Influence of Carbon Nano Tube on Dielectric Behaviour of Poly (Vinylidene Fluoride) Composite Films

A

Thesis

Submitted in partial fulfilment

Of

The requirement for the award of the degree

Of

MASTER OF TECHNOLOGY (M. Tech.)

In

MATERIAL SCIENCE & ENGINEERING

By

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UNDER THE GUIDANCE

Of

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SCHOOL OF PHYSICS & MATERIAL SCIENCE

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2007

Dedicated

To

My Parents

CERTIFICATE

This is to certify that the thesis entitled **" Influence of Carbon Nano Tube on Dielectric Behaviour of Poly (Vinylidene Fluoride) Composite Films"** which is being submitted by ***Vajinder Singh*** in Partial fulfilment of the requirements for the award of the degree of ***Master of Technology (M.Tech.) in Material Science and Engineering*** of Thapar University, Patiala (India), is a record of the study conducted by him under my supervision and guidance and that no part of this thesis has been submitted for the award of any other degree.

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M.Tech (Material Science & Engg)

Contents

LIST OF SYMBOLS AND ABBREVIATIONS

CNT	Carbon nanotube
CVD	Chemical vapor deposition
^{o}C	Degree Celsius
ε	Dielectric Constant
C	Capacitance
CNT	Carbon Nanotubes
d	Sample Thickness
DC	Direct Current
DMF	N,N-Dimethylformamide
DSC	Differential Scanning Calorimetry
ΔH	Heat Capacity
LBL	Layer-by-layer
MWNT	Multiwall carbon nanotube
PTFE	Polytetrafluoroethylene
PVDF	Poly (vinylidene fluoride)
SWNT	Single wall carbon nanotube
T_g	Glass Transition Temperature
T_m	Melting Temperature

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Abstract

The state-of-the-art properties of PVDF-MWCNT materials have been reviewed in the context of their structural, electrical, and dielectric properties. The novel idea of nano dispersion to make nano-composite has been discussed and future directions investigated. PVDF-MWCNT composites are widely used in sensor, transducer and actuator application. In Comparison to pure PVDF or CNT materials, they have an advantage of mechanical flexibility. In this research work, an attempt way made to understand the processing and characterization of PVDF-MWCNT nanocomposites and to determine the changes in the PVDF morphology and other material parameters. In addition PVDF-MWCNT composites show a linear increase in the percentage of crystallinity with the increase of MWCNT concentration in the composite. Dielectric spectroscopy results indicate that by increasing the MWCNT concentration in the composite, the dielectric constant and the polymer conductivity increase.

Chapter 1

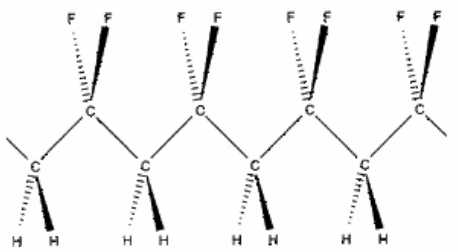
1.1 Review

In recent years, polymers materials have attracted the attention of chemists, physicists and material scientist & technologist alike considering their novel physical properties, their electrical and dielectric properties have made an important futuristic material. The phenomenon of piezoelectricity can be observed in crystalline materials or in crystalline region of semi-crystalline materials due to lack of center of symmetry. It is possible to develop a piezoelectric amorphous polymer by adding dipoles that behave similar to the dipoles in the crystalline region of piezoelectric polymers. If the unit cell of the crystal lattice is such that the center of gravity of its positive charges does not coincide with that of the negative charges, it creates a permanent dipole. A macroscopic electrical polarization is observed if the dipoles are aligned throughout the crystal. Applying external mechanical stress will strain the dipoles, which alters the polarization so that electric charges appear on the surface of the crystal; this is the direct effect mentioned. Conversely, applying an external electric field to the crystal will deform the natural dipoles inducing strains that change the dimensions of the crystal. The practical use of piezoelectric materials became possible with Paul Langevin's discovery of the sonar in 1917 during World War I. The use of piezoelectricity in sonar, create intense interest in piezoelectric devices.

The existence of piezoelectric polymers has been known since 1924. However, the early known piezoelectric polymers did not receive much attention because of their weak electro-mechanical response. A growing interest starts after the work by Fukada in the 1950’s and 1960’s, which is the discovery that rolled films of polypeptides and numerous other polymers induce surface charges when stressed. A major milestone in this field was recorded with Kawai's discovery of the strong piezoelectric effect in polyvinylidene fluoride (PVDF) in 1969. Later, other PVDF co-polymers were also reported to be piezoelectric, including P (VDF-TrFE) and P (VDF-TFE).

1.2 PVDF polymer

Ppoly (vinylidene fluoride). It is also known as poly (1, 1-difluoroethlene) with a repeat unit (CH2-CF2) **as** shown in fig 1**.** PVDF was discovered as part of Dupont's research on fluoropolymers; the company went on to develop polyvinylidene fluoride (PVDF) in 1961 and commercially introduce it in 1965. The breakthrough came in 1969, when Kawaii discovered the exceptional piezoelectric behavior of PVDF, which at that time was the highest among the known synthetic polymers. After more than 30 years of study and development, the piezoelectricity and electromechanical properties of PVDF and its copolymers have been improved significantly. Today, this class of polymer still possesses the highest electromechanical responses over a broad temperature range among known synthetic organic materials and it is the only commercially available piezoelectric polymer.



Molecular structure of PVDF polymer chain

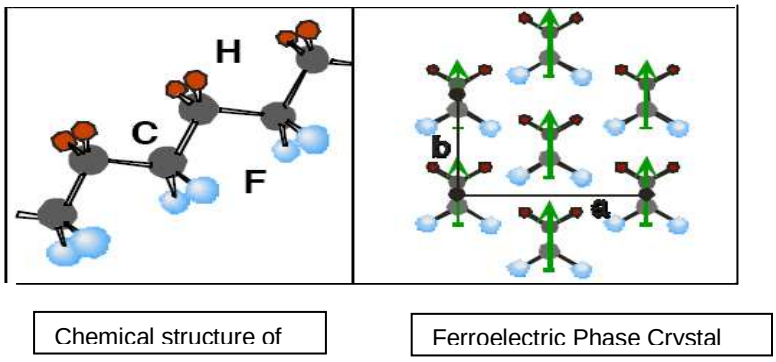


Fig1: Molecular structure, chemical structure and ferroelectric phase crystal structure

PVDF has a simple chemical formula, intermediate between polyethylene (PE) (CH2-CH2), and polytetrafluoroethylene (PTFE) (CF2-CF2-). This simplicity of chemical structure gives PVDF both strength and toughness as reflected by its tensile properties and impact strength. In thin sections, such as films, filament, and tubing, PVDF components are flexible and transparent. PVDF has outstanding properties, such as high dielectric constant, high strength, high thermal stability, resistance to most chemicals and solvents, resistance to ultraviolet and nuclear radiation, and resistance to weathering. PVDF can take many molecular and crystal structures, which change depending on the preparation conditions of the sample .Table1 shows some important Physical properties of PVDF film

Table 1 Piezoelectric, pyroelectric, thermal expansion coefficients and mechanical properties of PVDF film.

Material property	Coefficient	Biaxially oriented film	Uniaxially oriented film
Piezoelectric coefficient (pC/N)	d_{31}	4.34	21.4
	d_{32}	4.36	2.3
	d_{33}	-12.4	-31.5
	d_h	- 4.8	- 9.6
	$d_{33}{}^a$	-13.5	- 33.3
Pyroelectric coefficient (10^{-5} C/m^2 K)	P_3	-1.25	- 2.74
	P_3 *calculated*	-0.44	-1.48
Thermal expansion coefficients (10^{-4} K^{-1})	α_1	1.24	0.13
	α_2	1.00	1.45
Mechanical Properties	E (10^9 Pa)	2.5	2.5
	K (10^{-10} Pa^{-1})	2.6	2.6
	ν	0.392	0.392
	S_{11} (10^{-10} Pa^{-1})	4.0	4.0
	S_{12} (10^{-10} Pa^{-1})	- 1.57	- 1.57
	C_{11} (10^9 Pa)	5.04	5.04
	C_{12} (10^9 Pa)	3.25	3.25

There are four known crystal forms of PVDF, three with permanent dipoles (β, γ and δ phases), where β-phase is highly polar compared to the other two phases, and one non-polar phase, which is the α-phase. The α-phase is the most common phase and can be obtained from melt directly. The chains are packed within the crystal lattice in specific conformation. The crystal structures are described by conformations of the chains as a series of trans (T) or gauche (G) linkages, by the orientation of these chains sequences about the chain axis (parallel or antiparallel) and by the relative directions of adjacent chains up-up (same direction) or down-down (opposite) direction as shown in fig1.2. Each phase will be described below.

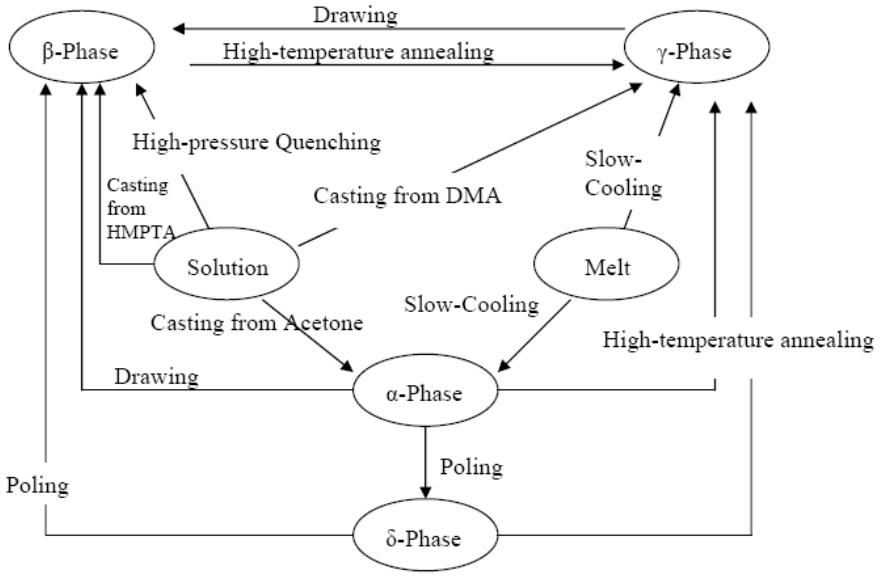


Fig1.1: Production and conversion of the crystal forms of PVDF

Form I or β-phase has all-trans (TTT) conformation. All chains are oriented essentially parallel to the b-axis as shown in fig 3 of the unit cell with dipoles pointed in the same direction, resulting in a non-centro symmetric crystal; β-phase PVDF has the highest piezoelectricity. Form II or α-phase has a trans-gauche-trans-gauche' (TGTG') conformation with individual chains arranged to yield a centro symmetric unit cell. Thus an anti-polar crystal resulted. Form IIp or δ-phase has the same conformation as form II and follows from this form by rotation of every second chain such that all chains are

aligned. Form III or γ-phase has a trans-trans-trans-gauche (TTTG) conformation; the molecular chains are packed in a parallel non-centro symmetric, polar crystal.

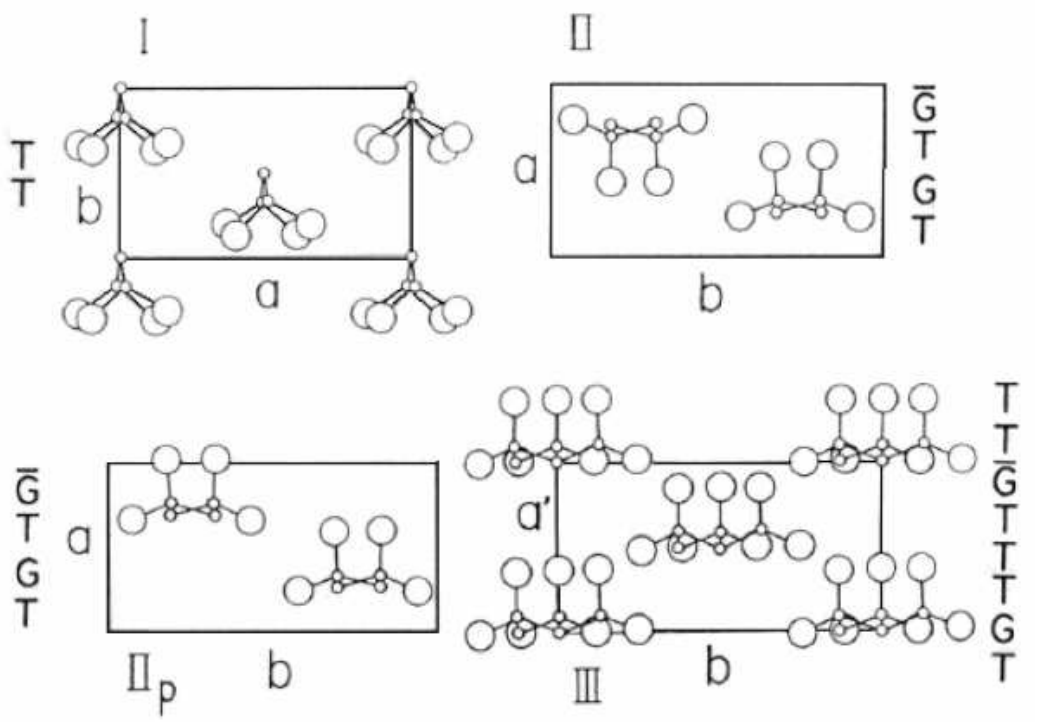


Fig1.2: The conformation of the four PVDF phases

1.3 Processing of Piezoelectric PVDF Film

The non-polar α-phase is obtained by cooling the melt at a normal rate (10-20°C or higher) as show in fig1.1.In the α-phase, the polymer crystals are very small and arranged as spherically symmetric polycrystalline aggregates called spherulites that have no net polarization. These spherulites are composed of 10-20 nm thick crystalline lamellae that grow out from the center of the spherulite and have the noncrystalline component interposed between them as shown in fig 1.3. The most common technique to obtain macroscopically polar PVDF film or conversion from α-phase to β-phase is by the mechanical stretching of the film and then electrical poling to align the dipoles in the same direction

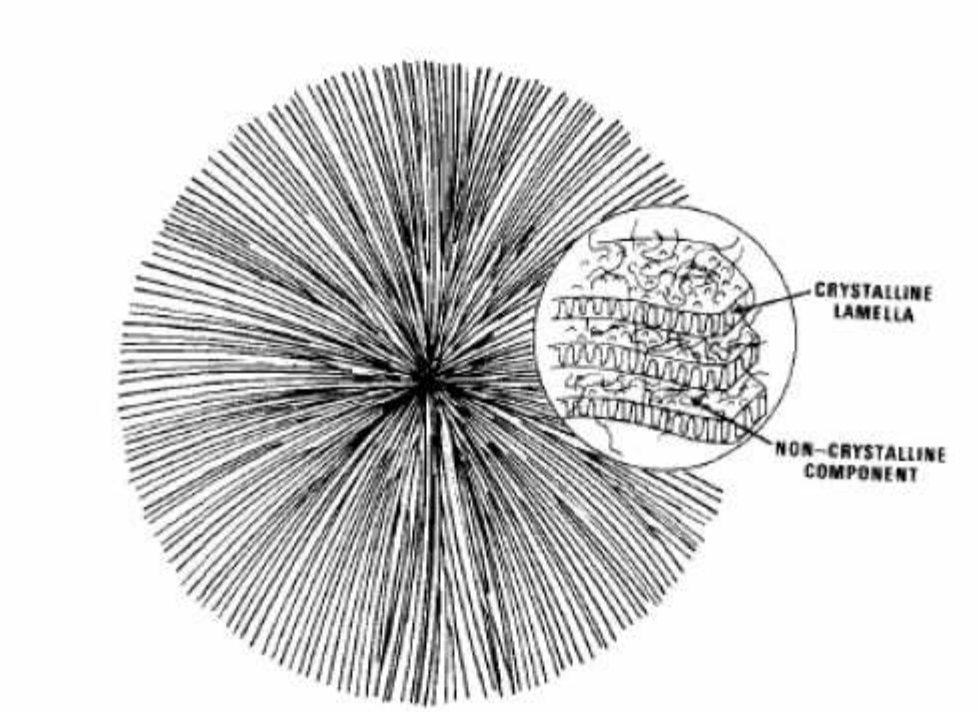


Fig1.3: A schematic diagram of a spherulite and detail of section emphasizing the Lamellar structure (3)

Typically, the film is stretched 3-7 times its length at elevated temperatures (60-140°C) and then cooled at a rate of 10-20°C/min or higher while still in the stretched state. Mechanical drawing or stretching of the sample causes a breakdown of spherulites and orientation of molecular chains in the direction of the force. The drawing also rotates the $-CF_2-$ dipoles in the direction of the film thickness. From this point, the film is poled to align the oriented dipoles of the β-phase and create the necessary strong resultant dipole moment and remnant polarization. The remnant polarization P_r is the polarization during poling minus the electronic and the atomic polarization that relaxes at room temperature once the field is removed. Remnant polarization is the measure of degree of piezoelectricity in the material; the higher the P_r the more piezoelectric is the material. fig1.4 shows a schematic diagram of the common process for obtaining piezoelectric PVDF film.

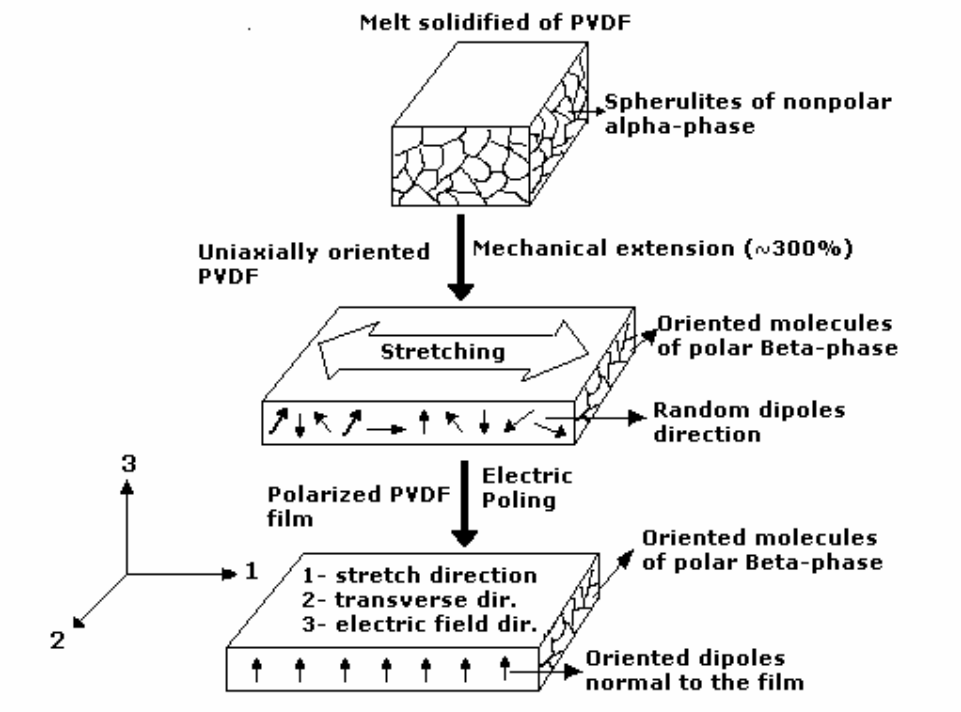


Fig 1.4: Schematic diagram of the common process in preparing piezoelectric PVDF

A common method of poling is to apply a static electric field on the order of 0.5 MV/cm at approximately 100°C with a low current, high voltage DC power supply for up to one hour; this is called thermal poling as shown in fig1.5. Commercially available PVDF films, however, are typically poled via corona poling fig1.5B because this technique is amenable to mass production and results in a product with a more stable polarization over time. In this process, a corona discharge caused by a high electric field, ionizes the air surrounding a grounded sample; these ions deposit and create a potential across the sample resulting in poling.

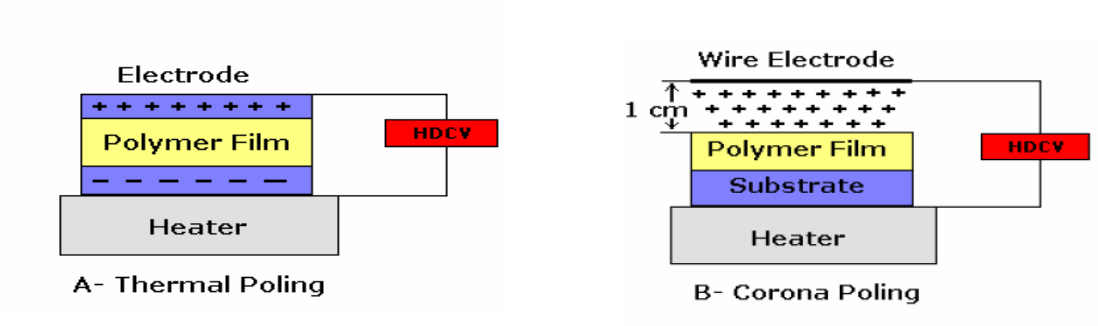


Fig1.5: Types of polymer poling.

1.4 Carbon nanotubes

The carbon nanotubes (CNT) were discovered in 1976 when Endo synthesized vapour-grown carbon fibers, however at the time, it was not given any thought and focus. It was only after Iijima's work in 1991that global scientific attention was turned to these interesting carbon structures and intense studies on the properties, structure, and applications of these unique materials have been carried out.

CNTs are considered to be a rolled-up graphene sheet that forms long concentric cylinders. Bonding in CNTs is essentially sp^2; the circular curvature causes σ bonds to be slightly out of plane, the π orbital is more delocalized outside the tube. The properties of nanotubes depend on the structure, morphology, diameter, and length of the tubes. The structure of carbon nanotubes is described in terms of the tube chirality, which is defined by the chiral vector C_h and the chiral angle θ as shown in fig1.6. The chiral vector indicates the way, in which graphene is rolled-up to form a nanotube. The chiral vector is described as:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$

where the integers (*n*, *m*) indicate the number of steps along the zigzag carbon bonds of the hexagonal lattice, $\vec{a}_1$ and $\vec{a}_2$ e unit vectors . The chirality of the carbon nanotubes has a huge impact on their properties, especially electronic ones.

There are two main kinds of CNTs:

 Single wall carbon nanotubes (SWNTs) are hollow single cylinders of a graphene sheet, which are defined by their diameter and their chirality. The diameter of SWNTs varies from 0.5 to 5 nm. Depending on the chirality SWNTs may either be metallic or semiconducting.

 Multiwall carbon nanotubes (MWNTs) are a group of concentric SWNTs often capped at both ends, with diameters in the range from several nanometers up to 200 nm. These concentric nanotubes are held together by vander Waals bonding. MWNTs form complex systems with different wall numbers, structures, and properties and additional features such as: tips, internal closures within the central part of the tube, forming a so called "bamboo" structure as shown in fig1.7 and even an angle Y-junction formation of MWNTs.

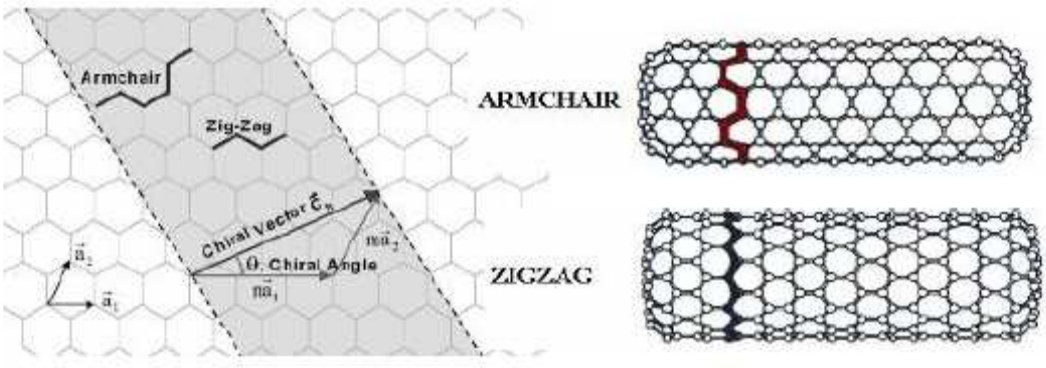


Fig1.6: By rolling a graphene sheet in different directions typical nanotubes can be Obtained

Due to their properties CNTs have become very promising fillers for the fabrication of new advanced composite systems. It is commonly understood that carbon nanotubes cannot be utilized without any supporting medium, such as a matrix, to form structural components. Therefore, significant developments have been the subject of numerous studies in processing CNTs and CNT/polymer composite films or fibers [4, 5, 6, 7, 8].

The effective utilization of CNTs in composite applications depends strongly on the ability to disperse them homogeneously throughout the matrix. Chemical modifications have become an important issue due to the poor solubility of the CNTs in almost any solvent. Therefore, various functionalization strategies of the surface of the carbon nanotubes have been developed. Chemical modification of CNTs ensures good dispersion of nanotubes in a medium, and enhances the interfacial bonding between filler and matrix, which is crucial to achieve a load transfer across the CNT-matrix interface.

This is a necessary condition for the improvement of the mechanical properties of such composites and better stability of the systems. Various studies include amorphous, semi-crystalline, thermoplastic, water-soluble and conjugated polymers; resins, ceramics, and metal matrices as a supporting material for CNTs. As a result of the presence of CNTs in composite, improvements of the properties of the matrix material such as: enhanced mechanical performance, high electrical conductivity, better thermal conductivity, and anisotropic optical properties.

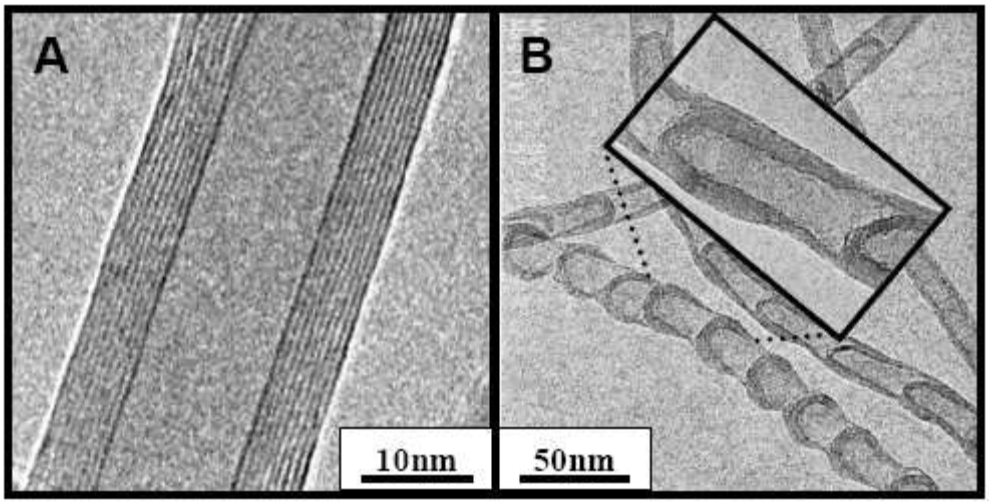


Fig1.7: High resolution transmission electron microscope images of MWNTs used in this study: A) multiwall carbon nanotube (“hollow”) and B) “bamboo” type of MWNT

1.5 Manufacturing methods

At present carbon nanotubes are manufactured by different methods in laboratories and industry. The production of CNTs with a high order of purity, large amount, low costs, and uniformity are still one of the biggest issues in the carbon nanotube society. The most common techniques are in Table 2

Table2: An overview on the most common CNTs synthesis techniques and their advantages and disadvantages

Method	*CVD*	*Arc Discharge*	*Laser Ablation*	*HiPCO*
Basics	Decomposition of hydrocarbon gases in the presence of metal catalyst particles	Electric arc discharge generated between two graphite electrodes under an innert atmosphere (argon, helium)	Graphite target is vaporized by laser irradiation under flowing innert atmosphere and high temperature	Gas-phase growth of singlewall carbon nanotubes with carbon monoxide as a carbon source at high temperature and pressure
SWNT	long, 0.6 - 4 nm diameter	short, 1.2 - 1.4 nm diameter	long, 1-2 nm diameter	~0.7 nm diameter, various lengths
MWNT	long, 10-200 nm diameter	short, 1-3 nm diameter	not applicable but possible	not applicable
Yield	up to 100 %	up to 90%	up to 65 %	up to 70 %
Advantages	high purity, large scale production, simple	easy, defect-free nanotubes, no catalyst	high purity, defect free SWNTs	large scale, high purity
Disadvantages	limited control over the structures, defects	short, tangled nanotubes, random structures	expensive, low scale production	defects

1.6 Properties of CNTs

Carbon nanotubes have gained in interest as nanoscale materials due to their exceptional, Outstanding properties such as: extremely high Young's modulus and ultimate strength, high electric and thermal conductivity. Moreover, CNTs provide a remarkable model of a 1D system. More details on the properties of carbon nanotubes are presented below.

- **Mechanical properties:**

The structural properties of CNTs with strong σ bonds between the carbon atoms give nanotubes a very high Young's modulus and tensile strength. The strength of the carbon-carbon bonds in-plane, along the cylinder axis, retains the structure exceptionally strong

resistance to any failure. CNTs also have very good elasto-mechanical properties. The two dimensional (2D) arrangement of the carbon atoms in a graphene sheet permits a large out-of- plane distortion. Both experimental and theoretical investigations show extraordinary mechanical properties of individual MWNTs with Young's modulus being over 1 TPa and a tensile strength of 10 - 200 GPa , which is several hundred times more than that of steel, while they are only one-sixth as heavy. The elastic response of a nanotube to deformation is also remarkable: CNTs can sustain up to 15 % tensile strain before fracture. Nanotubes are shown to be very flexible, with the reversible bending up to angles of 110º for both SWNT and MWNT. Due to the extremely high strength of CNTs, they can bend without breaking. All of these properties open up broad possibilities for the use of CNTs as lightweight, highly elastic, and very strong composite fillers.

- **Electrical properties**

Carbon nanotubes possess unique electrical properties. The diameter being in the nanometer range gives rise to quantum effects. The differences in the conducting properties are caused by the molecular structure. CNTs can either be conducting or semiconducting, depending on their chirality. They are metallic if the integers of equation are: $n=m$ (armchair structure) and $n-m=3i$ (where i is an integer). All other structures are predicted to be semiconducting. The geometry of the nanotubes determines band structures and thus the energy band gap. The energy band gap of semiconducting CNTs highly depends on the nanotube diameter and is given by:

$$E_{gap} = \frac{2\gamma_0 a_{C-C}}{d}$$

Wher γ_0 denotes the C-C tight binding overlap energy (2.45 eV), a_{C-C} the nearest neighbor C-C distance (~1.42 Å), and d is the diameter of a nanotube.

Multiwall carbon nanotubes are expected to behave like quantum wires due to the confinement effects on the tube circumferences. The conductance for carbon nanotubes is given by

$$G=G0M=(2e^2/h)M$$

where $G0=(2e^2/h)=(12.9 k\Omega^{-1})$ is the quantum unit of the conductance, *e* is electron charge, *h* is Planck's constant, *M* is an apparent number of conducting channels including electron-electron coupling and inter-tube coupling effects in addition to intrinsic channels. In general, MWNTs are quite often found to be one-dimensional conductors with a high electrical conductivity (even $>10^3$ S/cm). The metallic properties of the MWNTs are due to their multiple-shell structure consisting of tubes with various electrical properties, where additional electronic coupling between shells takes place. Moreover, MWNTs are predicted to have ballistic electron transport at room temperature (it refers to conduction where Ohm's law does not apply; the resistance is not dependent on the CNT's length).The electrical current that could be passed through a multiwall nanotube corresponds to a current density in excess of 10^7 A/cm2. If nanotubes were classical resistors, the power dissipated by such a current would heat the nanotube so much that it would vaporize. The fact that this does not happen suggests that the electrons in nanotubes are strongly decoupled from the lattice

- **Chemical properties**

Functionalization of the carbon nanotubes (chemical or physical modification of the surface of CNTs, e.g. by the attachment of certain molecules or functional groups) is a very important issue in order to overcome their poor solubility in solvents. Functionalized CNTs are very attractive for chemical and biological applications because of their strong sensitivity to chemical or environmental interactions. This leads to a broad range of applications, e.g. as sensors. Covalent and non-covalent functionalization, doping, decoration with organic as well as inorganic species of the surface of CNTs lead to direct changes of the properties of carbon nanotubes (optical, electrical, and mechanical).

- **Other properties**

Besides the outstanding mechanical and electrical properties, CNTs exhibit interesting thermal and optical properties. Defect-free nanotubes, especially SWNTs, offer a direct band gap and a well defined band and sub-band structure, which is ideal for optical and optoelectronic applications. The experimental measurements of the optical absorption of a bundle of single-walled carbon nanotubes show that there are several groups of absorption peaks and each group is closely related to the nanotube geometry. Typically, the optical absorption spectra of the SWNTs reveal peaks that correspond to the transition

between the density of states , which strongly depends on the structure of nanotubes, e.g. chirality and the diameter.

CNTs are thermally stable up to 800 °C in vacuum; their thermal conductivity in the axial direction is about twice as high as of present commercial synthetic diamond but has very small values in the radial direction. CNTs with high aspect ratio and small tip radius of curvature are found to be excellent field emitters (electron emission). It was shown that relatively low voltages are needed for effective field emission with a high field amplification factor, this offers an advantage over other metallic emitters which need a high voltage for emission.

1.7 CNT- Polymer composites

Nowadays polymers play a very important role in numerous fields of everyday life due to their advantages over conventional materials (e.g. metals) such as lightness, resistance to corrosion, low-cost production, and ease of processing. Further improvement of their performance is still being intensely investigated. Altering and enhancement of the polymers' properties occur, for example, through doping with various fillers such as metals, semiconductors, organic and inorganic particles and fibers, as well as carbon structures and ceramics; thereby enabling polymers to be used as a structural unit .

Fillers are used in polymers for a variety of reasons: improved processing, density control, optical effects, thermal conductivity, and control of thermal expansion, electrical properties, magnetic properties, flame resistance, and improved mechanical properties, such as hardness, elasticity, and tear resistance. Polymer composites can be used in many different forms in various areas ranging from structural units in the construction industry to the composites of the aerospace applications.

There are several important requirements for an effective improvement of CNT-based composites' properties, such as: a large aspect ratio of a filler, good exfoliation and dispersion of nanotubes, and good nanotube-nanotube and nanotube-polymer interfacial bonding. Numerous studies have shown already, that an effective performance of the carbon nanotubes in composites for a variety of applications strongly depends on the ability to disperse the CNTs homogenously throughout the matrix. Good interfacial bonding and interactions between nanotubes and polymers are also necessary conditions for improving mechanical properties of the composites. Due to the nanoscale size of the

CNTs the active CNT/matrix interface is significantly higher than that of other conventional fillers

1.8 Various approaches for the fabrication of CNT/polymer composites:-

1. Solution processing of composites: The most common method based on the mixing of the CNTs and a polymer in a suitable solvent before evaporating the solvent to form a composite film. The dispersion of components in a solvent, mixing, and evaporation are often supported by mechanical agitation (e.g. ultrasonication, magnetic stirring, shear mixing).

2. Melt processing of bulk composites: This method concerns polymers that are insoluble in any solvent, like thermoplastic polymers. It involves the melting of the polymers to form viscous liquids to which the CNTs can be added and mixed.

3. Melt processing of composite fibers: CNTs are added to the melts of the polymers. The formation of CNT/polymer fibers from their melts occurs through e.g. the melt-spinning process.

4. Composites based on thermosets: A thermoset polymer is one that does not melt when heated such as epoxy resins. The composite is formed from a monomer (usually liquid) and CNTs, the mixture which is cured with crosslinking/catalyzing agents.

5. Layer-by-layer assembly (LBL): CNTs and polyelectrolytes are used to form a highly homogeneous composite, with a good dispersion, good interpenetration, and a high concentration of CNTs. This method involves alternating adsorptions of a monolayer of components which are attracted to each other by electrostatic interactions resulting in a uniform growth of the films.

6. In-situ polymerization: The polymer macromolecules are directly grafted onto the walls of carbon nanotubes. This technique is often used for insoluble and thermally unstable polymers which cannot be melt processed. Polymerization occurs directly on the surface of CNTs . In general, all of these different techniques give various results in

terms of the efficiency of the nanotubes' dispersion, interfacial interaction between components, properties of the composites, and possible applications.

1.8. Potential applications of CNTs and their composites

Carbon nanotubes are being wildly considered for the use as energy storage materials (fuel cells), advanced aerospace composites, co-axial cable, field emitting devices, transistors, EMI shielding in electronic devices, nanoprobes and sensors, composite materials, to name a few. The potential applications of carbon nanotubes and their composites are listed below:

a) Field emitters: Carbon nanotubes have been shown to have excellent emission characteristics: emission has been observed at fields lower than 1 V/m, and high current densities of over 1 A/cm2 have been obtained

b) Energy storage: The advantages of considering CNTs to store energy are their cylindrical and hollow geometry, nanometer scale diameter, and perfect surface specificity. Energy carriers such as hydrogen can be stored in an adsorbed form on CNTs, which are capable of absorbing and releasing large quantities of this element easily and reliably .

c) Sensors: Strong dependence of the properties of CNTs on surface modification, mechanical deformation, doping, coating, etc. make them a very attractive material for chemical, biological, and physical sensors. Small changes in the environment of the CNT can cause drastic changes to its electrical properties .

d) High strength composites: The outstanding properties of CNTs have enabled the development of composite systems with improved mechanical performance.

e) Conducting polymer composites: A high aspect ratio of CNTs allows for lower percolation than other fillers .

f) Heat dissipation coatings: Extraordinary thermal properties make CNTs a promising filler for heat dissipating materials

g) EMI shielding materials: CNTs act as an absorber/scatterer of radar and microwave radiation.

h) Aligned CNT systems: for data storage, optical transmitters, and detector sensory systems etc.

1.9 Aim of the present Work:-

Poly(vinylidene fluoride), is a polymer that has been studied for over four decades due to its stability and durability in various environments The literature review that the polymer (PVDF) has low dielectric properties as compared to other inorganic ceramic materials. The main objective of this project was to develop homogeneous dispersion of the MWNT in PVDF polymer matrix and also studies its effects on the dielectric properties of pure PVDF polymer system. This research focuses on the processing and characterization of PVDF-carbon nanotubes (PVDF-MWCNT) nanocomposites, and to determine the changes in the PVDF morphology due to the addition of carbon nanotubes in the polymer matrix. In addition, PVDF-CNT nanocomposites show a linear increase in the percentage of crystallinity with the increase of CNT concentration in the composite. Dielectric spectroscopy results indicate that by increasing the CNT concentration in the composite, the dielectric constant and the polymer conductivity increase. The thermal and electrical properties of the PVDF and PVDF-MWCNT composites we investigated several characterization process, including Differential Scanning Calorimetry (DSC), Dielectric spectroscopy as well as optical microscope analysis.

Chapter 2

Experimental

2.1 Materials

Multiwall carbon nanotubes with “hollow” and “bamboo” morphologies with a diameter in the range of 110 - 170 nm, lengths between 5-9 micron, and purities of 98% (Aldrich), were used in this study. The chemicals that have been used in the functionalization processes and composite fabrications are described in the text below.

2.1.1 Functionalization and dispersion of MWNTs

Various methods of functionalization of multiwall carbon nanotubes were used in order to achieve a good level of exfoliation of the bundles and agglomerations of CNTs. Since chemical modification of CNTs is crucial for obtaining uniform dispersions and a high stability of nanotubes in organic or aqueous solvents, both covalent and non-covalent functionalization of the surface of MWNTs were introduced

2.1.1.1 Oxidation with acids.

Carbon nanotubes were oxidized with a mixture of sulfuric and nitric acids (1:3 v/v, (H_2SO_4: Sigma-Aldrich, >95 %; HNO_3: Sigma-Aldrich, >70 %). MWNTs were suspended in this solution followed by sonication (ultrasonic bath) for 4 hr. The magnetic stirring was done about 24 hrs at 50^{o}C. Oxidation disrupts the π bonding symmetry of the sp^2 hybridize carbon atoms and therefore leads to numerous side defects along the entire length of CNTs. Oxidized CNTs (carboxylic groups are dominant, therefore the CNT-COOH abbreviation is used to refer to oxidized nanotubes) remain stable in aqueous solvent for months as shown in Fig. 2.

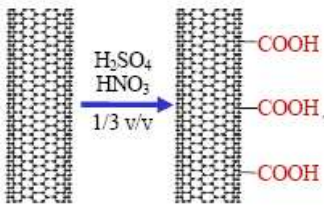


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Fig2:- Schematic of covalent functionalization of the oxidized CNT

2.1.2 Composite preparation:

Functionalized carbon nanotubes were incorporated into polymers utilizing different approaches including solution processing and sol gel method. Since various experimental setups used in this study require different samples (in size and shape, assembled on different substrates or free-standing films, solution dispersions or solid materials), the CNTs-polymer composites were suitably processed and prepared to meet all necessary experimental conditions and requirements of applied investigation methods. A general description of the preparation techniques that have been used in this study is presented below.

2.1.2.1 Solution Processing

Carbon nanotube dispersions were mixed together with the polymers in suitable solvents. To form a composite, the solvents were then evaporated from the mixture. The formation of a homogeneous mixture was supported by intensive ultrasonic agitation and mixing. MWNT-based composite was obtained utilizing this method:

MWNT-PVDF Composite

An appropriate amount of poly (vinylidene fluoride) (Sigma-Aldrich, Mw=530,000) was added to well dispersed MWNT with the PVDF in an organic solvent N,N-dimethylformamide (DMF) and the solution was ultrasonic treated for 2 hrs..The final mixture was then thoroughly mixed with magnetic stirrer at 50^{o}C for 24 hrs until a stable, black-colored DMF solution of MWNT-PVDF composite was formed. The MWNT-PVDF samples were prepared with 0.05, 0.07 wt% of PVDF. This final mixture is further treated for making of thin film and powder by using various techniques i.e. Dip Coating, Spin Coating, Chemical Precipitation, and Solution Cast Method. We have used solution cast method and spin coating techniques.

2.1.2.2 Dip coating:

This process divided into five stages; immersion, start-up, deposition, drainage, and evaporation.

With volatile solvents, such as alcohol, evaporation normally accompanies the start-up, deposition, and drainage steps. The thickness of the deposited film is related to the position of the streamline dividing the upward and downward moving layers. Film thickness depends on six forces;

a) Viscous Drag Upward On the Liquid by the Moving Substrate.

B) Force of Gravity

C) Force of Surface Tension

D) Internal Force of the Boundary Layer

E) Surface Tension Gradient

F) Pressure

After dip coating the film was heat treated in vacuum oven for15- 18 hrs and then characterized for further investigation.

2.1.2.3 Spin Coating:

Spin coating process is also divided into four stages; deposition, spin-up, spin-off and evaporation. An excess of liquid is dispersed on the surface during the deposition stage. In the spin-up stage, the liquid flows radially outward, driven by centrifugal force. In the spin-offstage, excess liquid flows to the perimeter and leaves as droplets. As the film thins, the rate of removal of excess liquid by spin-off slows down. In the last stage, evaporation takes place over as the primary mechanism of thinning.

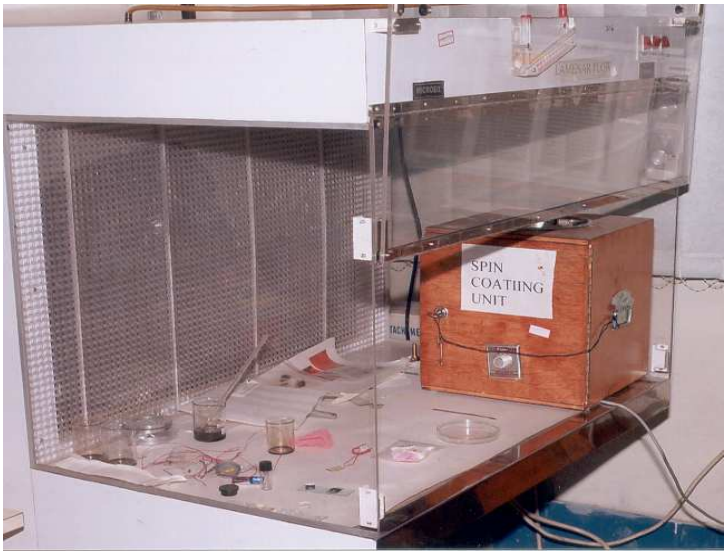


Fig. 2.1 Spin Coating Unit

An advantage of spin-coating is that a film of liquid tends to become uniform in thickness during spin-off. The balance between two main forces is important; Centrifugal force,

which drives flow radially outward, and viscosity force which acts radially in ward. Again after the deposition, the film is annealed in vacuum oven about 15-18 hrs and then characterize for further investigation.

2.1.2.4 Chemical Precipitation

By using this process we prepared nano composite powder various steps have been followed given as:

An appropriate amount of poly (vinylidene fluoride) was added to well disperse MWNT with the PVDF in an organic solvent N, N-dimethylformamide (DMF) and the solution was ultrasonic treated for 2 hr. The final mixture was then thoroughly mixed at $50^{o}C$ for 24 hrs until a stable under constant stirring, black-colored DMF viscous solution of MWNT-PVDF composite was formed. Then this viscous solution was water treated to remove nitrate ion, sulfate ion, chloride ion, and phosphate ion existed by using filter paper .By adding water in the solution, it is convertend in wet powder form .Then this wet material was further heat treated in vacum oven for 15-19hrs. With the help of Morser-pistill as shown in fig2.2 we further reduced the size of particle and pallet of this powder for further investigations.

Fig.2.2Morser-pistill

2.1.2.5 Solution Cast Method:

In this method, we first prepared the solution by using solution processing as written above. Then this viscous solution was kept between two hot plates and pressed. The resultant material was come in the form of disk.

2.2 Characterization Techniques:

The structural, dielectric, and thermal properties of the MWNT-based composites were characterized utilizing various experimental techniques including LCR meter, differential scanning calorimetry (DSC). The general description of the experimental setups used in this study, as well as conditions and parameters of each experiment are the purpose of the following section.

2.2.1 Differential Scanning Calorimetry:

Differential Scanning Calorimetry (DSC) is a thermal analysis technique used to study the thermal transitions in polymers, such as the melting point temperature, T_m, and the glass transition temperature, T_g. Two pans sit on a pair of identically positioned platforms connected to a furnace by a common heat flow path. The polymer sample is placed in one pan while the other is used as the reference pan. The two pans are then heated or cooled until they reach the selected starting temperature. A typical temperature program is set to increase the temperature at a fixed rate. As the program runs, the system monitors the temperature of each pan and keeps the heating rate constant throughout the experiment. It is important for the system to keep the two separate pans heated at the same rate. The pan with the polymer sample will take in more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan. If the temperature differs from the programmed temperature in either pan, the pan is heated or cooled to keep a constant temperature.

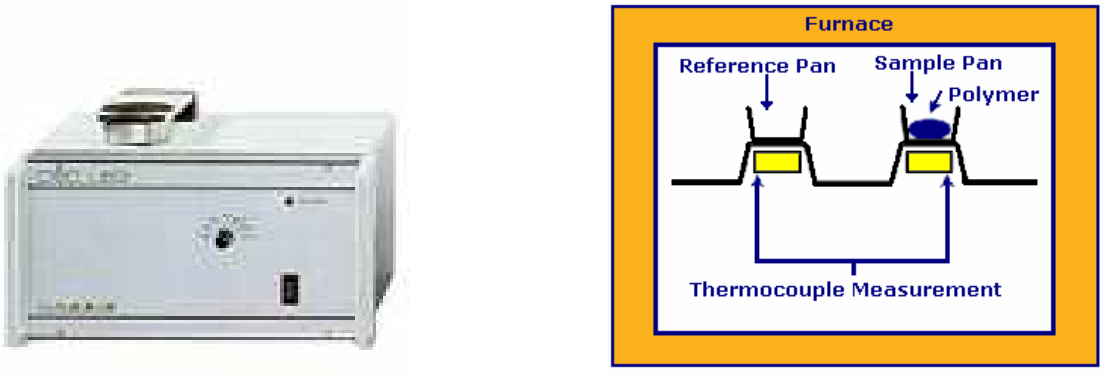


Fig. 2.3 Differential Scanning Calorimeter

The difference in the energy supplied to the two pans per unit time (dq/dt) is proportional to the heat capacity of the sample.

2.2.2 Optical polarizing microscopy

The optical studies observed in CNTs dispersed PVDF investigated using an Olympus optical polarizing microscope (Model BX51P) at a magnification of 50X under crossed polarizers using long working distance objective lens. The optical micro-textures of LC materials were also investigated as a function of temperature, voltage and other physical parameters.

Fig 2.4 Optical Microscope and temperature controller

2.2.3 Dielectric measurements

The dielectric measurements were carried out using a programmable automatic RCL meter (FLUKE PM 6306) in the frequency range 50Hz to 1MHz. The cell was calibrated using air and benzene as standard references. The frequency and bias dependence of the

real and imaginary parts of the complex dielectric permittivity have been studied in detailed at different temperatures. The dielectric properties of the PVDF/MWNT were taken at off voltages.

Fig. 2.5 LCR Meter

Dielectric spectroscopy technique measures the dielectric properties of a medium as a function of frequency. In the case of polymeric medium, dielectric spectroscopy is a powerful technique that is capable of probing the molecular motion and the electric properties. The dielectric constant or relative permittivity of a material is the ratio of the dielectric constant of the material to that of vacuum (Equation 1). The capacitance measures the extent to which charge can be stored.

$$\varepsilon_r = \frac{\varepsilon'}{\varepsilon_0}$$

The complex dielectric properties, the relative permittivity (ε') and the loss factor (ε") are determined by scans as a function of frequency. An alternating current (V_{rms} = 0.005-1.1 volts) external electric field is applied across the material placed in a capacitor plate configuration (Figure2.2). The displacement of the charge by applying the electric field is called "polarization". The dielectric properties of a material are defined by a complex dielectric permittivity, ε^*

$$\varepsilon^* = \varepsilon' + i\varepsilon''$$

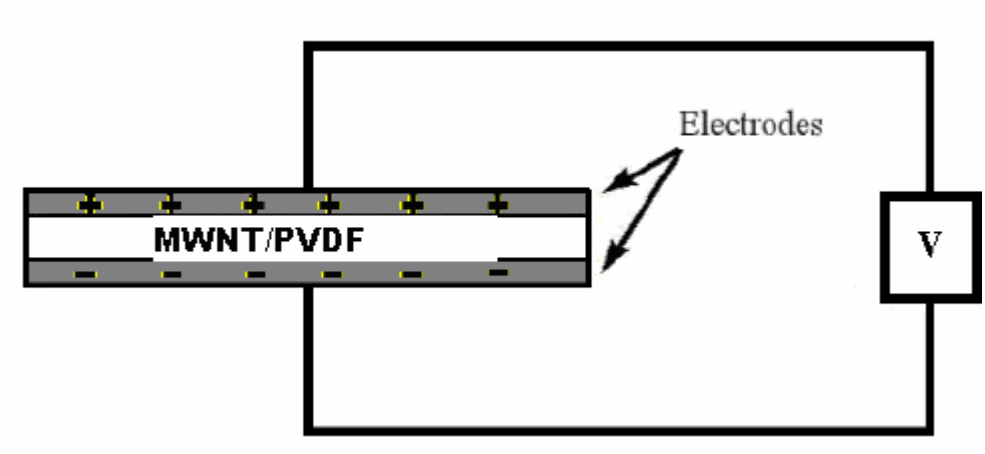


Fig. 2.6 Parallel plate works as a capacitor for dielectric measurement

Where ε' is the dielectric constant of the material, also known as the relative dielectric permittivity, and it is used to define the ability of the material to store electrical charge. ε" is the imaginary part, which is related to the material loss and known as the dielectric loss. The dielectric constant ε' is calculated, where C is the capacitance, d is the thickness of the sample, A is the area of the parallel electrodes and ε_0 is the dielectric permittivity of vacuum (ε_0 = 8.85 x 10-12 F/m).

$$\varepsilon' = \frac{C.d}{A.\varepsilon_0}$$

The dielectric constant of the material depends on the material's polarization, the higher the polarizability of the molecules, the higher the dielectric constant. Polarization mechanisms have several types discussed below.

There are four different types of polarization mechanism that can affect the dielectric constant and dielectric loss of the material: electronic polarization, atomic polarization, orientation polarization and interfacial polarization. In a given dielectric material, the total polarization is a sum of all the polarizations resulting from each one of them.

The polarizability of non-polar molecules arises from two polarization mechanisms, electronic and atomic. While in polar molecules depend on dipolar and interfacial polarization mechanisms.

Electronic polarization mechanism occurs at the molecular level and arises from a shift of the center of mass of the negative electron charge cloud surrounding the positive atomic nucleus when an electric field is applied, as shown in fig 2.6(a). This charge displacement acts to neutralize part of an applied field. This occurs in materials where the structure is formed from the molecules of different atoms with different electro negativities. Forming molecules of different types of atoms, results in the displacement of their electron clouds towards the stronger binding atom. This shift of the electron cloud results in change of atoms polarity, whose equilibrium position is further changed when electric field is applied

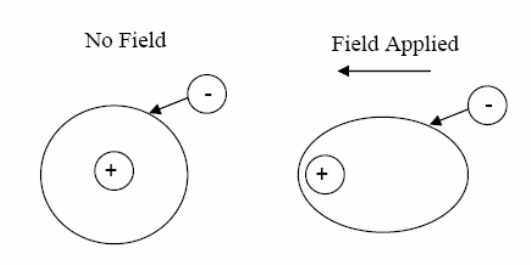


Fig. 2.6(a) Effect of electric field on electronic polarization

Atomic polarization mechanism occurs due to the shift of the atom itself, and it is usually due to the deformation of positive and negative atoms under the force of the applied field. fig 2.6(b) is a schematic diagram of the atomic polarization.

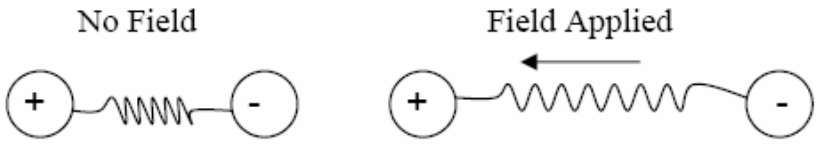


Fig 2.6(b) Effect of electric field on atomic polarization

Dipolar polarization mechanism, also known as orientation polarization, occurs when applying field to a randomly oriented dipolar material, in which the applied field cause a net orientation parallel to it, as illustrated in fig 2.6(c).

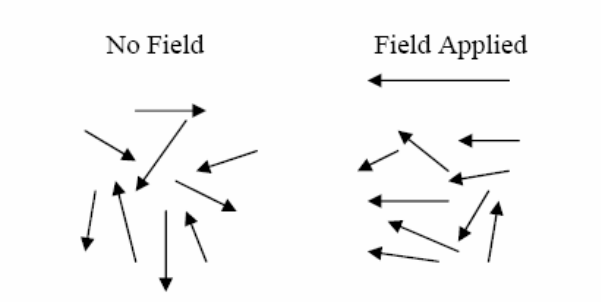


Fig 2.6(c) Effect of electric field on dipolar polarization

Interfacial polarization, also known as ionic relaxation, is comprised of ionic conductivity and space charge relaxation. Ionic conductivity predominates at low frequencies and introduces only losses to the system. Interfacial relaxation occurs when charge carriers become trapped at interfaces of heterogeneous systems. A schematic of interfacial polarization mechanism is shown in fig. 2.6(d).

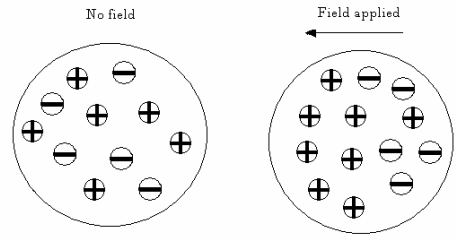


Fig .2.6(d) Effect of electric field on interfacial polarization

Each dielectric mechanism effect has a characteristic relaxation frequency. As the frequency becomes larger, the slower mechanisms drop off. A dielectric permittivity spectrum over a wide range of frequencies includes the real and imaginary parts of permittivity are shown in fig 2.7. Electronic and atomic polarizations due to the inertia of orbiting electrons, known as the inertia effect, have a small magnitude except at the resonant frequency. Electronic polarization occurs at a characteristic frequency of about 10^{15} Hz and atomic polarization occurs at about 10^{12} Hz. Lower frequencies of Each dielectric mechanism effect has a characteristic relaxation frequency. As the frequency becomes larger, the slower mechanisms drop off. A dielectric permittivity spectrum over

a wide range of frequencies includes the real and imaginary parts of permittivity are shown in fig 2.8. Electronic and atomic polarizations due to the inertia of orbiting electrons, known as the inertia effect, have a small magnitude except at the resonant frequency. Electronic polarization occurs at a characteristic frequency of about 10^{15} Hz and atomic polarization occurs at about 10^{12} Hz.

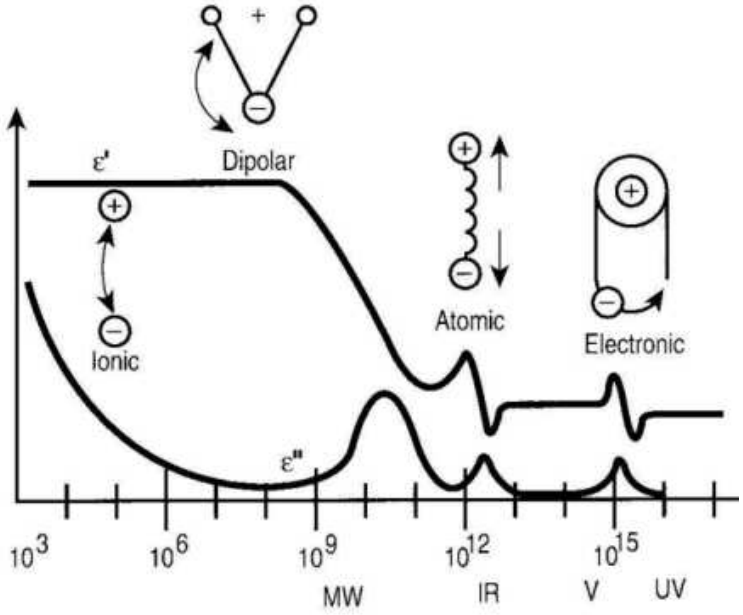


Fig2.7. Frequency response of the dielectric mechanism

The effect of crystalline phase on the real (ε') and imaginary (ε") parts of the relative complex permittivity on PVDF has been studied at both room temperature and under linear heating of the sample as shown in fig 2.8. At room temperature measurements, Gregorio et al. observed increase in the dielectric constant ε' in the whole frequency range with the increase in the β-phase present in the sample, which also increases with the drawing ratio. The difference in morphology of the samples may also affect the orientation of PVDF dipoles resulting in different dielectric constant (ε') values. It is observed that results may vary due to the porosity of samples. Samples obtained from solutions are more porous than those obtained from melt and these results in different dipole densities. These results can also be affected by the difference in morphology related to the sample thermal history. The dielectric constant ε' value increases by

heating the sample because an increase in temperature reduces the tension on the molecules caused by drawing, reducing packing and making the dipoles free to orient. This increases the dipolar orientation and results in the increase of ε' value.

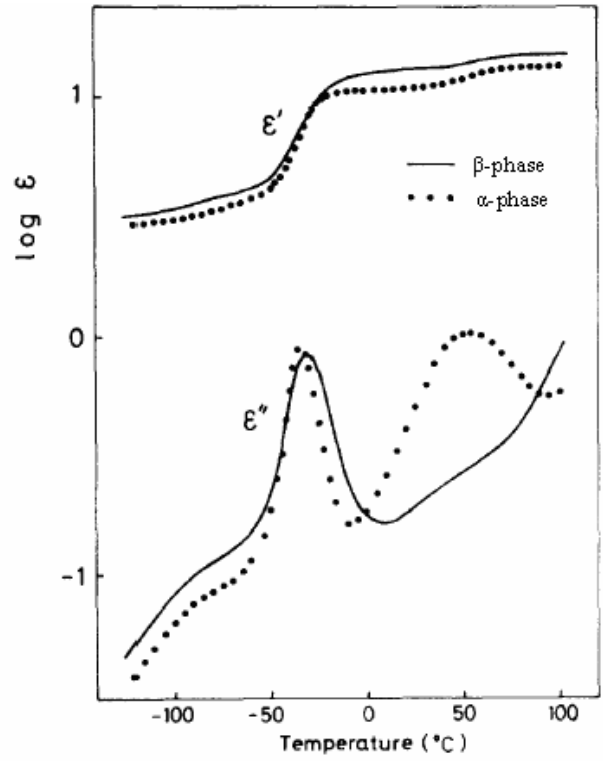


Fig. 2.8 PVDF Dielectric relaxation

CHAPTER 3

Results and discussions

3.1 Structural properties of the samples

This chapter discusses results obtained from the various characterization techniques like optical microscopy, thermography and dielectric spectroscopy, results from optical microscopy for structural and related investigation for pure and CNT doped .

3.1.1 Morphological studies of composite films

Fig. 3.1 shows micrographs of optical textures exhibiting large MWNT dispersed in the continuum of PVDF prepared by solution processing technique. The films were prepared by spin coating technique and were given heat treatment for solvent evaporation as well as annealing to achieve the solid film form and then characterize. For various compositions we studied the uniform dispersion of MWNT in PVDF.

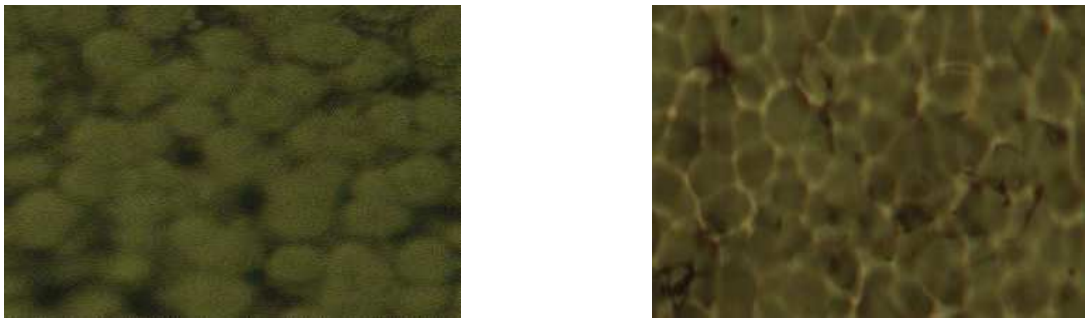
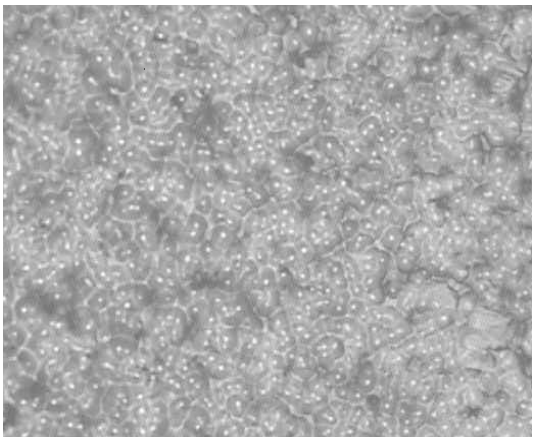
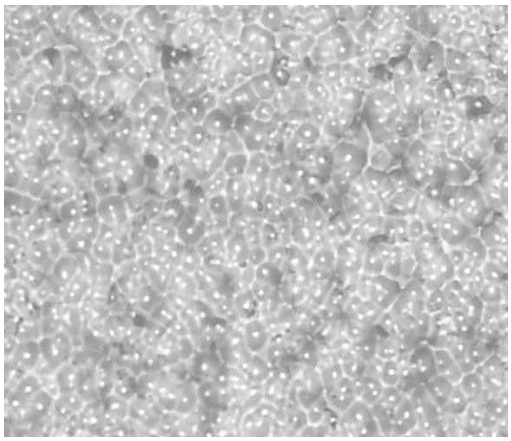


Fig 3.1 Microstructure of Pure PVDF film at 50X

0.05% MWNT were dispersed uniformly in PVDF by oxidation technique .the corresponding optical textures are shown in fig 3.2(a) at 200X, (b) at 200X, (c) at 50X.



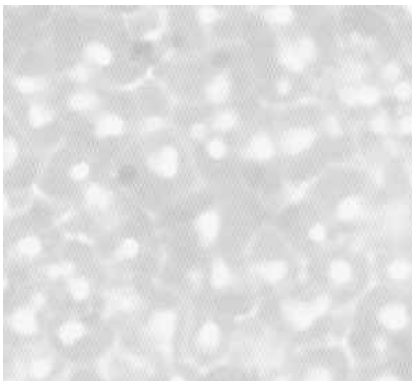


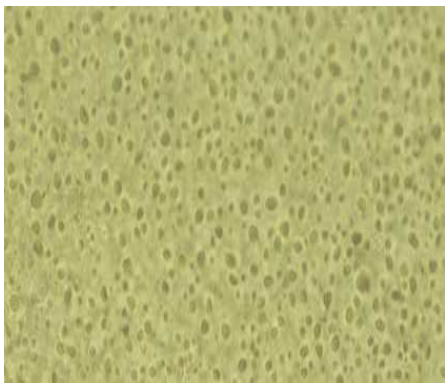
(a) (b)

Fig.3.2 Optical microscopy at 0.05%MWNTin PVDF

(c)

Fig3.2c Optical microscopy at 0.05%MWNTin PVDF





(a) **(b)**

Fig 3.3 Optical microscopy at 0.07%MWNTin PVDF at (a) 200X, (b) 50X

Fig 3.3 shows micrographs of a 0.07% MWNT concentration obtained at room temperature.

3.2 Thermography Investigation:

Differential Scanning Calorimetry (DSC) was used to determine the changes in the thermal behavior of different PVDF samples after the addition of CNT to the polymer matrix. The results were compared with respect to the concentration of the CNT dispersed amount in PVDF polymer matrix

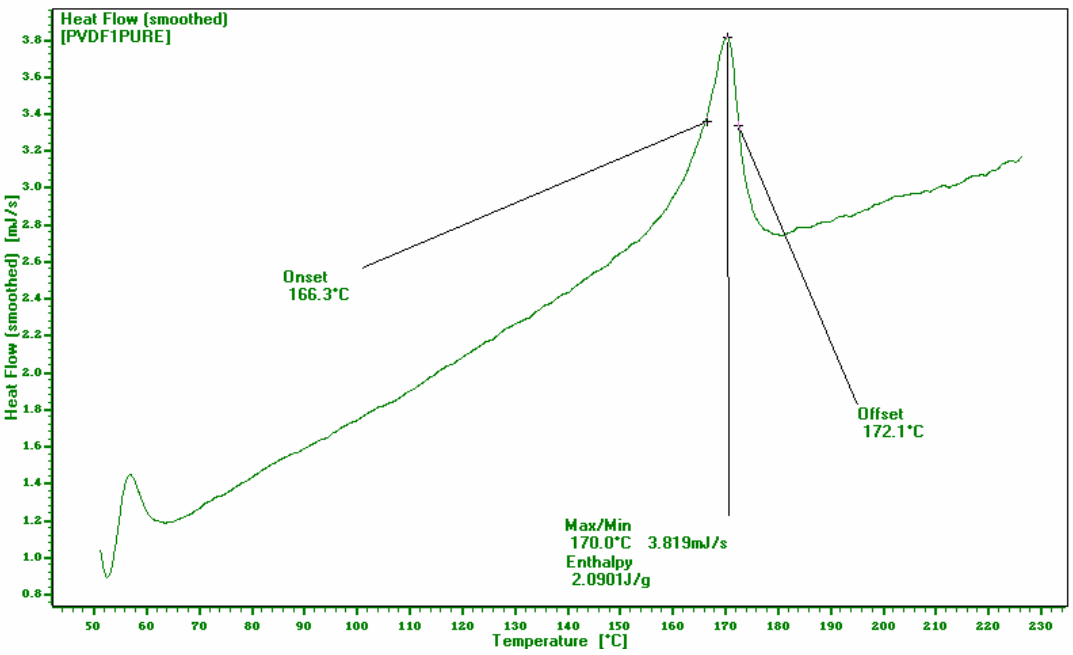


Fig.:- 3.4 DSC profile of the pure PVDF sample

The scanning rate of the temperature profile was controlled at 5oC per minute from room temperature to 250^{o}C. The transition temperature was found at 170^{o}C. We found that, transition peak in pure PVDF shifted to lower temperature with the addition of MWNT as shown in fig 3.5, and fig 3.6. This may be due to the increase in conductivity of the PVDF. All figures shows linear relation, whereby increasing CNT concentration increases the percent crystallinity.

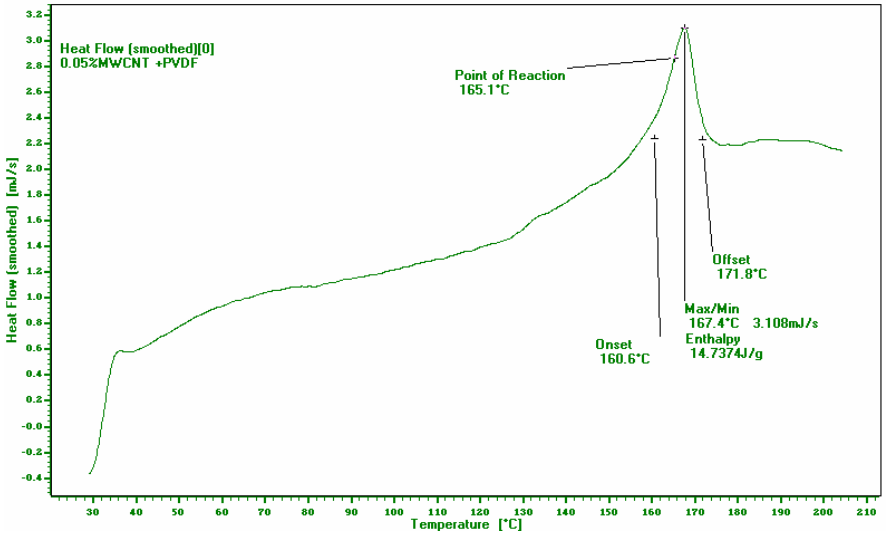


Fig 3.5 DSC profile for 0.05MWNT in PVDF

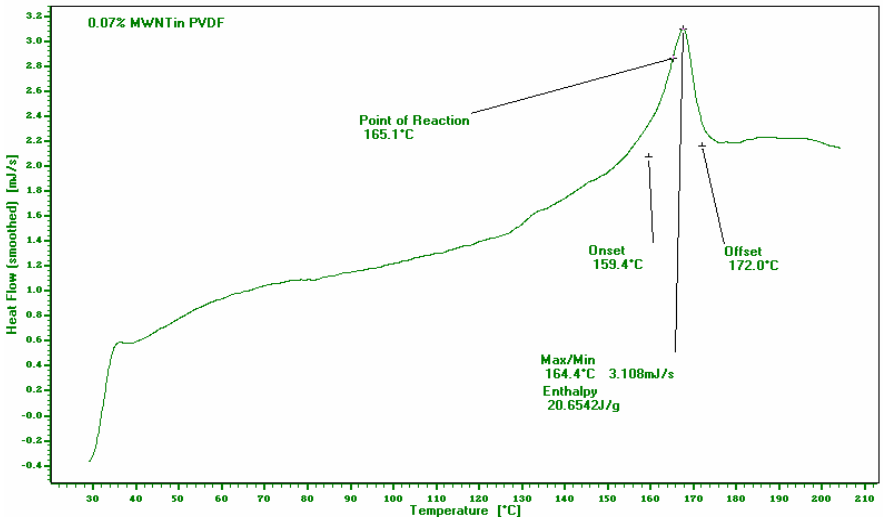


Fig 3.6 DSC profile for 0.07%MWNT in PVDF

3.3 Dielectric Spectroscopy

In the dielectric measurements section, the dielectric constant was measured for the PVDF and PVDF-MWCNT composite samples prepared by solution casting method and the results were compared with the control sample results. The dielectric constant (ε) of the samples used in the current study was first measured at room temperature.

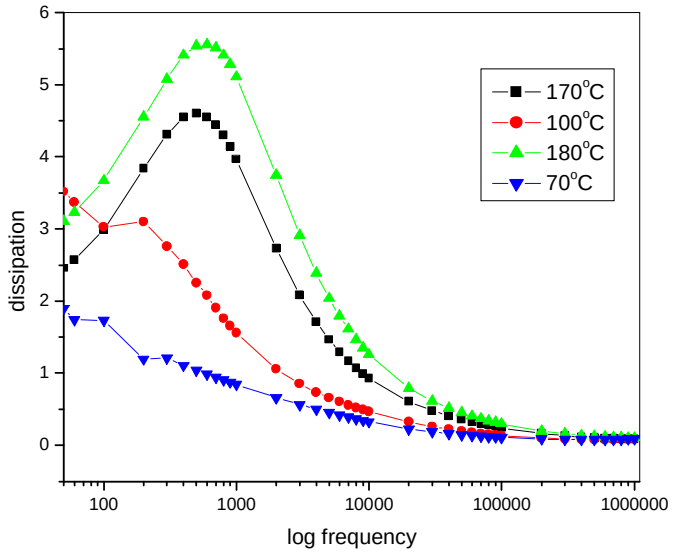


Fig3.7: Graph between dissipation vs frequency at different temperature (PVDF)

As it is clear from the graph shown in fig3.7 that dissipation was decreasing with increasing frequency but at higher frequencies it is almost constant. Also it's clear that there is no effect of temperature on the loss at higher frequencies.

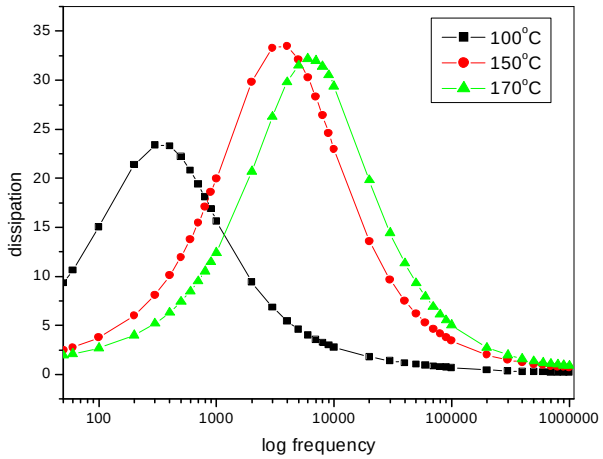


Fig 3.8 Graph between dissipation vs frequency at high temperature (0.07% CNT in PVDF)

At higher temperature and lower frequency, the losses are dominant but as we increase the frequency the loss decreases and become constant at high frequency. This behavior is shown in above fig 3.8.

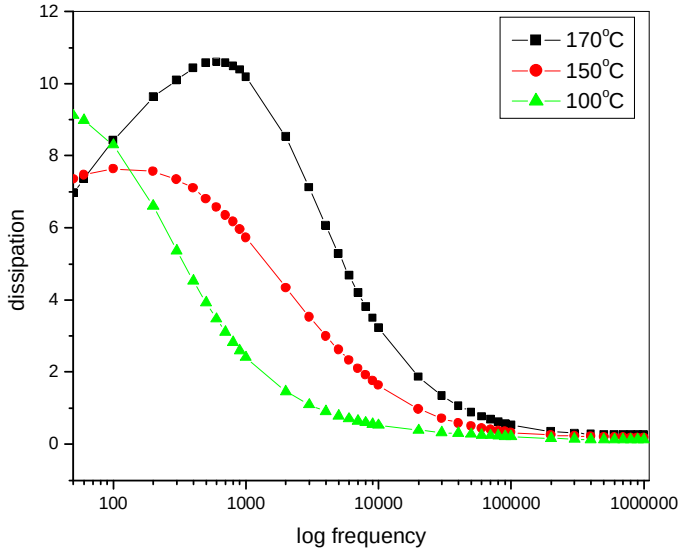


Fig3.9: Graph between dissipation vs frequency at higher different temperature (0.05%CNT)

With the addition of CNT, there was a decrease in loss at higher temperature and lower frequency, but at higher frequency it is almost constant as is clearly shown in the fig3.9.

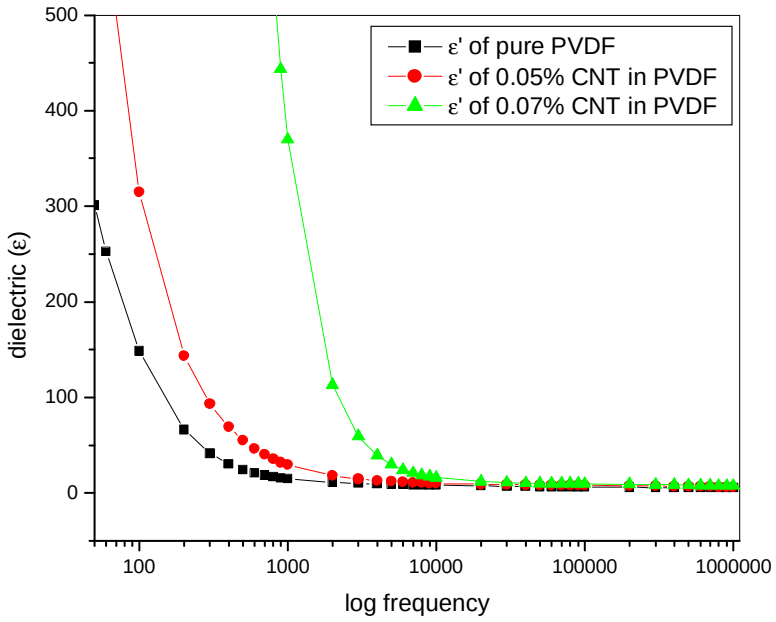


Fig 3.10:- Graph between dielectric vs frequency at different concentration of CNT in PVDF at room temperature

These observations prove that the electric properties of the polymer improved by adding CNTs to the polymer matrix. The increase in the dielectric constant of PVDF-CNT is due to the conductive properties of the CNTs. The increase in the dielectric constant allows the material to carry more current and energy to the piezoelectric dipoles, which improved the material's piezoelectric effects resulting in a better sensor or actuator properties.

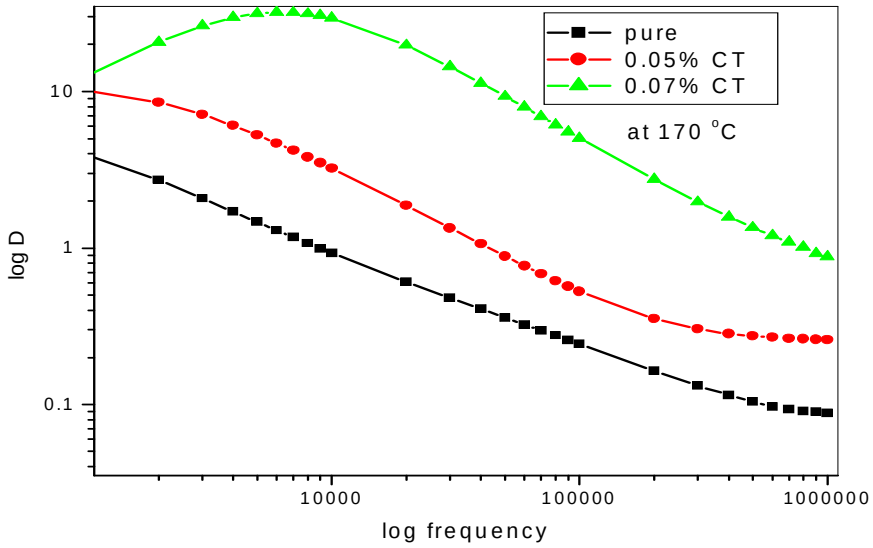


Fig3.11: Graph between dissipation(in log) Vs frequency at 170^{o}C temperature for different concentration of CNT in PVDF

On increasing the concentration of MWNT on PVDF we found that there was increase in loss at lower frequency but as the frequency increases it become constant as shown in fig 3.11.

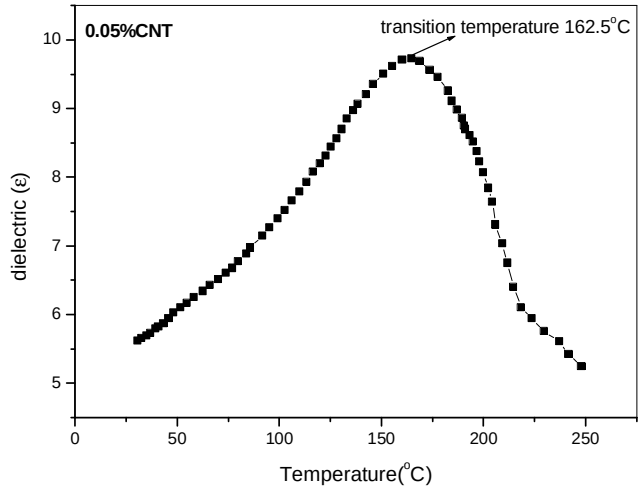


Fig3.12: Graph between dielectric vs. temperature at 100 kHz frequency of 0.05% CNT

At 100 KHz or at higher frequency .We found a increase in dielectric value at transition temperature and achieve a maximum dielectric permittivity, this transition temperature can also be shown DSC curve. At higher temperature a sudden decrease in Dielectric value is shown in fig 3.12

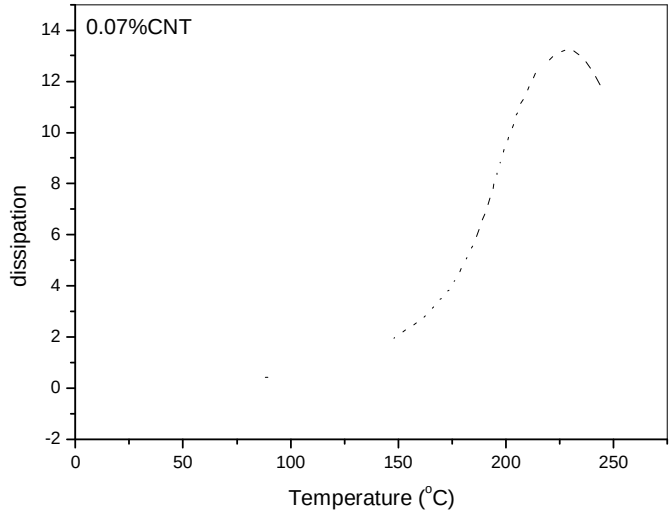


Fig3.13.Graph between dissipation factor Vs temperature at 100 kHz frequency of 0.07% CNT

As shown in fig 3.13 at transition temperature there was sudden increase in dissipation factor and it was maximum at melting temperature of PVDF after this it start to decrease may be due to the presence of CNTs

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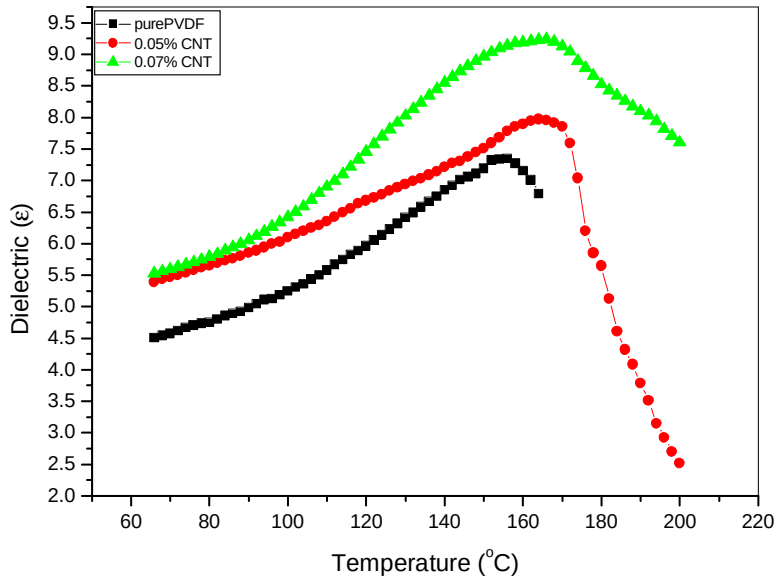

Fig 3.14 (a): Graph between dielectric vs. temperature at 100 kHz

In the fig 3.14 (a) we found that by addition of CNT in PVDF there was increase in dielectric value, at higher frequency and temperature (transition temperature).On increasing the temperature there was sudden decrease in dielectric value.

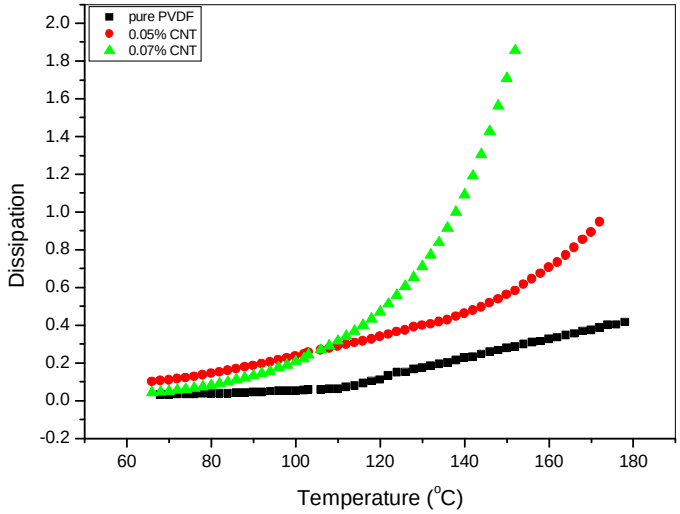

Fig3.14 (b): Graph between dissipation vs. temperature at 100 kHz

As shown in fig 3.14(b) by addition of CNTs there was a increase in dielectric loss but at higher temperature or temp near to melting point there was a sudden decrease in dielectric loss as shown in above fig 3.12 and fig 3.13.

CHAPTER 4

CONCLUSIONS

We have introduced novel approaches and solutions for effective uniform dispersion of carbon nanotubes in solvents and polymers, which are crucial for further commercial exploitation of these unique materials. It is shown that carbon nanotubes as components of nanocomposites have a significant effect on electrical and optical properties of these hybrid materials. The results presented here indicate the potential of utilizing CNT-based nanocomposites for electrical and sensing applications.

The effective utilization of CNTs in composite applications strongly depends on the ability to homogeneously disperse them throughout the matrix. Therefore, various surface functionalization strategies were employed in order to overcome the poor solubility of CNTs in solvents and polymers.

In a fairly simple process high stability, good exfoliation, and dispersion of CNT in solvents and polymer were achieved. This is advantageous over other reported methods, which mainly require complex chemical treatment, resulting in dispersion in only organic or aqueous solvent.

Multiwall carbon nanotubes were covalently functionalized by commonly used oxidation methods. These strategies resulted in a good dispersion of the nanotubes in various solvents.

The fabrication of composites with a high dielectric constant but with low losses can be achieved by efficient separation of the individual conductive particles in a host material. Silica coating of the CNTs forms insulating shells that prevent the charge flow between filler particles in the polymers.

In dielectric spectroscopy the electric properties of the polymer improved by adding CNTs to the polymer matrix. The increase in the dielectric constant of PVDF-MWCNT is due to the conductive properties of the CNTs. The increase in the dielectric constant allows the material to carry more current and energy to the piezoelectric dipoles, which

improved the material's piezoelectric effects resulting in a better sensor or actuator properties.

Finally, we presented a new approach for the preparation of MWNT-polymer composite with highly defined morphologies. The structural, optical, thermal and dielectric properties of these composites were characterized by optical microscopy, differential scanning calorimetry and LCR meter etc. The acquired knowledge can be useful for a further optimization of the CNT nanocomposites materials and towards their practical applications. Outstanding steps in the development of this research should entail comprehensive studies on dispersion techniques of CNTs with different morphologies, optimized large-scale production of CNT-polymer composites. In order to achieve a better understanding as well as better characteristics of different nanocomposites with MWNTs, further mechanical, electrical, and optical measurements are required.

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