A STUDY OF POLYMER-GRAPHENE CONDUCTING

THIN FILMS AND THEIR PROPERTIES

By

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Abstract:

Polyaniline (PANI) is a polymer which can be doped by charge-transfer doping and protonation to make it conductive. Not only because of electrical properties but also because of good stability of PANI, it is potentially attractive as electronic material. It has been shown that that the addition of 3 parts polyvinylpyrrolidone (PVP) to 1-part polyaniline can drastically enhance the conductivity of the resulting blend. PVP can also be blended with every major and significant resin matrix system used in polymer composites, which can improve the through thickness electrical and thermal conductivities of the composite materials. On the other hand, high conductivity of graphene is well understood subject. In this present work, conductive composite thin films are prepared by dispersing the graphene in PVP solution and followed by in situ polymerization of PANI in acidic medium by oxidative method. The goal of this work is to synthesis high conductive composite thin flexible films which are highly demanding in defense and aerospace industries. The conductivity of thin composite films was measured with four probe method. FTIR spectrum analysis confirms the in situ polymerization of PANI: PVP blend without losing the conductive properties of both PANI: PVP blend and graphene nanoplatelets. The Dynamic Mechanical Analysis shows the increase in yield strength and decrease in % strain of composite thin films with increase in percentage of Graphene. The Thermogravimetric Analysis shows increase in thermal stability with addition of graphene in the composite films.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1   Conductive Polymer

In general polymers are considered as an insulating materials. The common application of carbon based polymer are also limited to the area only where conductivity has no meaning like packaging, groceries bags and so on. The first electrically conducting organic polymer - Polyacetylene $(CH)_x$ halides were reported by three chemists: Alan Heeger, Alan MacDiarmid and Hideki Shirakawa in 1977. They demonstrate that when trans-polyacetylene is exposed to halogen (Chlorine, Bromine and Iodine) group at room temperature, its conductivity increases significantly [1]. For this noble research work in conducting polymer Heeger, MacDiarmid and Shirakawa were
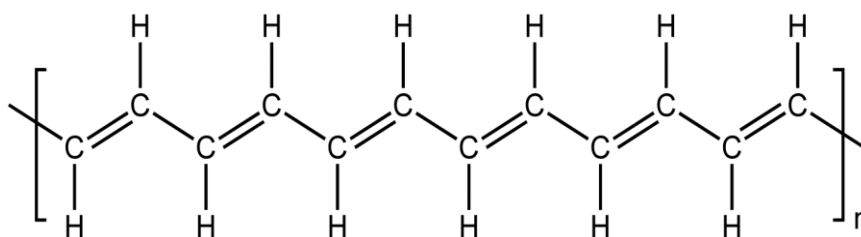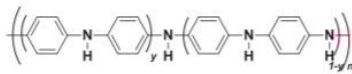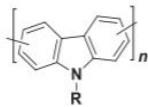
Figure 1: A Segment of trans-polyacetylene

awarded with Nobel prize in Chemistry 2000 [2].   In last four decads, the research work on conducting polymer has been rapidly increased. This significant research work in conducting polymer itself illustrate the potential application of conducting polymers in near future.

Since conducting polymers shows the combined properties of metal, semiconductor and conventional polymers, research on these areas are growing significantly. The electrical properties of metal and semiconductor with advantages of conventional polymers like easy and cheap preparation process can be achieved simultaneously in conducting polymer. Some of the most common conductive polymer with their chemical structure are presented in Table 1.

Table 1: Some conductive polymers, their abbreviation and chemical structure adopted from [3]

Name	Abbreviation	Polymer structure
polyaniline	PANI	
polythiophene	PTh	
poly(3,4-ethylenedioxythiophene)	PEDOT	
polypyrrole	PPy	
polyacetylene	PA	
polycarbazole	PC	

The conducting or non-conducting characteristics in polymer are determined by whether valence electron are under σ-bond or π-bond. In traditional polymer the valence electrons are under sp^3 hybridization which will lead to σ-bond for valance electron. Such σ-bonded electrons have very low mobility of electron. Because of lack of mobile electrons, such polymer exhibits non-conducting in nature. On the other hand, conducting polymer have sp^2 hybridized carbon center backbone with valance electrons in P_z orbitals. All such P_z orbitals will form delocalized orbits throughout the molecular chain. Electrons on those delocalized orbits are under π-bond and highly mobile even with small doping by oxidation. Hence such mobile electrons determine the conducting characteristics of polymers [4]. In general oxidizing or reducing material is the doping in conducting polymer. In addition, protonic solvent may also lead to the self-doped conductive

organic polymers. Depending upon the nature of doping agent, the conductivity values can be different. In Table 2 conductivity values of different conducting polymers with specific dopants are presented.

Table 2: Conductivities of different polymers with selected dopants adopted from [5]

Polymer	Doping materials	Conductivity (s/cm)
Polyacetylene	I_2, Br_2Li, Na, AsF_5	10^4
Polypyrrole	BF_4^-, ClO_4^-, tosylate	$500-7.5\times10^3$
Polythiophene	BF_4^-, ClO_4^-, tosylate, $FeCl_4^-$	10^3
Poly(3-alkylthiophene)	BF_4^-, ClO_4^-, $FeCl_4^-$	10^3-10^4
Polyphenylenesulphide	AsF_5	500
Polyphenylene-vinylene	AsF_5	10^4
Polythienylene-vinylene	AsF_5	2.7×10^3
Polyphenylene	AsF_5 Li, K	10^3
Polyisothi-anaphthene	BF_4^-, ClO_4^-	50
Polyazulene	BF_4^-, ClO_4^-	1
Polyfuran	BF_4^-, ClO_4^-	100
Polyaniline	HCl	200

1.2 Polyaniline (PANI)

Among the list of conducting polymer, Polyaniline (PANI) is the one which grabbed the researcher's interest significantly in last few decades. Since PANI can be doped both by charge-transfer doping and protonation, its electrical properties can be controlled reversibly. That's why it is more interesting and unique among conducting polymers. Not only because of electrical properties but also because of good stability of PANI, it is potentially attractive as electronic material too[6].
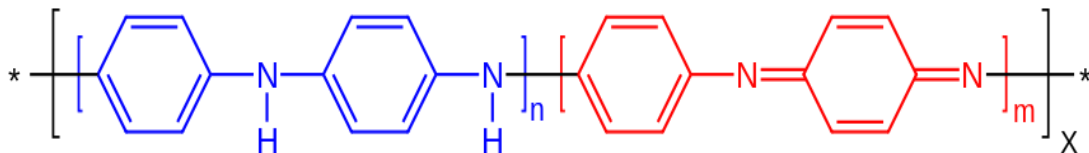
Figure 2: General Polyaniline Structure

3

There are two common synthesis process of PANI, one is Chemical oxidative polymerization and another is electrochemical polymerization. In this work, we are following the chemical oxidative polymerization, which will be discussed later. Figure 2 shows a general

Leucoemeraldine base

Emeraldine base

Emeraldine salt

Pernigraniline base
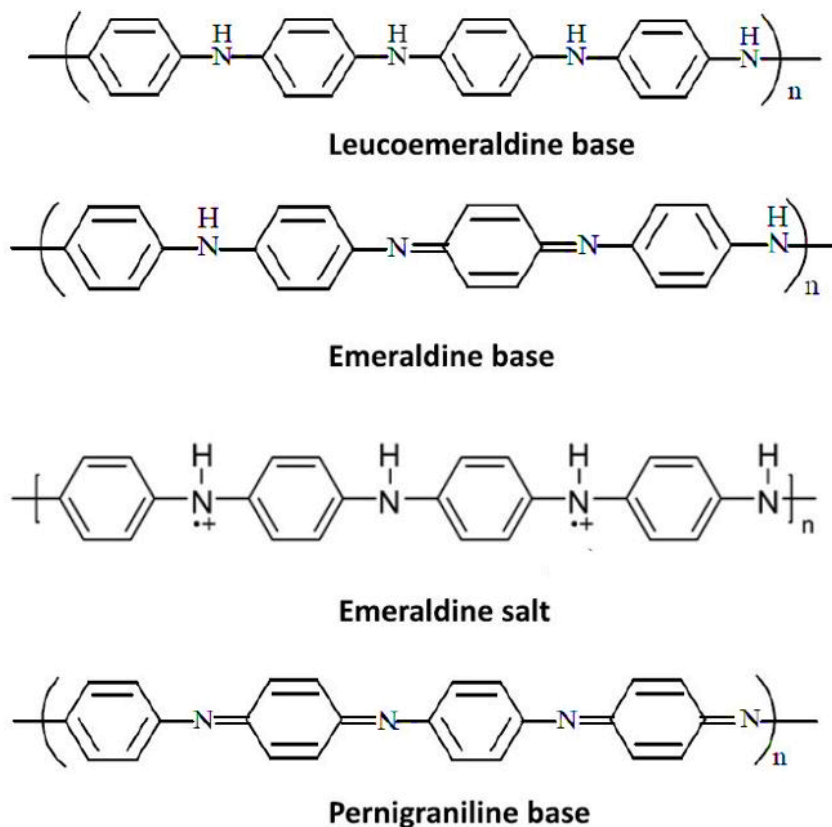
Figure 3: Different oxidation state of Polyaniline

structure of PANI where it contains 'n' reduced unit and 'm' oxidizing units. The reduced units are called benzenoid and oxidizing units are called quinonoid.

The value of 'n' and 'm' can range from 0 to 1 such that their sum is always one. The state of PANI where n=1and m=0 i.e. benzenoid units are only present is called "Leucoemeraldine" and the state with n=0 and m=1 i.e. all quinonid units are present is called "Pernigraniline". The state where the oxidized and reduced units are equal i.e. n=m=0.5 is called "Emeraldine base (EB)". Emeraldine is considered as most stable form of PANI and most conductive when doped [7, 8]. The different oxidation states of Polyaniline are illustrated in figure 3.

Polyaniline Emeralldine Base (EB) can be protonated with different acids. Depending upon the nature of acid and the degree of protonation, the conductivity of Polyaniline Emeraldine Salt (ES) will be different [9, 10]. Figure 4 illustrates the protonation mechanism of PANI Emeraldine base (EB) to PANI Emeraldine salt (ES), where A^- represents arbitrary anion of acid HA.
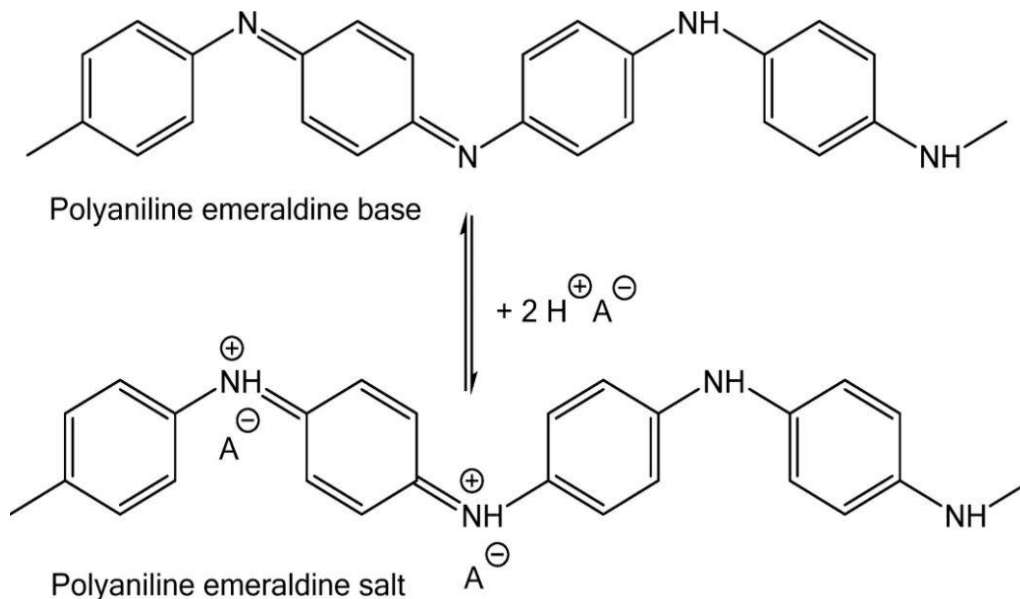
Figure 4: Protonation mechanism of PANI EB to PANI ES adopted from[10]

1.2.1 Protonation of Polyaniline(PANI) in Sulfuric Acid Medium

The conjugated double bond present along the backbone of conducting polymer is one of the key point to understand. Conducting state of PANI is achieved only after protonation of emeraldine base. On the basis of degree of protonation of emeraldine base, the conductivity can change from form insulating state ($\sigma = 10^{-10}$ S/cm) to metallic conduction state ($\sigma = 10^{-1}$ to 10^2 S/cm). The physical and chemical properties of conducting polymer can be controlled by controlling the pH, doping level and polyaniline's polymerization [11-14]. In this work, we have obtained the emeraldine salt from emeraldine base by protonating PANI in sulfuric acid medium. Doping of polyaniline in sulfuric acid media, introduced multiple charge carriers which determine an

improvement of the electrical conduction along the polymer chain. Fig. 5 illustrate the standard form of sulfonated PANI with the ion conducting polymer where HSO_4^- represents inorganic anions which are ionically bonded with –NH groups of polymeric chain. These type of ionic bond are weak and can be changed easily by changing the pH value of aqueous solution of sulfuric acid[14].
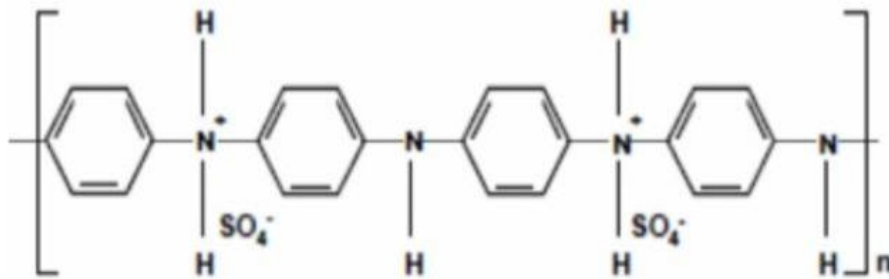
Figure 5: Polyaniline as Emeraldine Salt (ES), in sulfuric acid media adopted from[14].

1.3 Polyvinylpyrrolidone (PVP)

Polyvinylpyrrolidone (PVP) is a polymer which has wide range of application. It has been used in medicine and industry equally. It was developed in late 1930's as a chain polymer of 1-vinyl-2-pyrrolidone. The polymerization of vinylpyrrolidone in aq. H_2O_2 gives the PVP with wide range of molecular weight ranging from thousand to few million Dalton. PVP with specific small range of molecular weight can be achieved with control in polymerization process [15, 16]. Because of being water, chlorinated hydrocarbons, alcohol, amides, amines soluble and nonionic in nature, PVP has wide range of application. It has very good affinity to other polymers and resins, excellent in film formation, high adhesiveness to wide range of substrate, excellent binding properties, etc. [17]. In addition, it has been shown that PVP has a tuning effect in the conductivity properties of PANI through its dopant [18]. A general molecular structure of PVP is shown in figure 6.
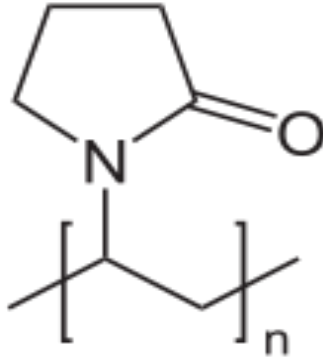
Fig. 6: General representation of PVP chain

1.4 Carbon Nanomaterial – Graphene

Graphene is not only the thinnest but also the strongest material ever known till date. It is a single atomic two-dimensional layer of carbon arranged in hexagonal pattern. In 2004, Prof. Andre Geim and Prof. Kostya Novoselov had isolated graphene from graphite and characterized its properties. For this novel research work, the prestigious Nobel Prize in physics 2010 was awarded for them. Graphene not only shows excellent mechanical, electrical and thermal properties but also it is almost 100% transparent [19]. In addition, the density of graphene is very low, comparable with the density of helium gas [20-22]. Producing a thin layer of graphene in a large scale is still a challenging, expensive, and time consuming process. The alternate possibility to harness those excellent mechanical, thermal, and electrical properties of graphene could be the excellent uniform distribution of graphene in polymer matrix [23].

1.5 Polymer-Carbon Composite Material and Processing

Polymer nanocomposites consist of a matrix which can be a thermoplastic, thermoset or elastomer and reinforced with a nanomaterial. It has been used widely for improving the mechanical properties, electrical conductivity, thermal stability, fire retardancy, and gas barrier properties. The use of carbon nanomaterials as fillers in the prepration of polymer/carbon

composite has grabbed significant interest owing to their unique properties and numerous potential applications in the automative, aerospace, wind turbine maufacturing, and electronic industries [24]. Significant researches were focoused on clay/polymer composite material but because of poor electrical and thermal poroperties of clay, an alternative fillers were desired. To overcome these drawbacks, carbon based nanoparticles like Graphene, Carbon nanotube (CNT), carbon black were introduced to prepare polymer nanocomposites.Although carbon nanotubes are effective nanofiller for conductive composite, the cost of CNT becomes an issue. Hence to overcome such issue, graphene nanoplatelets are considered as suitable replacement[25-27].

The area of research where the dispersion of graphene in polymer matrix in nanolevel has been opened, a new promising area is opened in material science and engineering. Such disperesion of carbon nanoparticles shows a remarkable improvement in mechanical and electrical properties, which can not be achieved through pure polymer or conventional composites. Such improvement in properties of polymer-graphene composites totally depends upon the degree of uniform dispersion of carbon nanoparticles in polymer matrix [28]. Hence the processing of composite playes a crucial role in determining the final properties of composites. Such processing is highly determined by the polarity, molecular weight, reactive functional groups present in the component of composite [29]. The common techniques that are generally adopted for high degree of dispersion of the carbon nanoparticles in polymer matrix are 1) In situ interactive polymerization 2) Solution intercalation and 3) Melt intercalation [29].

For in situ interactive polymerization, carbon nanoparticles are dispersed uniformely in the liquid monomer. The dispersion usually carried out by the ultrasonication or bath sonication process. Then, an initiator is diffused under suitable reaction condition and the polymerization starts on the surface of carbon nanoparticles [30, 31]. For solution intercalation, solublized polymer and graphene dispersed solvent are mixed with each other and the evaporation of solvents will lead to the sandwiching the polymer in between carbon nanocomposite [32]. In case of melt intercalation

method, carbon nanoparticles like graphene, CNT are mixed mechanically in the molten state of polymer matrix at elevated temperature. This process is suitable for the prepration of composites having thermoplastic polymer as matrix [32-34].

1.6   Hypothesis

The in situ polymerization of polyaniline (PANI) in the graphene dispersed polyvinylpyrrolidone (PVP) solution could be an effective way to prepare conductive flexible thin composite films.

Hypothesis 1: The dispersion of graphene in polyvinylpyrrolidone (PVP) solution will be an effective method in order to obtain the excellent dispersion of graphene with significant reduction in agglomeration.

Hypothesis 2: The in situ polymerization of polyaniline in the graphene dispersed PVP solution can improve the mechanical, thermal and electrical properties of the composite material.

Hypothesis 3: During in situ polymerization, polymerization occurs on the surface of graphene nanoplatelets. No chemical reaction occurs in between graphene and polyaniline. Thus leading to the better conductive composite thin film keeping the conductive property of graphene and PANI/PVP blend unchanged. Hence, conductive polymer can bridge the graphene nanoplatelets and creates a conductive path.

Hypothesis 4: Composite material market has interesting growth rate. Commercialization of conductive composite thin film can be a great idea towards a student startup company.

1.7   Literature Review

In the past years, lots of researches have been carried out on PANI, PVP, and graphene. Most of the researchers considered only pair of two materials out of these three. Very few researches has been carried out by considering all three materials for synthesis of composite materials and characterized their properties. Somani et al. has shown that the size of PANI particles

can be effectively controlled by the chemical oxidative polymerization of aniline in presence of PVP [35].

Sulimenko et al. has demonstrated that the presence of conductive particles has small positive effect to increase conductivity. The significant contribution to the conductivity appears from the increase in the ionic strength of reaction medium and increase in production on conducting PANI particles. It is also reported that the exothermic oxidation of aniline contribute to the increase in temperature with increase in conductivity [36].

Subramanian et al. investigated the constructive modification method for conducting polyaniline with the neutral polymer PVP. It was found that tuning effect in conductivity of PANI appears through dopant, supporting matrix and steric stabilizer. PVP is found acting as co-dopant along with the dopant from acidic medium. Different molar ratio of PANI and PVP (PANI: PVP = 4:1, 2:1, 1:1, 1:2 and 1:3) was studied. Out of these five different molar ratio, ratios with more molar mass of PVP has shown a significant increase in conductivity in comparison to other molar ratio. It has been found an increase in conductivity by ~ 700% for 1:2 and 1:3 molar ratio [18]. Those results are quite interesting.

Vijayakumar et al. studied the AC impedance behavior of PANI and its blends with PVP. AC conductivity for PANI-PVP blends has found higher than that of PANI in proportion to PVP incorporated. The study of frequency dependence of conductivity shows that at AC frequency lower than the critical frequency (f_C), conductivity remains unchanged. For the AC frequency above the critical frequency (f_C), raise in frequency causes increase in conductivity. The total AC conductivity at given temperature was studied using following equation.

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac}(\omega)$$

Where σ_{dc} is frequency independent DC conductivity, σ_{ac} is frequency dependent AC conductivity. At frequency lower than critical frequency, $\sigma(\omega)$ is fairly constant validating the equation $\sigma(\omega) = \sigma_{dc}$ but at frequency higher than critical frequency, DC component becomes

negligible and corresponding equation becomes$\sigma(\omega) = \sigma_{ac}(\omega)$. The study of temperature dependence of the conductivity was also found interesting. For PANI-PVP blend, decrease in conductivity is observed with increase in temperature up to 423K and afterward the conductivity increases with increase in temperature [37].

Domingues et al. has reported a one-pot synthesis process for graphene/polyaniline transparent conductive thin films. This procedure is based on an interfacial polymerization process and it is very easy and convenient for transferring to suitable substrate. The Raman spectroscopy analysis of graphene/polyaniline nanocomposite shows the interaction through oxidized segments with bi-polaronic and less planar PANI structure. This result is very interesting and exciting in comparison to the result where carbon nanotubes/PANI prepared through same procedure shows more planar and polaronic PANI structure [38, 39]. Regarding the conductivity of prepared graphene/PANI composite, it was evidently observed that the conductivity directly depends upon the amount of graphene in the films. These films have potentiality to replace ITO electrodes. The best result achieved for such films is with sheet resistance of 60.60 Ω sq^{-1} with transmittance 89%. Overall, this work showed the interfacial polymerization is one of the best route for getting self-standing, transparent conductive graphene/polyaniline nanocomposite thin films. Such films have great potential in the area of electrochemical and electrochromic devices, photovoltaic and sensor devices [39].

Liu et al. has investigated the nanocomposites of conductive thermoplastic elastomers nanocomposite at very low graphene loading level for the application of strain sensor. They dispersed 0.1 wt% graphene homogeneously in the thermoplastic polyurethane and found significant enhancement in mechanical properties of thermoplastic polyurethane at very low graphene loading (0.2 wt%). In such nanocomposites, graphene provides a wide range of sensitivity for repeated stress cycle. In addition, these nanocomposites perform excellent for recoverability and reproducibility [40].

Frackowiak et al. has investigated the super capacitive behavior of conducting polymer/carbon nanotube (CNT) composites. They have shown that CNT acts as a backbone for the electronically conductive polymer enhancing the mechanical properties. This enhanced mechanical property preserve polymer from the repeated mechanical changes like shrinkage and breaking. In addition, CNT improves the ability of charge transfer which ultimately increases the charge/discharge rate. They have reported that 20 wt% of CNT shows the best performance in such supercapacitor application [41, 42]. Feng et al. have studied the graphene/PANI nanocomposite for super capacitive application. They have reported that the graphene/PANI nanocomposite shows very promising electrochemical behavior. They also reported that the morphology of PANI in graphene/PANI composite also determines the electrochemical properties. They found that the nanowire morphologies exhibit higher specific capacitance than that of nanocone morphologies. The specific capacitance of graphene-PANI nanocomposite is reported as 724.6 F g^{-1} with cycle reversibility of 90% [42, 43].

1.8   Objectives of this study

This present work focuses on in situ polymerization of conducting polymer PANI in a graphene dispersed PVP solution. There are lots of research carried out considering graphene/PANI, graphene/PVP or PVP/PANI for improved electric, thermal and capacitive properties of composites. In addition, some researches were carried out using N-Methyl-2-pyrrolidone for synthesis process of composites. Most of the literature cited have prepared the thin film in nano or micro scale or they come up with the powder form and made pallets for characterization. There is a need of simple, scalable technique using environmental-friendly reaction medium for preparation of lightweight flexible conductive composites thin films.

Blaha et al. has recently studied the effect of various acidic medium for oxidation of aniline with strong and weak oxidants [44]. Shen et al. also investigated a flexible polymer/graphene thin

films, prepared like a sandwich structure having thermoplastic polyurethane as matrix for graphene nanoparticles and polyester as reinforcing interlayer [45].

In this work we have reported a simple, scalable techniques for the preparation of conductive flexible thin polymer-graphene films without using any hazardous solvents. A water soluble environment friendly polymer PVP is used as solvent which is effective in stabilizing the graphene dispersion as well as improvement in the conductive nature of PANI by co-doping process. The in situ polymerization of PANI in graphene dispersed PVP solution gives the synergetic output of PVP, PANI and graphene to form a flexible conductive thin composite film with improved mechanical and electrical properties.

CHAPTER II

MATERIALS AND METHODOLOGY

2.1   MATERIALS

Graphene nanoplatelets (GNS) of average particle diameter 5 microns was purchased from XG-Science. Polyvinylpyrrolidone (K-90) of average molecular weight 360000, Sulfuric Acid of formula weight 98.08 g/mole and density 1.84 g/ml, Hydrochloric acid of formula weight 36.46 g/mole and density 1.2 g/ml, Aniline (99.5% pure) of molecular weight 93.13 and Ammonium persulfate (APS) of molecular weight 228.20 were purchased from Sigma-Aldrich.

2.2   Synthesis of PANI/PVP/Graphene Composite

PVP: PANI/Graphene composites were prepared in situ polymerization by solution method. Three different solution were prepared in three different steps. First solution was prepared by pouring 1.86 gm of 99.5% pure Aniline on 20 ml of 1M aqueous Sulfuric/Hydrochloric acid and then kept for stirring at 300 rpm for 1 hr. Second solution was prepared with 6.667 gm of PVP and different wt% (i.e. 0, 5, 10, 20 wt%) of Graphene nanoplatelets in 80 ml of distilled water and kept under ultra-sonication for 30 minute with amplitude 40, 30sec pause on time & 10 sec pause off time. The third solution was prepared by adding 4.56 gm of APS in 100 ml of double distilled water. After stirring first solution for 1 hour and ultra-sonicating second solution for 30 minute, they were mixed and kept for stirring at 400 rpm for 1 hr. This process was carried out in ice bath to maintain temperature around 0°C.
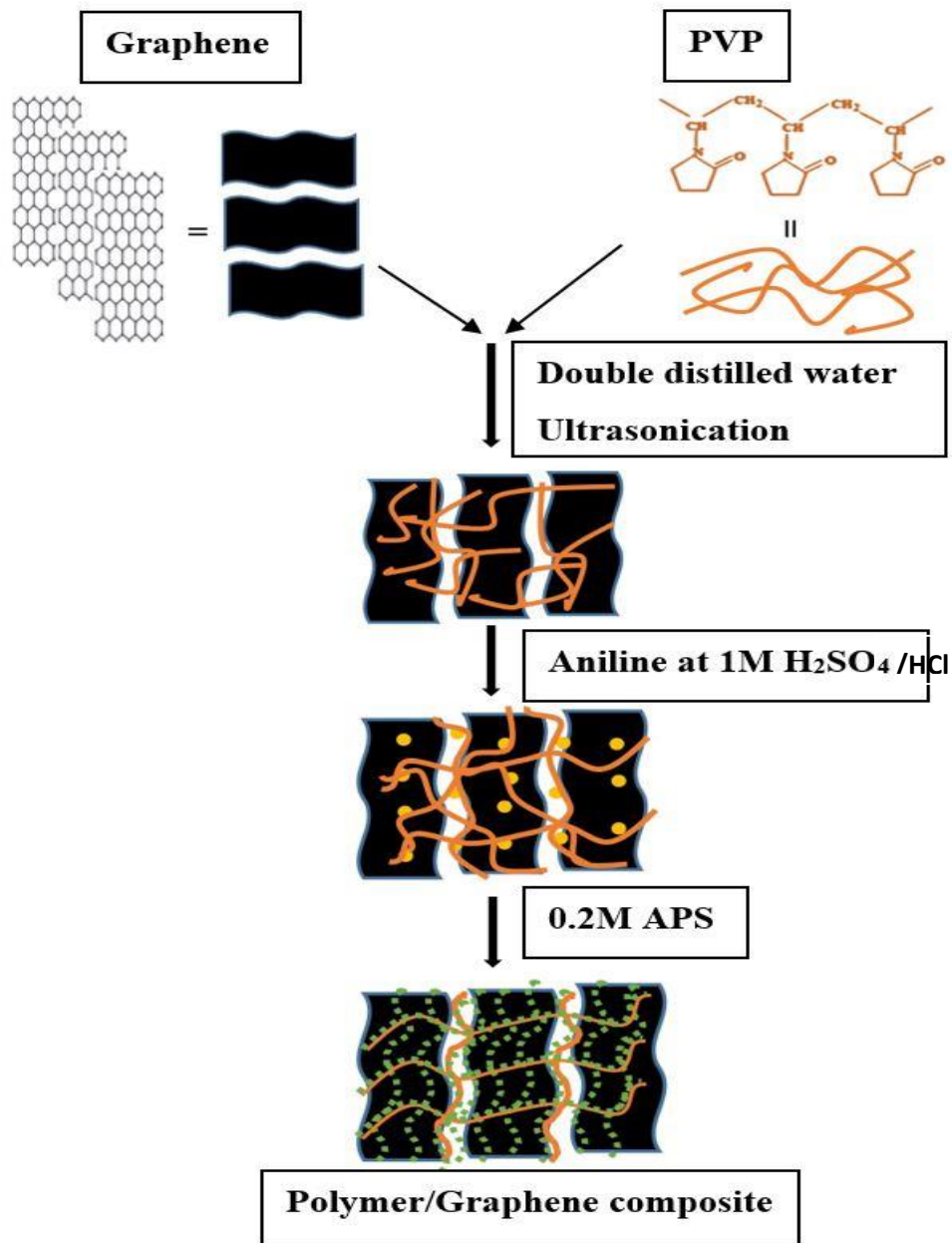
Figure 7: Schematic representation of polymerization and preparation of polymer/graphene composite

After 1 hour, the APS solution was added drop by drop with constant stirring at 400 rpm and maintaining temperature around 0ºC. When a dark green color appears on the solution, the stirring was stopped and poured in a Teflon coated mold and the mold was kept in Nitrogen flowing atmosphere for 10 hours to get the thin polymer-graphene composite film.

2.3   Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy in attenuated total reflection (ATR) mode was used to characterize the graphene and polymer-graphene composites. The IR spectra of polymer-graphene composite samples were collected using a Nicolet iS50 Spectrometer Thermo Scientific Inc. (Waltham, MA) equipped with a diamond crystal (45° angle) as an ATR accessory. Each sample was run using 64 scans versus the background that was also collected using 64 scans to generate a single beam spectrum at 4 cm^{-1} resolutions in the range of 600 to 4000 cm^{-1}. The data spacing was 0.482 cm^{-1}.
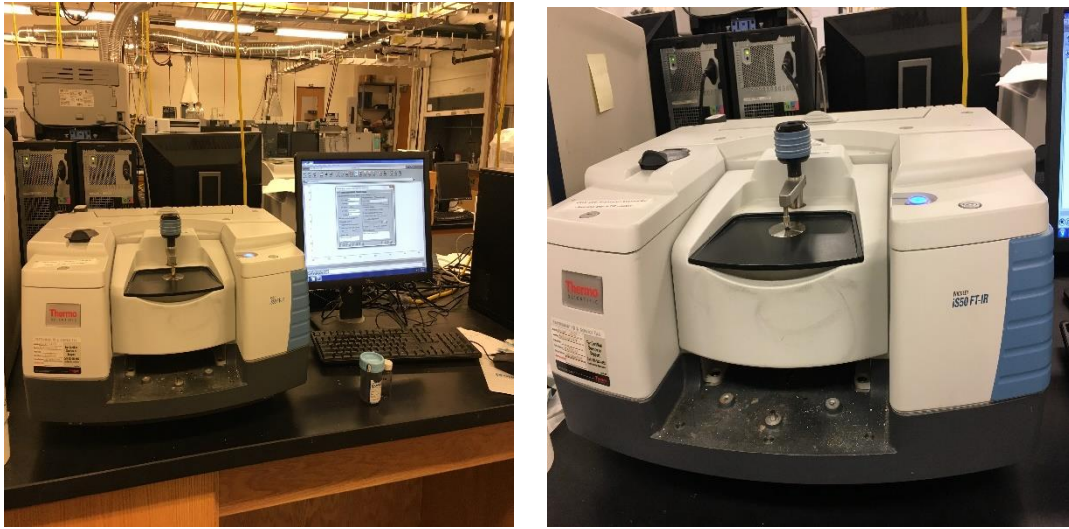
Figure 8: Fourier Transform Infrared Spectroscopy (FTIR) setup and Nicolet iS50 Spectrometer

2.4   Four Point Conductivity Measurement

Four-probe method was used to analysis the conductivity and resistivity of the polymer-graphene thin film. A source meter (KEITHLEY 2400) with lucas/Singatone corporation Model SP4 4-probe head and S-302 test stand were used during the measurements. The fundamental

property of conductive material is electrical resistivity which is the function of the availability of free electrons in the material. The availability of free electron depends upon how the materials are
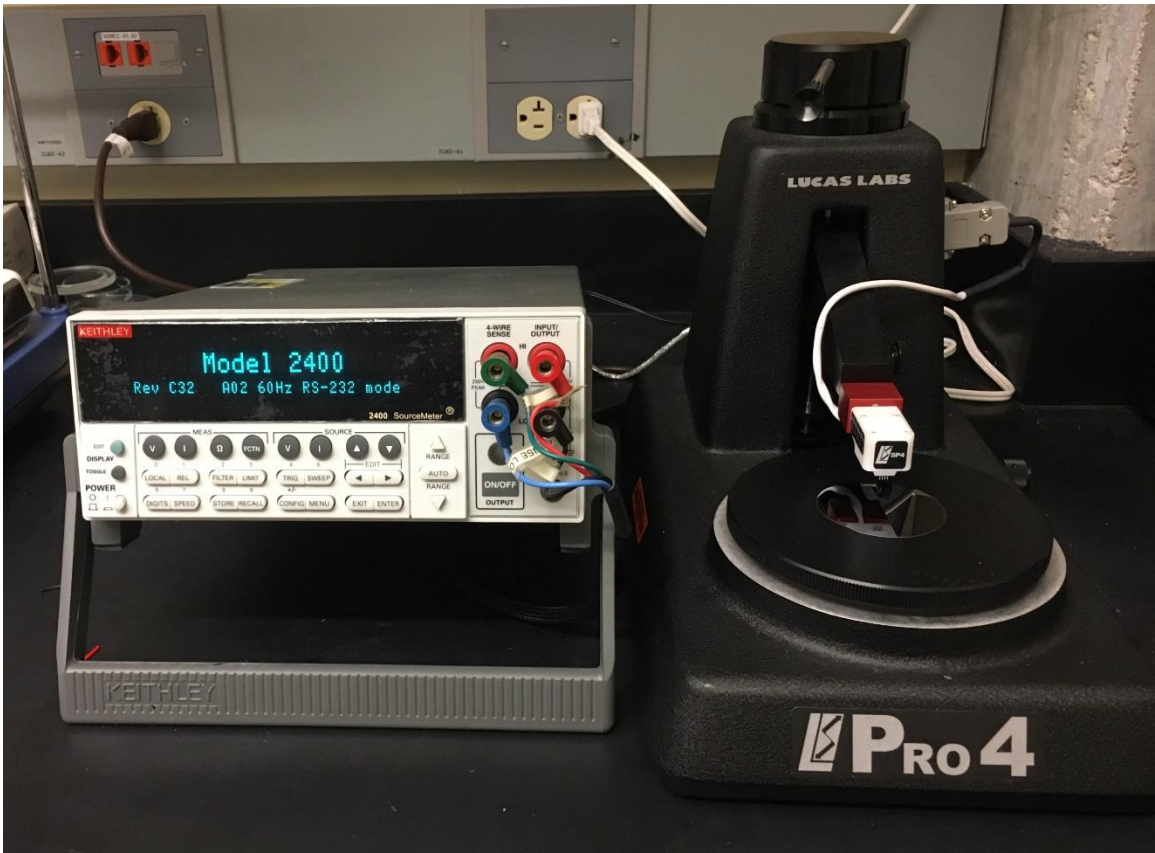
Figure 9: Four Point Setup with KEITHLEY 2400 source meter and S-302 test stand

physically bounded at molecular level. Since lots of other important properties are also function of physical binding of material at molecular level, measurement of electrical resistivity of material makes a lot sense in characterizing the material. The resistivity measurement of polymer-graphene thin film is measured on the basis of following theory.

By Ohm's law, the average resistance (R) between two surfaces (In reference to figure 10 surface 1 and surface 2) of the composite thin film having length (L) and cross sectional area (A) is given by

$$R = \frac{V}{I} \text{ (Ohms)}$$

Where V is voltage difference between two surfaces and I is current.

Again, the resistivity (ρ) is expressed as

$$\rho = \frac{R \times A}{L} \text{ (Ohm-cm)}$$

Where the cross sectional area A can be expressed as

$$A = W \times t \text{ (cm}^2\text{)}$$

W and t are width and thickness of the cross sectional area.

So, resistivity can be expressed as

$$\rho = \frac{R \times W \times t}{L} \text{ (Ohm-cm)}$$

For the special case of square sample where length = width

$$\rho = R \times t \text{(Ohm-cm)}$$

By measuring the resistance (R) and thickness (t) we can find the resistivity of the sample.

Conductivity (σ) is defined as the resiprocal of resistivity (ρ). So,

$$\sigma = \frac{1}{\rho} \text{ (S/cm)}$$

In actual measurement, the 4 point probe contacts the top surfce of the material. The final resistance value on four probe system are obtained on the basis of following assumption :

    a)   horizontal length of the sample is infinite.

    b)   thickness of sample is < 0.4 times the spacing of the probe.

    c)   measurement temperature is room temperature (~25°C).
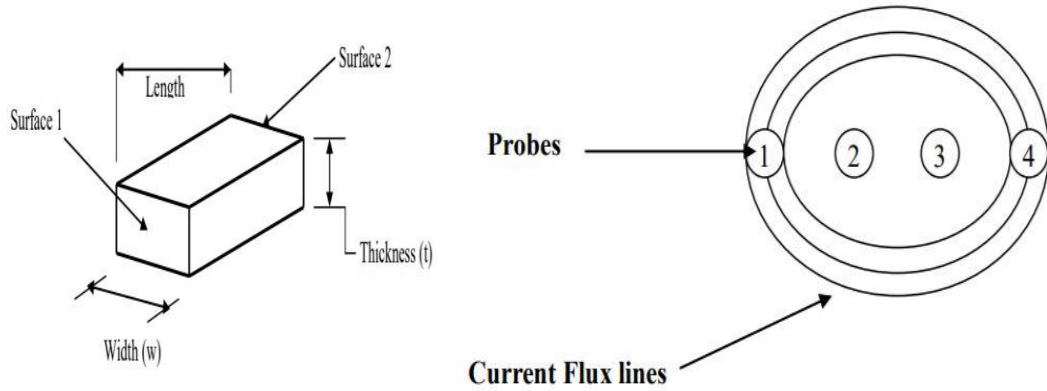
Figure 10: Schematic representation of four probe sample (left) and position of probe with lines of electric flux (right)

Under these assumption the relation for average resistance with voltage V and current I is found as

$$R = \frac{\pi}{\ln(2)} \times \frac{V}{I}$$

2.5   Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) was carried out to analyze the stress-strain relationship on DMA Q800 (TA Instruments, USA). A tension film clamp was used at custom
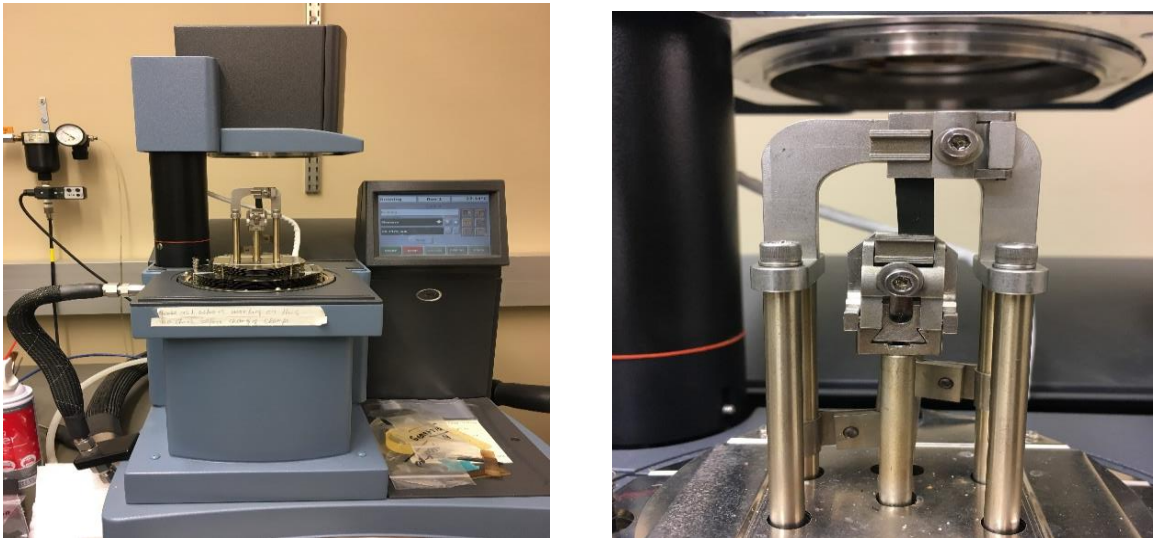
Figure 11: Dynamic Mechanical Analysis (DMA) setup (Left) and tension film clamp (Right)

mode for a rectangular specimen of length around 15 mm (varies slightly from sample to sample

slightly), width 6.5 mm and thickness 0.35 mm. Data sampling interval was 2.00 sec/pt with minimum dynamic force 0.00001 N. All the tests are conducted between temperatures 25^0C and 400 ^{0}C with temperature ramp 5^0C/min.

2.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of PANI, PANI: PVP and PANI: PVP/Graphene composite samples were performed using high-resolution Thermogravimetric analyzer (TA Q-50, TA instruments, New Castle, DE). The samples were heated with a rate of 20 °C/min from room temperature to 950 °C under 40 ml/min of continuous nitrogen flow.

2.7 Scanning Electron Microscopy (SEM)

The surface morphology of polymer-graphene thin film was investigated using FEI Quanta 600 field-emission gun Enviromental Scanning Electron Microscope. The scanning was carried out with 10 KV for magnification 1000X and 10,000X.

CHAPTER III

RESULTS AND DISCUSSION

3.1 FTIR SPECTRA ANALYSIS

Study of FTIR spectrum of samples of graphene, PANI:PVP with 0% graphene, PANI:PVP with 10% graphene and PANI:PVP with 20% graphene were done. The FTIR analysis confirms the in situ polymerization of PANI on the surface of graphene. There is no chemical bonding between
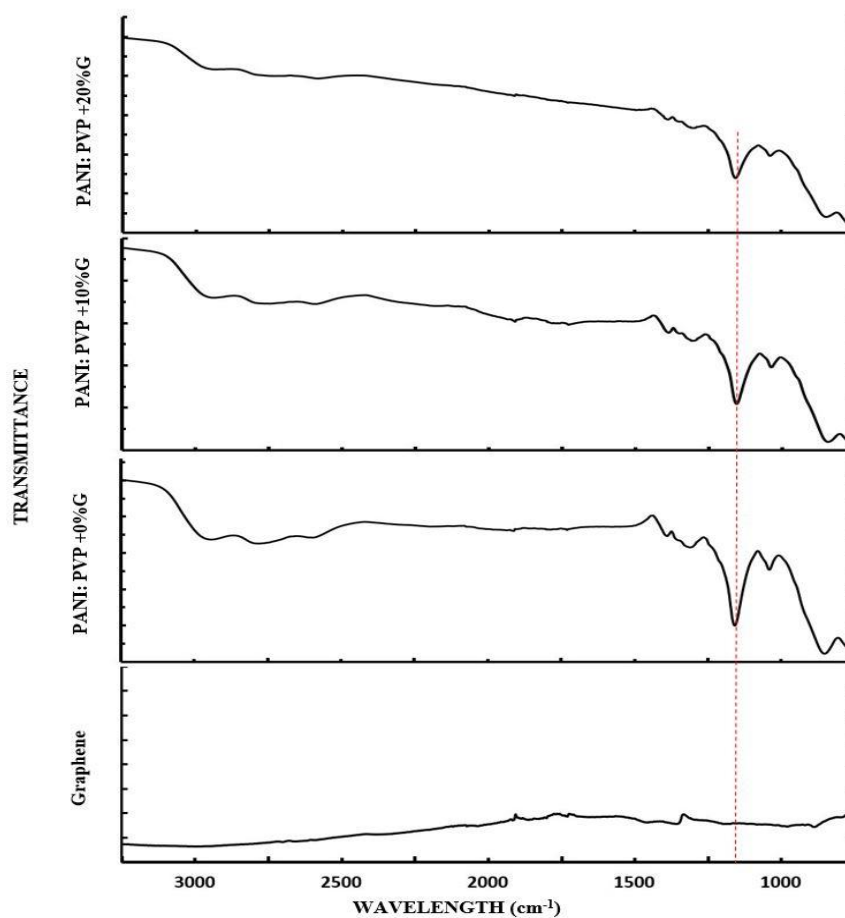
Figure 12: FTIR Spectra of Graphene, PANI: PVP+0%Graphene, PANI: PVP+10%Graphene, PANI: PVP+20%Graphene

graphene and polymer, which ultimately preserves the high conductive property of graphene nanoplatelets. The conductive polymer blend PANI:PVP is working as a binding agent to form the graphene/polymer composite flexible films.

In graphene, broad peak about 3200 cm^{-1} indicates the O-H stretching. Other peaks at 1700, 1400 and 1100 cm^{-1} corresponds to C=O, O-H and C-O stretching. Because of the puirity of graphene we used, the C=O and C-O peaks are not distinguished significantly[46, 47]. In PANI, PVP and graphene composite, peaks at 1050 cm^{-1} appears due to S-O and S=O vibration. The observed band at 1153 cm^{-1} is defined as the electronic-like band which is correlative to the conductivity nature. This band also gives the information about the measure of the degree of delocalizetion of π electrons[18, 48, 49]. The existance of those peacks for all composition of graphene confirms that the in situ polymerization is happening on the surface of graphene without distrubing the conductive properties of polymer and graphene. No reaction is confirmed between graphene and polymer matrix.

3.2   SEM
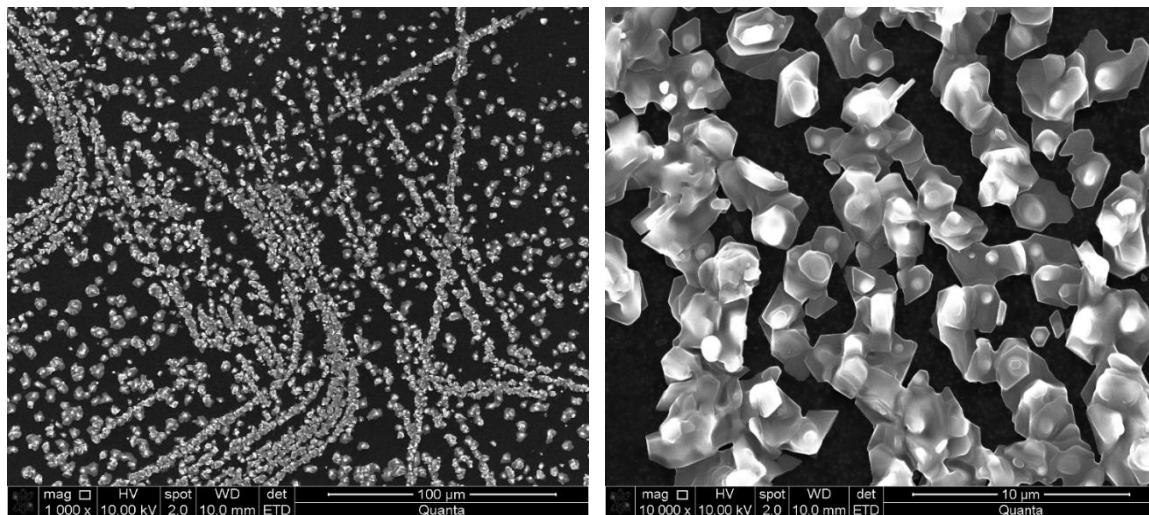
Figure 13: Electron Microscopy image of PANI: PVP+0%Graphene at 1,000X (left) and 10,000X (Right)
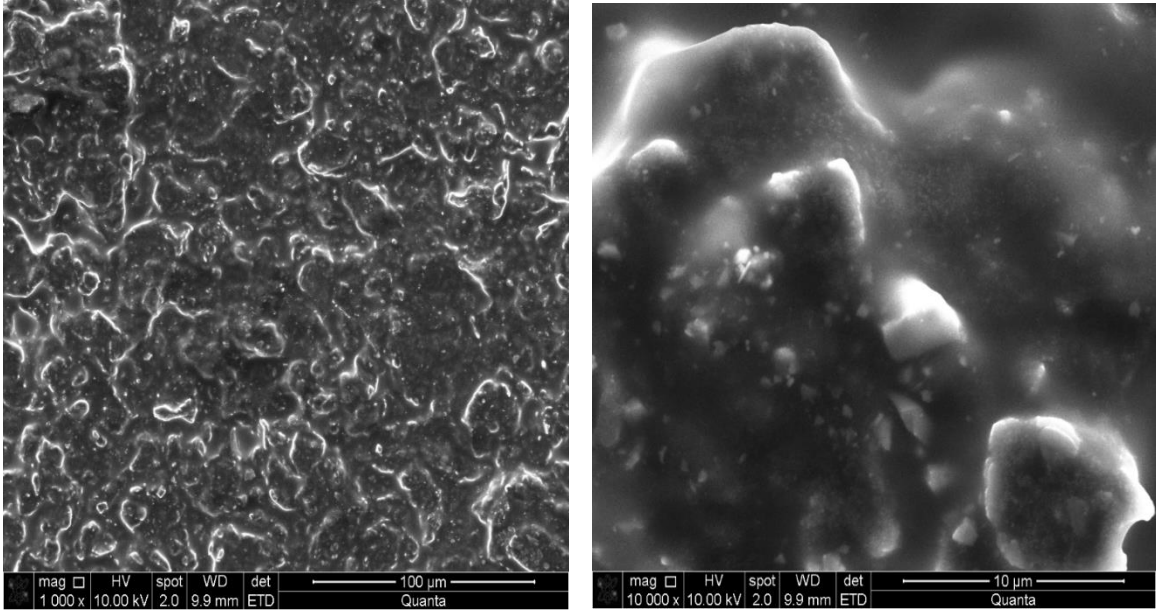
Figure 14: Electron Microscopy image of PANI: PVP+5%Graphene at 1,000X (left) and 10,000X (Right)
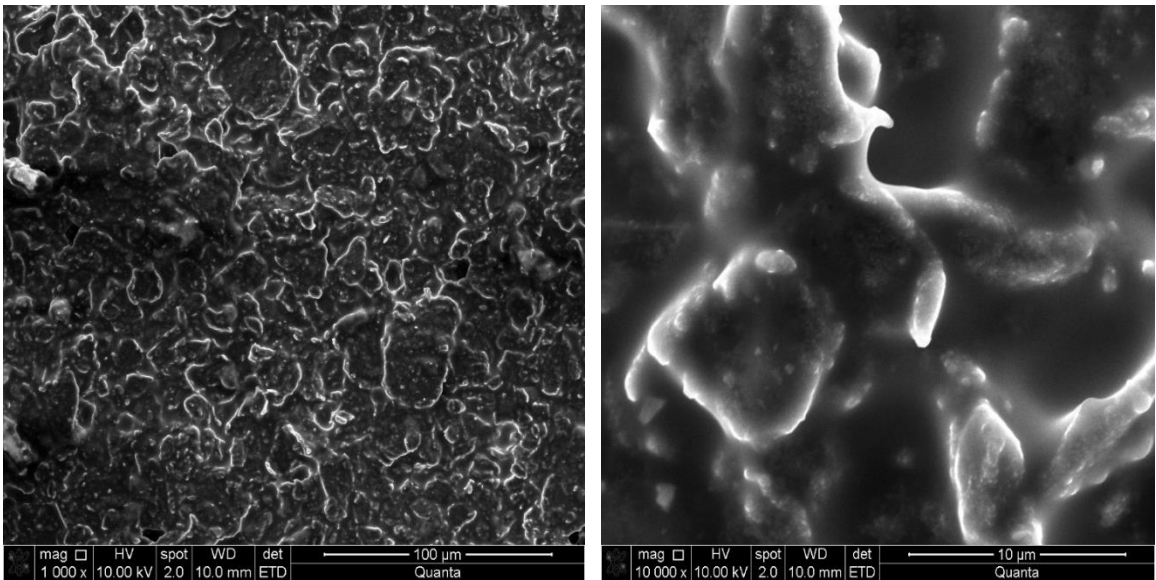
Figure 15: Electron Microscopy image of PANI: PVP+10%Graphene at 1,000X (left) and 10,000X (Right)
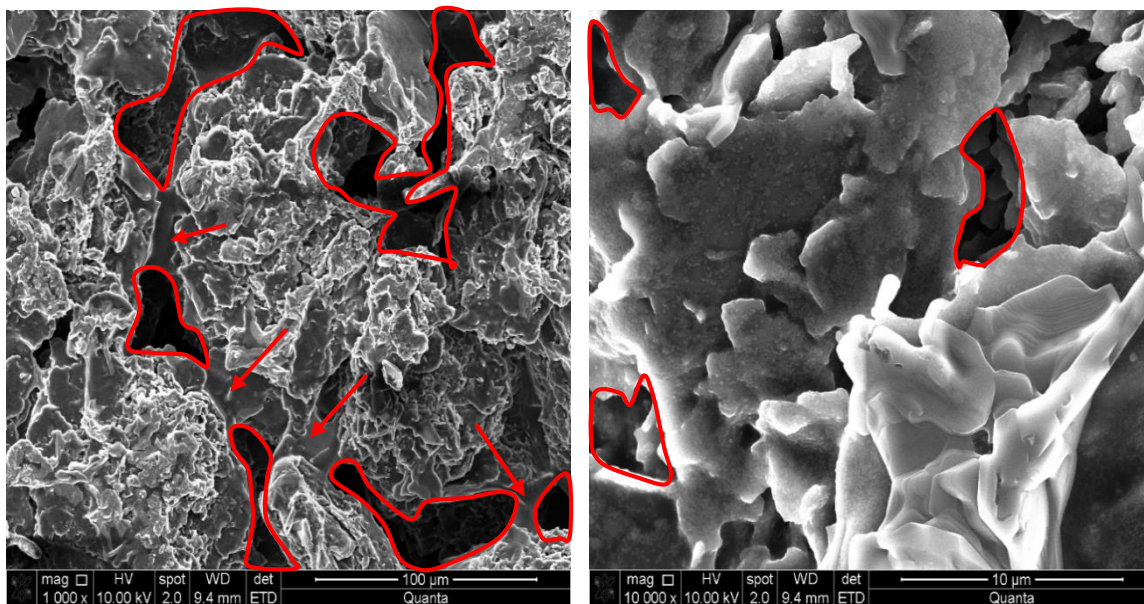
Figure 16: Electron Microscopy image of PANI: PVP+20%Graphene at 1,000X (left) and 10,000X (Right)

The surface morphlogy of PANI/PVP/Graphene composite films were investigated through scanning electron microscopy. Figure 13 shows the surface morphology of PANI/PVP film with no graphene. A well defined thread like chain sturcture of PANI crearly noticed. Usually such threadlike structure of PANI are favourable to achieve higher conductivity values. Figure 14 and Figure 15 represent the electron microscopy of PANI/PVP/5wt% graphene and PANI/PVP/10wt% graphene composite thin films respectively. In both case a uniform distribution of graphene nanoplatelets wrapped with PANI chain in the polymer matrix is noticed. Figure 16 shows the surface morphology of PANI/PVP/20wt% graphene composite thin film. Although uniform PANI coating of graphene nanoplates are achieved, large size voids are also observed. Presense of such voids increases the brittleness of thin films along with decreases in film forming capability. Because of formation of such significant large voids above 20%wt graphene, a conductive continious flexible thin film couldn't be achieved.

3.3 TGA

Conductive composite films are expected to be used in composites for improving the through thickness conductivity. Since composites will be cured around 175℃, we need to characterize their ability to withstand the temperature changes and also observe their stability at elevated temperatures. We did this by performing TGA. Thermal stability of PANI, PANI:PVP and
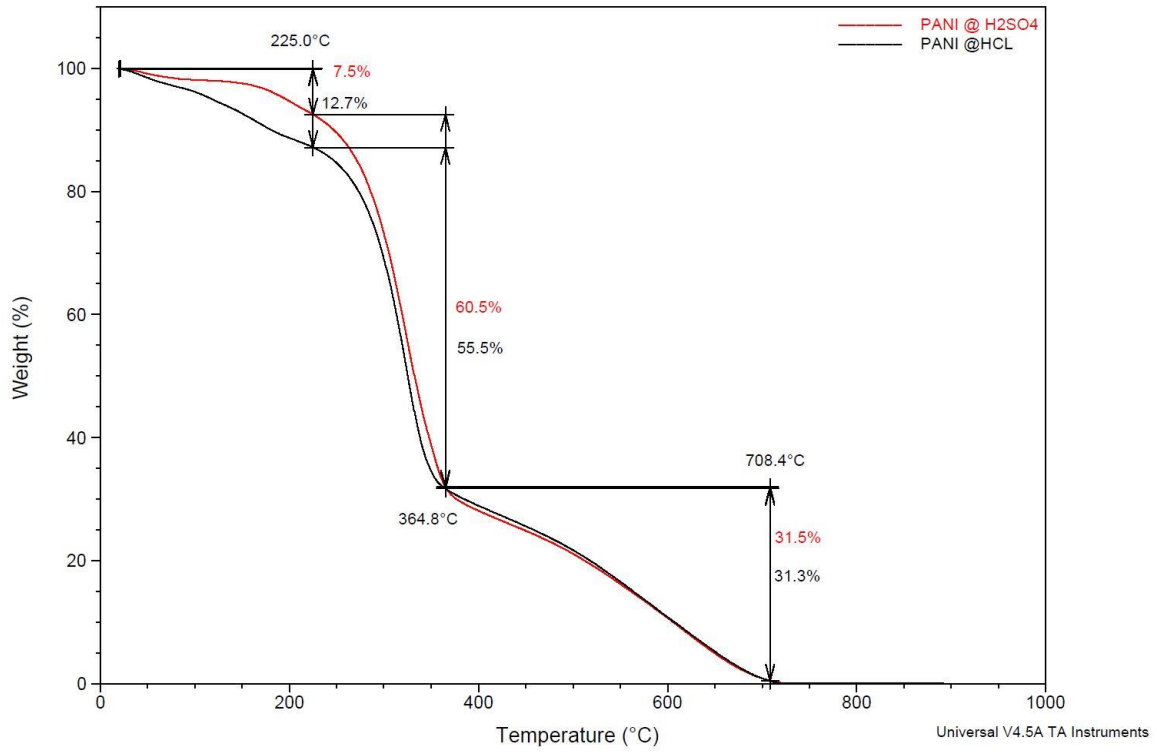
Figure 17: TGA curves for Polyaniline with polymerization medium of Sulfuric acid and Hydrochloric acid

PANI:PVP/Graphene composites were investigated from room temperature to 950 ^{O}C in nitrogen atmosphere. Figure 17 shows the TGA curves for polyaniline prepared by polymerization in the Sulfuric acid and Hydrochloric acid medium respectively. Three step weight loss process was observed for polyaniline.

The % weight loss upto 225 ^{O}C is mainly due to elemenation of water molecule and loosely bounded molecule. This loss is higher by 4.9% for PANI polymerized on hydrochloric (HCl) acid medium. Which shows that the polymerization of PANI on HCl medium contains more water

25

molecules and loosely bounded impurities. The other two weight loss by removal of dopents and degradation of polymer for both sample are identitical[18, 50]. Most composites are cured around 175°C - it can be seen that PANI is still stable till 225°C - therefore, conductivity of the films will not be compromised.

Table 3: TGA data for PANI with polymerization medium Hydrochloric and Sulfuric acid

Sample	Temperature range (^{0}C)	% of weight loss	%of residue at 715(^{0}C)	Comments
PANI at Hydrochloric acid	Upto 225	12.70%	No residue	Elemination of loosely bounded or water molecule
	225 to 364.8	55.50%		Removal of ion dopents and small molecule
	363.7 to708.4	31.30%		Degradation of PANI itself.
PANI at Sulfuric acid	Upto 225	7.50%	No residue	Elemination of loosely bounded or water molecule
	225 to 364.8	60.50%		Removal of ion dopents and small molecule
	363.7 to708.4	31.50%		Degradation of PANI itself.

Figure 18 shows the TGA curves for PANI and PVP blend in 1:3 ratio, polymerized in two different acidic medium. This blend also shows three steps of weight loss. The first weight loss
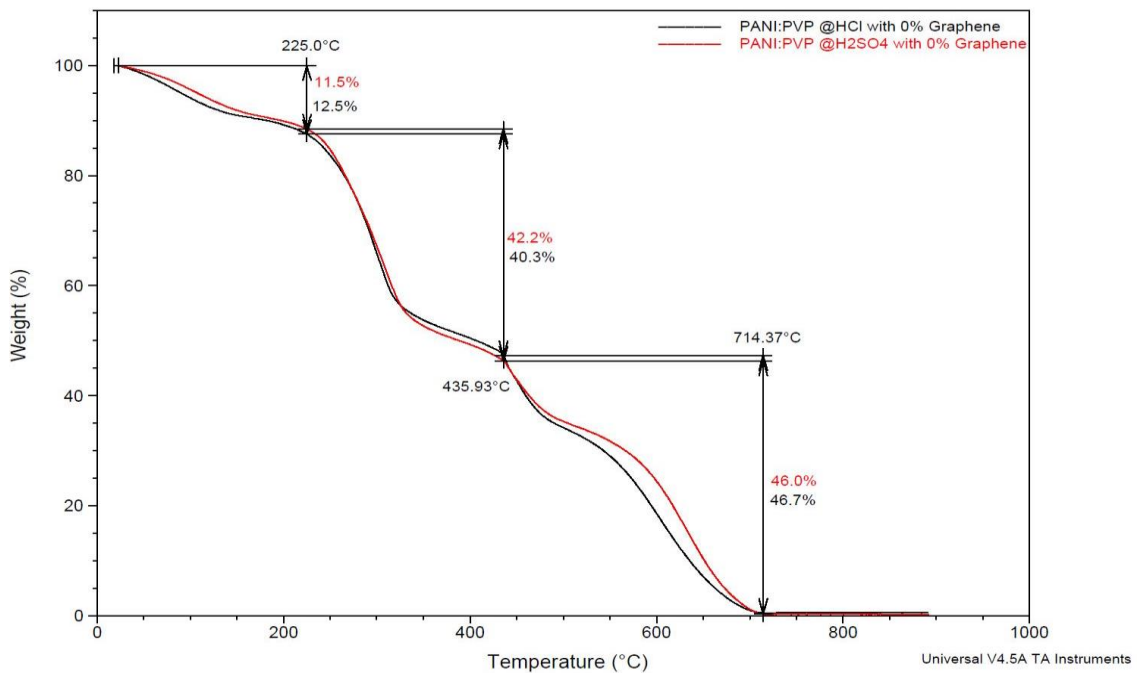
Figure 18: TGA curves for PANI: PVP blend with polymerization medium of Sulfuric acid and Hydrochloric acid

Table 4: TGA data for PANI: PVP plus no graphene with polymerization medium Hydrochloric and Sulfuric acid

Sample	Temperature range (^{0}C)	% of weight loss	%of residue at 715(^{0}C)	Comments
PANI:PVP at Hydrochloric acid with 0%Graphene	Upto 225	12.50%	No residue	Elemination of loosely bounded or water molecule
	225 to 435.9	40.30%		Removal of ion dopents and small molecule
	435.9 to714.4	46.70%		Degradation of PANI:PVP blend.
PANI:PVP at Sulfuric acid with 0%Graphene	Upto 225	11.50%	No residue	Elemination of loosely bounded or water molecule
	225 to 435.9	42.20%		Removal of ion dopents and small molecule
	435.9 to714.4	45.90%		Degradation of PANI:PVP blend.

upto 225^{0}C is because of evaporation of water and loosely bound molecules. Here also the PANI:PVP at hydorchloric medium shows more incorporation of water and loosely bound molecules. The second weight loss process corresponds to removal of SO_4^{--} dopant present in conducting polymer. It is noticed that the loss of such dopent in PANI:PVP blend,which are responsible for conductive properties of polymer, is decreased by 10% to 15% in comparision to the only PANI. This happens because of high tendency of PVP to absorbe anions[51]. The third step of weight loss corresponds to the decompositon of PANI:PVP blend. The third step weight loss is higher by 14 % to 15% in comparision to only PANI. This is resonable because PANI and PVP undergo for decomposition in this third step weight loss. In addition, the incorporation of PVP in PANI shifted the decomposition of polymer to higher temperature.

Figure 19 shows a comparative TGA analysis of PANI/PVP blend with no graphene and 20 wt% graphene in Sulfuric acid medium. It also shows the three step weight loss process which are summerized on Table 5. The comparatative study of these two curves showed that the incoporation of water and loosely bound molucule decreases for PANI:PVP/Graphene composite film. The incorporation of graphene in PANI:PVP blend does not bring a significant change on degradation of SO_4^{--} ion dopants but there is small decrease in % weight loss for this weight loss

step. The third weight loss corresponds to the degradation of polymer backbone. There is complete

degradation of PANI:PVP with no graphene blend at 709.6 $^{\circ}$C but there is 4.6% resedue present at

Table 5: TGA data for PANI: PVP plus 20% graphene with polymerization medium
Hydrochloric and Sulfuric acid

Sample	Temperature range ($^{\circ}$C)	% of weight loss	%of residue at 715($^{\circ}$C)	Comments
PANI:PVP at Sulfuric acid with 0%Graphene	Upto 225	11.50%	No residue	Elemination of loosely bounded or water molecule
	225 to 435.9	42.20%		Removal of ion dopents and small molecule
	435.9 to714.4	45.90%		Degradation of PANI:PVP blend.
PANI:PVP at Sulfuric acid with 20%Graphene	Upto 225	10.80%	4.60%	Elemination of loosely bounded or water molecule
	225 to 435.9	40.80%		Removal of ion dopents and small molecule
	435.9 to714.4	43.80%		Degradation of PANI/PVP/Graphene blend.

that temperature when 20% graphene is incoporated in the PANI:PVP blend. Which clearly

indicates that the incorporation of graphene nanoplatelets in PANI:PVP blend increase the thermal
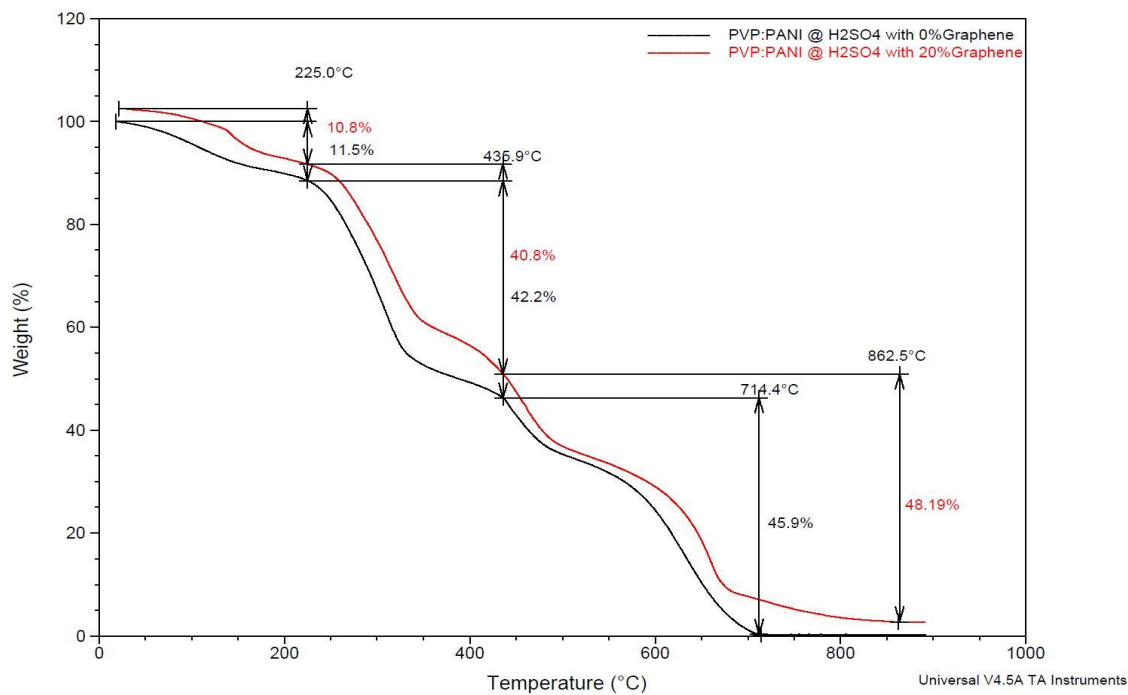
Figure 19: TGA curves for PANI: PVP with 0% graphene & 20% graphene loading and
polymerization medium of Sulfuric acid

stabalaity of composite thin film. The complete decomposition of PANI:PVP/Graphene sample is achieved at 862.5 $^\text{O}$C which is higher by 148.1 $^\text{O}$C.

3.3   Conductivity

The four-point probe method was used to make electrical conductivity measurement of PANI: PVP/Graphene composite samples. The conductivity results of different graphene content in the PANI: PVP/Graphene composites are shown in Table 6 which shows that the increase of

Table 6: Conductivity data for polymer/Graphene composite with different loading wt% of graphene nanoplatelets

Sample	Thickness (Cm)	Resistance (Ω)	Resistivity (Ω-cm)	Conductivity (S/Cm)	Avg. Conductivity (S/Cm)
PANI:PVP+0%G	0.013	6305	81.965	0.012	
	0.016	5953	95.248	0.010	0.012
	0.014	5180	72.52	0.014	
PANI:PVP+5%G	0.026	1222	31.772	0.031	
	0.024	1348	32.352	0.031	0.029
	0.028	1398	39.144	0.026	
PANI:PVP+10%G	0.031	261	8.091	0.124	
	0.03	243	7.29	0.137	0.129
	0.028	284	7.952	0.126	
PANI:PVP+20%G	0.033	66	2.178	0.459	
	0.031	68	2.108	0.474	0.465
	0.035	62	2.17	0.461	

the graphene content had increased the conductivity of the PANI: PVP/Graphene composites. There are several components which might be responsible for the enhancement in the conductivity. One of those cause is the dopant effect. The presence of sulfate ion as a dopant in polyaniline emeraldine salt caused the hydrogen bonding. In addition, the absorption of polyaniline on the surface of graphene has led to the successful formation of PANI/graphene composite. PANI provides a good conductive path on the surface of graphene layers, thus activates the participation of more electrons in the directional movement. PANI is reported as a good electron donor while the graphene acts as the electron acceptor where both facilitated the π–π* interaction between the graphene surface and the quinoid rings of PANI. So applied potential

difference cause the delocalized electrons to move resulting in an enhancement of the electrical conductivity. The electrical conductivity was enhanced due to charge transfer between PANI and graphene. From the Table 6 it is observed that the conductivity of PANI/PVP/20% Graphene composite film has increased by ~39 times than that of no graphene composite film.
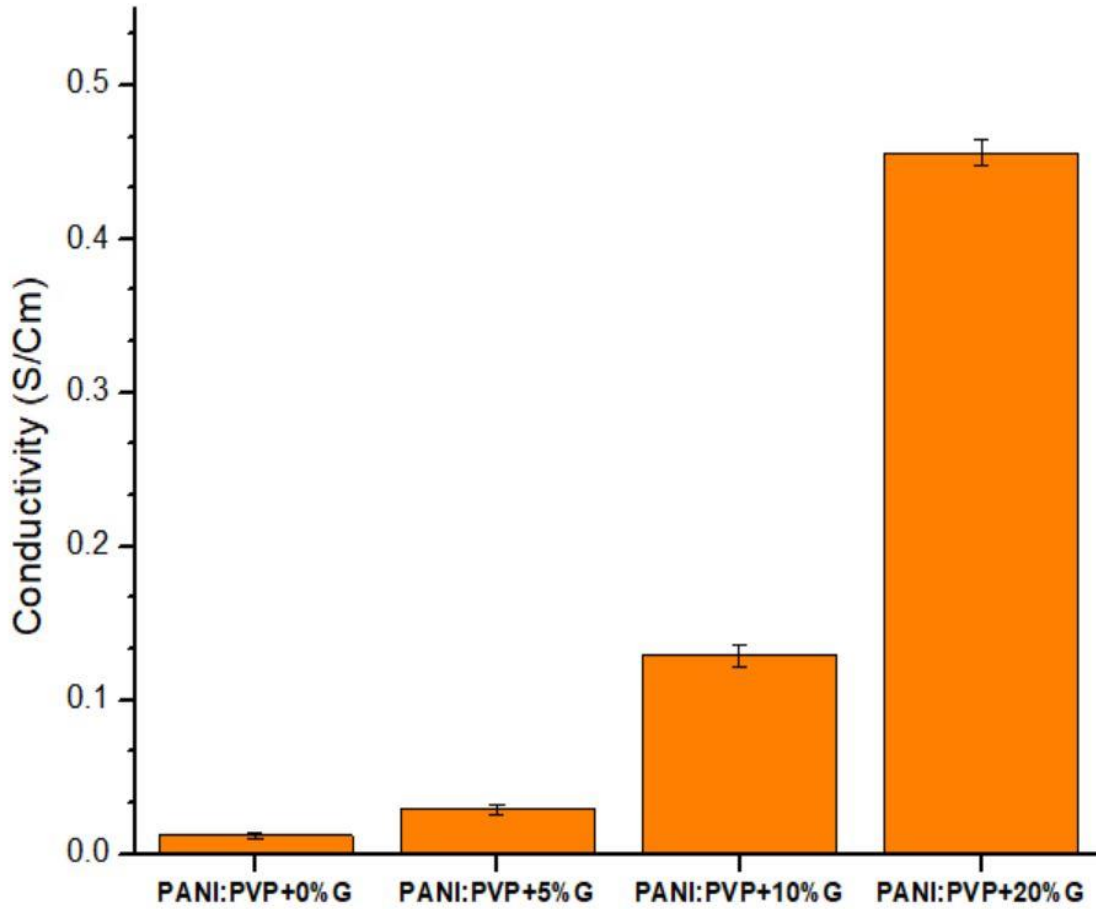
Figure 20: Illustrative bar diagram of increae in conductivity for different loading wt% of graphene in composite films

3.4   DMA

Considering the flexibility of composite thin film one of demanding feature, a stress-strain analysis was done on DMA for different loading of graphene in polymer matrix. Table 7 and Figure

Table 7: Average stress and strain% data for polymer/Graphene composite with different loading wt% of graphene nanoplatelets

Sample	Stress (Mpa)	Avg. Stress (Mpa)	Strein %	Avg. Strain%
PANI:PVP+0%G	1.549		25.47	
	1.848	1.699	34.68	30.075
	1.699		30.075	
PANI:PVP+5%G	2.171		21.96	
	2.054	2.025	26.07	25.91
	1.849		29.7	
PANI:PVP+10%G	2.199		19.29	
	1.728	1.874	27.08	23.34
	1.695		23.65	
PANI:PVP+20%G	3.005		14.37	
	2.442	2.52	13.43	16.61
	2.113		22.03	

21 shows the trend on increasing in stress and decreasing in strain percentile. From the experiment, it was observed that the ultimate tensile strength of the thin film increased by 48.32% with the
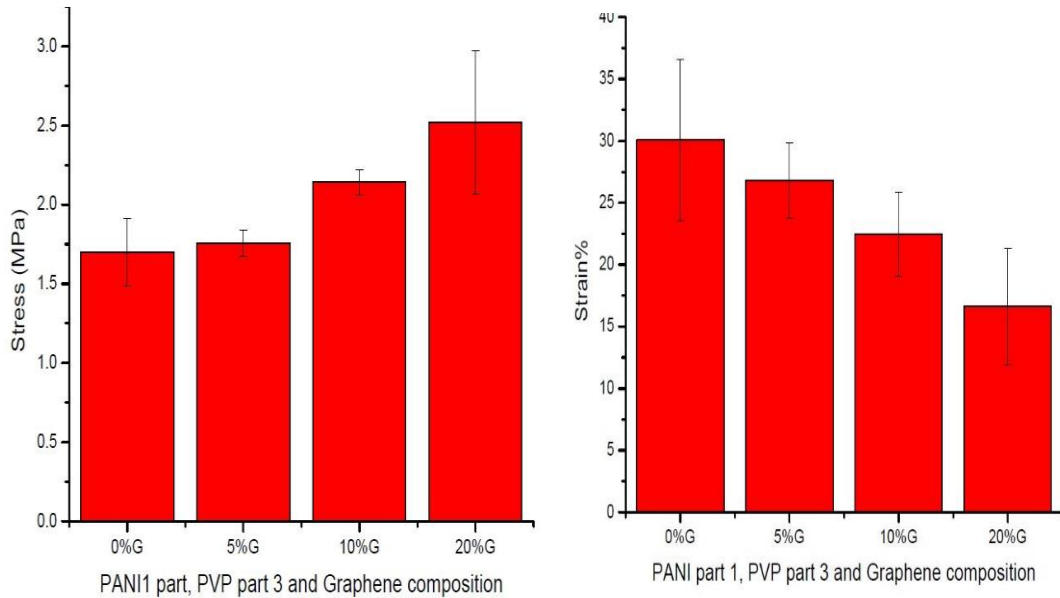
Figure 21: Illustrative bar diagram of increase in average stress (Left) and decrease in average strain % for different loading wt% of graphene in composite film

increase in graphene by 20wt% while the strain decreased by 13.465% with the increase in graphene loading by 20wt% in conducting polymer matrix. Figure 22 shows the stress-strain curve for different loading of graphene.
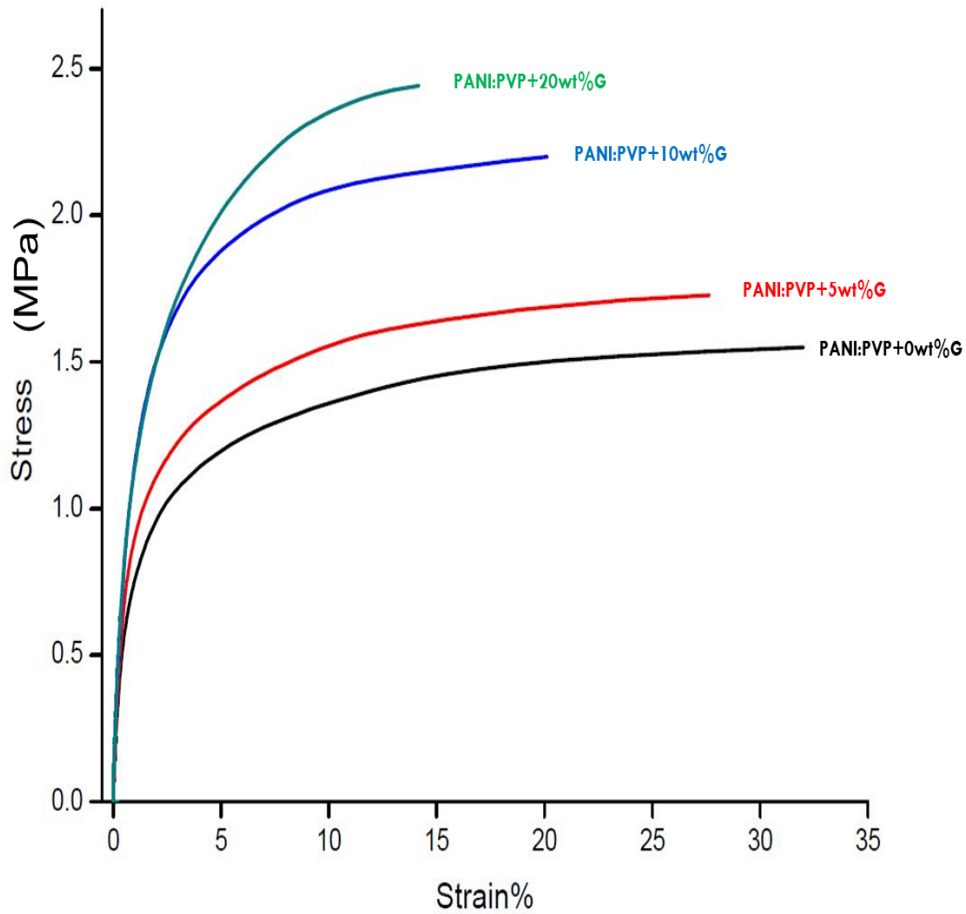
Figure 22: Stress-strain curve for polymer/Graphene composite films with different loading wt% of graphene nanoplatelets

CHAPTER IV

Business Model Canvas

4.1 Technology and value proposition

In composites used in aerospace and wind turbines, lightning strike mitigation properties are enhanced by adding a single layer of copper or aluminum mesh to improve their surface and through thickness conductivity, since they typically have very low conductivity in the thickness direction. The inability of composites to dissipate the generated heat due to either thermal loads or lightning strikes can be overcome by increasing the thermal and electrical conductivity in the thickness direction. The current copper or aluminum mesh used in composites for lightning strike protection is good only for one single lightning strike. By increasing the composite through thickness conductivity, it would be possible to enhance their durability against such catastrophic events. This can be introduced into the current manufacturing practices without modifying any of the current manufacturing approaches. If the through thickness conductivity can be increased, such a composite system may also be potentially used to store energy and make the composite into an active electrode. Researchers have attempted to make such a composite material but have not been successful. The other important problem that we have overcome is the issue with using conductive polymers as carriers for nanoparticles such as graphene and carbon nanotubes. By blending two different polymers (one conductive and another non-conductive but acting as a dopant), we can enhance the conductivity of the overall system, which can be used to make flexible conductive films. These films have other potential applications that have not even been discovered yet.

The team's on-going work has led to a simple and affordable process to manufacture flexible and conductive films using safe and affordable graphene fillers and blends of polymers. This technology has a high commercialization potential based on limited customer discovery. We believe that it can lead to radical improvements in the ability of composites to have high conductivity and flexibility and increase its capability to withstand multiple lightning strikes.
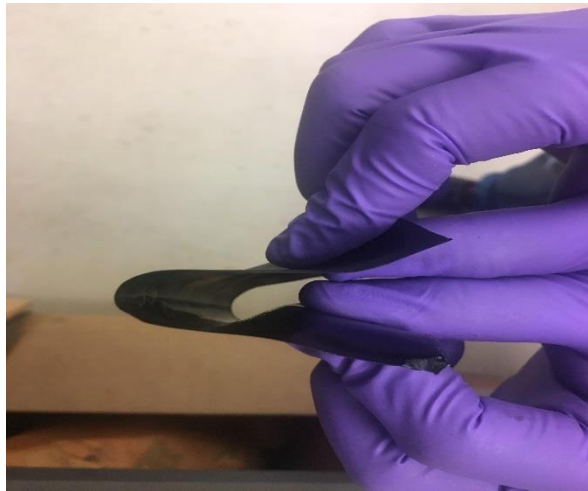
Figure 23: Digital image of conducting polymer/graphene composite thin film

As a result of this research, our team has filed a patent disclosure with OSU Technology Development Center and will be filing a non- provisional patent. As an IP-protected technology, the patent-pending process and the flexible film production methods are an intellectual property of the team. OSU's   Technology Development Center (TDC), the Intellectual Property Screening group at Oklahoma State and the School of Entrepreneurship managing the I-Corps site program at Oklahoma State provided initial funding of $3,000 for conducting scale-up of the technology and assisted in discussing the technology with a very limited number of potential customers. In addition, our team has also received $5000.00 funding from E-team Venturewell for additional technical development, additional customer discovery, supporting business development efforts, and for a better understanding of the competitive landscape.

4.2 Positive Social Impact

The Lightning Strike Mitigation films have the potential to impact a number of industries in the aerospace and wind energy industries. One example of a social impact will most likely be seen in the aerospace industry. As the aerospace and the space sectors have pushed for reduced weight structures, the need for preventing damage to those structures due to lightning strikes without copper or aluminum meshes is high. Our additives and films will solve some of the problems related to lightning strike mitigation and the need to repair those structures after every single strike. Utilizing cured composites with lightning strike mitigation technology will make aircraft and wind turbines lighter and more durable, which will help meet fuel efficiency and CO_2 emission goals.

4.3 Value Propositions

❖ **Increased Conductivity** of composite thin films by 50% will help to replace Cu and Al mesh by polymer/graphene composite films that can withstand multiple lightning strikes.

❖ Lightning Strike Mitigation layer will **reduce weight** of lightning strike protection layer by 40%, leading to less fuel consumption for the aerospace industry. It will increase the **efficiency of windmills** for wind energy industries.

❖ Graphene in polymer-graphene composite thin film can absorb UV radiation. The primer layer is entirely eliminated, **reducing manufacturing costs by 30%.**

❖ Polymer/graphene conductive thin films or spray can be installed or applied with an automated system, which will **decrease the labor cost of LSM installation by 50%.**

❖ **No Change in Manufacturing Process:** our direct customers, can simply blend in the desired amount of LSM or add the film/ Spray in their standard production process. Therefore, for a composites manufacturer to adopt this technology, there is no change needed. No additional asset cost, labor cost or learning curve is associated with the LSM

on the production line because it is simply an additional material ingredient. The LSM film/ Spray may also be added directly between the composite laminates.

4.4 Market Overview and Potential

The overall market of Lightning Strike Mitigation Materials spans across multiple industries because composite materials with high trough thickness conductivity have multiple useful benefits. According to IBIS world, Carbon Reinforced Composite usage has grown by 13% over the last five years and high growth potential is predicted for well-documented industries such as aerospace and wind energy industries, however strong growth is foreseeable across all industry segment.

Our immediate target market is any company that fabricates primary and secondary structure for the aerospace industry and the wind energy industry, as well as the composite repair shops that repair such structure to bring them back to service as quickly as possible. The fabricators of composite materials who then sell to our end user, which is either the original equipment manufacturer or a consumer. Interviews with people from GE Global Research Center and other customer indicates that up to 5% of the cost of components used to fabricate a composite part could be spent on lightning strike mitigation. Assuming this and that the industry growth would positively correlate with our proposed technology, we believe our product could have an obtainable market volume of $50 million in the US alone by 2020. That number is based on acquiring only five percent of the total addressable multibillion-dollar market. If customer acceptance could be gained, it is possible that the OSU-student led company could gain a major share of this volume.

The composite market is projected to grow between 7% to 9% at a compounded annual growth rate over the next five years in the composites sectors [52, 53]. The top manufacturers in the composite sector include the aerospace, RV, automotive, recreation, transportation, marine and

wind energy industries. Total composite market in North America is estimated at $10 billion with a 7% Compound Annual Growth Rate (CAGR) over the next 5 years. Conservatively estimating 5% of this market to be covering electrically conductive composites and composites for lightning strike mitigation, the composites market is currently at $500 million per year. The projected market for the conductive films by themselves could be estimated to be $50 million.

4.5 Competition

The major player in the market is a company supplying the copper and aluminum mesh to the composites industry. However, based on our discussions with the composites design group at GE R&D in Schenectady, NY, GE is interested in improving the through thickness thermal and electrical conductivity and not just the surface conductivity. The only company supplying the copper mesh to the composites industry for lightning strike mitigation is Dexmet Corporation in CT, who appear to have almost 75% of the market. Based on our discussion with Dexmet representative, Dexmet is interested in development of conductive light weight thin films. Discussion with Boeing representative revels that the labor cost for applying Cu and Al mesh is costly and they are interested in alternative ways to reduce the labor cost as well. Astroseal products Manufacturing Corporation is yet another company from CT manufacturing similar copper mesh for the composites industry. There is no US manufacturer making graphene or carbon nanotube based films for lightning strike mitigation, although N12 technologies from Cambridge, MA is manufacturing CNT films for improving interlinear fracture toughness of composites. It appears that they have not considered their films for lightning strike mitigation but it is possible that they could be a potential competitor. XG Sciences started by Prof. Larry Drzal in Michigan sells high conductivity graphene films, although it is not flexible nor

can it be easily introduced into the composite manufacturing process. The approach of XG Sciences is to provide the additive that needs to be added to the resin system in order to improve the conductivity of the composite matrix, but since the addition of such nanoparticles drastically increases the resin viscosity, we believe that we have a competitive advantage. Currently, XG Sciences has 100% market share of the non-flexible graphene film market.

4.6 Commercialization Plan

This plan indicates that Lightning Strike Mitigation Solutions will be a student-led venture operating as a limited liability company (LLC) as a for-profit business. With the help of VentureWell funding as well as funding from the Technology Development Center at OSU, our team will have the means to employ Ms. Dunzy to focus directly on business development and commercializing our conductive composite thin films.

During the 50+ customer interview by entrepreneurial lead (EL), several potential partners validated the value propositions hypothesized by the EL, which clearly indicated the commercial potential of the technology. Companies such as Pro-set and Evonik who have established partnerships with end users and composites manufactures could also help us to reduce the lead time and establish the benefit of our product at the beginning of the supply chain, move throughout the supply chain and create demand from different user types with our versatile application proves. We have also established collaborations with Huntsman Advanced Materials and Applied Graphene Materials. We are planning to collaborate with Spares School of Business, OSU for the help of a creativity, innovation and entrepreneurship scholar team to initiate additional, targeted customer interviews with additional customers. Our Preliminary set of interviews suggests us that we can go for National I- Corps team funding to do a detailed customer discovery project.

Based on 50+ customer interviews, we found that companies like Dexmet Corporation and Boeing are interested in lightweight conductive thin films and are also ready to help us with designing the LSM test. We plan to work with GE, for testing and characterization of the final product and LSM capabilities. The product from this project could be sold as films compatible with epoxy resin or BMI systems and is also compatible with glass fiber or carbon fiber reinforced composite systems.

Actual or potential interest by companies: Boeing, Dexmet Cooperation, NORDAM, Advanced composite materials, Axiom, Evoink and Pro-Set are interested in receiving samples for testing and evaluation, with GE composites also interested in working with us to evaluate the product.

Based on our overall market research, we believe that the composite materials market is open to innovative idea that keep industries moving forward with new technologies. Therefore, our main marketing avenues will be attending trade shows, advertising with Composites World, joining trade associations and networking within the industry.

4.7 Work Plan and Outcomes

The work plan of this technology consists of both technical tasks as well as business-related tasks for obtaining the needed funding to complete the technical tasks. Establishment of success will be based on both business and technical task accomplishments. Technical success will be based on establishing conductivity of composite materials and the ability to withstand multiple lightning strikes. Business success will be based on proving or changing the business model canvas hypothesis to establish a successful student start-up company at OSU.

Table 8: Technical milestone for year 2018

Tasks	2018											
	Month											
	1	2	3	4	5	6	7	8	9	10	11	12
Procurement of materials	▮	▮										
Preliminary high conductivity formulations and optimization of films	▮	▮	▮	▮	▮	▮						
Conductivity and mech. property measurements			▮	▮	▮	▮	▮	▮	▮			
Composite fabrication with graphene films			▮	▮	▮	▮	▮	▮	▮	▮		
Measurement of composite properties				▮	▮	▮	▮	▮	▮	▮		
Preliminary lightning strike tests									▮	▮		
IP & patent formalization			▮	▮	▮	▮	▮	▮	▮	▮	▮	▮

Table 9: Funding and business milestone for year 2018 and 2019

Milestone descriptions	2018												2019											
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12
Establishing startup company				▲																				
I-Corps, NSF grant applications for future R&D	▮	▮	▮	▮	▮	▮	▮	▮																
Venturewell E-team Stage I	▮	▮	▮																					
Venturewell E-team stage II application and stage II				▮	▮	▮	▮	▮																
Provisional patent	▲																							
Non-provisional patent														▲										
OSU TDC Stage I project (application in Spring 2018, Project to start in Fall 2018							▮	▮	▮	▮	▮	▮	▮	▮	▮	▮								
Customer discovery and establishing customer interest	▮	▮	▮	▮	▮	▮	▮	▮																
Business Plan competitions (Love's cup, Baylor, Rice, Oregon)			▲											▲		▲	▲							
NSF Phase I SBIR application											▲													

40

CHAPTER V

CONCLUSIONS

The objectives of this research is to identify an easy process to develop conducting composite thin film without using any hazardous solvent during processing. To achieve this research goal, the dispersion of graphene nanoplatelets were carried out in viscous solution of PVP followed by oxidative polymerization of PANI in presence of SO_4^{--} and Cl^- ions as dopant. The evaporation of this final solution was carried out in nitrogen atmosphere to obtain a flexible conductive thin film.

The in situ polymerization of Polyaniline in the graphene dispersed PVP solution was carried out successfully. The FTIR result confirmed that even after addition of 20 wt% graphene, there is no change in the electronic-like band of PANI: PVP blend. Which confirms that there is no additional functional group or chemical bonding with graphene. The conductive film is as a result of binding of graphene nanoplatelets with one another via conductive polymer blend. The effective conductive path is achieved via PANI: PVP blend.

The surface topology of polymer/graphene thin films were investigated using SEM. It is confirmed that with the current process of dispersion of graphene, 20 wt% graphene is the maximum limit that can be incorporated in polymer matrix in order to get continuous flexible conductive composite thin films. It is found that at 20 wt% graphene, large size and number of voids are created increasing the brittleness and discontinuity of composite thin films.

Thermal stability of PANI, PANI/PVP and PANI/PVP/Graphene composite were studied using TGA. For only PANI sample, the incorporation of water and loosely bound molecules is

higher when dopants are Cl^- ions in comparison to when dopant is SO_4^{--} ion. Which confirmed that the Sulfuric acid is preferred than the Hydrochloric acid as polymerization medium. For PANI/PVP blend, both acidic medium result shows same thermal stability but in comparison to PANI, incorporation of PVP in PANI decreases the weight loss due to degradation of dopant ions by 10% -15%. This confirms that the incorporation of PVP improves the stability of thermal and conductive properties of PANI. The TGA curves of PANI/PVP/0%graphene and PANI/PVP/20%graphene shows that the incorporation of graphene in polymer reduces the incorporation of water and loosely bound molecule. In addition, the thermal stability of polymer chain increases because of incorporation of graphene. An increase of 148.1^{O}C is confirmed for degradation of polymer backbone because of presence of graphene nanoplatelets.

Conductivity measurement were carried out using four probe set up for polymer/graphene composite with graphene content from 0 wt%, 5 wt%, 10 wt% and 20 wt%. It is noticed that the conductivity of composite with 20 wt% of graphene is about 39 times higher than the no graphene composite. This confirms the charge transfer between PANI and graphene because of delocalized electrons.

The change is stress and strain % were evaluated through tensile testing via DMA. A trend of increase in stress and decrease in strain % is noticed. The increase in stress by 48.32% and decrease in strain % by 13.465% is confirmed for polymer/20 wt% graphene composite thin film.

A clear and well defined potentiality of commercialization of conductive composite thin film was recognized through 50+ customer interview. Companies like GE, Dexmet cooperation and Boeing are interested to coordinate for further research, development and testing. This innovative idea of commercialization of conductive composite thin film establish a strong base for student Start-up Company.

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

This research work can be taken as a starting phase for the preparation of conductive composite films. Since some previous work has shown the IR treatments during polymerization of aniline increases chance of formation of thin fiber like structure[54] which is supportive for increasing conductive properties, in future, the formation of polyaniline chain in presence of IR radiation could be looked. From literature, the super capacitive properties of PANI has been found an interesting work. In order to get an idea about the capacitive properties of conductive composite thin films, impedance analysis can be performed in future. We have explored the Ultrasonication process for the dispersion of graphene in polymer, in future, wet ball-milling process can be exploited to achieve good level of dispersion[55, 56] as large voids were noticed in SEM for higher wt% of graphene in the present work. Additive manufacturing is another growing industry in recent timeframe. In future, preparation of 3D printing conductive ink for printing antenna structure on composite materials will be another interesting topic for research and development. In addition, the study of through thickness conductivity of composite with conductive thin films in between carbon prepreg layers would be an interesting work in future.

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