

Synthesis and Characterization of PVA/Graphene Nano Composite for Packaging Material



Name: Maaz Khan Jadoon

Reg No: 00000119453

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Supervisor Name: Dr. Ahmad Nawaz Khan

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

H-12 Islamabad, Pakistan

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*All of my work is
dedicated to
My loving parents*

**“I COULDN’T HAVE DONE IT WITHOUT
THEIR LOVE AND SUPPORT”**

Acknowledgement

All prays and glory is due to **ALLAH**, whose worth cannot be described even by the greatest rhetoricians of all times whose blessings and bounties cannot be enumerated by beckoners and enumerators of all ages, and homage due to Him cannot be adequately paid even by the most assiduous and revering attempters. It is my privilege to express my deep sense of gratitude to my research **supervisor, Dr. Ahmad Nawaz Khan**, for his constant persuasion, affectionate guidance and efficient supervision at each and every stage of this research work. I would also like to thank my **committee members Dr. Iftikhar H.Gul and Dr. Malik Adeel Umar** for giving valuable guidance and suggestions to improve my thesis.

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Maaz Khan Jadoon

Abstract

Nano composite based on PVA and varied concentration of Graphene nano particles have been prepared in order to analyze their structural, morphological, thermal, dielectric and mechanical and antimicrobial response. The concentration of Graphene is varied from 0.1 wt% to 5 wt%. Graphene is homogenously dispersed within the PVA matrix up to 0.5 wt%, but some densification occurs at high weight percent of graphene observed through Scanning Electron Microscope. XRD analysis also confirms the exfoliation of graphene in the PVA matrix at lower loading of graphene but increasing the weight percent of graphene sheets re-stack and give a peak at $2\theta = 26.6^\circ$ which means that agglomeration of graphene sheets occurs at higher loading. FTIR analysis also shows a strong interaction between the PVA matrix and graphene. The -CO stretching peak at 1028 of Graphene/PVA nanocomposite become weak in comparison with pure PVA also suggesting the presence of interaction between PVA and Graphene. Dielectric properties also increase by incorporating Graphene into PVA matrix. The enhanced dielectric behavior of composite in the given frequency range is attributed to interface polarization. Modulus increases by increasing Graphene content. Tensile strength increases up to 0.5 wt% of graphene and then decreases at high concentration of graphene. The PVA/Graphene nanocomposite show bacterio-static behavior at higher loadings of graphene.

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Chapter 1

1 Introduction

1.1 Composite materials

Multiphase materials that depict the required properties of the constituent phase are called composites. The materials that are composed of two or more materials without change in the original properties of the materials themselves are mentioned as composites. These materials are also defined as materials with high strength containing reinforcements that are bind by the matrix system. These materials are highly under study due to their unique ability to constitute the properties of the reinforcements. The combination of these materials can be used for enhanced properties. Majority of the composite materials have two phases

- Matrix phase
- Dispersed phase

Matrix phase is a consistent phase while dispersed phase is enclosed by this matrix.

There are many reasons for which composite materials are preferred over all the other materials.

Specific modulus and strength mark these materials with extravagant properties. Higher specific modulus and the quality of polymer based composites with enhanced strength provide a decrease in the weight. Such materials are highly discussed due to their notable efficiency and conversion of energy with decreased weight. Figure 1.1 shows the types of composites.

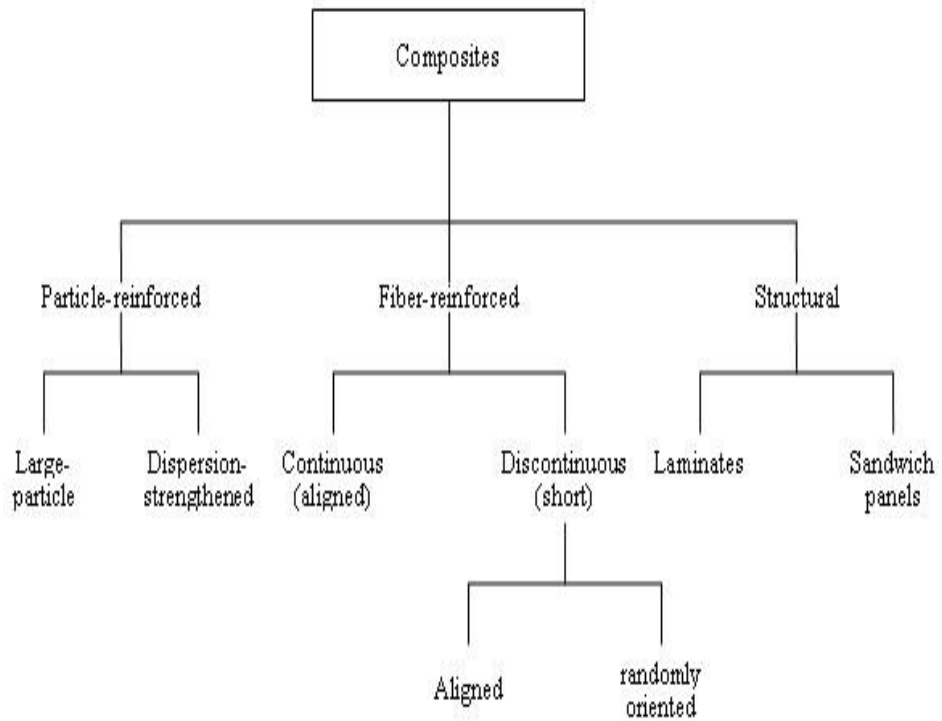


Figure 1.1: Composite

1.2 Polymer:

The word polymer is a derivation of Greek words “polus” and “meros” that mean many and parts respectively. Long chains of molecules possessing high molecular weight are called polymers. Such chains are often referred to as macromolecules. The chains possess specific characteristics depending on the molecules present in the chain. These molecules when combine to form long chains, give specific characteristics and properties like strength, viscosity, toughness etc.

The first usage of polymeric materials was observed with cotton, starch, fleece and proteins. Synthetic polymers were introduced in the mid of 20th century. Bakelite and nylon were the engineered polymers that showed the valuable characteristics in the new materials. In the past the focus was on the products that were made of covalent bonding between molecules or repeating units of the polymers but now the focus on polymeric studies has been enhanced to non-covalent bonding between these repeating units. Biological and natural polymers have gained special interest in this respect one of the major examples of a natural polymers is polyisoprene. Nearly all biological components are made up of polymeric macromolecules. Proteins and nucleic acids that are the basic building block of human body consist of biological polymers.

The vast research in the field has enabled the researchers to enhance the properties of the polymers. These properties rely on the synthesis process of the polymers and their solidification. Alteration in the processes allows to change the shape, size and association of the crystallites in the polymer. Molecular organization of the polymers decides the strength of the polymer. The state of the polymer solely depends on the organization of the molecules and repeating units. The classification of polymers depends on the process of their synthesis and whether they occur in nature or not, their structure and the orientation of the repeating units, forces between their molecules and the mode of their polymerization. Figure 1.2 shows the classification of Polymers

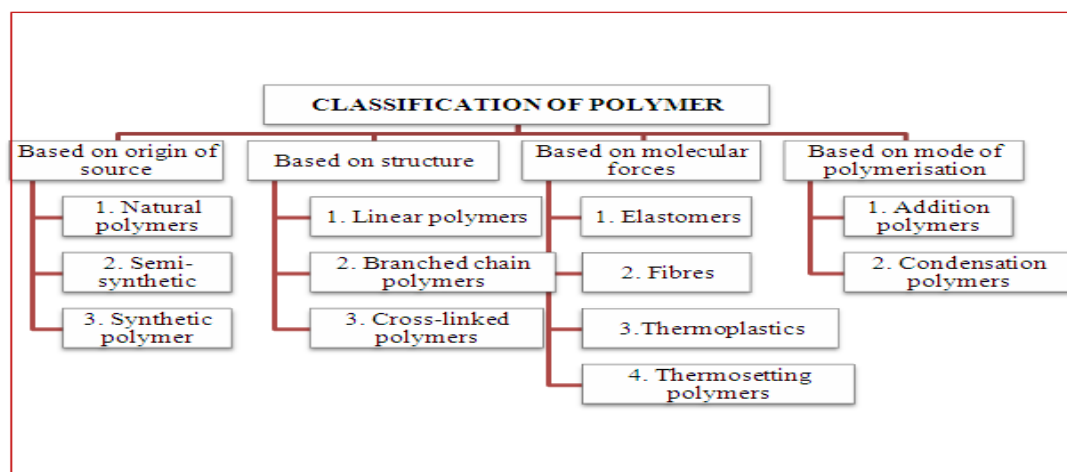


Figure 1.2: Classification of polymers

1.3 Polymer's Classification:

Polymer's classification has done by taking their molecular interaction, nature **and** structure in account. On the basis of their molecular interaction they are classified into four types

- Thermoplastic polymers
- Thermosetting polymers
- Elastomers
- Fibers

1.3.1 Thermoplastic polymers:

Thermoplastic polymers are those materials that upon reaching a specific temperature become malleable and below that temperature become solid. High molecular weights are observed in thermoplastic polymers The monomers or repeating units are linked with each other in a continuous manner with Vander Waal forces which become weak

when the temperature is raised. Due to weakening of these forces the solid materials turns into a viscous liquid that can be molded and shaped. Thermoplastic polymer can acquire two different types of structures depending on the extent of intermolecular forces i.e. amorphous structure or crystalline structure. The amorphous structure contains a bundled structure that defines the elastic properties of the material while an ordered and compact structure is observed by crystalline or semi crystalline structure that defines the mechanical performance of the material. Therefore, the thermoplastic polymers properties are defined by the structure they possess.

Thermoplastic polymers are highly recyclable due to no change in material properties upon increasing temperature, show high impact resistance, are chemically resistant and have a hard or rubbery surface.

1.3.2 Thermosetting polymers:

Thermosetting polymers also called thermoset are polymers linked with chemical bonds making an extremely cross-linked polymeric structure. High mechanical properties and excellent physical strength are attributed to this formation of highly cross-linked polymeric structure due to chemical bonds. A thermoset polymer is capable of irreversibly curing upon exposing to high temperatures nearly of 200 °C. Gel point is the known parameter when the viscous liquid state changes to a more solid and firm condition. Upon reaching its gel point this material is no more capable of molding or shaping. These materials hold a disadvantage of being unrecyclable. Once these materials are cured it is not possible to return them to their moldable form. Thermoset polymers have distinguished properties of not melting, being insoluble and showing high resistance to creep. Some of the renowned thermosetting materials are resins which includes phenol, unsaturated polyester and epoxy. They are notable in their use for coating, manufacturing of fiber glass and insulating materials, tool handles, fillers etc.

1.3.3 Elastomers:

An elastomer is a polymeric material that is both viscous and has elasticity. Elastomer has weak intermolecular forces along with a small Young's modulus. In contrast with other material an elastomer contains high failure strain. Elastomers are also given the name rubbers due their properties. Hydrogen, oxygen, carbon and silicon are the major molecular components of each of the monomers present in the elastomer. Above their glass transition temperature elastomers are amorphous. At recognizable temperatures

rubbers become deformable and soft. They are primarily used as seals and for adhesion purposes. Long chains of elastomers have the ability to rearrange themselves when an external stress is applied to it. Due to presence of covalent bonding in crosslinked chain, the chain returns to its original arrangement when the stress is removed. Temperature also affects the properties of elastomers. Less mobile chains are observed in elastomers that have gone below the glass transitioning temperature while the elastomers above the glass transitioning temperature will have more elasticity and chain mobility.

1.3.4 Fibers:

Fibers are synthetic materials whose length is exponential as compared to their width. Fibers exist in nature as biological fibers however polymeric fibers are man made fibers with long chains based on synthetic chemicals. These fibers are made by using different polymeric materials like nylon, polyester, phenol-formaldehyde polyolefin, elastomers etc.

1.4 Types of Polymers on the basis of “mer” in the chain:

- **Homo polymers:**

A homo polymer is a type of polymer that contains similar kind monomers that mix or join with each other to make a macromolecule.

- **Co-polymer:**

When different types of monomers especially greater than two different types are combine to make a macromolecule than the polymer is called co-polymer.

- **Polymer Blend:**

Use of physical bonding to combine different types of monomers results in the formation of a polymer blend.

1.5 Recognition of polymers:

Polymers are recognized on the basis of their linear or ring like structure into two categories.

- **Aliphatic polymers:**

Polymers that contain hydrocarbons in a linear structure e.g. PE, PP

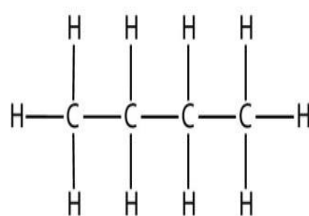


Figure 1.3: Aliphatic Polymers

- **Aromatic Polymers:**

Polymers that have a benzene ring in them or a naphthalene ring that acts as a backbone of the chain.

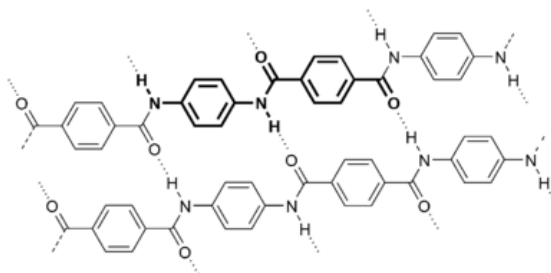


Figure 1.4: Aromatic polymer

1.6 Molecular structure of Polymers:

Polymers can be characterized into the following types based on their molecular structure

- **Linear Polymers:**

Polymers that form long chains by connecting monomers linearly

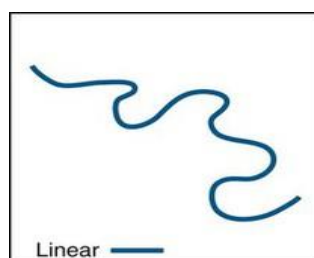


Figure 1.5: Linear polymers

- **Branched Polymers:**

These type of polymers are formed when secondary chains connect to the central long chain.

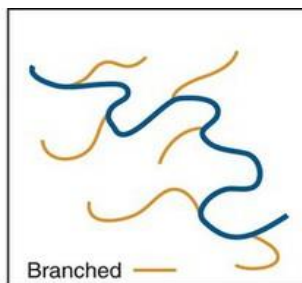


Figure 1.6: Branched polymers

- **Cross-linked Polymers:**

These types of polymers contain long chains that can be either branched or linear but are capable of forming a chemical bond between the monomers.

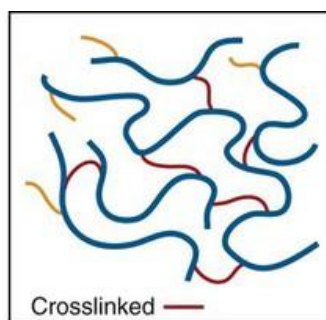


Figure 1.7: Cross-linked polymer

1.7 Vinyl Polymers:

This is a group of polymeric materials that is derived from vinyl monomers. An extended alkane chain acts as their backbone. An alkene group ($C=C$) is polymerized into a chain ($\dots-C-C-C-C\dots$) to form the alkane backbone. Generally, vinyl only refers to polyvinyl chloride (PVC). Most common plastics are polyvinyl

- Simple alkenes are polymerized i.e. Polyethylene from ethane, polypropylene from propene and polybutadiene from butadiene.
- Vinyl benzene is used to make polystyrene.
- Monomers of vinyl chloride are polymerized to derive polyvinyl chloride $CH_2=CHCl$.
- Vinyl acetate is polymerized to obtain polyvinyl acetate. It is used as a glue when suspended in water.
- Polyvinyl acetate is hydrolyzed to obtain polyvinyl alcohol.
- Acrylonitrile is used to prepare polyacrylonitrile.

1.8 Polymer Composites:

Polymer composites have matrix phase made of polymer in which different types of fillers can be added depending on the required properties. Polymer composites have gained much attention since the use of nanostructures as fillers. When nanostructures are used as fillers in polymer composites they are given the name Polymer Nanocomposites.

1.9 Why Polymer Nanocomposites.

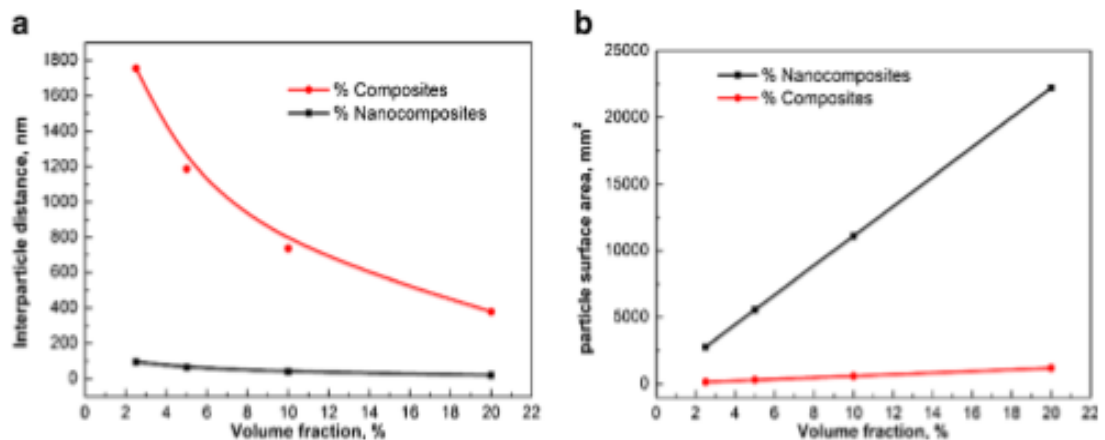


Figure 1.8: Comparison of composite and nanocomposite (a) distance between particles (b) surface area of Particle.

Micro fillers and nano fillers both have been used extensively in polymer nanocomposites however drastic differences can be observed in the use of both these fillers. The above graphs show a comparison between the use of micro fillers and nano fillers. Both nano fillers and micro fillers are added to the polymer matrix to observe their characteristics. It can be observed in Fig1.8(a) that the change in inter particle difference in nano filler does not have considerable effect as observed in case of micro filler. Increase in volume fraction results in decrease of inter particle distance in micro fillers while this effect is negligible in case of nano fillers. This shows that the matrix binding in nano fillers is good as compared to micro fillers because nano fillers provide more space for the matrix to fill in. therefore good interfacial bonding is observed in nano fillers as compared to micro fillers. [3]

Fig 1.8(b) gives a comparison of nano fillers and micro fillers with respect to increase in surface area by addition of the filler. A noticeable increase in the surface area is observed when nano filler is added into the polymer matrix while micro fillers show

no increase in the surface area upon their addition. In case of nano fillers surface area increases upon their addition hence providing more interaction between the matrix and nano fillers which results in good interfacial bonding. This comparison shows the preference to use nano fillers in polymer composites. [3]

1.10 Nano Filler Geometries:

The properties of Nanocomposite materials not just rely on upon the properties of their every single constituent, however on the filler's surface attributes and morphology. In Selecting Nano filler, the important points which must be kept in mind are Size and shape of filler which have a huge impact on the properties of Nanocomposites and their handling systems. filler geometries have three main kinds which are used in polymer Nanocomposites those includes Particle, fiber also layer types of fillers. When we Compare the geometries of Nano filler we jumped to a conclusion about highest specific surface area which only layer Nano fillers have. [3]

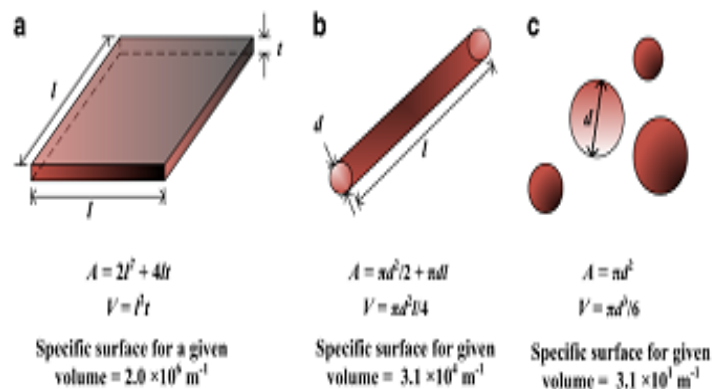


Figure 1.9: Nano filler geometry

1.11 Polyvinyl Alcohol

It is semi-crystalline, atactic, homo, water soluble and synthetic polymer. We can write its formula as $[\text{CH}_2\text{CH}(\text{OH})]_n$. It is colorless and odorless. It is available in the form of beads or as solutions in water.

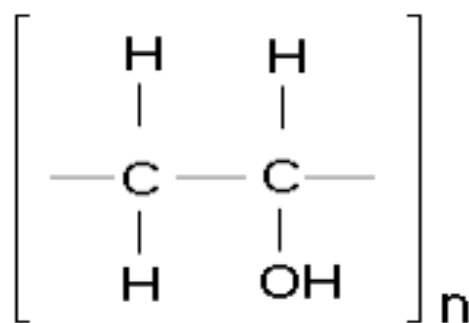
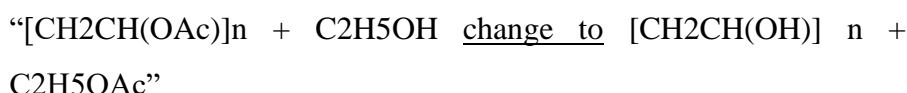


Figure 1.10:PVA structure

1.11.1 Manufacturing

PVA is different from vinyl polymers, the driving cause for this difference is that it can never be easily manufacture by using its own monomer during polymerization. The monomer vinyl alcohol is not stable which is used in its polymerization when we compare it to acetaldehyde. Manufacturing process includes following steps

- a. Polymerization of the vinyl acetate
- b. we will get PVA from the Polyvinyl acetate
- c. Other than acetate polymer precursors we can also use different one as chloroacetate groups and formate.
- d. By using ethanol in base-catalyzing Trans esterification polyester can be converted to it.



The properties are totally dependent upon the total amount of extra ester groups. PVA have demand of about 1 million metric tons in 2006. Some of the producers that produce large amount of PVA are Kuraray and Sekisui Specialty Chemicals (USA) but china is leading these Companies from the past decade and is producing about 45 percent of the total of the world

demand. The North Korean produces a Vinalon which is produced from PVA. As we know it is having inferior properties as clothing fiber but still, we produce it for reason of self- sufficiency as no oil is necessary to manufacture it.

1.11.2 Uses of PVA

It can be used as Paper adhesive

- It can be used as sizing agent in textile industries

- It is used as Paper coatings in paper industries and also as a release liner
- It can be used is packaging.
- It can be used as a film in water transfer printing
- It can be used in eye drops in order to make the dry eyes wet and as a lubricant for hard contact lens
- The fibers of PVA can also be used in concrete as reinforcement material
- It can be used as raw material to manufacture polyvinyl nitrate
- It can be also used in the formation of encapsulated Nano beads of polymer as a surfactant
- When PVA is doped with iodine it can polarize light
- It is used in 3d printing as it supports the structure of the 3d printed object
- It is used as thickener, modifier, in polyvinyl acetate glues

1.11.3 Properties of PVA

Some of the properties are listed in table 1.

Table 1 :Properties of PVA

T _g	40°C - 45°C
Melting Point	160°C - 170°C
Density	1.19 g/cm ³
Boiling Point	228°C

1.11.4 Tacticity in PVA:

PVA is an atactic polymer, having OH group attached randomly on either side of the polymer chain. The structure is given in the figure 1.15. Due to the consistency and non-variant nature along chains both structures syndiotactic and isotactic will be able to crystallize easily. In any case, their unit cells and melting temperatures are not the same. In general, Atactic polymers are totally amorphous only to that extant when the side group is so small or it may be polar which allow some regular arrangement means crystallinity. PVA is this type of crystalline atactic polymer which is also

referred as polyvinyl alcohol. Atactic polyvinyl alcohol is somehow crystal on account of syndiotactic.

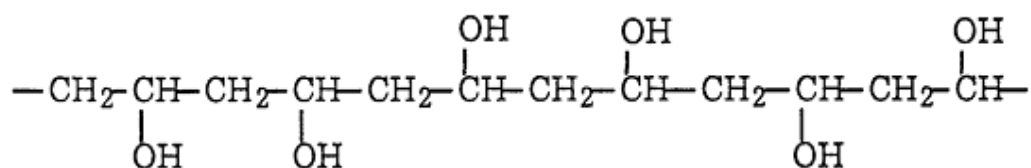


Figure 1.11: Tacticity of PVA

1.12 Graphene

Graphene, having a remarkable two-dimensional structure, is containing numerous planar sheets of carbon atoms which are sp²- bonded [7]. Its discovery was made in 2004. It is having great properties and is becoming the most wanted material of the coming future and today. [1]

1.12.1 : Synthesis of Graphene

Some of the methods are as follows.

- Adhesive tape or scotch tape method
- liquid phase
- From graphite oxide
- Epitaxial growth
- CVD

Chapter 2

2 Literature Review

2.1 Alumina/Polyvinyl Alcohol (PVA) Composites

Archana, Nigrawal, Navin Chand they worked on dielectric properties of Alumina/Polyvinyl Alcohol (PVA) nanocomposites. Figures 2.1 to 2.2 show the alteration of ϵ' with rise of temperature and frequency for pure PVA and samples 1, 2 and 3 respectively. [9] At initial temperature (30°C) these plots Figures 2.1 to 2.2 do not show any change in ϵ' value which shows that there is no amassing of interfacial charge in nanocomposites. As there is increase in the temperature improvement in the dielectric constant is detected. At 150°C, the sample with the higher weight percent of alumina has highest value of ϵ' . The rise in dielectric constant can be credited to the fact that because of the enhanced segmental mobility at or near glass transition gave high rise in dielectric constant for all samples.[10] [11]

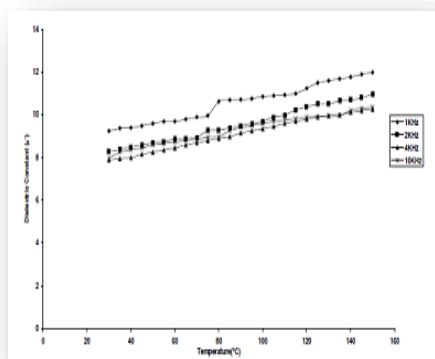


Figure 2.1: Dielectric constant of PURE PVA

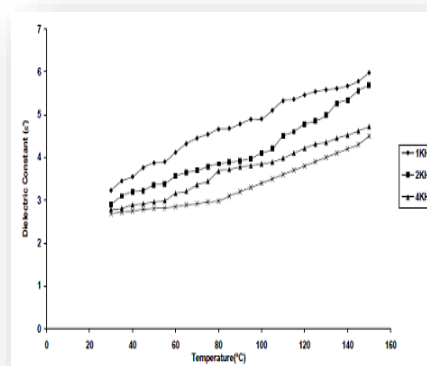


Figure 2.2: 0.5wt% of nano alumina in PVA

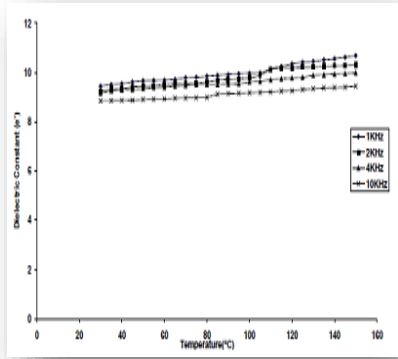


Figure 2.3: 1% nano alumina in PVA

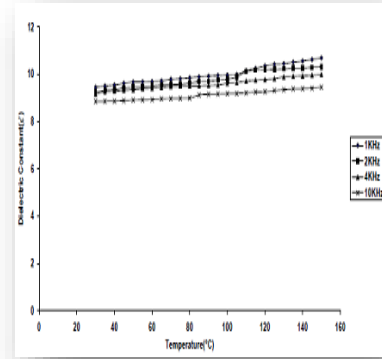


Figure 2.4: 5% nano alumina in PVA

2.2 PVA/Graphene Composite

Xin Zhao et al worked on PVA/Graphene composites. They have made PVA composite films with graphene having enhanced uniform and good dispersion were synthesized accurately by integrating graphene oxide in PVA matrix and reducing graphene oxide into graphene sheets at nano level [5]. The PVA/Graphene composite films showed substantial enhancement in the mechanical performance[14]. For example, The figure 2.6 show that by adding 1.8 vol % graphene nanosheets 150% increase of tensile strength is achieved, representing the effectual load transfer within the graphene sheets also in the matrix. The composite's modulus with 1.8 vol % graphene addition is increased 10 times than the PVA sample as indicated in figure 2.5. The evaluation between the experimental outcomes and the Halpin-Tsai theoretical interpretation specified that graphene may be arbitrarily scattered within polymer matrix[14]. Furthermore, On adding graphene nanosheets to the matrix of PVA it effects though very small on crystal arrangement of the composites. [7]

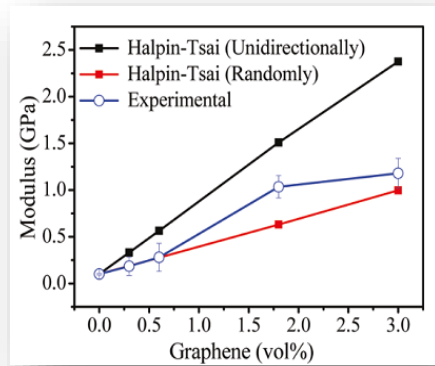


Figure 2.5: Young's modulus and Halpin-Tsai theoretical models of graphene/PVA nanocomposites

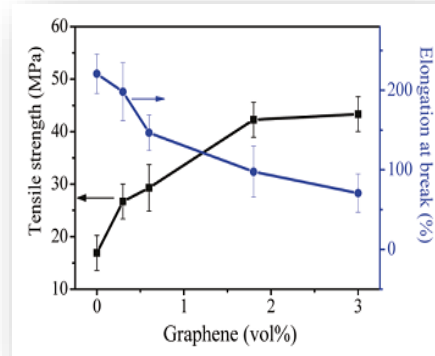


Figure 2.6: Mechanical properties of graphene/PVA nanocomposites

2.2.1 Mechanical Percolation

Figure 2.8 shows the mechanical percolation. When the filler quantity approaches a threshold value with which the space within two sheets gets smaller enough that they may attempt to pile or stack on one another conveniently because of the van der Waals force, then they change to the stacked form (figure 2.8(4)). [8] There is a threshold point for mechanical performances due to the Nano sheet content, i.e., a loading of 1.8 vol%, and this occurrence is termed as mechanical percolation[21][28]. Among these, the second one (figure 2.8(2)) is the perfect situation, presenting the definitive contribution to the mechanical performances with the highest effectiveness. [8]

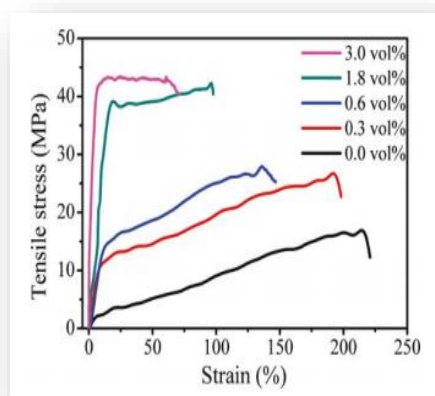


Figure 2.7: Stress-Strain graph of Nanocomposite

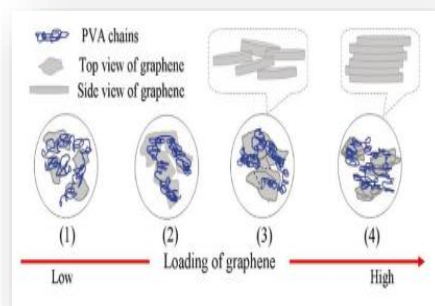


Figure 2.8: Mechanical percolation of PVA

2.2.2 PVA/Graphene XRD Results

XRD is an effective technique to calculate the inter-layer alterations of graphene - related materials and properties related to crystallinity of composite. In the Figure 2.9, the XRD patterns show a broad peak of graphene and PVA has its characteristic peak at $2\theta=19.5$. However, as the graphene nanosheets is dispersed into the PVA matrix (figure 2.9 curve c), the broad peak disappears in the composites, suggesting the disorder of structure regularity of the graphene. Figure 2.10 shows the same results as graphene loadings increase in the composite. Therefore, Exfoliation of the graphene nanosheets are considered at the molecular level into the PVA matrix. To further confirm this point, an equivalent sample of 0.6wt% of graphite is prepared, in PVA. The characteristic peak of graphite remains at $2\theta=26.5$. It is because the graphite has a regular structure. PVA is semi-crystalline, having a peak of XRD at $2\theta =19.4$ of strong intensity. Figure 2.10 shows a weak hump at $2\theta=40.4$ and a large part of the intensity is at $2\theta=19.4$ that is the (101) diffraction peak of PVA. Because of the packing of PVA chains there is an increase in the intensity of the (101) diffraction peak, causing in a large size PVA sol-gels crystallites As addition of the graphene nano-sheets into PVA polymer, the (101) diffraction intensity increases first and then descents, it concludes that at 0.6wt% of graphene the crystallinity is maximum[14].

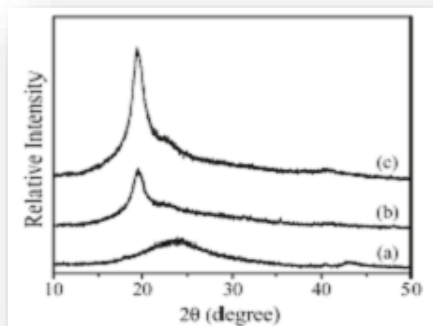


Figure 2.9 :XRD pattern of (a) graphene powder, (b) pure PVA, and (c) graphene/PVA composites with 0.6 vol % loading of graphene

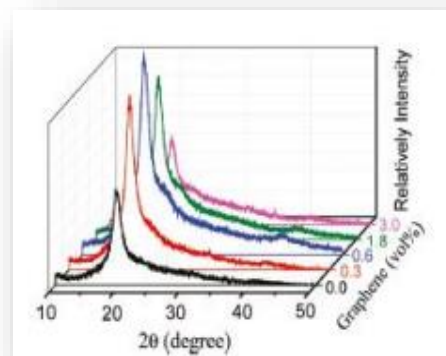


Figure 2.10 :XRD patterns of graphene/PVA composites with various graphene contents

2.3 PVA/GO nanocomposite:

Graphene nano sheets with polymer matrix have been processes in an aqueous solution, such work has been reported by many as Xiaoming Yang, Xiao-ming Tao, Songming Shang and Liang Li. Rather simple practical approach for developing properly dispersed nano-composites with aligned Graphene nano sheets in PVA (Poly

vinyl alcohol) matrix is explained. Effects of Graphene on PVA structure have been studied[17]. Crystallinity of PVA is reduced by adding Graphene, however the film of matrix PVA is surely strong and ductile. Uniform distribution of Graphene in PVA at molecular level and its alignment with matrix is responsible for change in structure and alteration of properties of PVA/Graphene composite material. The strong interfacial interactions between PVA and Graphene also plays the important role to the overall properties and structure. [14]

2.3.1 FTIR analysis of the Composite:

FTIR analysis was done for functional group analysis, like for determining the interaction of PVA and Graphene sheets. As we know that –OH stretching and –C–OH stretching bands are both sensitive to hydrogen bonding. Shifts towards lower wavelengths have been observed for strong hydroxyl band for free and hydrogen bonded alcohols bands at 3100-3500 cm^{-1} , this shift is attributed to the increase in amount of Graphene sheets in poly vinyl alcohol (Fig.3). This may be due to the hydrogen bonding dissociation among hydroxyl groups of the polymers[29][30]. As by the results from FTIR, it is revealed that hydrogen bonding existing between the two components i.e PVA and Graphene, which is responsible for hydrogen bonding present within the polymer chains and which decreases the polymer crystallinity.

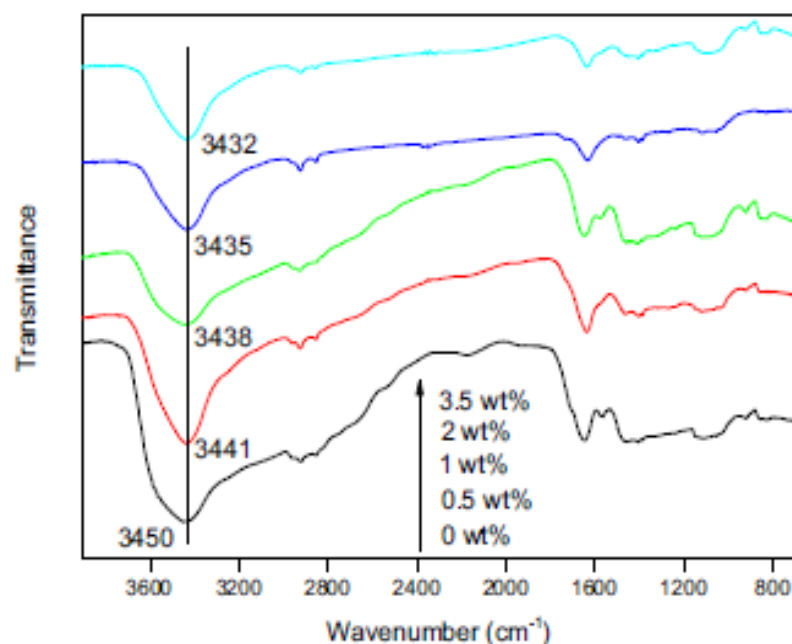


Figure 2.11: FTIR spectra of PVA/GO nanocomposite

2.4 Antimicrobial activity of graphene materials.

Liu et al analyses the antimicrobial activity on the basis of altering lateral dimensions of well distributed GO nano sheets from nano meters to micro meters. They demonstrate that wrapping of cells is done efficiently by larger GO sheets and block the active sites on membrane thereby inhibiting bacterial proliferation. In contrast smaller GO nano sheets showed weaker anti-microbial activity due to incomplete bacterial surface covering because the uncovered membrane surface could still take up nutrients from the environment for survival. [2]

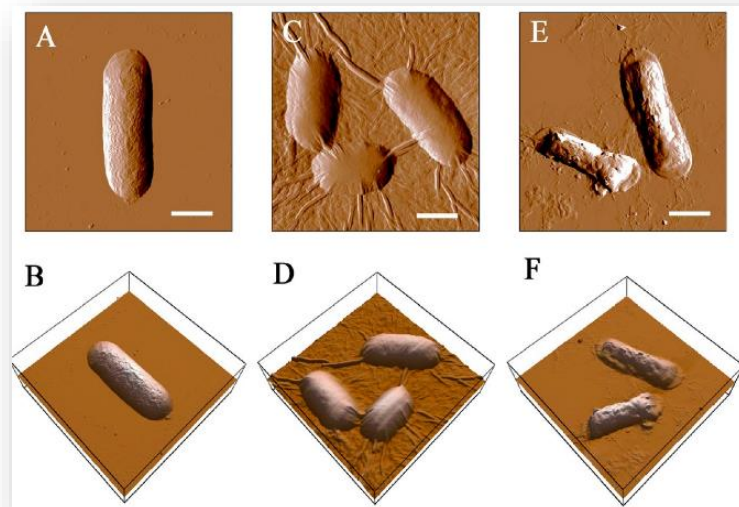


Figure 2.12: AFM images of incubated *E. coli* with GO (A,B) *E. coli* incubation, (C,D) incubated *E. coli* with GO-0, (E,F) incubated

AFM was utilized to see the interaction between *E. coli* cells and GO sheets. Figure 11 shows the images of incubated *E. coli* with large GO (GO-0) and small GO (GO-240) sheets. The Figure A and B shows that cell retains its membrane integrity after incubation for 2hr in deionized water. In figure C and D, *E. coli* cells are shown after wrapping by large GO sheets. Figure E and F shows small GO sheets adhesion on the cell surface. [2]

2.5 Objectives

- Developing Graphene/PVA nanocomposite through solution casting method
- Investigating the properties of Graphene/PVA nanocomposite:
 - ❖ Mechanical Properties
 - ❖ Dielectric Properties

- ❖ Thermal Properties
- Anti-microbial Activity
 - ❖ Anti-bacterial
 - ❖ Anti-fungal

Chapter 3

3 Experimental Procedure

3.1 Materials

The materials used are PVA(mw=72000) purchased from MERCK and the graphene used is purchased from Korea.

3.2 Preparation of PVA sheet

Required amount of PVA is taken and de ionized water was added and the solution was kept on constant stirring at 500 Rpm and 90°C. After 40 min we get a clear solution. Then graphene is added to the solution and the mixture were ultrasonic treated for 40 min with a probe sonicator. The obtained dispersion was poured into a Teflon mold and placed in vacuum oven at 40°C for drying and 450mbar pressure. The PVA/Graphene composite film was carefully peeled of the mold the thickness obtained was approximately 0.20mm.

There is five easy steps involved in the preparation:

- Take PVA + Deinosed water
- Dissolved at 90°C with magnetic Stirrer and then graphene is added
- Probe Sonication for 40 minute
- Casted in Teflon Mold
- Dried in vacuum oven at 40°C at 450mbar pressure
- Nanocomposite Film is peeled off



Step 1 PVA + Distilled water



Step 2 Dissolved at 90°C with magnetic Stirrer.

Graphene is added



Step 3 Probe Sonication for 40 minutes



Step 4 Casted in Teflon Mold



Step 5 Dried in vacuum oven at 40°C
at 450mbar pressure



Step 6 Nanocomposite Film

3.3 Composition and Number of samples prepared

Table 2 :Samples composition.

PVA (wt %)	Graphene (wt%)
100	0
99.9	0.1
99.7	0.3
99.5	0.5
99	1
95	5

3.4 Characterization Methods

3.4.1 X-Ray Diffraction (XRD)

The structural analysis of nano hybrid composites were done by WAXD at room temperature with a Cu K α Radiations ($1\frac{1}{4}$ 0.15418 nm). The range of WAXD was $2\theta = 5^\circ$ to 50° in order to evaluate the crystalline phases in the solution casted films and the scanning rate was $2^\circ/\text{min}$ was employed for the samples.

3.4.2 Differential scanning calorimetry

Further information about crystalline phases were determined by DSC (Perkin Elmer) results. Thermal properties of samples can also have attained by DSC results by heating the sample at 10°C per minute. Zinc and Indium standards were maintained at temperature and heat flow rates.

3.4.3 Scanning electron microscope

Highly resolution and magnified images of nanocomposites were obtained by SEM (JOEL JSM-6490A) in order to examine the morphology and distribution of nano

fillers within the PVDF matrix. The samples were treated with liquid nitrogen to make it brittle and then broke to form a clear surface of nanocomposite. Gold coating was employed to make the samples conductive.

3.4.4 Dielectric Analysis

Dielectric constant, dielectric loss and AC conductivity were calculated using Impedance Analyzer (Wayne Kerr 6500B) at room temperature verses frequency from 100 Hz to 5 MHz. The 12 mm diameter samples were prepared using die with 0.22 mm average thickness of samples.

3.4.5 Mechanical properties

Tensile properties of nanocomposites were measured using Universal Testing Machine (Trapezium-X , model no. AG-20KNXD Plus) manufactured and assembled by Shimadzu Co.

Chapter 4

4 Results and Discussion

4.1 XRD Results

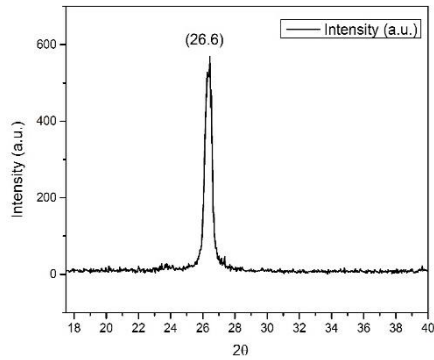


Figure 4.1: XRD of Graphene

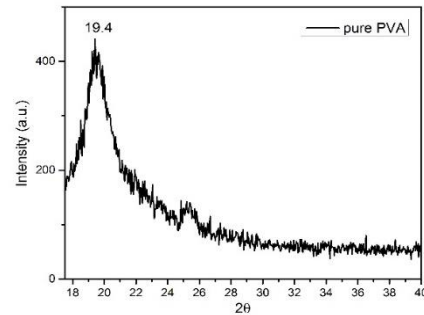


Figure 4.2: XRD of Pure PVA

Figure 4.1 gives us the XRD pattern of Graphene. For Graphene, the crystalline peaks appear at $2\theta = 26.6$, corresponding to (0 0 2) crystal planes of Graphene [1-3]. Figure 4.2 gives us the XRD of pure polyvinyl alcohol. The crystalline peaks appear at $2\theta = 19.4^\circ$, corresponding to (101) crystal planes of PVA [16-21].

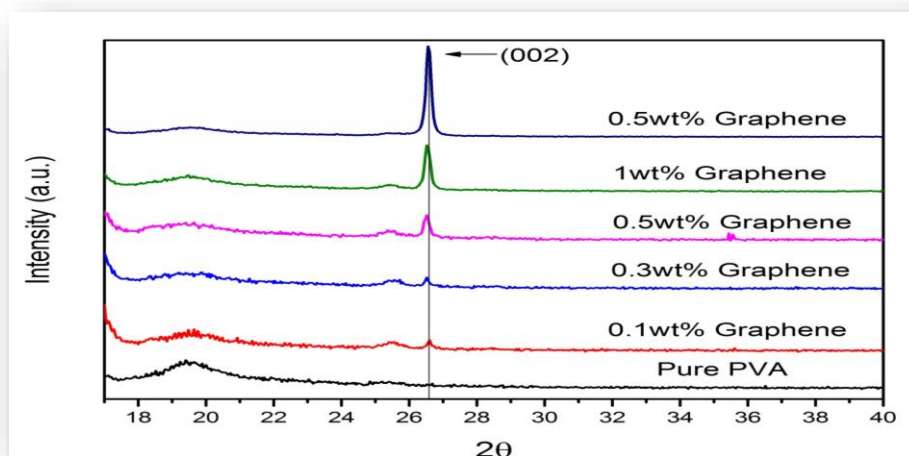


Figure 4.3: XRD comparison of pure PVA, 0.1wt% graphene, 0.3 wt % of graphene, 0.5wt% of graphene, 1wt% of graphene, 5wt% of graphene

Figure 4.3 give us the comparison of pure PVA,0.1wt% graphene,0.3 wt % of graphene,0.5wt% of graphene,1wt% of graphene,5wt%of graphene. The XRD profile of lower concentration of graphene wt% of PVA composite film shows a peak of diminished intensity at 26.6. These results indicate that graphene has been efficiently exfoliated within the PVA matrix. But for the higher concentration then 0.3wt% the intensity of graphene peak is increased. This means that now graphene sheats were not individually dispersed in PVA matrix but rather in the form of stacks of graphene platelets.

In addition the crystalline structure of the matrix was also affected due to the incorporation of the graphene there is a decrease in the packing of PVA chains and hence results in either less order packing.

It also means that PVA chains have penetrated into the graphene layers which also gives improvement in the mechanical properties such as tensile strength and modulus.

4.2 FTIR Analysis

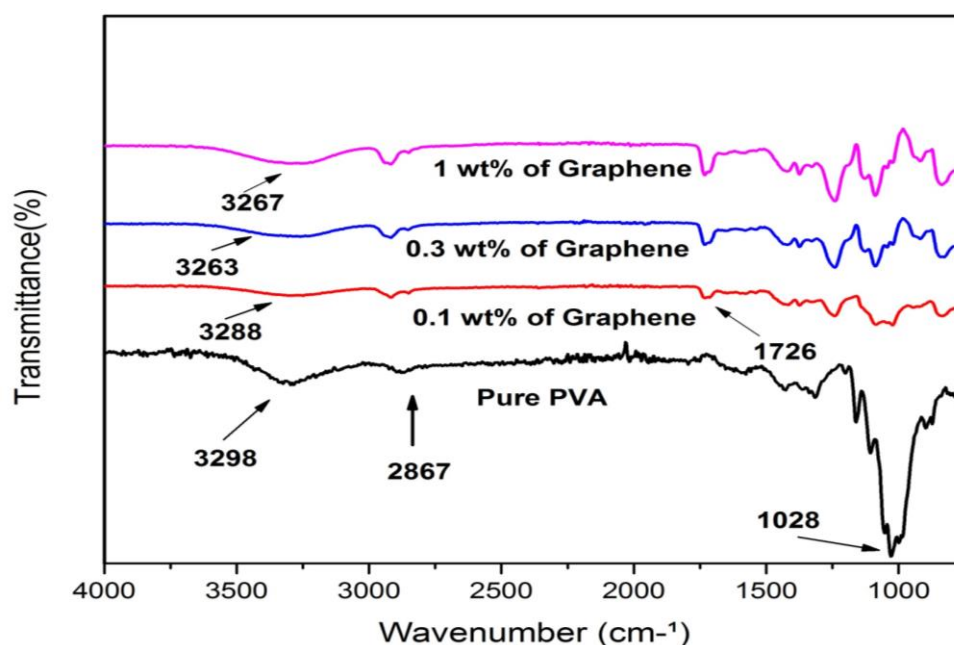


Figure 4.4: FTIR analysis of pure PVA, 0.1wt%, 0.3wt%, 1wt% of graphene

Figure 4.4 shows the FTIR analysis of PVA, 0.1wt% graphene, 0.3 wt % of graphene and 1wt% of graphene. The hydrogen bonding has great influence on the C-OH and -OH stretching bands which are sensitive to it. As shown in the fig.4.4 the band

3298 cm^{-1} involving the strong hydroxyl band shifts to lower wave number when graphene content is increased in the matrix of PVA. It would be attributed to the breaking down of the hydrogen bonds among the hydroxyl groups in polymer. Acquired results shows that there is a hydrogen bonding between PVA and graphene and reduces the polymer crystallinity.

The -CO stretching peak at 1028 cm^{-1} of Graphene/PVA nanocomposite become weak in comparison with pure PVA also proposing the existence of interaction between PVA and Graphene.

The peak at 1726 cm^{-1} , which can be ascribed to C=O stretching, stretching of ester group, increased after addition of graphene indicating the formation of ester bond.

4.3 SEM Analysis

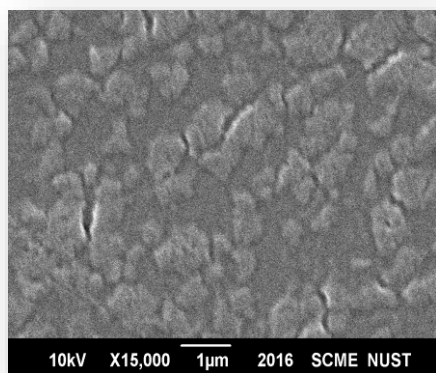


Figure 4.5: SEM images of Pure PVA

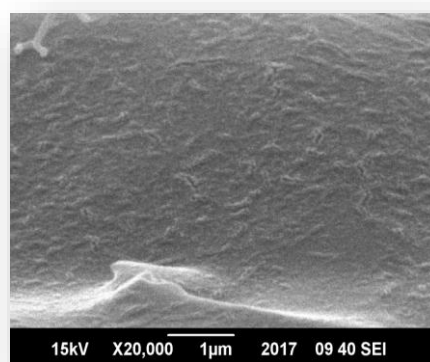


Figure 4.6: SEM images of 0.5wt% of graphene

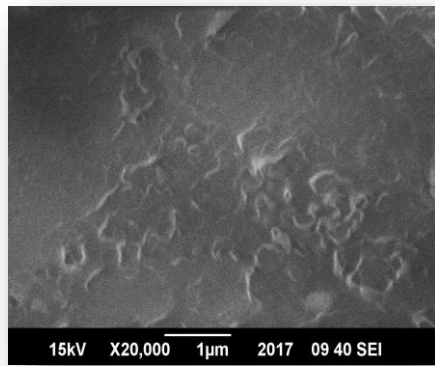


Figure 4.7: SEM images of 5wt% Graphene

Figure 4.5 ,4.6 and 4.7 shows the SEM images of pure PVA,0.5wt% of graphene and 5wt% of graphene dispersed in PVA matrix respectively. The first image is of pure PVA in which there are irregular spherulites present in PVA. This is because PVA crystals have reminiscent of structures as those from row nucleated crystallization in their early stages, dendrites in the mid to later stages and spherulitic in the final stage after the impinge and fully developed. The image 4.6 and 4.7 shows that when the graphene content was low as for 0.5wt% the graphene is well dispersed in the PVA/Graphene nano composite. But when the graphene concentration is increased the graphene platelets stack together and agglomerates causing the densification of graphene in the nanocomposite.

4.4 DSC analysis:

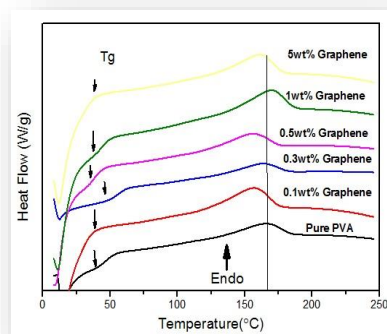


Figure 4.8: Heating curve of Pure PVA and PVA/Graphene nano

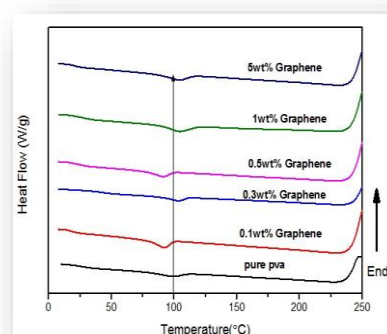


Figure 4.9: Cooling curve of Pure PVA and PVA/Graphene nano composite

The figure 4.8 and 4.9 shows heating and cooling DSC thermo-gram of pure PVA and PVA/graphene nanocomposite films of different weight concentrations. The Glass transition temperature for pure PVA is 39.8 There is overall increase in the Tg .This increase in Tg shows that the chains of polymer were indeed constraint due to H-bonding , an effect also demonstrate in other reports. The Melting temperature of pure PVA is observe at 167°C and decrease in addition of graphene till 1wt%. At 1wt% Tm is around 169°C.The decrease in Tm attributes to the relatively smaller crystal size of PVA due to intercalation of graphene platelets. It was observed that cooling curves promoted to high temperature with increased concentration of Graphene, this is because with addition of Graphene which acts as a heterogeneous nucleation sites for growth, leading to a faster crystallization process.

Table 3:Thermal properties of PVA/Graphene nanocomposite

Concentration wt%	Tm(°C)	Tg(°C)	Tc(°C)
Pure PVA	167.17	39.8	99.13
0.1	157.33	40	92
0.3	163.18	46	104
0.5	156	38.032	91
1	169	43.03	105
5	162	40.43	104.50

4.5 Mechanical analysis:

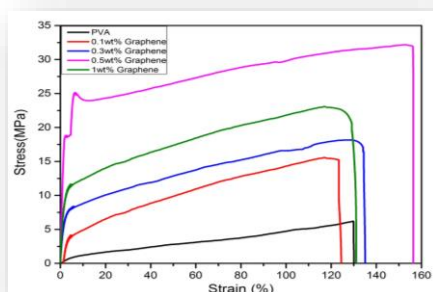


Figure 4.8: Stress-strain curve of PVA/Graphene Nano composite

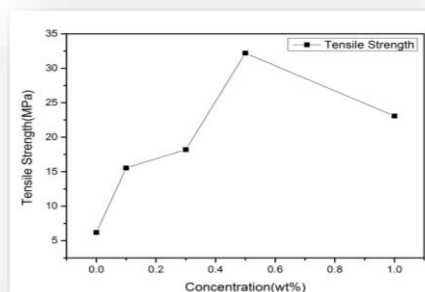


Figure 4.9: Variation of tensile strength with increase in Graphene content

Figure 4.10 shows the typical stress strain curve for PVA/Graphene nanocomposite with various graphene contents. As graphene is added upto 0.5 weight% the tensile strength of PVA/graphene was found to increase. However, when the graphene amount exceeds 0.5 wt % the tensile strength reduces but still it is higher than the pristine PVA matrix. It was therefore demonstrated that the mechanical performance of PVA/Graphene nanocomposite film depends upon the graphene content. There is an optimal value in my case it was 0.5 wt %.

The hydroxyle groups of PVA can serve on either hydrogen bonding acceptor or donor. However, the covalent bond in the PVA main chain make them stronger multi-valent bridges compared to separate hydroxyl groups when the content of graphene is fairly low the graphene sheets were surrounded thoroughly by PVA chains, so the tensile strength increases. However, when the graphene content is too high. The graphene sheets were re-stack and would not fully distributed into the PVA matrix.

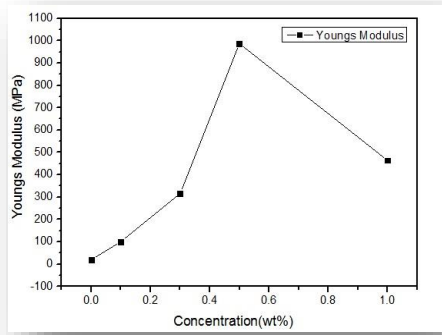


Figure 4.12: Variation of modulus with increase in Graphene

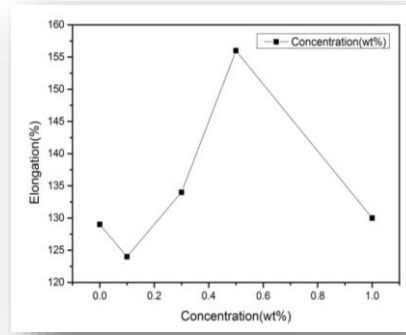


Figure 4.13: Variation of Elongation with increase in Graphene concentration:

The young's modulus of 0.5 wt % is about 986.8 MPa. The tensile strength of composite increases by 357% for 0.5wt% Of graphene. A 20% increase in elongation for the 0.5wt% of graphene is obtained.

4.6 Dielectric analysis

4.6.1 Dielectric constant

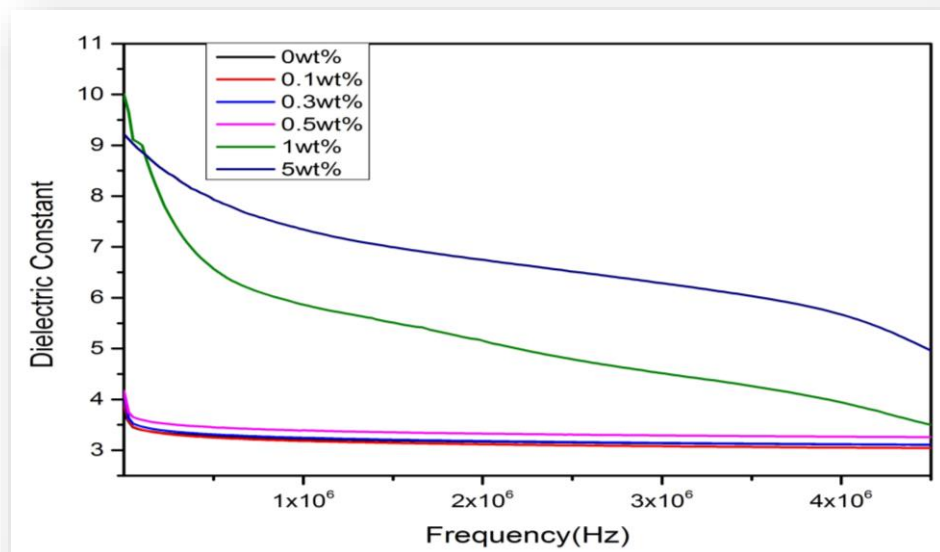


Figure 4.10: Variation of Dielectric constant of PVA/Graphene nanocomposite

The figure 4.14 shows the dielectric constant (ϵ') behavior PVA/Graphene nanocomposite at various concentrations with respect to the frequency at room temperature. As we add graphene in PVA matrix ϵ' is increases till 1wt% loading in the lower frequency region. However, at 5wt% of graphene, Dielectric constant is

decreased yet remains higher than the pure PVA. A variation in the dielectric behavior of composite in the given frequency range is attributed to interface polarization. Due to interfacial polarization which is slow relaxation process large local fields are produced inside the PVA/Graphene nanocomposite that increase the dielectric constant. [2] The dielectric constant value reduced on increase of frequency due to increase in frequency of applied field, it was supposed that the dipoles in the composite are not able rearrange or orient themselves quick enough so there is decrease in the dielectric constant.

Another aspect of the result is a decrease in the dielectric value of PVA/graphene nanocomposite at 5wt% of graphene. The reason can be attributed to the percolation of threshold value. Beyond the threshold value that is 5wt% of graphene the conductive path networks are started to form and therefore the permittivity values are relatively decreased

4.6.2 Dielectric loss

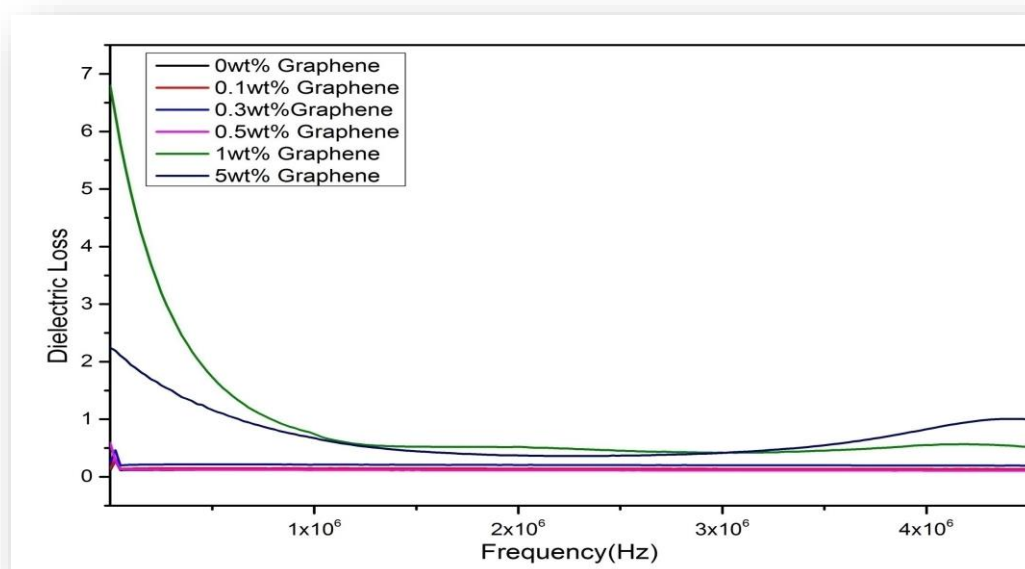


Figure 4.11: The variation of dielectric loss of PVA/Graphene nanocomposite with frequency

The figure 4.15 shows the varying dielectric loss with variation of the frequency. We know that the dielectric loss is the dissipation energy. As we increase the graphene concentration the dissipation energy increase as there is no conductive network form yet, but as the concentration of graphene reaches a critical value that is 5wt% of graphene in PVA at which conductive path networks are formed so the dielectric loss is decreased. [14]

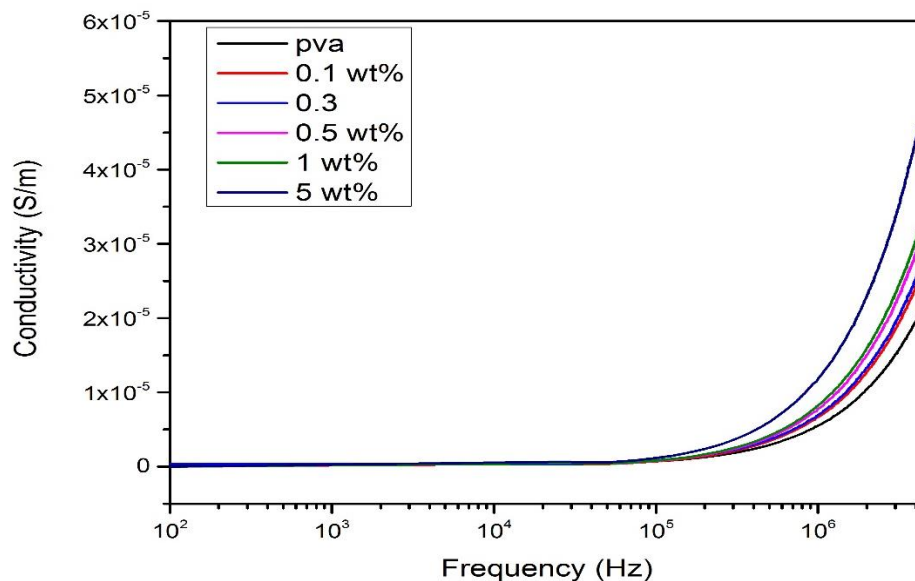


Figure 4.12::The variation of AC conductivity of PVA/Graphene nanocomposite with frequency

The increase in AC conductivity in the higher frequency region is pertaining to the hopping mechanism in which the charge carriers due to the excitation hop around the conductive sites which are boosted up causing an increase in effective conductivity.

4.7 Antibacterial Analysis:

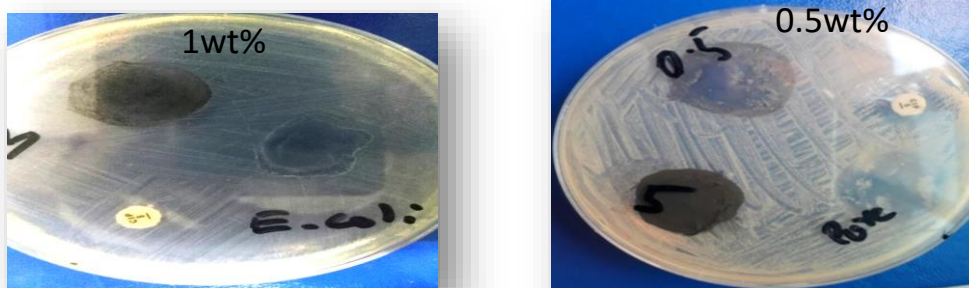


Figure 4.13:Anti-bacterial activity of PVA graphene nano composite

The anti-bacterial activity of PVA/Graphene nanocomposite film were tested against E. coli. The figure shows that PVA did not show any anti-bacterial activity and also the composite with lower loading of graphene. Graphene loadings higher than 0.5wt% are bacterio static and show contact inhibition. This is because that wrapping of cells is done efficiently by larger Graphene sheets and block the active sites on membrane

there by inhibiting bacterial proliferation. In contrast, smaller Graphene nano sheets showed weaker anti-microbial activity due to incomplete bacterial surface wrapping because the uncovered membrane surface could still take up nutrients for the environment for survivals. [1][2]

Chapter 5

5 Conclusion and Future

Recommendation:

5.1 Conclusion

Graphene, 2D material having outstanding electrical and mechanical properties. One of the interesting and promising properties of Graphene is its conductivity (25000cm² per volt-second i-e 200 times of silicon). PVA is semi-crystalline, atactic, homo, water soluble and synthetic polymer. Its T_g is around 40C and has good mechanical and thermal properties. By combining such materials together, would give good properties such as Dielectric, thermal, EMI Shielding and mechanical properties.

Initially polymer nanocomposite were made with graphene as a conductive nano filler and PVA as insulated polymer matrix and five different weight percentages of such compositions were prepared. It was observed that by increasing Graphene concentration mechanical properties were enhanced up (i-e ultimate tensile strength, modulus) to 0.5 weight percentages and after that ultimate tensile strength decreases. The young's modulus of 0.5 wt % is about 986.8 MPa. The tensile strength of composite increases by 357% for 0.5wt% Of graphene. A 20% increase in elongation for the 0.5wt% of graphene is obtained. Similarly, Dielectric properties were enhanced by increasing weight percentage of Graphene due to its conductive nature.

5.2 Future Recommendations

In this work PVA/Graphene nanocomposite is prepared with exceptional mechanical, dielectric thermal and anti-bacterial properties. In future we can work on hybrid composite of PVA/Graphene with other nano particles for many applications like EMI shielding better anti-fungal and anti-bacterial properties in packaging and in food industries .The 0.5wt% of graphene has the highest strength so we can further work on it for protective covering and also in textile industry.

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