Three Component Hybrid Nano Composite System of PVA/PANI/Graphene for Improved Dielectric Properties

Name: Munawar khan

Reg No: NUST201362320MSCME67713F

Supervisor: Dr. Ahmad Nawaz Khan

Thesis submitted to the School of Chemical and Materials Engineering (SCME) in partial fulfillment of requirements for the Degree of MS Materials and Surface Engineering

SCHOOL OF CHEMICAL AND MATERIALS ENGINEERING

NATIONAL UNIVERSITY OF SCIENCES AND TECHNOLOGY

H-12, ISLAMABAD PAKISTAN

August 2015

All of My Work Is Dedicated
To

My Loving Parents

"I couldn't Have Done It
Without Them"

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. Zakir Hussain and Dr. Iftikhar H.Gul** for giving valuable guidance and suggestions to improve my thesis.

I would like to thank all the faculty members, nonteaching staff and my fellow students Specially **Mr. Tanveer ul Haq Zia** for the help provided to me at various stages during this research work.

Munawar khan

Abstract

The development of radar absorbing materials is a flourishing field of research in both the commercial and defense sectors for stealth technology. In this research work, three phase system is prepared, having the insulative matrix blended with conductive matrix that is further embedded with Nano filler. Polyaniline (PANI) is synthesized using emulsion method, containing the conductive character. Polyvinyl alcohol (PVA), semi-crystalline in nature, is chosen as an insulator matrix and few layer graphene (FLG) is incorporated as a Nano filler in the PVA/PANI blend. Various concentrations of PVA/PANI blends were prepared and in selected blend concentrations, FLG is incorporated up to 1 wt%. Polymer blend of PVA/PANI and Hybrid composite of PVA/PANI/FLG are prepared via solution casting method and characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM), extensometer, impedance analyzer and microwave absorption test. PANI forms a heterogeneous immiscible phase with PVA matrix confirmed by XRD and SEM. FLG is dispersed uniformly in the PVA/PANI blend, although at concentrations up to 0.5 wt% of FLG, the sample shows exfoliation of graphene layers in the blend matrix but at 1.0 wt% of FLG, some agglomerations started to form.

The tensile strength of PVA is decreased up to 64 % from 29.3 to 8.5 MPa with increasing concentration of PANI owing to the disruption of the packing of PVA chains in the presence of PANI. By the addition of FLG in PVA/PANI blends, the tensile strength is increased up to 75% from 29.3 to 51.5 MPa and similarly the modulus is increased up to 1017 % from 0.17 to 1.9 GPa, inducing the reinforcement effect of FLG by anchoring the polymer chains. Similarly, the dielectric properties are significantly enhanced for the PVA/PANI/FLG system in which dielectric constant is increased from 4 to 8000 and dielectric loss is increased from 0.5 to 500000 at 100 Hz. The microwave absorption test revealed that the material having highest dielectric loss showed the highest value of absorption up to 21.3dB at 18.3GHz. The promising mechanical and dielectric results of PVA/PANI/FLG make it a suitable system for microwave and radar absorption applications.

Contents

List of Figures..8

List of Tables 11

1 Introduction...12

1.1 Composite materials..12

1.2 Polymer..13

1.3 Classification of Polymers..14

1.3.1 Thermoplastic Polymers...14

1.3.2 Thermosetting Polymers..14

1.3.3 Elastomers/Rubbers...14

1.4 Types of polymer on the basis of ‘mer’ in the chain...........................15

1.5 Recognition of Polymers:..15

1.6 Molecular Structures of polymers...15

1.7 Vinyl polymer..16

1.8 Polymer composites..16

1.9 Why polymer Nano composites..17

1.10 Geometries of Nano fillers...17

1.11 Polyvinyl Alcohol...18

1.11.1 Manufacturing..18

1.11.2 Uses of PVA..19

1.11.3 Properties of PVA...19

1.12 Polyaniline (PANI)..19

1.12.1 Applications..20

1.13 Tacticity in Polymers..20

1.13.1 Isotactic..20

1.13.2 Syndiotactic..21

1.13.3 Atactic..21

1.14 Tacticity in PVA..21

1.15 Graphene...22

1.15.1 Few layer graphene..22

1.16 Synthesis of Graphene..22

1.16.1 Scotch tape method..22

1.16.2 Liquid phase method 23
1.16.3 From Graphite oxide 23
1.16.4 Epitaxial growth 23
1.16.5 Chemical vapor deposition 23
1.17 Properties of Graphene[4] 24
1.18 Graphene-based polymer composites 24
1.19 Different types of graphene-based polymer composites 25
1.20 Factors affecting properties of Graphene composites 25
1.21 Manufacturing techniques of Polymer Nanocomposites 26
1.21.1 In Situ Intercalative Polymerization 26
1.21.2 Solution Intercalation 26
1.21.3 Melt Intercalation 26
1.22 Applications 27
1.22.1 Electronic Devices 27
1.22.2 Energy Storage 28
1.22.3 Sensors 28

2 Literature Review/Objectives 29

2.1 PVA /PANI Polymer Blend 29
2.2 PANI-PVA and PANI-PEO Blends 30
2.3 Alumina/Polyvinyl Alcohol (PVA) Composites 33
2.4 Mg-doped PbS/PVA Nanocomposites 35
2.5 Mechanical thinning to make Few-Layer Graphene from pencil lead 36
2.6 PVA/Graphene Composite 37
2.6.1 Mechanical Percolation 38
2.6.2 PVA/Graphene XRD Results 40
2.7 Objectives 41

3 Experimental 42

3.1 Materials 42
3.2 Preparation of Polyaniline 42
3.3 Preparation of PVA sheet 43
3.4 Preparation of Polymer blend 44
3.5 Preparation of PVA/PANI/FLG Composite 45
3.6 Composition and Number of samples prepared 45
3.7 Specimen Characterization 46

3.7.1 X-RAY Diffraction (XRD) 46
3.7.2 Scanning Electron Microscopy (SEM) 46
3.7.3 Tensile Mechanical properties 46
3.7.4 Dielectric Properties 46
3.7.5 Radar Absorption 46
3.7.6 Thermal Gravimetric Analysis(TGA) 46
4 Results and Discussion 47
4.1 XRD Results 47
4.2 SEM Results 50
4.3 Tensile results of PVA/PANI blend system 51
4.4 Dielectric results of PVA/PANI blends 53
4.5 Tensile Results of PVA 99%- PANI 1% composite with FLG 57
4.6 Dielectric results of PVA 99%- PANI 1% composite with FLG 58
4.7 Tensile Results of PVA 90%- PANI 10% composite with FLG 61
4.8 Dielectric results of PVA 90%- PANI 10% composite with FLG 62
4.9 EMI-Shielding 66
4.10 TGA Results 68
5 Conclusions/Future Recommendations 69
5.1 Conclusions 69
5.2 Future Recommendations 70
References 71

List of Figures

Figure 1.1: Composites 12
Figure 1.2: Flow chart Materials 13
Figure 1.3: Aliphatic Polymers 15
Figure 1.4: Aromatic Polymers 15
Figure 1.5: linear polymer 15
Figure 1.6: branched polymer 15
Figure 1.7: Cross linked polymer 16
Figure 1.8: Comparison of Nano composites with composites in terms of (a) surface-surface inter particle distance and (b) total particle surface area of $\boldsymbol{1mm3}$[1] 17
Figure 1.9: Geometries of Nano fillers.[3] 18
Figure 1.10: Structure of PVA. 18
Figure 1.11: Structure of polyaniline 20
Figure 1.12: Isotactic polymer 20
Figure 1.13: Syndiotactic polymer 21
Figure 1.14: Atactic polymer 21
Figure 1.15: PVA structure 21
Figure 1.16: 2d graphene, 0-d bucky balls, 1d carbon nano tubes, 3d graphene [5] 22
Figure 1.17: CVD method .[1] 24
Figure 1.18: Distance between two layers of graphene 24
Figure 1.19: Graphene based polymer nano-composite[4] 25
Figure 1.20: Application of graphene based polymer Nano composites.[4] 27
Figure 1.21: Capacitive touch screens 27
Figure 1.22: Energy storage 28
Figure 1.23: Sensors 28
Figure 2.1: “TEM image of PANI dispersion showing PANI particles” 29
Figure 2.2: “Four point probe conductivity of PANI–PVA composite films as a function of polyaniline loading” 29
Figure 2.3: “Electroactivity of the composites with varying polyaniline content.(a)aniline loading 34% (w/w), (b): aniline loading 23% (w/w), (c):aniline loading 9% (w/w)”. 30
Figure 2.4: “XRD pattern of Pure PANI, Pure PVA and PANI+PVA” 31
Figure 2.5: “XRD pattern of Pure PANI, PEO and PANI+PEO” 31
Figure 2.6: “Mechanical properties of polymer blends” 32
Figure 2.7: SEM results. 32
Figure 2.8: “Dc conductivity of polymer blends” 33
Figure 2.9: “Pure PVA dielectric constant” 33
Figure 2.10: “PVA+0.5% Nano alumina” 34
Figure 2.11:” PVA+1% Nano alumina” 34
Figure 2.12: “PVA+1.5% Nano alumina” 34
Figure 2.13: XRD pattern for (a) undoped, (b) 5 and 7.5 mol % of Mg doped PBS/PVA nano composite 35
Figure 2.14: “TEM images of FLG obtained by the mechanical ablation of the pencil lead, (A) the assembly of FLG, (B) Bilayer graphene with different crystallinity, (C) the perfect hexagon lattice, (D) the lattice with a lack of carbon atoms or the presence of ripple” 37

Figure 2.15: "TEM micrographs of the FLG borders with different graphene sheets numbers, (B) Tem micrograph and electron diffraction of a monolayer graphene (C) SEM image showing the presence of thick FLG in the sample." 37
Figure 2.16: "Young's moduli of the nanocomposite and Halpin-Tsai theoretical models. The theoretical simulations were taken as two cases: the random orientation and unidirectional distribution of graphene nanosheets in the polymer matrix". 38
Figure 2.17: "Mechanical properties of graphene/PVA nanocomposites with various graphene loadings: tensile strength (left) and elongation at break (right) versus graphene loadings" 39
Figure 2.18: "Typical stress- strain plots of the composites with various graphene loadings" 39
Figure 2.19: Mechanical percolation 39
Figure 2.20: "XRD pattern of (a) graphene powder, (b) pure PVA, and (c) graphene/PVA composites with 0.6 vol % loading of graphene." 40
Figure 2.21: "XRD patterns of graphene/PVA composites with various graphene contents" 40
Figure 3.1: Preparation of polyaniline 42
Figure 3.2: Polyaniline powder 43
Figure 3.3: PVA solution casted in Teflon mold 43
Figure 3.4: PVA sheet 43
Figure 3.5: Solution casting method for preparing polymer blend and Hybrid composite 44
Figure 4.1: XRD Polyaniline 47
Figure 4.2: XRD Polyvinyl alcohol 47
Figure 4.3: XRD comparison of Pure PVA, PANI, (PVA 99%-PANI 1%) and (PVA 90%-PANI 10%) 47
Figure 4.4: The Black line showing PVA chains while the red region showing the secondary bonding due to -OH group along the chains 48
Figure 4.5: The black lines showing PVA chains while he red DOT region showing PANI phase 48
Figure 4.6: XRD Few layer graphene 48
Figure 4.7: XRD comparison of (PVA 99%-PANI1%) with varying FLG concentration 49
Figure 4.8: XRD comparison of (PVA 90%-PANI 10%) with varying FLG concentration 49
Figure 4.9: SEM (99/1) polymer blend 50
Figure 4.10: SEM (90/10) polymer blend 50
Figure 4.11: SEM (90/10) polymer blend with 0.5 wt % FLG 50
Figure 4.12: SEM (99/1) polymer blend with 0.5 wt % FLG 51
Figure 4.13: Stress-Strain graph of PVA, PVA/PANI blends 51
Figure 4.14: Variation of tensile strength with increase in PANI concentration 51
Figure 4.15: Variation of modulus with increase in PANI concentration 52
Figure 4.16: "Variation of Dielectric constant of polymer blends with frequency" 53
Figure 4.17: "Variation of dielectric loss factor of polymer blend with frequency" 53
Figure 4.18: "variation of Ac conductivity of polymer blend with frequency" 54
Figure 4.19: "Variation of dielectric loss tangent of polymer blend with frequency" 54
Figure 4.20: Hopping Mechanism.[2] 56
Figure 4.21: Stress strain graph of Polymer blend (PVA 99%- PANI 1%) with varying concentration of FLG 57
Figure 4.22: Variation of tensile strength with varying concentration of FLG 57
Figure 4.23: Uniqueness in Nano structured materials[3] 57
Figure 4.24: Variation of Modulus with increase in FLG loading in polymer blend 57

Figure 4.25: “Variation of dielectric constant with frequency (PVA 99%/PANI 1%/FLG 0.1%-0.5%-1%)” 58
Figure 4.26: “Variation of dielectric loss with frequency (PVA 99%/PANI 1%/FLG 0.1%-0.5%-1%)” ... 59
Figure 4.27: “Variation of AC conductivity with frequency (PVA 99%/PANI 1%/FLG 0.1%-0.5%-1%)” 59
Figure 4.28:” Variation of Loss tangent with frequency (PVA 99%/PANI 1%/FLG 0.1%-0.5%-1%)” 60
Figure 4.29: Stress strain graph of Polymer blend (PVA 90%- PANI 10%) with varying concentration of FLG 61
Figure 4.30: Variation of tensile strength With varying concentration of FLG 61
Figure 4.31: Variation of Modulus with increase in FLG loading in polymer blend 61
Figure 4.32: Mechanical percolation [1] 61
Figure 4.33: “Variation of dielectric constant with frequency (PVA 90%/PANI 10%/FLG 0.1%-0.5%-1%)” 62
Figure 4.34: “Variation of dielectric loss with frequency (PVA 90%/PANI 10%/FLG 0.1%-0.5%-1%)” . 63
Figure 4.35: “Variation of Ac conductivity with Frequency of (PVA 90%/PANI 10%/FLG 0.1%-0.5%-1%)” 63
Figure 4.36:” Variation of tan δ with Frequency of (PVA 90%/PANI 10%/FLG 0.1%-0.5%-1%)” 64
Figure 4.37: Variation of shielding efficiency with frequency PURE PVA 66
Figure 4.38: Variation of shielding efficiency with frequency (99-1) polymer blend 66
Figure 4.39: Variation of shielding efficiency with frequency (90-10) polymer blend 66
Figure 4.40: Variation of shielding efficiency with frequency (90-10-0.1) Hybrid composite 66
Figure 4.41: Variation of shielding efficiency with frequency (90-10-1) Hybrid composite 67
Figure 4.42: Variation of shielding efficiency with frequency (99-1-1) Hybrid composite 67
Figure 4.43: Variation of shielding efficiency by adding FLG with (90-10) polymer blend 67
Figure 4.44: Variation of shielding efficiency by adding FLG with (99-1) polymer blend 67
Figure 4.45: TGA comparison of PVA, PANI and hybrid composite (99/1) 68
Figure 4.46: TGA comparison of PVA, PANI and hybrid composite (90/10) 68

List of Tables

Table 1.1: Properties of PVA 19
Table 1.2: Overview of the performances of the different methods of synthesis of Graphene.[1] 22
Table 1.3: Filler type and %loading of graphene and their effect on mechanical properties.[6] 25
Table 2.1: Mechanical properties of films after dehydration 30
Table 2.2: Lattice constant, average particle size, Eg and ρ values of PVA 36
Table 3.1: Specifications of materials used for experimentation 42
Table 3.2: Different composition of (PVA/PANI) polymer blend 45
Table 3.3: Different composition of Hybrid composite (PVA/PANI) (90-10) with variation in FLG concentration 45
Table 3.4: Different composition of Hybrid composite (PVA/PANI) (99-1) with variation in FLG concentration 45

Chapter 1

1 Introduction

1.1 Composite materials

Composite is known as a multi-phase material that shows essential extent of the properties of both constituent stages. Composite Materials alludes to every single strong material made out of more than one substance. Another meaning of composite materials is, these are the strong materials made out of a matrix system which surrounds and binds together the reinforcements. In combined action principle, better properties can be accomplished by the mixing two or more particular materials.

Numerous composite materials have two phases

- Matrix, which is consistent Phase.
- Dispersed stage, which is encompassed by the matrix.

Why to choose polymer over other metals?

- Specific Modulus
- Specific Strength

Higher specific modulus & quality of polymer strengthened composites expounds that the weight can be decreased. This is an element of incredible concern where decreases in weight result in more prominent efficiency and energy conservation.

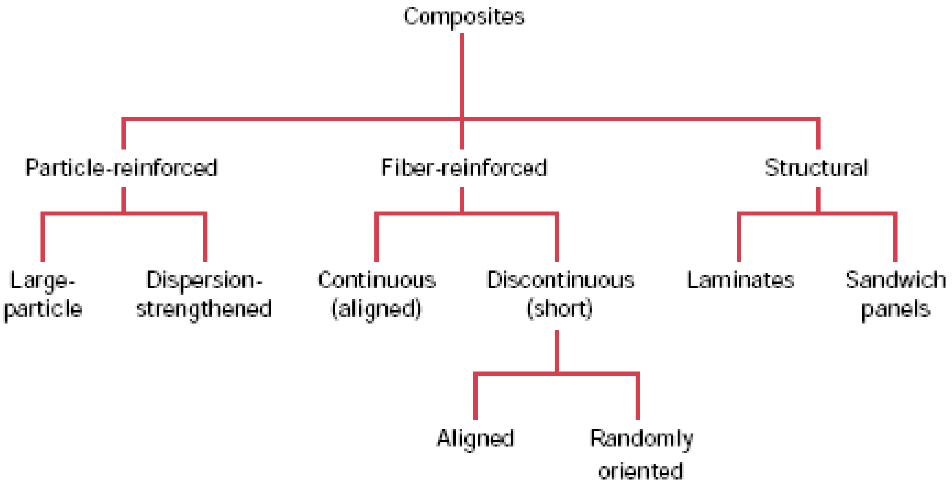


Figure 1.1: Composites

1.2 Polymer

Polymers are long-chain atoms of high molecular weight, the expression "macro-particles" is habitually utilized when alluding to polymeric materials. The introductory polymers which were utilized they were, particularly cotton, starch, proteins, and fleece. **Synthetic** polymers term came into known in the mid twentieth century. The engineered polymers were Bakelite and nylon, demonstrated the colossal conceivable outcomes of the new materials. Nonetheless, the researchers of that day understood that they didn't comprehend a considerable lot of the connections between the substance structures and the physical properties that came about. The exploration that followed structures the premise **for physical polymer science.** Numerous polymers take shape, and the size, shape, and association of the crystallites rely on upon how the polymer was solidified. Such impacts as strengthening are vital, as they have a significant impact on the last condition of molecular organization. Different polymers are amorphous, frequently in light of the fact that their ties are excessively sporadic, making it impossible to allow general pressing. The onset of chain atomic movement proclaims the glass transition and softening of the polymer from the shiny (plastic) state to the rubbery state. Mechanical conduct incorporates such fundamental angles as modulus,

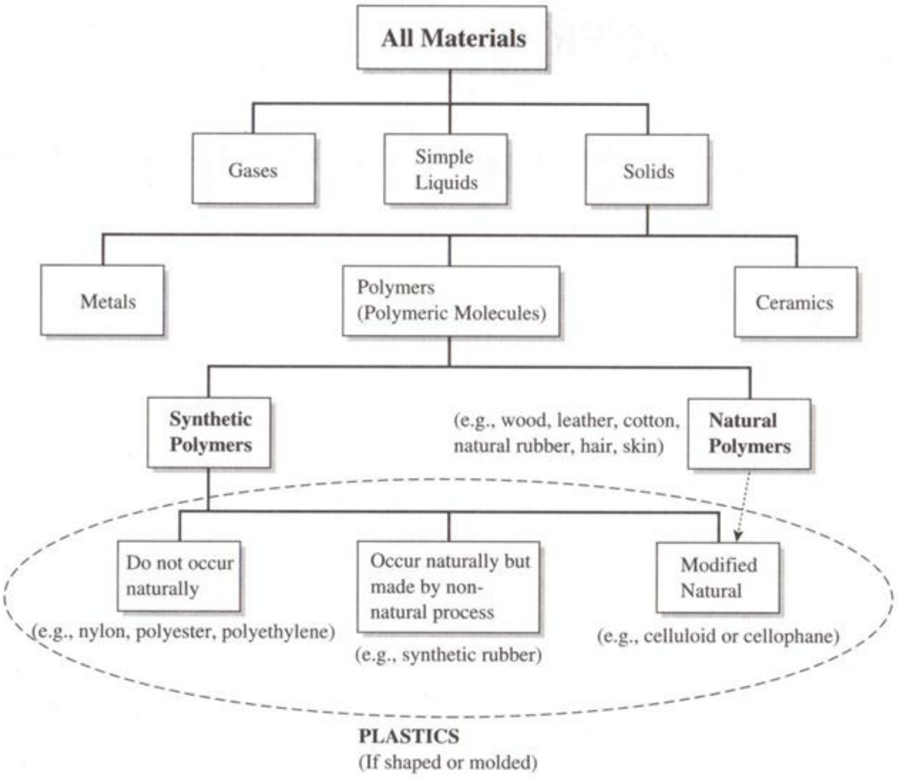


Figure 1.2: Flow chart Materials

1.3 Classification of Polymers

On the basis of inter-molecular forces, it is classified into three main categories

1.3.1 Thermoplastic Polymers

A **thermoplastic** is a plastic material, a polymer that can be molded when the temperature is raised from a specific value and it can become solid by cooling. Many of them have a high molecular weight. Thermoplastic have secondary bonding between the chains, by heating they become weak. So we can conclude that they can be molded into any shape by heating. So parts can be produced by applying various methods such as injection molding, compression molding, calendaring, and extrusion. They can differentiated from thermosetting polymers, as thermosets form chemical bonds in curing process. Thermosets cannot be melted, but they can be decomposed and cannot be reformed when cooled.

1.3.2 Thermosetting Polymers

A **thermosetting polymer**, also known as a **thermoset**, is petrochemical material that is cured when heated. Their curing temperature is generally above 200 °C (392 °F). They can be normally found in liquid state and they can be designed in such a way that they can be molded in any form. They can also be used as adhesives. Some them are solids like that of the molding compound which can be used in semiconductors and integrated circuits (IC). When hardening of thermoset is done they cannot be reshaped or reheated. Thermosetting resin may be contrasted with thermoplastic polymers which are commonly produced in pellets and shaped into their final product form by melting and pressing or injection molding.

1.3.3 Elastomers/Rubbers

An **elastomer** is a polymer which is viscoelastic and have weak forces between the chains. It have a low young modulus and high strain as compared to other materials. Elastomer is basically derived from elastic polymer and can be used with term rubber. But rubber is vulcanized. Its monomer is usually composed of carbon, hydrogen, oxygen or silicon. These are usually amorphous in nature and are used above their glass transition temperature, so their chains can move easily. At ambient temperatures, rubbers are thus relatively soft (E~3MPa) and deformable. Their primary uses are for seals, adhesives and molded flexible parts. Application areas for different types of rubber are manifold and cover segments as diverse as tires, shoe soles as well as dampening and insulating elements.

Formless polymers existing over their glass transition temperature, so that impressive segmental movement is conceivable.

1.4 Types of polymer on the basis of 'mer' in the chain

- **Homo Polymers:** Only one type of 'mer' units are repeating throughout for the formation of polymers
- **Blending Polymers:** Two or more types of 'mers' are combined by physical bonding
- **Copolymers:** Two or more types of 'mers' are combined by chemical bonding

1.5 Recognition of Polymers:

- **Aliphatic Polymers** are Hydrocarbons based on linear chain structures e.g. PE, PP

$$\left(CH_2 - CH_2 \right)_n$$

Figure 1.3: Aliphatic Polymers

- **Aromatic Polymers** are Hydrocarbons that contain benzene or naphthalene ring in the Backbone of the chain e.g. PET, PTT, PTN

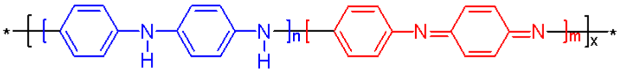


Figure 1.4: Aromatic Polymers

1.6 Molecular Structures of polymers

- **Linear Polymers:** Monomeric units are joined in the form of long straight chains

Figure 1.5: linear polymer

- **Branched Polymers:** secondary chains are connected to the central chain.

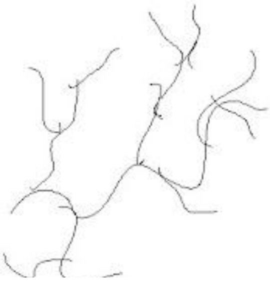


Figure 1.6: branched polymer

- **Cross-linked Polymers:** Monomeric units are linked together by chemical bonds.

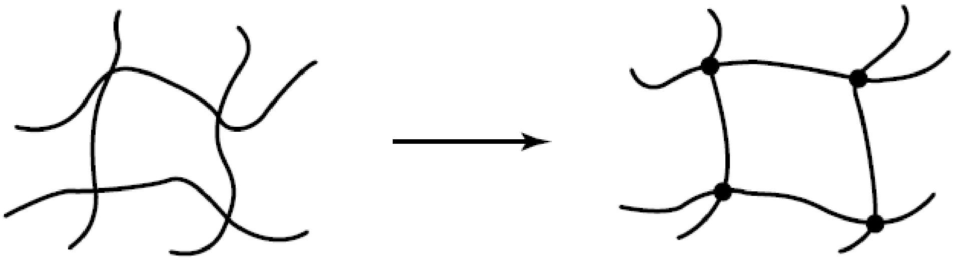


Figure 1.7: Cross linked polymer

1.7 Vinyl polymer

Vinyl polymers are a group of polymers derived from vinyl monomers. Their backbone is an extended alkane chain, made by polymerizing an alkene group (C=C) into a chain (..-C-C-C-C-..). In popular usage, "vinyl" refers only to polyvinyl chloride (PVC). Vinyl polymers are the most common type of plastic

- Polymerized simple alkenes: polyethylene from ethene, polypropylene from propene and polybutadiene from butadiene.
- Polystyrene is made from styrene or "vinyl benzene".
- Polyvinyl chloride (PVC) is made by polymerization of the monomer vinyl chloride (chloroethene) $CH_2=CHCl$
- Polyvinyl acetate (PVAc) is made by polymerization of vinyl acetate. In a water suspension, this is used as a glue.
- Polyvinyl alcohol (PVA) is produced by hydrolysis of polyvinyl acetate. (Not by polymerization of the monomer vinyl alcohol or ethenol, which is an unfavored keto-enol tautomer of acetaldehyde.)

1.8 Polymer composites

Those composites which have polymer as a matrix phase are termed as polymer composites. The filler can be of any type, shape and size. If we use filler of Nano size those are called as Polymer Nano composites.

1.9 Why polymer Nano composites

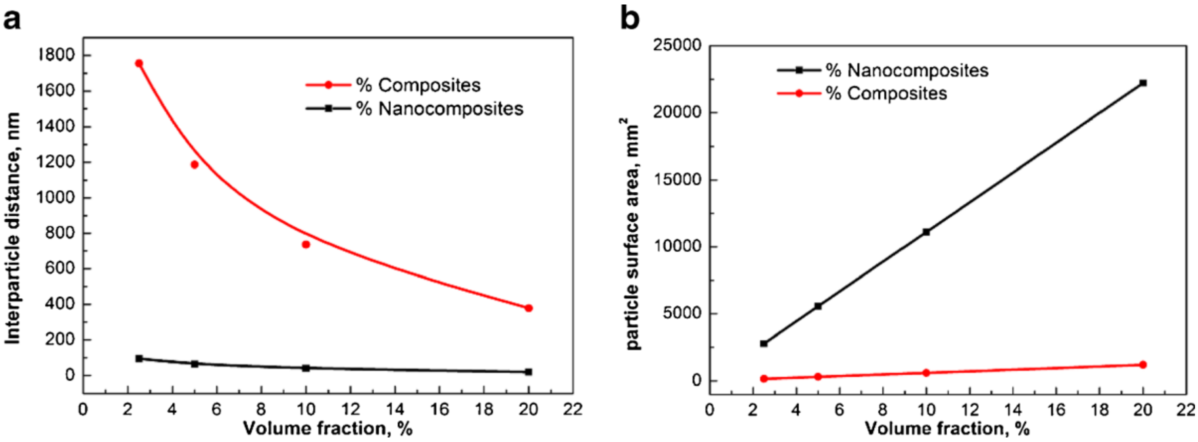


Figure 1.8: Comparison of Nano composites with composites in terms of (a) surface-surface inter particle distance and (b) total particle surface area of $1mm^3$[1]

The following graphs shows the effect of the Nano filler and Macro filler as we add it to the polymer matrix so in figure1.8(a) we can see as we add Nano filler there is no considerable effect on the interparticle distance of Nano filler while the macro filler interparticle distance is decreasing as the volume fraction is increased so the point here is that the Nano filler is providing room for the matrix to fill in the spaces between two consecutive fillers while the macro filler is relatively decreasing the its space for the matrix to fill in so the Nano filler will give good interfacial bonding as compared to the macro filler.[3]

The Figure1.8(b) shows the graph between particle surface area and volume fraction of the filler so as we see as we add the macro filler so the surface area is not increasing as compared to Nano filler which is abruptly increasing and thus giving more interaction area to the matrix to form interfacial bonding so based on the above discussion Nano filler gives good bonding with the matrix so they are a better choice.[3]

1.10 Geometries of Nano fillers

The properties of Nano composite materials not just rely on upon the properties of their individual constituents, however on their morphology and surface attributes of fillers. Selections of Nano fillers, such as filler shape and filler size have a huge impact on the properties of Nano composites and their handling systems .There are three main categories of filler geometries that have been adopted in polymer Nano composites including Particulate, fibrous and layered fillers.Comparing these three geometries leads to a conclusion that the layered Nano fillers have the highest specific surface area.[3]

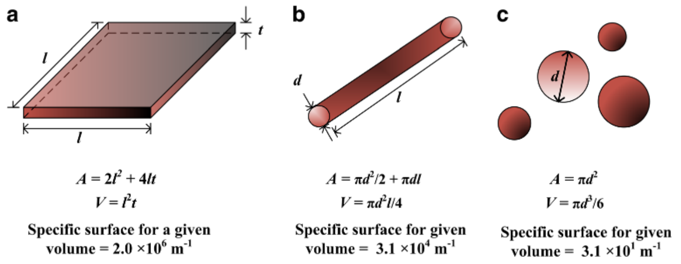


Figure 1.9: Geometries of Nano fillers.[3]

1.11 Polyvinyl Alcohol

It is semi-crystalline, atactic, homo, water soluble and synthetic polymer. We can write its formula as $[CH_2CH(OH)]_n$.It is colorless and odorless. It is available in the form of beads or as solutions in water.

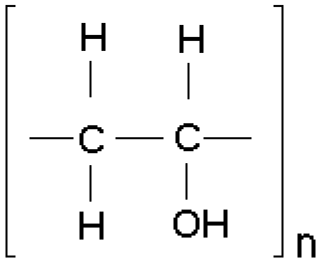


Figure 1.10: Structure of PVA

1.11.1 Manufacturing

PVA is not same as vinyl polymers; the main reason behind is that it cannot be manufactured by polymerizing its own monomer. The vinyl alcohol which is its monomer is unstable as compared to acetaldehyde. It is manufactured by the following steps

- First thing is to polymerize the vinyl acetate
- So from the Polyvinyl acetate we get PVA
- Some of the other precursor polymers can be used chloroacetate groups, formate, instead of acetate.
- we can convert the polyester by base-catalyzing Trans esterification using ethanol:

“$[CH_2CH(OAc)]_n + C_2H_5OH \rightarrow [CH_2CH(OH)]_n + C_2H_5OAc$”

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

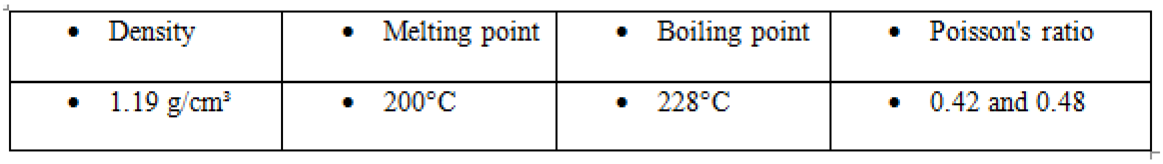
Companies from the past decade and is producing about 45 percent of the total of the world demand. The North Korean produces a Vinalon which is produced from PVA. As we know it is having inferior properties as clothing fiber but still, we produce it for reason of self- sufficiency as no oil is necessary 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

Table 1.1: Properties of PVA



• Density	• Melting point	• Boiling point	• Poisson's ratio
• 1.19 g/cm³	• 200°C	• 228°C	• 0.42 and 0.48

1.12 Polyaniline (PANI)

It is a conducting polymer of the semi-flexible rod polymer family and having aromatic structure. In spite of the fact that the compound itself was found more than 150 years prior, just since the mid-1980s has polyaniline caught the serious consideration of established researcher. Polyaniline is a standout amongst the most encouraging possibility for mechanical utilization of leading polymers this is because of the rediscovery of high electrical conductivity .It is synthesized by means of simple chemical or electrochemical oxidation of aniline. It is not readily processable in non-toxic solvents due to limited solubility and the materials are normally not melt processable.

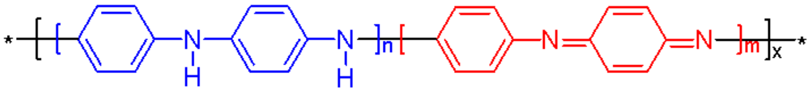


Figure 1.11: Structure of polyaniline

1.12.1 Applications

Polyaniline and the other conducting polymers, for example, polythiophene, polypyrrole, and PEDOT/PSS have potential for applications because of their light weight, conductivity, mechanical adaptability and minimal cost. Polyaniline is particularly alluring in light of the fact that it is moderately cheap, has three oxidation states with diverse color and has a acid/base doping response. This recent property makes polyaniline an appealing for acid/base substance vapor sensors, super capacitors and biosensors. The diverse colors, charges and conformations of the different oxidation states additionally make the material promising for applications, for example, actuators, super capacitors and electrochromics. They are suitable for production of electrically directing yarns, antistatic coatings, electromagnetic protecting, and flexible electrodes. Attractive fields for present and potential usage of polyaniline is in antistatic, charge dissemination or electrostatic dispersive (ESD) coatings and mixes, electromagnetic interference shielding(EMI), anticorrosive coatings, opening infusion layers, straightforward channels, indium tin oxide substitutions, actuators, compound vapor and solution based sensors.

1.13 Tacticity in Polymers

1.13.1 Isotactic

If the R groups on successive pseudochiral carbons all have the same configuration, the polymer is called isotactic.

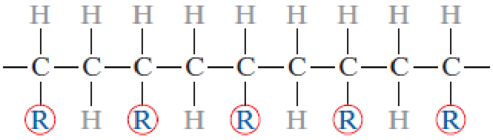
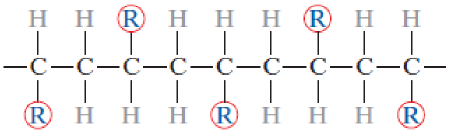


Figure 1.12: Isotactic polymer

1.13.2 Syndiotactic

When the pseudochiral centers alternate in configuration from one repeating unit to the next, the polymer is called syndiotactic.

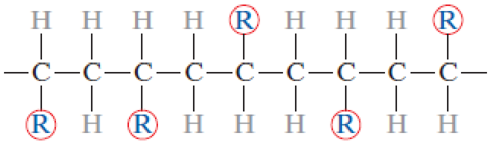


$$\begin{array}{ccccccccccc} & H & H & R & H & H & H & R & H & H & \\ & | & | & | & | & | & | & | & | & | & \\ - & C - & C - & C - & C - & C - & C - & C - & C - & C & - \\ & | & | & | & | & | & | & | & | & | & \\ & R & H & H & H & R & H & H & H & R & \end{array}$$

Figure 1.13: Syndiotactic polymer

1.13.3 Atactic

If the pseudochiral centers do not have any particular order, but in fact are statistical arrangements, the polymer is said to be atactic.

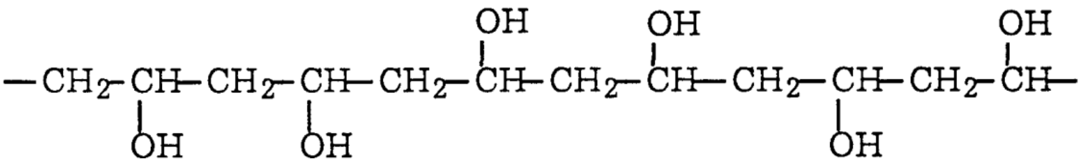


$$\begin{array}{ccccccccccc} & H & H & H & H & R & H & H & H & R & \\ & | & | & | & | & | & | & | & | & | & \\ - & C - & C - & C - & C - & C - & C - & C - & C - & C & - \\ & | & | & | & | & | & | & | & | & | & \\ & R & H & R & H & H & H & R & H & H & \end{array}$$

Figure 1.14: Atactic polymer

1.14 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. The isotactic and syndiotactic structures are both crystallizable as a result of their consistency along the chain. In any case, their unit cells and melting temperatures are not the same. Atactic polymers, then again, are generally totally amorphous unless the side group is so little or polar as to allow some crystallinity. One such crystalline atactic polymer is polyvinyl alcohol. Atactic polyvinyl alcohol is somewhat crystalline on account of syndiotactic "runs."



$$-CH_2-\underset{OH}{CH}-CH_2-\underset{OH}{CH}-CH_2-\overset{OH}{CH}-CH_2-\overset{OH}{CH}-CH_2-\underset{OH}{CH}-CH_2-\overset{OH}{CH}-$$

Figure 1.15: PVA structure

1.15 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.

1.15.1 Few layer graphene

When we get 5 to 8 layers of graphene stacked together so we can call it Few layer graphene.[8]

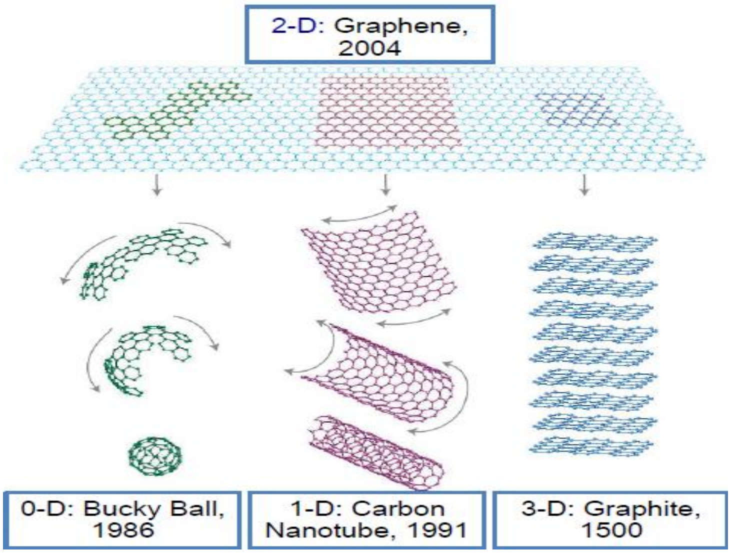


Figure 1.16: 2d graphene, 0-d bucky balls, 1d carbon nano tubes, 3d graphene [5]

1.16 Synthesis of Graphene

Some of the methods are as follows.

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

Table 1.2: "Overview of the performances of the different methods of synthesis of Graphene.[1]"

Method	Quality	Size	Amount	Complex.	Control.
Adhesive Tape	✓	×	×	(✓)	×
Liquid phase	✓	×	✓	✓	×
Graphite oxide	–	×	✓	×	×
Epi. growth	×	(✓)	×	✓	✓
CVD	×	✓	✓	✓	✓

1.16.1 Scotch tape method

In this method, graphene is peeled off from the graphite crystal with the assistance of a sticky tape. As the tape is removed from graphite, the graphene with multi layers is still on the tape. So if we do the peeling repeatedly so the multilayer graphene can be converted in to few layers

Of graphene. So after the peeling process is completed we attach the tape to a substrate, the glue solved by acetone, in order to remove the tape. At the end we do peeling for the last time with an unused tape.[1]

1.16.2 Liquid phase method

This method which will permit us to upscale the yield, with a specific end goal to get a much higher quantity of graphene. One of the least difficult strategies will be, to disperse it in a natural organic solvent with just about the same surface vitality as graphite. So this is how we reduce the energy barrier, which must be overcome so as to separate a graphene layer from the crystal. We then sonicated the solution in an ultrasound bath for a few hundred hours or a voltage is connected. After that, the solution must be centrifuged with a specific end goal to discard the thicker flakes.[1]

1.16.3 From Graphite oxide

Rule which is included in liquid-phase exfoliation, that standard can likewise be connected to shed graphite oxide because of numerous functional groups as we can say like hydroxyl or epoxide, graphene oxide dissolved in water by a method called sonication as it is hydrophilic in nature. These layers are negatively charged and some combinations of these layers are surrounded by electrical repulsion. As the centrifugation the graphene oxide is done so it is reduced to graphene which is regular in nature thermally and chemically. This is not really conceivable to wind up the majority of the oxygen. Point of fact, an atomic proportion of around 10 is still remaining.[1]

1.16.4 Epitaxial growth

Graphene can synthesized by this method by simultaneous heating and cooling down a SiC crystal Where Few-layer graphene has started growing on C face. Results are depending on the condition such as temperature, pressure or heating rate. Indeed, if temperatures and pressure are too high the development of nanotubes rather than graphene can happen. The graphitization Of SiC established in 1955, however it is produced as unwelcome side results rather than a technique for making graphene.[1]

1.16.5 Chemical vapor deposition

CVD is a well-known technique in which a substrate is uncovered to Gaseous mixes. This compound will be deteriorated on the surface of the substrate keeping in mind the end goal to grow a meager film, while the by-items will vanish.[1]

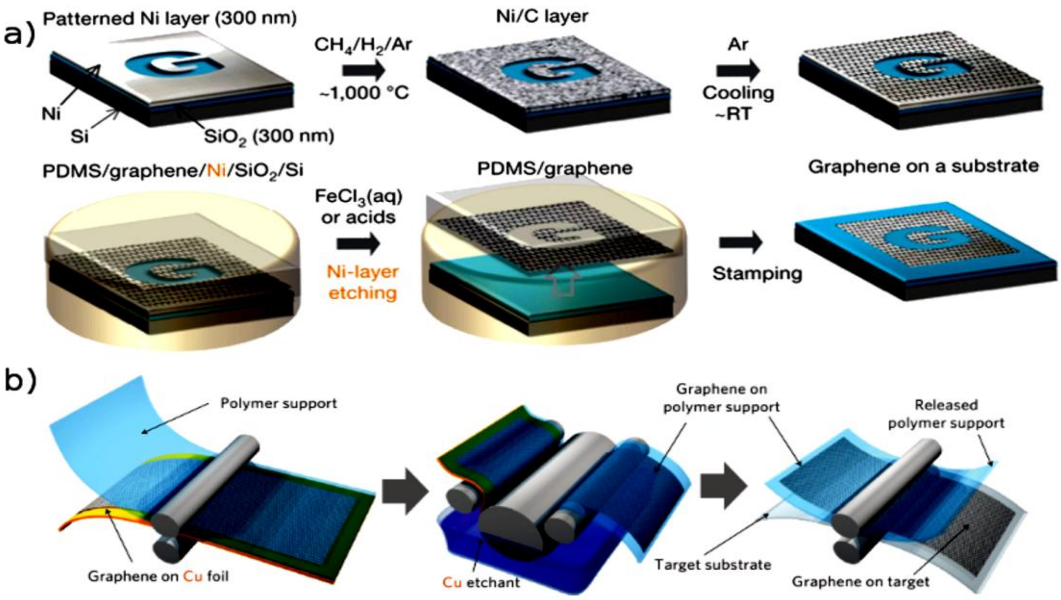


Figure 1.17: CVD method .[1]

1.17 Properties of Graphene[4]

- "Young's modulus (1000 GPa)"
- "Fracture strength (125 GPa)"
- "Elastic modulus (0.25 TPa)"
- "Thermal conductivity (5000 Wm^{-1} K^{-1})"
- "Mobility of charge carriers (200 000 $cm^2V^{-1}s^{-1}$)"
- "Specific surface area (2630 m^2 g^{-1})"
- "Quantum Hall effect"

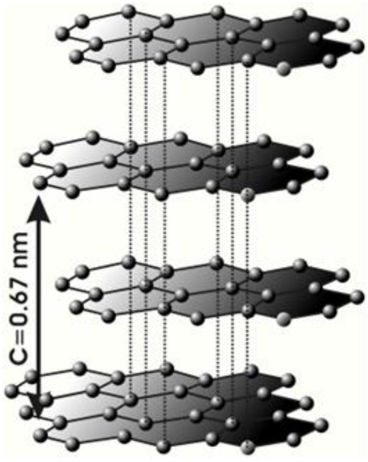


Figure 1.18: Distance between two layers of graphene

1.18 Graphene-based polymer composites

Graphene-based polymer composites show superior properties like[4]

- Flame retardant properties
- Gas barrier
- Thermal
- Mechanical
- Electrical

1.19 Different types of graphene-based polymer composites

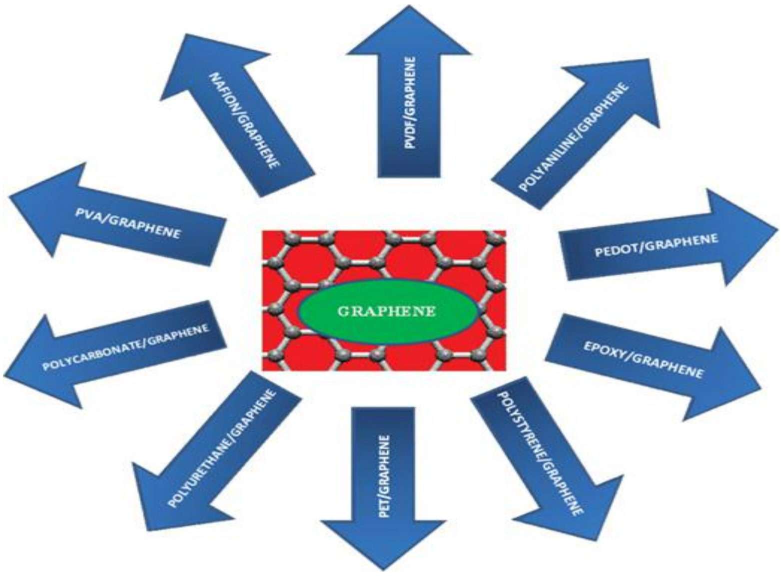
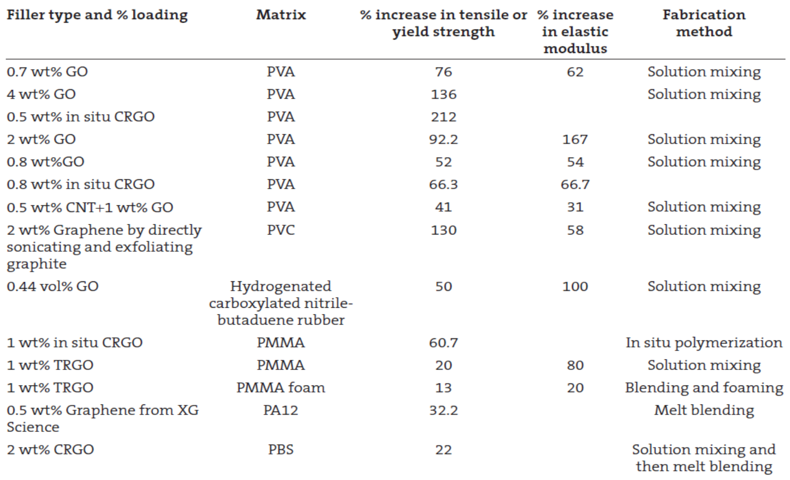


Figure 1.19: Graphene based polymer nano-composite[4]

Table 1.3: Filler type and %loading of graphene and their effect on mechanical properties.[6]



Filler type and % loading	Matrix	% increase in tensile or yield strength	% increase in elastic modulus	Fabrication method
0.7 wt% GO	PVA	76	62	Solution mixing
4 wt% GO	PVA	136		Solution mixing
0.5 wt% in situ CRGO	PVA	212		
2 wt% GO	PVA	92.2	167	Solution mixing
0.8 wt%GO	PVA	52	54	Solution mixing
0.8 wt% in situ CRGO	PVA	66.3	66.7	
0.5 wt% CNT+1 wt% GO	PVA	41	31	Solution mixing
2 wt% Graphene by directly sonicating and exfoliating graphite	PVC	130	58	Solution mixing
0.44 vol% GO	Hydrogenated carboxylated nitrile-butaduene rubber	50	100	Solution mixing
1 wt% in situ CRGO	PMMA	60.7		In situ polymerization
1 wt% TRGO	PMMA	20	80	Solution mixing
1 wt% TRGO	PMMA foam	13	20	Blending and foaming
0.5 wt% Graphene from XG Science	PA12	32.2		Melt blending
2 wt% CRGO	PBS	22		Solution mixing and then melt blending

1.20 Factors affecting properties of Graphene composites

Properties of the Nano composite depend on

- How the graphene layers are distributed in the polymer matrix.
- Interfacial bonding along the polymer matrix and graphene layers.
- Aspect ratio of graphene.

1.21 Manufacturing techniques of Polymer Nanocomposites

- “In Situ Intercalative Polymerization”
- “Solution Intercalation”
- “Melt Intercalation”

1.21.1 In Situ Intercalative Polymerization

The filler utilized is graphene or altered graphene which is at first absorbed inside of the monomer which is in liquid state. A second step would be to add a compatible initiator and polymerization is started by heat[4].

- “polystyrene (PS)/graphene”
- “Poly methyl methacrylate (PMMA)/expanded graphite (EG)”

1.21.2 Solution Intercalation

Pre-polymer or Polymer must be having solubility in the solvent system and then graphene or modified graphene layers are allowed to swell. It is then added and dispersed in to compatible solvent like toluene, water or acetone. Then the polymer is going to be adsorbed on the delaminated sheets of the graphene and in the end solvent is evaporated, examples are[4]

- Polystyrene (PS)/graphene
- Epoxy/LDH
- Polyethylene-grafted maleic anhydride (PE-g-MA)/graphite

1.21.3 Melt Intercalation

Modified graphene or Graphene is added to the polymer, which is the matrix and is in molten state using conventional techniques e.g. extrusion and injection techniques .A variety of polymer Nano composites such as polypropylene (PP)/expanded graphite (EG), High dense polyethylene (HDPE)/EG etc[4]

1.22 Applications

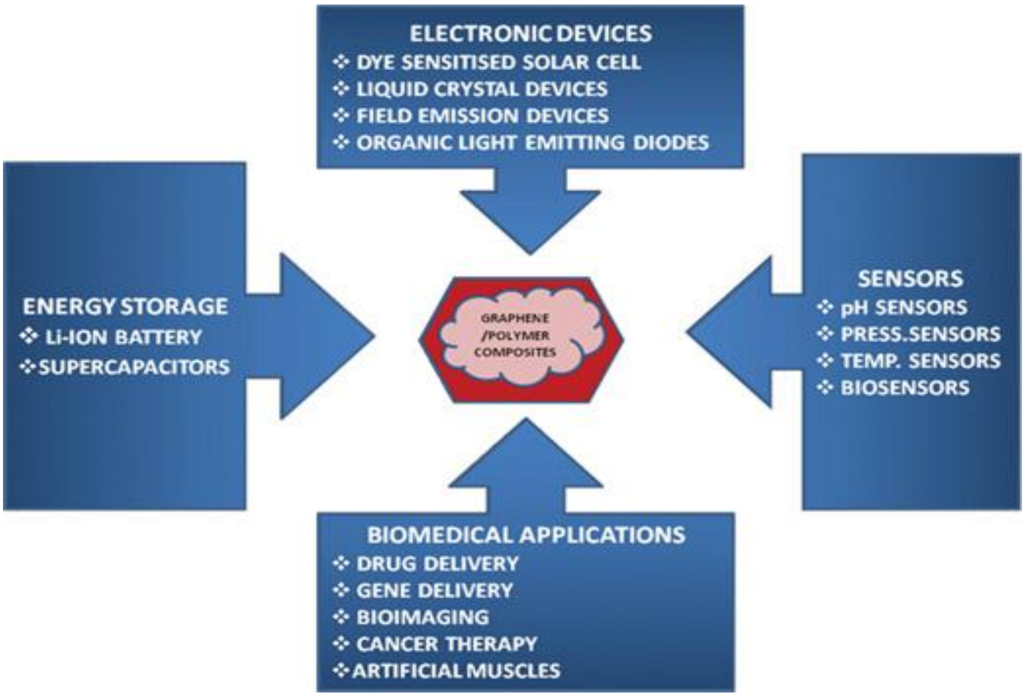


Figure 1.20: Application of graphene based polymer Nano composites.[4]

1.22.1 Electronic Devices

- Electrode

  DSSCs, OPVs, LCDs, OLEDs and field emission devices

- Transparent conducting films

  Solar cells, touch screens, flat panel display

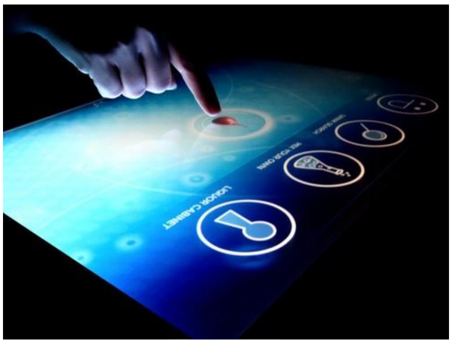


Figure 1.21: Capacitive touch screens

1.22.2 Energy Storage

- **Li ion battery**
    - cathode materials, poly-(anthraquinonyl sulfide) and polyimide
- **Super capacitor or Ultra capacitor**
    - Conducting polymers like PANI with GO and r-GO sheets

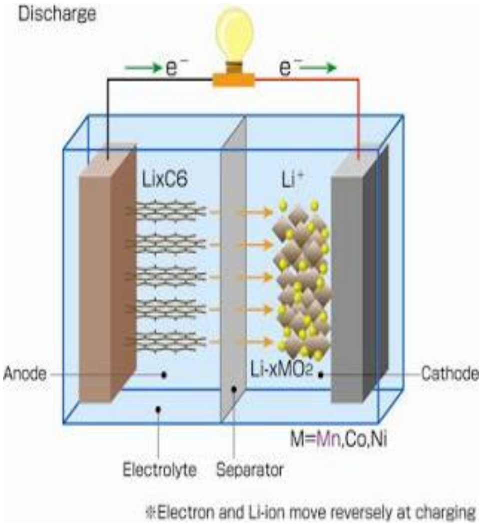


Figure 1.22: Energy storage

1.22.3 Sensors

- Many types of molecules can be detected such as biomolecules, Also used as pH, Pressure and temperature measuring sensors

Figure 1.23: Sensors

Chapter 2

2 Literature Review/Objectives

2.1 PVA /PANI Polymer Blend

A. Mirmohseni and G.G. Wallace worked on PVA/PANI blend. Manufacturing and characterization of polyaniline–polyvinyl alcohol composites is discussed. The PANI composite is manufactured by chemical polymerization of aniline in solvent comprising PVA (10%, w/w). When aniline is oxidized it consequences in an unwavering water based PANI dispersion, which is casted to make a film which is mechanically strong. Polyaniline–polyvinyl alcohol blends with variation in polyaniline concentration are prepared. Sheets prepared with these concentrations shows exceptional mechanical properties. They show flexibility and have the capability to be elongated to 190%. 40 MPa of tensile strength of is obtained and electrical conductivity of the composites is enhanced by increasing the quantity of PANI and got a value of 2.5 S cm^{-1}. Cyclic voltammetry exhibited that the composite material is electroactive.[9]

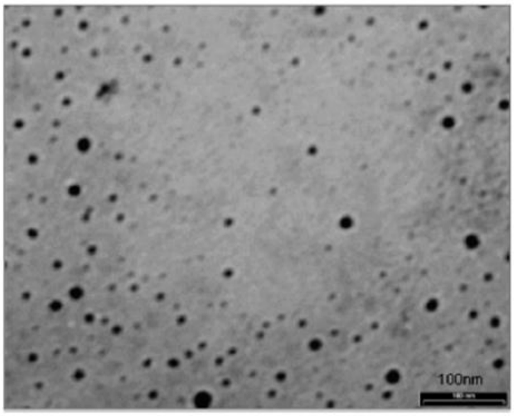


Figure 2.1: "TEM image of PANI dispersion showing PANI particles"

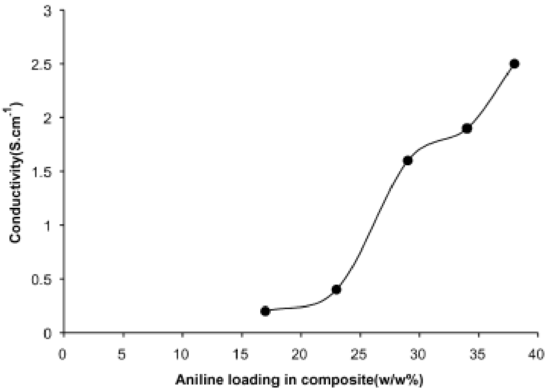


Figure 2.2: "Four point probe conductivity of PANI–PVA composite films as a function of polyaniline loading"

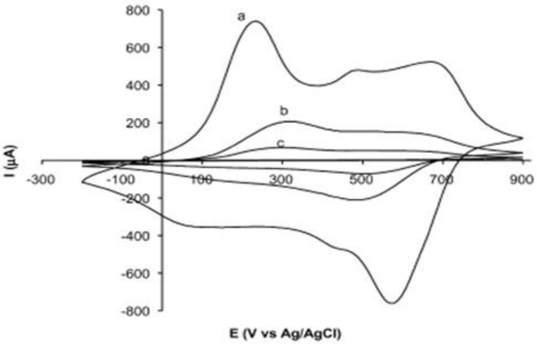
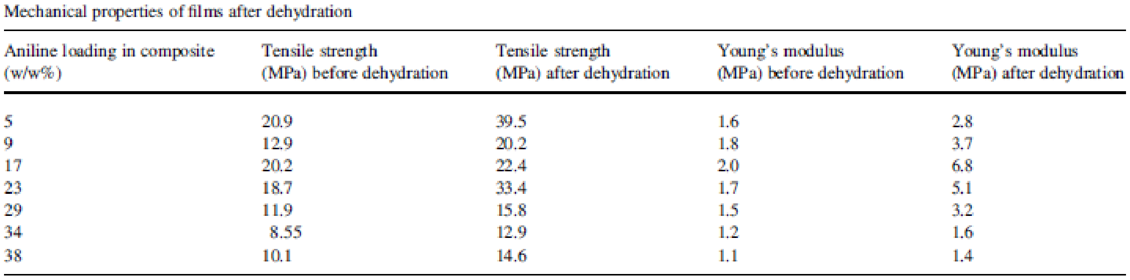


Figure 2.3: "Electroactivity of the composites with varying polyaniline content.(a)aniline loading 34% (w/w), (b): aniline loading 23% (w/w), (c):aniline loading 9% (w/w)".

Table 2.1: Mechanical properties of films after dehydration


Mechanical properties of films after dehydration

Aniline loading in composite (w/w%)	Tensile strength (MPa) before dehydration	Tensile strength (MPa) after dehydration	Young's modulus (MPa) before dehydration	Young's modulus (MPa) after dehydration
5	20.9	39.5	1.6	2.8
9	12.9	20.2	1.8	3.7
17	20.2	22.4	2.0	6.8
23	18.7	33.4	1.7	5.1
29	11.9	15.8	1.5	3.2
34	8.55	12.9	1.2	1.6
38	10.1	14.6	1.1	1.4

2.2 PANI-PVA and PANI-PEO Blends

A.Alakanandana, V.Geetha, Atul kumar, J.Siva, A.R.Subrahmanyam and Kumar worked on "Mechanical and Electrical Conductivity Studies of PANI-PVA and PANI-PEO Blends". PANI is autonomously blended with PVA. PEO is synthesized by solution casting process using NMP as common solvent. The change in structure of these films is premeditated by FTIR and XRD methods. XRD and FTIR studies established the complex development in polymer blends. The change in the intensities in the polymer blend and appearance of new peaks in the FTIR spectra revealed the blending of poly aniline with PVA and PEO. Tensile testing and scanning electron microscopy techniques are used to study the physical properties. SEM revealed the change in surface characteristics of pure PANI with blending. From tensile testing, it was observed that PANI-PVA blend is the most promising composition for several industrial applications. The dc conductivity of these polymer blends has been determined in the temperature range 300K to 373K. The dc conductivity of pure PANI is found to be more than PANI-PVA and PANI-PEO blends.

The change in the conductivity of this polymer blending at different temperatures depends on intra-chain and inter-chain mobility and is explained by two phase model.[10]

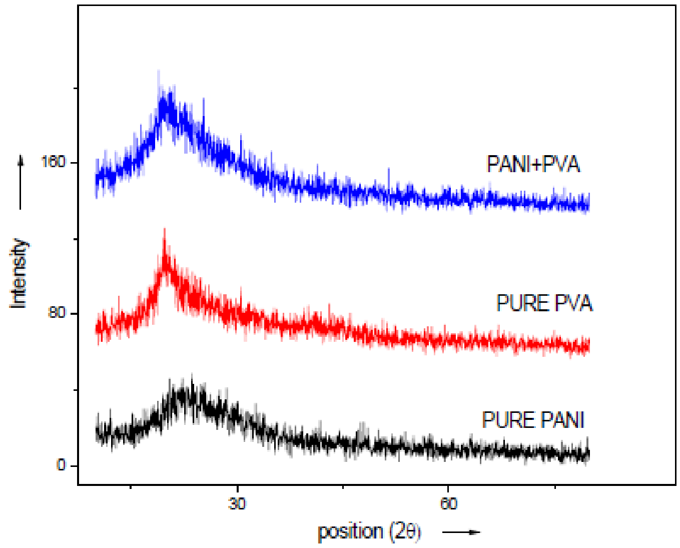


Figure 2.4: "XRD pattern of Pure PANI, Pure PVA and PANI+PVA"

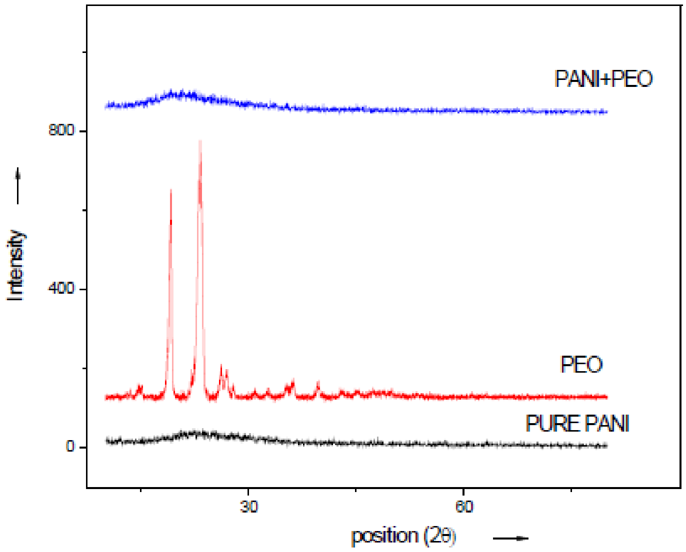


Figure 2.5: "XRD pattern of Pure PANI, PEO and PANI+PEO"

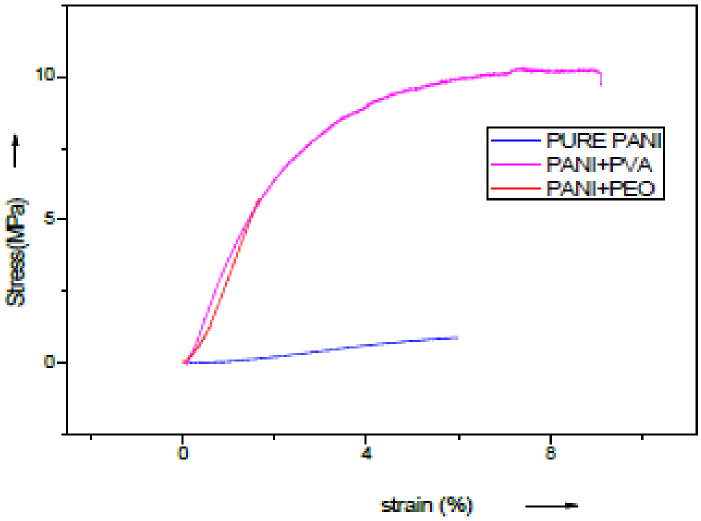
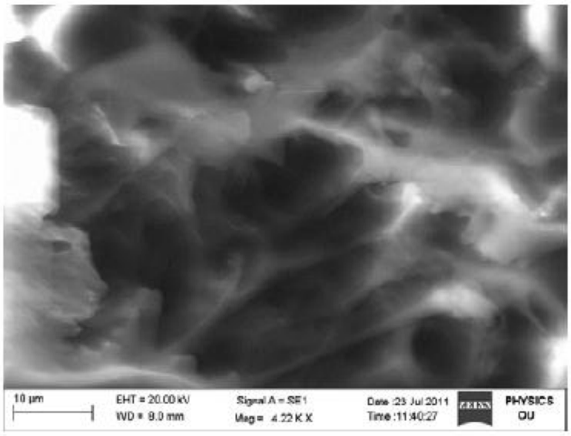
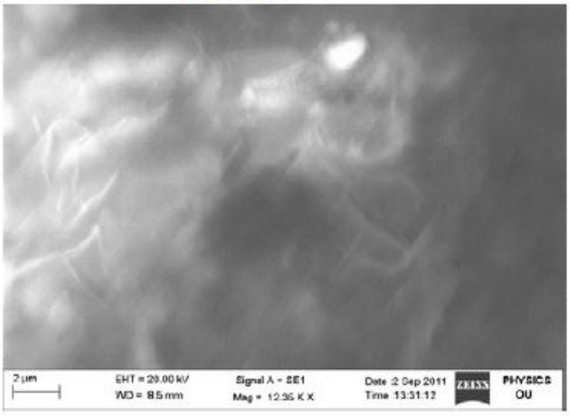


Figure 2.6: “Mechanical properties of polymer blends”



PURE PANI



PANI+PVA

Figure 2.7: SEM results

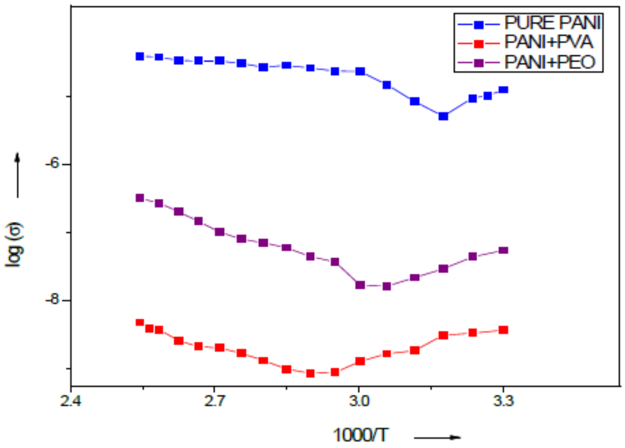


Figure 2.8: “Dc conductivity of polymer blends”

2.3 Alumina/PVA Composites

Navin Chand, Archana Nigrawal they worked on dielectric properties of Nano Alumina/Polyvinyl Alcohol (PVA) Composites. Figures 2.9 to 2.12 show deviation of Ɛ′ with temperature and frequency for PVA and samples 1, 2 and 3 respectively. At initial temperature (30°C) these plots Figures 2.9 to 2.12 do not show any change in ε’ value which shows that there is no amassing of interfacial charge in composites. As temperature is increased the dielectric constant is also increased and at 150°C, Ɛ′ value for the sample having higher percent of nano alumina is highest. The rise in dielectric constant can be credited to a reason that when we are close to the Tg, The mobility of the segments of the polymer chains gave high increase in dielectric constant.[11]

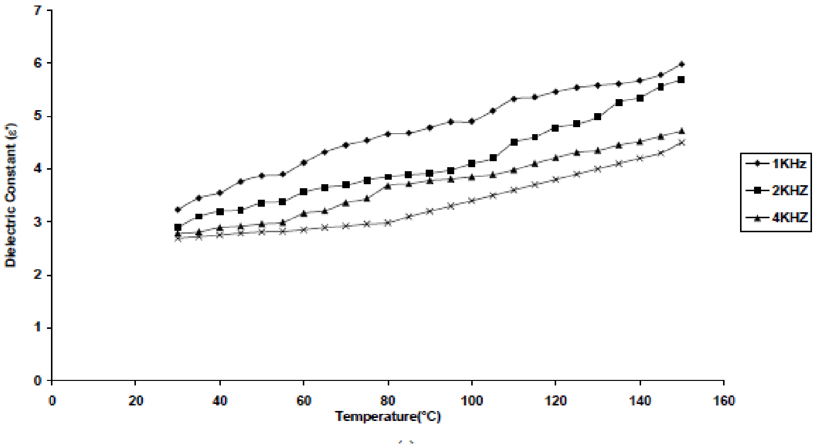


Figure 2.9: “Pure PVA dielectric constant”

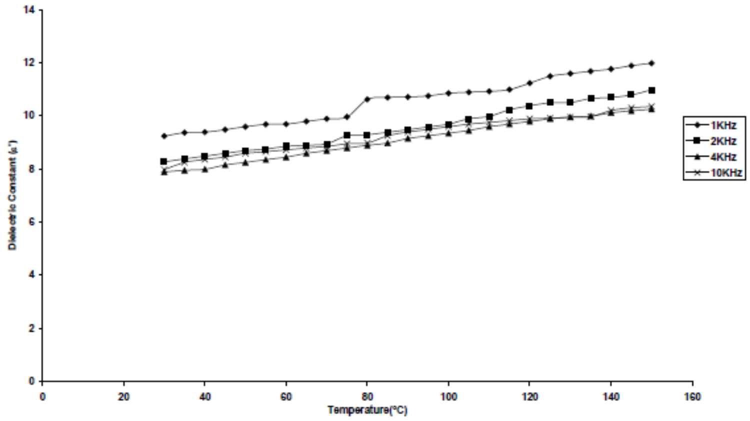


Figure 2.10: “PVA+0.5% Nano alumina”

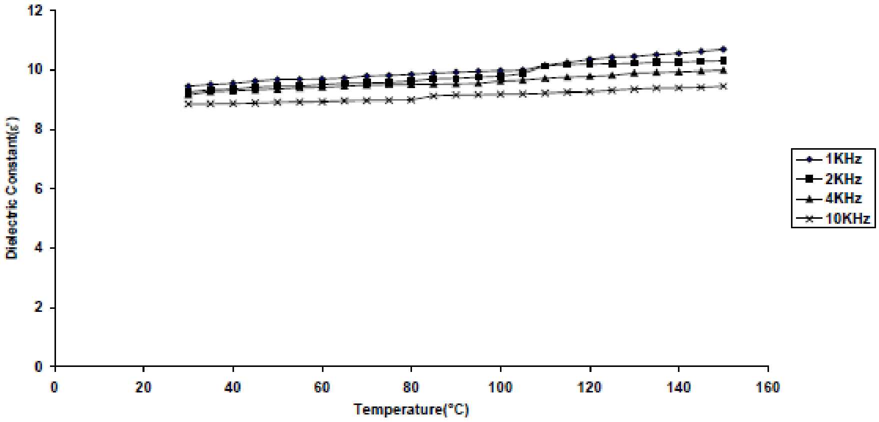


Figure 2.11:” PVA+1% Nano alumina”

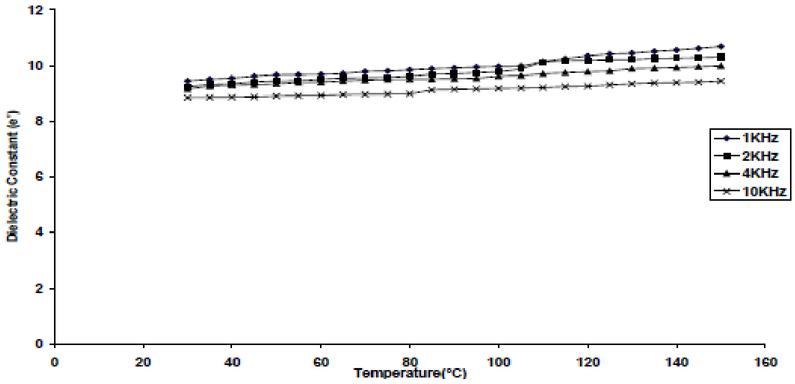


Figure 2.12: “PVA+1.5% Nano alumina”

2.4 Mg-doped PbS/PVA Nanocomposites

R Nagalakshmi, G Shanmugam and V Krishnakumar, worked on Mg-doped PbS/PVA nano composites. XRD results shows that Pbs is having cubic phase. Figure 2.13 gives us the XRD results of un-doped and Mg-doped PbS/PVA nanocomposite. Un-doped, 5 and 7.5 mol% have their diffraction peaks greater than 20°. Mg-doped films have cubic phase of PbS which is confirmed from JCPDS file No 05-592. Mg-doped films do not have Mg-related secondary phase according to XRD, which shows that Mg: PbS/PVA films are pure. Figure 2.13 also shows that diffraction peaks of Mg-doped films faintly shifted to greater value of 2θ with rise in Mg concentration, from which we conclude that PbS lattice is enlarged for all doped samples. [12]

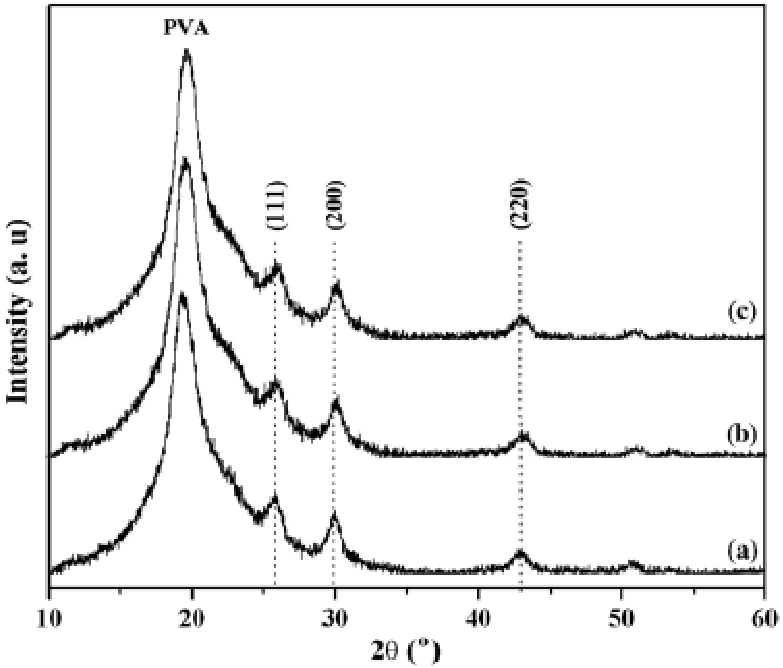
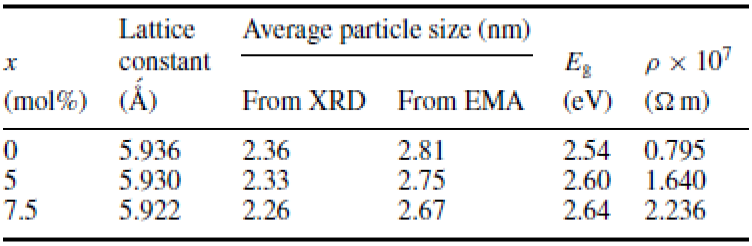


Figure 2.13: XRD pattern for (a) undoped, (b) 5 and 7.5 mol % of Mg doped PBS/PVA nano composite

Table 2.2: "Lattice constant, average particle size, Eg and ρ values of PVA"



x (mol%)	Lattice constant (Å)	Average particle size (nm)		E_g (eV)	$\rho \times 10^7$ (Ω m)
		From XRD	From EMA		
0	5.936	2.36	2.81	2.54	0.795
5	5.930	2.33	2.75	2.60	1.640
7.5	5.922	2.26	2.67	2.64	2.236

Table 2.2 shows the lattice constant '*a*' of the Mg/PbS/PVA films with change in the Mg and PbS/PVA pure film have lattice constant of about 5.936 Å however for 5 and 7.5 mol% Mgdoped PbS/PVA films the values of 'a' is decreased. The lessening in lattice constant is accredited to the integration of Mg2+ into the Pb2+ sites in the lattice; it is due to smaller ionic radius of Mg2+(0.066 nm) compared with Pb2+ (0.149 nm)

2.5 Mechanical thinning to make Few-Layer Graphene

I. Janowska, F. Vigneron, D. Be´gin, O. Ersen, P. Bernhardt, T. Romero,M.J. Ledoux, C. Pham-Huu they worked on mechanical thinning of FLG using pencil lead, they gave a fast and low cost method to make (FLG). The synthesis comprises of rubbing pencil lead on a tough glass surface then doing continuous ultra-sonication after that purification is done to eliminate the inorganic binder. Characterization techniques such as SEM, TEM and Raman elucidates that FLG have lateral dimension is of few micrometers, which is composed of 1,20 and sometimes 50 sheets.

The size of FLG is about 2µm. The flawless carbon lattice (Fig. 2.14C) and some with flaws that deliver higher stability of system for the thinner particles can be differentiated by TEM (Fig. 2.14D). The statistical TEM analysis is done on FLG border which clearly shows that on an average there are 5–8 layers of FLG (Fig. 2.15A). Single layers are also seen in the sample; which can be shown in Fig. 2.15 B. SEM analysis also showed FLG which composed of about fifty graphene layers (Fig. 2.15C) (not observed by TEM due to the lower scrolling tendency than the thinner ones).[8]

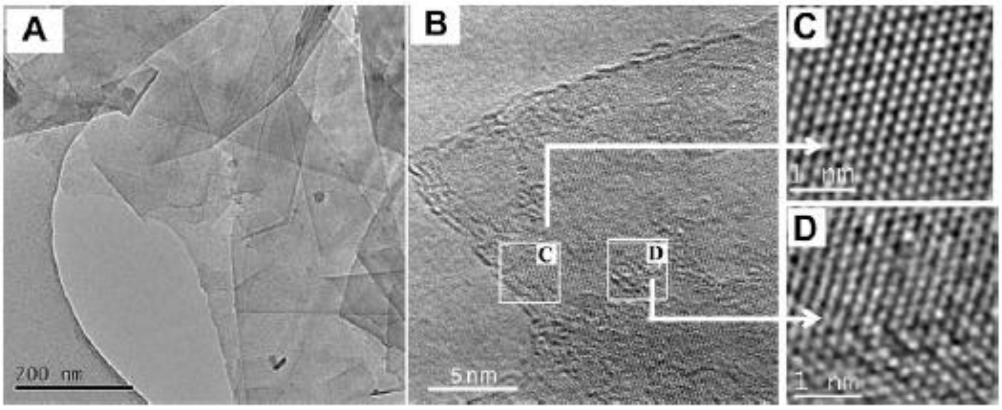
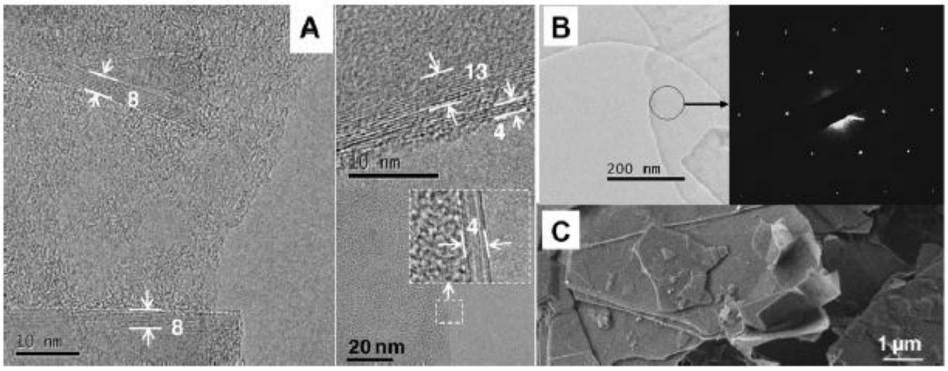


Figure 2.14: "TEM images of FLG obtained by the mechanical ablation of the pencil lead, (A) the assembly of FLG, (B) Bilayer graphene with different crystallinity, (C) the perfect hexagon lattice, (D) the lattice with a lack of carbon atoms or the presence of ripple"



•

Figure 2.15: "TEM micrographs of the FLG borders with different graphene sheets numbers, (B) Tem micrograph and electron diffraction of a monolayer graphene (C) SEM image showing the presence of thick FLG in the sample."

2.6 PVA/Graphene Composite

Xin Zhao, Qinghua Zhang, and Dajun Chen worked on PVA/Graphene composites. PVA/graphene composites are synthesized by adding graphene oxide to PVA matrix and after that graphene nanosheets are obtained by reducing graphene oxide. The composite films have enhanced mechanical properties. Tensile strength is increased by 150 % by only adding 1.8 vol % graphene, which shows the effectual load transfer between the graphene and the matrix. By 1.8 vol% loading the modulus is 10 times increased as compared to pure PVA.

As experimental and Halpin-Tsai prediction is compared, they indicate that graphene Nano-sheets may be randomly dispersed in the matrix. By adding graphene to the PVA the crystallinity of the composite is barely affected.[7]

2.6.1 Mechanical Percolation

Figure 2.19 shows the mechanical percolation .When the filler quantity reaches a value after which distance between any two sheets can get so little that sheets easily stack together due to the van der Waals force (figure 2.19(4)). In this study the critical value is 1.8 vol % loading of graphene and aforementioned phenomenon is called as mechanical percolation. Among these, the second one (figure 2.19(2)) is the perfect situation, presenting the vital influence to the mechanical behaviors with highest effectiveness.

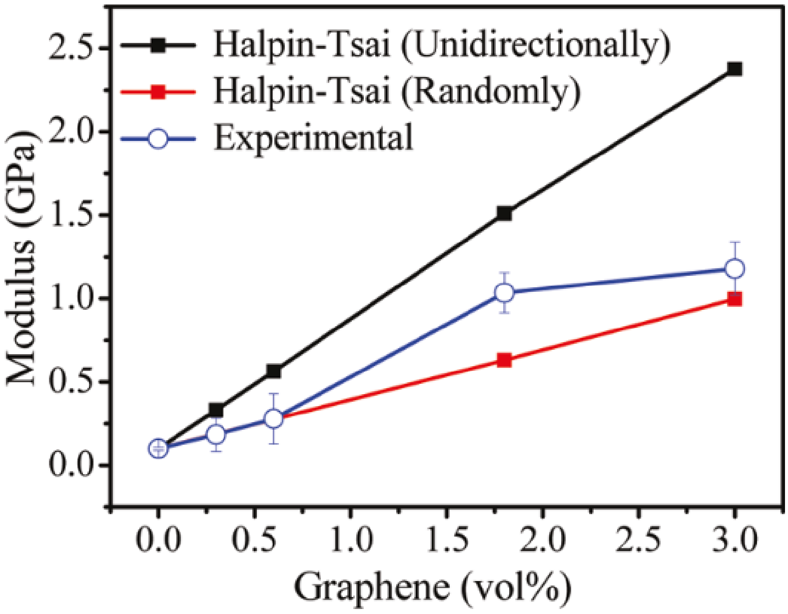


Figure 2.16: "Young's moduli of the nanocomposite and Halpin-Tsai theoretical models. The theoretical simulations were taken as two cases: the random orientation and unidirectional distribution of graphene nanosheets in the polymer matrix".

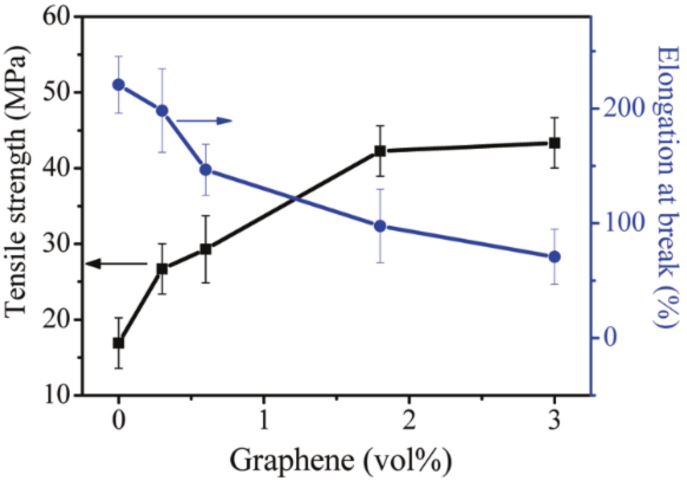


Figure 2.17: "Mechanical properties of graphene/PVA nanocomposites with various graphene loadings: tensile strength (left) and elongation at break (right) versus graphene loadings"

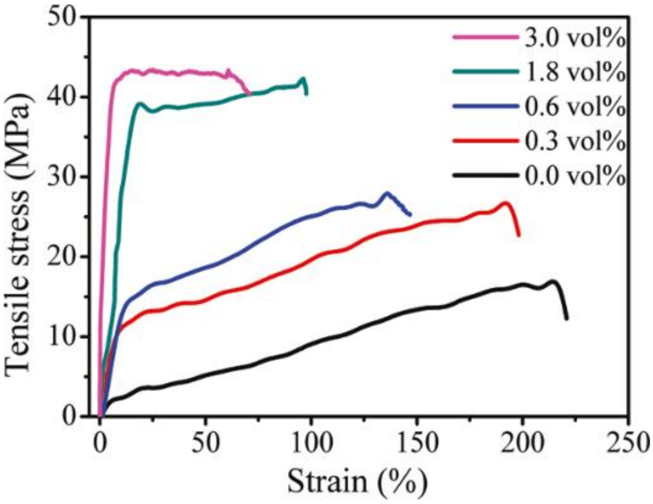


Figure 2.18: "Typical stress- strain plots of the composites with various graphene loadings"

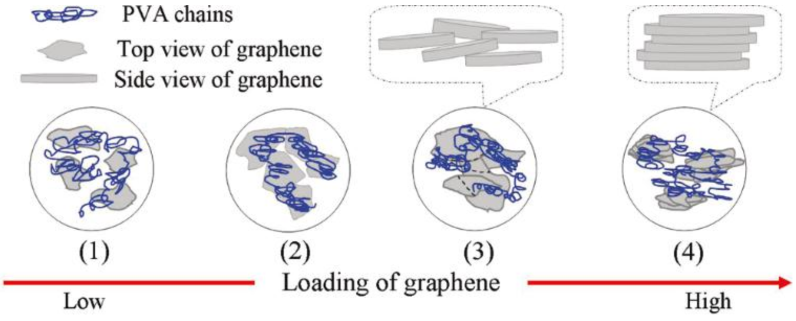


Figure 2.19: Mechanical percolation

2.6.2 PVA/Graphene XRD Results

XRD technique is used to calculate the crystalline properties of composite. As shown in the Figure 2.20, Graphene shows a broad peak while PVA peak is at 2θ=19.5.As Graphene is added to PVA matrix the graphene broad peak disappears while the characteristic peak of PVA remains intact (figure 2.20 curve c). Figure 2.21 also gives us the aforementioned results. Therefore, we can conclude that graphene Nano sheets are fully exfoliated and dispersion is at molecular level. To further clarify this point, we prepare a sample which contains 0.6 vol% of pristine graphite in PVA. As Graphite have a regular structure the composite gives the characteristic peak of graphite at 2θ=26.5. PVA is semi-crystalline in nature and shows a peak at 2θ =19.4. Figure 2.21 shows a weak bulge 2θ=40.4 while the rise in the intensity of the (101) diffraction corresponds to the rise in the number of PVA chains packing together, causing in a large size of crystallite in PVA sol-gels. As we add Graphene to the PVA till 0.6 vol % of graphene the characteristic peak of PVA is increasing then there is decrease which clearly show that at 0.6% vol we have maximum crystallinity.

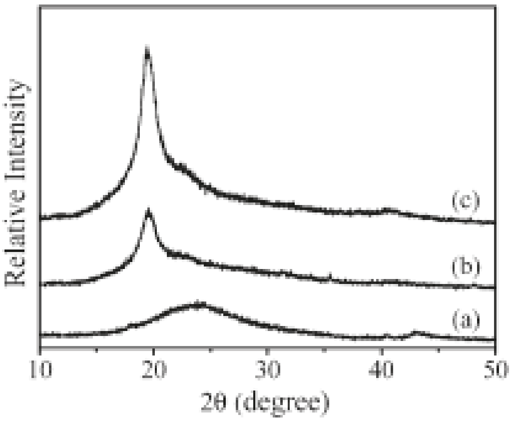


Figure 2.20: "XRD pattern of (a) graphene powder, (b) pure PVA, and (c) graphene/PVA composites with 0.6 vol % loading of graphene."

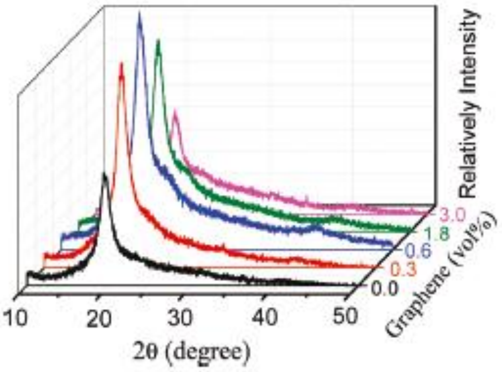


Figure 2.21: "XRD patterns of graphene/PVA composites with various graphene contents".

2.7 Objectives

- Investigating the mechanical and dielectric properties of PVA/PANI blends at various concentration
- Investigating the mechanical and dielectric properties by adding few layer Graphene (FLG) at different weight percentages to PVA/PANI polymer blend.
- Investigating the Emi-shielding property for RAM by adding Few Layer Graphene (FLG) at different weight percentages to PVA/PANI polymer blend

Chapter 3

3 Experimental

3.1 Materials

The following table gives us an overview of the materials used.

Table 3.1: Specifications of materials used for experimentation

Material	**Manufacturer**
Polyvinyl alcohol	ERKOL
Polyaniline	**Prepared in lab**
Few layer graphene	I. Janowska

3.2 Preparation of Polyaniline

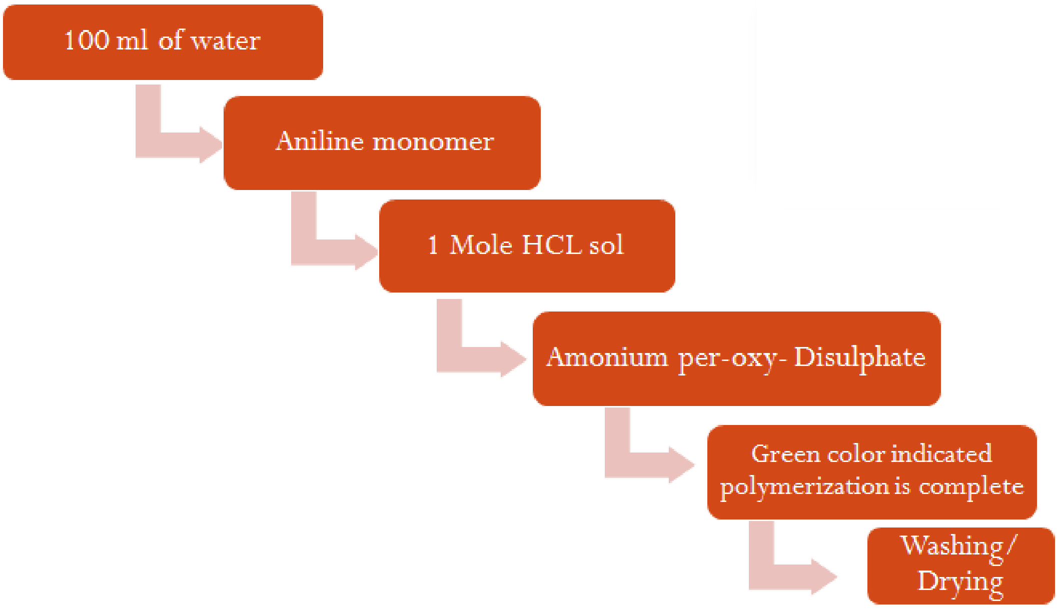


Figure 3.1: Preparation of polyaniline

Figure3.1 illustrates the method for the preparation of polyaniline 100 ml of de ionized water was taken and aniline monomer was added then 1 mole HCL sol was slowly added. Ammonium per-oxy-disulphate was added as an initiator and as the green color started to appear the polymerization was completed. The solution was washed several times and then dried to get the required Polyaniline powder that can be seen in figure 3.2.

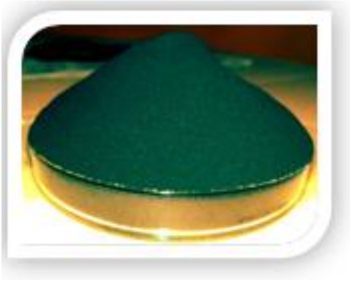


Figure 3.2: Polyaniline powder

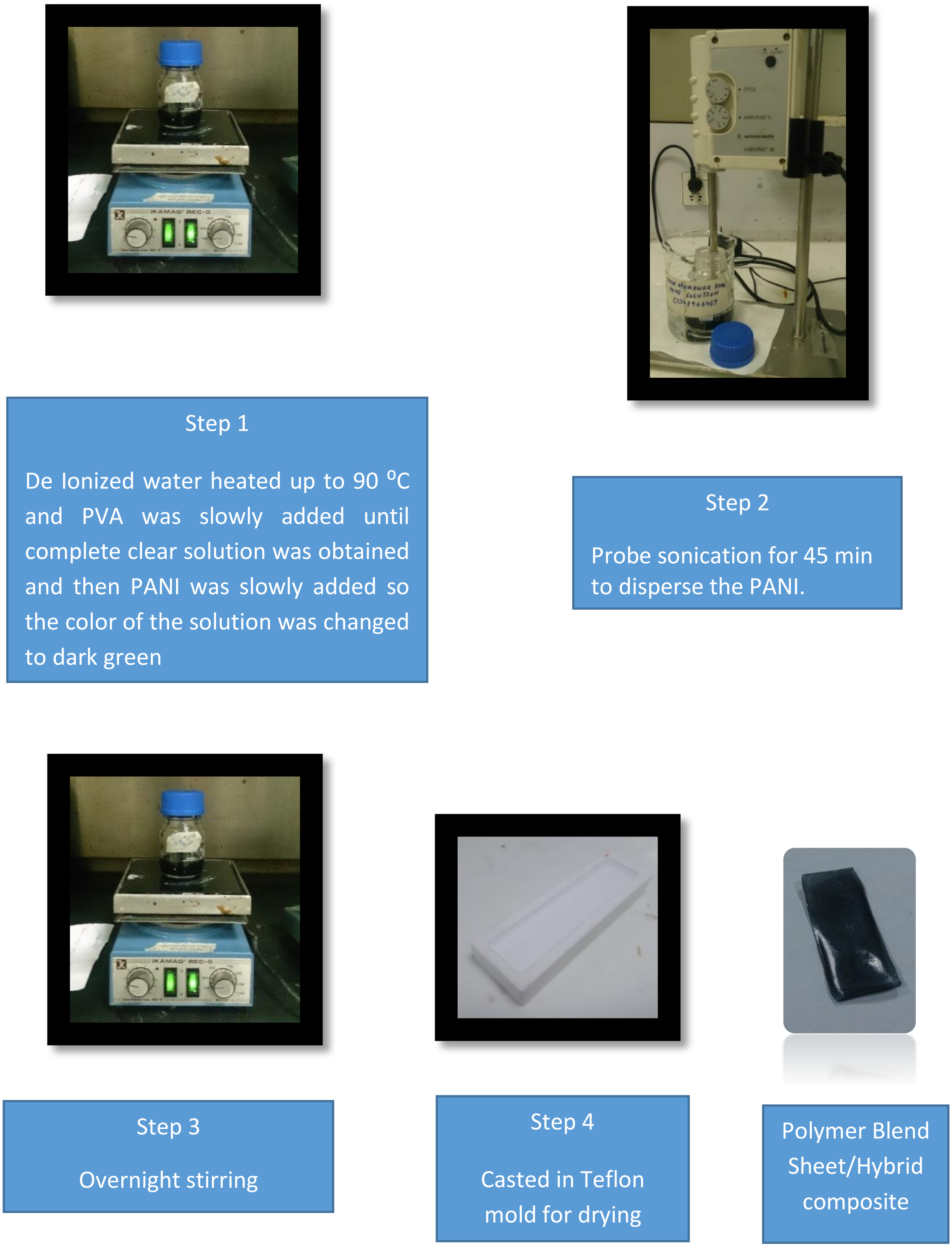
3.3 Preparation of PVA sheet

Required amount of de ionized water was taken and was heated up to 90 ^{0}C, then the required amount of PVA powder was added and the solution was kept on constant stirring at 500 Rpm. After 20 min we get a clear solution. This solution is casted in Teflon molds Figure 3.3 and left in the atmosphere for drying after 4 days we get the required sheet. Figure 3.4

Figure 3.3: PVA solution casted in Teflon mold

Figure 3.4: PVA sheet

3.4 Preparation of Polymer blend



Step 1

De Ionized water heated up to 90 ^{o}C and PVA was slowly added until complete clear solution was obtained and then PANI was slowly added so the color of the solution was changed to dark green

Step 2

Probe sonication for 45 min to disperse the PANI.

Step 3

Overnight stirring

Step 4

Casted in Teflon mold for drying

Polymer Blend Sheet/Hybrid composite

Figure 3.5: Solution casting method for preparing polymer blend and Hybrid composite

3.5 Preparation of PVA/PANI/FLG Composite

The same process is adapted as mentioned in polymer blend figure 3.5 preparation but at step 1 the required amount of FLG is added after PVA and PANI is dissolved.

3.6 Composition and Number of samples prepared

Polymer Blend

PANI %	PVA %
0	100
1	99
5	95
10	90
15	85
30	70

Table 3.2: Different composition of (PVA/PANI) polymer blend

Three component hybrid Nano composite

PVA/PANI %	FLG %
90/10	0.1
90/10	0.5
90/10	1

Table 3.3: Different composition of Hybrid composite (PVA/PANI) (90-10) with variation in FLG concentration

PVA/PANI %	FLG %
99/1	0.1
99/1	0.5
99/1	1

Table 3.4: Different composition of Hybrid composite (PVA/PANI) (99-1) with variation in FLG concentration

3.7 Specimen Characterization

PVA hybrid films were characterized using following techniques:

3.7.1 X-RAY Diffraction (XRD)

XRD patterns were measured at room temperature using a Theta-Theta instrument by STOE-Germany with a Cu $K\alpha$ Radiations ($\lambda = 0.15418$ nm). The scanning rate was 2˚/min over the range $2\Theta = 5^\circ - 40^\circ$

3.7.2 Scanning Electron Microscopy (SEM)

The morphologies of PVA Hybrid films were investigated using a JOEL JSM-6490A Analytical Scanning Electron Microscope. A cryogenic crack was created in the films using liquid Nitrogen i.e. the samples were frozen in liquid nitrogen where they became fragile and were broken to generate the fresh surface.

3.7.3 Tensile Mechanical properties

The tensile properties of PVA Nanocomposite solution-cast films were determined using Trapezium-X Universal Testing Machine (AG-20KNXD Plus) manufactured by Shimadzu Corporation at a crosshead speed of 5 mm per minute (ASTM D882). All the samples were tested at room temperature and at least 5 individual determinations were used to obtain an average value.

3.7.4 Dielectric Properties

Dielectric properties of specimens were determined using Precision Impedance Analyzer (Wayne Kerr 6500B) at room temperature in the frequency range of 100Hz to 10MHz. The capacitance C and dissipation D were measured through impedance analyzer.

3.7.5 Radar Absorption

Emi-shielding test was performed with the help of E8362B PNA Network Analyzer at room temp and in the frequency range from 8 to 20 GHz.

3.7.6 Thermal Gravimetric Analysis(TGA)

TGA analysis was done with the help of YRIS Diamond TG-DTA High Temp Vacuum in the range from 0°C to 1000° C at 10° C per min.

Chapter 4

4 Results and Discussion

4.1 XRD Results

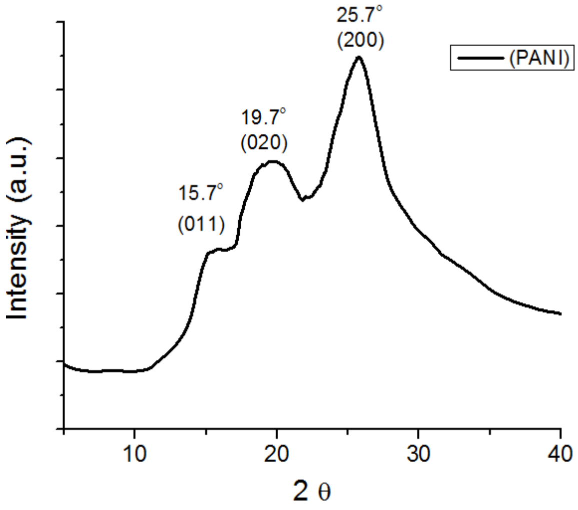


Figure 4.1: XRD Polyaniline

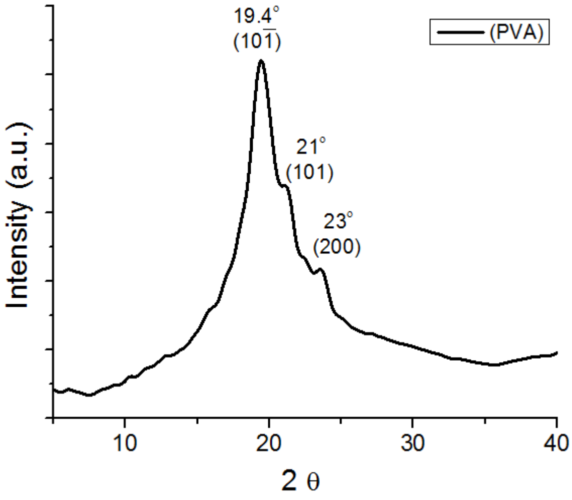


Figure 4.2: XRD Polyvinyl alcohol

Figure 4.1 gives us the XRD pattern of Polyaniline that is synthesized in lab. For pure PANI, the crystalline peaks appear at 2θ= 15.7, 19.7 and 25.7, corresponding to (0 1 1), (0 2 0) and (2 0 0) crystal planes of PANI in its emeraldine salt form, respectively.[13-15]. Figure 4.2 gives us the XRD of pure polyvinyl alcohol. The crystalline peaks appear at 2θ=19.4^0, 21^0 and 23^0, corresponding to (10$\bar{1}$), (101) and (200) crystal planes of PVA respectively [16-21].

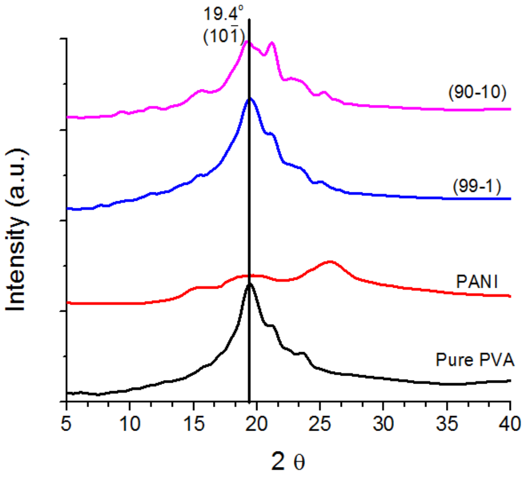


Figure 4.3: XRD comparison of Pure PVA, PANI, (PVA 99%-PANI 1%) and (PVA 90%-PANI 10%)

Figure 4.3 gives us the XRD comparison of Pure PVA, PANI, PVA 99%-PANI 1% and (PVA 90%-PANI 10%). As the PANI concentration is increased so the intensity of the characteristic peak of PVA that is $2\theta=19.4^0$ $(10\bar{1})$ is decreased. The $(10\bar{1})$ diffraction peak of PVA is due to the intermolecular interface between PVA molecular chains in the direction of intermolecular hydrogen bonding. The decrease in the intensity of the $(10\bar{1})$ diffraction peak after incorporation of PANI, as shown in Figure 4.3, corresponds to the decrease in the packing of PVA chains and hence results in either less ordered packing or a smaller crystallite size in PVA/PANI blend[20].

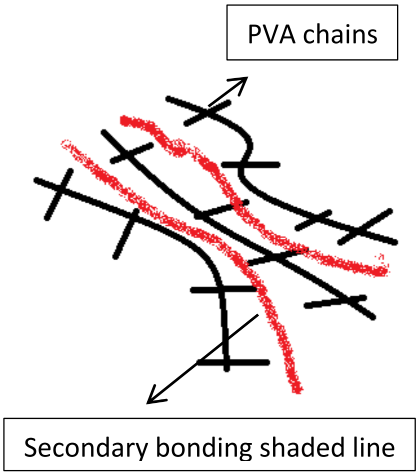


Figure 4.4: The Black line showing PVA chains while the red region showing the secondary bonding due to -OH group along the chains

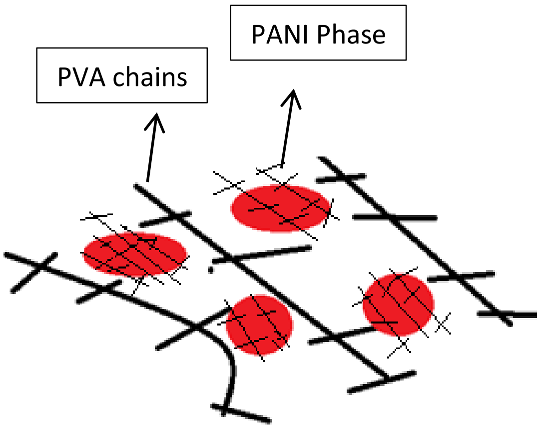


Figure 4.5: The black lines showing PVA chains while he red DOT region showing PANI phase

Figure 4.4, 4.5 shows the schematic diagram to explain the decrease in the peak intensity of PVA $2\theta=19.4^0$. Figure 4.4 shows the secondary bonding as shaded line where an order exists between PVA chains along the hydrogen bonds while in Figure 4.5 PANI phase is lying with in the PVA phase thus disrupting the packing of the PVA chains hence decreases the intensity of the respective peak. Figure 4.6 shows the XRD of FLG and it gives a very high intensity peak at 26.4^0 which corresponds to the graphitic planes.

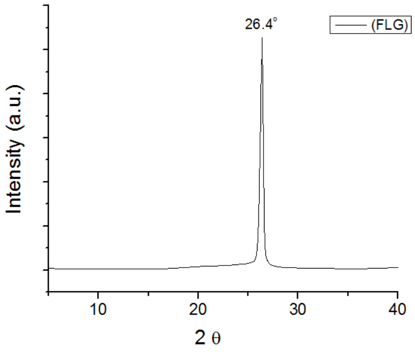


Figure 4.6: XRD Few layer graphene

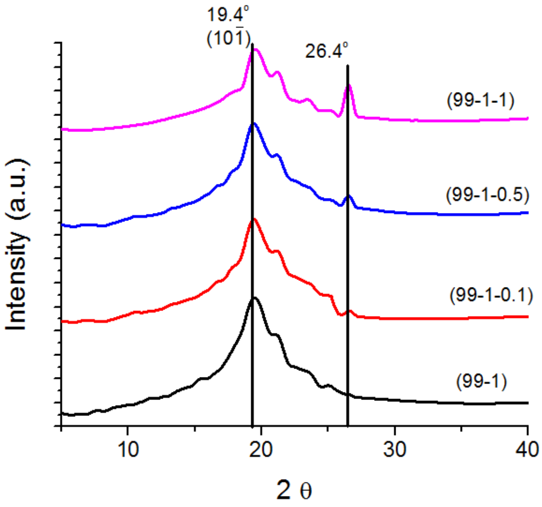


Figure 4.7: XRD comparison of (PVA 99%-PANI1%) with varying FLG concentration

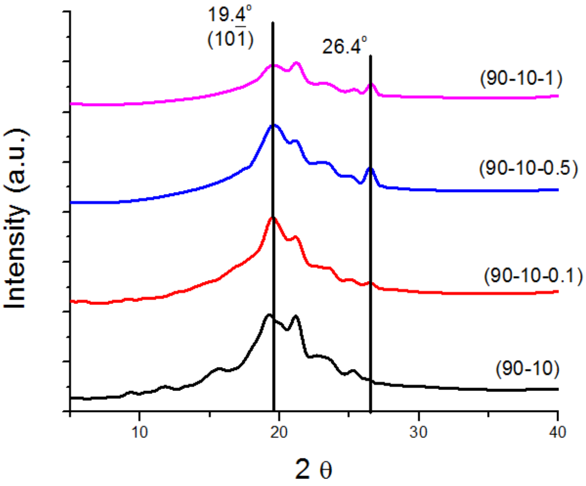


Figure 4.8: XRD comparison of (PVA 90%-PANI 10%) with varying FLG concentration

Figure 4.7, 4.8 shows the XRD pattern of of (PVA 99%- PANI 1%) and (PVA 90%- PANI 10%) polymer blend with varying concentration of FLG from 0.1 wt % to 1wt %. This comparison gives an idea that was discussed earlier that is decease in the characteristic peak intensity of PVA that is $2\theta=19.4^0$ $(10\bar{1})$ the same reason also applies here as explained by Figure 4.4, 4.5. The second idea is that as we add FLG to the Polymer blend there is an abrupt decrease in the peak intensity of the FLG $2\theta=26.4^0$ hence PVA has penetrated in to the graphene layers, which gives improvement in the mechanical properties such as tensile strength and modulus. The intensity of FLG peak is also increasing by increasing its amount that would give us an idea of stacking of FLG layers in which the PVA has not penetrated. In (90-10) composite system Till 0.5 wt% FLG loading the peak intensity is increasing, at 1 wt% FLG the intensity again decreasing which gives an idea that PVA has penetrated more as compared to 0.5 wt% FLG, so the properties must increase but the properties are decreased at 1 %wt loading of FLG. The reason is that at 1 wt % loading the characteristic peak of PVA $2\theta=19.4^0(10\bar{1})$ is relatively more decreased as compared to 0.5 wt % so which clearly tells that the secondary bonding along the PVA chains is much reduced and that is due to both increase in the amount of FLG and PANI.

4.2 SEM Results

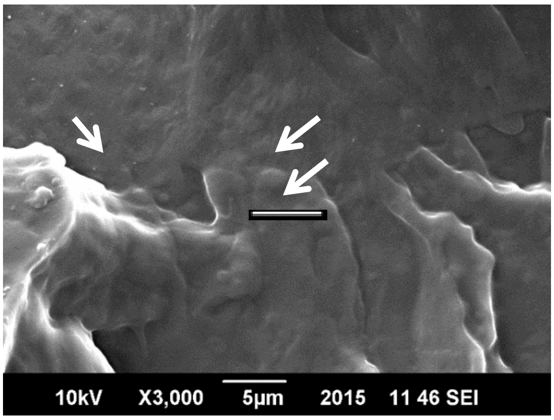


Figure 4.9: SEM (99/1) polymer blend

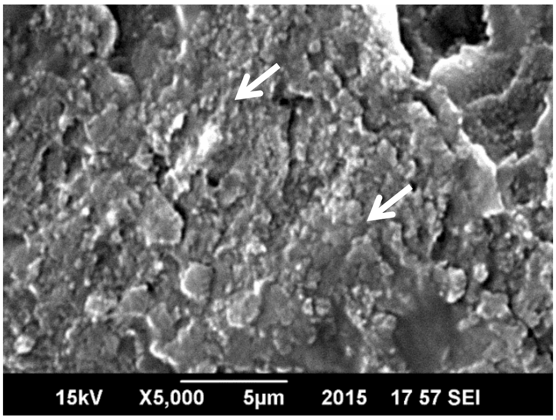


Figure 4.10: SEM (90/10) polymer blend

Figure 4.9, 4.10 shows the SEM results of (99/1) (90/10) polymer blend system. The arrows show the PANI phase which is heterogeneous though out the polymer. PANI phase is circular in shape; white lines are having a scale of 5µm so the average size of the PANI phase is roughly 2.5µm. As the PANI concentration is increased PANI forms a network in PVA and can be clearly seen in figure 4.10 marked by red arrows. The dispersion of PANI can be verified by XRD results figure 4.3.

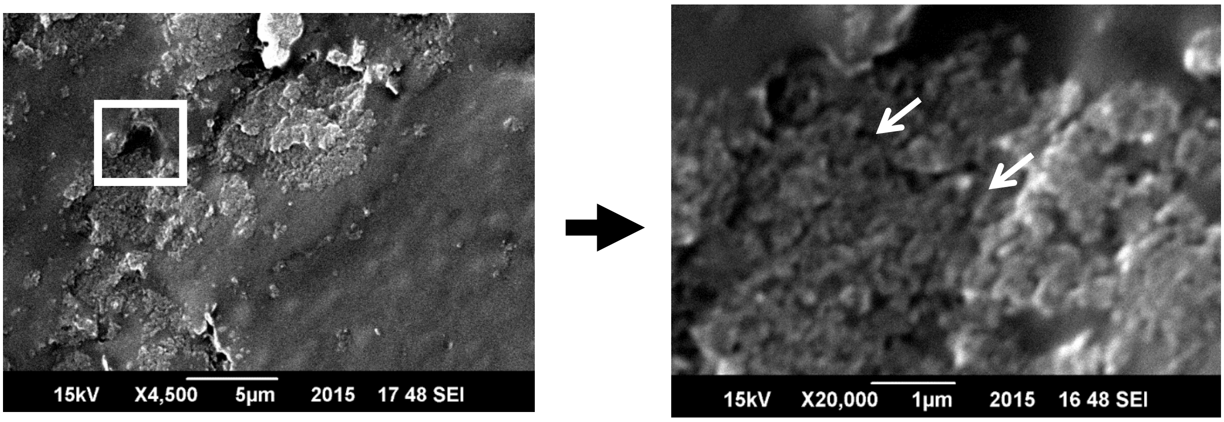


Figure 4.11: SEM (90/10) polymer blend with 0.5 wt % FLG

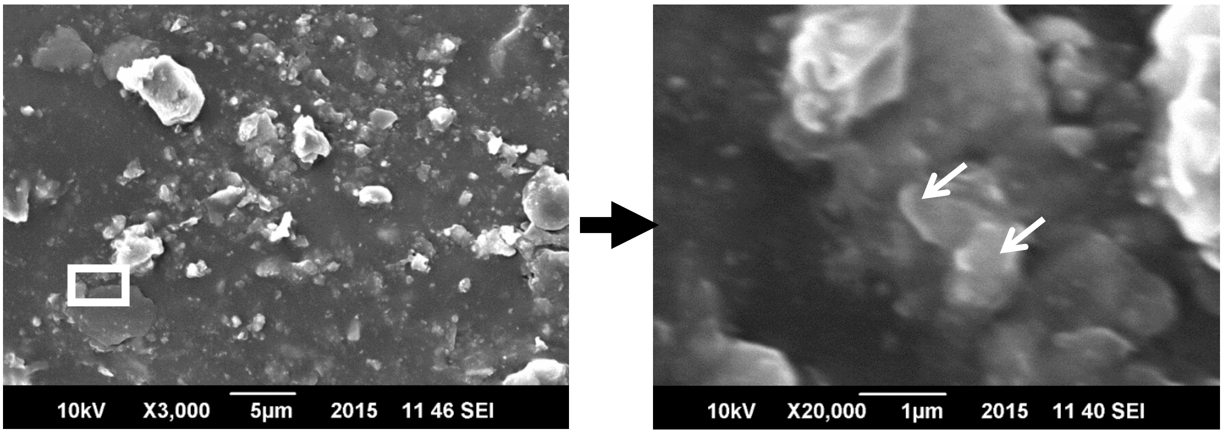


Figure 4.12: SEM (99/1) polymer blend with 0.5 wt % FLG

Figure 4.11 and 4.12 shows the dispersion of FLG in the polymer blends (90/10), (99/1) respectively. PANI along with FLG is forming a network marked by the red arrows the bright region shows PANI phase while dark region shoes FLG. In the (90-10) system with FLG the network is denser as compared to the network formed in (99-1) system with FLG

4.3 Tensile results of PVA/PANI blend system

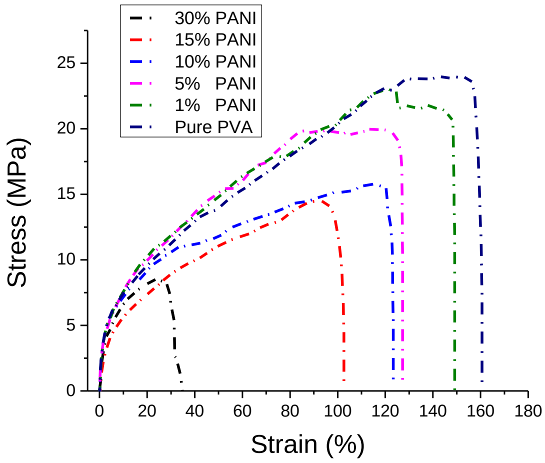


Figure 4.13: Stress-Strain graph of PVA, PVA/PANI blends

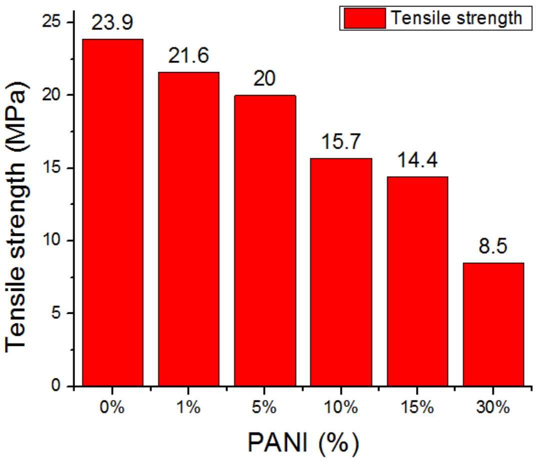


Figure 4.14: Variation of tensile strength with increase in PANI concentration

Solution casting technique is used to synthesize PVA/PANI standalone films of about 0.1 mm thickness. PVA/PANI polymer blend was made at different weight percentages (figure 4.13). PVA forms good quality films with considerable tensile strength (23.9 MPa) and Young's modulus (0.098 GPa) on introducing polyaniline in PVA, the strain (figure 4.13) and tensile Strength (figure 4.14) is decreased from 160 % to 37 % and 23.9 MPa to 8.5 MPa respectively.

While there is no significant change in modulus (figure 4.15).By adding PANI in PVA the crystallide size of PVA is decreased that can be confirmed from XRD results (Figure 4.3), the peak intensity of PVA/PANI blend is decreasing [10]. So the decrease in the tensile strength (Figure 4.14) of the polymer blend could be attributed to the decrease in crystallide size. The second reason for the decrease in tensile strength is attributed to the shrinkage of the matrix on the dispersed phase that allows for better stress transfer under situations of very little deformation. As higher deformation is applied to the sample this contact will be disturbed since there is no chemical bonding present at the interface[22].The same phenomena leads to decrease in strain as PANI is added to the PVA[22](Figure 4.13).

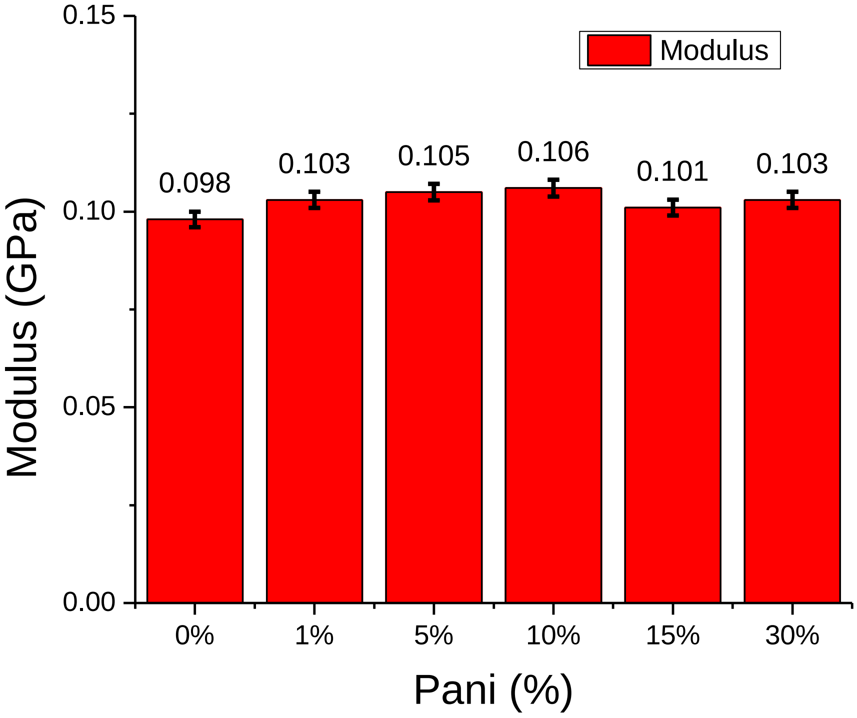


Figure 4.15: Variation of modulus with increase in PANI concentration

4.4 Dielectric results of PVA/PANI blends

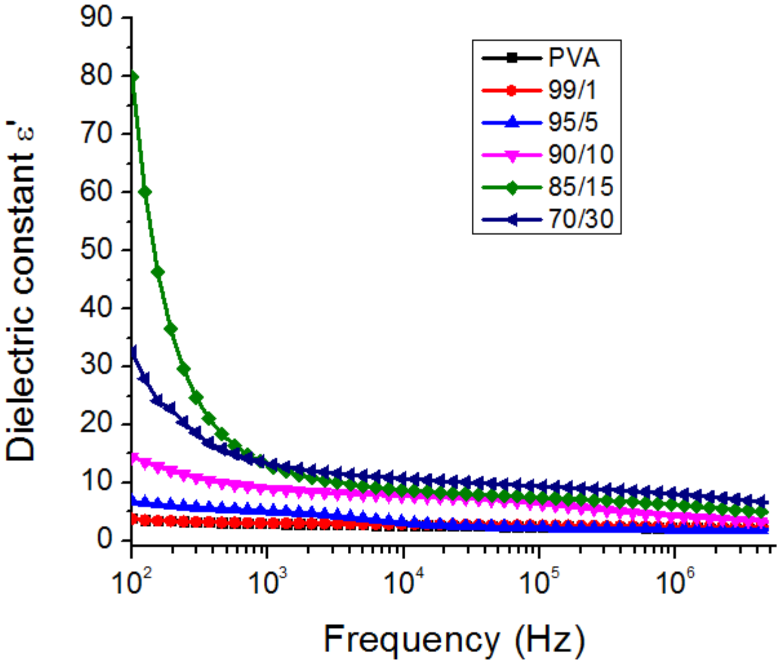


Figure 4.16: "Variation of Dielectric constant of polymer blends with frequency"

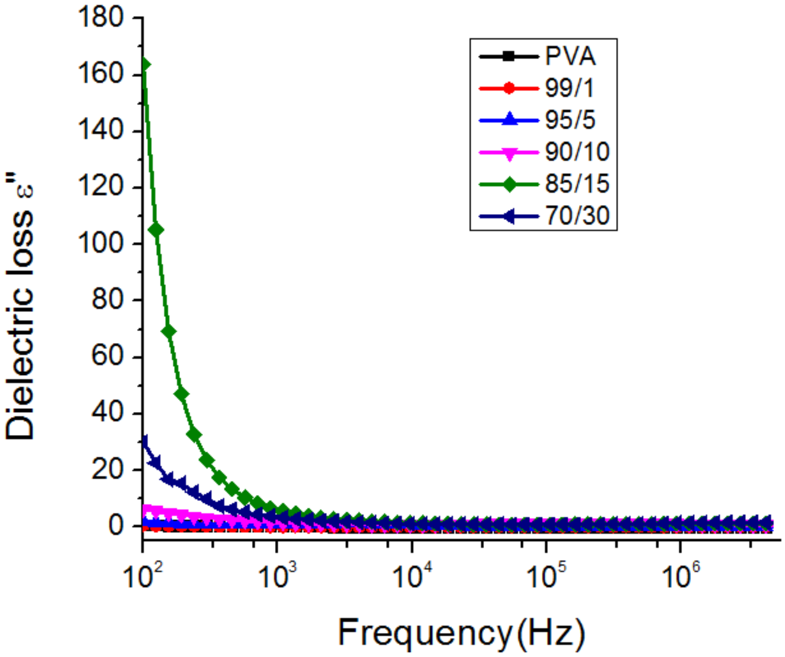


Figure 4.17: "Variation of dielectric loss factor of polymer blend with frequency"

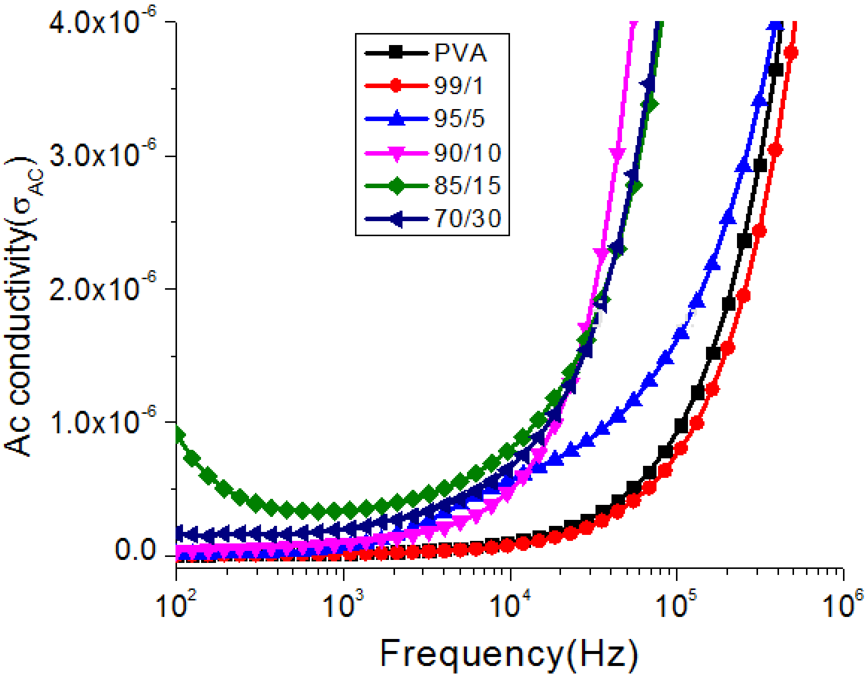


Figure 4.18: "variation of Ac conductivity of polymer blend with frequency"

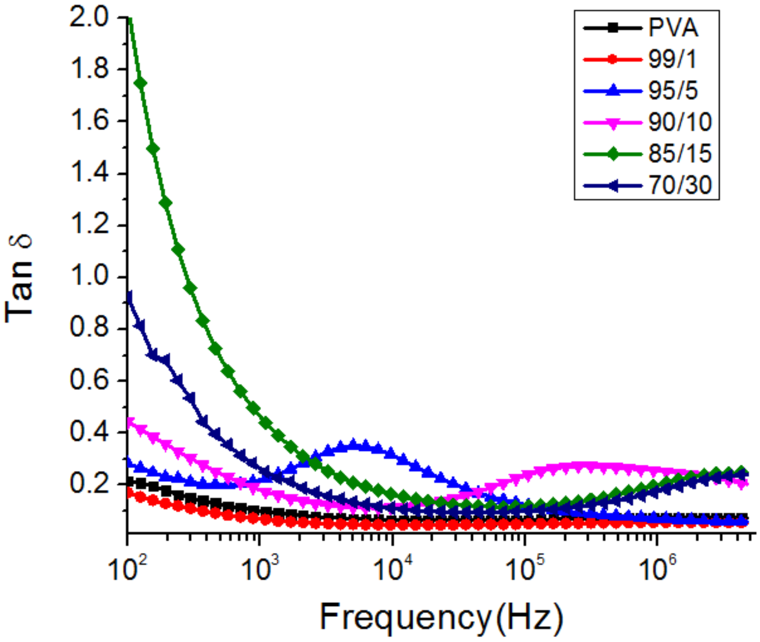


Figure 4.19: "Variation of dielectric loss tangent of polymer blend with frequency"

Figure 4.16 shows the dielectric constant ($\varepsilon^{/}$) behavior of PVA/PANI blend at various concentrations of PANI in PVA/PANI blend with respect to the frequency at room temperature. The values of dielectric constant as well as dielectric loss of PVA are stable with respect to the frequency of alternating current making it suitable candidate for dielectric materials[11]. As we add PANI in PVA matrix $\varepsilon^{/}$ is increasing till 15 % wt loading of PANI in the lower frequency region, while at higher frequency region, $\varepsilon^{/}$ remains intact as compared to PVA showing its good stability over wide frequency range. The influence of the second phase of PANI in PVA is quite evident from the significant enhancement of $\varepsilon^{/}$ of PVA. By the incorporation of PANI up to 15 wt% into the PVA, $\varepsilon^{/}$ is significantly enhanced in the lower frequency region. However, at 30 wt% of PANI, $\varepsilon^{/}$ is relatively decreased yet remains higher than neat PVA. The variation in the dielectric behavior of composites in the given frequency range is attributed to the interface polarization.

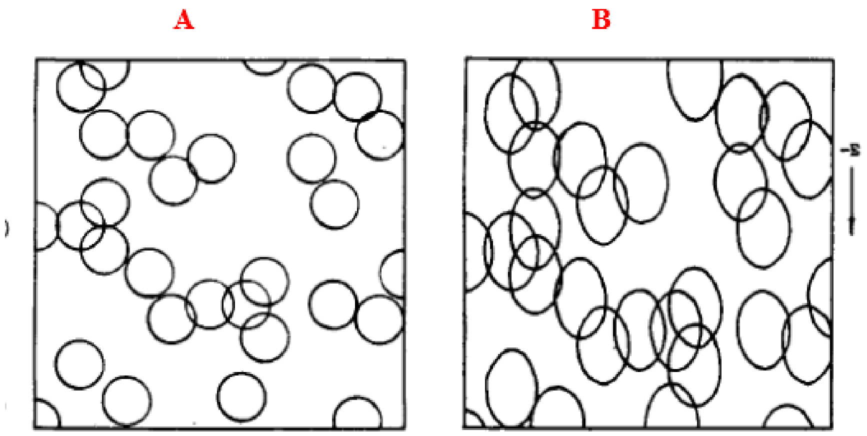
Due to the interfacial polarization, which is a slow relaxation process (Maxwell-Wagner-Sillars effect) large local fields are produced within PVA/PANI blend that increased the dielectric constant[11].Generally, the high polarizability of the molecule leads to a higher relative dielectric constant of the material. Dielectric constant values reduced on increasing frequency because when the applied field frequency is increased, it was assumed that the dipoles present in the composite cannot reorient themselves fast enough and therefore dielectric constant decreases. Another aspect of result is the decrease in dielectric value of PVA/PANI blend at 30% wt of PANI the reason can attribute to the percolation thresh hold value of PANI. Beyond the percolation threshold that is 15% wt of PANI, conductive path networks are started to form and therefore the permittivity values are relatively decreased.

Figure 4.17 shows the variation of dielectric loss with variation In frequency. The PANI we are using is HCl doped and is conductive in nature[23].we know that dielectric loss is the dissipation energy as we increase the PANI concentration the dissipation energy increases as there are no conductive network form yet, but as the concentration of PANI reaches a critical value that is 30 wt% of PANI in PVA , where conductive path network is formed so the dielectric loss is decreased.[24]

Figure 4.18 shows the AC conductivity (σAC) when the frequency is in increased for all the samples. σAC is increased in the lower frequency region as well as in the higher frequency region for PVA/PANI blend systems.

The increase of σ*AC* in the lower frequency region is related to the interfacial polarization mechanism in which the induced dipoles have enough time to orient themselves (relaxation phenomena) along the direction of the field[11]. Whereas the increase of σ*AC* in the higher frequency region is pertaining to the hopping mechanism[25] in which the charge carriers due to the excitation hop around the conductive sites are boosted up, causing an increase in the effective conductivity.

Figure 4.19 shows us the variation of tan δ with change in frequency in the lower frequency region the tan δ is increasing by adding PANI till 15 wt% which is the percolation value after which the value is decreased. The increase is due to the conductive behavior of PANI[26]. Secondly we are having a peak shifting towards the right side which clearly indicates the amorphous part of PANI is dominating and the molecules increase their segmental motion as they get more free volume. As the peak is shifting towards the higher side, thus it reduces the relaxation time. The fast motion which is coupled with mobile ions improves the transport properties.[27]



The distribution of localized states at low field strength

At high field strength, the shape of localized state is changed to ellipse.

Figure 4.20: Hopping Mechanism.[2]

Figure 4.20 gives us an idea of hopping mechanism. Figure 4.20 A shows the distribution of localized states at low filed strength, as high field strength is applied figure 4.20 B the localized states take the shape of ellipse increasing their area thus these states overlap each other forming a conducting path network and hence at higher frequency the AC conductivity is increased.[2]

4.5 Tensile Results of PVA 99%- PANI 1% composite with FLG

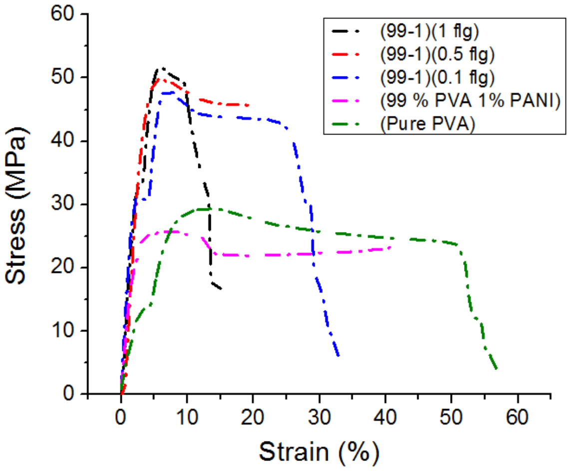


Figure 4.21: Stress strain graph of Polymer blend (PVA 99%- PANI 1%) with varying concentration of FLG

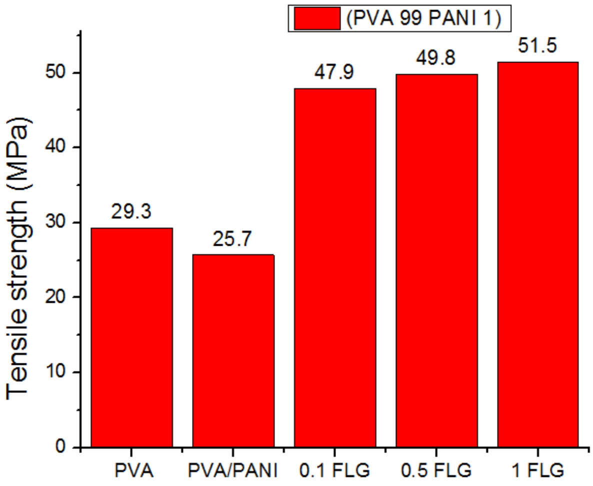


Figure 4.22: Variation of tensile strength with varying concentration of FLG

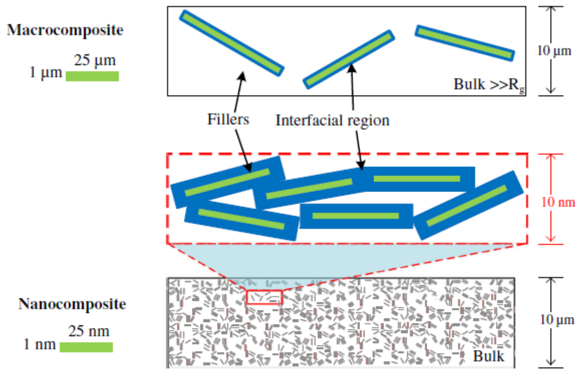


Figure 4.23: Uniqueness in Nano structured materials[3]

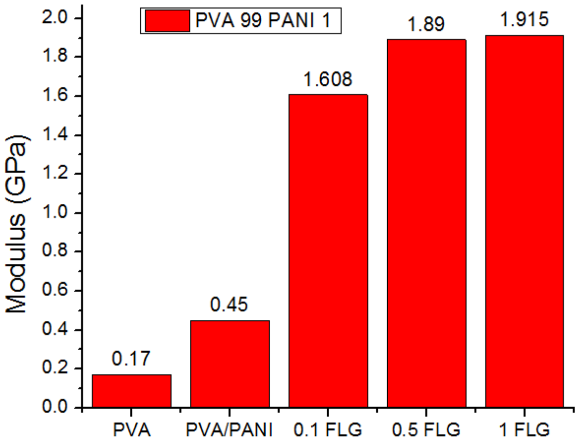


Figure 4.24: Variation of Modulus with increase in FLG loading in polymer blend

Figure 4.21 shows the stress and strain graph of PVA/PANI/FLG with varying FLG loading and PVA/PANI fixed at 99/1 respectively. As FLG is added to the polymer blend system the tensile strength (figure 4.22) is increased from 29.3 MPa to 51.5 MPa. The same phenomena occurs as previously discussed in the polymer blends on cooling the semi crystalline part PVA shrinks[22] around the FLG along with the PANI phase, so good stress transfer take place between the FLG as well as PANI particles but with PANI phase, the interfacial bonding is not strong enough so the tensile strength reduces but in case of FLG Nano filler there is strong interfacial H-bonding that is between the PVA hydroxyl group and oxygen containing groups of graphene sheets and thus the tensile strength increases[7, 28].

Figure 4.21 gives us the decrease in the strain from 56.8% to 15.5% as the FLG concentration is increased. Figure 4.24 shows the increase of modulus with increase in the FLG loading that is modulus is increased from 0.17 GPa to 1.915 GPa. “As the volume fraction increases, the surface–surface interparticle distance is far more reduced in nanocomposites than composite. This means that at a similar volume fraction, the interaction between nanoparticles is much higher than that between micron-sized particles. Therefore, nanoparticles under loading are able to interact each other more effectively to restrain the matrix molecular deformation. The total surface area of nanoparticles enhances significantly with their volume fractions when compared to composites. This is because, by being small, nanoparticles have a far higher surface area to volume ratio, therefore leading to more interaction with matrix for higher reinforcement as illustrated in (Figure 4.23) [3]”. As FLG are added they restrain the PVA matrix so the strain is decreased and the modulus is increased, that is due to restraining effect, high interfacial bonding and less interparticle distance.

4.6 Dielectric results of PVA 99%- PANI 1% composite with FLG

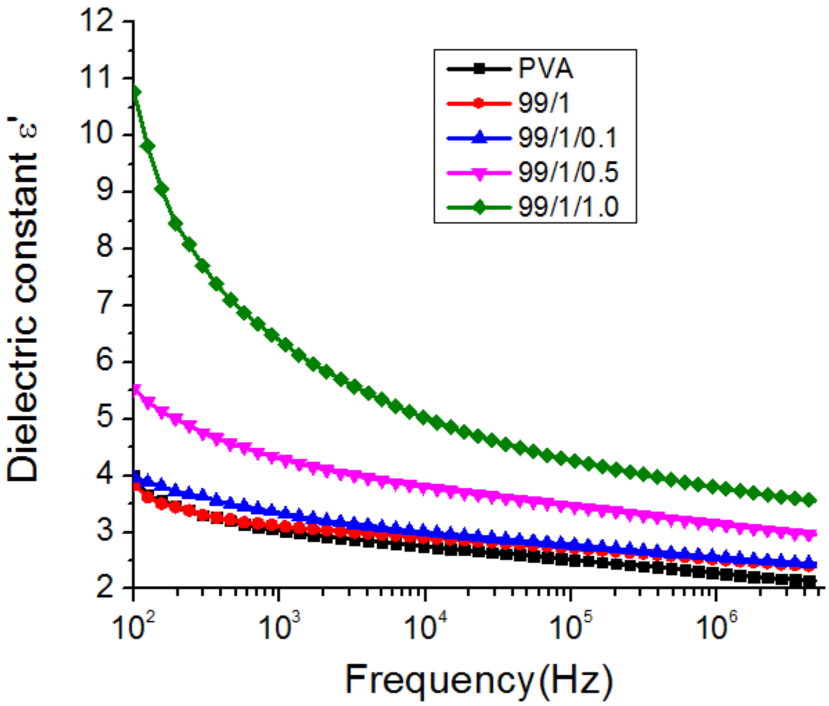


Figure 4.25: “Variation of dielectric constant with frequency (PVA 99%/PANI 1%/FLG 0.1%-0.5%-1%)”

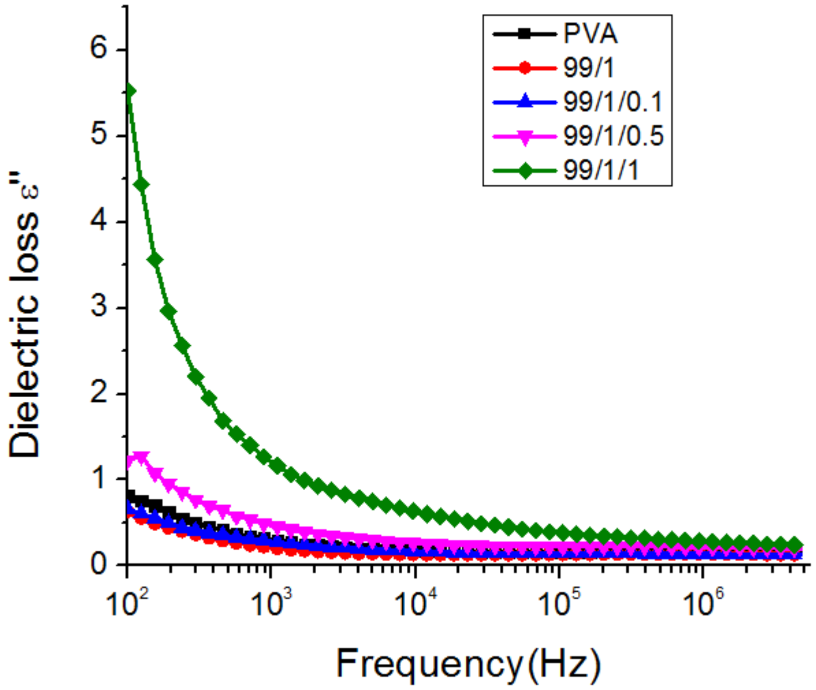


Figure 4.26: "Variation of dielectric loss with frequency (PVA 99%/PANI 1%/FLG 0.1%-0.5%-1%)"

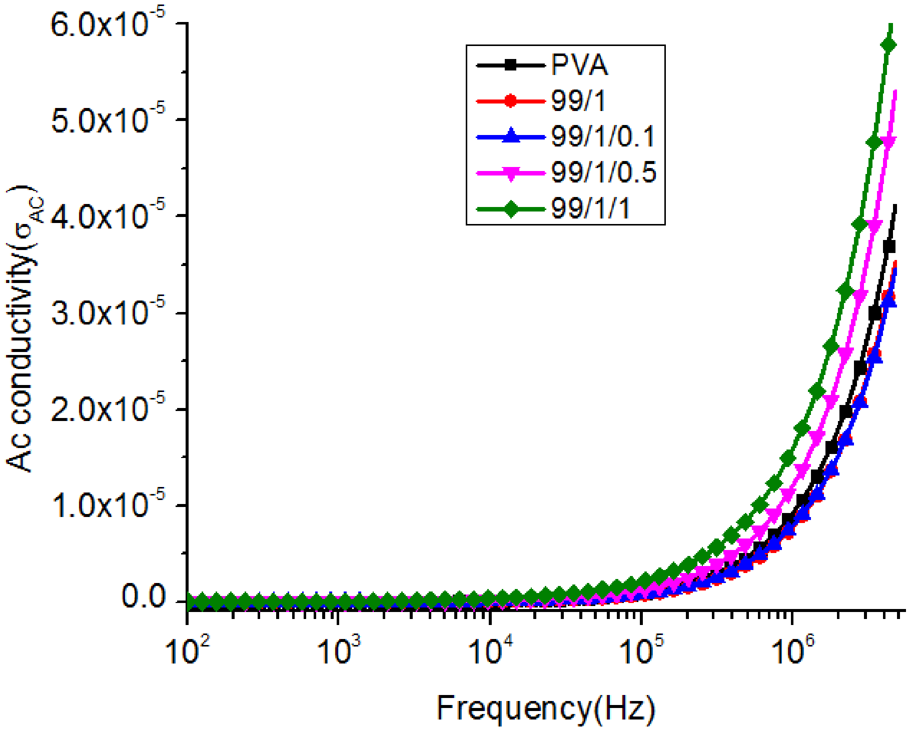


Figure 4.27: "Variation of AC conductivity with frequency (PVA 99%/PANI 1%/FLG 0.1%-0.5%-1%)"

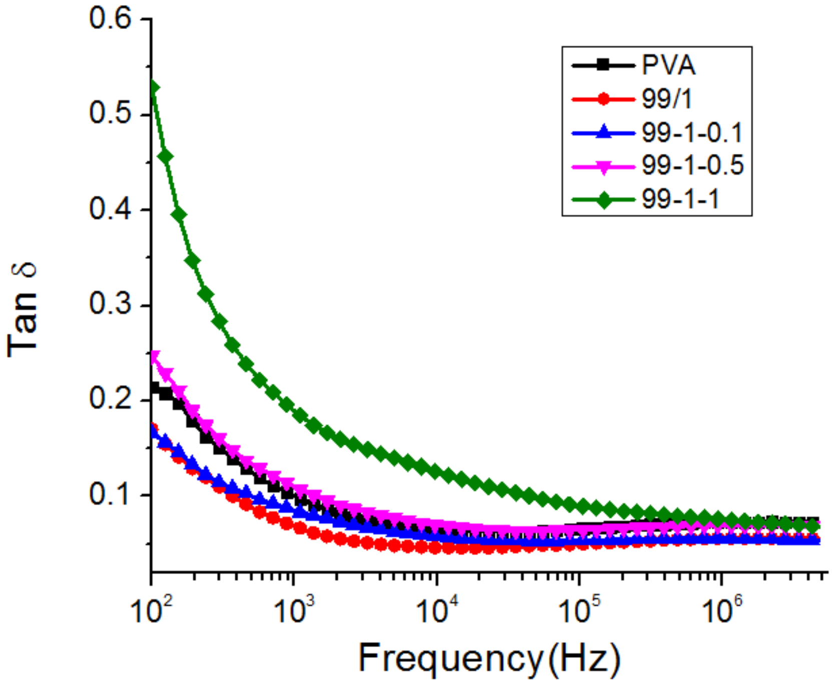


Figure 4.28:" Variation of Loss tangent with frequency (PVA 99%/PANI 1%/FLG 0.1%-0.5%-1%)"

Figure 4.25 shows the variation of dielectric constant with change in frequency of polymer blend of PVA 99%/PANI 1% and with FLG varying from 0.1 % to 1%. As we see the graph the value of permittivity is increasing as the concentration of FLG is increased. The pure system having value of about 3.5 which is increased to 11 in the lower frequency region whereas in the higher frequency region the value is relatively very low. One of the reasons for the increase in the permittivity at low frequency is attributed to the interfacial polarization that is explained previously in the polymer blend results. The second reason is the mini capacitor phenomena[29] With increase of FLG content in polymer phase, separation distances among neighboring FLG are constantly reduced. Lastly, a network of mini-capacitors with FLG as electrodes and PVA between them as insulater. Each mini-capacitor contributes to increase the capacitance, which can then relate with the substantial increase in dielectric permittivity.

Figure 4.26 gives us the variation of dielectric loss with change in frequency of polymer blend of PVA 99%/PANI 1% with FLG varying from 0.1 % to 1%.As we increase the FLG concentration so there is increase in the dielectric loss. The dielectric loss is increased from 0.8 to 6 with max FLG loading 1wt%. we know that dielectric loss is the dissipation energy as we increase the FLG concentration the dissipation energy increases as there are no conductive network form yet.

Figure 4.27 gives us the variation of AC conductivity (σ_{AC}) with change in frequency. The (σ_{AC}) is not increasing in the lower frequency region as the polyaniline percentage is very less so the phenomena of interfacial polarization are reduced, which is discussed previously in polymer blend results but the σ_{AC} is increasing in the higher frequency region and that is due to Non-ohmic conduction. Non-Ohmic conduction is frequency dependent and it is happening through the barrier-tunneling between FLG separated by PVA layer

Figure 4.28 gives us variation of tan δ with frequency by increasing the conductive filler FLG the values of tan δ are increasing in the lower frequency region[27]. While we cannot see any peak shifting as the filler is highly crystalline.

4.7 Tensile Results of PVA 90%- PANI 10% composite with FLG

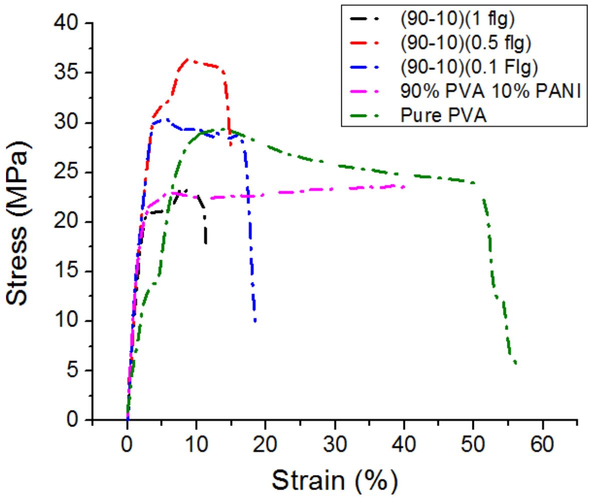


Figure 4.29: Stress strain graph of Polymer blend (PVA 90%- PANI 10%) with varying concentration of FLG

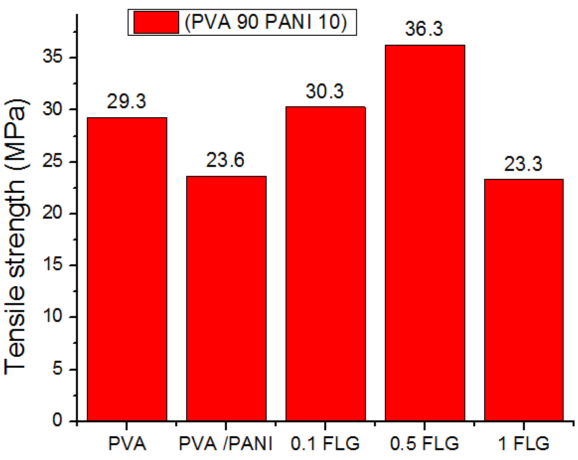


Figure 4.30: Variation of tensile strength With varying concentration of FLG

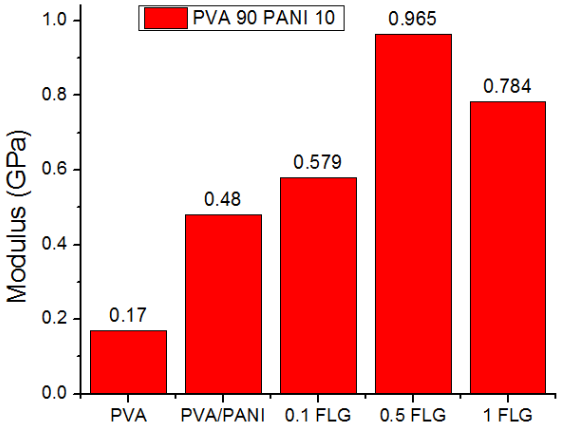


Figure 4.31: Variation of Modulus with increase in FLG loading in polymer blend

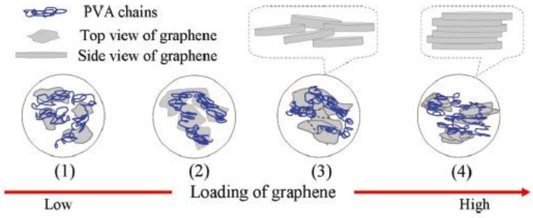


Figure 4.32: Mechanical percolation [1]

Figure 4.29 shows stress strain graph of PVA 90%/PANI 10% with varying FLG loading from 0.1 wt % to 1 wt %. By adding FLG to PVA/PANI blend strain is decreased that is from 56.8% to 11.36% and tensile strength is improved from 29.3 MPa to 36.3 MPa by loading of 0.5 wt% of FLG after that there is abrupt decrease in the strength to 23.7 MPa at 1 wt % of FLG (figure 4.30), which is lower than pure PVA system. Modulus is also increased from 0.17 GPa to 0.965 GPa at 0.5 wt% of FLG loading after which an abrupt decrease in modulus occurs the modulus reached a value of 0.784 GPa at 1 wt % loading of FLG (figure 4.31).The purpose for the rise in the tensile strength and modulus and decreased in the strain is the same phenomena as discussed previously in the PVA 99%/PANI 1%/FLG(0.1%-1%) three component system. The decrease in the tensile strength and modulus after 0.5 wt % of FLG is attributed to the mechanical percolation phenomena[7](Figure 4.32).Mechanical percolation can be explained form a critical concentration is reached where the layers or stack of layers (3 to 4 layers) pile up on each other reducing the overall contact area with matrix and thus the properties at percolation are decreased in our system of PVA 90%/PANI 10% the percolation value for FLG is 1 wt % at which the modulus and tensile strain is decreased.

4.8 Dielectric results of PVA 90%- PANI 10% composite with FLG

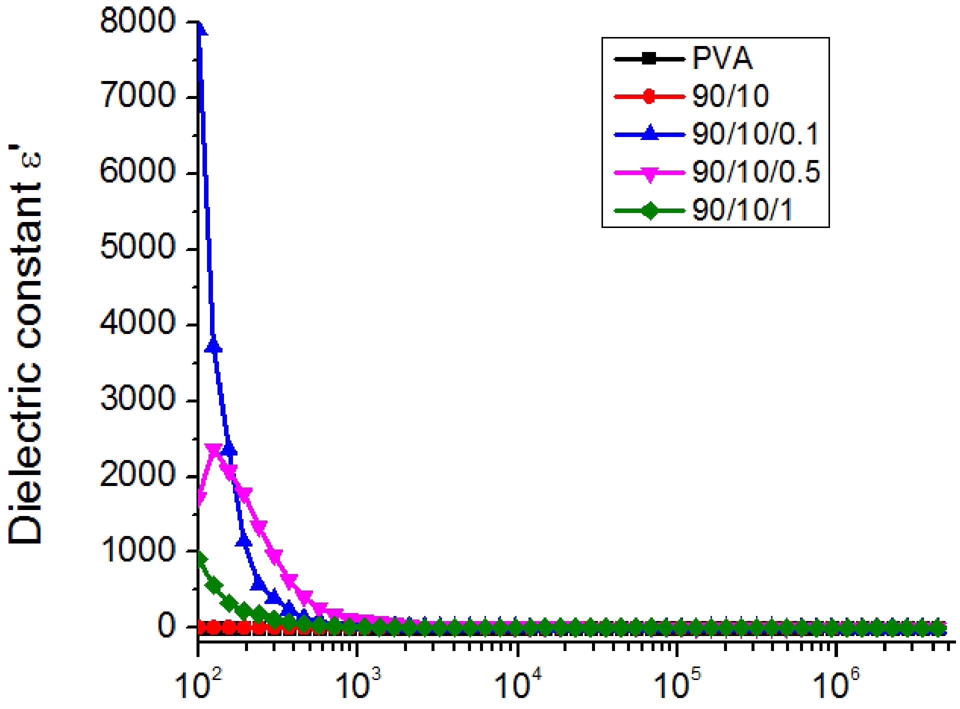


Figure 4.33: "Variation of dielectric constant with frequency (PVA 90%/PANI 10%/FLG 0.1%-0.5%-1%)"

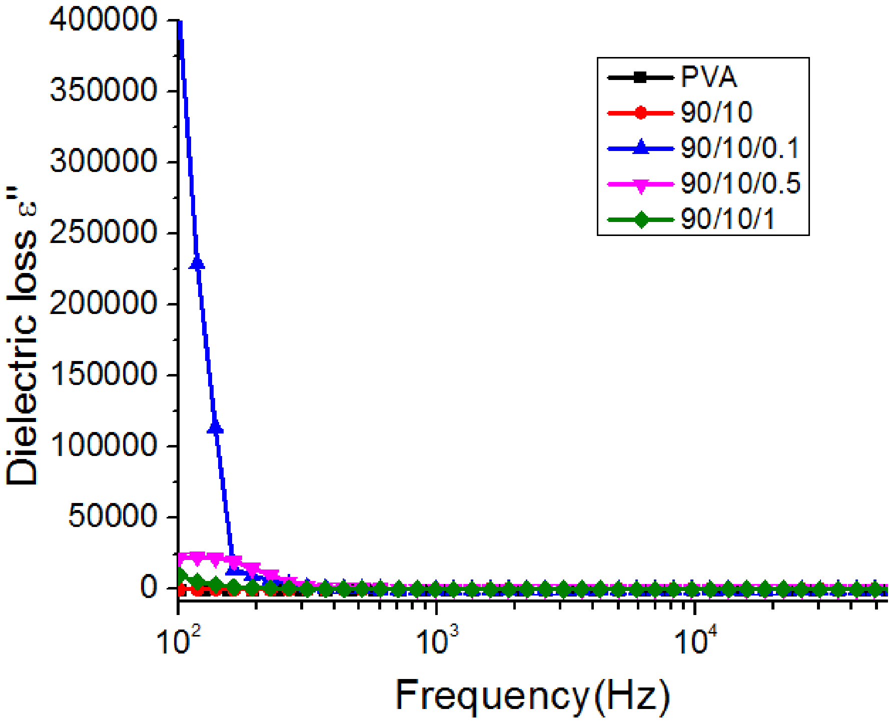


Figure 4.34: "Variation of dielectric loss with frequency (PVA 90%/PANI 10%/FLG 0.1%-0.5%-1%)"

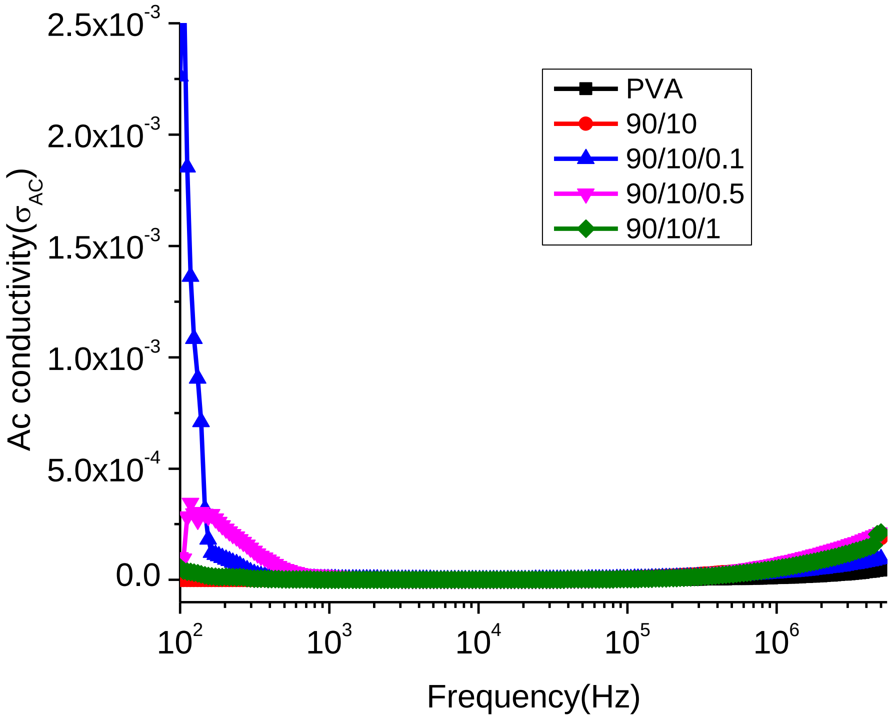


Figure 4.35: "Variation of Ac conductivity with Frequency of (PVA 90%/PANI 10%/FLG 0.1%-0.5%-1%)"

\

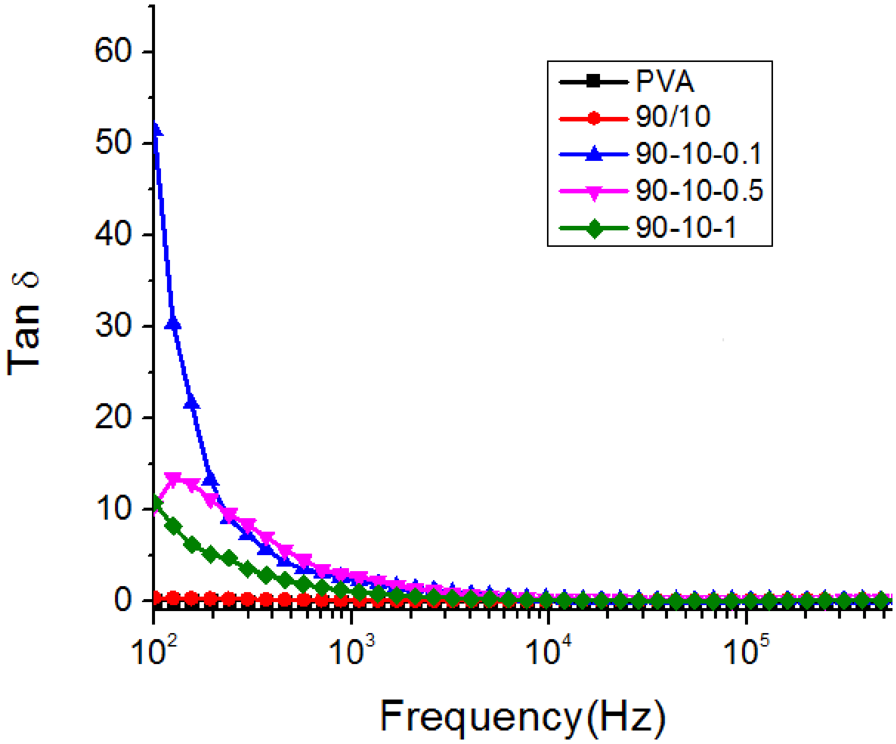


Figure 4.36:" Variation of tan δ with Frequency of (PVA 90%/PANI 10%/FLG 0.1%-0.5%-1%)"

Figure 4.33 shows the variation of dielectric constant with change in frequency of polymer blend of PVA 90%/PANI 10% and with FLG varying from 0.1 % to 1%. As we see the graph the value of permittivity is increasing as the concentration of FLG is increased. The pure system having value of about 3.5 this is increased to 8000 in the lower frequency region by adding of 0.1 wt % of FLG which is the percolation value in PVA 90%/PANI 10% polymer blend, after which the dielectric constant is decreased. After 0.1 wt % loading at 0.5 wt % and on wards of FLG loading conductive path networks are formed and thus the dielectric constant decreases. In the higher frequency region the value of permittivity is relatively very low. One of the reasons for the increase in the permittivity at low frequency is attributed to the interfacial polarization that is explained previously in the polymer blend results. The second reason is the mini capacitor phenomena[29] With increase of FLG content in polymer phase, the isolation distances between neighboring FLG are continuously reduced. Finally, a network of mini-capacitors with the FLG as electrodes and PVA between them. Each mini-capacitor contributes to increase the capacitance, which can then correlate with the significant increase in the dielectric permittivity.

Figure 4.34 gives us the variation of dielectric loss with change in frequency of polymer blend of PVA 90%/PANI 10% with FLG varying from 0.1 % to 1%.As we increase the FLG concentration so there is increase in the dielectric loss till 0.1 wt% loading FLG. The dielectric loss is increased from 0.8 to 500000 with FLG loading 0.1wt%. we know that dielectric loss is the dissipation energy as we increase the FLG concentration the dissipation energy increases as there are no conductive network form yet, but as the concentration of FLG reaches a critical value that is 0.1 wt% of FLG in PVA/PANI blend , where conductive path network is formed so the dielectric loss is decreased.[24]

Figure 4.35 shows the AC conductivity (σ*AC*) with increasing frequency σ*AC* is increased for all the samples. σ*AC* is increased in the lower frequency region as well as in the higher frequency region for PVA/PANI blend systems. The increase of σ*AC* in the lower frequency region is related to the interfacial polarization mechanism as discussed earlier[11]. Whereas the increase of σ*AC* in the higher frequency region is due to 2 reasons, the first one is the hopping mechanism[25]as discussed earlier in the polymer blend results. Figure 8 gives us an idea of proton hopping. The second reason of the σ_{AC} increasing in the higher frequency region is due to Non-ohmic conduction. Non-Ohmic conduction is frequency dependent and it is happening through the barrier-tunneling effect between FLG separated by PVA layer.

Figure 4.36 shows the variation of Tan δ with change in frequency. we can see the values of tan δ is increasing in the lower frequency region that is due to addition of conductive filler but as we compare the (90-10-FLG) and (99-1-FLG) so the values of (90-1-FLG) are relatively high, specifically the at (90-10-0.1) the reason is high quantity of conductive PANI and FLG[27]. There is no visible peak shifting as the filler is highly crystalline.

4.9 EMI-Shielding

On the basis of the dielectric results some the samples along with the pure and polymer blend were chosen for study of EMI-Shielding.

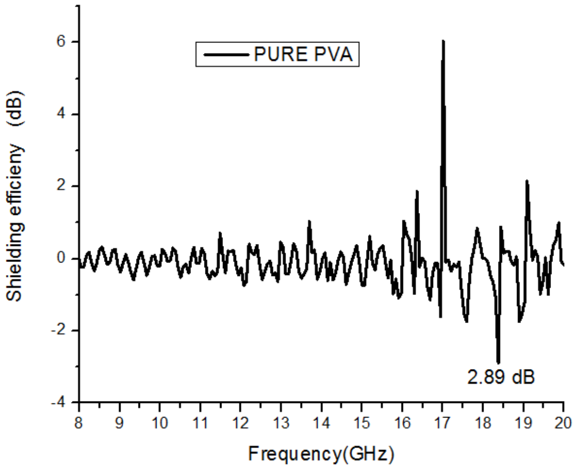


Figure 4.37: "Variation of shielding efficiency with frequency PURE PVA"

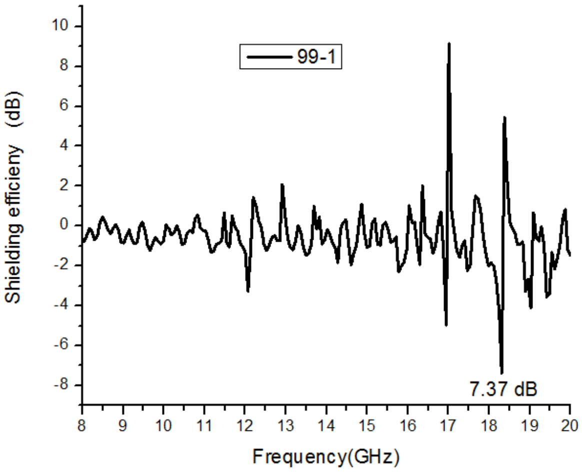


Figure 4.38: "Variation of shielding efficiency with frequency (99-1) polymer blend"

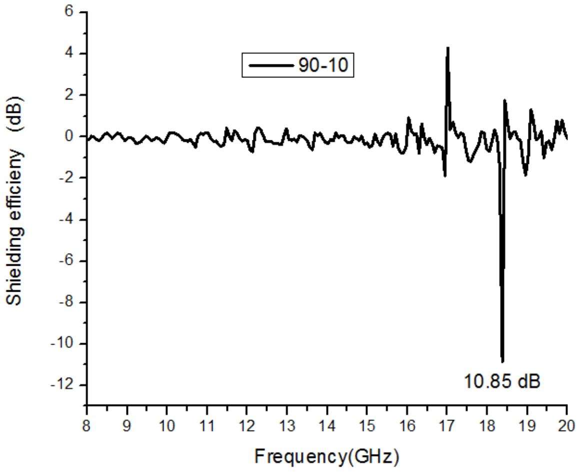


Figure 4.39: "Variation of shielding efficiency with frequency (90-10) polymer blend"

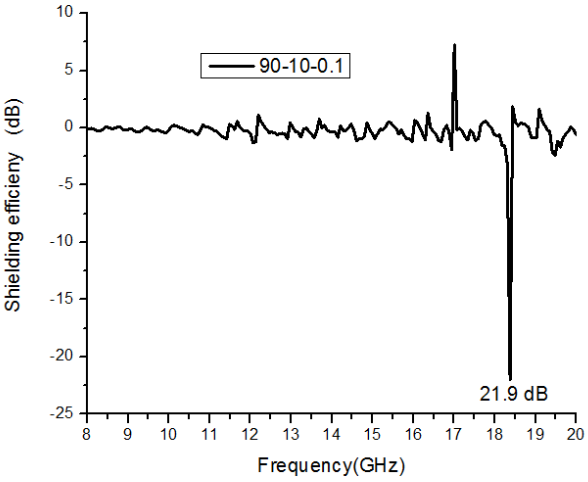


Figure 4.40: "Variation of shielding efficiency with frequency (90-10-0.1) Hybrid composite"

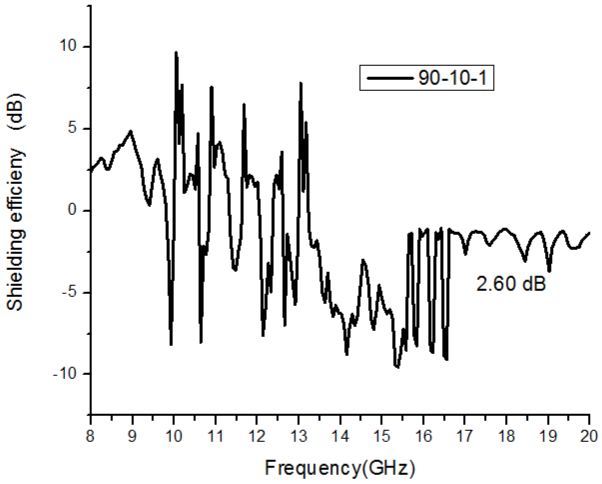


Figure 4.41: "Variation of shielding efficiency with frequency (90-10-1) Hybrid composite"

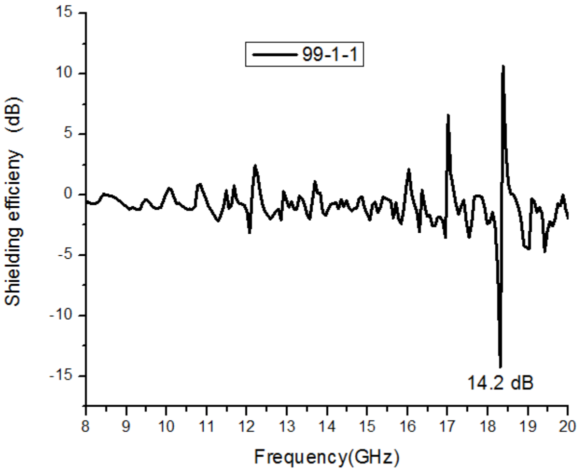


Figure 4.42: "Variation of shielding efficiency with frequency (99-1-1) Hybrid composite"

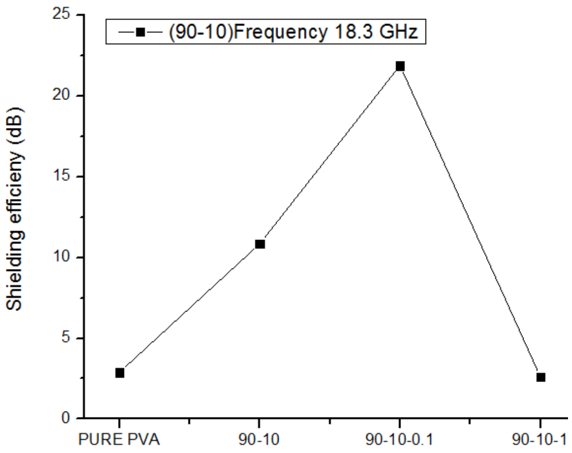


Figure 4.43: "Variation of shielding efficiency by adding FLG with (90-10) polymer blend"

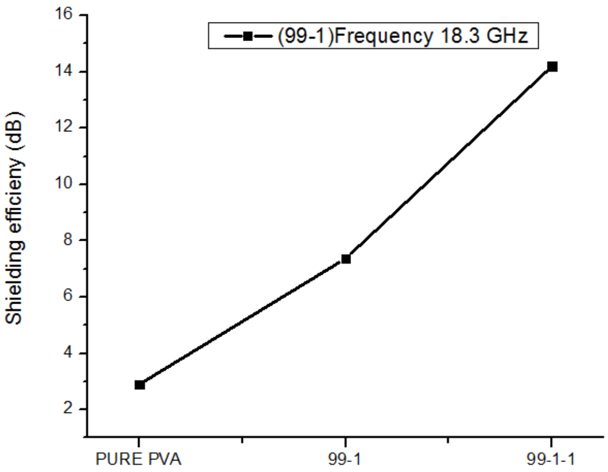


Figure 4.44: "Variation of shielding efficiency by adding FLG with (99-1) polymer blend"

Figure 4.37-4.42 represents shielding efficiency as a function of frequency. It is observed that all the samples shows increase in absorption at 18.3GHz.Figure 4.43 and figure 4.44 shows variation of shielding efficiency by adding FLG to polymer blends (99-1),(90-10) respectively. As PANI and FLG is added to the PURE PVA the absorption is increasing in (99-1) system by adding FLG the values goes to a maximum of 14.2 dB while in (90-10) system by adding FLG the maximum value (21.9dB) is attained at 0.1 wt % loading of FLG after which the value is decreased to 2.60dB.

“The structure of microwave absorbing materials generally consists of shapes of materials with properties that allow electromagnetic (EM) waves to penetrate into the regions where electric and magnetic fields experience loss. This loss usually occurs due to conductivity of material. When incident Electromagnetic waves penetrate a surface of a conductive material, the electric field interacts with electrons inside the material and then they induce current. Some of the loss also happens through molecular polarization phenomena, such as space charge relaxation, dipole rotation and hopping of confined charges and in the end the electrical energy is dissipated as heat due to the resistance of materials. We can say that the energy is absorbed by the material. So a good absorber must have high value of tan δ,Ɛ′′”.[30]

4.10 TGA Results

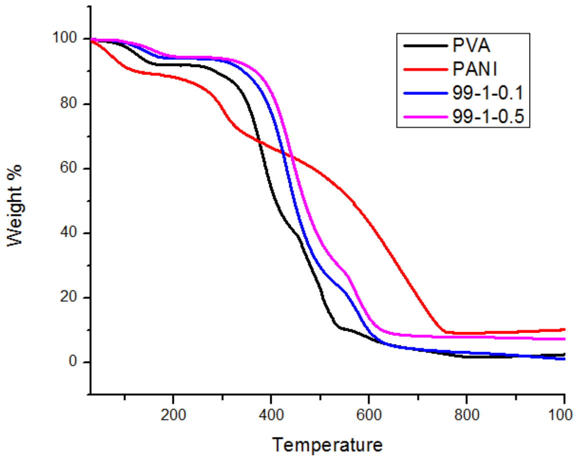


Figure 4.45: TGA comparison of PVA, PANI and hybrid composite (99/1)

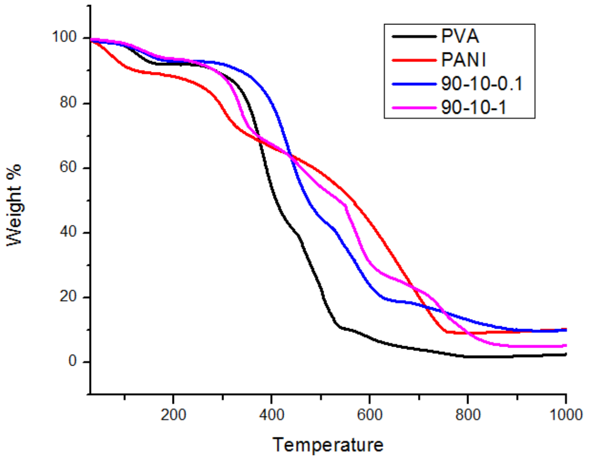


Figure 4.46: TGA comparison of PVA, PANI and hybrid composite (90/10)

The thermal stability of the composite materials was assessed by thermo gravimetric analysis (TGA) in inert atmosphere. Figure 4.45, 4.46 shows the comparison of Pure PVA, PANI with (99-1) and (90-10) hybrid composite systems. The TGA graph of Pure PVA shows two steps. The first step, 76^0C to 178^0C that is due to the presence of solvent and the second step, 246^0C to 540^0 at which the polymer is decomposed. As FLG, PANI is added to the pure PVA the degradation of the hybrid composite (99-1-FLG) and (90-10-FLG) is mildly shifted to a higher temperature range with respect to the neat polymer matrix. This indicates that there is a strong interaction between PVA, PANI and FLG. The thermal stability of the 99/1 hybrid composite with FLG was increased by 39^0 C and that of 90/10 system was increased by 19^0C increase.

Chapter 5

5 Conclusions/Future Recommendations

5.1 Conclusions

Graphene, 2D material, is becoming the most wonderful material due to its unprecedented electrical and mechanical properties. One of the exciting properties of 2D graphene is its conductivity (25000cm² per volt-second i.e 200 times of silicon) PVA is semi-crystalline, homo, water soluble synthetic polymer. It is having nonconductive nature. we can write its formula as $[CH_2CH(OH)]_n$. Tg=85ºC[8] Poly aniline(PANI)is a conducting polymer of the semi-flexible rod polymer family and having aromatic structure and its Tg=163ºC [9].while having conductivity=6×10^{-2} S/m. By combining such materials would give great properties such as mechanical, dielectric, thermal and Emi-shielding.

Initially polymer blend is made with PVA as matrix and PANI as filler and with 5 different weight percentages and it is observed that by increasing the Polyaniline concentration the mechanical properties were decreased that is due the weak secondary bonding of PANI phase with PVA, strain is decreased by78%, strength decreased by 64.4%.While the dielectric properties were increased due the conductive nature of PANI that is dielectric constant is increased by 3100% and dielectric loss is increased by 1100%.

Among the 5 different weight percentages two of them (99-1) and (90-10) were selected to further add few layer graphene. The (99-1) system by adding FLG gives great increase in mechanical properties that is strength is increased by 75.7%, modulus is increased by 1017%.Dielectric properties are also increased dielectric constant is increased by 175%, dielectric loss increased by 1100%.

The (90-10) system by adding FLG also showed increase in properties as compared to polymer blend. the mechanical properties shows a little increase, strength increased by 23.8 % modulus increased by 464 %.

While the dielectric properties were enormously increased, dielectric constant increased from 4 to 8000 and dielectric loss is increased from 0.5 to 500000. Emi-Shielding results of (90-10-0.1) Hybrid composite gave maximum shielding efficiency of 21.9 dB. So it can be used in Stealth technology. It was observed that (99-1) with FLG is a good better choice where mechanical properties are significant. While (90-10) with FLG is a good choice for storing charges as it gives high values of dielectric constant.

5.2 Future Recommendations

Initially polymer blend is made with PVA as matrix and PANI as filler, with 5 different weight percentages. Among these 5 percentages two extreme concentration of PANI that is 1 % at lower concentration and 10 % at higher concentration were selected to add FLG. The higher side that is 10% PANI showed huge increase in dielectric properties but percolation was reached at earlier stage of 0.1 wt % of FLG.(PVA 99%-PANI 1%) system with FLG also showed increase in the dielectric properties but comparatively less as compared to (PVA 90%-PANI 10 %) with FLG system and no percolation was reached so we can conclude that the properties of the (PVA 99%- PANI 1%) must be further investigated by increasing FLG concentration. while the properties of (PVA 95%-PANI 5%) system must be investigated by adding FLG. For EMI-Shielding samples with different structures such as holes in the sheets must be prepared to see the effect on the absorption properties, As EMI-Shielding property is strongly dependent on morphology.

References

1. Krane, N., *Preparation of Graphene.* Physics of Nanoscale Carbon, 2010.
2. Kai, W., X. Hengkun, and G. Jingpang, *Percolation and Dielectric Breakdown* Proceedings of the 4th International Conference on Properties and Applications of Dielectric Materials, 1994.
3. Zaman, I., et al., *From clay to graphene for polymer nanocomposites—a survey.* Journal of Polymer Research, 2014. **21**(5).
4. Das, T.K. and S. Prusty, *Graphene-Based Polymer Composites and Their Applications.* Polymer-Plastics Technology and Engineering, 2013. **52**(4): p. 319-331.
5. Zhang, C. and T. Liu, *A review on hybridization modification of graphene and its polymer nanocomposites.* Chinese Science Bulletin, 2012. **57**(23): p. 3010-3021.
6. Du, J. and H.-M. Cheng, *The Fabrication, Properties, and Uses of Graphene/Polymer Composites.* Macromolecular Chemistry and Physics, 2012. **213**(10-11): p. 1060-1077.
7. Zhao, X., et al., *Enhanced Mechanical Properties of Graphene-Based Poly(vinyl alcohol) Composites.* Macromolecules, 2010. **43**(5): p. 2357-2363.
8. Janowska, I., et al., *Mechanical thinning to make few-layer graphene from pencil lead.* Carbon, 2012. **50**(8): p. 3106-3110.
9. Mirmohseni, A. and G.G. Wallace, *Preparation and characterization of processable electroactive polyaniline–polyvinyl alcohol composite.* Polymer, 2003. **44**(12): p. 3523-3528.
10. A.R.Subrahmanyama, et al., *Mechanical and Electrical Conductivity Studies of PANI-PVA and PANI-PEO Blends.* IJMS, 2012. **2** (1): p. 4.
11. Nigrawal, A. and N. Chand, *Electrical and Dynamic Mechanical Analysis of Nano Alumina Addition on Polyvinyl Alcohol (PVA) Composites.* Apr. 2013. **Vol. 2**(Iss. 2): p. 25-33.
12. Krishnakumar, V., G. Shanmugam, and R. Nagalakshmi, *Large third-order optical nonlinearity of Mg-doped PbS/PVA freestanding nanocomposite films.* Journal of Physics D: Applied Physics, 2012. **45**(16): p. 165102.
13. Yan, J., et al., *Preparation of a graphene nanosheet/polyaniline composite with high specific capacitance.* Carbon, 2010. **48**(2): p. 487-493.
14. Yan, J., et al., *Preparation of graphene nanosheet/carbon nanotube/polyaniline composite as electrode material for supercapacitors.* Journal of Power Sources, 2010. **195**(9): p. 3041-3045.
15. Bhattacharya, P., et al., *Graphene decorated with hexagonal shaped M-type ferrite and polyaniline wrapper: a potential candidate for electromagnetic wave absorbing and energy storage device applications.* RSC Advances, 2014. **4**(33): p. 17039.
16. Bajpai, A.K., J. Bajpai, and S.N. Soni, *Designing Polyaniline (PANI) and Polyvinyl Alcohol (PVA) Based Electrically Conductive Nanocomposites: Preparation, Characterization and Blood Compatible Study.* Journal of Macromolecular Science, Part A, 2009. **46**(8): p. 774-782.
17. HONG, P.-D., J.-H. CHEN, and H.-L. WU, *Solvent Effect on Structural Change of Poly(vinyl alcohol) Physical Gels.* Journal of Applied Polymer Science, 1998. **69**: p. 2477–2486.
18. Strawhecker, K.E. and E. Manias, *AFM of Poly(vinyl alcohol) Crystals Next to an Inorganic SurfaceAFM of Poly(vinyl alcohol) Crystals Next to an Inorganic Surface.* Macromolecules, 2001. **34**: p. 8475-8482.
19. Ma, X.-D., et al., *Preparation and characterization of polyvinyl alcohol–selenide nanocomposites at room temperature.* Journal of Materials Chemistry, 2002. **12**(3): p. 663-666.
20. Lei, C., Q. Wang, and L. Li, *Effect of interactions between poly(vinyl alcohol) and urea on the water solubility of poly(vinyl alcohol).* Journal of Applied Polymer Science, 2009. **114**(1): p. 517-523.
21. Qian, X.F., et al., *Polymer-inorganic nanocomposites prepared by hydrothermal method: Preparation and characterization of PVA-transition-metal sulfides.* Journal of Applied Polymer Science, 2001. **82**(11): p. 2744-2749.
22. Leclair and D. Favis, *The role of interfacial contact in immiscible binary polymer blends and its influence on mechanical properties.* Polymer, 1996. **37**.

23. Pud, A., et al., *Some aspects of preparation methods and properties of polyaniline blends and composites with organic polymers.* Progress in Polymer Science, 2003. **28**(12): p. 1701-1753.
24. P.Dutta, S.Biswas, and S.k. De, *Dielectric relaxation of PANI-PVA composite* Materials research Bulletin, 2002. **37**: p. 193-200.
25. Zuo, Z., Y. Fu, and A. Manthiram, *Novel Blend Membranes Based on Acid-Base Interactions for Fuel Cells.* Polymers, 2012. **4**(4): p. 1627-1644.
26. Stan, C.S., et al., *Synthesis and Characterization of PSSA-Polyaniline Composite with an Enhanced Processability in Thin Films.* Open Chemistry, 2014. **13**(1).
27. Pradhan, D.K., R.N.P. Choudhary, and B.K. Samantaray, *Studies of Dielectric Relaxation and AC Conductivity Behaviorof Plasticized Polymer Nanocomposite Electrolytes.* Int. J. Electrochem. Sci., 2008. **3** p. 597 - 608.

28. Wang, J., et al., *Preparation of graphene/poly(vinyl alcohol) nanocomposites with enhanced mechanical properties and water resistance.* Polymer International, 2011. **60**(5): p. 816-822.
29. Min, C., et al., *A graphite nanoplatelet/epoxy composite with high dielectric constant and high thermal conductivity.* Carbon, 2013. **55**: p. 116-125.
30. Phang, S.W., et al., *Microwave absorption behaviors of polyaniline nanocomposites containing TiO2 nanoparticles.* Current Applied Physics, 2008. **8**(3-4): p. 391-394.