A

Dissertation

On

Morphological, Spectral and Electrical Investigation of PVDF/MWCNT composites

In partial fulfillment of requirement for

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In

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Submitted by

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UNDER THE SUPRVISION

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CERTIFICATE

This is to be certify that the thesis entitled "**Morphological, Spectral and Electrical Investigation of PVDF/MWCNT Composites**" which is being submitted by **Hitesh Kumar Mehtani** in partial fulfillment of requirement for the award of **Master of Technology (M.Tech) in Materials & Metallurgical Engineering** from School of Physics and Materials Science, Thapar University, Patiala (India) is a record of study counted by him under my supervision and guidance. No part of this thesis has been submitted for the award of any other degree.

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(Hitesh Kumar Mehtani)

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List of Symbol and Abbreviations

CNT	Carbon Nanotube
MWCNT	Multiwall Carbon Nanotube
PVDF	Poly (vinylidene Fluroide)
THF	Tetrahydrofurane
DMF	N, N-Dimethylformamide
Δ H	Heat Capacity
^{o}C	Degree Celsius
TEM	Transmission Electron Microscopy
DSC	Differential Scanning Calorimetry
SEM	Scanning Electron Microscopy
FT-IR	Fourier Transformation- Infrared Spectroscopy
PL	Photo- Luminescence Spectroscopy

Abstract:

The nanocomosite composed of Poly (vinylidene Fluroide) and oxidized MWCNT has been synthesized via solution mixing process. The COOH functionalizations of MWCNT were performed to prevent the agglomeration in the PVDF matrix. The PVDF/COOH+MWCNT mixture was spin coated on the ITO coated conducting glass substrates. The morphological, optical and electrical measurements were carried out of these nanocomposites with various concentration of MWCNT. Results indicate that the appropriated addition of oxidized MWCNT improved their structural and morphological behavior of β phase of these nanocomposite films. DSC thermograms demonstrate their crystalline behavior in β phase.

Chapter 1
Introduction

Polymers shows a great variety of material characteristics (e.g., mechanical flexibility, optical transparency, biocompatibility, chemical stability, *etc.*) enabling them to be used in applications such as micro-fluidic and bio-implantable systems. A polymer produced in huge volumes thanks to the development of manufacturing industry. For example microelectromechanical systems (MEMS) can be easily made from polymer by showing such as cast molding, injection molding, hot embossing and photolithography [3].

Due to less electrical conductivity in polymers, the role to use these materials has finite to a structural component in applications. Most of the times, polymer-based MEMS devices required conductive material to control or collect the electrical signals from system. While coherent metal suffers incompatibility with polymers, whereas polymer/nano-composite provides alternate of conductivity in polymer systems. These types of material is different in sense of retains many features in polymers like (biocompatibility, flexibility, process ability) and now also electrical conductivity and piezoresistivity from the nanomaterial which is not property of most polymers. Now we use polymer nano-composite, to make components such as conductive electrodes and acoustic and lightweight sensor.

In Polymer/nanocomposite polymer acts as amatrix material and nanomaterial like CNT, Grephene act as a filler material. Due to this there are good changes of properties take place in material. We use different ways to disperse nanomaterial in polymers. By different ways we enhance different properties of composites. To enhance more properties we used MWCNT as filler material.

In this research, we use a semi crystalline material PVDF which has wide range of applications in electronic industry as well as in chemical industry due to its ferroelectric behaviour and chemical resistance respectively. PVDF shows five well known crystalline phases α, β, γ, δ, ε [2]. Out of these phases, β phase plays an important role due to its ferroelectric property. The β phase is forming ‘Trans (TTT) planer Zigzag’ formation [2]. Now a days we use different filler

materials in polymer to make composites example of this types of filler are PZT, gaphene, CCTO etc. Recently carbon nanotubes (CNT) also used to make composites because of their unique physical and chemical properties like strength, thermal stability [3, 15]. CNT as a filler and polymer as a matrix to make polymer/CNT nano-composites [1] which may have high thermal stability, mechanical properties. The COOH-Functionalized Multi Wall Carbon Nanotube (MWCNT) prevents agglomeration. But to get good properties we try to get β-phase so we convert non-polar phase into β-phase by different ways. 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 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 –CF2- 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 polarization.

In this work, we made an attempt to make PVDF/COOH-Functionalized MWCNT nano-composites membrane with enhanced ferroelectric properties.

1.1 Polymer: - The word polymer is derived from Greek words poly and meros, meaning many parts. The covalent bond present has intermolecular forces which keep the molecule intact. In addition, the types of intermolecular forces hydrogen bond, dipole-dipole forces, landon forces hold these molecules together in bulk. In this, many polymer molecules are produced by covalently bonding together only one or two types of repeating units. These units are parts from which chains are generated; as a class of compounds called **Monomer.**

The degree of polymerization is simply the number of repeat units in a molecule. The degree of polymerization n is given by the ratio of molecular weight of the polymer to the molecular weight of the repeat units.

$$n=M/M0$$

1.1.1 Polyvinylidene fluoride: - PVDF is a semi-crystalline material which having a various application in electronic industry and in chemical industry due to its ferroelectric behavior and chemical resistance. PVDF is highly non reactive and pure thermoplastic polymer. PVDF develop in 1961 and commercially introduce in 1965. PVDF shows five different crystalline phase (α, β, γ, δ, ε) in these phases [2], β phase is plays an important role to enhance material property like ferroelectric property. The β phase forms trans (TTT) planer Zigzag formation [2].

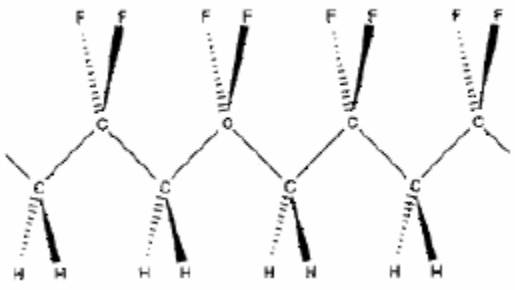


Figure 1.1: Molecular structure of PVDF

The spherulitic structure in β phase is control the grain size which enhances the piezoelectric coefficient by electromechanical coupling [3]. The formation of β phase by α phase is taken by either mechanical stretching or by high temperature annealing. The orientation of crystal moment is also possible by the application of large electric field.

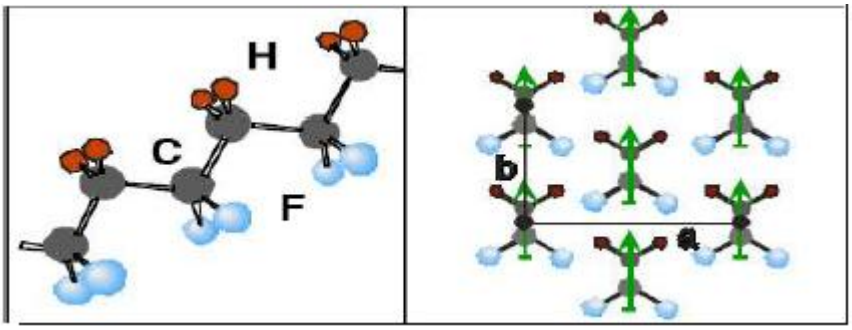


Figure 1.2: Chemical and ferro-electric phase structure of PVDF

PVDF has simple molecular formula of CH_2- CF_2. Due to its chemical structure it shows good strength and toughness which is reflected by its tensile strength. PVDF films are transparent and flexible. Polymer shows good dielectric constant, high thermal stability, and resistance to ultraviolet and nuclear radiation. Due to different preparation condition it shows different molecular structure. Polymer shows five different phases in five three of them have permanent dipole moment, but β phase show good dipole as compare to other two phases. When we melt the polymer we get basic common phase which is called as α phase. By applying different methods we change this phase into β phase. This phase (β) shows TTT all Trans' conformation. It shows highest piezoelectricity because in this all chains are in same direction and parallel to b axis and shows a dipole in same direction and form Non- Centro symmetric crystal. The α phase shows tran-gauche-trans-gauche (TGTG) conformation and Cento symmetric crystal unit due to its anti polar crystal. The δ phase shows same conformation as α phase. But γ shows TTTG conformation and shows Non- Centro symmetric.

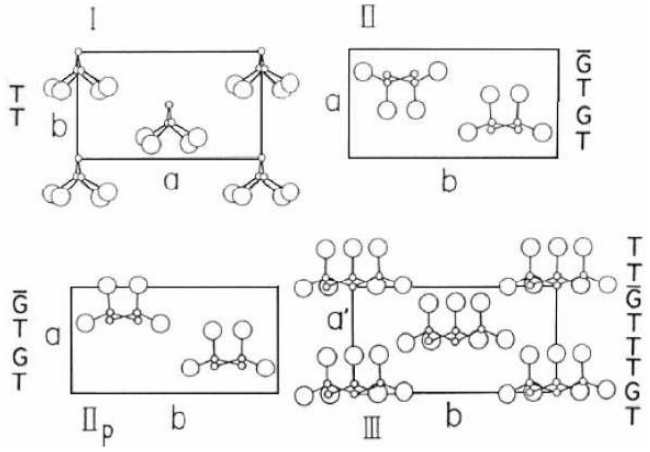


Figure 1.3: Four Phases of PVDF

1.1.2 Morphology of PVDF: - When we grow polymer from melt it shows no net polymerization. It grows in spherical symmetric aggregates which are called as spherulites structure. In this microstructure appear as radial fiber which is thin and pallet like structure called as lamellae. In polymer there is some amorphous region containing disordered conformation. In PVDF polymer about to be 50% is amorphous region.

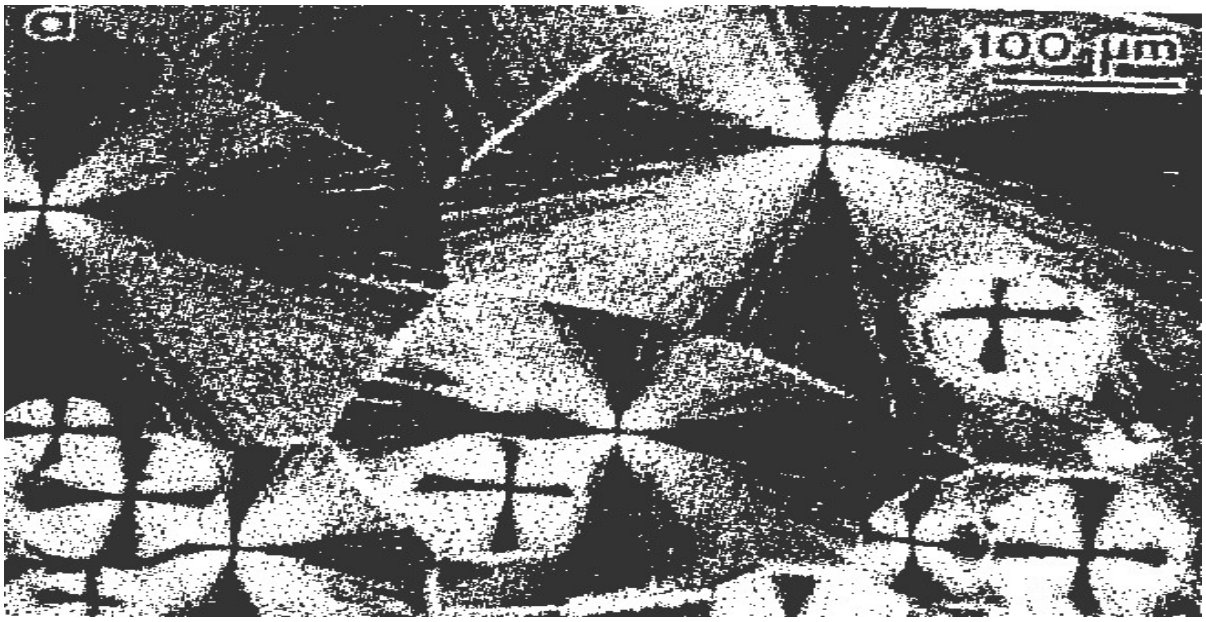


Figure 1.4: Spherulites structure of PVDF polymer

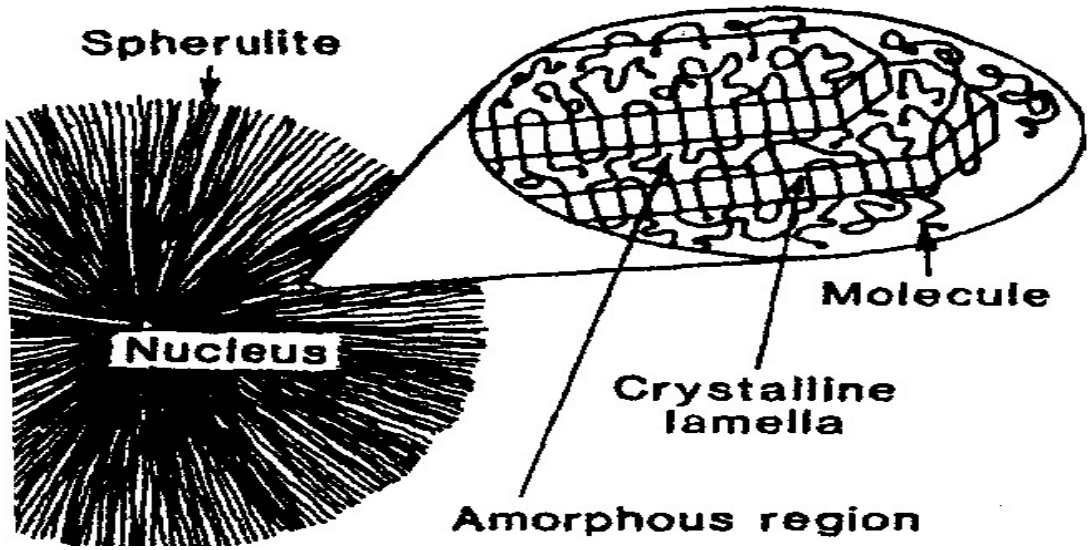


Figure 1.5: Schematic representation of polymer

1.1.3 Properties of Polymer: - PVDF shows piezoelectric and ferroelectric properties. In 1880 first time piezoelectric behavior was observed. Curie observed when we compressed the crystal in some direction we get some positive and negative charge on some portion of the surface and the charge depend upon the pressure which is form due to the applied force. Then they observe the behavior of some materials like quartz, topaz, Rochelle salt etc.

During 1st world war they used the piezoelectric plates to detect the submarine in the sea water by applying high voltage crystal will expand and when wave strike to material then it expand and vibrate which produce some voltage with the help of that we detect the submarine.

Piezoelectric Properties: - PVDF is a material which changes its behavior as the response of external stimulus. In this when we apply mechanical stress it generate piezoelectricity this effect is called as Piezoelectric Property.

$$D=d.\ T$$

In this D is electric charge density, d is piezoelectric constant of the material, T is the applied stress. Due to this PVDF are also used sensors materials.

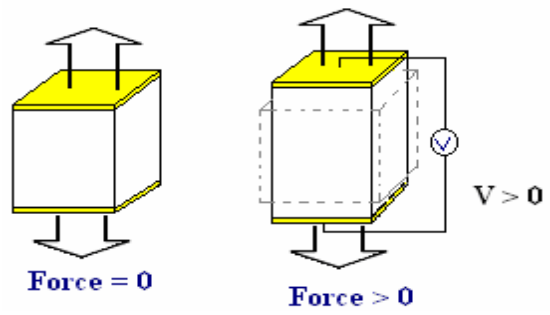


Figure 1.6: Piezoelectric Effect on PVDF

Converse of Piezoelectric means when we apply the voltage then shape of material is also changed.

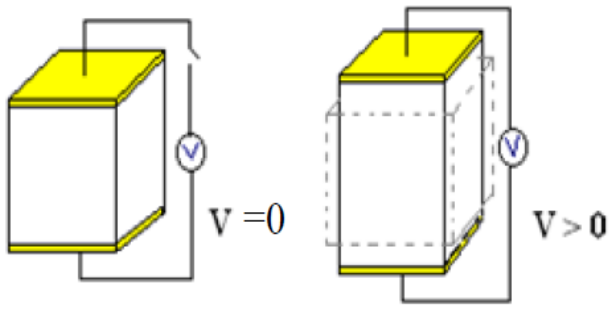


Figure 1.7: Converse Effect of PVDF

Pyro-electricity: - It is the property of material in which electrical signal generates when temperature is changed.

$$\Delta P = p\,\Delta T$$

ΔP reversible change of polarization and ΔT is change of temperature. Polarization constant (p) is defined as the change in polarization per unit temperature.

$$p = \frac{1}{A}\left(\frac{dQ}{dT}\right)$$

Ferro electricity: - The group of materials which exhibits polarization in absence of electric field called ferroelectrics. In PVDF there is some net dipole moment in crystalline phase after applying external electric field they align in a particular direction and shows magnetic field. These occur by rotation of segment in a particular direction.

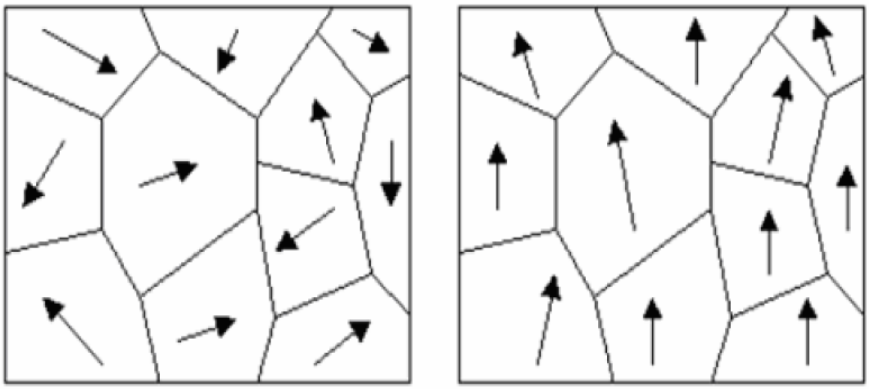
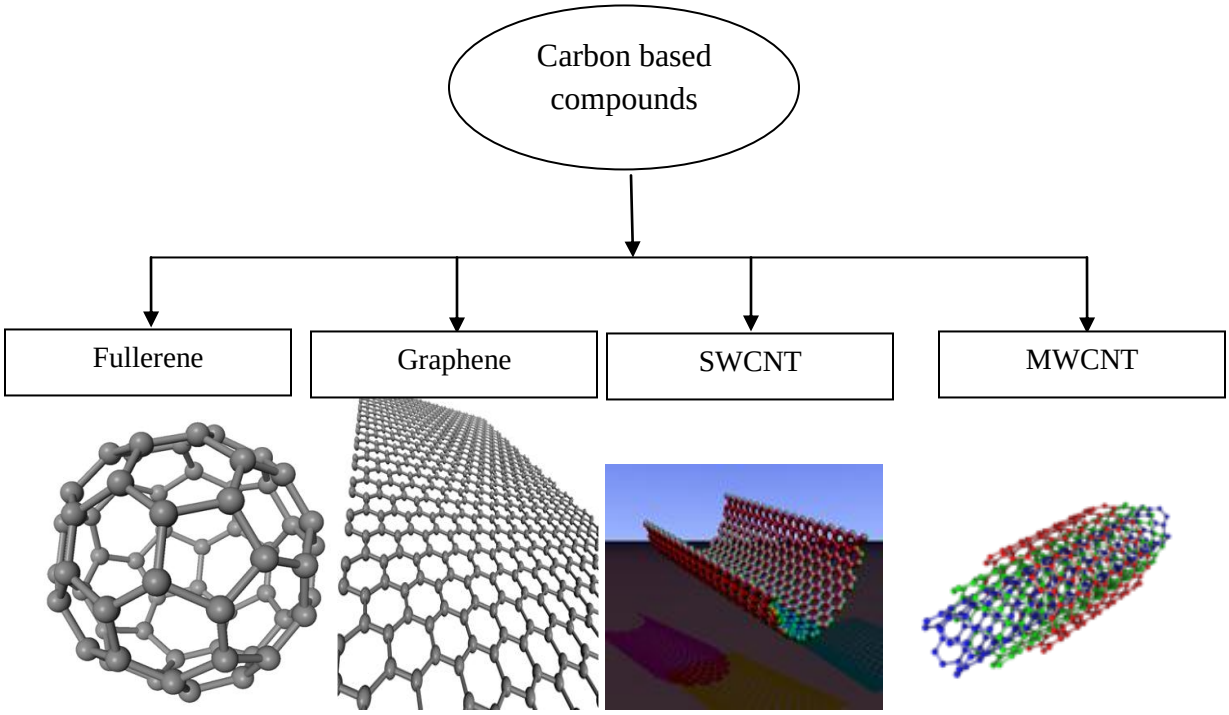
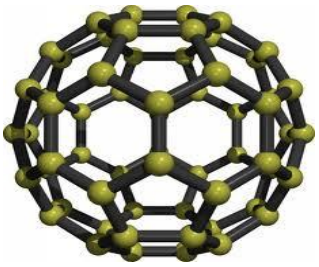


Figure 1.8: Ferroelectric Behaviour of PVDF

1.2 Carbon Based Compounds: - Carbon is very unique, versatile and is tetravalent element which is capable of forming different compounds (nanostructure) by the interesting property known as Catenation. Cationation is a linkage of atom of same element in longer chains. From last 30 years few new members of carbon family are coming. There properties are versatile. They form different structure in different dimension like in zero dim, 1-D, 2-D etc. Carbon form sp^2 hybridization. Some of their structure having important applications in areas related to electronic, spintronics, medicines and many other.



1.2.1 Fullerene: - Basically it is a zero dimensional structure. Molecule composed entirely of carbon in form of hollow sphere or tube. These are also called as buckyballs. These having similar structure to graphite which is composed to stack of graphene sheets of hexagonal rings. This structure contains 20 hexagons and 12 pentagons. The fullerene molecule is a fundamental building block of the crystalline phase, and through doping and chemical reactions it forms a large family of materials, many of which have special, intriguing properties.



1.2.2 Graphene: -When infinite graphene crystals become finite, surface and boundaries appear, forming non-three coordinated atoms at the edges, and if the size is in the order of nanometers, we have a graphitic nanostructure that exhibits different properties from those observed in bulk. This distinction is made because it has been demonstrated that the Properties of graphene can be recovered in systems with several sp_2 hybridized carbon layers when stacking disorder is introduced. However, the physicochemical properties of graphene appear to be very different from bi-layer Graphene and few layer graphene.

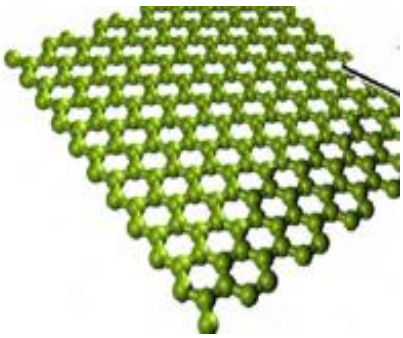


Figure 1.9: Graphene

1.2.3 Carbon Nano-tubes:-

These are discovered in 1976. But after 1991 a lot of work is going on this carbon structure especially on its properties, structure and its outstanding application. These are the allotropes of carbon with cylindrical structure. 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 nano-tubes depend on the structure, morphology, diameter, and length of the tubes. The structure of carbon nano-tubes is described in terms of the tube chirality, which is defined by the chiral vector C_h and the chiral angle θ. The chiral vector Indicates the way, in which graphene is rolled-up to form a nanotube.

$$\boldsymbol{C_h = n a_1 + m a_2}$$

In this m, n are the number of steps of zigzag carbon bonds on the hexagonal lattice and other two are the unit vectors. These tubes show extraordinary properties in thermal conductivity, mechanical and electrical properties. Nano-tubes are fullerene structure family.

1.2.4 Properties of CNT:-

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. CNTs also have very good elasto-mechanical properties. Due to the high strength of CNTs, they can bend without breaking.

Electrical Properties: - CNT shows both properties like conducting and as well as semiconductor properties this depends 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.

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 nano-tubes.

1.2.5 Classification of CNT: - On the basis of their property they can divided into two parts. These are

Single Wall: - The diameters of these tubes are 0.5 to 5 nm. These are hollow single sheet of graphen which are also defined by their chirality which tells us the tubes are metallic or semiconducting and the morphologies of the SWCNTs grown by thermal chemical vapor deposition (CVD) and grown by high-pressure carbon-monoxide (HiPCO) are significantly different from those of the laser ablation and the arc discharge samples. The CNT films prepared by the laser ablation and arc discharge reveal low CNT density but better network formation by an entanglement of the SWCNT bundles.

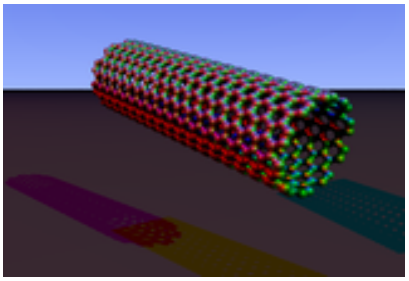


Figure 1.10: SWNT

MWCNT: - These are the group of single wall tubes whose diameter 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. These cannot be utilized without any supporting medium such as matrix that's why we made composite in which CNT dispersed in polymer.

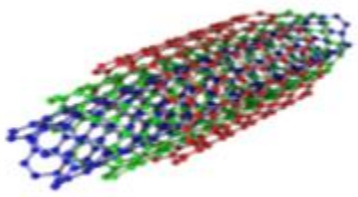


Figure 1.11: MWCNT

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.

1.3 Literature Review

In 2003 A. Salimi et al. [7] they studied that to increase the properties like dielectric and piezoelectric in PVDF increase the β phase content it could be increase by transformation mechanism from α to β phase via formation of necking during stretching.

In 2005 Ye-Tse Lai et al. [10] in this sensing element comprises a PDLC sensing film doped with carbon nanotubes (CNT-PDLC) and a planar inters digital electrode pair. The concentration of DMMP exposed to the CNT-PDLC material is detectable by measuring the change in conductivity of the material. Compared to conventional LC-based sensors, the proposed PDLC device is robust against mechanical shocks, and can fully operate with a simple read-out circuit.

In 2007 Vajinder Singh Arora et al. [17] studied that Transition peak in pure PVDF shifted to lower temperature with the addition of MWNT. This may be due to the increase in conductivity and Dielectric Spectroscope by increasing the concentration of MWCNT in the PVDF.

In 2008 Jan P. Lagerwall et al. [19] they studied the dispersion of CNT in liquid crystal they also enhance the thermotropic LC by CNT doping.

In 2008 Gaurav Mago et al. [18] in this polyvinylidene fluoride (PVDF) and PVDF nano-composite membranes were prepared via an isothermal immersion precipitation method using two different anti-solvents (ethanol and water). The structure and morphology of the resulting membranes were investigated by wide angle X-ray diffraction (WAXD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC).

In 2010 Kai Ke et al. [22] they studied that the dispersion state of MWCNT affect the crystallization behavior and electrical properties of polymer. They get more visible effect of visco-elasticity at lower frequency and high electrical conductivity of composites.

In 2010 Mauricio Terrones et al. [23] in this they studied the morphology, properties and defects of the graphene and graphite nanoribbons and they try to use them in electronic, spentronic, medicines and many other places also.

In 2010 Zdenko Spitalsky et al. [24] in this they studied the chemical, electrical and mechanical properties of CNT-Polymer Composites. Their high electrical conductivity has roused interest in the area of electrical appliances and communication related applications. However, due to their miniscule size, the excellent properties of these nanostructures can only be exploited if they are homogeneously embedded into light-weight matrices as those offered by a whole series of engineering polymers.

In 2011 Chandan Biswas et al. [25] in this they studied the electrical properties of grephene versus CNT. They try to use this type of material in the electronic device like in communication, computation, automation. They also review the progress of Carbon Nanotubes and Graphene researches and compare their electronic properties and electric device performance.

In 2011 Linghao He et al. [26] they conclude that to the enhanced of dispensability and stability of MWCNT endowed by the HBCs, which significantly favors the formation of β phase of PVDF.

In 2011 Qin Zhang et al. [27] they studied that by adding MWCNT in PVDF enhances its properties like stiffness and dielectric constant. After this a proper poling process these thin films could be used to construct a light weight and acoustic sensors.

In 2011 T. Hasan et al. [28] they studied the application of Polymer Composites with grapheme and CNT. They conclude that their uses in transparent conductor, saturable absorbers, electroluminescent and photovoltaic devices.

In 2012 Chao-Xuan et al. [29] conclude that by improved the desperation of carbon nano-tubes in polymer at higher concentration and achieve uniform distribution of carbon nanotubes within the polymer, an optimized dispersion process was developed featuring strong organic solvent

chloroform, which dissolved PDMS base polymer easily and allowed high quality dispersion of MWCNTs.

In 2012 Qing-Liang Shou et al. [34] they studied the CNT and EG fillers to prepare PVDF composites and also increase its thermal conductivity by these fillers. To make composite of both is very economical and environmental friendliness.

In 2013 Eric D. Laird et al. [36] in this they focus on the structure, morphology and application of semi-crystalline properties. In this we see structure and morphology of semicrystalline PCNs and polymer crystalenabled applications. They see CNT is work as nucleating agent in Polymer-CNT Composites after polymer crystallization.

In 2013 Junwei Li et al. [37] they concluded that the rising the cooling rate decreased the crystallization rates of PVDF.

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In 2013 Linghao He et al. [38] they conclude that by an oxidative unzipping process of MWCNT before dispersing in PVDF they enhanced the interference and piezoelectric β phase.

In 2014 Wenjing Huang et al. [41] by using grephene and CNT β form nanowires were crystalline under some specific conditions.

In 2014 Javad Heidarian et al. [42] studied that by dispersing of CNT in FE enhance the glass transition temperature T_g which form γ phase in material and also see the enhancment in material physical, mechanical and thermal properties of the material as compare to other samples.

In 2014 Jie Chen et al. [43] concluded that organoclay clay changes morphology of the material and also more influence on resistivity as compare to CNT but in large content CNT influences more than organoclay. They showed CNT at blend surface is beneficial to reducing the percolation threshold.

1.4 Gaps in Study: - Large numbers of reports are found for development of MWCNT nanocomposites but the gaps are found in doping of MWCNT in phase separated films for optimize its optical and electrical properties. We will make an attempt to functionalize the MWCNT and then doped in polymer phase separated films to optimize the enhanced optical, electrical and dielectric parameters of these composites.

1.5 Objective of Thesis Work: -

- To study the morphological properties of functionalized MWCNT- Polymer based composites Films.
- Investigation of electrical properties of these composites films.
- To optimize the various parameters that affects the optical and thermal properties of these composites.

Chapter 2

Experimental and Characterization Techniques

2.1 Materials: - The materials which are going to use in this study are poly (vinylidene) fluoride PVDF pallets having M_w=530.000 (Aldrich), Multiwall Carbon Nanotubes (MWCNT) with hollow structure having diameter = 110-170 nm and length = 5-9 μm. Purity of MWCNT is about to be 98% (Aldrich). Solvents which are going to use are tetrahydrofurane (THF), C_4H_8O (M_w=72.11 stablized) (S.D.fine-chem Ltd), N,N-Dimethylformamide DMF, C_3H_7NO (M_w=73.09) (S.D.fine-chem Ltd), H_2SO_4 (98%) pure and HNO3 (69-72)% pure from Loba Chemie Pvt. Ld.

2.2 Synthesis of β phase: -

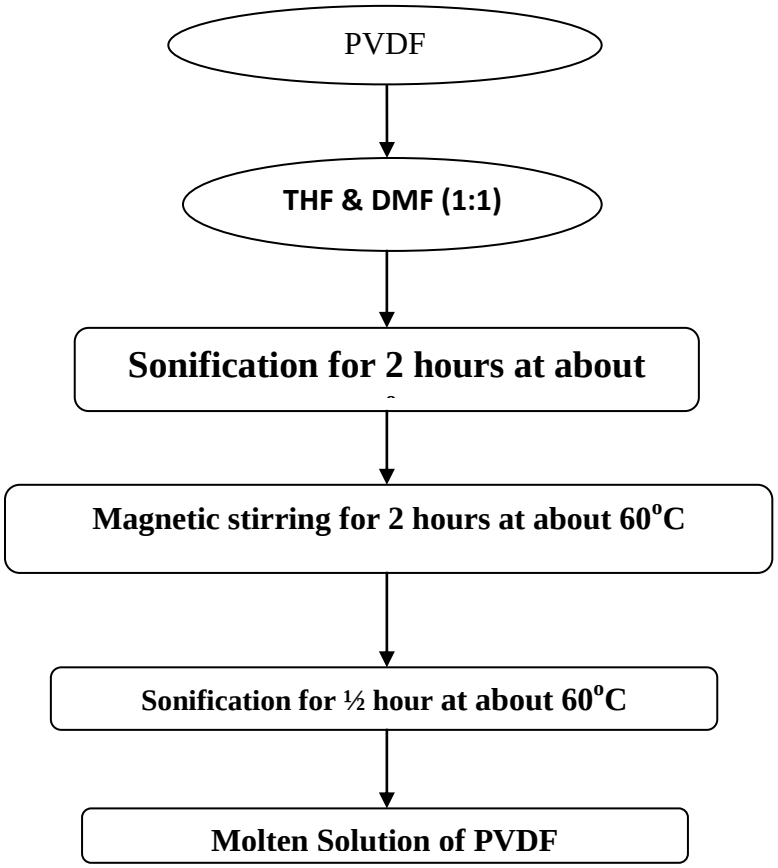


Figure: 2.1 Flow chart of Synthesis of PVDF

In this we take a proper composition of PVDF with THF and DMF at 1:1 and then we pour the PVDF and mixture in the conical flask. Then sonicate the solution at 60^{o}C for 2 hours so that proper mixing of the solution takes place. Then we put the flask on the magnetic stirrer for blending the solution at temperature 60^{o}C. The stirrer will take place at about 4 hours to blend the solution in proper manner then sonicate the solution again to make proper solution for half hour only and after that we get the molten solution for making composites.

2.3 Chemical Composition of PVDF and Solvents: - These are the solvents which is required to making molten solution of PVDF.

Table: 2.1 List of Chemicals

Sr.No.	Material	Chemical formula	Quantity
1.	Poly(vinylidene fluoride) (PVDF)	-(CH_2-CF_2)-	1g
2.	Tetrahydrofurane (THF)	C_4H_80	5ml
3.	N, N-Dimethylformamide (DMF)	C_3H_7NO	5ml

2.4 Functionalization of MWCNT: - In this work we functionalized the MWCNT because nanomaterials have a property of agglomeration this cause a huge problem in proper dispersion of MWCNT so to solve this problem we are going to do Functionalization. It is the one way of reduced agglomartion because it also reduced the properties of the material. For functionalization first we weighing the MWCNT on weighing machine and take the MWCNT at about 1 gm. Then take H_2SO_4 and HNO_3 in the ratio of 1:3 and pour it in conical flask with MWCNT. Then sonicate the solution at about 60^{o}C for 4 hours so that proper mixing of the solution takes place. After mixing we stirrer the solution for 24 hours at about 60^{o}C. During stirring oxidation will

take place and COOH (carboxyl) group was attached to the MWCNT. Then we first reflux the solution trying to enhance its pH at 7 or we can say we normalized the solution with the help of distilled water then we centrifuge the solution and get powder form of MWCNT and filter it and then we disperse the oxidized MWCNT in chloroform because by dispersion it enhance the life of functionalization at about 2 months. Then we characterized the solution by TEM and FTIR for confirmation of functionalization. By FTIR we just confirmed the presence of carboxyl groupand by TEM we analyze the changes about agglomeration is going to reduced or not.

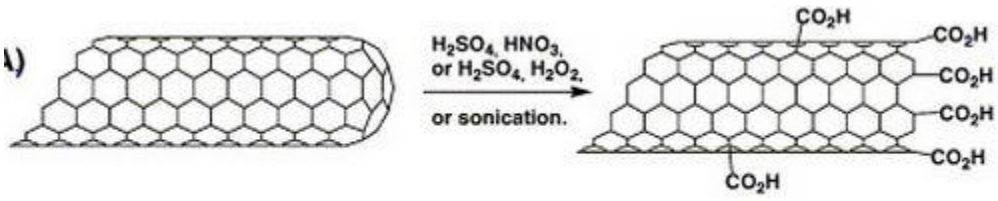


Figure: 2.2 Functionalization

2.5 Flowchart: -

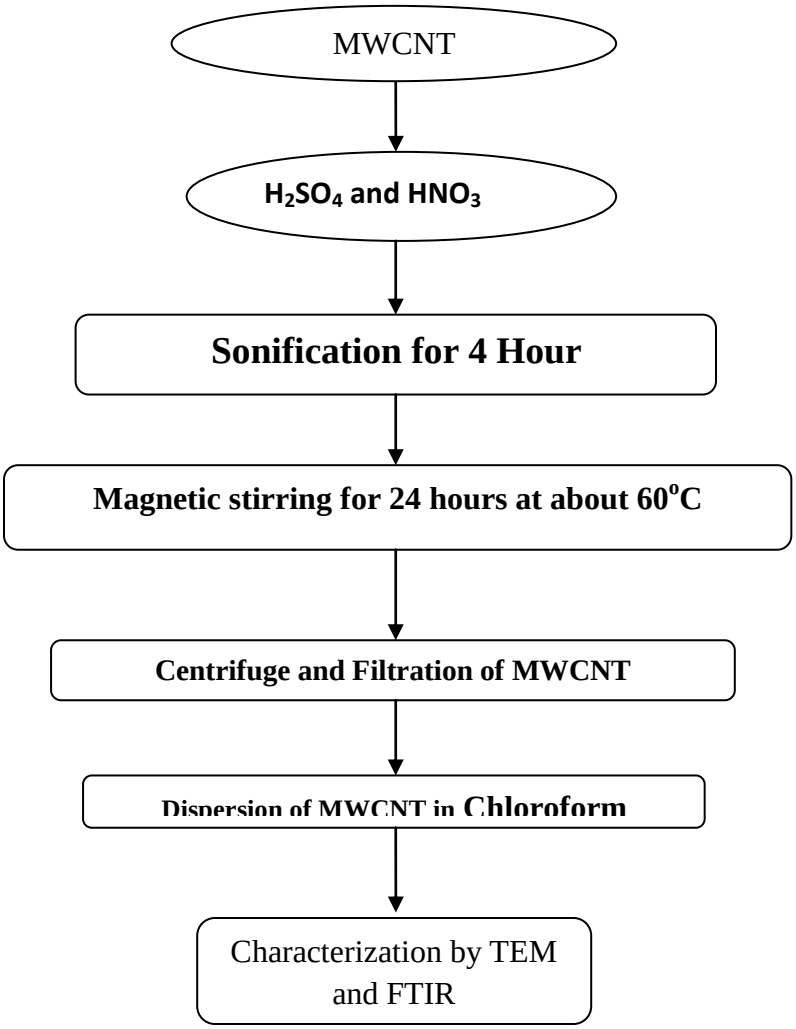


Figure: 2.3 Flow chart of Functionalization

2.6 Methodology of Composites: - In this we take Functionalized MWCNT because without this MWCNT will not make mix in Polymer they form amelgation in the polymer which affects the property of a polymer as well as MWCNT. Then we mix the MWCNT in different amount in polymer. After that we sonicate the solutions about to be 1 hour. Then after cooling, the mixture was spin cast (1000 rpm) on the conducting ITO coated substrate to form the film of PVDF-MWCNT+COOH nanocomposites. At high speed by centrifugal force the thickness of the film is controlled. Then cool it room temperature with passage of time the evaporation of the

solvent take place then opaque films is formed. Then we sealed it with epoxy. After that we characterized this in different ways like we find its electric, morphology, thermal studies by this we characterized the Composites and compare with pure PVDF film.

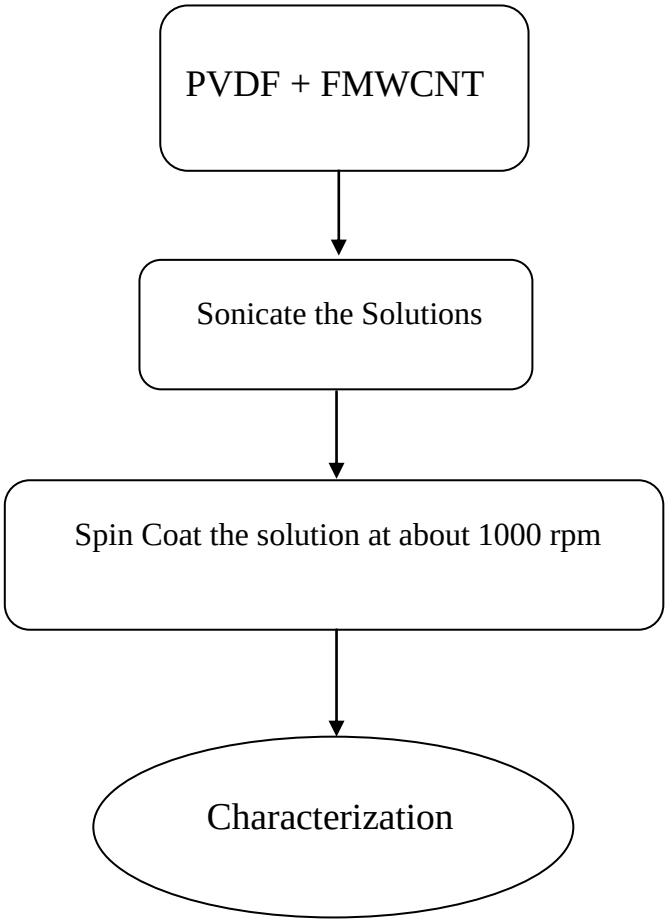


Figure: 2.4 Flow chart of Composites Synthesis

2.7 Characterization Techniques: - The structure, morphological, chemical analysis, thermal and electric measurement are done by different experimental techniques. The techniques which are using in this research are Transmission Electron Microscope, Fourier transformation IR Spectroscopy, X-ray diffraction (XRD), differential scanning calorimetery (DSC), Scanning Electron Microscope (SEM), LCR meter (frequency range 50Hz to 1MHz), optical polarizing microscope. The descriptions of these techniques are

Scanning Electron Microscope: - SEM is used for morphological analysis at higher rate. It gives the images of surface of sample scanning by high energy beam of electron at higher rate. These electrons interact with the surface gives the information about the topology, composition and other properties. The signals which are produced by electron could be secondary electron, Back Scattered Electrons. Then these are detected by detectors for different scattering there are different detectors they all come in a single machine. When we get information from SEI mode that give high resolution about to be 1-5 μm. For SEM sample should be conducting if there is non conducting samples like ceramics etc. then for SEM we make them conducting by spray the conducting material like silver, gold etc. with the help of spray we form a conducting layer of them to resolve the charging problem. In this there is condenser and object lenses they just focusing the electron beam on the sample not for the imaging the sample. According to SEM principal it could work without condenser and objective lenses but with help of them we get good resolution images.

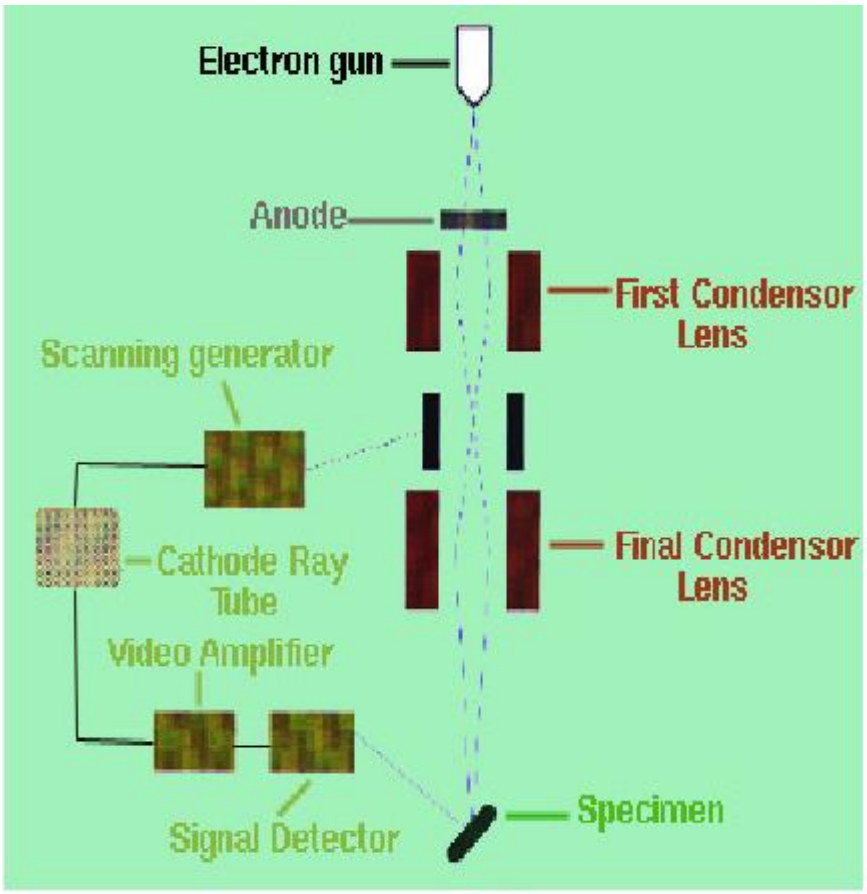


Figure: 2.5 Ray Diagram of SEM

Fourier transformation IR Spectroscopy: - The method which is used in this is of infrared spectroscopy. FTIR is used to identify organic (in some cases inorganic) materials. This technique measures the absorption of infrared radiation by the sample material versus wave number. The absorption bands are identifying to the molecular components and structures which present in the material. Some of the radiation is passed through the sample these are the IR radiation. Some of IR radiation is absorbed and some of it was transmitted by the sample. When a material is exposed in infrared radiations, so when some of IR radiation was absorbed by specimen it usually excited the molecules to higher vibrational state. The wavelength which is absorbed by molecule shows the function of difference in energy between the at-rest and excited vibrational states. The absorbed wavelength that absorbed by the sample are used to

characterized the molecular structure of the sample. Some of the analysis which is done with the help of that spectroscopy.

Applications are:

- To identify the foreign materials
  - Particulates
  - Fibers
  - Residues
- To identify the bulk material compounds
- To identify the constituents in multilayered materials
- It can also determine the amount of components in mixture

These types of instrument generated individual frequency from their sources. Because of that we used grating or prism. It works on the principal of Michelson Interferometer. Grating is used to separate the IR radiation. In this we plot the spectra between intensity vs frequency in which intensity is detect on the basis how much it fall on the specimen and how much passed in the sample.

Figure: 2.6 FTIR spectometry

X-Ray Diffraction: - X-ray diffraction technique is non-destructive analytical technique, which tell us the information about the crystallographic, structure, chemical composition, and physical properties of materials either is in powder form or in thin films. These are based on observing the scattered intensity of X-ray beam which is hitting the sample as a function of incident and scattered angle, polarization, and wavelength or energy. It (Panalytical X'Pert) is an experimental technique that explains the fact that x-rays are diffracted from crystals. Its proper wavelength (in the Angstrom range, ~ 10^{-8} cm) from which it is scattered by the electron cloud of an atom of its compatible size. Based on its diffraction pattern obtained by X-ray scattering of tell us that which of molecules or atoms present in the crystal, electron density can be reformed and if there is an another phase present in material that can also be collected either from of the diffraction pattern.

Figure: 2.7 X-ray diffractometer

X-ray is a technique which is used to determine the crystalline structure of the material. It is based on the principal of Bragg's law. In this we plot the graph between intensity and 2θ angle.

Differential Scanning Calorimetery: - Differential Scanning Calorimetry (DSC) (LINSIS L-63) is analysis technique which is used to study the thermal transitions in materials, it could be melting point temperature, T_m, and the glass transition temperature, T_g.in this technique we put two pans sit on a pair of identically positioned which is connected to a furnace by a common heat flow path. The sample is placed in one pan and while the other pan is used as reference pan. Both of the pans are then heated and after that also cooled until they reach the selected starting temperature. In this a particular temperature program is set to enhance the pans temperature with a fixed rate. As we run the program, the temperature of each pan increase at a constant heating rate throughout the experiment which is monitor by the system. One thing which is very important for the system during the process is to keeping two separate pans heated with the same rate. The pan which having the sample will take more heat to keep the temperature of the sample pan increasing with the same rate as the reference pan. If temperature differs due to some reason from the programmed temperature in any of pan, then the pan could be heated or cooled that depends upon the change to keep the constant temperature. The difference in energy which is supplied to the both of pans per unit time (dq/dt) is directly proportional to the heat capacity of the sample.

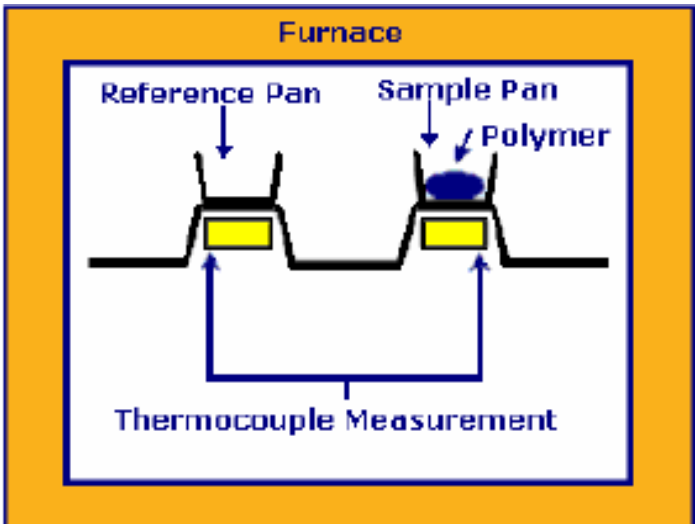


Figure: 2.8 Ray Diagram of DSC

Dielectric Measurement: - The dielectric measurements were taken out by using a programmable automatic RCL meter (FLUKE PM 6306) with the frequency range 50Hz to 1MHz. in this first we use benzene as standard references and then sample can be calibrated in air. The frequency and bias dependence of the real and imaginary parts of the complex dielectric permittivity have studied in detailed with different temperatures also. Dielectric spectroscopy technique measures the dielectric properties of sample as a function of frequency. In the case of polymeric medium with the help of dielectric spectroscopy we are capable of probing the molecular motion and the electric properties of the polymer. The dielectric constant or dielectric permittivity of a material is the ratio of the dielectric constant of the material in that vacuum. We measure the capacitance at that extent where 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 scanning the specimen as a function of frequency at different temperature. The displacement of the charge which takes place in specimen by applying the electric field is called "polarization". The dielectric properties of a material are explained by a complex dielectric permittivity, ε^*

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

Figure: 2.9 LCR meter

Where ε' is the dielectric constant of the material, which is also known as the relative dielectric permittivity of the material and it is also define as the ability of the material to store as the electrical charge. ε" is the imaginary part, which is related to the loss in the material and also known as the dielectric loss. Dielectric constant of material also depends upon the material polarization higher will be the polarization higher well be the dielectric properties of material. There are four types of different polarization mechanism these effect the dielectric constant and loss of the material. These mechanisms are electronic polarization, atomic polarization, orientation polarization and interfacial polarization. Overall polarization is the sum of above all. In above all two are non polar polarization mechanisms electronic and atomic.

In electronic polarization occurs at molecular level due to the shifting of centre of mass of negative electron and positive nucleus when an external field is applied. This type of polarization basically forms where we form the structure with electronegative atoms. Due to this electron move towards the higher electron negative atom. This shifting forms the polarization in the material and it further change as we apply external field.

Atomic polarization occurs due to the shifting of atom itself which is generally form due to the deformation of positive and negative atoms due to the external force which is applied.

Dipolar polarization these types of polarization are Polar. These occurs when we apply randomly oriented dipolar material then all the movements form a parallel polarization and we get net polarization.

Interfacial polarization occurs due to ionic conductivity due to this at low frequency loss will take place. It occurs when charge carriers trapped into the heterogeneous system.

Optical polarizing microscopy: - In this study we observed PVDF and PVDF/FMWCNT nanocomposites using Polarized Optical Microscopy with magnification of 10 X to 50 X crossed or un-crossed polarizer using object lenses. A block digram of the experimental set up is given below

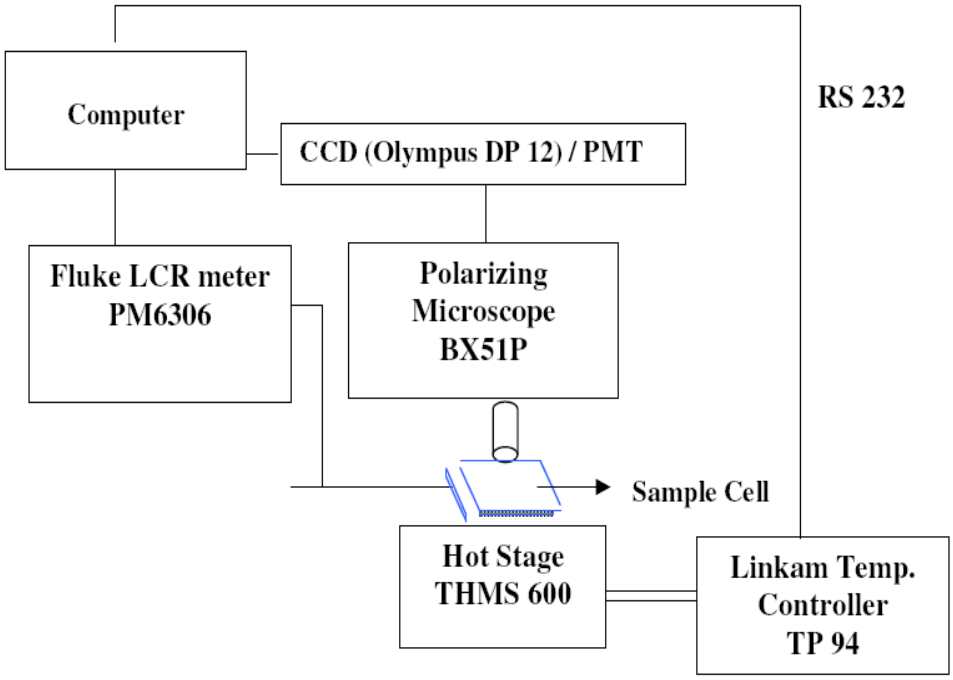


Figure: 2.10 Ray Diagram of Polarized Optical Microscopy

During electrical study we used Linkam teempearture Programmer and hot stage THMS 600. It is designed for temperature control during heating and cooling. By stage sensors which is digitally give accurate temperature readout whose controls and function have been carefully chosen and easy in operation. Its temperature range is from -196 to 600^{o}C. Its heating or cooling rate could be changing easily. The heating range is from 0.1 to 0.9^{o}C/min at 0.1 degree to 1.0 to 9.0^{o}C at 1.0 degree intervals.

Photo-Luminescence Spectroscopy: - It is related to the study of absorption and emission of radiation by the material. In this when light is fall on the material or interact with the material then due to interaction its electric vector oscillates that oscillation define the polarization of light. Basically light is electromagnetic wave in which most of the time we neglect its magnetic part.

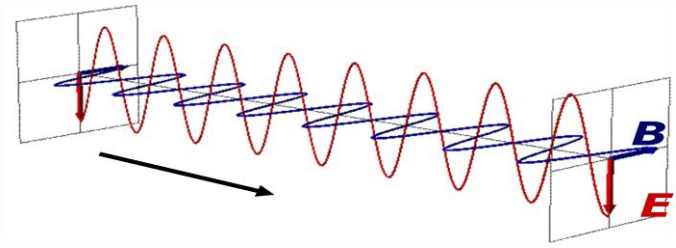


Figure: 2.11 Orientation of electric vector of light

In this we use polarizer which is basically used to polarize a light in given direction. Some of the common polarisers are:

- CaCO3 which polarized light into perpendicular plans under different angles.
- Filters which basically absorb one plane of polarization

In 1920, F.Weigert discovered that by fluorescence solution of dyes are polarized. Then he noticed the effect of temperature and viscosity on the polarization. Then he discovered that if increase the size of dye and viscosity the solution then polarization is going to increased but it decreased when temperature is decreased. Polarization state of fluorescence is described by

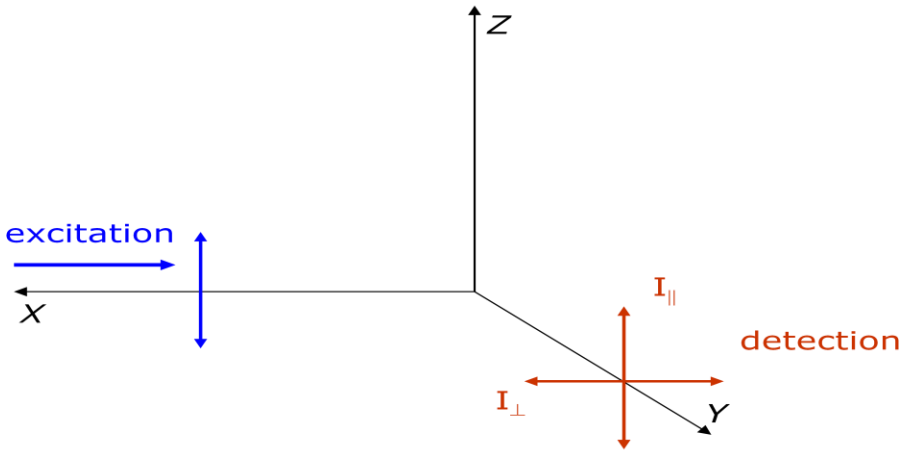


Figure: 2.12 Polarization state of Fluorescence

$$S=\frac{R-1}{R+2}$$

In this equation R is the ratio of intensity of parallel over intensity of perpendicular. In above fig. X is the direction of polarization and Y having the same intensity which is known as perpendicular direction.

In experimental set up of PL first we have leaser which is produced in it after that it passed through filler which excited the energy of laser after that it fall on the specimen after that it pass through the emission filler then it will be collected by PMT. The whole analysis of the material depends upon its radiative events it is a big fundamental limitation of this technique.

Figure: 2.13 Photograph of experimental set up of PL.

Transmission Electron Microscopy: - TEM helps in characterizing the particle size and morphology of nanomaterial. The basic function of TEM is same as in Optical Microscopy. But in TEM we generate photons in place of electron and glass lenses replaced by electro-magnetic lenses. Those changes enhance its resolution. Some of the basic components of the TEM are:

- Electron Source
- Thermionic Gun
- Electron beam
- 2 Condensers
- Electro-magnetic lenses
- Vacuum Chamber
- Sample Stages
- Fluorescent screen
- Computer

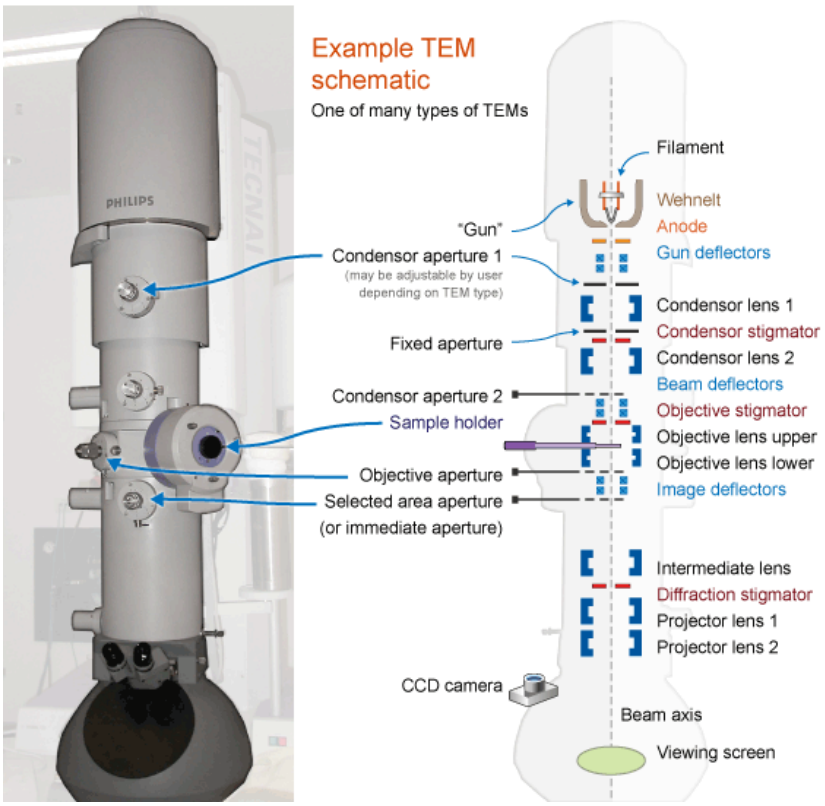


Figure: 3.14 Schematic Ray Diagram of TEM

In TEM powder sample or thin film on which incident beam is transmitted these types of samples are allowed. We prepared the sample by dispersing the sample in ethanol. Then the dispersed solution pours on the carbon paper. After some time ethanol evaporate and then carbon paper placed on the copper grid after that a beam is passed on the specimen and then we get the TEM images and studied them.

Chapter 3

Result and Discussion

3.1 Characterization of Oxidized MWCNT: -

3.1.1 TEM Analysis

The dispersed solution of MWCNT in ethanol was poured down on carbon grating for the morphological analysis [Fig. 1] through Transmission Electron Microscopy (TEM) (Model Hitachi H-7500). The micrograph clearly shows that oxidation of MWCNT can prevent it from the agglomeration [Fig. 1 (a)] where as in case of non oxidized MWCNT form the bundle of agglomerated MWCNT was observed in the TEM micrograph (marked by circle) in [Fig. 1(b)].

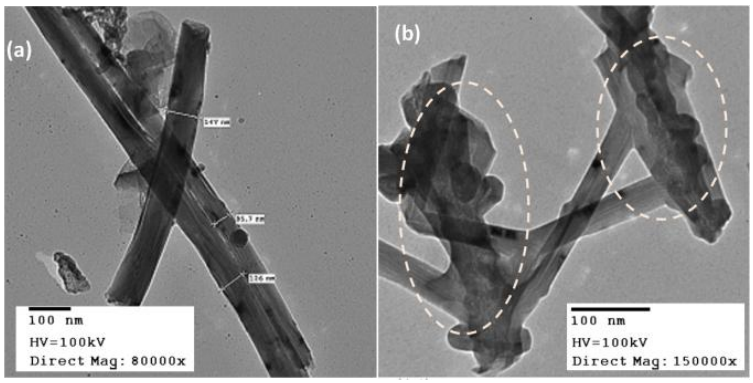


Figure: 3.1 TEM morphology of a) MWCNT+COOH, b) MWCNT Dispersed in ethanol solvent

3.1.2 FTIR Spectroscopy

Fig. 2 represents the COOH functionalized MWCNT which was chemically detected through FTIR Spectrophotometer (Model Perkin Elmer RX-I). Because of their black character of CNT's stronger absorbance was observed in a very weak concentration of nanotubes while taking IR spectra. The peak analysis corresponding to the absorption of treated MWCNT at 1740 cm^{-1} detects elongated C=O stretching of carboxylic group. While 1385 cm^{-1} indication of bend from O-H bond. While these peaks were not present in untreated MWCNT during the IR analysis [Fig. 2]. Hence FTIR conforms the functionalization of MWCNT, which further used as a filler in the PVDF matrix while making PVDF-MWCNT nanocomposites.

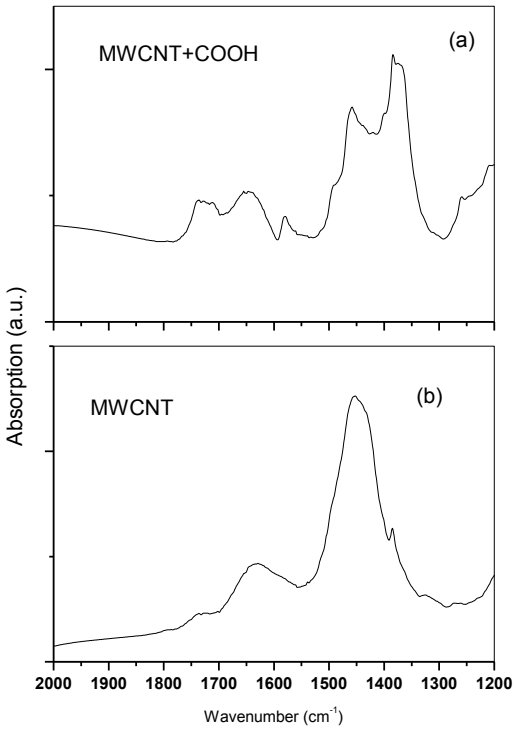


Figure: 3.2 shows the FTIR of (a) functionalized MWCNT, (b) MWCNT

3.2 Characterization of PVDF/PVDF+FMWCNT: -

3.2.1 Crystalline Behavior

Fig. 3 provides the heating scan of PVDF and PVDF/MWCNT nanocomposites films, which was performed through Differential Scanning Calorimeter [Model NETZSCH STA449F3]. In heating scan of different crystallization peaks were observed in pure PVDF film which is due to the presence of α phase along with β phase in PVDF film. As the melting temperature of β phase in PVDF film is lower than α phase [4], so it confirms the peak corresponds to 178.8 ^{o}C shows the melting of α phase where as another peak corresponds to 159.36 ^{o}C shows melting of β phase in PVDF. In another case while incorporation of oxidized MWCNT in PVDF provides only Endo up peaks showing only the melting of β phase, which shift to the higher melting points as well as goes on broaden with raise in concentrated of oxidized MWCNT. In cooling it observed that crystallization temperature shifted towards higher temperature as compare to pure PVDF. It proves that oxidized MWCNT works as an nucleating agent that's why temperature is shifting.

Table: 3.1 calculated the crystallinity of the material

Sample	T_m	ΔH_m	X_m	T_m	ΔH_c	X_c
Pure PVDF	159.36	31.85	30.47	131.90	33.01	31.62
PVDF + 0.1% MWCNT	157.65	32.90	31.51	135.60	34.46	32.05
PVDF + 0.3% MWCNT	157.92	26.37	25.31	135.25	34.52	33.13
PVDF + 0.5 % MWCNT	157.62	22.76	21.81	135.51	34.68	33.35

The crystallinity (X_m) of nanocomposites calculated by this formula.

$$X_m\ (\%) = \frac{\Delta Hm/ø}{\Delta H_m^*} \times 100$$

In this ΔH_m^* is the melting enthalpy (104.5 J/g) at 100 % crystalline PVDF and ø is the weight fraction of concentration of MWCNT in this nanocomposites. Hence from the calculated parameter [Table 1], we observed that the degree of crystallinity was enhanced in 0.1wt % oxidized MWCNT than pure PVDF film while it further get reduced when the concentration of oxidized MWCNT was 0.3 & 0.5wt % in PVDF film. This fact was clearly observed with the morphological studies of these membranes. But in cooling crystallinity goes on increasing because in control rate cooling MWCNT work as an nucleating agent.

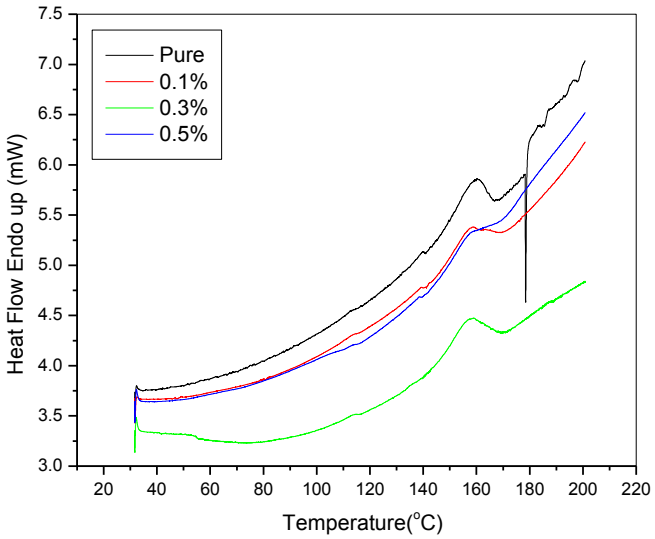


Figure: 3.3 shows the DSC thermographs of heating curve of pure PVDF and PVDF / Functionalized MWCNT nanocomposites.

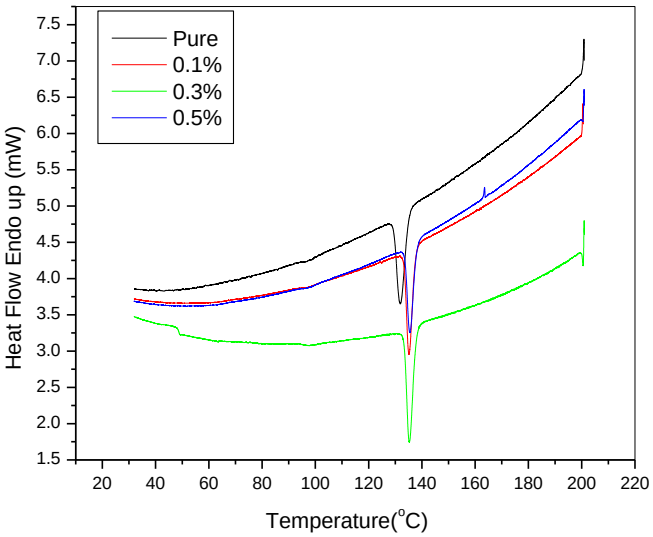


Figure: 3.4 shows the DSC thermographs of cooling curve of pure PVDF and PVDF/Functionalized MWCNT nanocomposites.

3.2.2 Morphological Analysis

The morphological analysis of PVDF nanocomposites films were investigated through scanning electron microscopy (Model: JEOL JSM-6510). The sample of nanocomposites was prepared by fine coating of gold nanoparticle (Model JEOL JFC-1600 Auto Fine Coater) was performed to avoid charging problem before taking micrograph. Fig. 4 shows the microstructure analysis of pure PVDF and oxidized MWCNT dispersed in PVDF nanocomposite film. The magnification in SEM was kept fixed at 5,000X during imaging process. The sponge like structure known as spherultic structure of β phase was observed in micrograph of pure PVDF [Fig. 4(a)] where as [Fig. 3(b)] shows the dispersion of (0.1wt %) oxidized multiwall carbon nanotubes which is homogenously distributed in film presence of MWCNT flatten the also spherultical structure in film and hence decreased the α phase in the film this is also seen in XRD pattern of those films and reduced the micro pores in this film. This can alter the ferroelectric properties of β phase. At 0.3 wt % of oxidized MWCNT in PVDF [Fig. 4(c)] the micropores start increasing as the size of sherulite get reduced, which reduced the ferroelectric properties of β phase whereas 0.5 wt % oxidized MWCNT dispersed PVDF nanocomosite, the sherultic structure of PVDF get perturbed due to agglomeration. Therefore it creates disordering in the composite film. As a result ferroelectric properties of β phase get reduced as compare to other PVDF films. Therefore from the microstructure analysis, it shows that the dispersion of oxidized MWCNT alter the morphological properties of spheruletical structure.

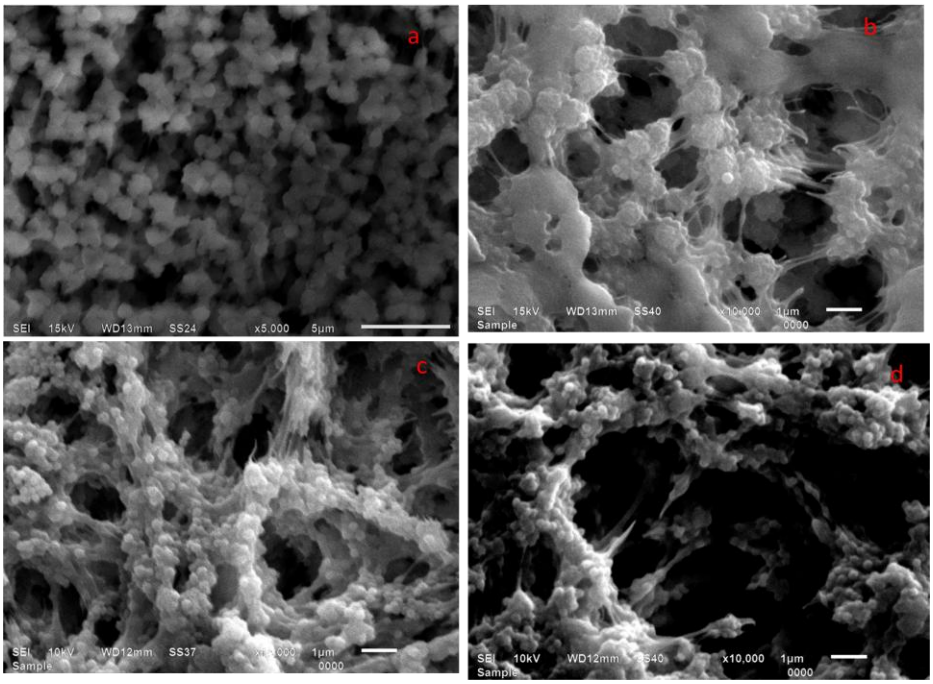


Figure: 3.5 SEM images of (a) Pure PVDF film, (b) PVDF + 0.1wt% of fMWCNT, (c) PVDF + 0.3 wt% of fMWCNT, (d) PVDF +0.5% fMWCNT at magnification of 5000X

3.2.3 Polarized Fluorescence Analysis

To confirm the ordering and disordering caused by oxidized MWCNT's in PVDF films, the polarized dichroism measurement were investigated [Fig. 5] in fluorescence spectrometer [Agilent Technologies, Mulgrave - Model Cary Eclipse]. The measurements were performed by rating the both polarizer's in parallel & perpendicular positions. The emitted intensities corresponding to the respective position was represented as I_{11} (I_{VV}) and I_{J} (I_{VH}) respectively. The order parameter was then calculated by

$$S=\frac{R-1}{R+2}$$

Where R is the Dichroic ratio which is the ratio of I_{VV} and I_{VH}. The recorded polarized from [Fig. 5] was represented in the table 2. It shows that 0.1wt % oxidized in PVDF create highest ordering which get enhanced 45% from un-doped where as the agglomeration get reduced shows only 12.5%. This ordering gets impact on dielectric properties of PVDF nanocomposites.

Table: 3.2 calculated the order parameter of the pure PVDF and PVDF/FMWCNT nanocomposites.

Sr. No.	FMWNT (concentration)	Polarized Intensity (I_{VV})	Polarized Intensity (I_{VH})	Order Parameter
1	Pure PVDF (0%)	708	550	0.08
2	0.1 wt%	673	482	0.116
3	0.3 wt%	711	523	0.107
4	0.5wt%	723	550	0.09

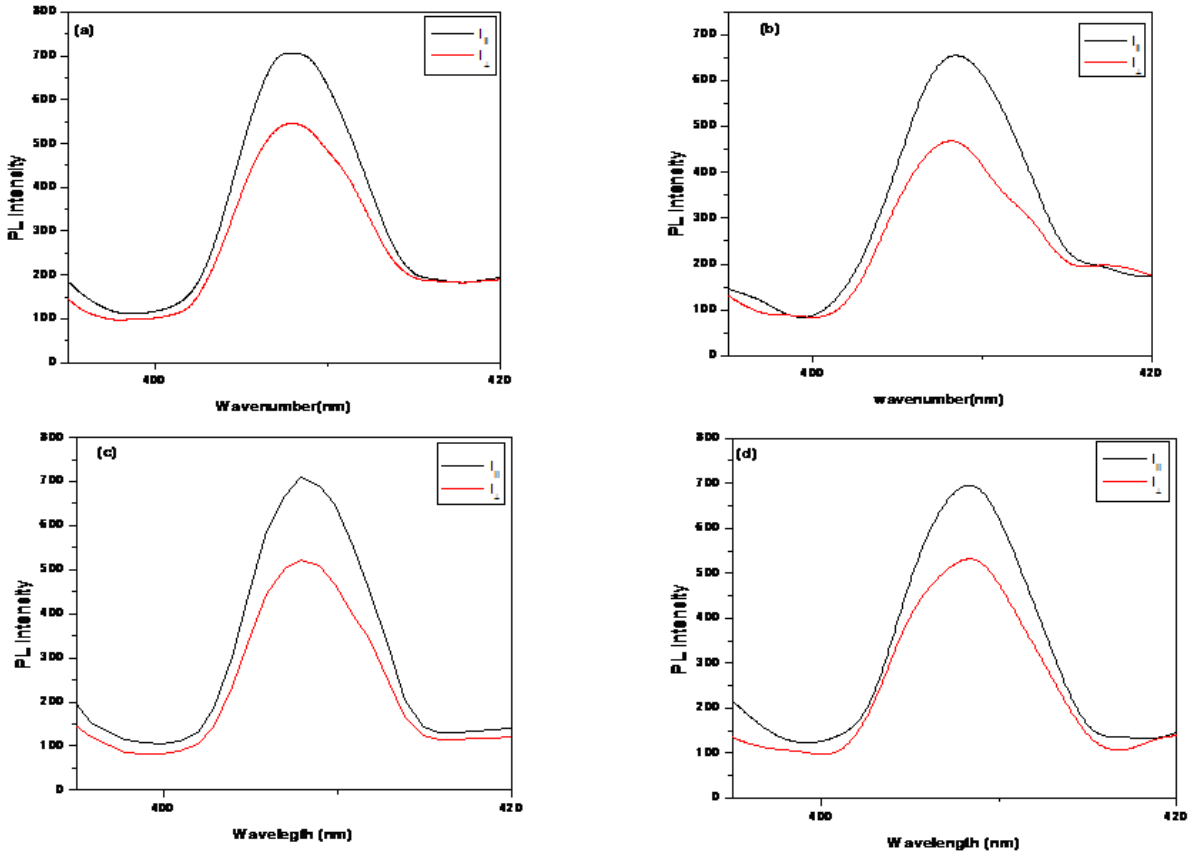


Figure: 3.6 Polarized Photo luminous spectra of (a) Pure PVDF, (b) PVDF +0.1wt% FMWCNT, (C) PVDF +0.3wt% FMWCNT, (d) PVDF + 0.5wt% FMWCNT

3.2.4 Structure Analysis:

Fig. 6 shows the X-ray diffraction pattern of pure PVDF and PVDF nanocomposites films performed in Goniometry PW3050/60 (Theta/Theta) with a step size of 0.001 and scan step time is 1s at 25 ^{o}C. In pure PVDF, strong diffraction peaks are at 2θ= 19.99, 20.35 which are the reflection of α and β phase in the film respectively there 2θ = 20.35 represents the β phase shows the reflection of 200/110 whereas 2θ = 19.99 represents α phase which reflects the plane of 100, 020, 100 and 021 whereas PVDF/FMWCNT nanocomposites shows a diffraction peak at 2θ = 20.33 which indicates only the presence of β phase whereas other configuration such as α, γ, δ, ε get eliminated so properties of PVDF gets enhanced. PVDF shows five different phases these are α, β, δ, γ, ε. In all of that β phase shows highest polarization with a chain formation of TTT trans formation. In last some decades, efforts have been made to enhance the β phase content in material using different techniques. Many reported the enhancement of β phase in PVDF but during that process α phase is also present but here we eliminate α phase in the material. The other phase like α, δ shows TGTG' chain formation and TTTGTTTG' formation shows by the ε and γ. Therefore by the XRD diffraction we concluded that we enhance the β phase percentage in the composites by adding FMWCNT.

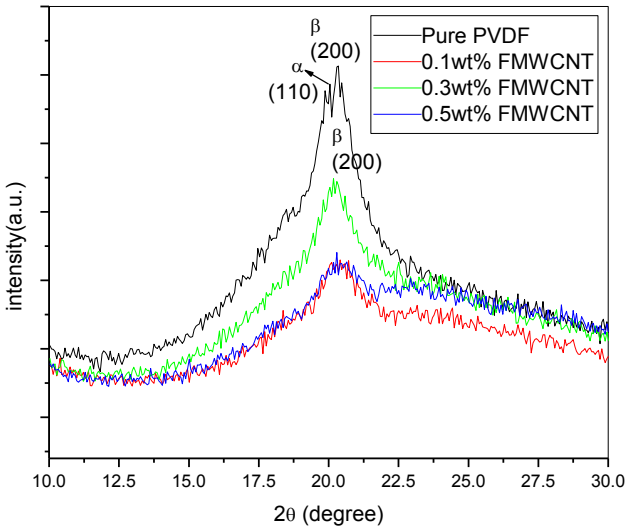


Figure: 3.7 X-ray diffraction of pure PVDF and PVDF/FMWCNT nanocomposites.

3.2.5 FT-IR Spectroscopy: It is also a good technique to identify the crystal structure of PVDF. FT-IR spectra of the comparison modified film are shown in [Fig.7]. In each sample, absorption peaks were appeared at 510 and 840 cm^{-1} both these peaks were indicate the presence of β phase in the films. Intensity of phase was high in 0.1 and 0.3 wt % FMWCNT. The β phase shows the TTT trans sequence which also examined in XRD results. But the intensity slightly goes down in 0.5wt% concentration.

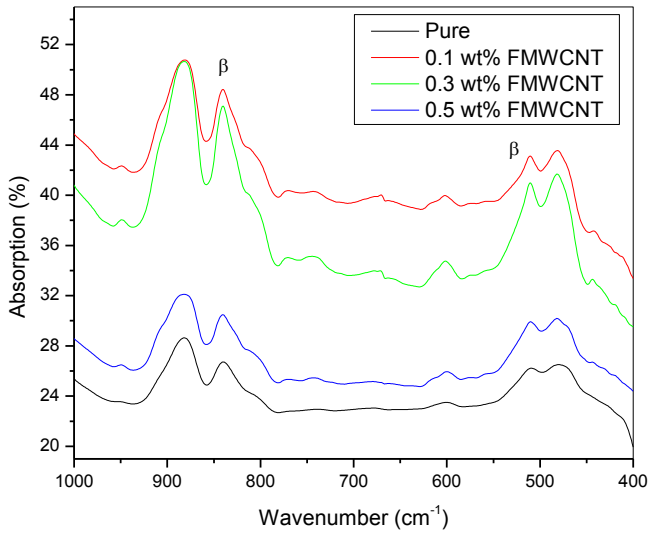


Figure: 3.8 shows the FT-IR of pure PVDF, PVDF +0.1%FMWCNT, PVDF +0.3%FMWCNT, PVDF+0.5% FMWCNT

3.2.6 Electrical Properties of Nanocomposites

Fig. 8 (a) shows the conductivity of the pure PVDF and PVDF/FMWCNT with different concentration of FMWCNT. In this we see the conductivity as a function of frequency from 50Hz to 1 MHz. Electrical conductivity depends upon the FMWCNT. On higher frequency conductivity goes on increasing. Carbon nanotubes are conductive material so when we enhance the wt concentration of MWCNT conductivity increases so pure PVDF shows less conductivity and wt% of MWCNT dominates the conductivity of material. Dielectric permittivity with applied field at a frequency of 50 Hz to 1MHz. PVDF is dielectric material which stores charges. Dielectric properties also depend the orientation of the structure in the material. In fig. 8 (b) shows the dielectric properties of PVDF and PVDF/FMWCNT nanocomposites at a particular

frequency 200 Hz. Dielectric permittivity of pure PVDF is around 10 and in nanocomposites we saw the dielectric permittivity enhanced in 0.1 wt% of FMWCNT and then decreased in 0.3 wt% and 0.5 wt%. This is done because the symmetry of β phase is more in 0.1 wt% as compare to other nanocomposites this is also proved by Fluorescence spectroscopy.

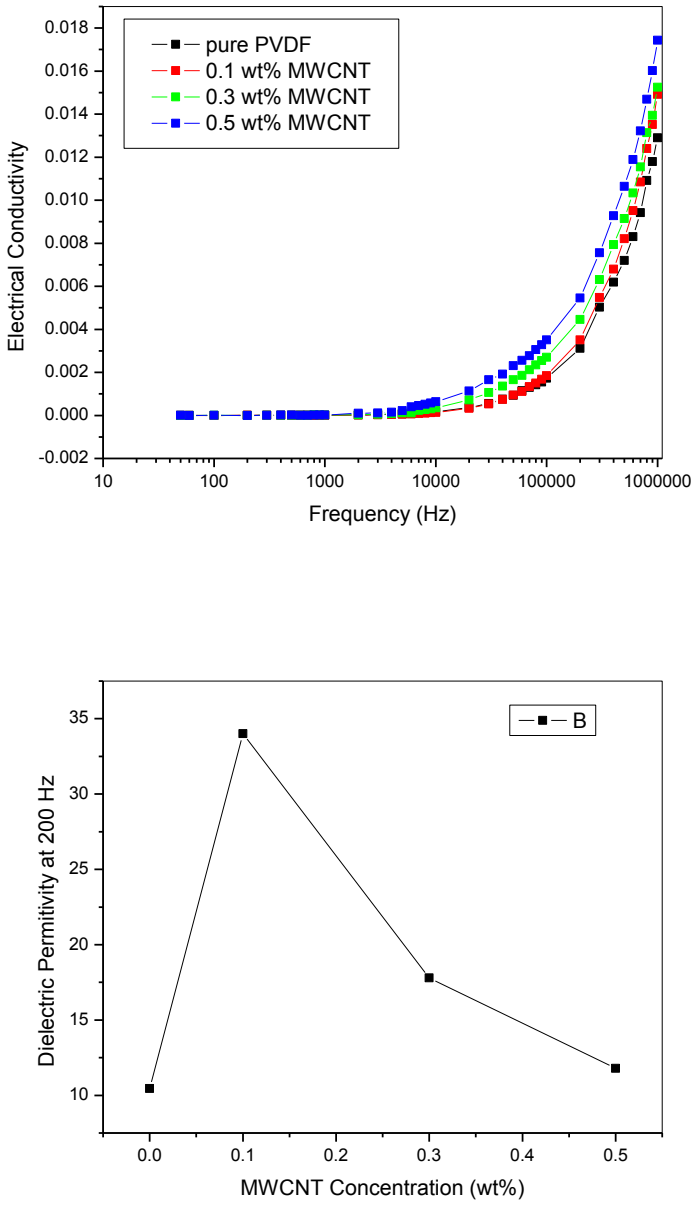
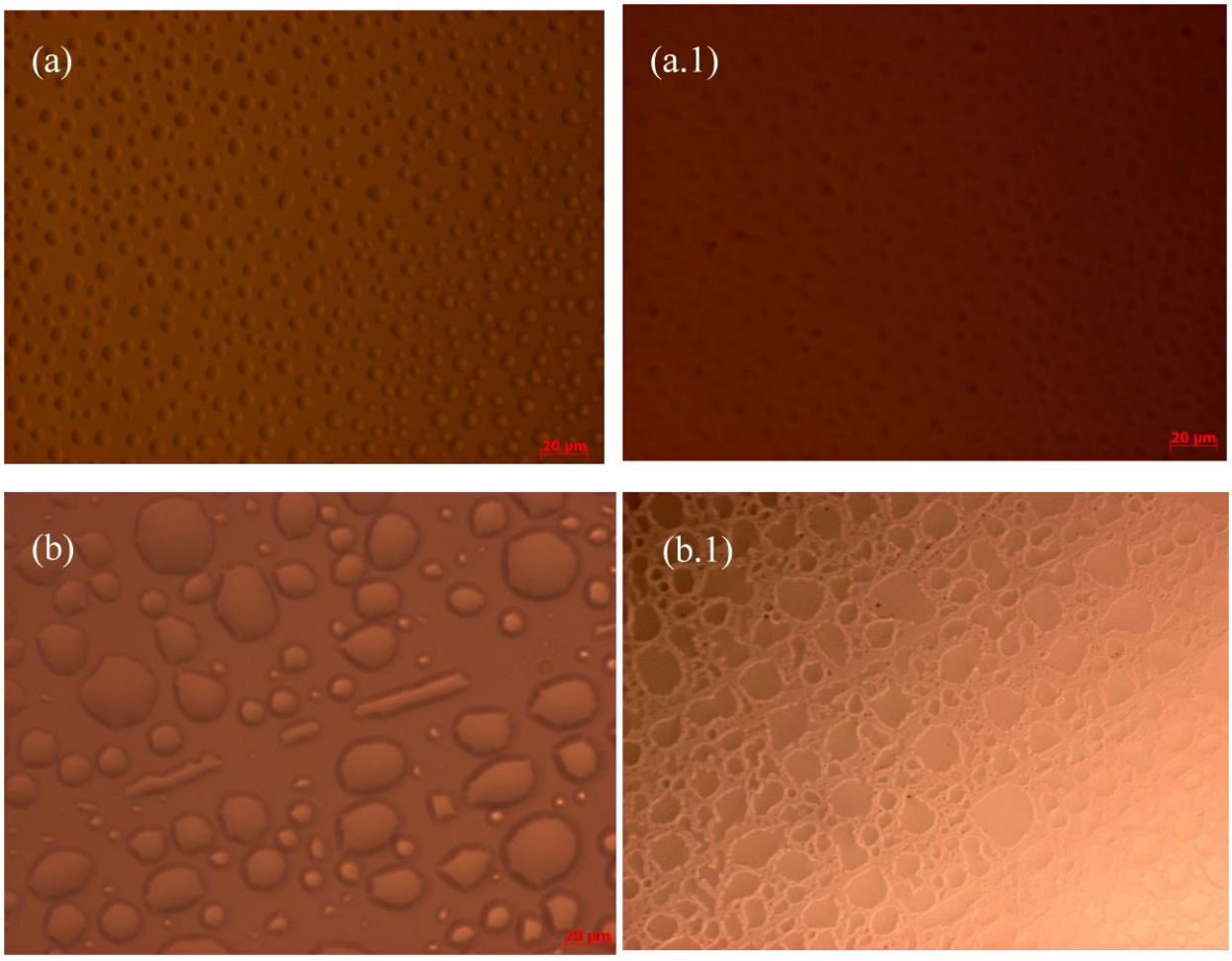


Figure: 3.9 (a) shows the Frequency depended electrical conductivity of pure PVDF and PVDF/FMWCNT nanocomposites and (b) shows the dielectric permittivity of pure PVDF and PVDF/FMWNT nanocomposites at 200 Hz.

3.2.7 Morphological Analysis by Optical Microscopy:

Fig. 3.10 shows the micrographs of pure PVDF thin film and PVDF/FMWCNT nanocomposites with different wt% of FMWCNT. Fig. 3.10 (a) clearly shows the spherltical structure of β phase at room temperature and with the help of linkam Temperature control we get micrographs with different temperature 3.10 (a.1) shows the micrographs at 160^{o}C it clearly shows the melting point which also clarify from DSC graphs. Fig. 3.10 (b) shows the micrographs of PVDF+ 0.1 wt % FMWCNT nanocomosites this micrograph clearly shows that ordering in the material at 50 X at room temperature and also shows the micrograph at melting temperature ordering will also clarify earlier by Polarized Fluorescence analysis. Fig. 3.10 (c) and (d) shows the micrographs of PVDF / 0.3 wt% and 0.5wt % FMWCNT at room temperature and melting temperature. Micrographs also shows that as wt % of FMWCNT increased spherultical structure is decreased.



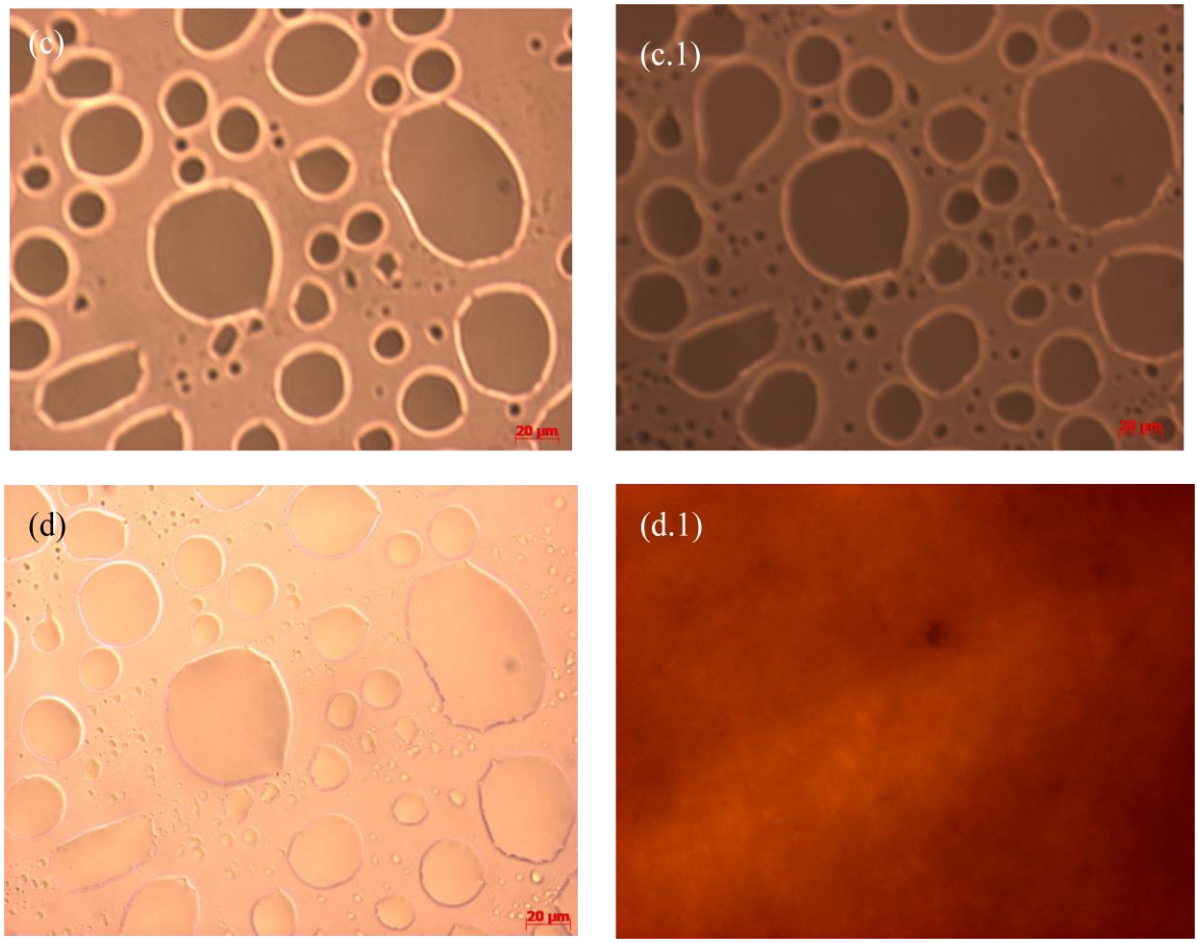


Figure: 3.10 shows the micrographs of PVDF and PVDF/FMCNT nanocomposites at room temperature and at melting temperature.

Chapter 4

Conclusion

In this research work, we successfully synthesized β phase in oxidized MWCNT dispersed in PVDF nanocomposites and well characterized.

- TEM analysis of COOH functionalized showed that the agglomeration of MWCNT was reduced and COOH Functionalization of MWCNT was well characterized with the help of FTIR spectroscopy.
- Morphological study with SEM showed that oxidized MWCNT was dispersed in PVDF until it reaches to its critical limit 0.3 wt% after it agglomerated with spherultical structure of PVDF.
- XRD analysis showed the reduction of α phase in the PVDF matrix and further supported by FTIR spectroscopy.
- Thermal analysis by Differential Scanning Calorimeter showed that addition of 0.1 wt% oxidized MWCNT enhanced the highest crystallinity in PVDF.
- PL spectroscopy showed that addition of oxidized MWCNT enhanced the ordering in PVDF material in which 0.1wt% of FMWCNT enhanced ordering about to be 45% than un-doped PVDF. That will also verified by the Optical Polarized Microscopy.
- The electrical investigation supports the enhancement of electrical conductivity with the dispersion of MWCNT in PVDF.

Hence we conclude that oxidized MWCNT effect the morphological response of PVDF matrix, which significantly improved the electrical properties over the prior approach. Therefore with the dispersion of MWCNT in PVDF, these nanocomposites may prove to be desirable potential candidates for the variety of applications in electronic industry.

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