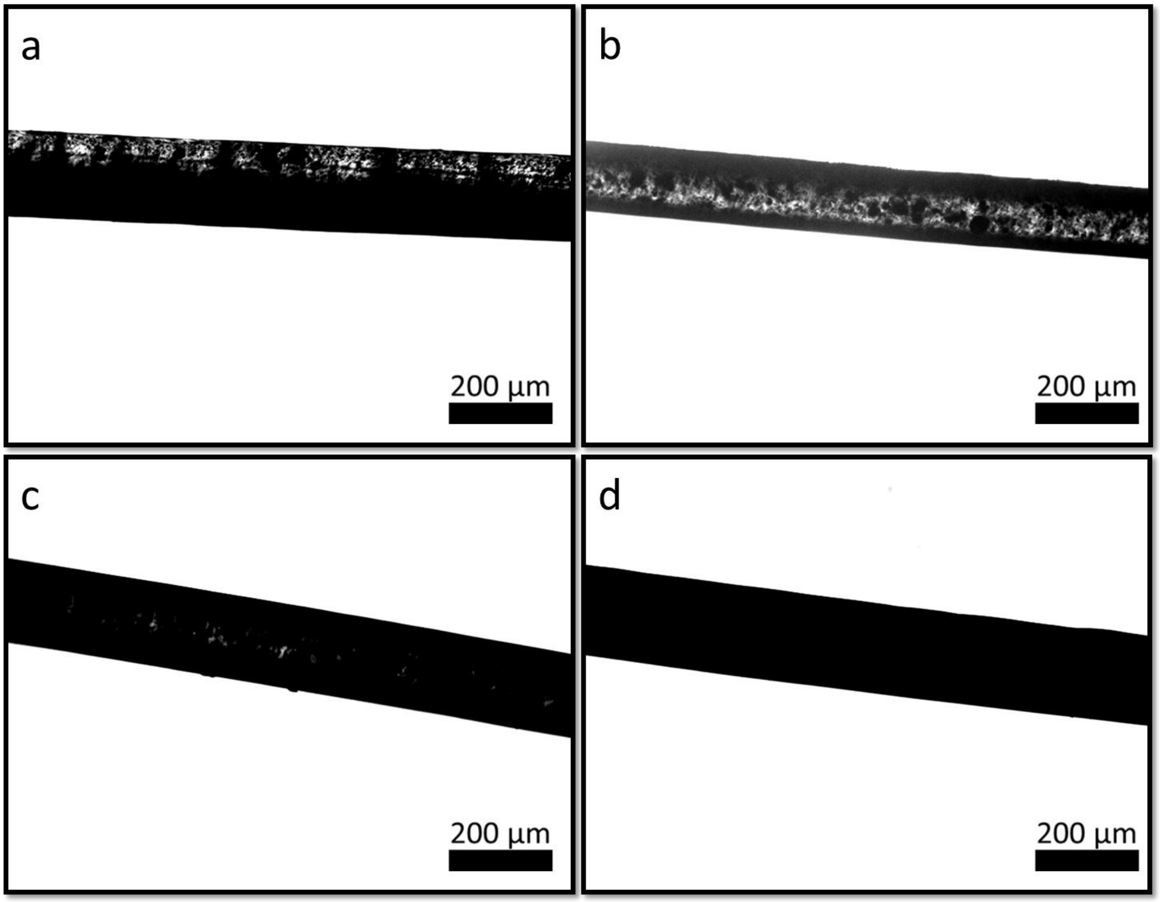

Figure 4.5 : Comparison between the synthesized CNT/PLA fibers with 1 wt.% CNT loading prepared via solution mixing. (a) HNO_3 functionalized CNT/PLA composite. (b) H_2SO_4+HNO_3 functionalized CNT/PLA composite. (c) N_2 plasma functionalized CNT/PLA composite and (d) Untreated CNT/PLA composite.

4.4 Conclusion

Synthesis of CPCs was carried out successfully by solution mixing and the extrusion methods for varied filler concentrations. The maximum electrical conductivity is showed by the 5% CNT concentration samples at 3.97 S/m and 25.16 S/m for the CPC fibers obtained via the solution mixing and the extrusion methods, respectively. The higher electrical conductivity of the CPCs made by extrusion method compared to solution mixing might be related to higher shear rates, which leads to smaller aggregates and better dispersion of the nano-fillers in the polymer. Regarding the functionalized CNTs, conductivity measurements showed a negative effect of the CNTs functionalization on the electrical conductivity of the CPCs. This limitation could be attributed to the formation of defects in the CNTs or agglomeration of functionalized CNTs in the CPCs. This work will be continued by performing more characterizations on the CPCs (i.e. TEM for showing the dispersion of CNTs in PLA, Raman for investigating the defects in CNTs structure, XPS and FTIR to analyze the functionalization groups on CNTs.

CHAPTER 5 ADDITIONAL RESULTS

The conference article presented in Chapter 4 shows the main results on the variation in the electrical conductivity values of the CPC with the manufacturing method and the effect of the various functionalization treatments of CNTs on the conductivity of the synthesized CPCs. However, other works have been carried out in context of this master's degree.

As shown in Figure 4.4, the functionalization of CNTs has a negative effect on the conductivity of the PLA/CNT composite. This can be attributed to the formation of defects in the CNTs or agglomeration of functionalized CNTs in the CPCs. The functionalization step makes the CNTs fragile and hence, when the functionalized CNTs are subjected to long sonication steps for the CPC synthesis there is more probability of the CNTs to break thus, shortening their length. These shorter CNTs are hypothesized as being responsible for lower conductivity of the polymer composites.

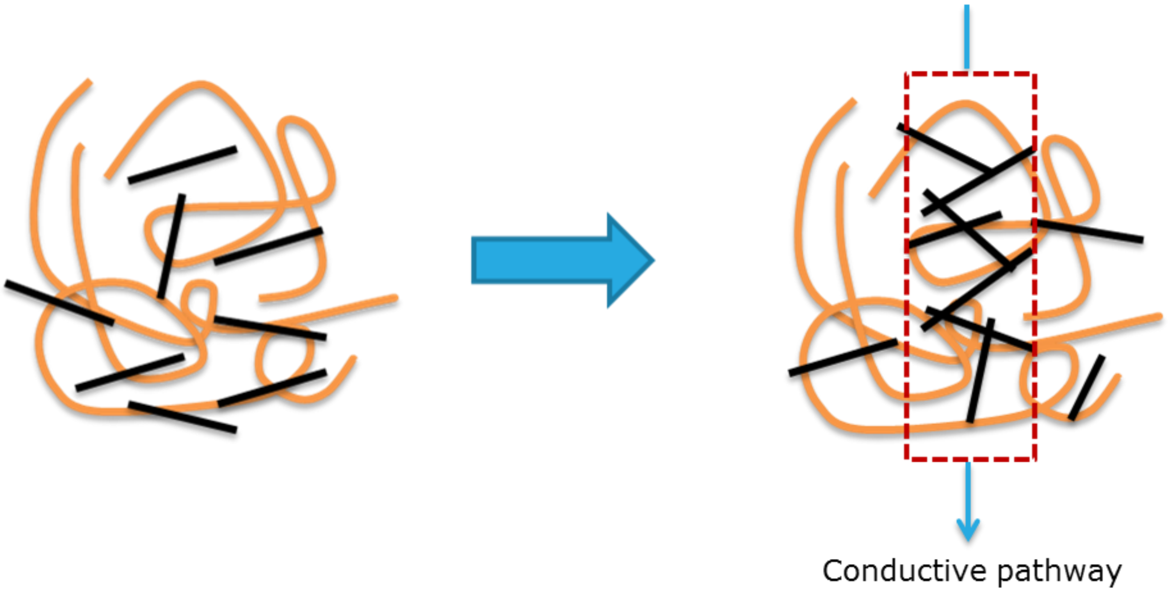

Figure 5.1 : Schematic explaining the formation of a percolation pathway by using "binders": uniform dispersion of fillers in the polymer (left) compared to selective distribution for max conductivity (right). The dotted box depicts the percolation pathway formation.

The formation of percolation pathway by using binding molecules can be defined as the probability of two CNTs coming in contact with each other is high if the CNTs are longer and thus have more surface area but when the length of the CNT is shortened the probability of them coming into contact with each other decreases and thus making it difficult for the formation of a conductive pathway. To overcome the damage caused by the functionalization step and to assist the percolation pathway formation, we try the use of binding molecules that act as bridges in between two functionalized CNTs (see Figure 5.1). These bridges act as links in-between two acid functionalized CNTs and thus help getting two nanotubes closer together and assisting the formation of a conductive pathway. CNTs are first subjected to a short acid functionalization step and are then treated with Para-phenylenediamine, which ensures the anilyation of the functionalized CNTs. These aniline treated CNTs are washed with deionized water and dried using the vacuum oven. CPC synthesis of these aniline treated CNTs along with PLA is then carried out using the solution mixing method as described in Chapter 3. The CPC obtained is again dissolved with DCM and fed into a syringe to be extruded as fibers using the deposition robot. The fibers are then dried and their electrical conductivity is measured using the two-point probe resistivity measurement method.

The electrical conductivity of the para-phenylenediamine treated CNTs/PLA composite samples is found to be 4.2 S/m at 5 wt. % of CNT loading. This value is slightly higher when compared to the functionalized as well as the un-treated CNT/PLA composite samples which are synthesized using the solution mixing method. Figure 5.2 shows a comparison between the previously achieved highest electrical conductivity of the un-treated CNT/PLA composite and the amine treated CNT/PLA composite, both of which are synthesized using the solution mixing method.

When the CNTs are treated with HNO_3, the carboxylic groups (-COOH) are attached to the surface of the CNTs. Such carboxylic functionalized CNTs when react with para-pehynelenediamine, the amine group ($-NH_2$) present in para-phenylenediamine binds with the carboxylic group on the CNTs, thus resulting to an amide formation (CO-NH). Each amine molecule has a 1:1 binding affinity ratio with a carboxylic molecule. The amide acts as a bridge between two acid functionalized CNTs, bringing the nanotubes closer together and assisting the formation of a percolative path, thus resulting in a higher electrical conductivity. Table 5.1 shows the variation in the resistivity and conductivity values of the 5 wt. % CNT/PLA polymer composites synthesized using the solution mixing method.

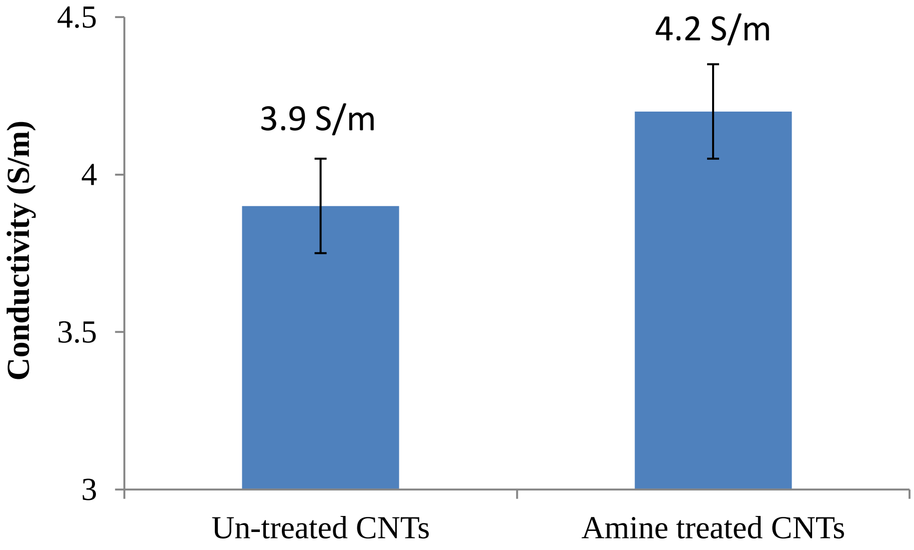

Figure 5.2 : Comparison between the conductivity values of the un-treated CNT/PLA and amine treated CNT/PLA composite samples prepared via solution mixing method.

As seen in Table 5.1, the amine treated sample prepared via the solution mixing method shows higher electrical conductivity compared to the un-treated CNT sample. This increase in conductivity is explained by the presence of binding molecules of amine from the para-phenylenediamine used.

Table 5.1 : Resistivity and conductivity values for the various 5 wt. % CNT/PLA samples synthesized using the solution mixing method.

Sample type	**Un-treated**	**HNO_3 treated**	**H_2SO_4+HNO_3 treated**	**N_2 plasma treated**	**Amine treated**
Resistivity (Ω.m)	0.26	1212.2	>10000	4.43	0.23
Conductivity (S/m)	3.9	Not conductive	Not conductive	0.22	4.2

A better conductivity can be attained via the extrusion method of CPC manufacturing, which is superior in comparison to the solution mixing method. Table 5.1 also shows the high resistivity values of the composite samples manufactured using the functionalized CNTs. Synthesized CPCs as mentioned previously can be then dissolved with measured quantities of DCM and filled into a syringe to be then extruded into various 2D and 3D structures, using the deposition robot via the solvent-cast printing method. Initially the CPC material is like a paste but post deposition when exposed to the air, the DCM evaporates, thus leaving behind a solid structure. These depositions are done using a wide variety of nozzle diameters which depends on the requirement and the viscosity of the CPC material used. Figure 5.3 shows the examples of the 2D and 3D structures like fibres and layered scaffolds that were designed using the deposition robot.

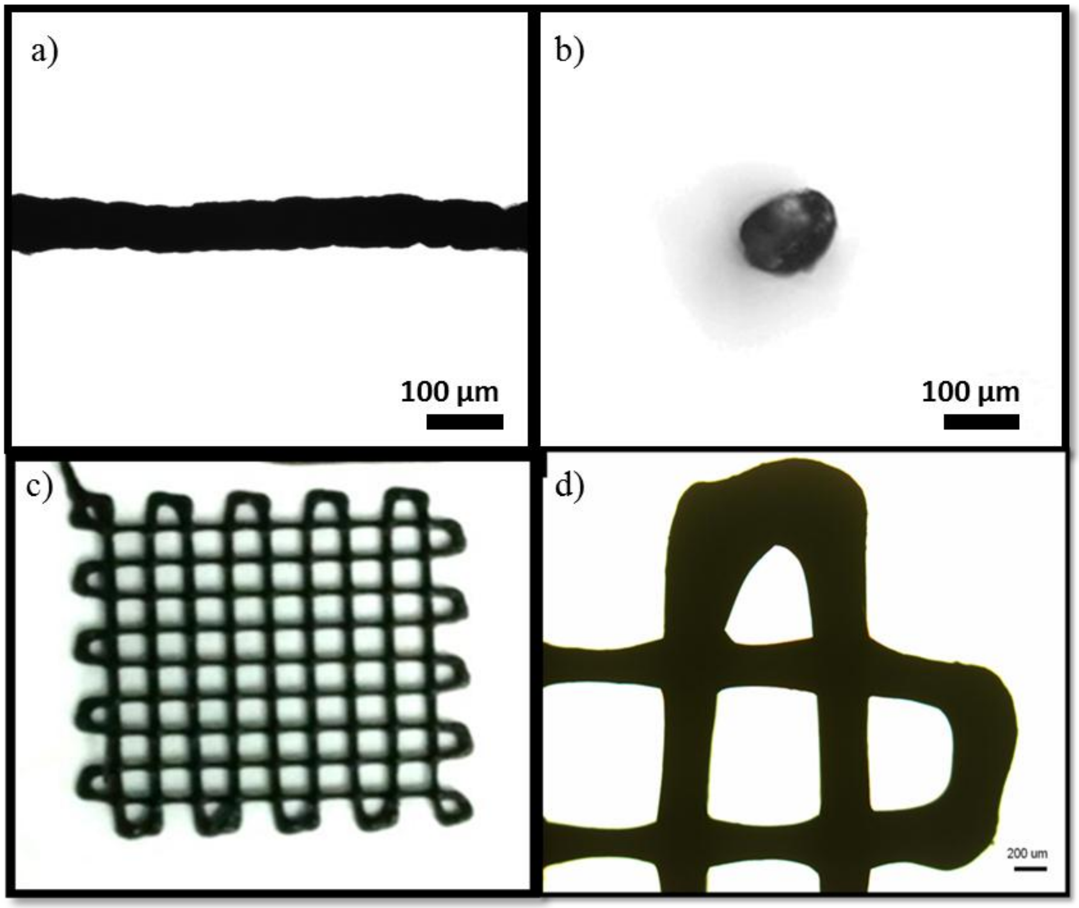

Figure 5.3 : Microscopic images of the designed 2D and 3D structures

a,b) longitudinal and cross-sectional view of the 5 wt. % CNT/PLA fiber

c,d) magnified view of a 4 layer scaffold structure designed using the 2 wt.% CNT/PLA.

Figures 5.3 a,b) show the microscopic images of the 5 wt. % CNT/PLA fiber printed using the amine treated CNT/PLA CPC manufactured using the solution mixing method via the deposition robot. The printing conditions are: nozzle diameter of 0.1 mm, the velocity of the robot head 3.1 mm/s and the pressure applied is 400 kPa. It exhibits a conductivity of 4.2 S/m. As seen in the figure the fiber printed has a rough and wavy surface and the cross-section is also not circular in shape. This can be due to the uneven mixing or poor compatibility of the CNT fillers with the PLA polymer. Figures 5.3 c,d) are the microscopic images of the 2 wt. % amine treated CNT/PLA CPC sample printed into a 4 layer scaffold using the deposition robot. The printing conditions for printing this sample are: nozzle diameter of 0.2 mm, velocity of the robot head 2.8 mm/sec and the pressure applied is 270 kPa. When compared to the fiber printed using the 5 wt. % CNT/PLA CPC sample, it exhibits a smoother surface and less pressure is needed to extrude the CPC through the syringe. This is due to the presence of less CNT fillers in the 2 wt. % samples.

CHAPTER 6 GENERAL DISCUSSIONS

The works presented in the previous chapters of this thesis compares the most commonly used methods of CPC preparation and their effect of various functionalization methods on the conductivity of CPCs. It also presents a method of using binding molecules as bridges to help connect the CNT fillers dispersed in the polymer so as to form a percolative pathway and enhance the conductivity value of the composite. The fibres drawn using the deposition robot shows that these CPCs can be printed into various 2D and 3D structures, for various applications.

6.1 Variation of the conductivity with method of synthesis

As discussed in Chapter 3, we use solution mixing and twin screw extrusion methods as methods of CPC synthesis. It is observed that in both the methods of synthesis, initially as the filler loading is increased the conductivity value increases gradually but at 2 wt. % of CNT loading the conductivity value drastically increases, hence it is conferred that threshold value lies around the 2 wt. % of filler loading. A similar trend is observed in the conductivity curves of the samples prepared using both the methods of synthesis, i.e., solution mixing and twin screw extrusion. But despite of having a similar conductivity curve, at each wt. % of filler loading the conductivity values for the samples prepared using the twin screw extruder are higher compared to the samples prepared using the solution mixing method. The higher conductivity obtained for the CPCs made by extrusion method is related to the better dispersion of the CNT fillers that can be obtained using extruder compared to solution mixing. This is confirmed from the microscopic images (Figure 4.2) of the fibre samples prepared using the two methods. The 0.2% and 0.5% CNT/PLA loaded samples showed a clear variation in dispersion as both these samples prepared using the extrusion method appears to be darker and hence better dispersed. While the samples prepared using the solution mixing show more clear spots along the fibre and thus, presence of agglomeration of the CNTs. The higher conductivity obtained for the CPCs made by extrusion method might be related to the movement of CNTs in the composite material due to the evaporation of the solvent, during the drying phase in the solution mixing method or it can be attributed to the better dispersion of the nano fillers due to the higher shear rates, which leads to smaller aggregates and better dispersion of the fillers in the polymer manufactured using the extruder compared to solution mixing.

6.2 Effect of CNT functionalization

The resistivity analysis of the CPCs of the functionalized CNTs dispersed in PLA show that the specific conditions of acid and the plasma functionalization attempted have a negative effect on the conductivity of the composite: all three functionalization methods increase the resistivity of the CPCs. But when compared to the acid functionalized CNT/PLA samples, the N_2 plasma functionalized CNT/PLA sample gives slightly better conductivity results. The higher resistivity of the treated CNTs might be related to lower dispersion and higher agglomeration (Figure 4.4) of the functionalized CNTs in the polymer matrix. The bad dispersion of treated CNTs in PLA can also be attributed to the hydrophobic nature of CNTs and PLA. When CNTs are subjected to acid treatments they are oxidized and this gives the CNTs a partial hydrophilic nature which reduces its compatibility with the hydrophobic PLA worsening the dispersion of CNTs in PLA. Also, the acid or plasma treatments can introduce defects in the structure of the CNTs and make them fragile, which when mixed along with PLA and synthesized as composites break into shorter lengths which in turn leads to lower conductivity of the CPCs. However, other hydrophobic functionalization techniques need to be tried to see their effect on the conductivity of the CPC samples produced. The effect of the different functionalization is confirmed by the microscopic images of the CPC fibres which show the most dispersion of the fillers in case of the un-treated CNT/PLA composite samples when compared to the three treated CNT/PLA composite samples.

6.3 Effect of binder molecules on the conductivity of the CPC

To reduce the extent of damage caused on the conductivity property of the CNTs due to the strong functionalization methods and to find a way to connect the functionalized CNTs within the polymer matrix, selective dispersion via the use of binding molecules that act as bridges between the CNTs, is investigated. These binding molecules act as bridges and connect the acid functionalized CNTs in the polymer matrix, thus may help the formation of a conductive pathway. This process is known as the selective dispersion of the fillers and needs to be applied to attain higher conductivity values. For this we use binding molecules (para-phenylenediamine) that act as bridges between the acid functionalized CNTs. The use of binding molecules also reduces the damage caused to the CNTs by long exposures to harsh acids and helps connected the shorter CNTs dispersed in the polymer. The amine group present in the para-pheylenediamine has an affinity for the carboxylic group present on the acid treated CNTs and forms an amide bond. This amide bond formation acts as a bridge between two acid treated CNTs, thus getting them closer and helping the conductive pathway formation. This can be concluded from the conductivity analysis results as the conductivity of the amine treated CNT/PLA CPC is measured at 4.2 S/m when compared to 3.9 S/m of the un-treated CNT/PLA CPC sample.

6.4 2D and 3D printing of the CPCs

The CPCs manufactured using the above techniques and treatments were then dissolved using measured quantities of the solvent DCM. This composite paste is filled into a syringe to be extruded using the deposition robot via the direct write method. Several 2D and 3D architectures like fibers, single and multi-layer scaffolds (Figure 5.3 (c,d)) can be printed using this technique. It is observed that for the CPC material when printed, as the concentration of the CNT fillers in the sample material increases the printability of the material decreases, i.e., more pressure is required to extrude the material containing higher filler loading. As observed from the Figure 5.3 (a,b) the surface of the printed filaments of the 2 wt. % CNT loaded samples is more smooth compared to that of the samples printed using the 5 wt. % CNT loading CPC. Hence, it can be inferred that apart from the ease of printability, the surface of the printed filaments becomes more irregular and rough as the concentration of the CNT loading is increased. The same printing technique can be applied to design and print other complex architectures like more complex scaffold structures and even free standing 3D structures.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

This project was an attempt to present a potential method to synthesize conductive polymer composites (CPCs) with maximum possible conductivity at the least amount of CNT filler loading, so as to reduce costs and maintain the ease of manufacturing. The project showed a comparison between the two most commonly used methods of composite synthesis and how the conductivity value varies with the method of synthesis despite having the same filler loading. It also discusses the effect of acid and plasma treatment of the CNTs on the conductivity of the prepared composite. Finally, it presents the possibility of the use of bridging molecules in between the CNTs that assist the formation of a percolative pathway within the polymer composite and thus helping achieve higher conductivity at relatively lower filler loadings.

Preliminary results show that regardless of the method of synthesis, the conductivity value of the PLA/CNT polymer increases with an increase in the filler loading. For both the methods of synthesis, i.e., the solution mixing and twin screw extrusion method, the threshold value for the electrical conductivity lies around the 2 wt. % CNT loading. While the conductivity value curve will follows a similar path in both cases, the conductivity value at each filler loading is greater for the CPC samples extruded using the twin-screw micro compounder when compared to the samples prepared using the solution mixing method. The resistance was found to be least in case of the 5wt. % CNT loading samples. In case of the 5wt. % CNT/PLA mix sample prepared by solution mixing the conductivity was found to be 3.97 S/m and for the 5wt. % CNT/PLA mix sample prepared by extrusion the conductivity was found to be 25.16 S/m.

In order to make the CNTs more reactive, help increase the CNT-CNT interaction within the polymer so as to help the formation of a conductive pathway, functionalization of CNTs using acid and plasma treatments were tried. The conductivity analysis for the CPCs of the functionalized CNTs dispersed in PLA via solution mixing method show that functionalization of CNTs had negative effect on the conductivity of the CNT nano-composites i.e., the resistivity increases in all the three cases. This increase is probably related to the lower dispersion and agglomeration of the functionalized CNTs in the PLA matrix due to the van der Waal bonding between the CNTs.

To achieve higher conductivity in the CPC, selective dispersion of the fillers needs to be applied. Para-pehnylenediamine was used as the binding agent, having an affinity for the carboxylic groups attached to the CNTs after the treatment with acid it helps getting two acid functionalized CNTs together via an amide group formation and helping the conductive pathway formation. This is verified by the resistivity analysis of the CPCs prepared using the amine treated CNTs via the solution mixing method. The conductivity value of the amine treated CNT/PLA CPC is found to be at 4.2 S/m when compared to the previously achieved high of 3.9 S/m.

Solvent-cast printing method is used for to draw the above synthesized CPCs into 2D fibers using the deposition robot, for their resistivity analysis using the two-point probe method. This shows the printability possibility of these conductive composite materials. Other 2D and 3D structures like single and multi-layer scaffolds were designed using the same technique by dissolving the composite in the solvent (DCM). The same technique can be applied to design and print other complex architectures and potentially freestanding 3D structures.

7.2 Recommendations

The following aspects are recommended for more exploration in future work:

1. Orientation of the CNTs inside the designed microstructures should be studied at different shear conditions, which could be used to find the correlations between the final electrical conductivities and the process parameters.
2. Use of other hydrophobic functionalization techniques to check their effect on the conductivity values of the CPCs.
3. Trying other binder molecules (other amines, esters, etc.) to quantify the “bridging” theory.
4. Using the extrusion method of synthesis for these binding molecule treated CNTs to achieve higher conductivity molecules.
5. Designing more complex 3D architectures like multi-layer scaffolds and free standing structures using the CPC materials.

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