MICROWAVE *IN-SITU* POLYMERIZATION OF POLY LACTIC ACID AND CARBON NANOTUBES AND STUDY OF ITS ELECTRICAL CONDUCTIVITY

A thesis submitted
in partial fulfillment of the requirements
for the award of degree of

Masters of Technology
in
Chemical Engineering

Submitted by:

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DECLERATION

I hereby declare that the work being presented in the thesis report entitled "**Microwave *in-situ* polymerization of poly lactic acid and carbon nanotubes and study of its electrical conductivity**" by me in the partial fulfillment of the requirements for the award of degree of Masters of Technology in Chemical Engineering, from Department of Chemical Engineering, Thapar University, Patiala, is an authentic record of my own work carried under the supervision of **Dr. Rajeev Mehta**, Professor, **Dr. S.K Ahuja,** Assistant Professor, Department of Chemical Engineering, Thapar University, Patiala. The matter presented in this report has not been submitted in any other University/Institute for the award of Masters of Technology or any other degree.

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CERTIFICATE

This is to certify that the dissertation entitled, **"MICROWAVE *IN-SITU* POLYMERIZATION OF POLY LACTIC ACID AND CARBON NANOTUBES AND STUDY OF ITS ELECTRICAL CONDUCTIVITY"** is an authentic record of my own work carried out as requirement for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, Punjab under the supervision of Dr. Rajeev Mehta, Professor, Department of Chemical Engineering and Dr. S.K Ahuja, Assistant Professor, Department of Chemical Engineering.

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ABSTRACT

Poly lactic acid (PLA) is linear aliphatic thermoplastic polyester produced from renewable resources. Its degradable nature makes it very useful. High molecular weight PLA is produced by condensation method ring opening polymerization of Lactide.

Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure. It has extraordinary thermal conductivity, mechanical and electrical properties. Carbon nanotubes find applications as additives to various structural materials.

Nanocomposite is a multiphase solid material where one of the phases has one or more than dimensions of less than 100 nanometers (nm). It is a solid combination of a bulk matrix and nano-dimensional phases differing in properties due to dissimilarities in structure. These materials show improvements in mechanical, thermal, electrical and barrier properties.

In this study properties of nanocomposite of PLA and carbon nanotubes are studied, in which lactide is the monomer and carbon nanotube as the nanofillers.The *in-situ* polymerization was done in a Monomode microwave reactor. Microwave heating has been used for the synthesis of composite. Microwave heating is a faster method of heating as compared to the other methods. Fourier transform infrared microscopy confirmed the formation of nanocomposites. SEM and TEM images showed that the CNT is dispersed over the polymer matrix.

CNT has very high electrical conductivity and thus synthesized nanocomposite expectedly shows high electrical conductivity. The electrical conductivity of nanocomposite spectacularly increases with the increase in concentration of nanofiller up to a certain value.

CONTENT

LIST OF FIGURES

CHAPTER 1 : INTRODUCTION

1.1 Degradable polymers

Degradable polymers are a specific typeof polymer that breaks down into natural by-products such as gases (CO_2,N_2), water, biomass, and inorganic salts due to microbial action. These polymers are found both natural and are also synthesized, and largely consist of ester, amide, and ether functional groups. The properties and mechanism of breakdown of these polymers are determined by their structure. These polymers are commonly synthesized by condensation reactions, ring opening polymerization (ROP), and metal catalysts. There are enormousexamples and applications of degradable polymers. Even though degradable polymers have several applications, there are properties that tend to be common among them. All the degradable polymers must be stable and durable enough for use in their particular application, but upon disposal they must easily break down.A broad description of types of degradable polymers is given below.

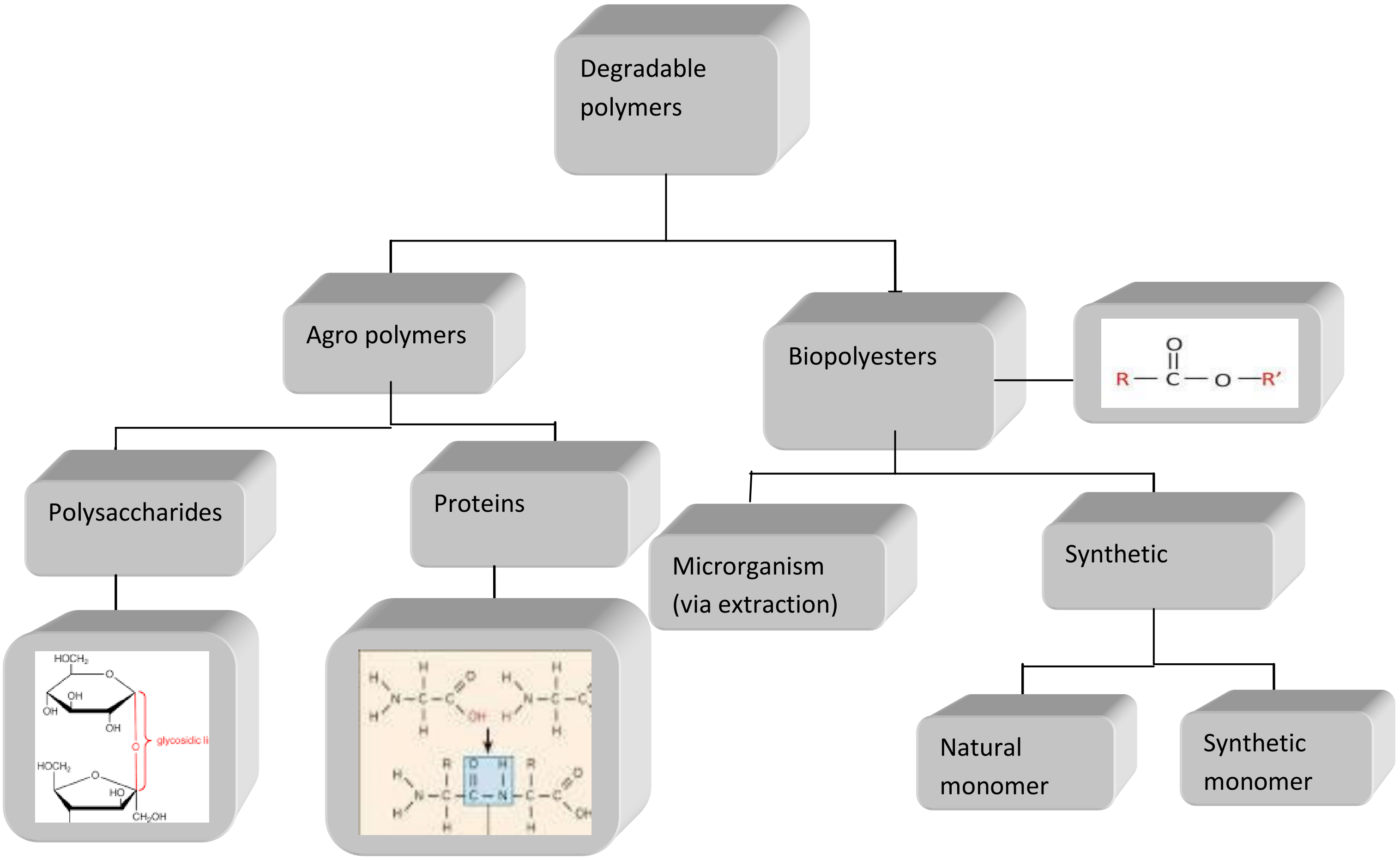


Fig 1: Types of degradable polymer.

PLA is a degradable polymer. It is widely studied now days. A lot of studies have been done to study its synthesis as well as its properties. Also using PLA as polymer matrix various nanocomposites are also synthesized using different fillers.

1.2 Poly (lactic acid)

PLAwas firstsynthesizedin 1932 by Carothers (at DuPont). The product synthesized by him was a low molecular weight PLA which was produced by heating lactic acid under vacuum while removing the condensed water. The main problem was the low molecular weight of the PLA. Finally, by ring-opening polymerization of the lactide, high-molecular weight PLA was synthesized.

PLA was preliminary used in combination with polyglycolic acid (PGA) as suture material and sold underneath the name Vicryl in the U.S.A. in 1974. A lot of research effort is presently concentrated on the development of different PLA modifications to make a material that is suitable for a wider range of products. In many cases the modification of PLA by copolymerization, surface treatment, stereocomplexation, or blending is being done. This modification leads to many changes in the properties and degradation pattern of the inherent polymer radically and consequently affects its suitability for different end-use applications.

Suitable analysis and characterization of PLA and its precursor during different stages of production is essential for controlling the properties and stability of the resulting product. The current industrial production of lactic acid is based mainly on microbial carbohydrate fermentation because it is more economical and more feasible chemicallyas compared to the chemical method. This method also enables the production of optically pure lactic acid.

The optical purity of lactic acid is vital during the synthesis of PLA becausea small amount of enantiomeric impurities can drastically change the properties such as crystallinity or degradation rate of the polymer. Because the fermentation broth includes a complex mixture of impurities, nutrients, and cell debris, the downstream processing of lactic acid plays a vital role in the overall production route of PLA. A figure showing the process of degradability of PLA is given below.

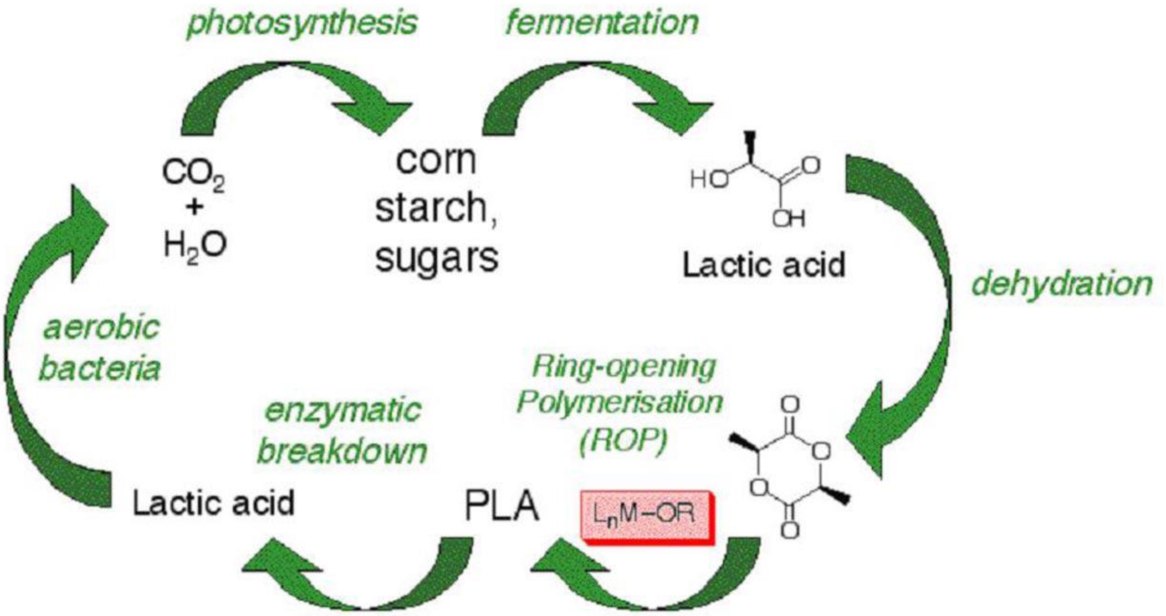


Fig.2: Cycle of synthesis and decomposition of PLA.

The detection and elimination of impurities is verynecessary because these impurities can strongly deteriorate the properties of the synthesized polymer. Lactide is a dimer formed by ring-opening of lactic acid. It is used in the production of high molecular mass PLA in byring-opening polymerization (ROP) method and hence, is a very important intermediate in the industrial manufacture of PLA. Because of the chiral nature of lactic acid, the intermediate lactide exists in three different forms

1. L,L-lactide
2. D, D-lactide
3. D,L-lactide.

A 50% mixture of L,L- and D,D-lactide is calledas racemic lactide. Lactide is the end-product of depolymerization process. In this process a low molecular mass lactic acid is formed by step growth polymerization and is further degraded thermally by the backbiting reaction.

The properties of crudelactide consequently depend upon the quality of the polymer used as a reagent for the reaction as well as on the various parameters of depolymerization reaction. Sometimes along with lactide the crude product also contain other contents like water, lactic acid, lactic acid oligomers and residual catalyst, when used for the polymerization of the oligomer. Precautionary control during the production procedure, starting from the monomers lactic acid and lactide to the polymerization process, whether it is step-growth polymerization or ROP, is necessary for the production of PLA of high optical purity and high molecular mass (Inkinen *et al.,* 2005).

Polycondensation method

In this method PLA is synthesized by step growth polymerization in which the growth of polymeric chain takes place by joining of two molecules and removal of small molecules like water, etc. In this process the PLA formed is low molecular weight.

Ring- opening polymerization

Ring opening polymerization of lactic acid is done to form to produce a high molecular mass PLA.Ring-opening polymerization (ROP) is a type of chain-growth polymerization, the terminal end of polymeric chain acting as an reactive center where further monomersreact by opening its ring and forming afurther longer polymer chain. The centre of propagating can beanionic, cationic orradical. Metallic catalysts are used to produce high molecular mass polymers. ROP is mostly used for the synthesis of biopolymers. The driving force in ring-opening polymerization of cyclic monomers is the relief ofsteric repulsions orbond-angle strain between the atoms in the center of the ring. Thus, as compared to other types of polymerization, the change in enthalpy in ring-opening is negative. The mechanism involved in the reaction is given below:

In the figure given below theLM indicates a single metalcenter and the set of its attendant ligands. The initiation step of the reaction takes placeafter coordination of the LA (lactic acid) molecule by its ketonic oxygen. This leads to the activation of the ketonic carbon to the nucleophilic attackbyX which is a nucleophilic ligand, leading to thering-opening of cyclic molecule and generation of bond between metal and alkoxide. The initiation reaction is started by X = OH, OR where, R = alkyl group, or an amide group. The propagation step involves the repeated attachment of the LA monomer in the polymeric chain and thenthe regeneration of the metal–alkoxide bond for attaching the next molecule. Therefore, competing with *trans*-esterification reaction takes place which competes with ROP. Usually, this reaction is less rapid as compare to the chain growth step of ROP, but with decrease in concentration of monomer the rate of *trans*-esterification reaction become significant. *Trans*esterification reaction leads to expansion of the distribution of the molecular weight of the polymer and hence, leading to the increase in Polydispersity index with time from 1.0 to2.0. Intra-chain *trans*-esterification producing cyclic-oligomers can also occur side by side with inter-chain *trans*-esterification. Moreover, ina stereoselective polymerization of either *rac*- or *meso*-LA, scrambling of the stereocenters will take place along the chain of polymer because of the *trans*-esterification and hence, leading to loss of stereoselctivity. chain transfer, reaction also takes place which is a bimolecular reaction. In this reaction two metal centers are bridged by alkoxide ligands.The steps explained above can also be explained through these reactions (Chisholm, 2010).

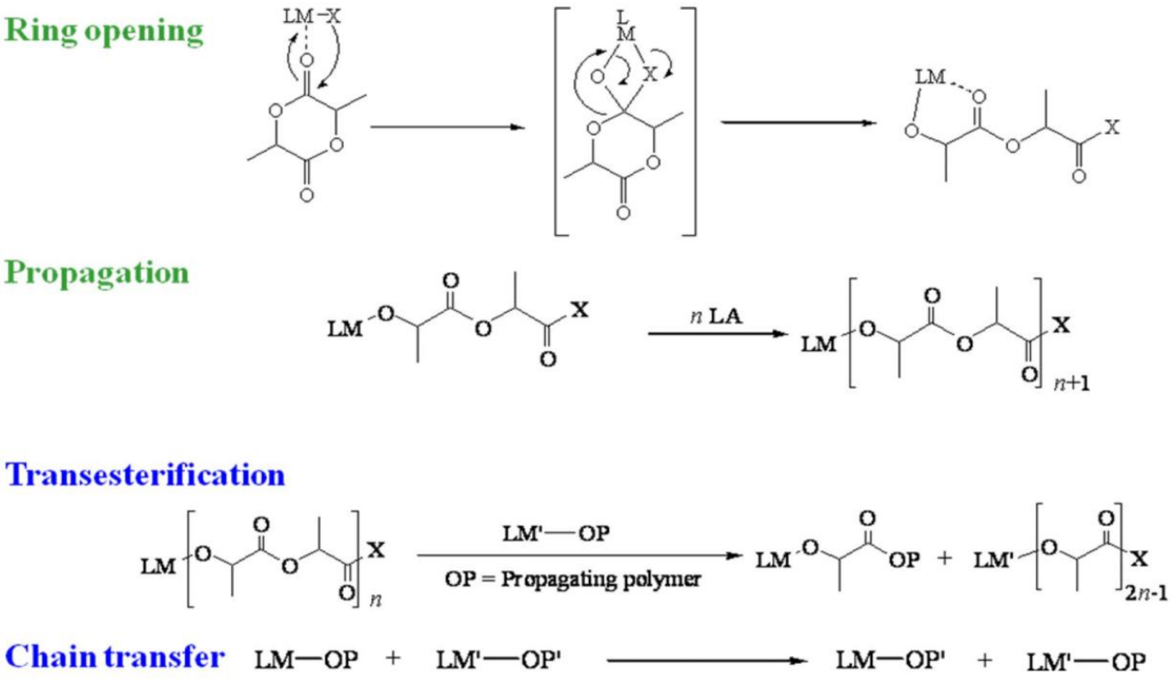


Fig.3: steps involved in Ring –opening polymerization (Chisholm, 2010).

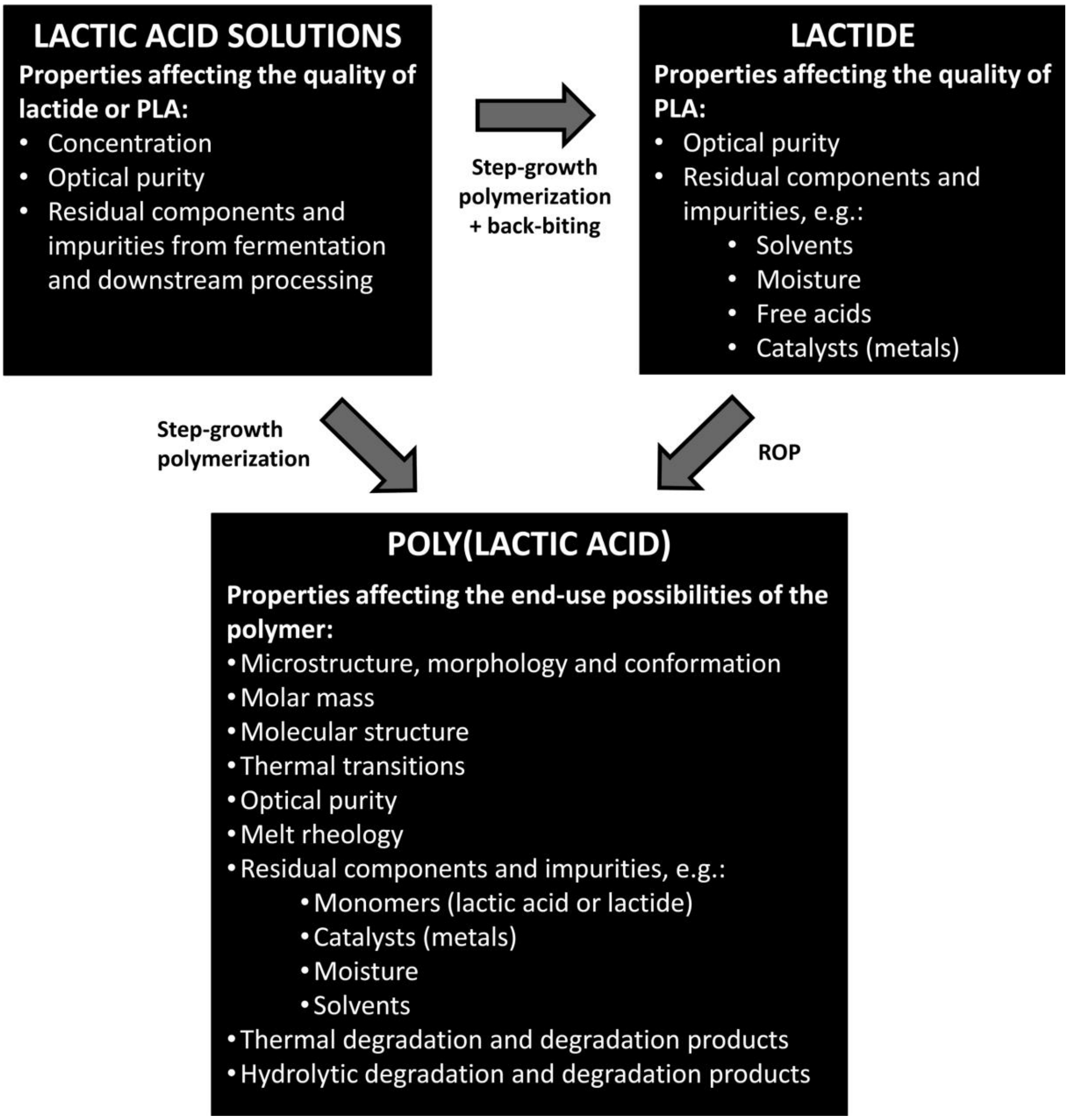


Fig.4: Preparation of PLA from Lactide and lactic acid and its properties(Inkinen *et al.*, 2005).

1.2.1 Thermal stability of Poly (lactic acid)

PLA is thermally unstable and exhibits rapid loss of molecular weight as the result of thermal treatment at processing temperatures. The ester linkages of PLA tend to degrade during thermal processing or under hydrolytic conditions. PLA undergoes thermal degradation at temperatures lower than the melting point of the polymer, but the degradation rate rapidly increases above the melting point. It has been postulated that thermal degradation mainly occurs by random main-chain scissions. Several reactions such as hydrolysis, depolymerization, oxidative degradation, and intermolecular and intramolecular trans-esterification reactions to monomer and oligomeric esters, are suggested to be involved in the degradation process during thermal treatments. The degradation of polymer increases with increasing temperature and time. Different factors like particle size and shape of polymer, temperature, moisture, crystallinity, % D-isomer, residual lactic acid concentration, molecular weight, molecular weight distribution, water diffusion, and metal impurities from the catalyst will affect the polymer degradation rate.

In comparison to other biopolymers, the production of PLA has numerous advantages including:

(a) Lactic acid is produced by the fermentation of a renewable agricultural source corn which produces monomer lactide.

(b) The fixation of significant quantities of carbon dioxide via corn (maize) production by the corn plant.

(c) A significant amount of energy is saved.

(d) It has the ability to recycle back to lactic acid by hydrolysis or alcoholysis.

(e) It has the capability of producing hybrid paper-plastic packaging that is compostable.

(f) It leads to reduction of landfill volume.

(g) Improvement of the agricultural economy

(h) The all-important ability to tailor physical properties through material modifications.

Briefly, PLA is based on agricultural (crop growing), biological (fermentation), and chemical (polymerization) sciences and technologies. It is classified as generally recognized as safe (GRAS) by the United State Food and Drug Administration (FDA) and is safe for all food packaging applications (Taubner *et al.*, 2001).

1.2.2 Properties of PLA

PLA has unique properties like good appearance, high mechanical strength, and low toxicity; and good barrier properties have broadened its applications. Numerous researchers have studied the different properties of PLA alone and in combination with other polymers as blend or copolymer. Low glass transition temperature of PLA limits its usages in thermally processed packages. Because of its deformation and its low melting temperature, it is better to use it for heat-sealing and thermoforming applications. The other important property of polymers is their rate of crystallization. Crystallinity is the indication of amount of crystalline region in the polymer with respect to amorphous content. Crystallinity influences many polymer properties including hardness, modulus, tensile strength, stiffness, crease point, and melting point. So, while selecting a polymer for a required application its crystallinity plays the foremost role. Some other properties of PLA are:

- PLA is soluble in various solvents like chlorinated solvents, hot benzene, and dioxane.
- PLA can be processed like most thermoplastics into fiber.
- PLA is a semi crystalline polymer with glass transition temperature 55 °C.
- The thermal decomposition of PLA takes place at a temperature range of 325-375 °C.
- The melting temperature of PLA is 170 °C
- The tensile strength of PLA is 69.91 MPa
- The Young’s modulus of elasticity of PLA is1968 MPa (Auras *et al.*, 2003).

1.2.3 Barrier properties of PLA

One of the most important factors in food packaging polymers is their barrier or permeability performance against transfer of gases, water vapor, and aroma molecules. Polymer chain branching and small changes in L:D stereochemical content have no effect on permeation properties, but film crystallinity profoundly impacted of the permeation of mentioned gases (Lehermeier *et al.*, 2001).

1.2.4 Applications of PLA

- PLA can be processed by extrusion, injection molding, film & sheet casting, and spinning, providing access to a wide range of materials.
- PLA can also be used as a compostable packaging material, either cast, injection molded, or spun (Rafal *et al.*, 2010).
- Cups and bags have been made of this material. In the form of a film, it shrinks upon heating, allowing it to be used in shrink tunnels.
- It is useful for producing loose-fill packaging, compost bags, food packaging, and disposable tableware.
- In the form of fibers and non-woven textiles, PLA also has many potential uses, for example as disposable garments.
- PLA is a growing alternative as a "green" food packaging polymer. New applications have been claimed in the field of fresh products, where thermoformed PLA containers are used in retail markets for fruits, vegetables, and salads.
- PLA brings a new combination of attributes to packaging, including stiffness, clarity, and twist retention, low-temperature heat sealability, as well as an interesting combination of barrier properties including flavor, and aroma barrier characteristics.

In the present work, in-situ polymerization of PLA-CNT has been carried out in a microwave monomode reactor. An introduction to microwave theory and CNT is given in the following section 1.3 and 1.4.

1.3 Microwave theory

Microwave irradiation heating has gained popularity in the past few years as a powerful technique for fast and efficient synthesis of a wide range of compounds. This is because of the selective heating of polar molecules by absorbing microwaves. The purpose of Microwave irradiation is to provide better reaction rate and formation of product in lesser time. It is proving quite successful in the formation of a variety of carbon-heteroatom bonds.Microwave heating have been used to speed up various chemical reactions in the laboratories which led scientists to investigate the mechanism of microwave dielectric heating and to identify the advantages of the technique for chemical synthesis (Desai *et al*., 2005).

In recent years, microwaves have been widely used for performing various chemical reactions and have become really useful non-conventional energy source for carrying out organic synthesis. This is seen in great number of publications in recent years, mainly in 2003, associated to the application of microwaves as aneffect of a great availability of microwave assisted instruments which are very reliable and dedicated. Thefirst recorded organic synthesis in which microwaves were used was the aqueous emulsionpolymerization using pulsed electromagnetic radiation of butyl acrylate, acrylic acid and methacrylic acid (Mingos *et al*., 1997); (Nuchter *et al.*, 2000); (Gedye *et al.*,1986).

1.3.1 Principles of microwave activation

In the electromagnetic spectrum the microwave radiation region is placed between infrared radiation and radio-waves. Telecommunication and microwave radar equipment occupymost of the band frequencies in this region. In order to avoid interference between these systemsthe industrial and household microwave ovens operate at a frequency of 2.45 GHz which is fixed.

The energy involved for a quantum can be calculated using Planck's law $E = h\nu$ which is found to be 0.3 cal mol^{-1}.

1.3.2 Method of heating

Conventional heating: In this method of heating, reactants are slowly activated by an external heat source. Heat is driven into the substance, passing firstly, through the walls of the vessel in order to reach the solvent and the reactants. After passing through the walls of vessel heating of solvent takes place and then the reactants are heated. This is a slow and inefficient method for transferring energy into the reacting system.

Microwave heating: Microwaves couple directly with the molecules of the entire reaction mixture, leading to a rapid rise in the temperature. Since the process is not limited by the thermal conductivity of the vessel, the result is an instantaneous localized superheating of any substancethat will respond to either dipole rotation or ionic conductivity. Only the reaction vessel contentsare heated and not the vessel itself; better homogeneity and selective heating of polar moleculesmight be achieved.

The acceleration of chemical reactions by microwave exposure results from the interactionsbetween the material and electromagnetic field leading to the thermal and specific (non-thermal)effects. For microwave heating, the substance must possess a dipole moment. A dipole issensitive to external electric field and tries to align itself with the field by rotation. If submittedto an alternating current, the electric field is inversed at each alterance and therefore dipoles tendto move together to follow the inversed electric field.

Such a characteristic induces rotation and friction of the molecules, which dissipates as internal homogeneous heating. The electric field of commonly used irradiation frequency (2450 MHz) oscillates 4.9 × 109 times per second.Thus, microwave heating is directly dependent on dielectric properties of a substance, dielectricconstant (ε’) and dielectric loss (ε”). The conduction mechanism leads, due to the much stronger interaction of ions with electric field,to the generation of heat. The ions will move under the influence of an electric field, resulting inexpenditure of energy due to an increased collision rate, converting kinetic energy into heat. Theheat generated by both mechanisms adds up resulting in a higher final temperature (Kingston *et al.*,1988).

Since the ability of a molecule to couple with the microwave radiation is a function of its dipole moment, just polar molecules interact withmicrowave energy compounds with high dielectric constants such as water, ethanol,acetonitrile, *N*,*N*-dimethylformamide (DMF), acetic acid, chloroform, dichloromethane, acetone,ethylene glycol etc. These tend to heat rapidly under microwave irradiation, while less polarsubstances, such as aromatic and aliphatic hydrocarbons or compounds with no net dipolemoment, such as carbon dioxide, carbon tetrachloride, diethyl ether etc. as well as highly ordered crystalline substances, are poorly absorbing. Thus, polar molecules in a non-polar solvent would absorb energy, but not the solvent or the reaction vessel, if it is made of Teflon.

At times it is possible to use mixtures comprisingmicrowave active reactants and microwave inactive solvents. It has also been suggested that if microwave energy is absorbed by the solvent and not by the substrate, only modest rate increase will result relative to those observed with conventional energy. If, on the other hand, the microwave energy is absorbed selectively by a reactant, by a complex or by an intermediate during the rate determining step, then large rate increase will result (Madhvi *et al.,* 2012).

1.3.3 Types of microwave reactor

There are two types of microwave reactors that can be used in the laboratory:

Multimode Microwave Reactors

Monomode Microwave Reactors

Multimode Microwave Reactor

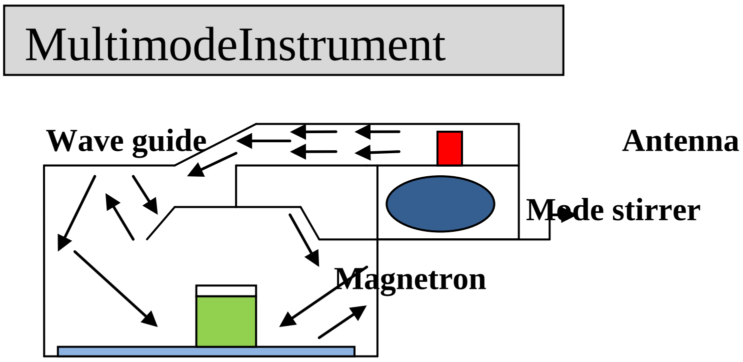


Fig. 5: Multimode Microwave reactor (Madhvi *et al.,* 2012).

Even though the microwave reactors have been introduced on the market as household devicesfor cooking, heating and thawing of food, they have found use in organic laboratory for carryingout organic synthesis on the laboratory scale. Most of the publications in the area of microwavechemistry from Asian countries involve use of domestic microwave ovens. These ovens (withlimited power 800–1000 W) are characterized by a non-homogeneous distribution of electricfield due to several reflections off the metallic walls of the oven.

Since the field isheterogeneous, so their use in synthetic purposes requires mapping of the field, involvingdetermination of hot spots of high energy using a filter paper sheet impregnated with a solutionof cobalt chloride (Loupy *et al., 2001*).

Some modifications of domestic microwave ovens have been suggestedby various workerssuch as introduction of condensersby boring through the top of theoven or reaction flasks being fitted with condensersand charged with pre-cooled,microwave-inactive coolants, like xylene, carbon tetrachloride etc. In addition to these, there aremany dedicated large multimode versions with rotors (8 or more reactions simultaneous), butclaimed to have (quasi) in-phase microwave irradiation achieved by special design of theirequipment.
The use of multimode reactors has however, following limitations:

a) The distribution of electric field inside the cavity results from multiple reflections off the wallsand reaction vessel and is consequently heterogeneous.

b)The temperature cannot be simply and accurately measured.

c) The power is not tunable

Monomode Microwave Reactors

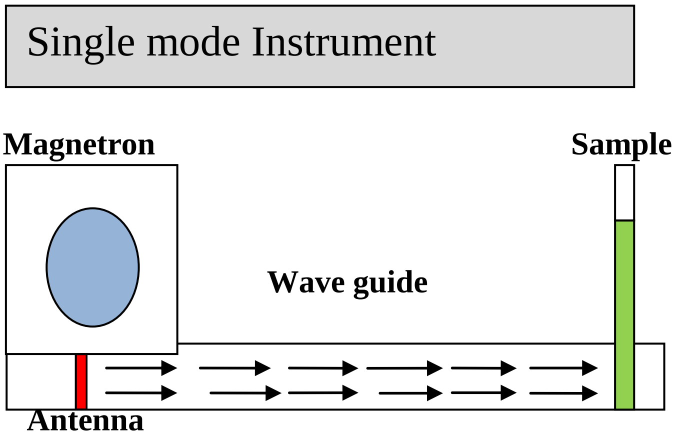


Fig.6: Monomode Microwave Reactor (Madhvi *et al.*, 2012).

In the monomode microwave oven the dimensions of wave belt (wave guide) and excitations are specially calculated so to allow only one mode of propagation or resonance. They are able to obtain a homogeneous distribution of the electric field in the wave belt (focalized fasciculus) and hence in the heated reaction mixtures. They are used with less power emitted with a high return of energy, and thus, the utilization of monomode reactor is energy efficient and leads to better yields in organic synthesis, while preserving the thermally unstable products(Zhang *et al.,* 1999).

1.4 Carbon nanotubes (CNT)

Until 1980’s pure solid carbon was thought to exist in only two physical forms,diamond and graphite. In 1991 CNT was discovered by Iijima, when he vaporized graphite and collected it. The unique geometric properties of this new allotrope of carbon did not end withsoccer shaped molecules, it was also discovered that carbon atoms can form longcylindrical tubes. These tubes were originally called “buckytubes” but now are betterknown as carbon nanotubes or CNT for short.

CNT molecules are shaped like a tube;like a sheet of graphite ("graphene sheet") or wire rolled into a tube. Carbon nanotubes have very unique physical and chemical properties that chemistsare trying to better understand through laboratory research. One of the physicalproperties of carbon nanotubes is that it’s possible to make them only a single atomiclayer thick. This means that they can be about 1/50,000 the thickness of a human hair.

Because of the bonding characteristics of carbon atoms, the physical appearanceof carbon nanotubes can often resemble rolled up chicken wire (see Fig. 7). One of the interesting physical properties about carbon nanotubes is that whenyou have two of them which have slightly different physical structures and they are joined together.This electronic behaviour depends upon the structure of the two tubes. Nowadays, scientists are trying to make carbon nanotubes in large amounts with a high degree of purity so that the physical structures are all thesame. If they have similar physical and chemical properties then it becomes easier topredict their behaviour which would ultimately make them more useful for possiblenanosensors. These nanosensors could behave like semiconducting materials inmicroelectronic circuits, or detect small changes in electric current, or register chemicalreactivity, or changes in air pressure or temperature. There are three unique geometries of carbon nanotubes. The three geometries are armchair, zig-zag, andchiral. These geometries can beclassified as how the carbon sheet is wrapped into a tube(Wang *et al.*, 2009).

(a) (b) (c)

Fig. 7: Geometries of CNT: (a) Armchair arrangement of carbon atoms, (b) Zig-zag arrangement of carbon atoms, (c) Chiral arrangement of carbon atoms.

1.4.1 TYPES OF CNT:

There are three main types of CNT which are given below:

- Single walled
- Multi walled
- Double walled

Single-walled carbon nanotube structure Single-walled carbon nanotubes can be formed in three different designs: Armchair, Chiral, and Zigzag. The design depends on the way the graphene is wrapped into a cylinder. For example, imagine rolling a sheet of paper from its corner, which can be considered one design, and a different design can be formed by rolling the paper from its edge. A single-walled nanotube's structure is represented by a pair of indices (n,m) called the chiral vector (Mintmire *et al.*, 1992).

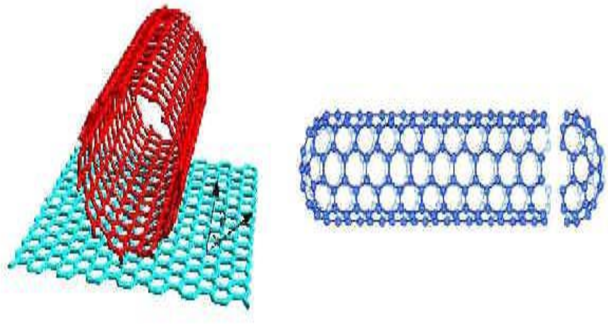


Fig. 8: Single walled CNT.

There are primarily two structural models of multi-walled nanotubes which are Russian Doll model and Parchment model. In the Russian Doll model, one carbon nanotube contains another nanotube inside it (the inner nanotube has a smaller diameter than the outer nanotube). In the Parchment model, a single sheet of graphene is rolled around itself multiple times, similar to a rolled up scroll of paper. Multi-walled carbon nanotubes have same properties as that of single-walled nanotubes.However, the outer walls on multi-walled nanotubes are able to protect the inner carbon nanotubes from chemical interactions with outside materials. Multi-walled nanotubes also have a higher tensile strength than single-walled nanotubes.

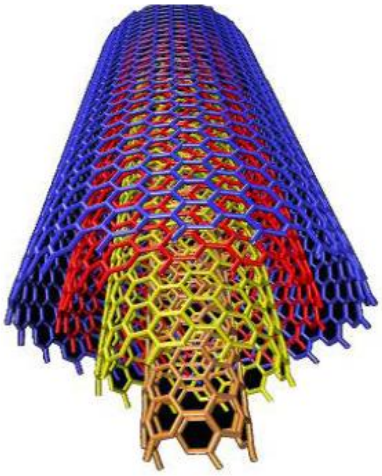


Fig. 9: Multiwalled CNT

Carbon Nanotubes are an example of true nanotechnology in that they are less than 100 nanometers in diameter and can be as thin as 1 or 2 nm. They are molecules that can be manipulated chemically and physically in very useful ways. They open an incredible range of applications in materials science, electronics, chemical processing, energy management, and many other fields. Some properties include:

- Extraordinary electrical conductivity, heat conductivity, and mechanical properties.
- They are probably the best electron field-emitter known, largely due to their high length-to-diameter ratios
- As pure carbon polymers, they can be manipulated using the well-known and the tremendously rich chemistry of that element.

Some of these properties provide opportunity to modify their structure, and to optimize their solubility and dispersion. These extraordinary characteristics give CNTs potential in numerous applications.

1.4.2 Properties of CNT

Some of the important properties of CNT are:

1.4.2.1 Mechanical properties

The mechanical properties of CNT are very important but it is very difficult to understand the conceptual explains behind them. Theory of elasticity explains concepts of the mechanical properties. The theory of elasticity defines series of moduli which are bulk modulus, young's modulus etc, which characterize the material's response to a perturbation which changes its shape or volume from its equilibrium configuration. For example the young's modulus (y) defines the responses of system when strained along a particular axis. Some studies also said that when nanotubes are subjected to compressive strain it was observed that tubes formed buckles at critical strain at which energy of system displayed slope of discontinuity. These buckles were like explained with continuum shell model with fitted parameters of flexural rigidity and stiffness. The model also accounted for buckling observed under bending and torsional deformations. The ability of SWCNT to sustain large structural distortions without any bond breaking or rearrangement is also explained by this model.

Carbon nanotubes have higher tensile strength than that of steel and Kevlar. The reason behind the strength is sp^2 bonds between the carbon atoms. This bond is stronger than even than the sp^3 bond found in diamond. Under high pressure, individual nanotubes can bond together, trading some sp^2 bonds for sp^3 bonds. Hence, it is possible to produce long nanotube wires. Carbon nanotubes are strong as well as they are elastic. The tip of the nanotube can be pressedleading to its bending without damaging to the nanotube, and the nanotube will return to its original shape when the force is removed. The elasticity of CNT has no limit and if a strong force is applied it can lead to permanent deformation of the shape of the CNT.The strength can be weakened because of the defects in the structure of nanotubes. nanotube's strength can be weakened by defects in the structure of the nanotube (Gullapalli *et al.,* 2011).

1.4.2.2 Electrical properties

As mentioned before, the conduction properties of carbon nanotubes depend upon their structure. When the collisions between conduction electrons and atoms are minimized by the structure of atoms in a carbon nanotube, a carbon nanotube is highly conductive. Carbon nanotubes can also withstand higher electric currents than copper.This is because of the strong bonds between carbon atoms. The transport of electron occurs just along the axis of the tube. Electrical signals at speeds up to 10 GHz can be routed by Single walled nanotubes when used as interconnects semi-conducting devices interconnects. Carbon nanotubes also have a constant resistively (Hong *et al.,* 2007).

1.4.2.3 Thermal properties

The carbon nanotubes can withstand high temperature this is because of the strength of the atomic bonds. Hence, carbon nanotubes are shown to be very good conductors of heat. As compared to copper wires, which are usually used as thermal conductors, 15 times the amount of watts per meter per Kelvin of heat can be transmitted by Carbon nanotubes. The thermal conductivity of carbon nanotubes dependsupon the temperature of the tubes and the environmental conditions.

1.4.2.4 Potential uses

There are a lot of potential applications for Carbon nanotubes such as waterproof and tear resistant cloth fabrics.Concrete and steel like applications like a space elevator has even been proposed based upon the strength, electrical circuits which are based upon the property of electrical conductivity, sensors which are based upon the property of thermal conductivity, vacuum food packaging, and as a vessel for delivering drugs.

Thus, it is easy to understand the potential use of CNT in various systems. One much system is PLA-CNT nanocomposites and the nanocomposite concept is briefly discussed below in section 1.5.

1.5 Nanocomposite

A nanocomposite can be defined as a solid phase material with one or more components having one, two or three dimensions in nanoscale regime. Nowadays, this definition has significantly broaden its boundary including large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly different components and are mixed at nanometer scale.

Nanocomposites material science is a rapid growing area of research. The main objective behind this research is to obtain control of the nanostructures through advanced synthetic approaches. The properties of Nanocomposites do not entirely depend on the component materials required to make Nanocomposite material but also on their morphology and interfacial characteristics. Therefore the mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the material are improved.

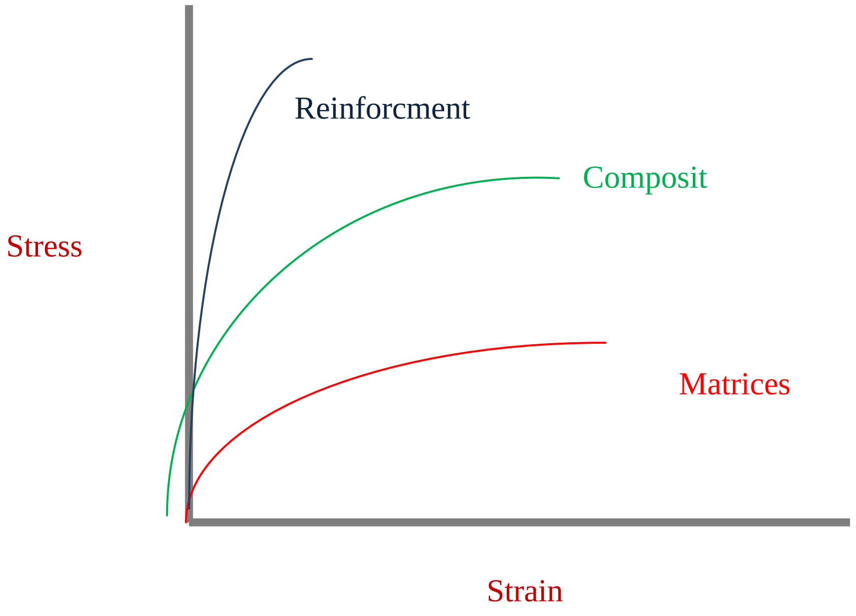


Fig. 10: Stress v/s strain graph of composites, fillers and monomer.

Generally, a nanocomposite contains a strong and stiff component (the reinforcement) which is embedded in a softer (relative to the reinforcement) component, the matrix. Therefore, the composite has strength properties between those of the reinforcement and the matrix.

Polymer nanocomposites consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. These materials are different from conventional composite materials as they exhibit different behaviour due to the presence of nano sized structural units and high surface–to-volume ratio. There are many types of polymer nanocomposites that can be tailored according to the desired applications. One of the most promising polymers in this direction is PLA. Currently various nanofillers are being reinforced on PLA matrix. Nanoclay, nanocellulose and many other types of nanofillers are used with PLA matrix which leads to the improvement of various properties. Also CNT is used as nanofiller with a variety of polymers because of good mechanical and electrical properties. The nanocomposite of PLA and CNT as nanofiller might have good mechanical properties.

CHAPTER 2: LITERATURE REVIEW

2.1 PLA SYNTHESIS

PLA is synthesized using two methods: Polycondensation and ring-opening polymerization using microwave irradiation as well as conventional methods of heating. Some of the studies are mentioned below:

2.1.1 Polycondensation

Achmad et al.,studied the production of PLA by direct polycondensation of lactic acid under vacuum without using catalyst and solvents to reduce the cost of the production. Experiments were done at polymerisation temperatures (T_p) of 150–250 °C. The maximum molecular weight obtained for PLAwas 90 kDa under vacuum at 200 °C and a time period of 89 h. Above 200 °C, PLA is degraded thermallybecause of the specific scission. The activation energy (E_a) of polycondensation reaction was also calculated and thus, was found to be larger than that of the (E_a)required in the catalyzed ring opening polymerization (ROP). In addition, the E_a was even higher than the deactivation energy (E_d) for both ROP and DP. At lower T_p, yield of PLA were higher while at higher$T_p$the yield of lactide were higher. Both PLA and lactide had an approximate yield around52–75 wt%. The method have applications in plants where compactness is necessary, and simple and same operating procedures.

2.1.2 Ring opening polymerization

Dider et al., (2014) prepared PLA which had Amide capped end by using the ability of amine groups to ring-open lactide. A two-step process was followed in which excess of lactide was reacted with primary and secondary amines before the addition of the ROP catalyst DBU. Polyfunctional amines were used as initiators for preparing amide-functionalised PLA of different structures like star-shaped, linear, telechelic. Unreacted monomer present in PLA was removed by the reaction of primary amines with the lactide.samples without affecting the polymer properties.

Robert and Aurbrecht, (2008) carried out the ring-opening polymerization of lactide using tin (II) bis(2-ethylhexanoate)/benzyl alcohol to form degradable polylactide (PLA). The mechanism of polymerization was similar to that of the transesterification reaction; the experiment also demonstrated the reactions of carboxylic acid derivatives. The polymerization was successfully carried out using standard laboratory conditions. Analysis of polymer stereochemistry was analysed byNMR. The effects of stereochemistry of monomer on the polymer,s stereochemistry was studied.Their effect on molecular weight was also studied.

2.1.3 Microwave synthesis of PLA

Aswath *et al*., (2008) studied the synthesis of PLA in a microwave reactor using tin octoate as a catalyst as well as without using the catalyst. The presence of catalyst enhanced the rate of reaction as compared with non catalyzed reaction. Polymer of molecular mass up to 25 kDa was synthesized without the need of any controlled environment. FTIR and gel permeation chromatography were done. Microwave assisted polymerization of lactic acid to produce PLA is a quicker and efficient method than traditional method.

Nikolic *et al.*, (2010) synthesized Poly (D,L-Lactide) by ring opening polymerization (ROP) process using tin (ii) 2-ethylhexanoate as an initiator.ROP was done in a microwave reactor which took 30 minutes at 100^0 C. The frequency of the reactor was 2.45 GHz and power was 150 W. Various monomer to initiator ratios were used (1000, 5000, 10000). Gel permeation chromatography was used to obtain the molecular mass of the product which was in the range of 26,700 to 112,500 g/mol. A polydispersion index of 2.436 to 3.425 was obtained.

Liu *et al*., (2001) synthesized PLA by ring opening polymerization (ROP) of D, L Lactide using stannous octaonate as catalyst, reaction was microwave assisted. The weight average molar mass obtained was in between 39000 to 67000. The polydispersity index lie between 1.3 to 1.7. The rate was reaction was enhanced after using the microwave in place of conventional method.

Frediani *et al*., (2010) studied the polymerization of L-Lactide by calcix[4]arene-titanium (iv) complex using conventional heating and microwave irradiation. NMR, IR, DSC, HPLC-SEC and WAXD were done. It was observed that the use of microwave irradiation increased the rate of polymerization. But the use of microwave also affected the molecular weight distribution as compared to conventional heating.

2.2PLA COMPOSITES

Nanocomposite using PLA as polymer matrix is being synthesized using various nanofillers. Some of the studies are mentioned below:

2.2.1 PLA/OMMT Composites

Cao *et al*., (2009) studied the microwave assisted synthesis of nanocomposite of Poly lactic acid with organomontmorillonite (OMMT) nanofiller in the bulk by in-situ ring-opening polymerization (ROP) of D,L-lactide. There werevarious factors that influenced the polymerization process like dosages of the catalyst and OMMT, the microwave power and irradiation time, in terms of tensile strength were studied. The time taken for polymerization wasdecreased to about 10 min when the reactor was under 90 W of microwave irradiation, and the thermal and mechanical properties of the nanocomposites of PLA/OMMT were considerablyenhanced. At 0.6 and 1.0% highest mechanical properties were obtained. The formation of nanocomposite was confirmed by TEM and XRD.

2.2.2 PLA/OMLSComposites

Ray *et al.*, (2003) used simple melt extrusion technique with PLA and OMLS for the synthesis of nanocomposites, in which silicate layers present in OMLS are either intercalated, partly exfoliated, intercalated-and-flocculated, or a combination of all the three. All the nanocomposites showed improvement in various material properties mainly mechanical properties simultaneously as compared to those of pure PLA. These improvements include various mechanical and flexural properties, the rate of crystallization, oxygen gas permeability, heat distortion temperature, with aninstantaneousenhancement in biodegradability. They studied the melt rheological properties also for thesynthesized nanocomposite of PLA and organically modified layered silicate based. With increasing C18-MMT content week frequency dependence is shown by both dynamic modules at low frequencies. This means that with increase in C18-MMT content there is ongoing change in behavior from liquidlike to solidlike.

2.2.3 PLA/SILICA and PLA/CLAY

Kontou *et al.,* (2011)studied the effect of two different types of nano-scale fillerssilica and montmorillonite. The comparison of three different weight fractions and their mixtures was done. The effect of reinforcing of nanofiller studied on thermo-mechanical properties of PLA was studied. Numerous experimental techniques were used to investigate the role of aggregates and interphaseincluding scanning electron microscopy (SEM), differential scanning calorimetry, wide-angle X-ray scattering (WAXS), dynamic mechanical analysis (DMA), thermogravimetric analysis and tensile measurements. It was concluded from the experimental results that montmorillonite andsilica have different toughening and reinforcement effects on PLA, while when these two different nanofillers are combined has anunfavourableeffect on the tensile strength and other properties of the material. Young's modulus of the nanocomposites was described by the four micromechanics models and was used to study the various matrix–nanofiller interactions. The model that assumes the presence of an interphase surrounding each nanoparticle was considered as the best fit model for obtaining experimental results. An increase in the nanofiller content above a definite amount didn’t lead to acorresponding increase in the interphase, because the total surface area of the nanofiller was counterbalanced by the formation of aggregates. It is postulated that interphase effect is affected by the aggregation effect.

2.3 Composities of CNT as nano filler

CNT is used as nanofiller with various polymers as it has excellent properties and modifies various electrical, mechanical and other properties. Some of the studies in which CNT is used as nanofiller are mentioned below:

2.3.1 Epoxy/ CNT composites

Liu *et al*., (2009) in this study the polyethylenimine was used as a dispersant for the reinforcement of MWCNTepoxy composites. The composit part which is covalently modified is 10 000 times more resistive as compared to the counterpart which isnoncovalently modified. As compared to the noncovalent composites the composite part with covalently functionalized nanotube has higher storage modulus. This is mainly because of the stronger interactions between nanotubes and polymer. Similar results were obtained by

Spitalsky et al.for MWCNT/epoxy composites which were treated with H_2O_2/ NH_4OH mixture.

2.3.2 POLYPROPYLENE and POLYAMIDE 6 blend / MWCNT and NICKLECOATED CARBON FILLER Composites

Seung et al., (2014) investigated the effects of hybrid fillers like multi-walled carbon nanotube (MWCNT) and nickelcoated carbon fiber (NCCF)on the electrical conductivity of polymer blend of polypropylene (PP) and polyamide 6 (PA6). Polypropylene-g-maleic anhydride (PP-g-MAH) was used as a compatibilizer for the PP/PA6 blends. TEM results of the PP/PA6 /MWCNT composites with 70 to 30 ratio showed that the MWCNT were preferably located in PA6 phase than in PP phase. This was possibly because of the lower interfacial tension of the PA6/MWCNT composite in comparison with PP/MWCNT composite. The values of the electrical conductivities were increased with the increase in content of the NCCF. The increase in electrical conductivity was because of the increased electrical pathway with the addition of NCCF content. Electrical conductivity and morphology results of the PP/PA6/NCCF/ MWCNT composites showed that the selective localization of the MWCNT in the PA6 phase affected the increased electrical conductivity of the composites. The hybrid fillers could produce a synergistic effect on the electrical conductivity and also the electromagnetic interference shielding efficiency (EMI SE) of synthesized composites.

2.3.3 PMMA/CNT composites

Jia *et al*., (2010) used in-situ process was used for preparing PMMA/CNT composites. The heat deflection temperatures and the mechanical properties of the composites rise with the an increase in concentration of CNTs. The ratio of dispersion CNTs into the PMMA matrix was directly proportional to the time taken by the polymerization reaction of MMA to form PMMA before the addition of CNTs into the PMMA matrix.

2.3.4 PU/CNT composites

Koerneret *al.,* (1999) added MWCNT as nanofiller in small amounts to thermoplastic elastomer polymer. The nanocomposites formed showed improvement in various properties mainly electrical and mechanical properties. It showed high electrical conductivity. Properties like yield stressand modulus were enhanced whereas, alow electrical percolation was shown.

2.3.5 PC/CNT composites

Fornes *et al.,*(2005) studied solution blending was used for the preparation of PC/CNT composites at different concentrations of CNTs. The solvent containing CNTs wassonicated for 1 hour for proper dispersion of CNTs in the solvent. PC solution was prepared in which the addition of dispersed solution was done. The mixture was then sonicated for 10 min and precipitation was done in methanol. The precipitates were dried under vacuum. Then solution casting was done for preparing PC/CNT films. The dispersion of nanotubes for synthesis of composites of PC fibers that were based on SWCNTs and MWCNTs was doneeither by via solvent blending or melt extrusion which was followed by melt spinning. TEM results disclosed that MWCNTswere more readily dispersed within the PC matrix than SWCNTs and also had higher aspect ratios than SWCNTs.

2.3.6 PVC/ CNT Composites

Brozaet *al.,*(2007) studied the preparation of MWCNT and SWCNT reinforced PVC matrix nanocomposites in THF solution which is then followed by film casting. The scanning electron microscopy allowed the confirmation of a homogeneous distribution of the CNT’s nanofillers in the PVC matrix. The changes inthe characteristic temperature of PVC transformation and sorption in methylene chloride, were determined by DSC measurements, were found depending upon the concentration of CNT’sThe electrical measurements showed an increase in the conductivity with the increasing CNT’s content in the PVC matrix.

2.3.7 Mg/CNT nanocomposites

Goh*et al.*,(2008) studied the improvement in ductility and fatigue behaviour of nanocomposite of magnesium which is reinforced with 1.3 wt% of carbon nanotubes (CNTs)was calculated. For the synthesized nanocomposites the determination of the deformation behaviour various dislocation studies were done. A comparison between monolithic Mg and Mg-1.3CNT nanocomposite was done in whichthe effects of CNTs in the improvement Mg. Ductility wasobserved which was because of high activity of the basal slip system. Constant stress amplitude cyclic tests showed that lower cycles for the failure for the Mg-1.3CNT nanocomposite were obtained than that of the monolithic Mg. Both the nanocomposites monolithic Mg and Mg-1.3CNT harden upon cycling. One of the main hardening causes was the formation of sessile forest dislocations.

2.4PLA/CNT Composites

Study of nanocomposites of PLA using CNT as nanofiller using different techniques and study of their properties is mentioned below:

PLA/CNT using water-crosslinking technique

Kuan *et al.,* (2008) studied (MWCNT)/poly (L-lactic acid) (PLLA) composites were prepared using the water-crosslinking technique for improving the physical characteristics of the synthesized nanocomposites. They observed with increasing of water-crosslinking time that PLLA crystallization temperature is decreased. At low carbon nanotube loading and in water-crosslinkingreaction high heat deflection temperature can be obtained for the nanaocomposite. There was a rise of 42^0 C in HDT of PLA(62^0C to 106^0C) with the addition of 1 phr MWCNT to PLLA. After water cross-linkingtreatment the composites exhibited enhanced mechanical properties than that of the non-crosslinked composite because of the strong chemical intramolecularbonding in the cross-linked composites. Also,thermo-gravimetric analysis (TGA) showed that with the increase in water cross-linking time the thermal degradation temperature of the nanocompositeincreases. Crystallization temperature of PLLA decreases with the increase of water cross-linking time, leading toa stable crystalline structure after water cross-linking reaction.Thermal degradation properties wereimproved by 121^0C and 201^0C with the addition of watercrosslinkage and also with and withoutcarbon nanotube addition respectively. Addition of 1 phr MWCNT improved the tensile strength of nanocomposite by 13%, this was shown by mechanical property tests.

Kuan *et al.*(2012)studied thepreparation of multi-walled carbon nanotube (MWCNT)/polylactide (PLA) composites. High electrical conductivity is achieved at a low carbon nanotube loading When 0.5 parts per hundred parts of resin modified multi-walled carbon nanotube was added to low-crystalline PLA (LC-PLA), the surface resistance of the composite was decreased. The degree of crystallinity of PLA can influence the electrical property of MWCNT/PLA composites MWCNTdispersion was enhanced by covalent or hydrogen bonding between modified multi-walled carbon nanotube and PLA. They concluded after the comparisons of carbon nanotubes-reinforced HC- and LC-PLA composites that carbon nanotubes cause the electrical conductivity and mechanical characteristics of LC-PLA to be better than those in HC-PLA.

PLA/CNT using melt-mixing

Quan *et al.*(2010) studied multi-walled carbon nanotubes (MWCNTs) filled poly(L-lactic acid) (PLLA) and PLLA/poly(D-lactic acid)(PDLA) composites, prepared through a directly melt mixing process. A crystalline structureof stereocomplex was formed by PLLA and PDLA. The electrical conductivities weregreatly improved by the formation of stereocomplex compared to that of PLLA/MWCNT composites at same MWCNT content. The X-raydiffraction, non-isothermal and isothermal crystallization results showed that the formation of stereocomplexgreatly increased the crystallinity of the composites,and MWCNTs acted as heterogeneous nucleating agent, which significantly accelerated the nucleation and spherulite growth. Hence,the PLLA/PDLA/MWCNT composites have a very low percolation threshold due to the volume exclusioneffect. Both of the composites undergo a transition from an insulator to a semiconductor by addition of MWCNTs. The electrical properties are greatly improved by the formation of stereocomplex compared to that of PLLA/MWCNT composites at same MWCNT content, and the percolation threshold of the PLLA/PDLA/MWCNT composites is much lower than that of PLLA/MWCNT composites, being 0.35 and 1.43 wt%, respectively. The DSC, POM and XRD results shows that the formation of stereocomplex combines with the strong nucleation effect of MWCNTs significantly increases the crystallinity of the composites, accelerate the crystallization process, finally resulting in a lower percolation threshold compared to PLLA/MWCNT composites due to volume exclusion effect.

Shanmugharaj *et al.*,(2013) prepared thenanocomposites based on the polymer blend of polyurethane (PU) elastomer which is a thermoplastic and polylactide (PLA) using surface modified carbon nanotubes as nanofiller which were prepared by simple melt mixing process after the synthesis various properties like mechanical, electroactive shape properties were investigated. Fourier Transform infrared (FT-IR) and wide angle Xray diffraction (WAXD) were done to confirm the synthesis as well as to study the chemical and structural behaviour. The surface modified carbon nanotube when used s nanofiller for PU/PLA polymer blends showed a significant improvement in the mechanical properties for example, tensile strength, as compared to the pure CNT with polymer blends. It was also observed in dynamic mechanical analysis that glass transition temperature (Tg) of PU/PLA blend was slightly increased on loading of pristine CNT and there was a more pronounced in case of surface modified CNTs. Electrical and thermal properties of polymer blend composites were increasedconsiderably with pristine or surface modified CNTs. Shape memory studies of the composites of PU/PLA/modified CNT exhibited that at lower applied dc voltages a notable recoverability of its shape as compared to pure or pristine CNT loaded system.

Table 1: literature review of synthesis of PLA using microwave reactor.

Monomer	**Catalyst**	**Microwave reactor type**	**Temperature (° C)**	**Time (min)**	**Power (Watt)**	**Molar mass g/mol**	**References**
d,l-lactide	Sn(Oct)$_2$	Domestic microwave		10-30	85 170	39,000-67,000	Liu et al., 2001
D,L-lactide	Sn(Oct)$_2$	monomode microwave	100	10-30	150	78,461-3,09,940	Nikolic et al., 2010
L-lactide	calix[4]arene-titanium (IV)]	monomode microwave	130	20-80	200	8100-18,600	Frediani et al., 2010

Table 2: literature review of nanocomposites of PLA using different nanofillers.

Monomer	**Nanofiller**	**Process**	**Reaction time**	**Properties improved**	**References**
PLA	OMMT	ring opening polymerization	10 min	Toughness tensile strength	Hailei Cao *et al.*
PLA	OMLS	melt extrusion		flexural properties, heat distortion temperature, oxygen gas permeability	Suprakas Sinha Ray *et al*
PLA	LDH	ring opening polymerization	4 hrs	PLA crystallinity and temperature of crystallization both increased higher degradation onset temperatures	Vimal Katiyar *et al.*

Table 3: literature review of CNT used as nano filler with different polymers.

Monomer	**nanofiller**	**process**	**Properties improved**	**references**
bisphenol-A epoxy resin	CNT	melt mixing	impact strength, bending strength, and thermal conductivity	Yang *et al*. , 2009
PE	CNT	screw extrusion	Young's modulus and tensile strength of the composites can increase by 89% and 56%,	Xiao *et al*. ,2006
PEI	CNT	casting and imidization	elastic module of the nanocomposites significantly improved by about 250%	Liu *et al*. , 2007

Table 4: Literature review of synthesis of PLA-CNT composite using various techniques.

Monomer	**nanofiller**	**process**	**Properties improved (Ref. No.)**	**References**
PLA	MWCNT	Water-crosslinking technique	thermal degradation temperature of the nanocomposite increases Improved tensile strength	Chen-Feng Kuan *et al*. ,2008
PLA	MWCNT	Melt mixing process	electrical properties are greatly improved	Hui Quan *et al.,* 2012

2.4 Summary of the literature

PLA can be synthesized using two methods which are polycondensation and ring-opening polymerization. The PLA formed by polycondensation are low molecular weight whereas, the PLA produced using ring-opening polymerization is of high molecular weight. There are two methods of heating that can be used to heat the reaction mixture in ring-opening polymerization conventional and microwave heating. Conventional method is very slow process and less efficient whereas, microwave heating is a better process as it reduces the time required for the reaction and is more efficient.

PLA is degradable polymer and shows many other properties because of which nanocomposites of PLA with various nanofillers are synthesized. One of those nanofiller is CNT which is used as nanofiller with various polymers because of its great electrical and thermal properties.

Some of the other nanofillers like OMLS AND OMMT when added various mechanical properties of PLA like toughness, rate of crystallinity, etc. were improved.

Whenever, CNT is used as nanofiller with any polymer then it modifies various mechanical properties like strength, toughness, storage module, young modulus etc. It also modifies the electrical properties as it a very good conductor of electricity.When CNT was used as nanofiller with polymers like PE and PEIvarious mechanical properties like young’s modulus was improved to a great extent. Also the electrical conductivity was achieved at a low concentration of CNT as compared to high concentration.

OBJECTIVE:

In this work microwave heating is used to synthesize a nanocomposite in which PLA is the bulk matrix and CNT is the nano filler. The objective of performing this reaction is that we want to synthesize a nanocomposite with improved properties like electrical conductivity. These properties are modifiedby adding CNT as nano filler in the polymer bulk matrix. PLA has good electrical insulation properties, whereas CNT is a good conductor of electricity. Hence, synthesis at different concentration of nanofillerhas been done to check at which concentration of CNT, the product shows the best properties.

Various tests of samples have been performed to measure certain properties of the product.

- TEM
- SEM
- FT-IR
- Impedance Analysis

Thus the objectives are as follow:

- To synthesize PLA-CNT nanocompositeusing in–situ polymerization under microwave radiation.
- Synthesis of PLA-CNT nanocomposite using amino functionalized CNT.
- Analysis of electrical properties of the nanocomposites prepared at different concentrations of CNT.

CHAPTER 3: METHODOLOGY

3.1 Materials and Methods

There are various techniques and materials that are employed for the synthesis of PLA-CNT nanocomposites. These are mentioned in this chapter.

3.1.1 Dispersion of CNT

To synthesize the nano composite of CNT and PLA was used solvent hexane for the dispersion ofCNT. The dispersion of CNT is a difficult step.There are certain operations that were used to disperse CNT in the solvent.There are two methods used for dispersion in the present study:

1. **Ultrasonication**
2. **Mechanical stirring**

3.1.1.1Ultrasonication

Ultrasonication is done using ultrasonicator probe. It consists of a probe which produces ultrasonic waves in the mixture. It provides a large amount of energy in very short period of time which is required for the process. It disintegrates the clusters of particles. High amplitude waves released by the probe in to the solution also helps to achieve high dispersion of solids in the liquids. The CNT is mostly dispersed using high amplitude 80-100for 10 minutes. Using this technique the CNT clusters are disintegrated. Then mechanical stirring is done for 5 minutes.

Fig. 11: ultrasonication probe.

3.1.1.2 Mechanical stirring

After ultrasonication, mechanical stirring of the sample is done and the stirrer operates at 500 rpm. Using mechanical stirring the disintegrated particles are properly dispersed in the solvent. Both processes are repeated twice.

3.1.2Solvent evaporation

Another important step is the evaporation of the solvent from the reaction which was done in a vacuum dessicator in which the sample is placed and vacuum is applied using vacuum pump.

Fig. 12: vacuum desscicator.

3.1.3Polymerisation of lactide

Polymerization of PLA nanocomposites was done using microwave synthesis reactor, which is very helpful in reducing the reaction time. The synthesis of PLA in this project has been carried out by the ring opening polymerization as it produces high molecular weight PLA. PLA is synthesized by the polymerization of monomer, lactide. The amount of lactide used can be calculated by the following procedure,

Weight of the lactide (7 m mol.) = $no.ofmoles,(n)= givenweight,(g)mol.weight,(M)$

$givenweight,(g)$ = 1.008 grams

[M] is monomer conc. and [I] is conc. of initiator.

When [M]= 1.008/ 144

Let, M_0/I_0 =2534

Therefore, $[I]$ = 2.76×10^{-6} mol.

We have to now find the volume of initiator or catalyst (SnOct2), which can be defined by the following formulae

Weight of catalyst, $SnOct_2$ = [I] × M.W OF $SnOct_2$= 1.12 mg

As we know that, $Volume=weight/density$

Therefore, volume of catalyst used = 0.895 µl

3.1.3.1Monomode Microwave Reactor:

Microwave reactor used in this project for the polymerization was Anton Paar Microwave synthesis Reactor (monowave). The microwave reactor was attached with the air compressor; the role of air compressor was to provide the efficient source for heat sink.

Fig. 13: Monowave microwave reactor.

3.2 Experimental procedure

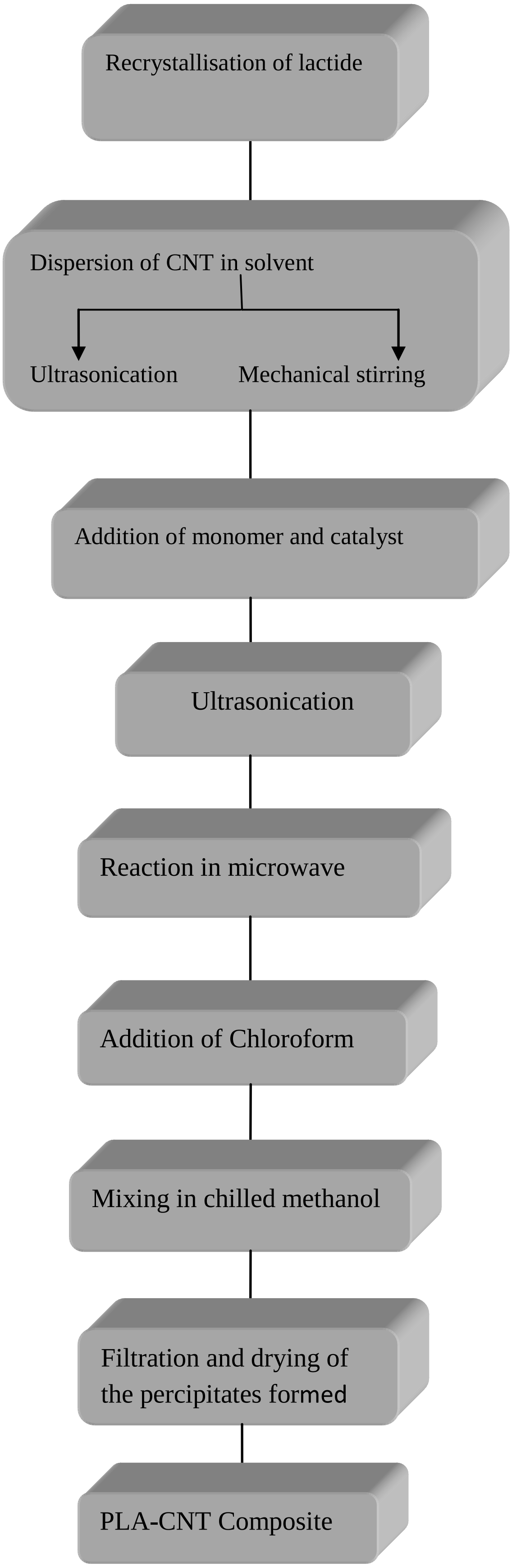


Fig. 14: Steps followed for the synthesis of PLA-CNT nanocomposite.

1. Recrystallization of lactide :

The first and foremost step in polymerization of lactide is the recrystallization of lactide. Recrystallization is mainly done to improve the purity of the lactide as it is the main attribute for the synthesis of high molecular weight polymer. Lactide, weighing 1.008 grams was slowly dissolved in the 10 ml ethyl acetate at 70^0C and was then kept in refrigerator to cool it down for 30 minutes. The crystallized lactide added ethyl acetate mixture was then vacuum dried in the vacuum dessicator for an hour to evaporate the ethyl acetate to obtain the crystallized lactide. These steps were repeated three times to finally obtain recrystallized lactide. It should be taken care of that, water should not contaminate lactide as impurities like water, even in ppm amount will affect the polymerization of lactide.

2. Dispersion of CNT and monomer

Organic solvents are used to disperse the nanofiller. CNT was dispersed in hexane using the techniques ultrasonication and mechanical stirring alternately. When the CNT was properly dispersed in the solvent then monomer lactide is added to the sample (1.008 gm) and then0.895 µl was added to the sample. The sample was again ultrasonicated for 5 minutes at high amplitude. After 5 minutes the monomer and nanofiller both were dispersed in solvent properly.

3. Solvent evaporation

Next main step was the evaporation of solvent which was done using vacuum descicator for about 2 hours. The beaker was kept in the dessicator it was covered with aluminium foil and small holes were made in the foil. This was done for the proper evaporation of the solvent from the sample.

4. Polymerisation using microwave reactor

The remaining mixture was then added to glass vial for the polymerization step. The amount of nano filler added depends upon the weight percent that we have taken. For the synthesis of high molecular weight polymer, ring opening polymerization technique is preferred over the polycondensation. Therefore, In-situ polymerization technique was used for the polymerization of PLA. Microwave synthesis reactor was used for the polymerization and thus provides the efficient energy required for the reaction. The vial containing the mixture of monomer, initiator and nanofillers was placed in the microwave reactor along with a magnetic bead to assist the stirring during the synthesis. The reaction parameters for the polymerization in microwave assisted reaction have to be defined and can vary from sample to sample. The parameters were defined for the synthesis of CNT nanofibers reinforced PLA nanocomposites.

Reaction conditions

Holding temperature was 150^0C and reaction time was 15 minutes. Stirring speed was 200, 400 and 600 rpm.

When the reaction was completed in the reactor next step was to extract the polymer. The polymer was extracted by adding 5 ml chloroformto the vial and kept overnight, so that the dissolution of polymer properly takes place. Then this sample was added to 30-40 ml methanol to form the precipitates of PLA. Then the solution was filtered and dried giving the nanocomposite as product.

The samples at various concentrations 0.1%, 0.2%, 0.5%, 1%, 2%, 7.5%, 15% of non-functionalized MWCNT were synthesized. For amino-functionalized CNT samples at 1% and 2% were synthesized.

CHAPTER 4: RESULTS AND DISCUSSIONS

The sample was subjected to various testing to find out whether the nanocomposites are formed or not and to study its electrical conductivity. A description of these testing and their results is explained in this section.

4.1 Yield of the products

The synthesis of nanocomposite at various concentrations of CNT was done.The following graph shows the yield of the nanocomposite obtained at different concentrations of CNT.

Table 5: Yield (%) of PLA-CNT nanocomposites at different concentrations of CNT

SNo.	Concentration of CNT(% of PLA)	Yield (%)
1.	0.1	87.5
2.	0.2	86
3.	0.5	88
4.	1	82.4
5.	2	83.7
6.	7.5	71.33
7.	15	68.2

Table 6: Yield (%) of PLA-ACNT nanocomposites at different concentrations of ACNT

SNo.	Concentration of ACNT(% of PLA)	Yield (%)
1.	1	62.23
2.	2	59.5

As we can see from the above tables that the yield of the two nanocomposites which are synthesized using amino functionalized CNT is less than those of non functionalized at same concentrations of CNT.

This is mainly because of the presence of amino group which is nucleophilic in nature and the presence of amino group hinders the growth of polymeric chain and hence terminates the long chains of polymer.

4.2FT-IR analysis result

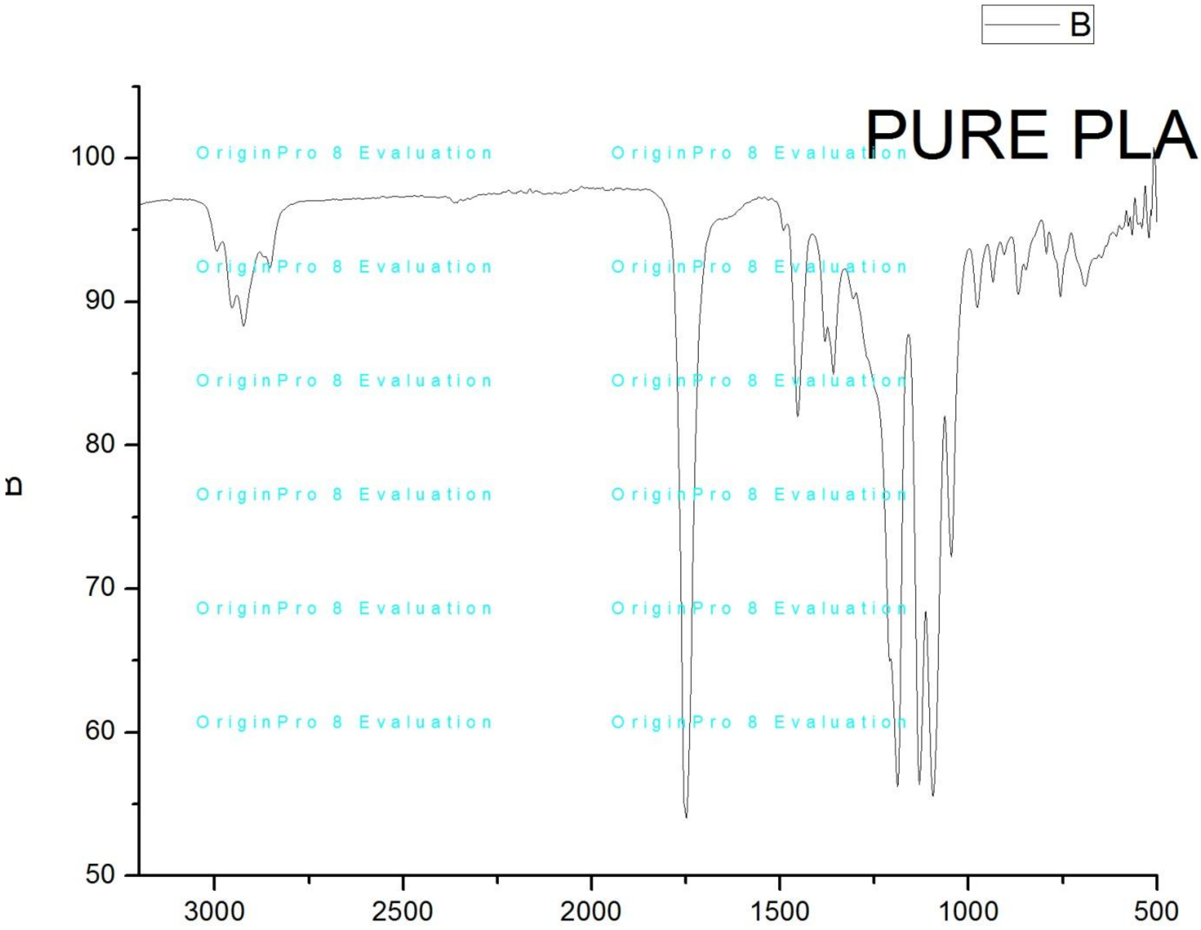


Fig. 15: FT-IR spectra of pure PLA

The above graph shows the FT-IR spectra of pure PLA in which two main peaks of PLA are observed at 1126.22 cm^{-1} and 1849.38 cm^{-1}

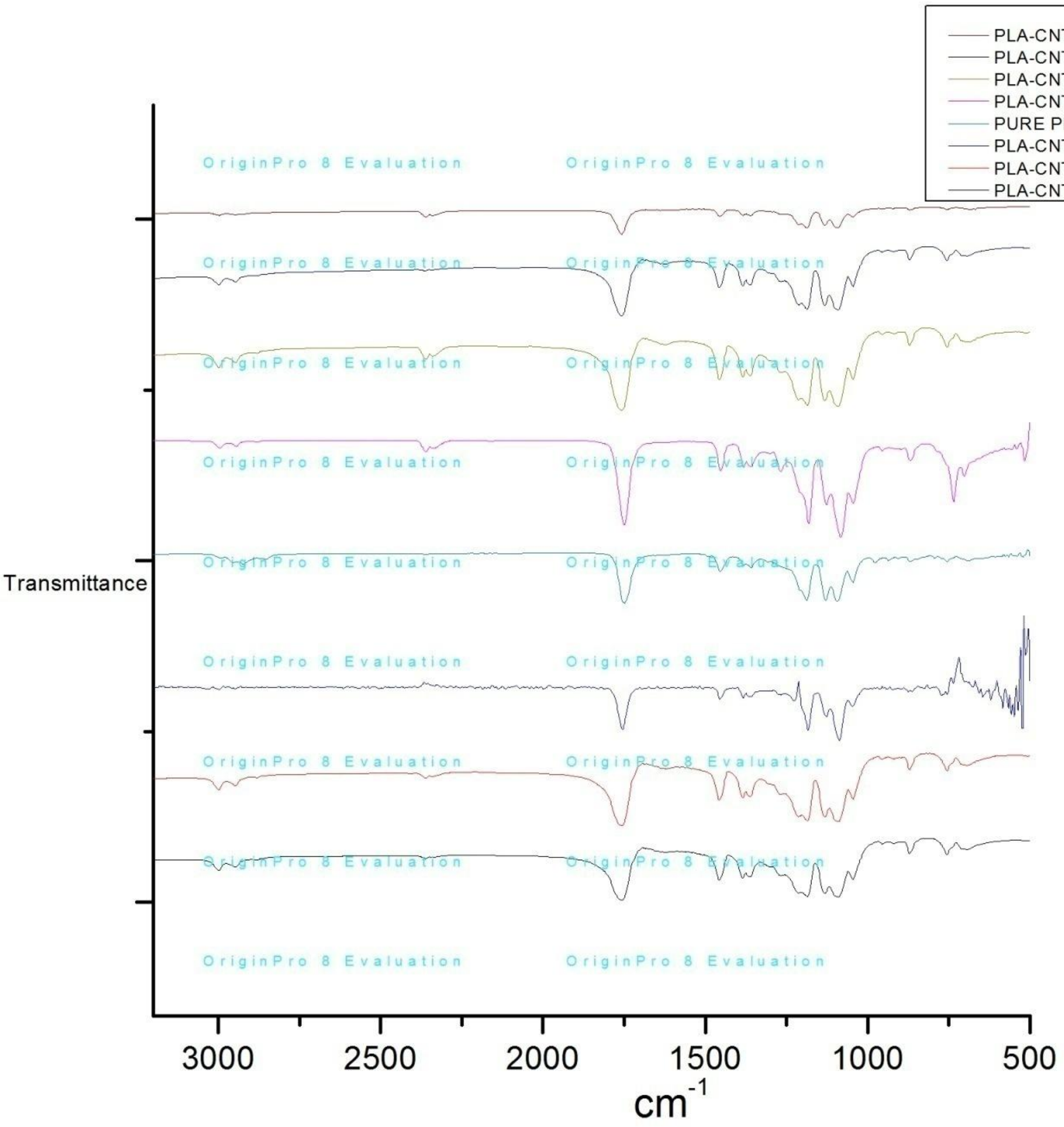


Fig. 16: FTIR Analysis of all the PLA-CNT nanocomposites.

In the above graph there are eight lines, the red line shows the bands of pure PLA and the other lines show the band of the PLA-CNT nanocomposite at different concentrations of CNT. As from the bands we can say that in our product PLA has been formed and as there are some modifications in the bands of PLA these shifts are mainly because of the presence of nanofiller CNT. Hence, we can conclude that nanocomposite has been formed.

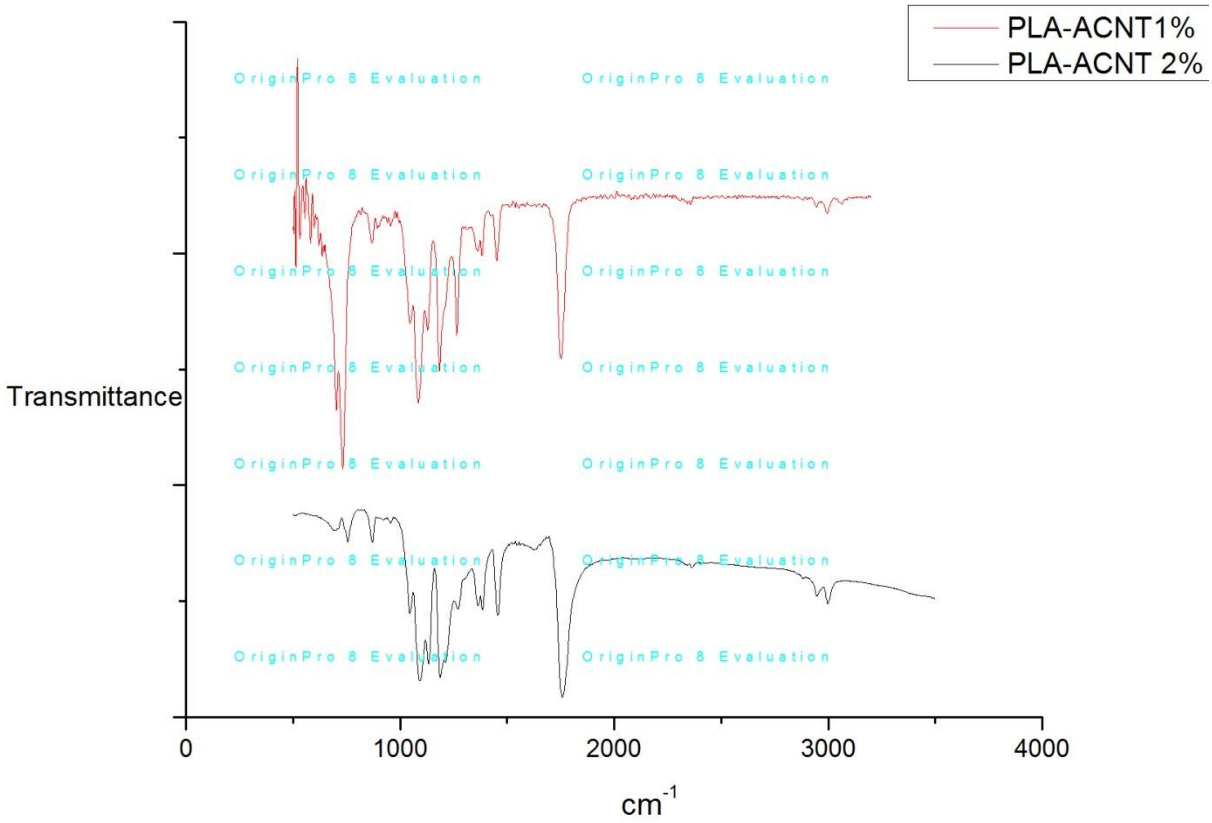


Fig. 17: FTIR results of PLA-ACNT nanocomposites.

The above fig shows the FTIR results of the amino functionalized CNT. As we can see there is less sharpness in the peeks of PLA. This is mainly because of the presence of nucleophilic amino group which terminates the growth of polymeric chain. Hence, low molecular weight product is obtained.

4.3SEM Analysis

The introduction of nanofibers to the PLA polymer matrix reinforces the polymer. The SEM pictures were taken to study the surface morphology of these nanocomposites. The SEM micrographs are shown in figure 18-22. These clearly show individual polymer nanocomposites having different CNT concentration and the effects of these nanofillers on the polymer matrix morphology.

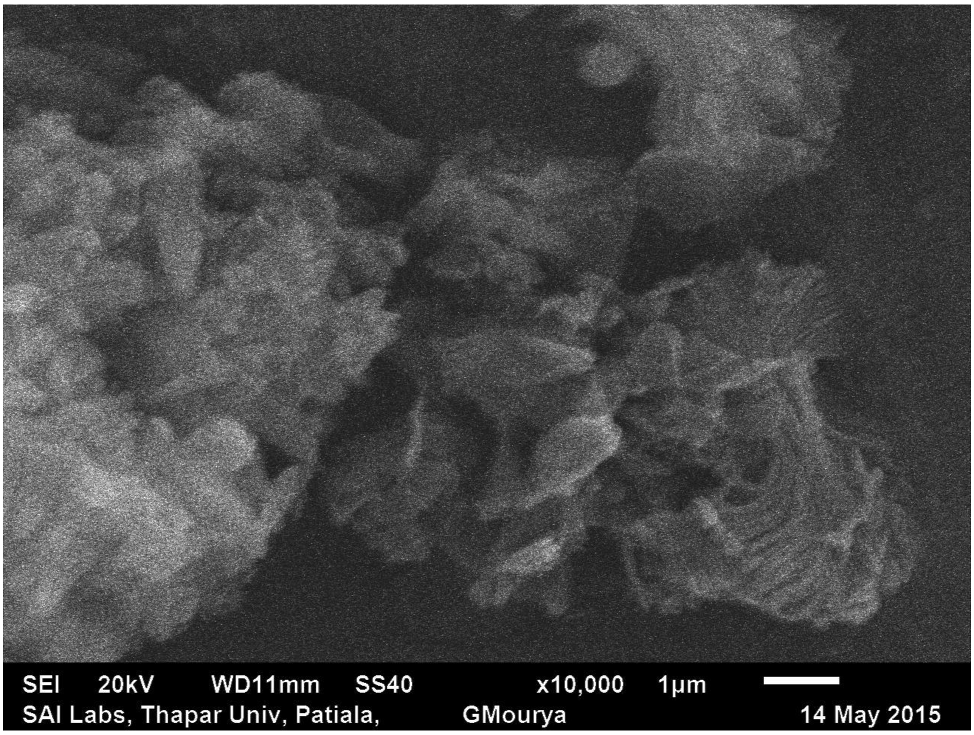


Fig. 18: SEM images of PLA-CNT composite at 0.5% concentration of CNT.

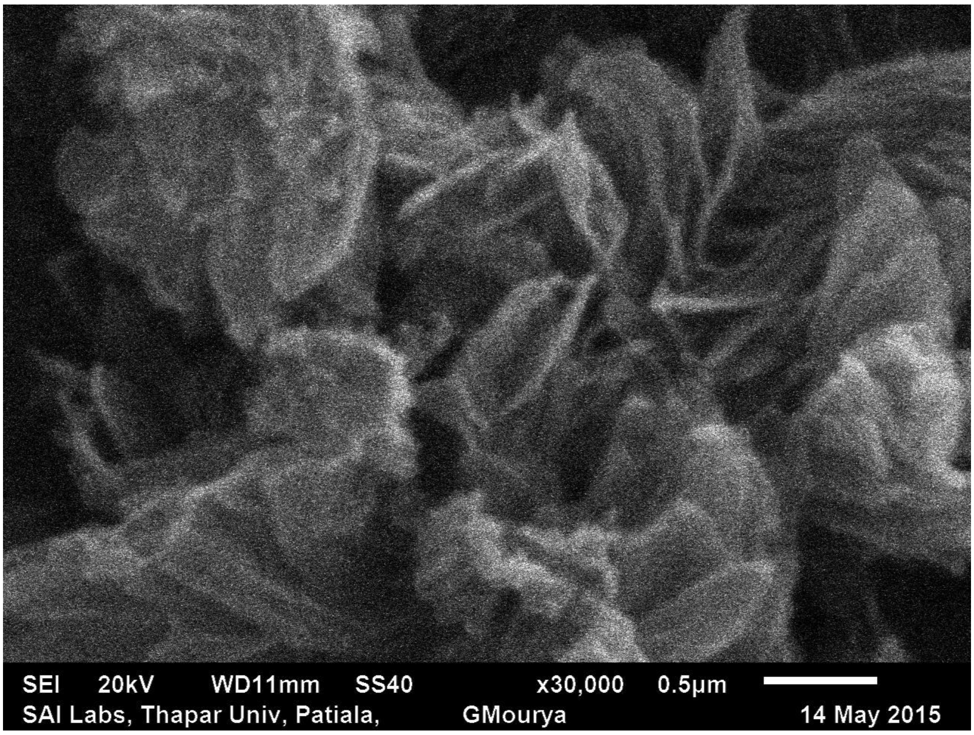


Fig. 19: SEM images of PLA-ACNT composite at 1% concentration of CNT.

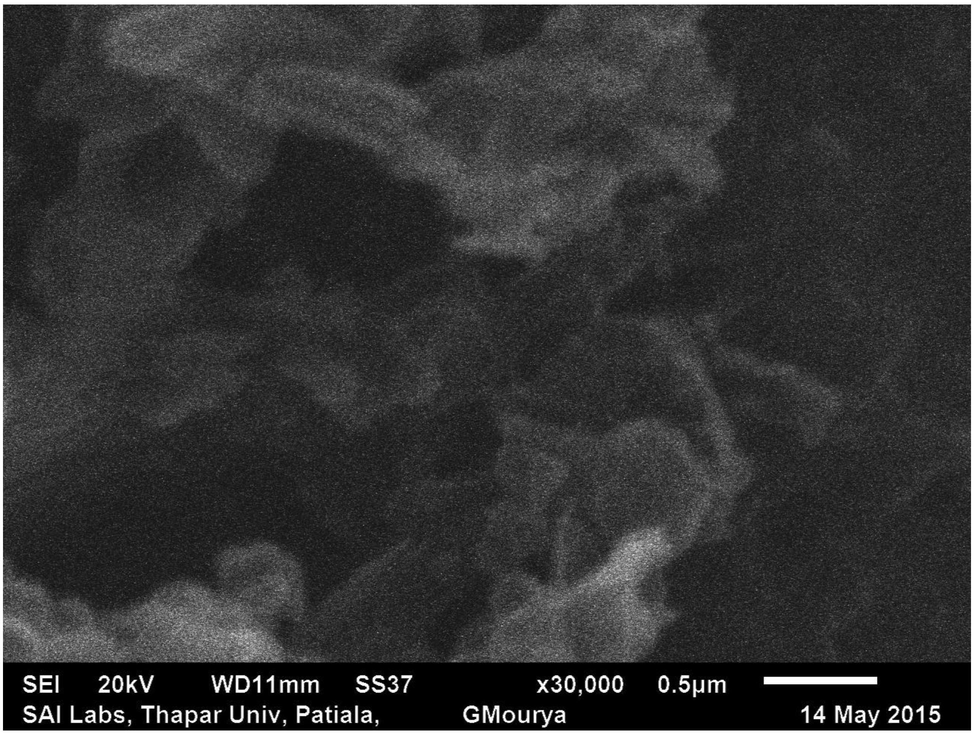


Fig. 20: SEM images of PLA-CNT composite at 2% concentration of CNT.

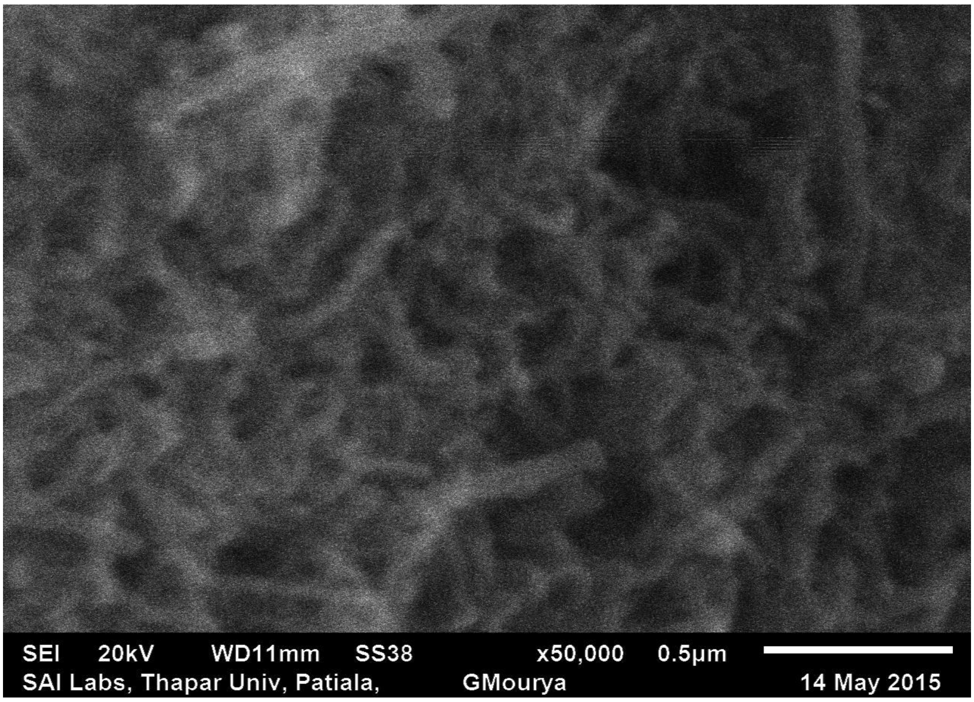


Fig. 21: SEM images of PLA-CNT composite at 15% concentration of CNT.

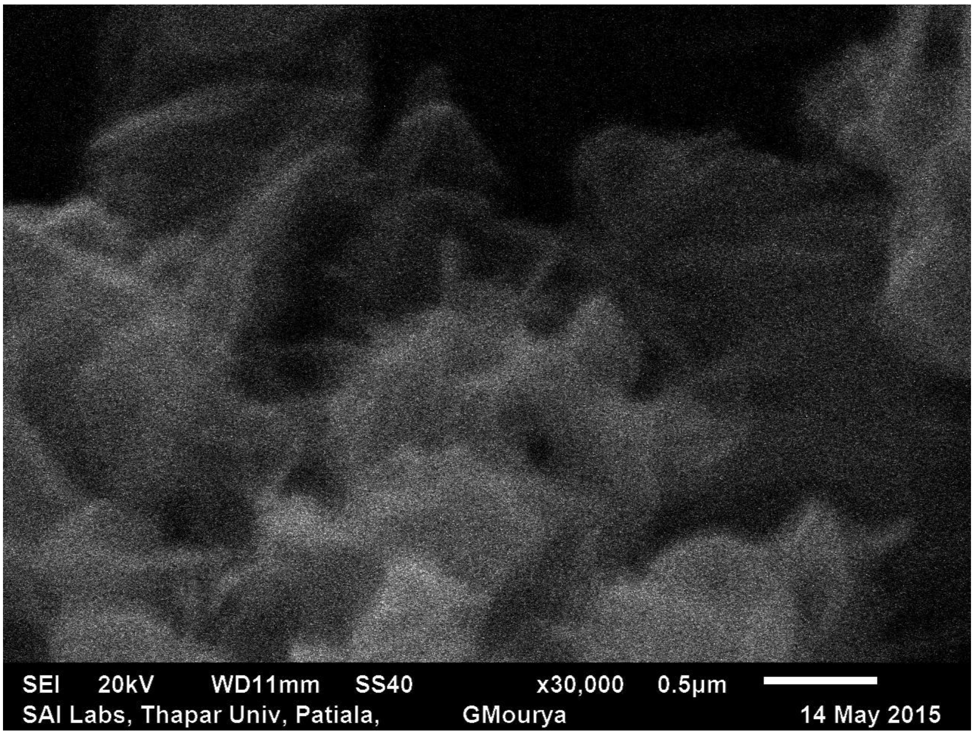


Fig. 22: SEM images of PLA-ACNT composite at 2% concentration of CNT.

4.3TEM analysis

Transmission electron microscopy is done to get to get clearer images showing the presence of CNT. From the images obtained, the presence of CNT in the polymer matrix at different concentrations of CNT is confirmed.The TEM images showed that there was a proper dispersion of CNT in the polymer matrix and hence, we can say that the nanocomposite was formed.

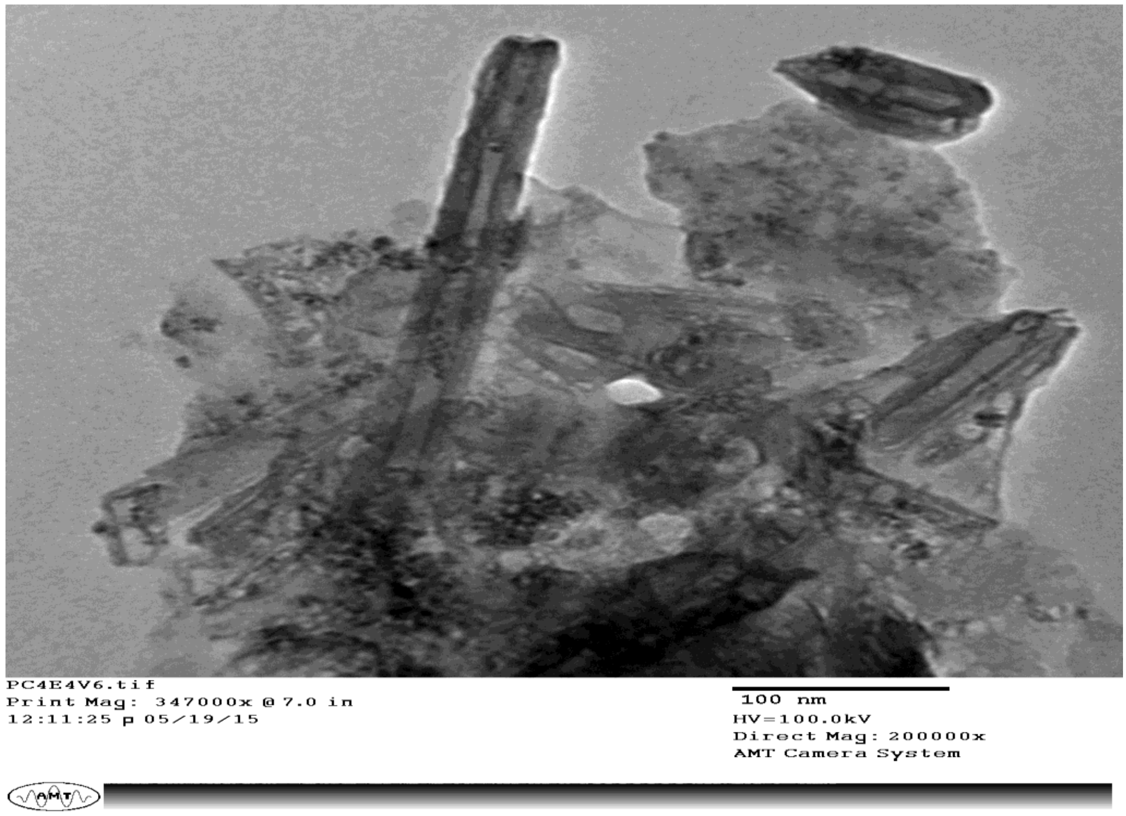


Fig. 23: TEM images of PLA-CNT composite at 0.5% concentration of CNT.

In the above image we can see the nanotubes present in the polymer matrix.

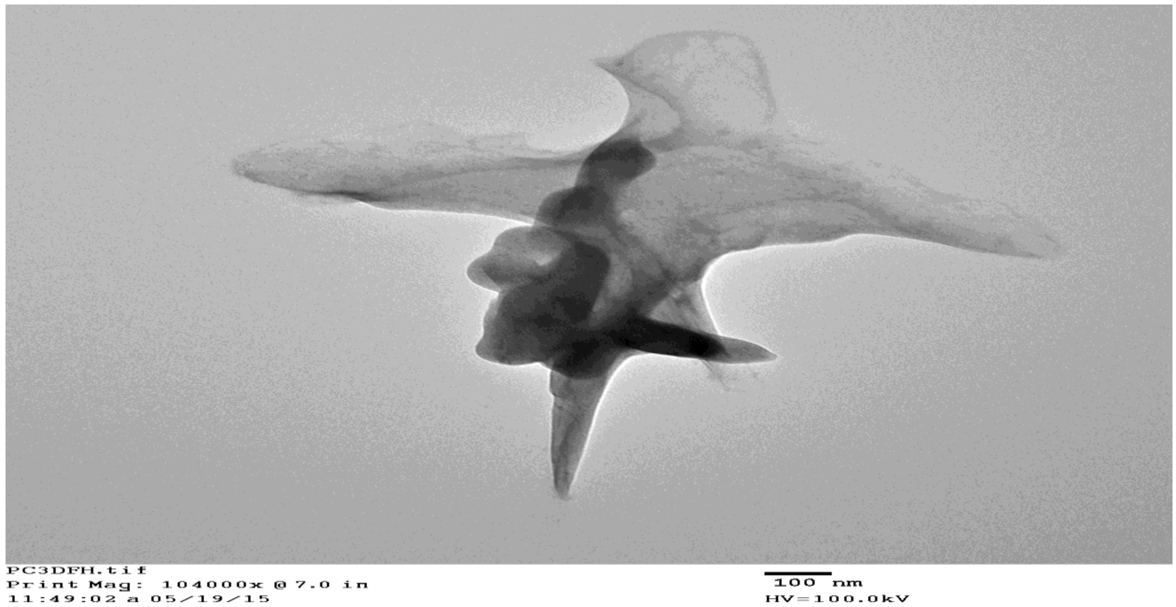


Fig. 24: TEM images of PLA-CNT composite at 2% concentration of CNT.

Fig. 25: TEM images of PLA-CNT composite at 7.5% concentration of CNT.

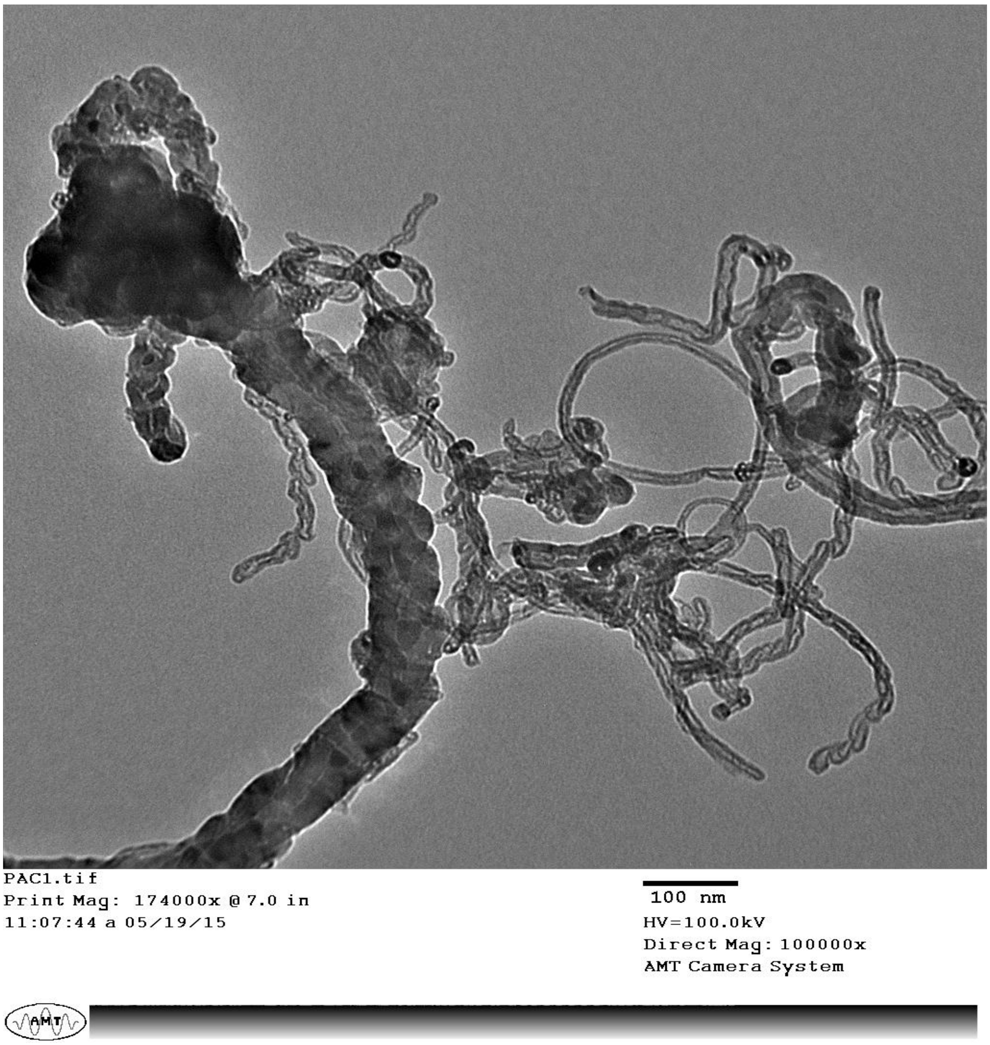


Fig. 26: TEM images of PLA-CNT composite at 15% concentration of CNT.

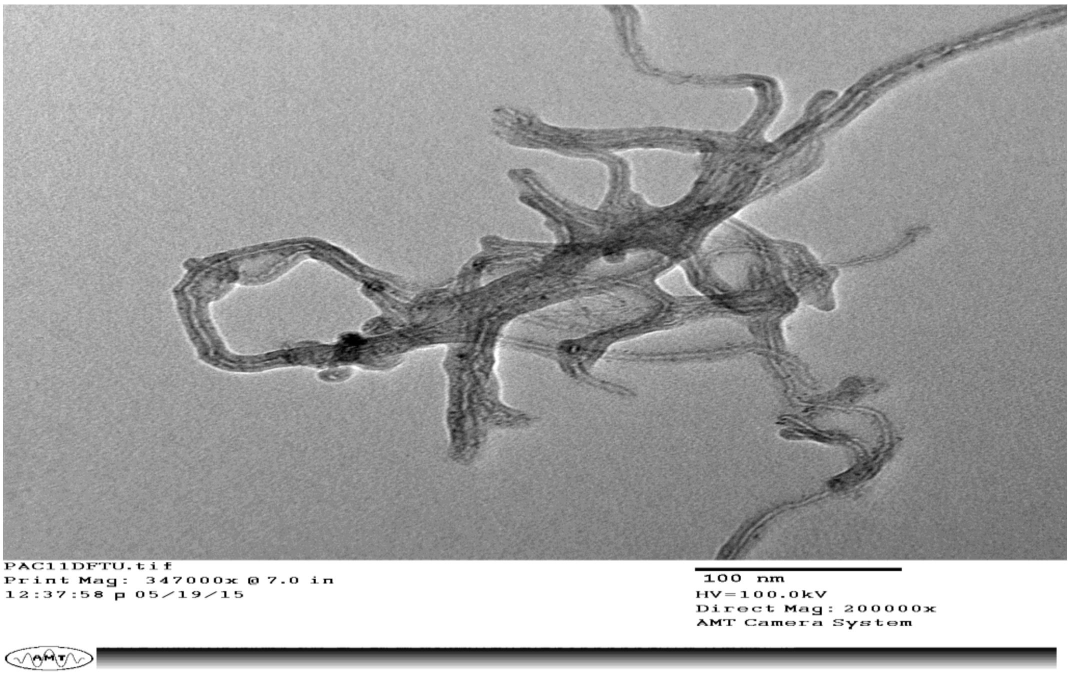


Fig. 27: TEM images of PLA-ACNT composite at 1% concentration of CNT.

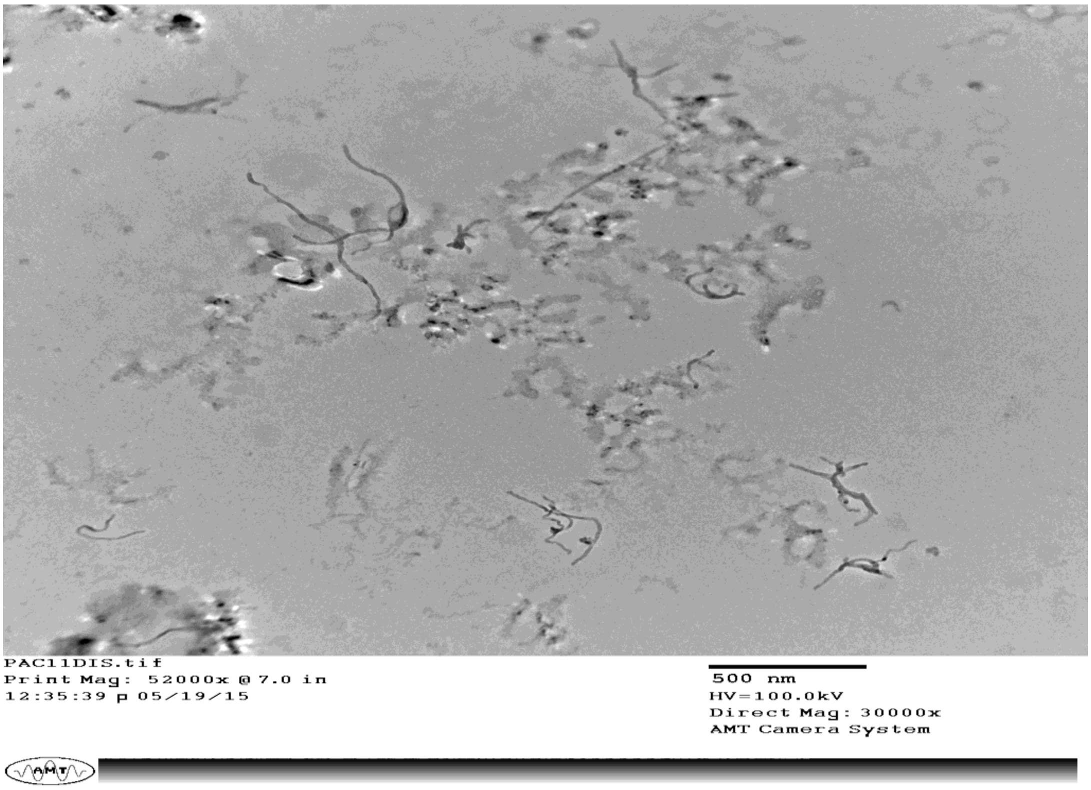


Fig. 28:TEM images of PLA-ACNT composite at 1% concentration of CNT

The above image shows the PLA-ACNT nanocomposite at 1% concentration of ACNT.From this image we can say that the presence of amino group in the product has affected the dispersion of CNT as well the formation of long chains of polymers as compared to the other products.

4.4 Electrical conductivity analysis

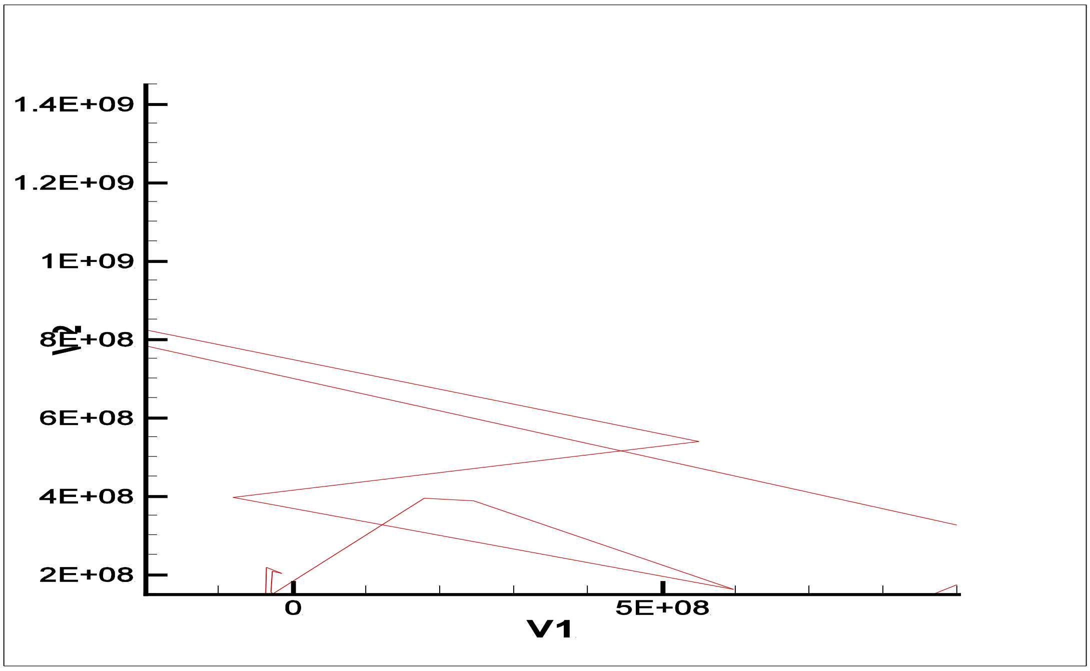
As we know PLA is an insulator it shows very low electrical conductivity whereas, CNT shows very good electrical properties, it is highly conductive in nature. The synthesized nanocomposite must show modification in electrical properties of PLA mainly electrical conductivity. Various samples that were synthesized at different concentration of CNT were analyzed using impedance analyzer. Various parameters were obtained at different frequencies and using these parameters electrical conductivity of the nanocomposites was calculated.

Real and imaginary impedance was obtained at different frequencies. Nyquist plot was plotted using real impedance as x- axis and negative of imaginary part on y-axis. Kole kole curve is obtained using this plot resistance of the sample is calculated a hence further electrical conductivity is calculated.

For this analysis a pellet of the sample was prepared (like a tablet). It was made using hydraulic press in mould of 1.034 cm diameter and the minimum thickness of the pellet that was required for this analysis was 1mm.

After making the pellet conductive silver paint was applied on the top and bottom surface of it and not on the sides. The sample was left opened in air for sometime as the paint was air drying.

Electrical conductivity of nanocomposite of PLA-CNT at 0.2% concentration



After the curve fitting of the data obtained from the analysis an approximate value of resistance was obtained which was about $6.5*10^8$ ohm. From this value approximate resistance can be calculated.

As we know,

Resistance = ρ * thickness/area

Where, ρ = Resistivity

$6.5*10^8$ ohm = ρ * 0.1/0.55

$\rho = 6.5* 10^8*0.55/0.1$

ρ = 5.1025e+9 ohm cm

$\kappa = 1/\rho$

$\kappa = 2.77 * 10^{-10}$ Scm^{-1}

Electrical conductivity of nanocomposite of PLA-CNT at 0.5% concentration

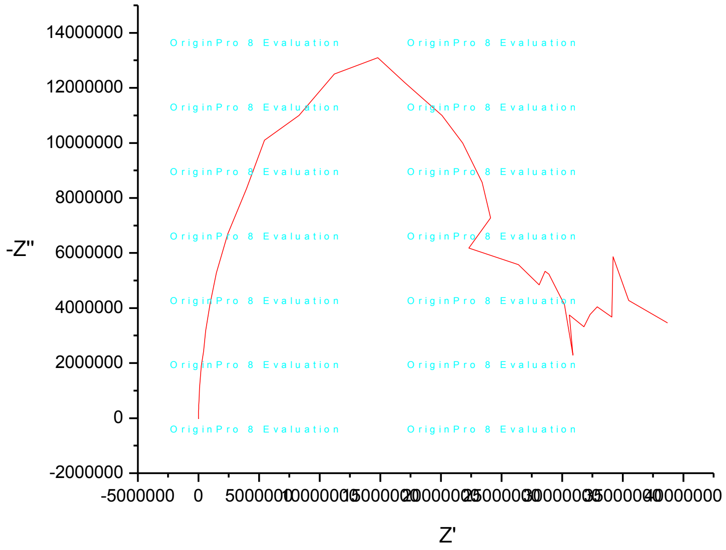


Fig. 29: Plot between real and imaginary impedance of PLA-CNT nanocomposite with 0.5% concentration of CNT for calculating resistance.

To find out the resistance the curve fitting of the above plot was done and hence, the resistance comes out to be $2.722*10^7$ ohm.

As we know,

Resistance = ρ * thickness/area

Where, ρ = Resistivity

$2.722*10^7$ ohm = ρ * 0.1/0.8392

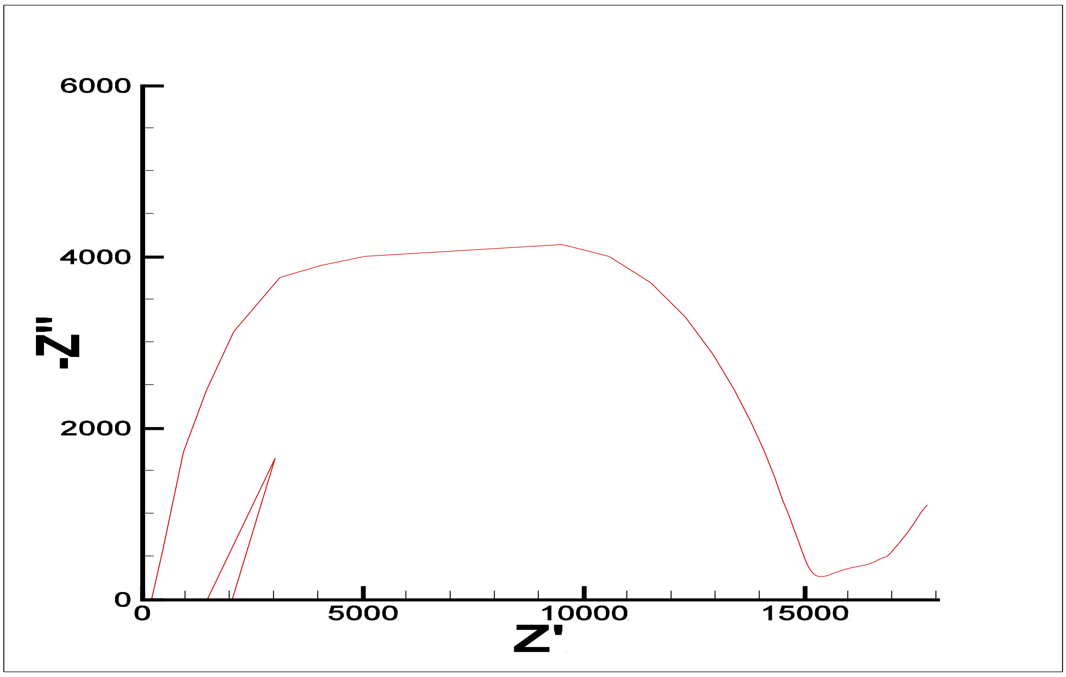
$\rho = 2.722 * 10^7 * 0.8392/0.1$

ρ = 2284302.4 ohm cm

$\kappa = 1/\rho$

$\kappa = 4.4 * 10^{-9}$ Scm^{-1}

Electrical conductivity of nanocomposite of PLA-CNT at 7.5% concentration



Similar to other samples curve fitting of the data obtained was done. An approximate value of resistance was obtained as we can see in the above graph the resistance is around 15350 ohm. Using this value an approximate value of resistivity and conductivity was calculated.

Resistance = ρ * thickness/area

Where, ρ = Resistivity

15350 ohm = ρ * 0.001/0.09

ρ= 15350*0.09/0.1

ρ = 13815 ohm cm

κ = 1/ ρ

κ = 7.23 * 10^{-5} Scm^{-1}

From, the above calculations we can that with increase in concentration of CNT the conductivity of PLA increase as at 7.5 % CNT very high conductivity was shown by the nanocomposite.

CONCLUSIONS

1. The polymer nanocomposite was synthesized at all the concentration of CNT.
2. TEM results showed that the CNT were properly dispersed and thus present with the polymer.
3. When amino-funcltionalized CNT was used a low yield of nanocomposite was obtained and with the increase in concentration of ACNT the yield further decreased. This was mainly because of the presence of amino group which are nucleophilic in nature and causes the breaking of polymer chain.
4. With the increase in concentration of CNT the conductivity of nanocomposite increases. As we can see with the conductivity values reported that at 7.5% concentration of CNT the conductivity showed a higher value.

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