

# **Studying physical and mechanical properties of PVA/CNTs nanocomposites**



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of

MS Materials Engineering

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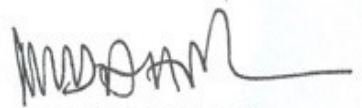
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## **Abstract**

MWCNTs (Multiwall carbon nanotubes) have unique physical and mechanical properties due to which research in this area has been greatly influencing researchers and scientists all over the globe. CNTs show unmatched properties in terms of mechanical, thermal and optical characteristics which promise a great position in numerous future applications.

But due to very high surface energy of these Nano particles scientists are facing problems in the effective dispersion of fillers in the matrices. To increase the dispersion of CNTs several methods are developed.

The morphology, thermal and mechanical properties of PVA based nanocomposites prepared by solution casting method using pristine and functionalized MWCNTs were studied. CNTs were functionalized by covalent method using mixture of nitric acid and sulfuric acid. FTIR spectroscopy confirmed the presence of functional bonds attached after functionalization. Morphology of PVA-CNT composite film were studied using SEM and AFM. SEM and AFM images confirmed the enhanced dispersion of fillers in the PVA matrix. Uniform dispersion of Nano fillers in result give good adhesion and improved stress transfer resulted in enhanced tensile strength and modulus of PVA-CNT composites. Enhanced Tensile strength and storage modulus was observed, 39% increase in tensile strength of pristine CNT composites and 60% increase in case of functionalized CNT composites.

During the course of this project, various characterization techniques such as Fourier Transform Infrared Spectroscopy, Scanning Electron Microscope, X-ray Diffraction, Thermo-gravimetric analysis, Differential Scanning Calorimetry, Tensile testing, Hardness testing (Vickers Hardness) and Atomic Force Microscope, were used.

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# Introduction

## 1. General

Carbon nanotubes, a 3D allotrope of carbon, has been a material of great attraction among the material science researches due to its extraordinary thermal, mechanical and physical properties. Due to these excellent properties, broad research has been done to use this material in efficient way in field of energy, electronics and biomedical applications.

Polymer nanocomposites (composites of polymers in which fillers are of nano scale) are one of the real uses of this material. Polymer nanocomposites show impressive improvements in their merits indeed, even at much lower loadings than polymer composites with customary micro scale fillers. Scientists have built up various nanocomposites for assortment of polymers affecting substantial changes in the potential properties for these polymers. Significant interest of the material expert is to make the cost of these materials more efficient. For this reason, nanotubes, alongside other recently created nano materials, are being use to increase the properties of these nanopolymers.

## 2. Structure and objectives of thesis

In this research work a polyvinyl alcohol/carbon nanotube nanocomposite was fabricated and characterization of this composite was done to calculate the effects of nanotubes on the behaviour of polyvinyl alcohol. This work also shows the effect of different loadings of nanotubes on the composite behavior.

Chapter 2 of this thesis discusses the background study of this research and shares an overview of the materials used, previous researches and advancements in this field. Chapter 3 discusses the methodology through which the samples and films of composites were created. The type characterization techniques and their basic working is also described briefly while the chapter 4 of this thesis presents the results obtained through these experimental techniques and detailed discussion on the effects of different loadings and conditions is discussed in this chapter.

Objective of this work is as follows

- i. To prepare nanofilms of PVA using different loadings of nanotubes in pristine and functionalized form using solution casting method.
- ii. To study the effects of incorporation of these two types of nanotubes in the mechanical, thermal and physical properties of PVA.
- iii. To compare these results and formulate a theory describing these results.
- iv. To establish whether incorporation of functionalized nanotubes improve the properties of nanocomposites or fails to do so efficiently.

# Theoretical Background

## ■ Polymers

“A chemical compound or mixture of compounds formed by polymerization and consisting essentially of repeating structural units.”(Merriam-webster.com)

Polymer is material which is a combination of long chains which are composed by an array of attached monomers. These monomers can be combined by addition polymerization or condensation polymerization. In addition polymerization a simple molecule adds on itself e.g. ethylene. In condensation polymerization when two molecules join together in result there is loss of small molecules in the form of by product.

Polymers have been used for centuries for versatile applications in the form of gums, resins and tars. However the scale on which today mankind is utilizing polymers started after the industrial

revolution. In 1830s, Charles Goodyear successfully produced synthetic rubber through vulcanization.(plc.cwru.edu 2012)

After 40 years a hard plastic produced synthetically from nitrocellulose was commercialized. Polymers are very diverse in their properties and structure. These materials are being used in nearly every industry such as PE, wool and rubber. One of the biggest advantages of polymers is their process ability. Processing of these materials is very versatile and cost efficient. With time and technological advancement polymers are replacing other materials in daily life use.

### 2.1.1 Polymer synthesis

To know the structure and properties of these materials the most important fact is to understand the processes of production. Polymers are produced in two different ways.

#### 2.1.1.1 Addition Polymerization

In addition polymerization a monomer gets attached to another monomer in a simple manner, unit by unit. The most common type is free radical polymerization. A free radical is created in a molecule which initiates the reaction through which polymerization starts. A free radical is a molecule which has a tendency to pair with another molecule due to absence of an electron. Free radicals are created with the molecules known as initiators. An initiator simply breaks the molecule in two different parts along a single bond which creates a free radical at the point of breakage.

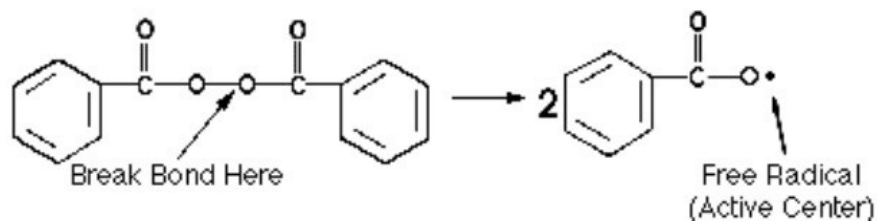


Figure 1(Free radical formation)

The first step is called initiation reaction in which free radical is created, the next phase is called propagation stage in which the free radical cause a chain reaction in

which electrons are transferred and long chains are formed. When supply of radicals comes to end the growth most likely also comes to an end in two ways, combination or disproportionation. In combination a single chain is formed after reaction of two chains, in disproportionation a hydrogen atom is removed from the chain and attaches itself to other chain.

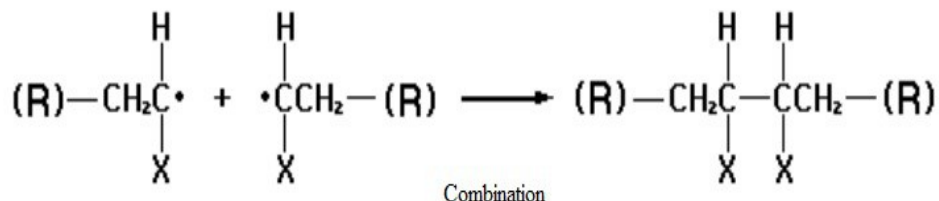


Figure 2 (Combination)

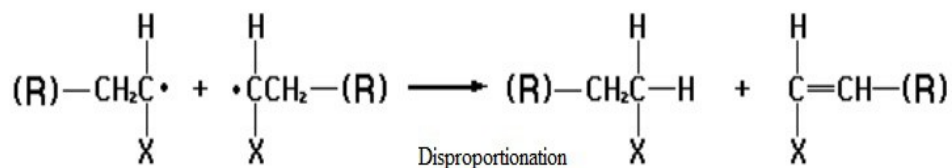


Figure 3 (Disproportionation)

### 2.1.1.2 Condensation Polymerization

In condensation Polymerization the reactions ends with byproducts, where different molecules join together, and lose small molecules attached to the chain as by products mostly water or methanol. It's a form of step growth polymerization.

### 2.1.2 Polymer Structure

Properties of polymers largely depends upon the extent to which polymerization is achieved but the structure of polymer chains too impacts the properties and nature of polymer products and solutions. There are two basic categories which describe the geometric structure of polymers.



### 2.1.2.1 Configuration

Configuration can be of two types, Cis and Trans. It is a chemical phenomenon, means this structure can't be changed unless the chain is chemically altered or the bonds are severed through which chains are stick together. When same groups are on the same sides then it is called Cis configuration but if on opposite sides then this configuration is called Trans.

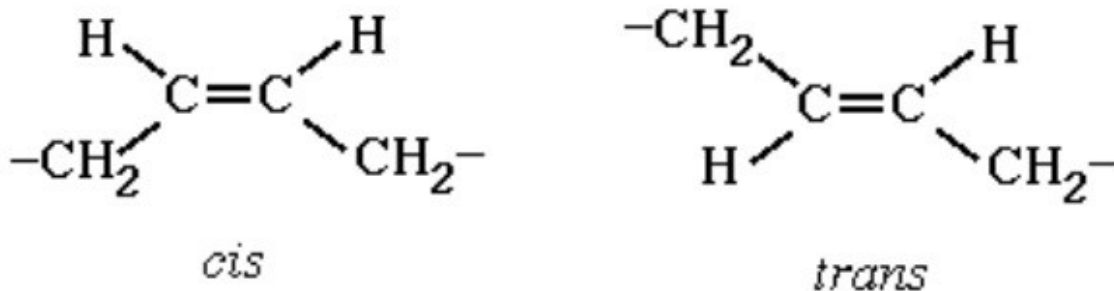


Figure 4 (The picture on the left is the example of cis configuration, The picture on the right side is the example of trans configuration)

### 2.1.2.2 Conformation

Due to presence of single bond, the functional groups present on both the sides of any molecule can rotate around the axis and form various forms due to which properties of molecules can slightly differ. This phenomena is called conformation.

### 2.1.2.3 Other polymer structures

There are, though, many types in which polymers can be arranged in branch shape. One of such kind is known as "star-branching". It comes about when a single atom causes a growth of branches from the central point and a star like structure is produced. Among this type of polymers those which have high level of expanding are called dendrimers. In this type the branches also have sub branches. This phenomena results in the spherical type of shape in 3D. If more than one type of monomer is present then structure will be slightly different called co-polymers. Generally there are three types of co-polymers that exist. These are block, random and graft polymers. In block polymers same type of monomer are attached in a sequence, in random polymer these are arranged in random manner and in graft polymer the primary chain of structure is made up of one monomer type and the branches are of different monomer. The accompanying graph shows the distinctive types of copolymers.

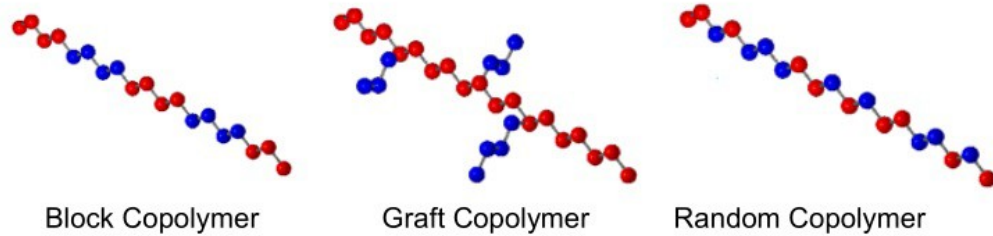


Figure 5 (Grahpic interpretation of Block, graft and random copolymer)

## Introduction to Polyvinyl Alcohol (PVA)

Polyvinyl alcohol is a thermoplastic polymer, that was developed with the reaction of polyvinyl acetate and potassium hydroxide.(S.K.Saxena 2004)

Polyvinyl Alcohol form an odorless and tasteless translucent solution when dissolved in water. It is soluble in water. Melting point of PVA is around 180 to 190° C and pH in range of 5 to 6.5 when formed as 5% solution in water. PVA is usually available in different hydrolyzed forms. Generally in the range of 85 to 98%.

### 2.2.1 Structure and properties of PVA

Polyvinyl alcohol has a simple structure. A hydroxyl group is present in the chain of PVA which dictates its properties. Monomer of this chemical is not stable at normal conditions. So production of PVA is indirectly achieved through polymerization of vinyl acetate. This polymerization ends with some byproducts and is not 100% efficient so various grades are formed depending on the degree of hydrolysis. It is always a co-polymer of polyvinyl alcohol and polyvinyl acetate. Commercially it is accessible with high degree of hydrolysis (85-98.5%). This degree of hydrolysis has huge impact on the properties of PVA such as its chemistry, solubility and crystallinity. Higher the molecular weight low is the solubility of

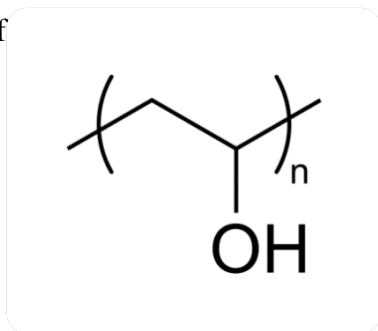


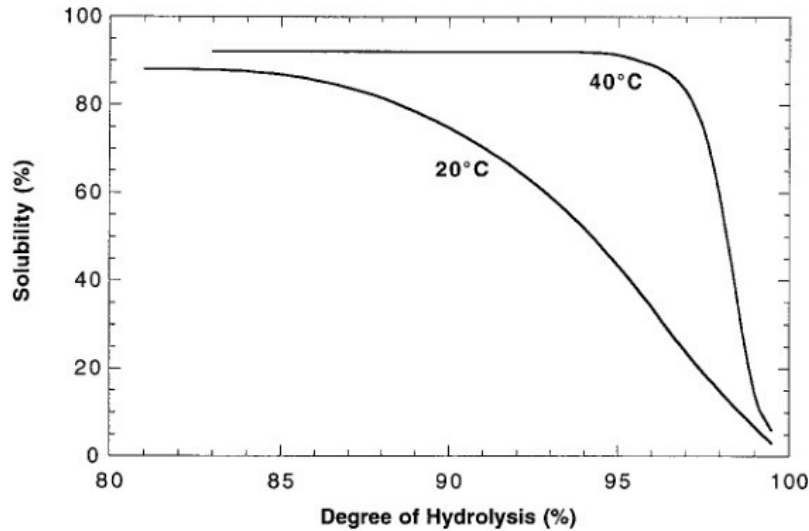
Figure 6 (Structure of PVA)

This OH group is responsible for the high solubility of PVA in water and it forms excellent films.

Form	Granular
Density kg/m <sup>3</sup>	400-432
hydrolysis	85-98.5%
Viscosity, mPa-s	27-33
Solution pH	5-6.5
Specific gravity	1.30
Refractive index	1.54
Specific heat, J/kg-K(cal/g/°c)	1674(0.4)

Table 2.1 (Properties of PVA)

Solubility of PVA increases with increasing temperature and decreasing molecular weight and hydrolysis.(Christie M. Hassan 2000)



Solubility as a function of degree of hydrolysis at dissolution temperatures of 20 and 40 °C

Figure 7 (Solubility graph of PVA with increasing hydrolysis)

PVA exhibits crystallinity because of the small size of –OH groups, they tend to fit into the lattices without disruption.

## Introduction to Carbon nanotubes (CNTs)

Among the various Nano fillers used to modify polymer matrices, carbon nanotubes have appealed great interest due to their higher physical, electrical and chemical properties.

Nano tubes can be visualized as plane graphite sheet rolled in a manner that it form a cylinder type shape which are bounded by covalently bonded carbon atoms, cylinder can be capped or open.

These are generally of two types according to the structure: single wall nanotubes and multi wall nanotubes.

MWNTs are made up of several layers of graphene sheets rolled coaxially in cylindrical shape with interlayer space of 0.34 nm. In this work all the work has been done on MWNTs

### 2.3.1 CNT structure

The basic structural classification of nanotube is divided into two categories one is called achiral and the other one is called chiral.(Wang 2007). The two nearly identical structures are known as ‘zigzag’ and ‘armchair’ illustrated in the figure below. In most cases nanotubes don’t show such level of extreme symmetry and atoms are found to be bounded in hexagonal form helically around the tube axis. This type is known as chiral and are found in mirror shapes.

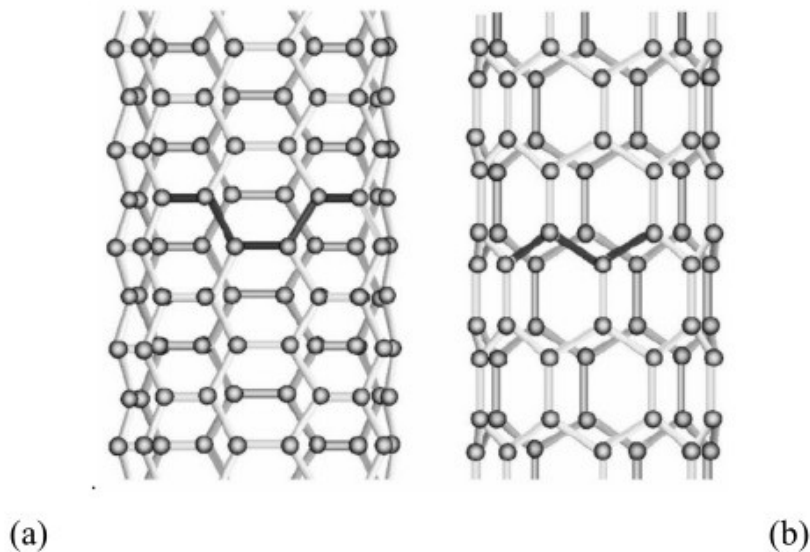


Figure 8 (a) =zigzag (b) =armchair

### 2.3.2 Properties of Carbon Nanotubes

#### 2.3.2.1 Mechanical Properties

Due to the presence of smooth cylinder-shape graphitic structure, nanotubes show high mechanical strength and can be an ideal candidate to be used as a filler material while producing light weight, high strength and efficient composite materials. In this work nanotubes are studied specially to calculate the mechanical behavior and increase in strength of composite after their insertion.

Theoretically CNTs has shown high modulus and tensile strength reaching upto 1 TPa and 180 GPa respectively and many researchers concluded similar results when using single nanotubes without forming composites.

CNTs can be tested mechanically with different set of apparatus and methods.

Figure 9 shows a similar setup in which CNTs are fused in SiO<sub>2</sub> substrate and a lateral force is applied on the tip of CNTs and the reaction is tested through highly sensitive sensors which shows the results in the form of graphs. Another method is shown in figure 10 in which atomic forces are applied on the tips of nanotubes.

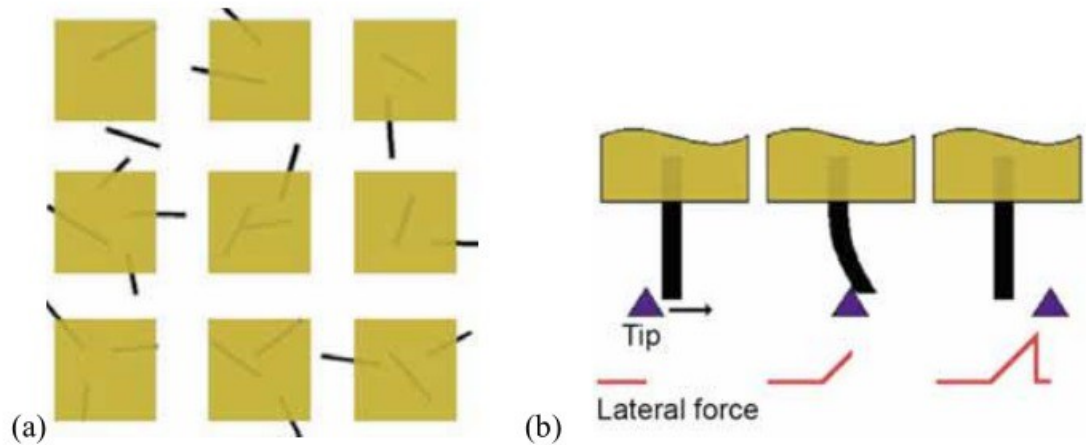


Figure 9 (Overview of the approach used to probe mechanical properties of carbon nanotubes.

(a) CNTs deposited on the substrate and held by SiO pads; (b) Representation of beam bending with the help of an AFM tip and lateral force changes

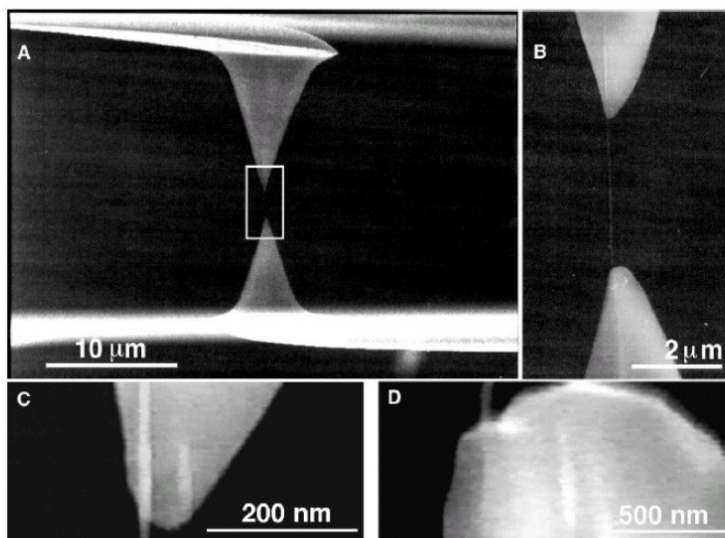


Figure 10 (SEM image of tensile test on carbon nanotube)

### 2.3.2.2 Chemical Properties

The reactivity of CNTs directly relates to the effect of higher curvature which is created during  $\pi$ -orbital mismatch which further increases reactivity in smaller diameter nanotubes. If the sidewalls or endcaps of nanotubes can be modified then the control over solubility of nanotubes in different solvents can be achieved.

### 2.3.2.3 Electrical and Thermal conductivity

In carbon nanotubes varying electrical conductivity has been observed. This depends upon varying molecular structure which gives rise to varying bandgap. Thermal conductivity of carbon nanotubes are calculated to be superior to diamond.

Materials	Thermal conductivity (W / m.K)	Electrical conductivity (S/m)
CNTs	>3000	$10^6$ - $10^7$
Copper	400	$6 \times 10^7$
Carbon fiber	1000	$2$ - $8.5 \times 10^6$
diamond	2200	$10 \times 10^{-12}$

Table 2.2 (Conductivity values of CNTs, Copper, Carbon fiber and Diamond)

### 2.3.3 Processing of nanotubes

CNTs can be formed by various methods and every process yield different type of properties which can be choose according to the application and use. Different processes are Arc expulsion method, laser ablation and CVD.

#### 2.3.3.1 Arc-discharge method

Basically, Short length multi-walled nanotubes with internal width of 1-3 nm and external breadth of roughly 10 nm are created. The technique makes CNTs through electric vaporization of carbon rods set as anode and cathode, isolated by pretty nearly 1mm, in a fenced area that is generally loaded with noble gas (somewhere around 40 and 650 mbar). An immediate current of 60 to 90 Amps more at 25 V develops temperature range very high between the rods. Vaporization of one rod undergoes and gets deposited on the other rod. Yield relies on temperature, graphite anode immaculateness and arc manageability.

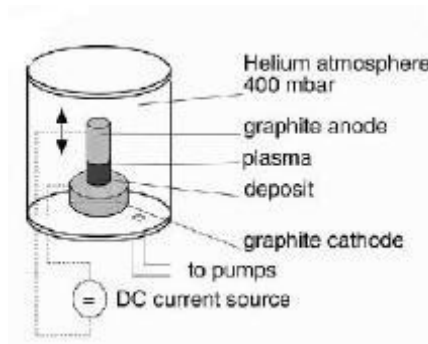


Figure 11 (graphic representation of Arc discharge Method)

#### 2.3.3.2 Laser Ablation

A continuous or pulsed, high-control laser is utilized to vaporize carbon from a graphite target. The subsequent soot is gathered by a water-cooled gathering finger. Sediment is then sanitized and MWCNTs are isolated. It is a expensive method for MWCNT generation. Immaculate graphite target is put in quartz tube heater at about 1200°C.



Heater has dormant climate of (Ar) or (He) at weight of 500 Torr. Laser vaporizes target and yield of CNTs differs from 20 to 80% by weight, though diameter distribution is generally somewhere around 2.5 and 10 nm.

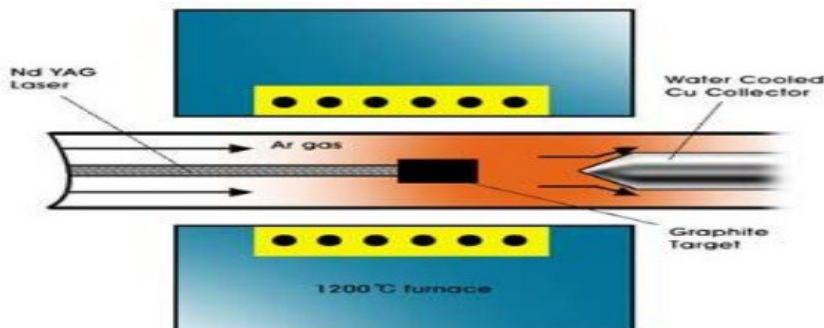


Figure 12 (Graphic representation of Laser ablation method)

### 2.3.3.3 Chemical vapor deposition

(CVD) amalgamation is accomplished by forming a high energy source with the help of any carbon source. When carbon source is located near any high energy zone such as plasma or heated coils this carbon source converts itself into vaporous form. Hydrocarbon gases, for example,  $\text{CH}_4$ , CO and  $\text{C}_2\text{H}_2$  acetylene are utilized as carbon source. The Hydrocarbon particle is then decayed into responsive carbon by energy source (heat/plasma). Carbon then diffuses towards the substrate which is at high temperature and contains a catalyst (for the most part a move metal e.g. Nano size Nickel, iron or Cobalt). The adsorption of carbon on catalyst happens which offers ascend to development of CNTs.

Development rate, size, width, length can be controlled by fluctuating different procedure parameters in this method. However the impediment could be high defect densities. CVD carbon nanotube blend is basically involves a two-stage process, first step comprises of an impetus arrangement step took after by the synthesis of the nanotube. The synthesis, which has a significant impact on nanotubes creation, may be arranged utilizing physical (sputtering) or compound (Etching/Sol gel, Co-precipitation) methods.

Nano particles of transition metal may be and set on the substrate, having broken up in solvent.

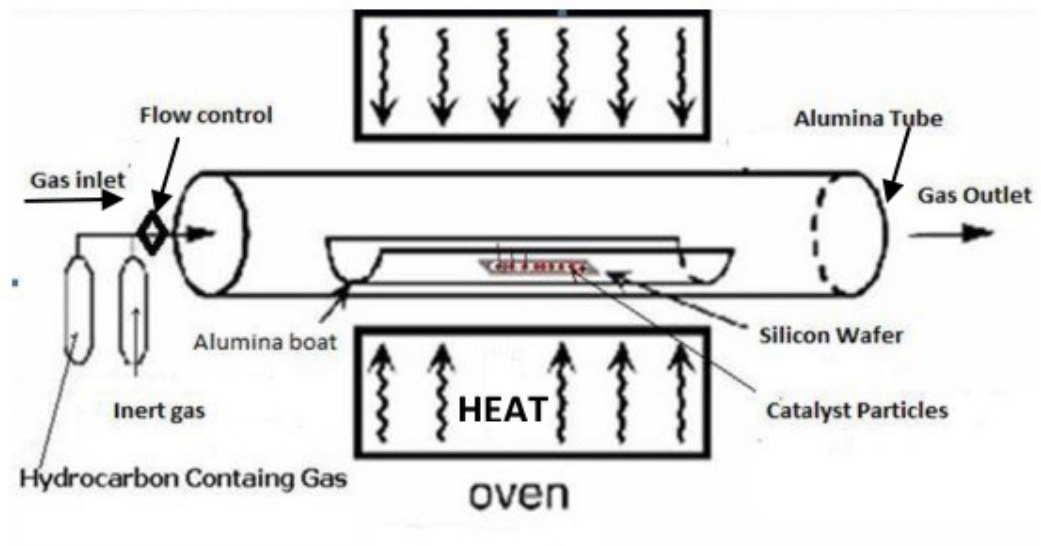


Figure 13 (Graphic representation of Chemical vapor deposition)

## **Polymer nanocomposites**

In the first chapter, different materials and their related backgrounds were introduced. Different type of CNT structures and their properties were discussed, then semi-crystalline PVA structure and its properties were discussed briefly.

In this chapter various aspects of progress and challenges of CNT / Polymer composites will be discussed. As carbon nanotubes show excellent mechanical and thermal properties, great enthusiasm has been shown by various researchers and scientific organizations. There are various inherent problems in the usage of CNTs. The first problem to be addressed is the variation in dimensions and purity of carbon nanotubes even taken from a single batch. The large surface area of nanotubes suggest that these difference can influence the final properties of the composites. Thus it is very difficult to perform reproducible and well controlled experiments which is giving a tough time to researchers to compare the results. The second biggest problem while dealing with nanotubes is the dispersion of tubes into the polymer matrix that directly effects the stress transfer from the matrix to tubes.

So fabrication of well-dispersed films of carbon nanotubes and PVA matrix is required in this research. In the first part of this chapter brief history and introduction of nanocomposites will be discussed before coming to the solution of above given problems.

## **Composites**

A composite is a material which is formed when two or more distinct materials combine to give enhanced properties. (e.g., weight, strength, corrosion resistance). The composite material has better properties as compared with individual components. The difference between an alloy and composite is that in composites the components retain their identity that is their chemical, physical and mechanical properties. There are two constituents in a composite

1. Reinforcement
2. Matrix

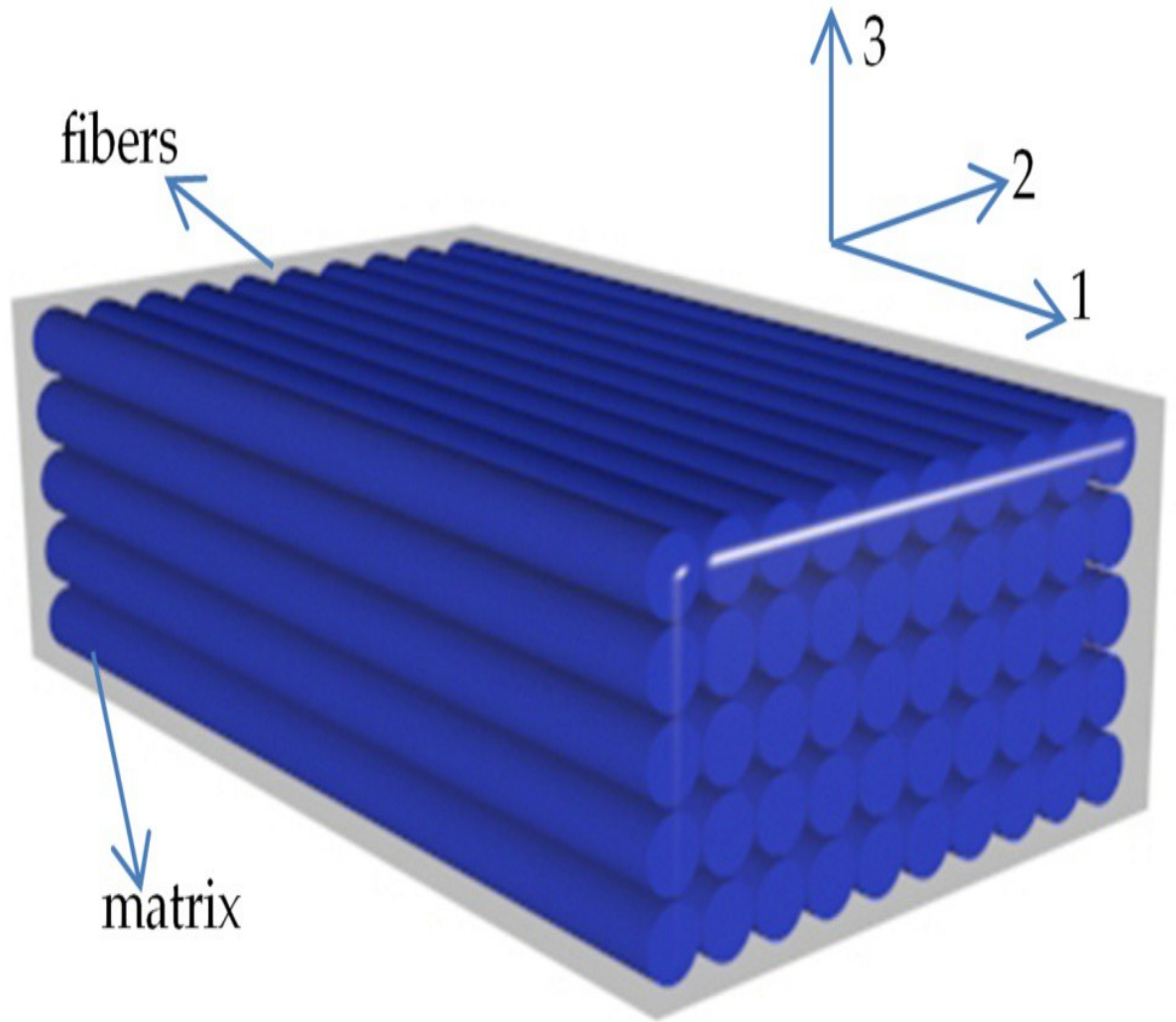


Figure 14(Schematic of Composite)

## 2.5.1 Classification of composites

### 2.5.1.1 Reinforcement based

Composites can be classified upon the kind of reinforcement used.

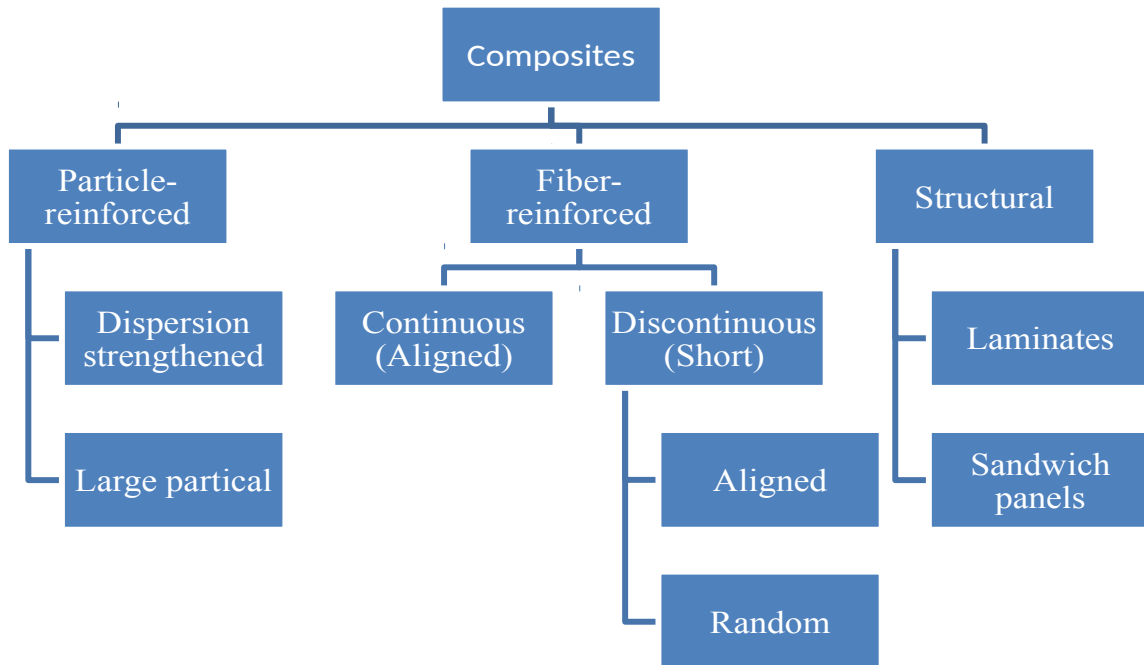


Figure 15(Classification of Composites)

The composites used generally are Kevlar, glass and carbon fibers. In some cases composites based upon stacking different laminates on one another are also used which is called as structural composites in which different size and shapes of fillers can be used. When different size fibers are used then these are called as anisotropic composites. (Daniel and Ishai 1994) But if the size of filler is very small then they exhibit properties like isotropic composites. One of the greatest advantages of using such composites is the minimum probability of getting any critical surface flaw at filler material which can lead to failure. On the basis of dimensions and diameter these can be divided in 3 categories.

*2.5.1.1.1 Short fibers (Whiskers)*

These are basically thin single crystals that have large aspect ratios. Due to their small dimensions they are seemed to be flawless and have nearly crystalline perfect structures. So these fillers give characteristic high strength composites. But the biggest disadvantage involved in this type of fillers is the

cost. The second problem is the good incorporation of filler into the matrix. Examples of this type of filler includes CNTs, graphite and silicon carbide.

#### 2.5.1.1.2 Continuous fibers

These are generally polycrystalline or amorphous materials with small diameters. These fibers are mostly made up of polymers or ceramics.

#### 2.5.1.1.3 Wires

Most wires have large diameters as compared with previous two categories. These include tungsten and steel etc. the most common example of this type of composite is in the construction industry where steel rods are dispersed in cement to form pillars and roofs.

#### 2.5.1.2 Matrix Based

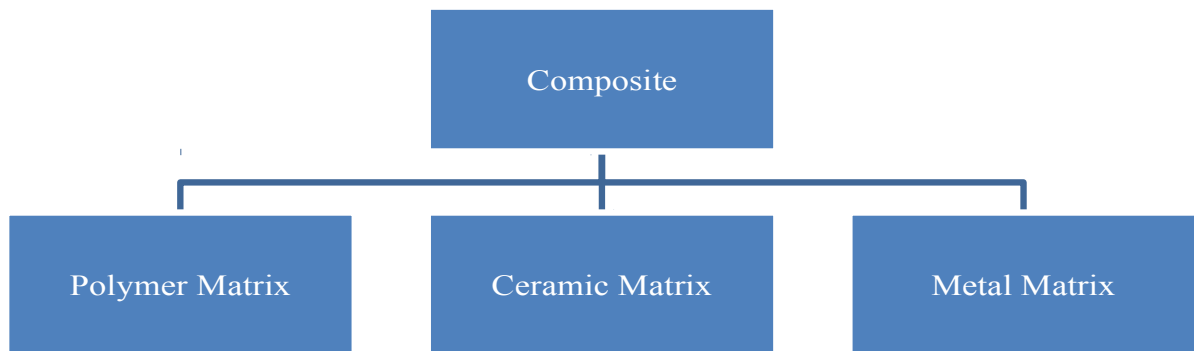


Figure 16(Classification of composites on the basis of matrix)

Matrix is that part of the composite which carries the fillers and gives the base to the material. Matrix surrounds the filler material and protects the reinforcement from external chemical and physical attacks. Matrix also gives shape to the final product and the stress applied on the composite is also transferred to the reinforcement through matrix material. This portion determines many of the parameters of materials e.g. operating temperature and chemical environment during working.

#### *2.5.1.2.1 Polymer Matrix composites (PMC)*

Polymers can be used as matrix in a composite material with reinforcement materials. There are 2 categories of polymeric materials which are thermosets and thermoplastics. Polymers are used in composites for their diverse properties as their ease of fabrication, low weight and cost play a critical role in manufacturing. Examples are carbon fiber sheets and PVA-CNT films.

#### *2.5.1.2.2 Metal Matrix composites (MMC)*

MMC generally consists of a low-density metal such as magnesium or aluminum and this matrix is reinforced with fibers or particulates of material like graphite or SiC. MMC offer high operating temperature and better wear resistance.

#### *2.5.1.2.3 Ceramic Matrix composites (CMC)*

These composites consist of a ceramic matrix and it is reinforced by a refractory fiber like SiC fiber. CMCs are light weight and offer high hardness and high resistance to thermal and chemical environments.

### **■ Nanocomposites**

These are a type composites in which one of the phases has at least one dimension in nanometers. These materials have been predicted to be the materials of 21<sup>st</sup> century due to the fact that they possess design uniqueness and such property combinations that can bring revolution in daily life and industrial materials. The number of pages published in the field of nanocomposites was about 13,420 in the last decade, which shows the level of interest shown by researchers around the globe. (Pedro Henrique Cury Camargo 2009)

#### **2.6.1 Classification of nanocomposites**

Nanocomposites are classified on the basis of the filler used. As the distinction between an ordinary composite and nanocomposite lies in the size of the filler material, there is no real difference in the matrix used. The broad classification of nanocomposites is given below

### 2.6.1.1 1D filler Nanocomposites

1 dimension nanocomposites are those in which one of the dimension is in nanoscale. CNTs are a type 1D fillers. The high aspect ratios of these fillers play the critical role in the properties. But using these materials demand careful working as alignment of fillers can change the properties massively.

### 2.6.1.2 2D filler Nanocomposites

2D fillers are in shape of sheets which have negligible thickness and have 2 dimensions in the nanoscale. Graphene sheets are an example of 2D nanomaterials. These materials have very high surface to volume ratios which make them very energetic and can be unstable. But this structure also gives very high mechanical strength to the material as the presence of voids and defects gets reduced.

### 2.6.1.3 3D filler Nanocomposites

3D Nano fillers are those materials which are like conventional fillers but are in Nano dimensions. Due to the size they differ in properties because they have very high surface area to volume ratios. But fillers when used in matrix are not homogenous they show heterogeneity as the result of uncontrolled agglomeration due to high Van Der Waals forces. Due to smaller sizes the surface atoms play significant role which is negligible in the case of micro particles.

Quantum effects are also observed largely due to the high surface area which in return give unexpected optical, magnetic and electric properties. For example when gold Nano particles are mixed in a solution they give deep-red color. Absorption of different wavelengths exhibit these contrary colors. Zinc oxide, silicates and ceramic silicon carbides are few examples of 3D fillers.

## 2.6.2 Synthesis of Nano fillers

Fillers in the dimensions on Nano meters can't be prepared by traditional methods due to several reasons, high energy due to high surface energy is one of the reasons. Alternative processes like sol-gel, CVD and hydrothermal are generally employed in labs and industry. Most of the methods are low temperature processes but ceramic fillers can be produced at high temperatures.

## 2.6.3 Synthesis of Nanocomposites

Nanocomposites are synthesized with the processes similar to synthesis of Nano fillers. Few of the examples are as follows.

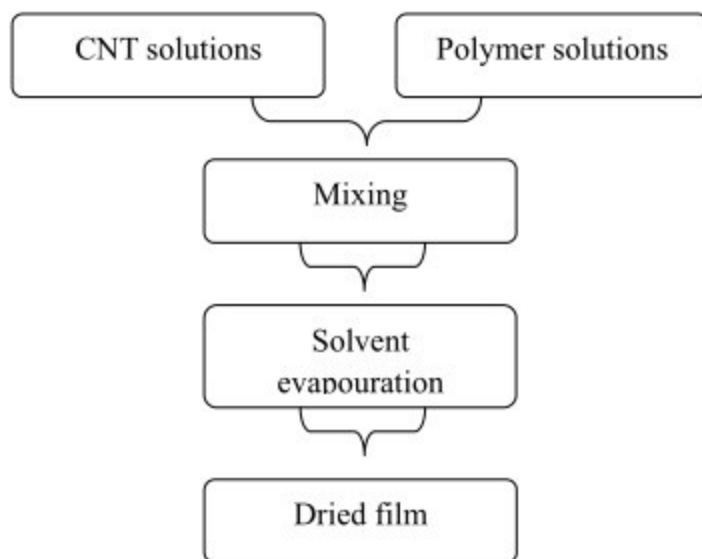
### 2.6.3.1 Solution processing

This technique is the most common method to produce Nano Composites. Different polymer matrix are treated in distinct ways but overall route employed is somehow very similar. First, we take Nano fillers



and disperse them in a solution at normal temperature or high temperature according to the choice of matrix material. Then the Filler solution is mixed with the matrix solution by carefully controlling the mixing rates and temperature of the setup. During mixing of both solutions evaporation has to be carefully controlled as these impurities can cause variation in the final product and can produce porous products with poor properties. Another problem while drying the solutions is the dispersion of filler material. To disperse the filler properly we have to adopt various techniques like agitation or modification of filler material.

Agitation is enforced with techniques like magnetic stirring, ultra-sonication or shear mixing. Further these agitation techniques can vary with respect to speed and temperature.



*Figure 17 Schematic showing procedure of solution processing*

### 2.6.3.2 Melt mixing

Most of the thermoplastics are processed with this technique. Thermoplastics become soft when applied temperature and these materials can be processed when heated over their melting temperatures. This technique is very time efficient and very simple. Large scale production can be achieved with melt mixing due to which this technique is preferred in the industry. Another benefit of this technique is that through these processes amount of contaminants, which are generally present in the product with other techniques, are absent.

High shear mixing is essential while mixing Nano fillers. When observing this technique certain parameters have to be taken in consideration like shear rate, shear time and type of the equipment used in shearing.

High shear rates can damage the Nano fillers and can degrade the polymer matrix used.

### 2.6.3.3 In-situ Polymerization

Polymer matrices which can't be processed with above mentioned techniques are processed through in-situ polymerization. The biggest advantage of this technique is the advantage of grafting fillers on the polymer chains at molecular scale. Which in result give excellent dispersion and good adhesion between the matrix and filler. High filler content can be achieved through this technique which in result give products with high mechanical strength and improved electrical properties.

# Experimental

## Introduction

When using CNTs to improve the physical properties of polymer composites there are several issues to be taken under observation. First prerequisite for the effective enhancement is the dispersion of nanofiller into the host matrix material. The better the dispersion we will get better product. In the case of carbon nanotubes this problem has been the most vital hurdle in getting the theoretical properties of carbon nanotubes to use.

When we use carbon nanotubes in pristine form they tend to form bundles and agglomerates which in result cause poor solution and with different experiments we observe that CNTs get settle on the base of the beaker. In addition to that for better composite properties good interfacial interaction between nanotubes and matrix is required, so that the stress applied on the composite gets transfer efficiently between the filler and matrix. Last but not the least orientation has a great role in the behaviour of composites. Pristine nanotubes can't be adjusted in the matrix in any particular orientation.

## Materials

CNTs were provided by Sigma-Aldrich, the outer diameter of CNTs is around 15 nm and length is in the range of 0.1 to 10  $\mu$ m. The Polyvinyl Alcohol ( $M_w = 84,000 - 124,000$  g / mole, 88% hydrolyzed) used in this experiment was purchased from ERKA and was preheated before use.

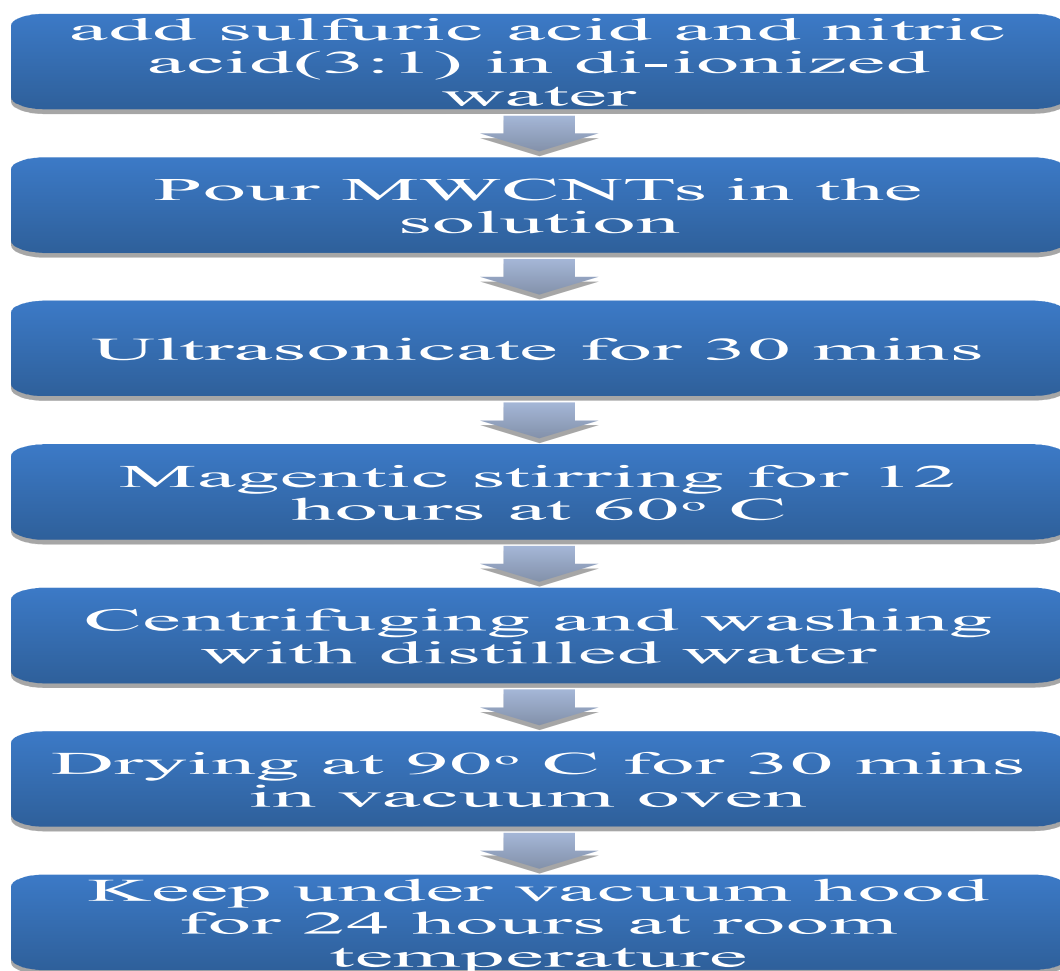
Nitric acid and sulfuric acid were purchased from a local distributor. Both acids were of laboratory grade.

## Functionalization of CNTs

To attach carboxyl group (COOH) and nitride group following method was undertaken:-66 ml of di-ionized water was taken in a 200 ml beaker. 34 ml of nitric acid and sulfuric acid in ratio 1:3 was mixed in this solvent to form mild solution of acid and water. After mild mixing of this solution 1 g CNTs were mixed.

This mixture was kept in the sonicator for 30 mins at room temperature. After that the beaker was placed on a hot plate and stirred magnetically for 12 hours at 60° C. then this solution was

placed under the vacuum hood undisturbed for 1 hour. After that this solution was filtrated with the help of a 0.45 microns nylon filter paper with the help of a filtration assembly powered by a vacuum pump. To neutralize the PH level of cnts and solution, water was mixed repeatedly during filtration. After filtration the cnts on the filter paper were collected on an aluminum foil and placed in vacuum oven. The powder was heated at 90° C for an hour to evaporate remaining solvent.



*Figure 18(Flow chart of procedure to functionalize the carbon nanotubes)*

After keeping the powder in a vacuum oven for 30 mins the powder was placed under a vacuum hood for 24 hours at room temperature.

## Composite preparation

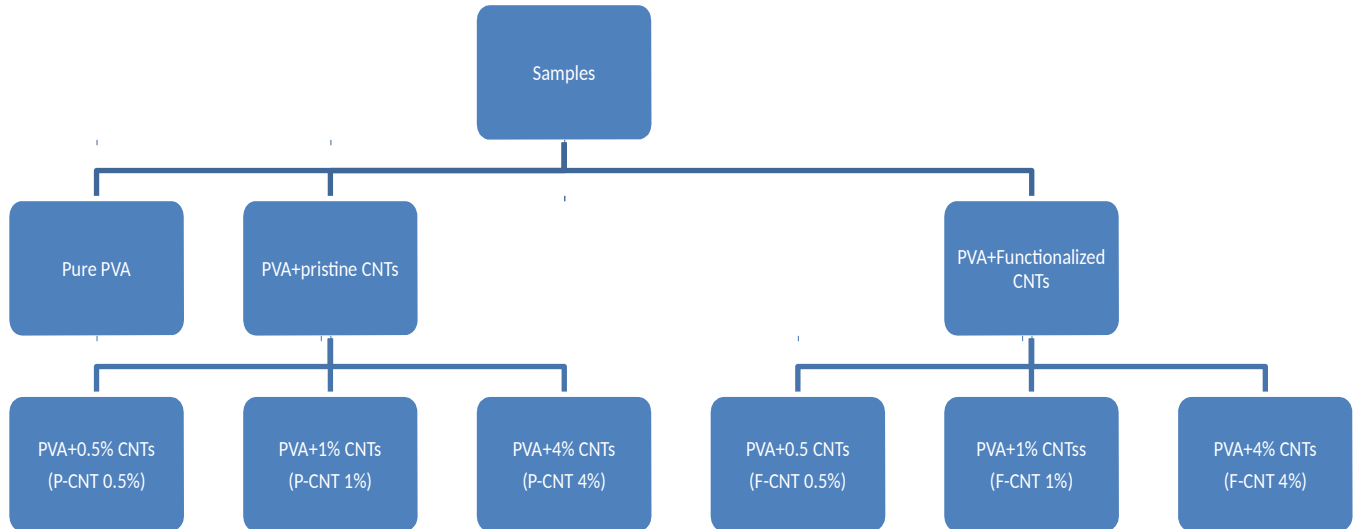


Figure 19(hierarchy chart representing the samples prepared in this research)

Seven different samples (upper image) were prepared with mold casting technique in the form of thin films. Teflon molds were used for this purpose, mold dimensions were 1\*1 inch in a square shape. 80 ml di-ionized water was taken in a beaker and was preheated at 80° C. Then polyvinyl alcohol in powder form was added slowly and temperature was raised to 90° C. The beaker was placed on a hot plate with a magnetic stirrer. This mixture was stirred at 700 rpm for 20 minutes and then at 1100 rpm for 40 mins. When the color of mixture turned transparent from milky then the temperature was cooled down and the beaker was then placed in a sonicator to extract the residue gases present in the mixture. After sonicating the mixture for 20 minutes then solution was ready for further processing.

To make composite films 6 different solutions were prepared in different beakers. The CNTs concentration in these solutions was calculated to form 0.5%, 1% and 4% loading in the required sample. This mixture was stirred mechanically for an hour. Then these mixtures were placed in a

sonicator for one hour. Then these mixtures were poured into Teflon molds and were placed in a vacuum oven at 80° C for degassing. Then the films were dried at room temperature under vacuum hood. The molds were kept under vacuum hood for 24 hours at room temperature.

## Characterization

### 3.5.1 FTIR

Infrared adsorption spectra were obtained from an Perkin-Elmer SPECTRUM1000 FTIR spectrophotometer (resolution 1 cm<sup>-1</sup>) using KBr pellets as standard to investigate that whether required functional groups were successfully attached to CNTs or not.

FTIR works on the basis of the fact that IR spectrum is basically molecular vibrational spectrum. So when any sample is exposed to infrared radiations, the sample molecule absorbs radiation in a specific wavelength. This absorption increases the energy level of molecule from ground state to excited state. The dipole moment of sample also changes due to this absorption. So in the FTIR spectra we calculate the number of peaks which relates to the freedom of vibration in numbers. The change of dipole moment can be calculated through intensity calculation. The number of peaks and intensity at particular wavelengths are analyzed and composition of sample is predicted.

### FTIR Instrumentation

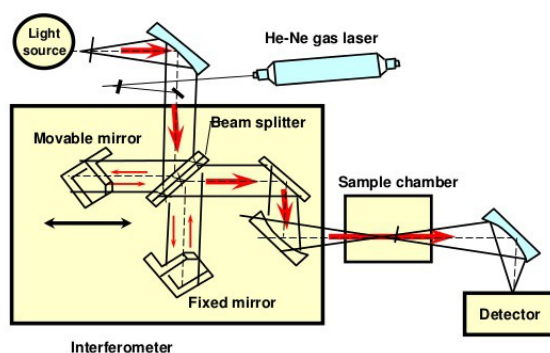


Figure 3.3(Schematic showing the working of FTIR machine)

### 3.5.2 Scanning Electron Microscopy (SEM)

To investigate the morphology of films a JOEL JSM-6490A SEM was used. The samples were coated with gold layer to increase the conductivity which is the basic parameter to test any sample with SEM. Samples were mounted on aluminum stubs for testing.

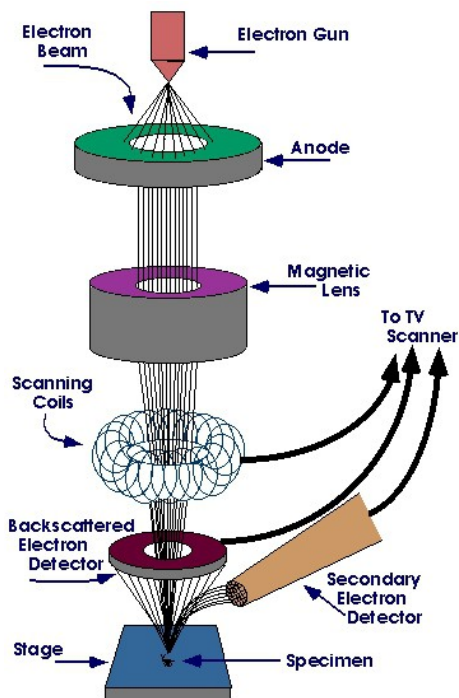


Figure 20(Schematic illustration of Working of Scanning Electron Microscope)

In SEM a gun fires an electron beam with the help of a tungsten wire which heats when current is applied. This beam is accelerated with the help of high voltage created between the anode and wire. This accelerated beam is then focused on the sample using electromagnetic lenses. When electron beams hits the samples several interactions are observed. These interactions are recorded on the detectors then are converted into an electric signal. This electronic signal is used to build an image on the screen.

### **3.5.3 Micro Vickers Hardness (MVH)**

The hardness of samples was measured using a Micro Vickers hardness tester (401 MND) developed by WOLPERT W GROUP. Samples were cut in square form ( $\frac{1}{2}$  inch<sup>2</sup>) and testing was performed 5 times on each sample and the average value was selected.

### **3.5.4 Tensile Testing**

Tensile testing of PVA and PVA-CNTs samples was performed using a TRAPEZIUM-X Universal Testing Machine (Model AG-20KNXD Plus) developed by SHIMADZU CORPORATION at a crosshead speed of 2 mm per minute (ASTM D882). The samples for this specific test were prepared by cutting the casted films in strips with dimensions of 10×80 mm<sup>2</sup> (10=width, 80=length). Gauge length was set at 20mm. 3 strips were prepared from each sample and were tested at room temperature and average value was selected for all the samples.

### **3.5.5 X-ray Diffraction (XRD)**

X-ray diffraction patterns were obtained with a Theta-Theta instrument developed by STOE-Germany at room temperature with Cu K $\alpha$  radiations ( $\lambda=0.15418$  nm) operating voltage was selected at 40KV and current at 40mA. Scanning rate selected was 2°/min over the range of  $2\Theta = 5^\circ - 40^\circ$ .

X-ray diffraction patterns were obtained to investigate the difference between crystallinity of pristine CNTs composites and Functionalized CNTs composites. These patterns can also be used to evaluate the composition of samples and it gives an idea about the functional groups present in the samples.

### **3.5.6 Atomic Force Microscope (AFM)**

AFM is a very precise equipment and yields images with high resolution. Its resolution is in the order of nanometers which is probably 1000 times higher than that of any general lab microscope. This equipment can not only image the sample in 3D topography, but can generate other surface features too. This device can generate images at atomic resolution with angstrom scale height information. This device used a cantilever with a very tiny and sharp tip which scans the surface of the sample. When this nano-sized tip gets closer to the surface the attractive atomic forces between the tip and the surface tend to deflect the cantilever which in response generates



an electric current in the processor of the machine which is shown as an output on the computer screen.

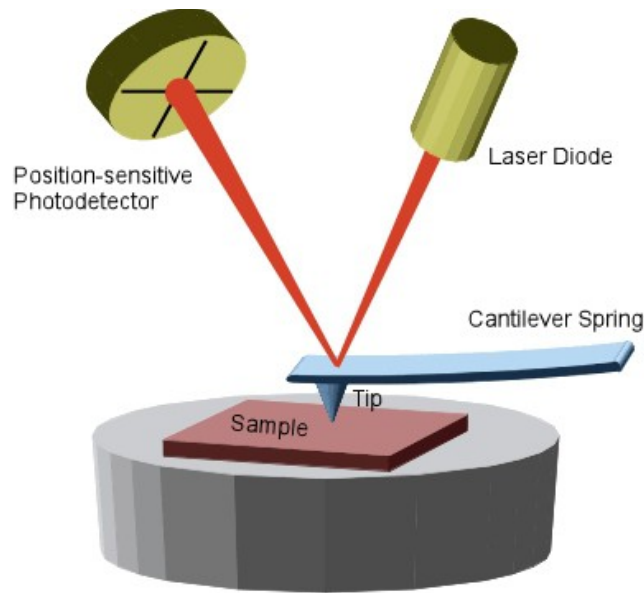
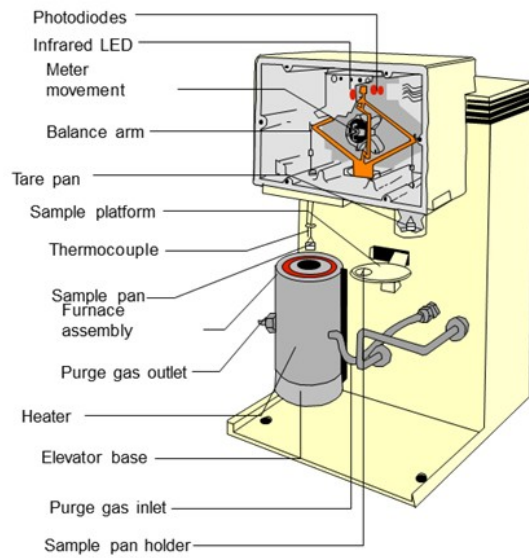


Figure 21(Schematic showing working of Atomic Force Microscope)

### 3.5.7 Thermogravimetric Analysis (TGA)

With the help of a TGA machine the chemical and physical behavior of a material is calculated as a function of mass loss vs temperature or mass loss vs time (constant T). With the help of this technique several material properties can be known such as second order phase transitions, at what temperature the material freezes or melts and glass transition temperature etc. this technique is best used to determine the thermal strength of any material. In Auto industry it plays an active role to determine the performance parameters of any material to be selected. The sample is placed on a ceramic pan, this pan hangs from a small hook which is connected with the balance. When heat is applied the balance sensor detects the weight change of the sample and gives output on a computer software which shows the results in the form of a graph. Schematic is shown in figure 3.5



*Figure 22 Schematic of TGA equipment*

# Results and Discussion

## Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra for PVA-CNTs (Pristine) is shown in figure below.

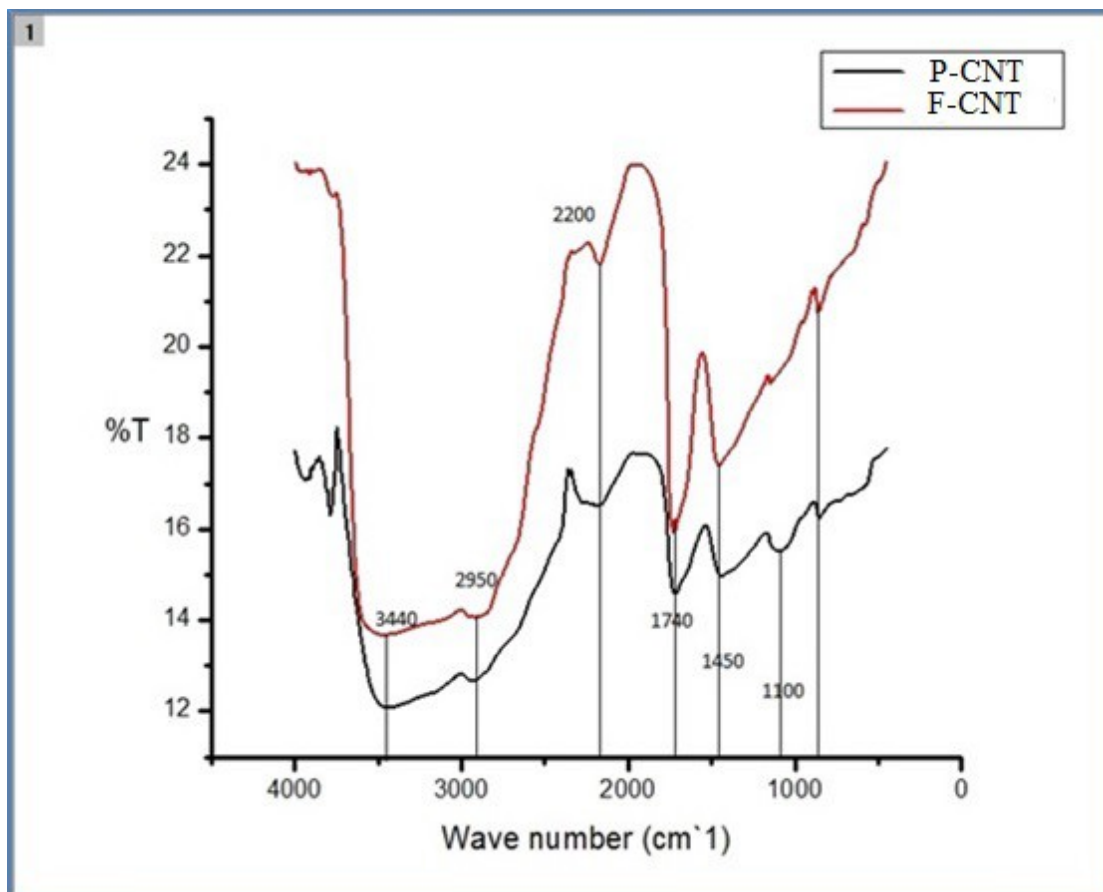


Figure 23(FTIR spectra of Composites)

In this spectra we can see a peak at  $1100\text{ cm}^{-1}$ . This peak represents the  $\pi$ - $\pi$  interactions between the walls of CNTs. By comparing the peaks at  $1100\text{ cm}^{-1}$  we can guess that in functionalized samples the disappearance of peak represents the decrease of CNTs interactions which indicates that functionalization was achieved. Peak at  $1490\text{ cm}^{-1}$  represents the N-O asymmetric stretch which is more prominent in the functionalized CNTs spectra which indicates the presence of an

additional functional bond due to treatment of  $\text{HNO}_3$ . The peak at  $1760\text{ cm}^{-1}$  indicates the presence of  $\text{COOH}$  bonds which again is the indication of functionalization being successfully done on CNTs. Asymmetric and symmetric stretching of  $-\text{CH}_2-$  group appears as absorption band at  $2950\text{ cm}^{-1}$ . Peak at  $3440\text{ cm}^{-1}$  corresponds to the O-H stretch of PVA molecule. Hence, by analyzing both the peaks we can precisely conclude that CNTs have been functionalized.

### **■ X-ray diffraction spectroscopy (XRD)**

X-ray diffraction patterns for pure PVA, PVA/PCNT and PVA/FCNT nanocomposites at different concentrations of MWCNTs is shown in figure below.

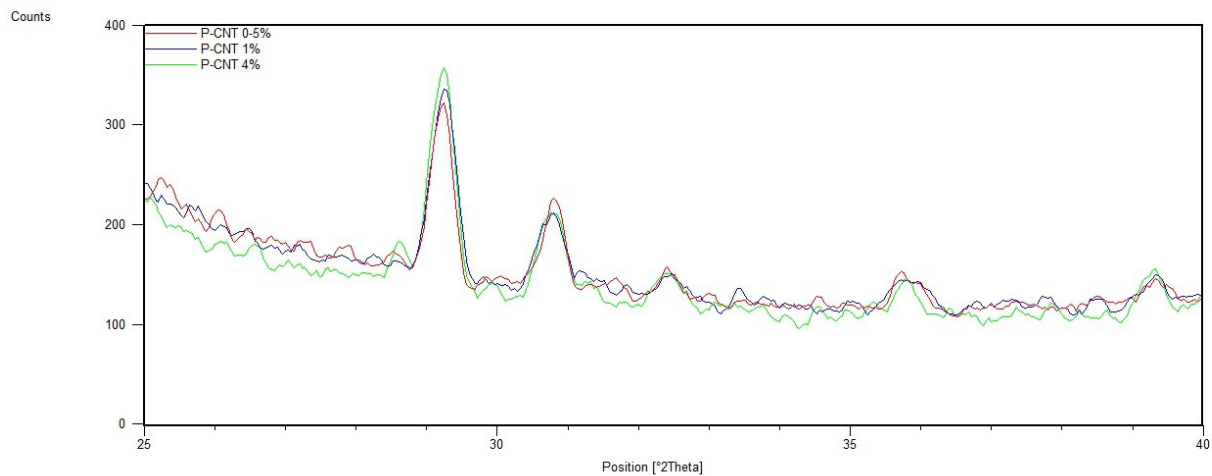


Figure 24(XRD-spectra of Pristine CNT-Composite)

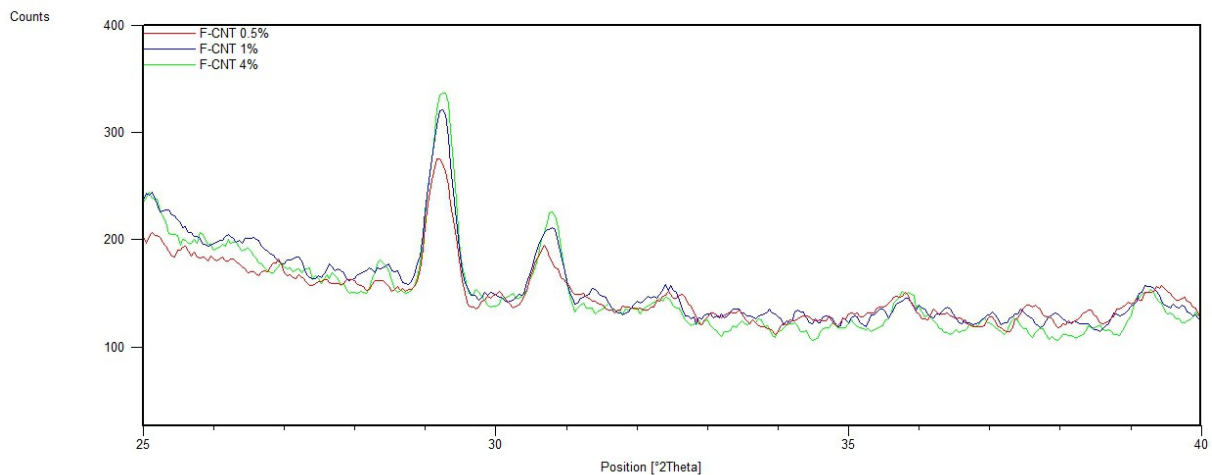


Figure 25(XRD-spectra of Functionalized CNT-Composite)

Both graphs exhibit peak at  $2\theta=29^\circ$  which corresponds with the presence of CNTs in the composite. In both the peaks there is an increase in intensity with increasing the filler ratio. As nanotubes are crystalline in nature they tend to increase the crystallinity of semi-crystalline PVA. This increase in crystalline nature of PVA due to addition of a crystalline filler is more prominent in the functionalized CNTs, which indicates the successful bonding of functional groups to the

nanotube walls. More increase in crystallinity in the functionalized composite also represents the decrease of agglomeration of the filler.

### Scanning electron microscope (SEM)

Figure below shows the SEM micrographs of PVA-CNT composite at different magnifications at loading of 4% filler. Only 2 of the samples were scanned in SEM.

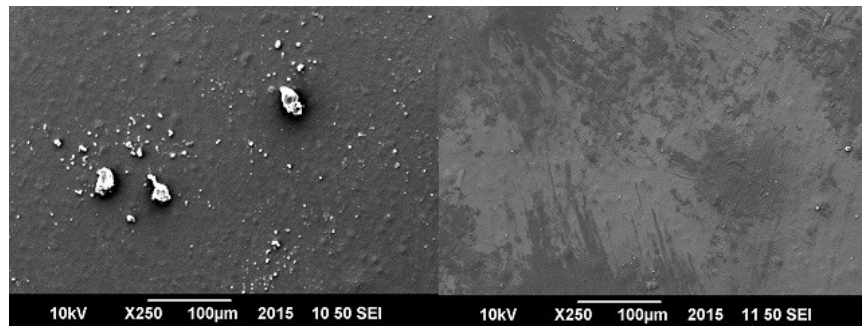


Figure 26 SEM image of P-CNT 4% at 250x on the left side, F-CNT 4% on the right side)

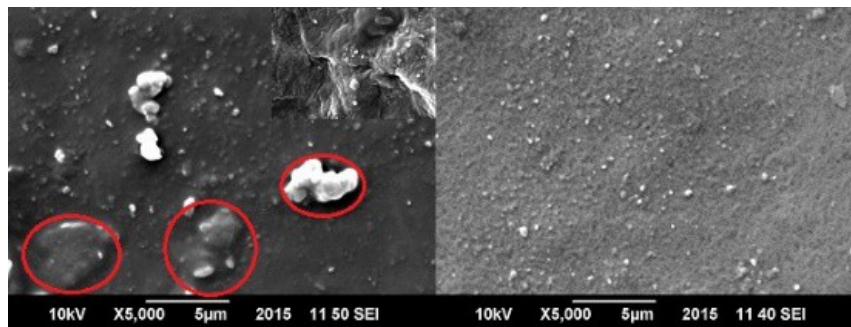


Figure 27 SEM image of P-CNT 4% at 5,000x on the left side, F-CNT 4% on the right side)

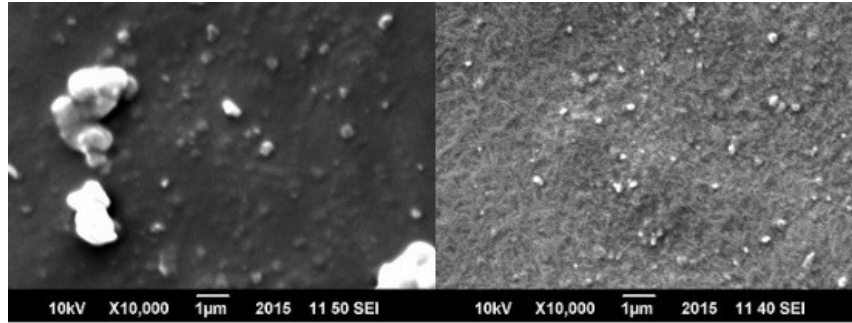


Figure 28(SEM image of P-CNT 4% at 10,000x on the left side, F-CNT 4% on the right side)

The left side of the images are the samples with pristine CNTs and right side of the images are from the samples that contain functionalized CNTs. As we can see that in the samples with pristine CNTs there are many bundles of agglomerated CNTs present and in the right side images the CNTs are very well dispersed and there are no signs of agglomerates.

The agglomerates present in the pristine sample in red circled in the SEM images.

## Atomic Force Microscopy (AFM)

3d AFM images of composite films of pristine and functional CNTs both with filler ratio of 4% are shown below.

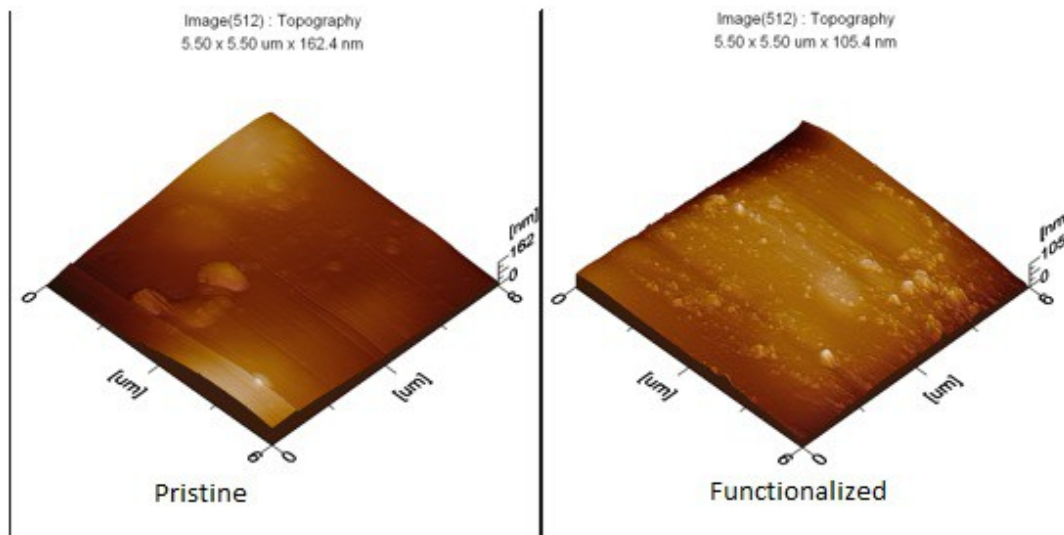


Figure 29(AFM images of Composite films. Pristine on the left side, Functionalized on the right side)

It can be seen that roughness of the sample is increased due to homogenous dispersion of CNTs in the sample. While the sample with Pristine CNTs shows a plane surface which can be identified as PVA. And CNTs can be found on the surface in the form of large agglomerate. In the sample on the right side there is no agglomeration of CNTs and surface is rough. However this trend gets reversed on the macroscopic level where the sample with pristine CNTs gets rougher due to agglomerates.

### Micro Vickers Hardness

The values of Micro Vickers Hardness for all the samples is given in the table below.

Sample name	Value 1 (HV)	Value 2 (HV)	Value 3 (HV)	Average value (HV = MPa)
PVA	9.9	9.9	10.3	10 = 98.1
P-CNT (0.5%)	11.9	12.2	12.1	12 = 117
P-CNT (1%)	12.4	12.5	12.8	12.7 = 124.5
P-CNT (4%)	14.1	14.2	13.8	14 = 137
F-CNT (0.5%)	13	13.6	13.2	13.25 = 130
F-CNT (1%)	15	15.1	14.6	14.8 = 146
F-CNT (4%)	15.7	16	15.9	15.8 = 155.7

Table 4.1 Table illustrating the Micro Vickers hardness values for the samples

Comparison of hardness values with increasing filler content is shown in the graph below.

It can be seen that with increasing the filler content the hardness values of samples progressively increase.

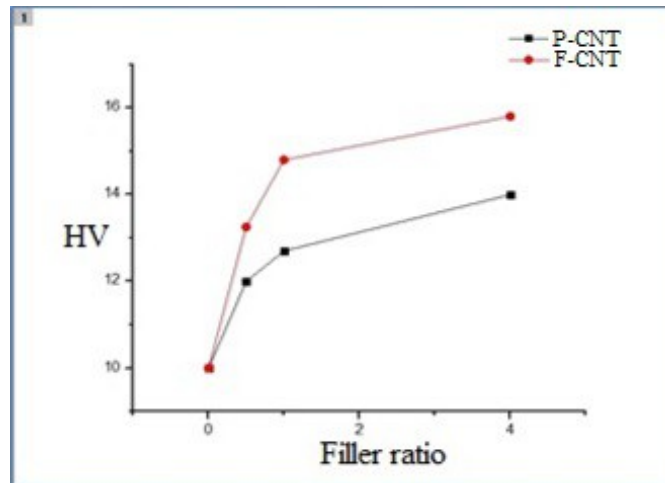


Figure 30(Graph of Hardness values)



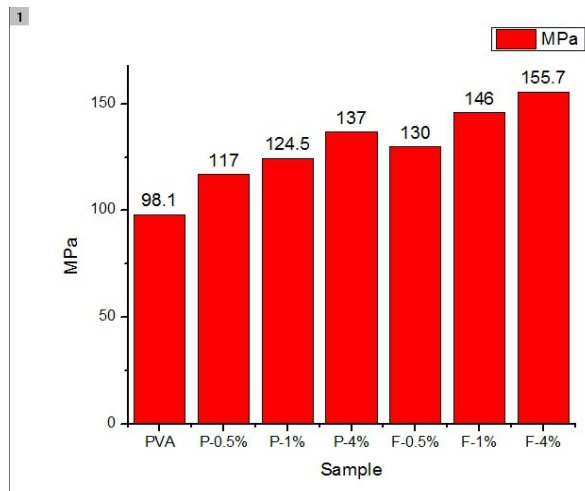


Figure 31(Bar graph of Hardness values In MPa)

This increase in hardness can be attributed to the binding effect of CNTs. As the length to diameter ratio of CNTs is very high that's why there is improvement in the stress transfer from matrix to the filler. At a given strain the filler carries more stress than the matrix as it is stiffer than the matrix.

When comparing pristine samples with the functionalized samples we can see that hardness value of samples increase considerably. This is due to better interaction of the filler with the matrix due to less agglomeration. The functional groups attached with CNTs restrict matrix movement which makes the composite stiffer and harder which can be seen from the hardness values given above.

## Tensile Testing

Sample name	Tensile strength(MPa)	Elongation (%)	Young's Modulus(GPa)
PVA	19.5	225	8.4
P-CNT (0.5%)	24	180	10.2
P-CNT (1%)	25.2	145	10.7

P-CNT (4%)	26.9	48	11.6
F-CNT (0.5%)	26.4	210	11.4
F-CNT (1%)	28.7	160	12.3
F-CNT (4%)	31.4	55	13.6

Table 4.3(Tensile testing results of Nanocomposites)

Tensile testing of the samples was carried out according to ASTM D-882, specified for reinforced polymer nanocomposites. The samples were cut in rectangular form in 10×80 mm<sup>2</sup> dimensions according to D-882. These samples were tested on a TRAPEZIUM-X Universal Testing Machine (Model AG-20KNXD Plus) developed by SHIMADZU CORPORATION. The data for tensile strength and modulus is given in the table 4.2. Figure 4.11 and figure 4.12 show the trends of tensile strength and modulus, it can be seen that both properties follow same trend. As the filler content is increased the strength and modulus also increase. But as the filler content is increased further we can see a decline in the slope of tensile strength, which indicates that the impact of Nano fillers on the properties starts decreasing after achieving a maximum point.

Figure 4.10 shows the graph of percentage elongation against filler content. We can see that with increasing filler content a sharp decline in the elasticity of films is observed which is largely due to the increased rigidity of material.

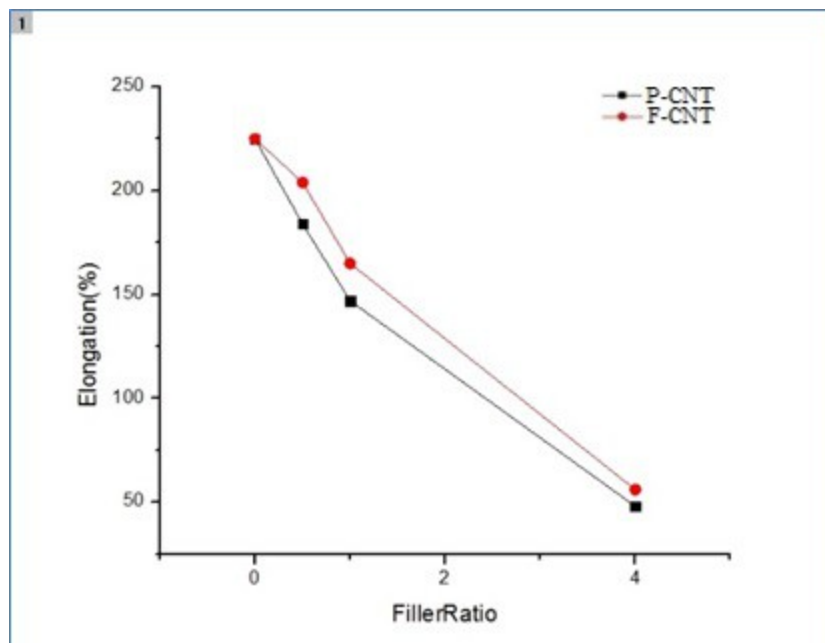


Figure 32(Graph of Results representing percentage elongation)

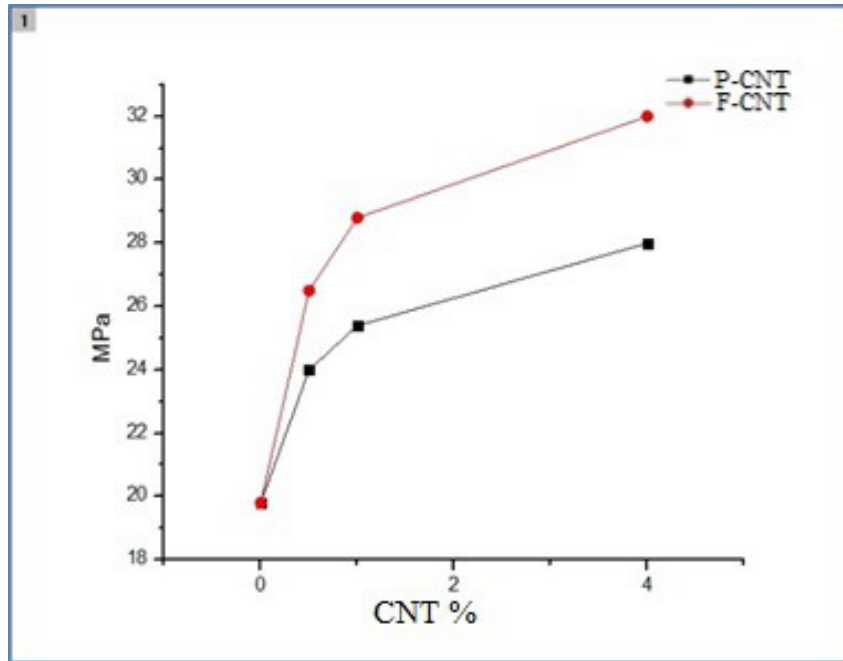


Figure 33(Graph of results representing Tensile Strength of Samples)

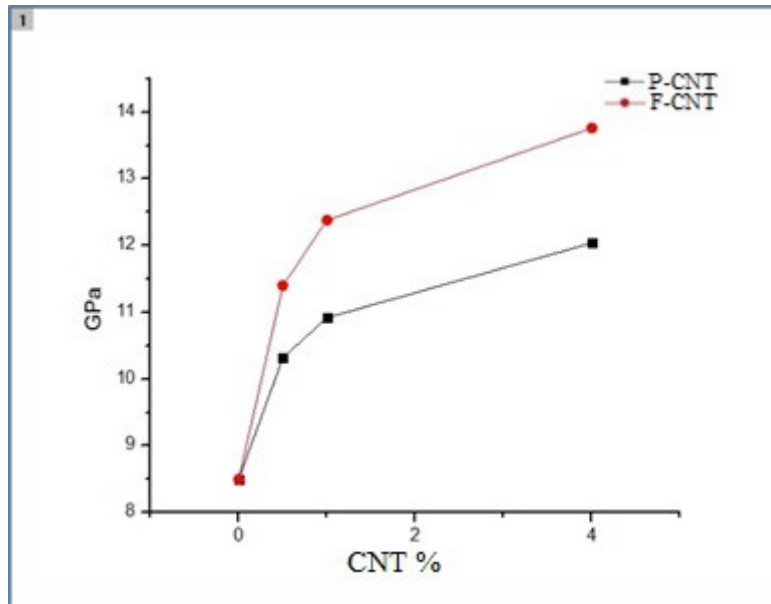


Figure 34(Graph of results representing Young's Modulus of Samples)

## Thermogravimetric Analysis (TGA)

The TGA curves of five of the samples were taken in N<sub>2</sub> atmosphere. In the graph below we can see that at 100° C all the samples show a decrease in weight due to vaporization of water content present in the samples. From 100° C to 280° C all the samples show linear behavior with no weight loss. At 280° C we can see weight loss in the pristine sample with CNT ratio of 0.5%. Sample of functionalized CNTs with filler ratio of 0.5% also show similar behavior. But at greater filler concentrations we can see an obvious difference between the degradation temperatures of samples. Pristine sample started degrading at 310° C and the functionalized sample started degrading at approx. 340° C, which is a very significant different.

Hence we can conclude that with functionalization of CNTs the thermal stability of nanocomposites increases significantly.

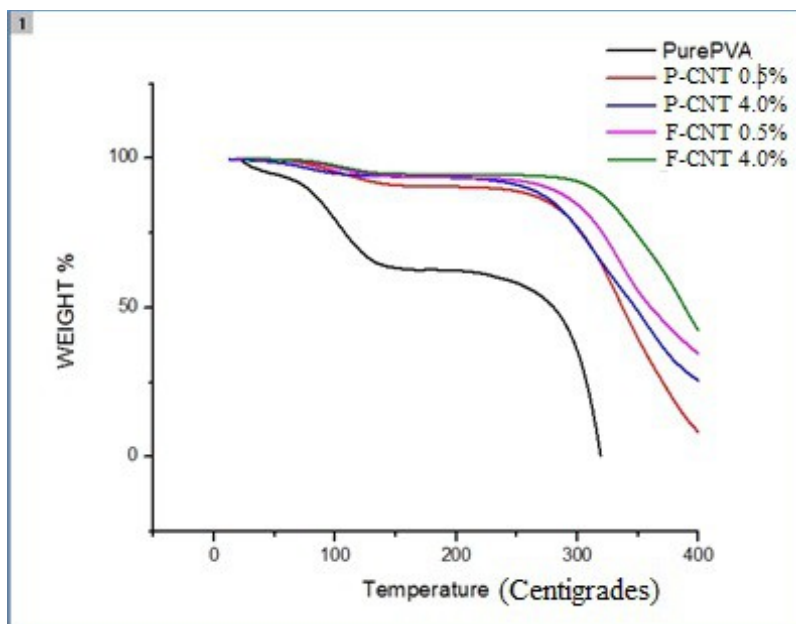


Figure 35(Thermogravimetric results illustrated in a graph)

### ■ Differential Scanning Calorimetry (DSC)

The DSC curves of four samples for comparison has been shown in the figure below. An endothermic peak can be observed in all four samples between the ranges of 300° C and 340° C. we can see a gradual increase in the temperature of these peaks with increasing filler ratio and functionalization also increases this temperature. If we calculate the area under the curves we can get the crystallization of samples which can be then compared with XRD data which will support the claim that with functionalization and increasing the filler quantity crystalline nature of nanocomposites increases.

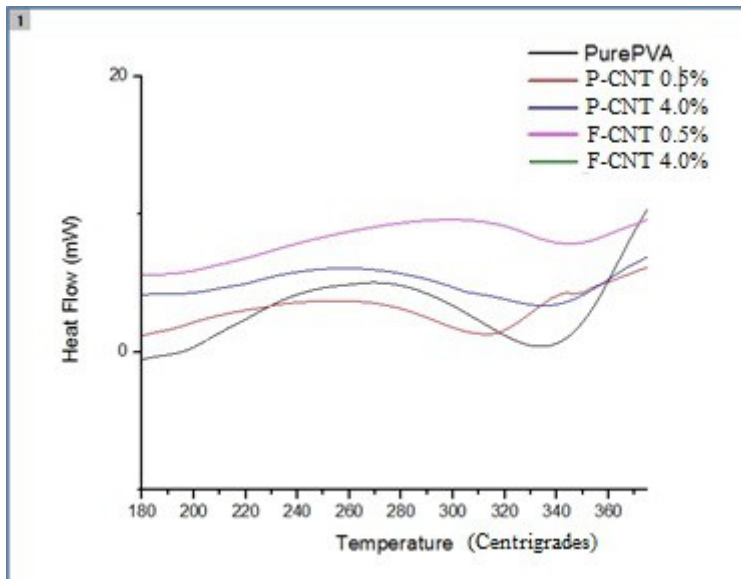


Figure 36(DSC graph of Samples)

## Conclusion

In this research several Polymer Nano composite samples with varying CNT ratio and modification were prepared. Polyvinyl alcohol was selected as a matrix and CNT's were functionalized with the help of nitric acid and sulfuric acid. Three samples were prepared with pristine CNTs in 0.5%, 1% and 4% ratio of filler respectively. Other three samples with the same

filler ratio were prepared but CNTs were functionalized in this case. 1 sample was pure PVA film which was used as a standard to compare the results.

To investigate the functionalization of carbon nanotubes FTIR of these samples was carried out which successfully showed the presence of carboxylic and nitric groups in the functionalized samples.

For the investigation of improved mechanical strength several techniques were employed such as Tensile and Vickers hardness test. Both the techniques showed an improvement in the hardness, tensile strength and young's modulus of the samples. All the results were compared with each other after which it was concluded that the hardness of samples was increased (22% in case of 0.5% pristine CNTs, 60% in case of 4% functionalized CNTs).

Similar trend was seen in the case of tensile strength. Sample containing 0.5% pristine CNTs showed an increase of 20%, and sample containing 4% functionalized CNTs showed an increase of 61%.

TGA results showed an increase in the thermal stability of nanocomposites with increasing filler ratio. The sample containing 0.5% filler content start degradation at 290<sup>0</sup>C and the sample having 4% functionalized CNTs show thermal degradation curve at 320<sup>0</sup>C.

The assumption that this improvement of mechanical and thermal properties is due to better dispersion of CNTs after functionalization was further proved from the images taken by SEM and AFM. Which showed homogenous dispersion of CNTs in the functionalized Nano-composites.

Hence, this research successfully proved that addition of Nano fillers in polymer matrices improve the mechanical and thermal properties. And these properties can further be efficiently enhanced when better dispersion and better interaction of filler and matrix is achieved through the process of functionalization.

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