

**Conducting flexible paper**  
**based on**  
**Bacterial cellulose and Polyaniline composites**

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# Declaration

I declare that this written submission represents my ideas in my own words, and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

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# Approval Sheet

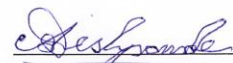
This thesis entitled “**Conducting flexible paper based on bacterial cellulose and polyaniline composite**” by **Divya Anand** is approved for the degree of Master of Technology from IIT Hyderabad.



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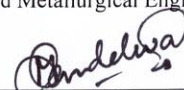
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*Dedicated to my parents*

*And*

*Dr.Mudrika Khandelwal*

# Abstract

Development of new greener material for conducting paper is sought for applications such as security paper, actuators, and anti-static packaging. In the present work a conducting paper/conducting polymer composite is prepared using bacterial cellulose and polyaniline. It is required that these materials possess high conductivity, low density and good mechanical integrity. This work aims to produce bacterial nanocellulose (BC) - polyaniline (PANI) nanocomposites by *in situ* polymerization. The advantages of using BC over filter paper are evident from the results in this report because of its ultrafine network structure, sufficient porosity, high purity and crystallinity, good mechanical properties, water holding capability and low environmental impact. Strategies to produce these composites from BC membranes and nanowhiskers have been reported. The BC/PANI composites thus formed are expected to possess good electrical conductivity and capacitance, in addition to excellent mechanical properties and flexibility. In this work, synthesis of polyaniline has been optimized and preliminary results on BC-PANI composites have been shown.

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# NOMENCLATURE

BC	Bacterial Cellulose
FP	Filter Paper
PANI	Polyaniline
MWCNTs	Multi Walled Carbon Nanotubes
HCl	Hydrochloric Acid
APS	Ammonium per Sulphate
FESEM	Field Emission Scanning Electron Microscopy
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infra-Red spectroscopy
PPMS	Physical Property Measurement System

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# Chapter 1

## Introduction and Aim

### 1.1 INTRODUCTION

The demand for lighter and flexible electronics, in applications including sensors, actuators and anti-static packaging, is increasing with the advancement of technology. A light weight material with good conductivity, mechanical strength and flexibility is needed to address the requirements. This thesis takes a baby step in developing such a conducting composite which can be made in form of a paper.

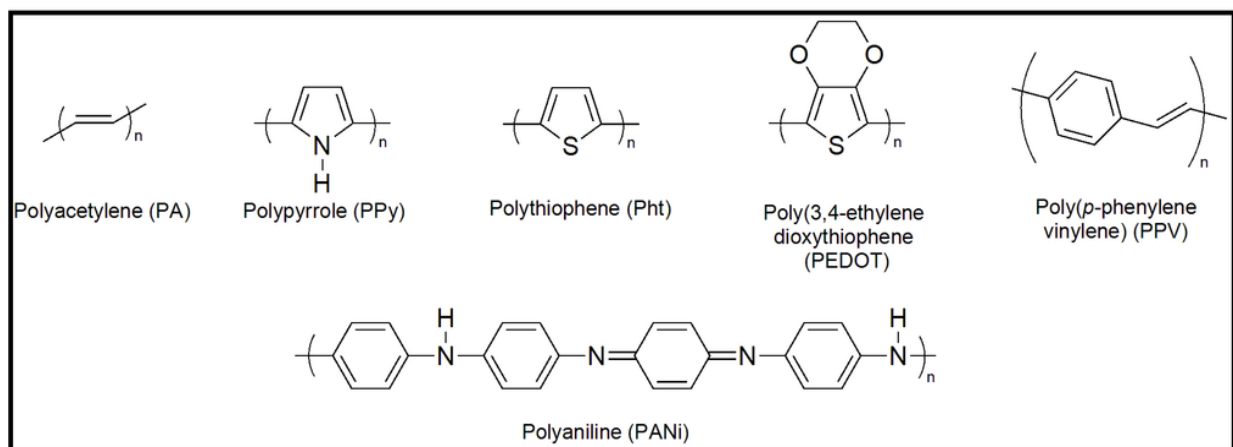
The needs for low weight and flexibility justifies the use of polymers in such applications. However, polymers have always been traditionally believed to be non-conducting. Interestingly, by 1970s some of the polymers were re-discovered with respect to their conducting properties [1,2]. Those polymers included polyacetylene, polypyrrole, and polyaniline, which have also been shown in Figure 1[1-3]. These polymers show conductivity along with being light weight and low in density. Amongst the library of conducting polymers, polyaniline has been found to be more promising. Some of the reasons include ability to exhibit different oxidation states characterised by the different colours, good environmental stability, easy and low cost synthesis and good conductivity. These properties are discussed in details in the next chapter.

While conducting polymers are a solution to the problem posed above, these polymers lack in mechanical integrity which inhibits formations of flexible paper-like material. Given this, it is required to produce polyaniline composites with substrates which are light weight, good in mechanical properties, processible, low in environmental impact, and cost effective. A reasonable amount of work has been done in recent years to develop composites with various polymeric substrates such as cellulose, rubber, plastic and textile to prepare PANI composites.

Cellulose and its derivatives are highly favoured because they are eco-friendly and found in abundance in nature. It can be obtained from many sources, however the most common forms used for composites include cellulose pulp, cellulose derivatives, cotton cellulose, micro-crystalline cellulose and bacterial cellulose membranes [4,5]. Amongst them, bacterial cellulose



(BC) is particularly advantageous because of its purity (close to 100%), high crystallinity and *in situ* manipulability. BC is generally produced as a dilute hydrogel with above 95% water, which implies high holding capacity [6,7]. It has attractive mechanical properties and unique nanostructure which implies that it is one of the best materials to be used as a substrate in such composites. It can also be used in the form of nanowhiskers with high aspect ratio.



**Figure 1. Structure of some conducting polymers**

The basic strategy to prepare the proposed polymer composite is *in situ* polymerization (i.e., polymerization at the time of composite formation) in order to obtain homogeneity and better bonding within the composite. The two strategies that are used for this work include using the BC sheet as it is and the second by preparation of nanowhiskers. These can be further subdivided into various other ways like the dip process, drop process, both solutions mixed together, matrix post polymerization and polymerization after sheet formation.

## 1.2 AIM

- Identification of the material to be used through literature review.
- Comparison of BC and FP as a substrate material
- Optimisation of polyaniline synthesis (IUPAC report, “There are as many polyaniline as the number of people who prepare them”[8])
- Composite preparation using various strategies by *in situ* polymerization of PANI on BC.
- Flexibility and conductivity measurements

### 1.3 THESIS OUTLINE

The research (in literature and from experiments), carried out towards the objectives stated in the previous section, is presented in the following seven chapters. A summary of all the relevant findings about conducting polymers, polyaniline, bacterial cellulose and conducting composites reported in the literature has been presented in chapter 2. The gap in literature and need to carry out the proposed research to partially fill the gap is evident. The relevant materials (substrates, chemicals), various characterization techniques (SEM, FTIR, PPMS, two probe) used for assessing the composition, internal structure, and properties in this project have been discussed in Chapter 3.

Chapter 4 presents a comparative study between filter paper and bacterial cellulose with respect to microstructure and solvent/liquid penetration. The difference is expected due to the difference in cellulose sources and different processing techniques. This chapter also deals with characterization of nanowhiskers produced from bacterial cellulose. Nanowhiskers have been used as an alternative substrate system which is discussed in chapter 6. Chapter 5 focuses on optimization in polyaniline synthesis with focus on parameters such as oxidizing agent (APS) to Aniline ratio, solvent systems, time and temperature of polymerization and drying.

Chapter 6 focuses on various strategies for composite formations. The focus of all the strategies is to perform *in situ* polymerization of aniline in the cellulosic matrix. Further in this chapter two kinds of matrices have been used - bacterial cellulose and filter paper. Another variation has been created by producing nanowhiskers which has been discussed in chapter 4 section 4.5. The first section briefly discusses various strategies for composite preparation. The subsequent sections are dedicated to the most encouraging strategy and characterization of the composites produced by this strategy.

Chapter 7 discusses about the scalability, cost of production, comparison to the existing products and most importantly effect on the environment. Chapter 8 presents the main conclusions made from the work presented in the thesis. This work has established a basic ground work in field of conducting paper from bacterial cellulose and polyaniline. Further work needed to optimize and produce a product useful for the society is also discussed.

# Chapter 2

## Literature Review

### 2.1 CONDUCTING POLYMER

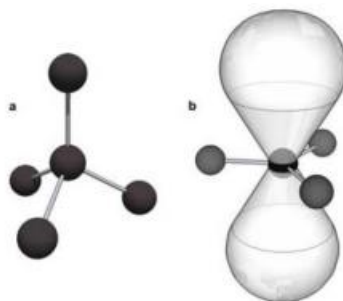
It was believed that polymers are excellent insulators which provide significant advantages for many application [9]. However, this concept was contradicted when reports of conducting or semiconducting polymeric materials such as polyacetylene and polyaniline began to appear in the literature [10]. It was only when the doping of polyacetylene had succeeded that a new class of conducting polymers with the remarkable ability to conduct electrical current began to develop enormous technological and scientific interest. Doped polymers are often referred to as “intrinsically conducting polymers”. This to differentiate them from other polymers because a polymer may acquire conductivity by loading with conducting particles such carbon black, metal flakes, or fibers of stainless steel.

The intrinsically conducting polymers (ICPs), more commonly known as “synthetic metals”, refer to the large class of organic polymers which possess not only the mechanical properties and processibility of conventional polymers, but also unique electrical, electronic, magnetic, and optical properties of metals, which conventional polymers do not have [1,2].The unifying characteristic property of this class of polymers is the intrinsic ability of the conjugated polymer backbone to support electrical conduction. Thus the fundamental property of conducting polymers is that electrical conductivity is achieved by charge carrier (electron or hole) through a  $\pi$  conjugated backbone. Since the initial discovery of polyacetylene and developments of methods to dope the polymer, the conducting polymer field has continued to accelerate at an unexpectedly rapid rate.

### 2.2 CONDUCTIVITY OF INTRINSICALLY CONDUCTING POLYMERS

Conventional and conducting polymers, both, are formed by the repetition of a monomer unit. While conventional polymers are formed only by  $\sigma$  bonds ( $sp^3$  hybridization), conducting polymers contains both  $\sigma$  and  $\pi$  bonds ( $sp^2$  hybridization) as shown in Figure 2.1. The localized electrons in the  $\sigma$ - bonds form the backbone in a polymer chain; they are very strong bonds

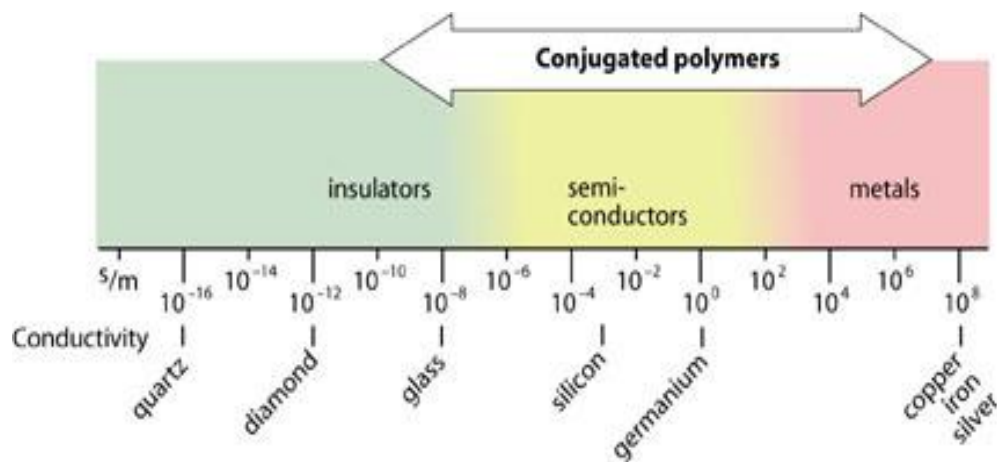
which make the polymer stable and electrically insulating as there are no free electrons in the system. On the other hand, the electrons in the  $\pi$ -bonds are delocalized along the chain, being easier to excite and conferring the optical and electronic properties to the polymer [1,2] . Therefore, in order to achieve electrical conductivity, the polymer should contain conjugation (an alternation between single and double bonds) along its chain. Moreover, conjugated polymers needs to be “doped” in order to render conductivity, by adding mobile charges and delocalizing the electrons along the backbone. This process is done through oxidation or reduction and the polymer becomes p-doped or n-doped. By oxidation, an electron is removed and the polymer becomes positively charged (being stabilized locally by an anion). Those charges then migrate in the polymer film creating electrical current. This type of doping is the most common, because in the reductive doping, the n-doped polymer becomes very unstable when exposed to ambient atmosphere as it will spontaneously oxidize, ending up in the neutral state again [11,12]. One important feature of this doping process is that the process is reversible, i.e. the doped polymer can be made neutral through a “de-doping” process. And this feature makes conducting polymers very interesting for many applications.



**Figure 2.1. Illustration of  $sp^3$  (a) and  $sp^2$  (b) hybridization [12]**

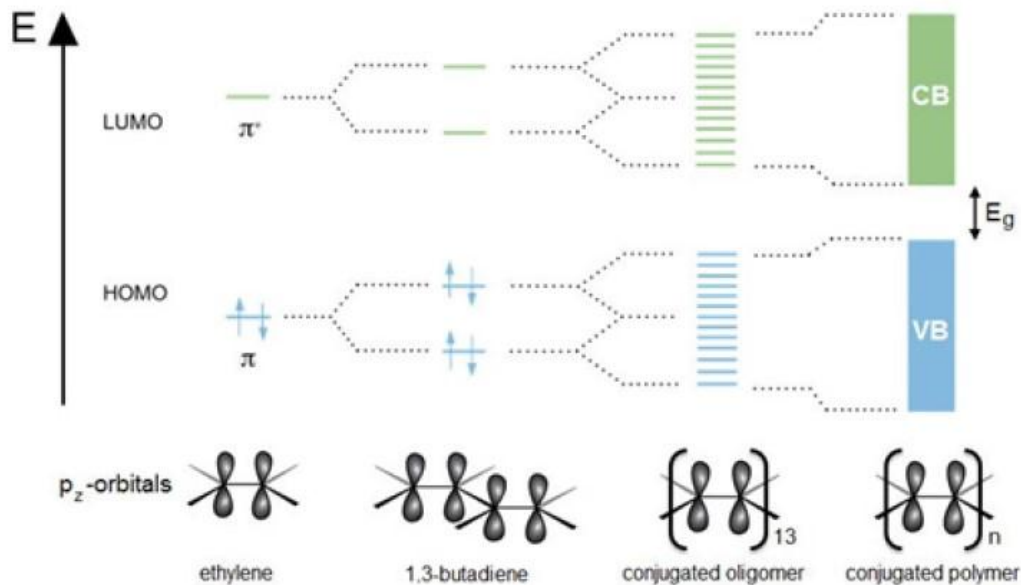
Conducting polymers are not one dimensional conductors, they are quasi one dimensional. If they were truly only one dimensional, no matter how high the conductivity of an individual chain, the bulk conductivity would be zero since a single molecule does not stretch from one end of a bulk piece of a conducting polymer to the other. The electrons have to be transported from one polymer chain to the other. At lower doping levels, this transportation is called “hopping” or “phonon-assisted quantum mechanical tunneling” [13]. At higher doping levels (metallic state), band structure will develop - both along the polymer chains and between chains. Conductivity

value for conducting polymers lies in between insulators and metal i.e., similar to semiconductors as shown in Figure 2.2. For example, doped polyacetylene has conductivity comparable to good conductors such as copper and silver, whereas in its original form it is a semiconductor.



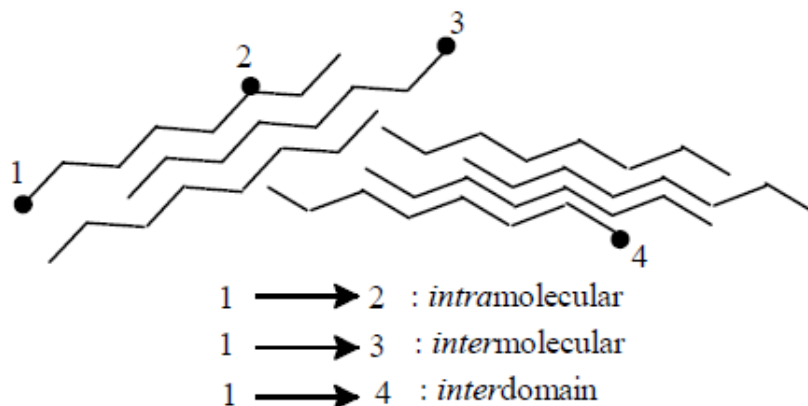
**Figure 2.2. Conductivity range for conducting polymers [1,2,14]**

The pi electron form conduction bands which is illustrated in Figure 2.3 for simple conjugated polymer.



**Figure 2.3. Energy band diagram of conjugated polymer**

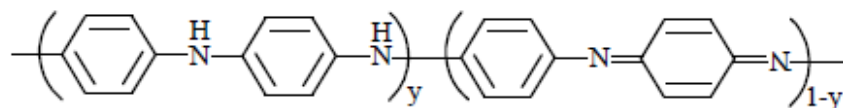
The bulk conductivity of conducting polymer consists of contributions from intramolecular, intermolecular and interdomain [1,2] . As schematically shown in Figure 2.4 (below), electrons have to move along a polymer chain (intramolecular contribution), then “hopping” to another polymer chain (intermolecular contribution) and from one domain to another (interdomain contribution) so that the polymer can be electrically conductive. Interdomain may be from one crystalline region to another crystalline region or between crystalline region and amorphous regions. Due to the “hopping” nature of charge transportation, the conductivity should increase with decrease in the distance between polymer chains. Therefore it is expected that increase in crystallinity or alignment of polymer chains will increase the bulk conductivity of conducting polymers [2].



**Figure 2.4. Schematic view of bulk conductivity of conducting polymers [83]**

### 2.3 POLYANILINE

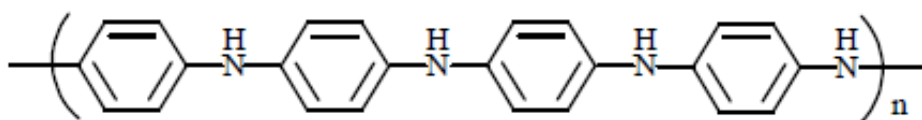
Polyaniline was first known in 1835 as “aniline black”, a term used for any product obtained by the oxidation of aniline. A few years later, Fritzche [15], carried out the tentative analysis of the products obtained by the chemical oxidation of this aromatic amine. Subsequent investigators [15,16] have verified these results, and similar observations have been made during the oxidation of aqueous hydrochloride acid solutions of aniline. The polyaniline, probably one of the earliest known synthetic polymer, [17,18], refer to a large class of conducting polymers which have the following general formula (Figure 2.5):



**Figure 2.5: Polyaniline general formula**

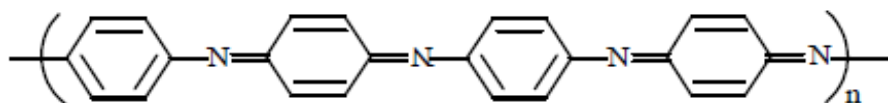
A large variety of derivatives can be prepared through substitution in the ring or on the N atoms. One of the special properties of polyaniline is that it can be doped by photonic acids. Thus, the properties of the doped polymer can be turned by incorporating different dopant anions. It has been found that polyaniline can exist in three different, isolable oxidation states at the molecular level [19]. They are the leucoemeraldine oxidation state, the emeraldine oxidation state, and the pernigraniline oxidation state. Other oxidation states are the result of physical mixture of these oxidation states.

(i) **Leucoemeraldine base:** the fully reduced form of non-doped polyaniline. It is composed solely of reduced units as shown below:



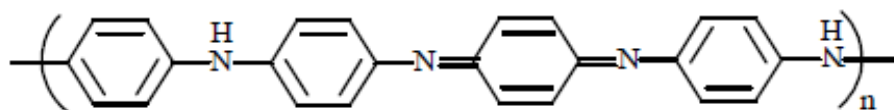
**Figure 2.6. Leucoemeraldine Base**

(ii) **Pernigraniline base:** the fully oxidized form of non-doped polyaniline. It is composed solely of oxidized base units as shown below:



**Figure 2.7. Pernigraniline Base**

iii) **Emeraldine base:** the intermediate oxidation state of polyaniline. It is composed of equal amounts of alternating reduced base and oxidized base units as shown below:



**Figure 2.8. Emeraldine Base**

The oxidation state of polyaniline can be precisely determined by volumetric titration methods using  $\text{TiCl}_3$  [20]. Several spectroscopic methods such as FTIR, Raman, and UV/Vis can also provide qualitative information about the average oxidation state of the polymer [21,22].

### 2.3.1 SYNTHESIS

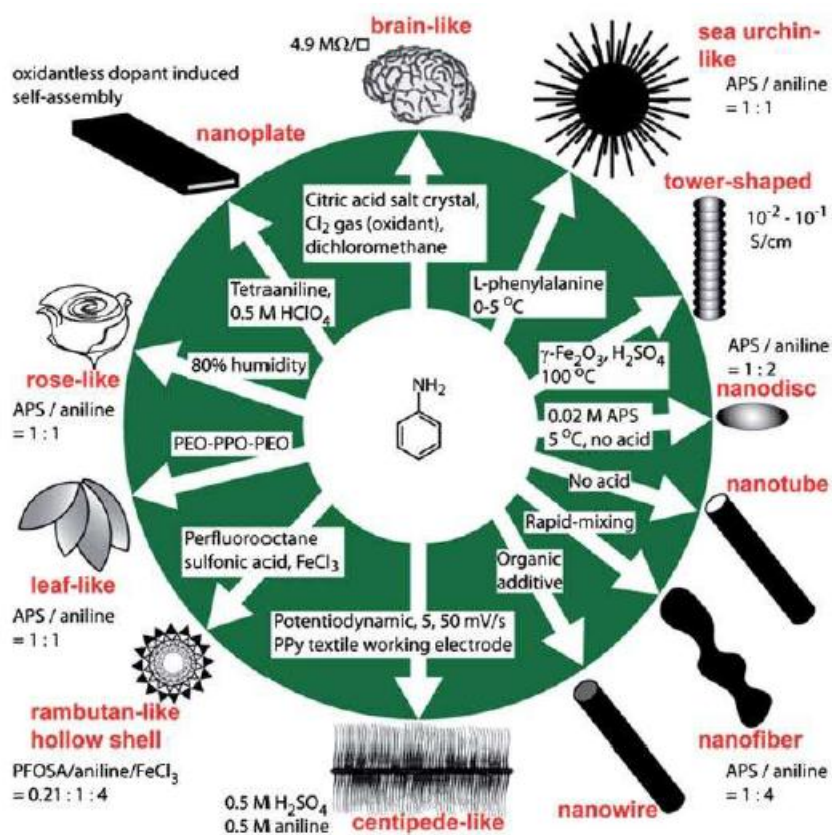
The interest in polyaniline as an important conducting polymer has increased significantly over the past decade, resulting in a number of review articles published a few years ago [17,23-26]. Polyaniline can be chemically or electrochemically synthesized by the oxidative polymerization of aniline monomer in the presence of aqueous acid e.g., 1M HCl solution [27]. The polymer obtained is an emeraldine salt. A number of groups have looked at the reaction conditions necessary to produce optimum quality polyaniline [23,28,29].

For chemical synthesis, there are many oxidizing agents, including ammonium peroxydisulfate [22,27] hydrogen peroxide [30], ferric chloride [31] and ceric nitrate and sulfate [32,33]. Typically the ratio of oxidizing species to aniline has been reported to be oxidant/aniline  $\sim 1.25$  (a stoichiometric equivalent of oxidant) [28,34]. Other chemical polymerizations incorporate a stoichiometric deficiency of the oxidant with respect to aniline (oxidant/aniline ratio  $\sim 0.25$ ) [22]. A typical chemical synthesis of polyaniline is carried out in aqueous 1M HCl at temperatures between  $\sim 0^\circ\text{C}$  and  $\sim -4^\circ\text{C}$  [24]. It has also been shown that higher molecular weight polyaniline ( $M_w > 100,000$ ) can be synthesized when the polymerization is carried out at temperatures below  $-20^\circ\text{C}$  [35]. More recently, reports of high molecular weight polyaniline synthesized at temperatures of between  $-30^\circ\text{C}$  and  $-40^\circ\text{C}$  appeared, which used lithium chloride as an inert solute to keep the reaction mixture mobile [29,31,35]. These used either a large molar deficit of ammonium persulfate oxidant to aniline, which gave a low yield of polymer, or electrochemical polymerization; but no attempts were made to assess the structural quality of the



polyaniline. The neutral form of polyaniline, emeraldine base, can be converted from the fully protonated emeraldine salt by de-protonation of the polymer with aqueous ammonium hydroxide.

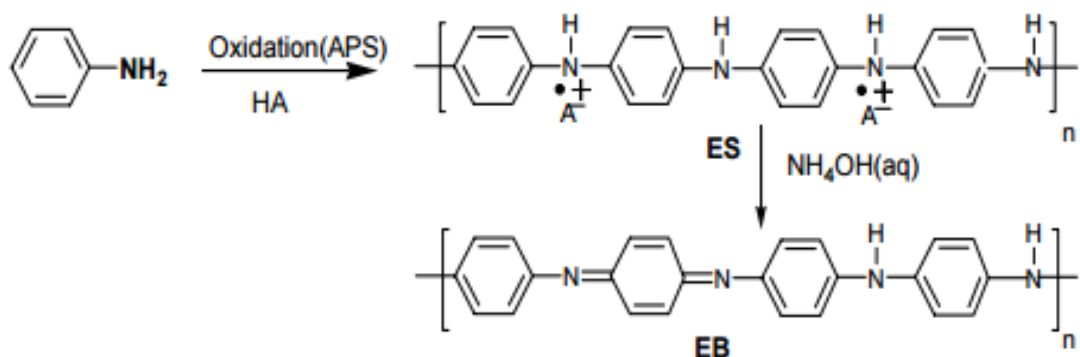
Polyaniline also exists in several nanostructured morphologies such as spheres, ribbons, fibres and so on. The morphologies are dependent on reaction conditions and synthesis chemistry. Some of the findings are summarized in Figure 2.9. The morphology of polyaniline plays an important role as it also affects mechanical properties and electrical conductivity.



**Figure 2.9. Variation in polyaniline morphologies obtained with different synthesis parameters [36]**

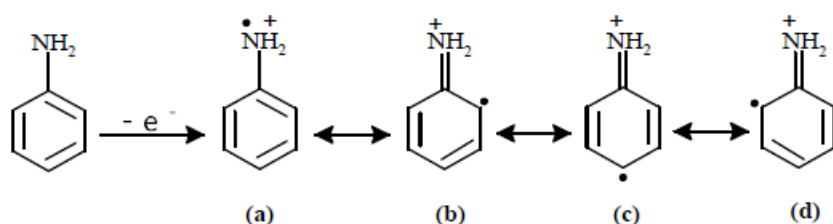
### 2.3.2 POLYMERIZATION MECHANISM

No matter whether polyaniline (PANI) is synthesized electrochemically or chemically, there is a close similarity in their polymerization mechanism. A general scheme for PANI formation is shown below in Figure 2.10 [37].



**Figure 2.10.** A general scheme for polymerization of aniline using APS as an oxidant [37]

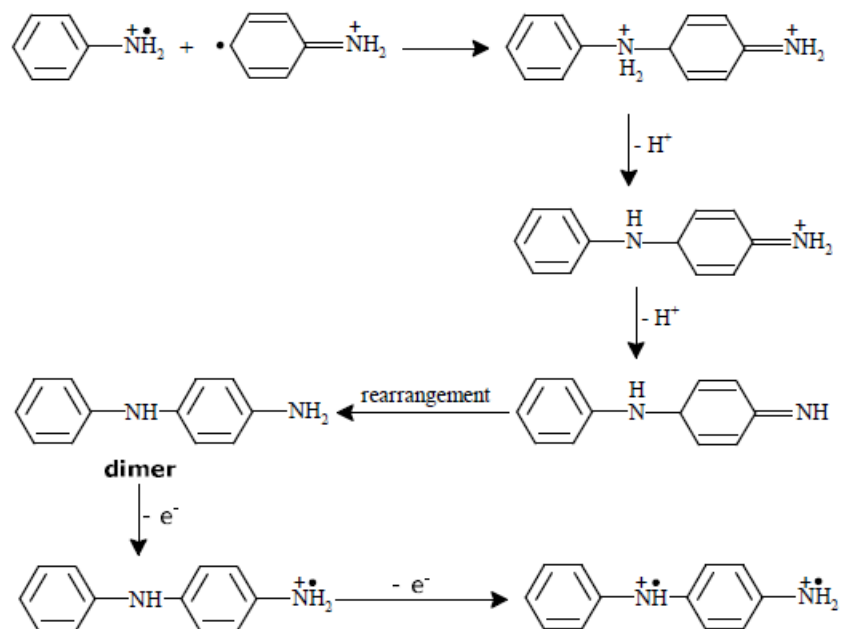
In both cases, the polymerization process proceeds via the following mechanism. The first step is the formation of the radical cation by an electron transfer from the  $2s$  energy level of the aniline nitrogen atom, as shown in Figure 2.11.



**Figure 2.11.** The formation of the aniline radical cation and its different resonant structures [37]

The formed aniline radical cation has several resonant forms, in which (c) is the more reactive one due to its substituent inductive effect and absence of steric hindrance. The next step corresponds to the dimer formation by the so-called “head-to tail” reaction between the radical

cation and its resonant form (most probably form (c)) in acidic medium. Then the dimer is oxidized to form a new radical cation dimer, as shown in Figure 2.12.



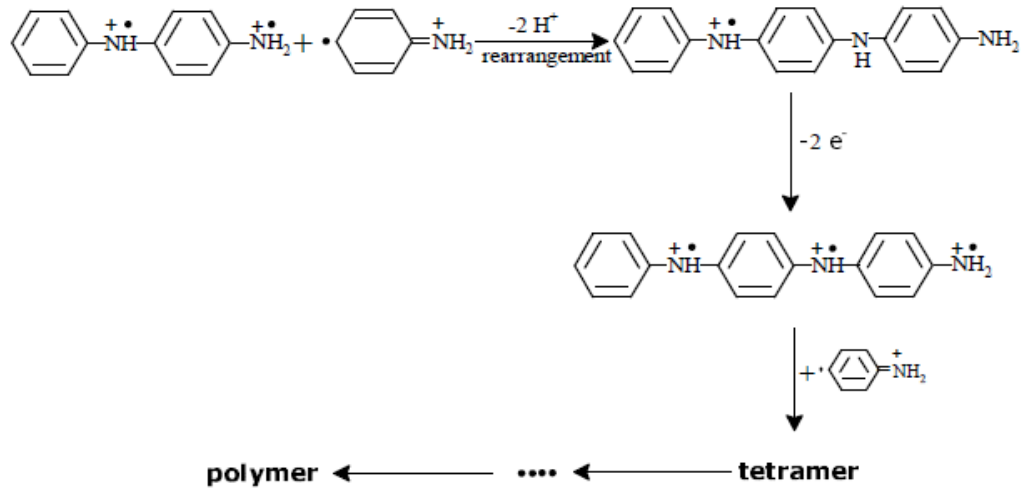
**Figure 2.12. Formation of the dimer and its corresponding radical cation [37]**

Next, the formed radical can react either with the radical cation monomer or with the radical cation dimer to form, respectively, a trimer or a tetramer. If this continues, similar to the above steps, the polyaniline (PANI) polymer is finally formed as shown in Figure 2.13.

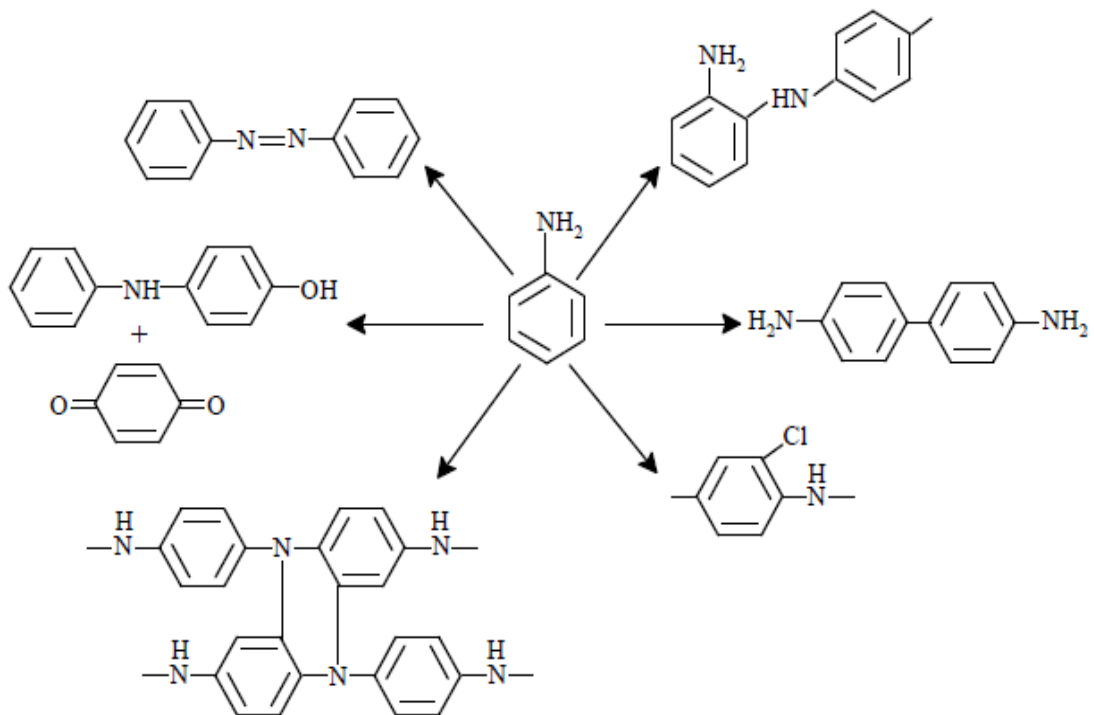
At the end, it should be mentioned that beside idealized formation of p-coupled PANI chain in the reactions described above, some side reactions have also been identified.

- coupling of aniline and its oligomers in “ortho” position;
- formation of benzidine groups (“tail to tail” coupling);
- chlorine substitution in aromatic ring (in systems with HCl and LiCl or NaCl);
- formation of N=N bonds (azo groups);
- formation of N-C<sub>Ar</sub> grafting bridges between chains;
- polymer hydrolysis (=O and -OH groups).

All those reactions introduce undesirable elements to the structure of PANI and are considered as chain defects.



**Figure 2.13. One possible way of PANI polymer formation [37]**

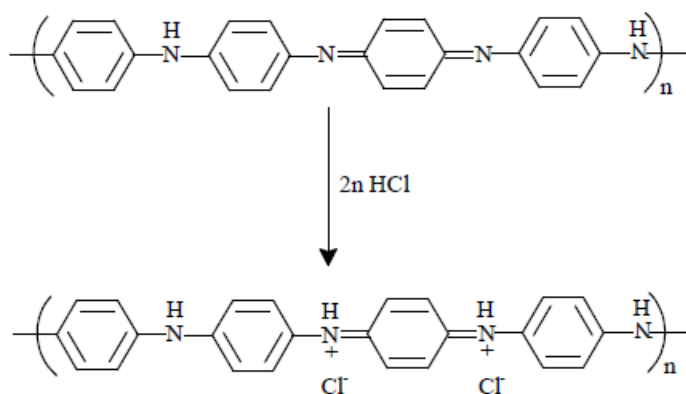


**Figure 2.14. Side reaction occurring during polyaniline synthesis [82]**

### 2.3.3 PROTONIC ACID DOPING OF POLYANILINE

Among the three oxidation states, only polyaniline in the emeraldine oxidation state can undergo non-redox doping process to convert it to a highly conductive form. The emeraldine base form of

polyaniline was the first example of the “doping” of an organic polymer to a highly conducting metallic regime by a charge transfer process in which the number of electrons associated with the polymer remained unchanged during the doping process [38]. This was first accomplished by treating emeraldine base with aqueous protonic acids as shown below. The conductivity of the doped polymer (by HCl) is about 9 to 10 orders of magnitude greater than that of non-doped polymer (~1-5 S/cm; 4 probe; compressed powder pellet).



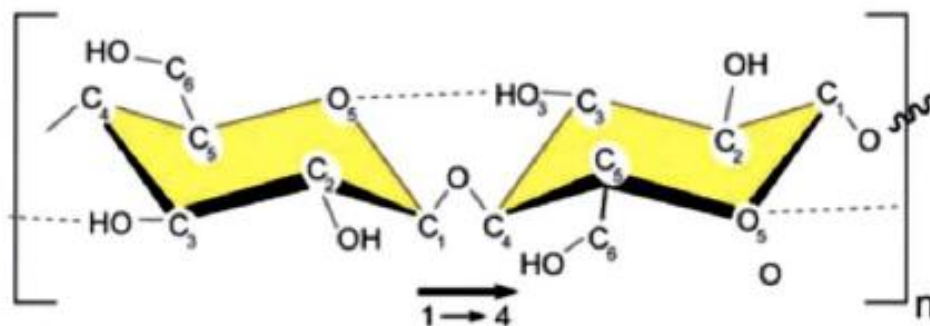
**Figure 2.15: Protonic Acid Doping of Polyaniline [83]**

## 2.4 BACTERIAL CELLULOSE

Cellulose is the versatile gift of nature [39]. It is one of the most abundant naturally occurring biopolymer[40]. Cellulose can be found from various forms depending upon its sources and processing techniques. Cellulose and its derivatives are highly favoured because they are eco-friendly. It can be obtained from many sources; however the most common forms used for composites include cellulose pulp, cellulose derivatives, cotton cellulose, micro-crystalline cellulose and bacterial cellulose membranes [3,4]. Amongst them, bacterial cellulose (BC) is particularly advantageous because of its purity which is close to 100%, high crystallinity and *in situ* manipulability. It is produced by the bacteria, principally of genera called as *gluconoacetobacter xylinus*[41]. It has attractive mechanical properties and unique nanostructure which implies that it is one of the best materials to be used as a substrate in such composites [5].

### 2.4.1 CHEMICAL STRUCTURE

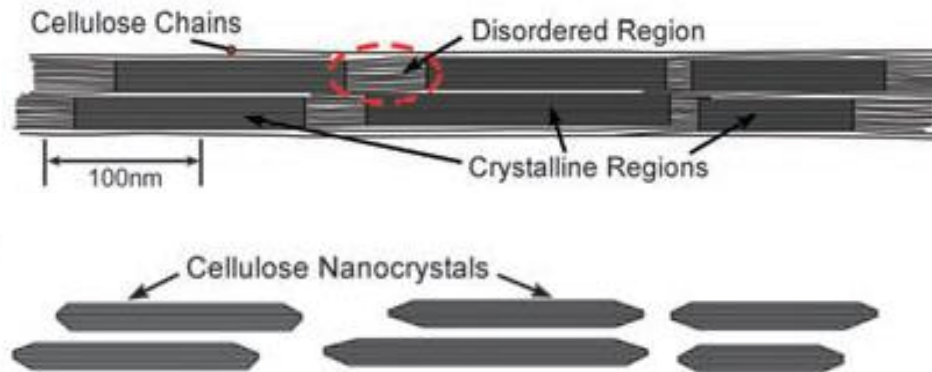
Cellulose is an organic compound with the formula  $(C_6H_{10}O_5)_n$  a polysaccharide consisting of a linear chain of several hundred to many thousands of  $\beta(1\rightarrow4)$  linked D-glucose units [42,43]. Figure 2.16 shows the chemical structure of cellulose showing  $\beta$ -1,4 linkage, where cellulose is the basic repeating unit [44].



**Figure 2.16. Chemical formula of cellulose showing  $\beta$ -1,4 linkage, where cellulose is the basic repeating unit [44]**

### 2.4.2 STRUCTURE OF BACTERIAL CELLULOSE

Cellulose occurs as a supra-molecular arrangement of poly-glucan chains in the form of thin long semi-crystalline microfibrils in all native cellulose forms, irrespective of its source. BC is generally produced as a dilute hydrogel with above 95% water, which implies high holding capacity [7]. Bacterial cellulose microfibrils are 6-10 nm by 30-50 nm in dimensions. The structure of bacterial cellulose microfibril is shown in Figure 2.14. The crystalline regions are separated by amorphous regions. These amorphous regions are more susceptible due to disorder and low density. Therefore, nanowhiskers can be derived from cellulose microfibrils by using acids which preferentially attack glycosidic bond in amorphous regions.



**Figure 2.17. Schematic representation of the effect of acid hydrolysis on microfibril [45]**

### **2.4.3 MECHANICAL PROPERTIES**

The techniques such as Raman, AFM indentation, AFM 3 point bend and inelastic X-ray scattering have been used for measurement of mechanical properties of cellulose nanoparticles. A wide distribution of properties have been reported, owing to the variation in the measurement techniques, and variation within the material such as crystallinity, relative distribution of the two polymorphs, anisotropy, and defects.

One of the common techniques has been *in situ* tensile test combined with XRD to measure strain. The values for elastic modulus in axial direction ( $E_A$ ) ranging from 120 to 138 GPa have been reported [46,47]. The elastic modulus in axial direction ( $E_A$ ) = 220 GPa and elastic modulus in transverse direction ( $E_T$ ) = 15 GPa have been reported using inelastic x-ray scattering (IXS) [46]. While the reported values of  $E_A$  for BC nanocrystals were 78 GPa [48] and 114 GPa [49] measured by AFM- three point bend and Raman, respectively.

### **2.5 CONDUCTING PAPER (COMPOSITE)**

Conducting paper constitutes a class of materials suitable for applications such as sensors, actuators, anti-static packaging, biomedicines, protective clothing and potential battery applications [50]. For the above mentioned applications, it becomes necessary to develop

materials which possess good conductivity, mechanical flexibility, along with light weight, low cost [50-52]. With increasing environmental concern, green materials and processing technologies are also sought.

Given these requirements, polymers are bound to play an important role due to their exceptional low density. Polyaniline (PANI) is one of the preferred conducting polymer, while others include polypyrrole, polyacetylene, polythiophenes and so on, because of its good environmental stability, high electrical conductivity, facile synthesis and relatively low synthesis cost [53]. Unlike other conducting polymers, PANI can be synthesized in water with an oxidizer [54]. It exists in various forms which differs in chemical and physical properties [55]. It exhibits three different oxidation states (a) leucoemeraldine- clear and colourless (b) emeraldine-green for the emeraldine salt and blue for emeraldine base (c) (per) nigeraniline-blue/violet [50,56]. The green protonated (emeraldine) state is usually preferred because it has conductivity higher than many polymers and similar to semi-conductors [50]. Its sensitivity to changes in its physicochemical properties makes it a suitable candidate in various applications such as organic electrodes, sensors, and actuators[55,57]. However, there are several problems associated with using PANI for the proposed purpose. One major problem with conducting polymers is lack of mechanical integrity. Therefore the difficulty in processibility limits its potential applications [58]. Also efforts are needed to optimize protocol of PANI synthesis in each lab [8].

Large ranges of materials with good mechanical properties have been used as substrates to produce PANI composites. These substrates include cellulose, rubber, plastic and textile [50,59-61]. Cellulose and its derivatives are preferred because of their abundance, low environmental impact. It can be obtained from many sources such as trees, plants, algae, fungi and bacteria. However, the most common forms used for conducting nanocomposites include cellulose pulp, cellulose derivatives, cotton cellulose, micro-crystalline cellulose and bacterial cellulose membranes [3,4]. Amongst them, bacterial cellulose (BC) is particularly advantageous because it is obtained as a highly pure and crystalline dilute hydrogel with above 95% water, which implies high holding capacity [7]. It has attractive mechanical properties and unique nanostructure which implies that it's one of the best materials to be used as a substrate in PANI composites [5].

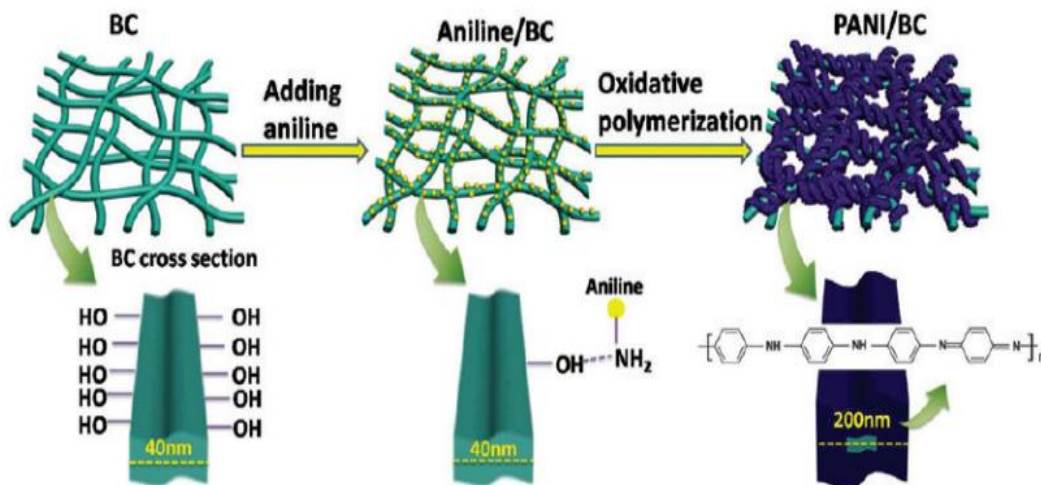


Recently, some research groups explored the preparation of BC/PANI conducting nano-composites through the *in situ* polymerization of aniline monomers in BC membrane because of their ability to conduct electrically and be used in flexible electrode materials [4,5,7,62-64]. Morphology and composition could be the key factors to obtain remarkable results from BC/PANI nano-composite [4,5,7, 62-64] . There have been several researchers with similar or different approaches working on it.

In one of the cases, BC/PANI Composite was prepared via *in-situ* polymerization on the surface of BC interfacially, but it has insufficient data with respect to milli-mole concentrations of reactants [5]. Another similar work by another group for attaining flexible electrically conductive nanocomposite based on BC & PANI was able to achieve the highest conductivity value of  $5 \times 10^{-2}$  S/cm [54]. According to them conductivity of the composite is dependent on dopants concentration and twistability which are directly proportional i.e., more the twist higher will be the conductivity, beyond a range. They showed that HCl is better than sulfuric acid, ammonium sulphate, benzene sulphonic acid etc., since they haven't mentioned the dimension or weight of BC used; replicating the results is not possible.

One of the group from Finland, published a paper on processible PANI Suspensions through *in-situ* polymerisation of nanocellulose concluded that the nanofibrillated cellulose/PANI composite paper exhibits a percolation threshold of electrical conductivity of 4.57 vol. % of PANI content, at which the corresponding conductivity was  $2.6 \times 10^{-5}$  S/cm, which was well above the antistatic criterion of  $10^{-8}$  S/cm[65]. Further people prepared BC/PANI composite using dodecyl benzene sulphonic acid (DBSA) using in-situ polymerization of aniline [66]. Time and temperature required for the polymerization reaction is missing in the paper though they concluded it by specifying the optimum in-take of DBSA/PANI to for higher bulk conductivity. The schematic diagram of formation of PANI/BC nanocomposites by them is shown below at Figure 2.14.

Some groups have worked to analyze the potential application of Cellulose/PANI composite for the treatment of synthetic reactive dye bath effluent [22]. They found that it can be used for removal of reactive dyes from the aqueous solutions and synthetic dye bath effluent. They last some supporting data for reference.



**Figure 2.18. Schematic diagram of the formation of PANI/BC nanocomposites [66]**

Flaked shape morphology of BC/PANI composite synthesized via *in situ* polymerization was also studied by a group in China [7]. They added oxidant and dopant drop-wise and finally filtered the suspension. According to them, they achieved an electrical conductivity of 5.1 S/cm by just manipulating the ordered flake-type nanostructure of the composite.

Another group working on BC composite with MWCNT and PANI[67], has proved the potential of the composite for flexible electronics application by stating that the flexible BC-MWCNTs-PANI hybrid electrode exhibits appreciable specific capacitance ( $656 \text{ F g}^{-1}$  at a discharge current density of  $1 \text{ A g}^{-1}$ ) and remarkable cycling stability with capacitance degradation less than 0.5% after 1000 charge–discharge cycles at a current density of  $10 \text{ A g}^{-1}$ [67].

Another group's studying cellulose/PANI nanocomposite indicated the removal of 95.9, 91.9, 92.7, and 95.7 % of RBBR, RO, RV, and RBK, respectively from textiles, and it decolorized 82 % of dye bath effluent [69] .

## 2.6 SUMMARY AND AIM OF THE THESIS

The proposed work aims to provide direction towards greener, mechanically stable, flexible, light weight conducting paper from bacterial cellulose and polyaniline composite.

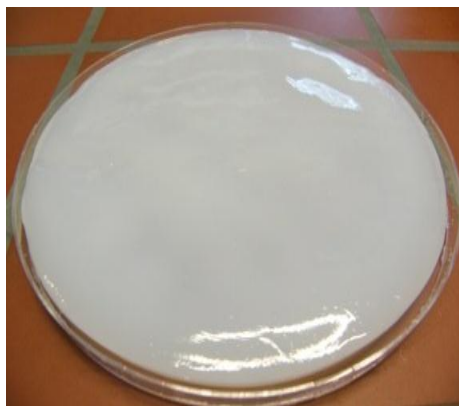
# Chapter 3

## Materials and Techniques

In the following sections, materials, various characterization techniques used for assessing the composition, internal structure, and properties in this project have been discussed. Preparation techniques for polyaniline and composites are discussed in the subsequent chapters.

### 3.1 MATERIALS

Aniline monomer ( $\geq 99.5\%$  pure) and ammonium persulphate (APS,  $\geq 98.0\%$  pure) were purchased from Sigma-Aldrich, India. Toluene and hydrochloric acid were ordered from Alfa Aesar India. Aniline was used in glove box which allows handling in inert environment as aniline is moisture sensitive. Laboratory prepared bacterial cellulose was donated by Dr. Mudrika Khandelwal from her previous work for this research (Figure 3.1).



**Figure 3.1. Bacterial Cellulose**

### 3.2 TECHNIQUES

#### 3.2.1 FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM)

FESEM is used to produce real space magnified images of the surface. It helps in determining the surface morphology i.e. the shape and size of topographic features on the sample surface.

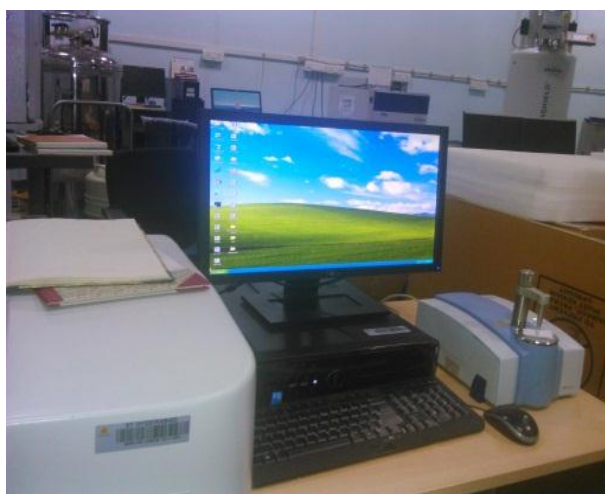
Zeiss Supra 40 (Figure 3.2) FESEM was used at an accelerating voltage of 5 kV. If the conductivity of the sample was low or nil, then the samples were gold coated using sputtering technique before microscopy.

### 3.2.2 FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FTIR)

TENSORS 37 Brukers FTIR (shown in Figure 3.3) was used for identifying polyaniline formation and characterization of composites. It is a powerful tool for identifying the chemical bonds (functional groups) which are activated by characteristic IR light region. Pellets made for conductivity measurement were used for FTIR before electrode coating. The scan was performed in the frequency range  $400$  to  $4000\text{ cm}^{-1}$ . Barium sulphate was used as the reference sample.



**Figure 3.2. Field Emission-Scanning Electron Microscopy**



**Figure 3.3. Fourier Transform Infra-red Spectroscopy setup**

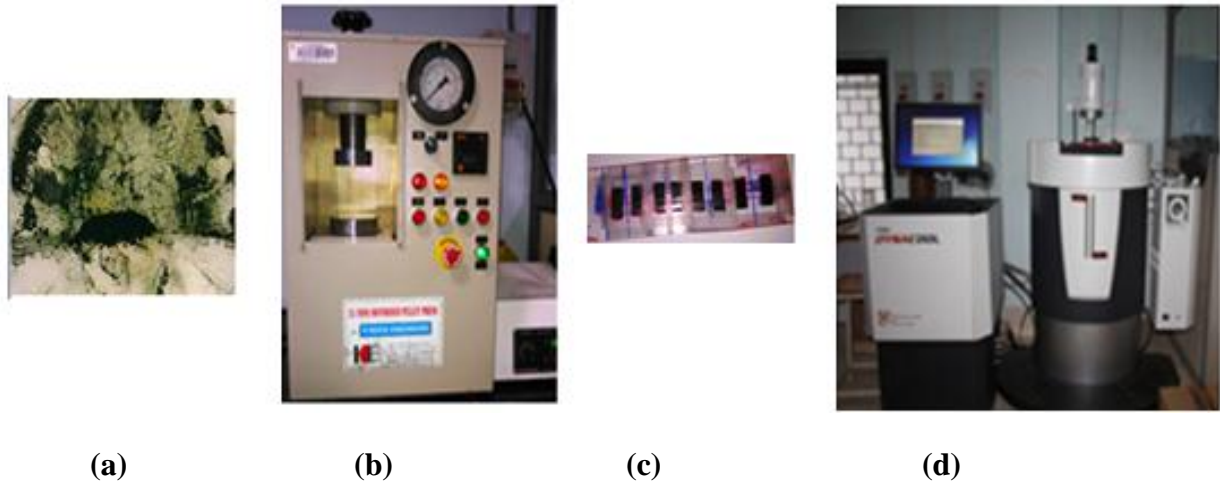
### 3.2.3 PHYSICAL PROPERTY MEASUREMENT SYSTEM (PPMS)

It is an open architecture, variable temperature-field system, designed to perform a variety of automated measurements. It is used to study electrical as well as magnetic behavior of materials. The instrument was used to measure resistance at variable temperature in order to obtain resistivity of the material or indirectly



**Figure 3.4. Physical property measurement system**

the conductivity. DYNACOOOL PPMS (Figure 3.4) was used with 4V. Polyaniline is obtained in powder form, from the synthesis, which is first converted into a pellet using a compaction press and then masked manually followed by coating platinum using e-beam deposition. Finally, the coated sample is kept inside the PPMS instrument at 4 probe mode and variation in resistance with temperature was obtained.



**Figure 3.5. Sample preparation to measurement in PPMS (a) PANI powder (b) compaction press used to make pellet (c) masking for electrode deposition and (d) PPMS instrument**

**Calculation:-**

$$R = \rho l/a$$

Where

R=Resistance in Ohm

$\rho$ =Resistivity in Ohm centimeter

l=length between the middle to probes in centimeter

a=cross-sectional area of corner probes in centimeter

With this formula resistivity is calculated and it is inversely related to conductivity

$$\text{Conductivity}(\sigma) = \frac{1}{\rho(\text{Resistivity})}$$

The unit of  $\sigma$  is Siemen per centimeter

Arrhenius equation was used to calculate activation energy

$$\sigma = \sigma_0 e^{\left(\frac{-E_a}{K_b T}\right)}$$
$$\ln \sigma = \ln \sigma_0 - \frac{E_a}{K_b T}$$

Where

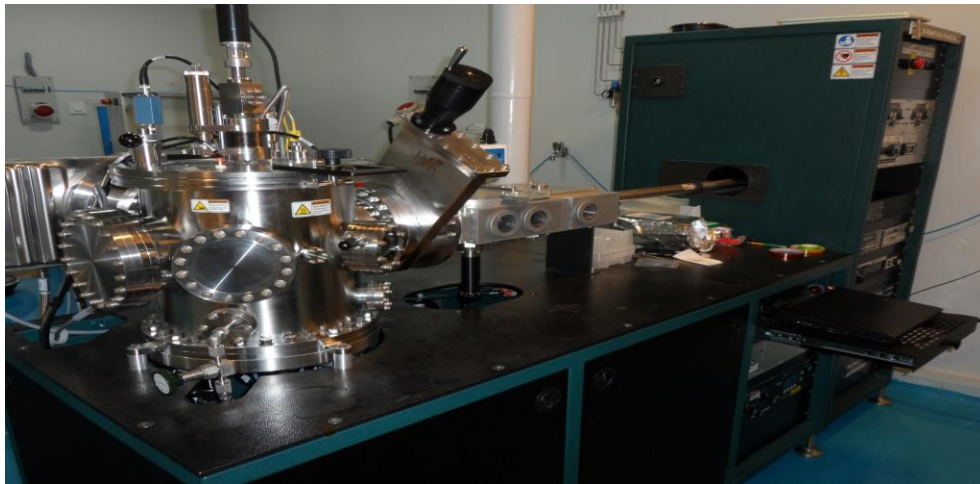
$E_a$ =Activation energy of the material

$K_b$ =Boltzmann constant

T =Temperature

### 3.3.4 HORIZONTAL MULTI-TARGET SPUTTERING

It is used for electrode deposition on the sample surface for conductivity measurement. It helps in coating the material sample with other materials such as silver, gold, and platinum with the desired thickness. It was purchased from AJA International, USA and it comprises of 3 Direct Current Guns and 1 Radio Frequency Gun (Figure 3.6).



**Figure 3.6. Horizontal multi-target sputtering**

### 3.2.5 LASER SCANNING CONFOCAL MICROSCOPY

Confocal microscope allows imaging at different focal planes in a transparent and translucent samples. Bacterial cellulose nanowhisker sheets were imaged at different depths to create a 3-D image. The instrument used for this work was Leica shown in Figure 3.7.



**Figure 3.7. Laser Scanning Confocal Microscopy**

### **3.2.5 TWO PROBE STATION**

It is used for conductivity measurement. The set-up was indigenously made and is shown in figure 3.8. It was also equipped to measure change in resistance with temperature.



**(a)**



**(b)**

**Figure 3.8: Two probe station a) front view and b) top view**

# Chapter 4

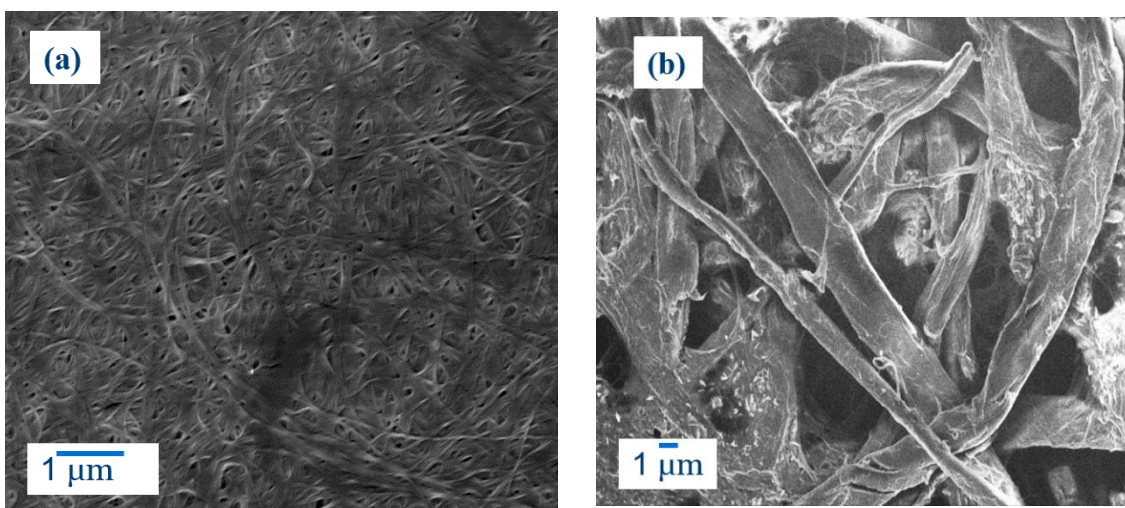
## Study of Substrate

### BACTERIAL CELLULOSE (BC) VS. FILTER PAPER (FP)

In the project, FP and BC have been proposed as suitable substrates for making composites with PANI. This chapter presents a comparative study between FP and BC with respect to microstructure, solvent/liquid penetration. The difference is expected due to the difference in cellulose sources and different processing techniques. This chapter also deals with characterization of nanowhiskers produced from bacterial cellulose. Nanowhiskers would serve as alternative substrate system which will be discussed in chapter 6.

#### 4.1 MICROSTRUCTURE

The microstructures of BC and FP were studied by SEM. Figure 4.1 shows the SEM images of BC and FP, which indicates fibrous structure in both. The difference lies in the dimension of fibers forming the two cellulose matrices. The BC fibers are of 20-30 nm in width whereas FP is composed of 20-30 microns fibers. The variation in width is more prominent in FP as compared to BC.



**Figure 4.1. SEM images of (a) bacterial cellulose and (b) filter paper**



## 4.2 SOLVENT PENETRATION KINETICS

In order to perform *in situ* polymerization, permeability of matrix is very important because for the polymerization to happen, the solvents carrying monomer and oxidizing agent should travel inside the matrix. From the literature, toluene and HCl are commonly used in polyaniline synthesis [67,70,71]; therefore the study has been carried out on these liquids. Figure 4.2 shows that the rise in weight is quicker and more for BC as compared to FP when they are immersed in the liquids. This is because of high porosity and higher holding capacity of BC [40,72,73].

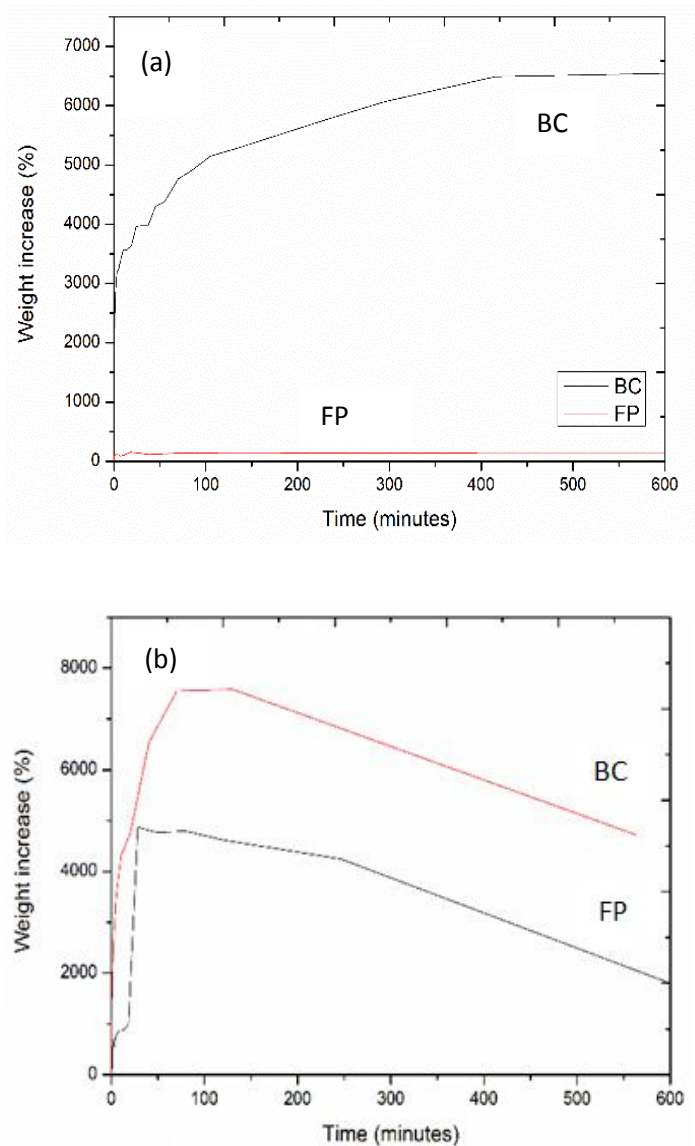
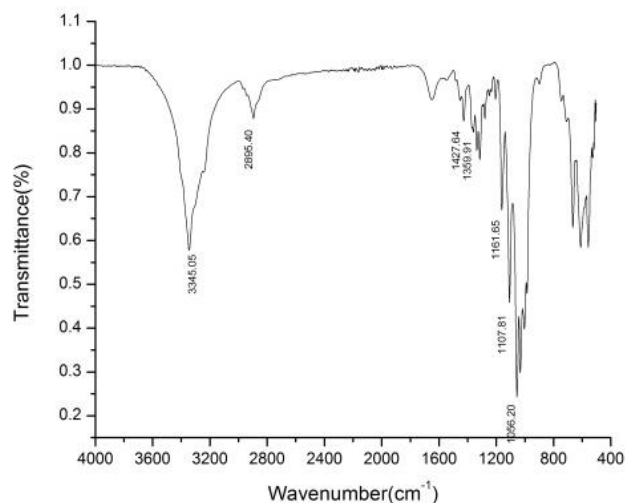


Figure 4.2: Gain in weight with time for BC and FP in (a) toluene and (b) 1M HCl

### 4.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

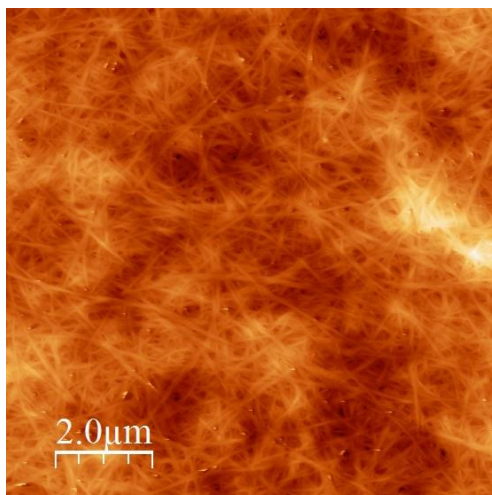
FTIR is used to identify the functional group present in the material. BC and FP are both made up of cellulose hence show similar peaks. FTIR spectra of BC is shown in Figure 4.3. The absorption band at 3345/cm and 2895/cm of BC can be assigned to the hydroxyl group of cellulose and C-H stretching of CH<sub>2</sub> respectively. Absorption band at 1427/cm can be assigned to CH<sub>2</sub> symmetric bending. Absorption band at 1359/cm corresponds to the stretching and bending modes of hydrocarbons in the cellulose backbone. The peak at 1161/cm can be assigned to the symmetric stretching of the bridge C-O groups. The absorption peaks at 1107.81 and 1056/cm can be assigned to the skeletal vibrations involving C-O stretching. Similar observation was obtained for FP, however the intensity of peaks were different.



**Figure 4.3. FTIR of Bacterial Cellulose**

### 4.4 ATOMIC FORCE MICROSCOPY (AFM)

The AFM images was obtained from Dr. Mudrika Khandelwal's doctoral thesis. For AFM analysis, dilute suspensions of microfibrils were prepared by sonication. However, the drying of the droplets on a silicon substrate for microscopy resulted into aggregation and thus the measurements were carefully done to avoid error due to overlap. Figure 4.4 shows the image of the BC microfibril suspension obtained by AFM. Like SEM, AFM confirmed the presence of long, uniform and even endless ribbon-like morphology. The heights of the microfibrils was found to vary from 7 to 10 nm.



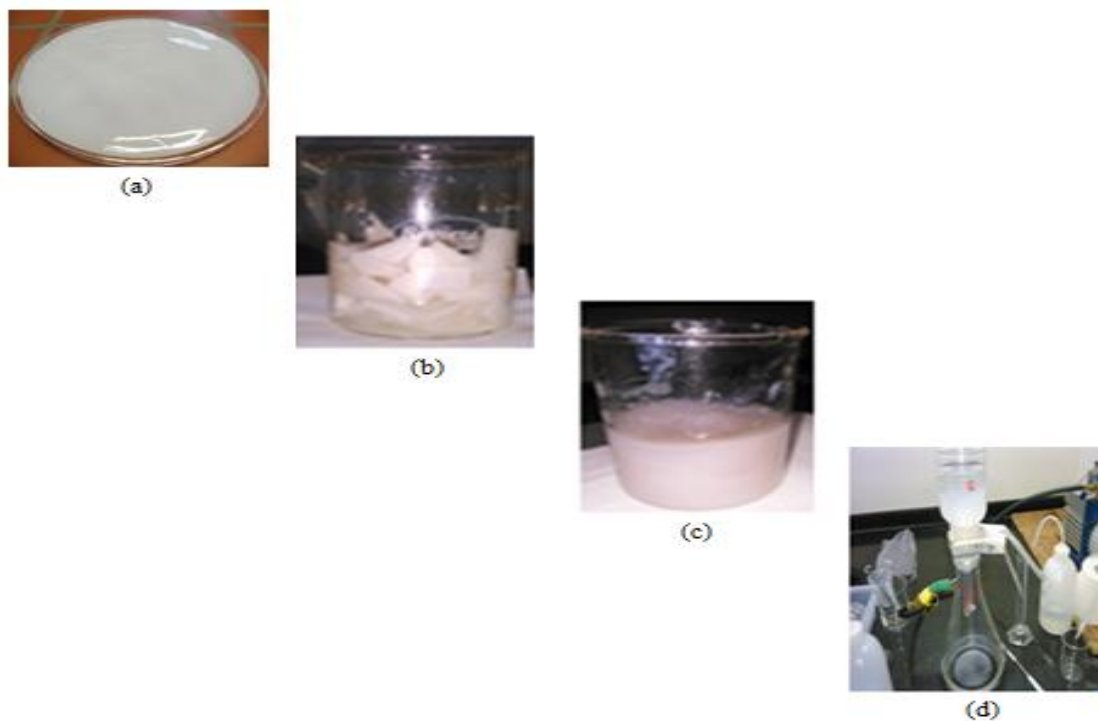
**Figure 4.4. AFM image of bacterial cellulose**

#### **4.5 CELLULOSE NANOWHISKERS AND FILM FORMATION**

Cellulose exists as microfibrils as shown in SEM and AFM above, which are long endless and entangled. A common practice to get rid of entanglement in cellulose is to produce nanowhiskers by acid hydrolysis which is discussed below.

##### **a) Preparation**

The dried cellulose was treated with dilute sulphuric acid to obtain dispersion of cellulose nanowhiskers. About 0.2 g of dried cellulose was treated with 20ml of 40% (vol/vol) sulphuric acid. The mixture was stirred with a magnetic stirrer and the temperature was maintained to be 45-50°C. This was continued till an off white to yellowish dispersion was obtained. The suspension was neutralised by exchanging the acid with deionised water using a 0.45 µm PTFE filter paper placed in a Buchner funnel. This was repeated till all acid was squeezed out and the pH of the suspension passing through the filter was close to 5-6. Finally, the suspensions were collected from the funnel.



**Figure 4.5. Stages for nanowhisker preparation (a) BC membrane (b) BC pieces in acid solution (c) after magnetic stirring at 40-50 °C for 4-5 hours (d) washing by filtration assembly with DI water**

#### **b) Nanowhiskers Film/Sheet**

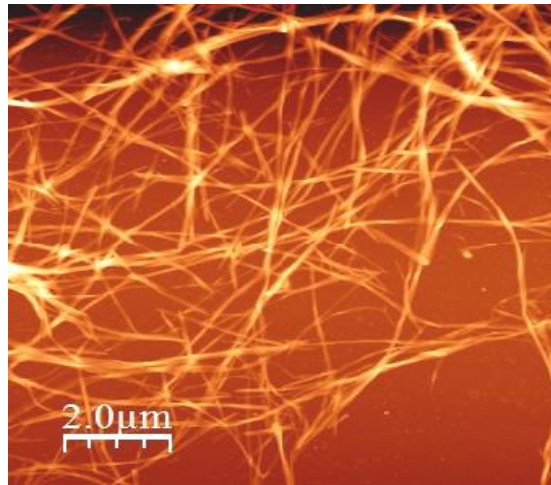
Films/Sheets were prepared from BC nanowhiskers using the filtration set up as shown in Figure 4.5. Optimization was carried out by varying the weight of nanowhiskers in order to obtain a flexible, uniform and preferably transparent sheet. It was seen that a reasonably good sheet was obtained by 27 mg in BC nanowhiskers as shown in Figure 4.6. It should be noted that flexibility of the sheet is dependent on the total weight of film.



**Figure 4.6. Photograph of nanowhisker film obtained from 27 mg of BC nanowhiskers**

### c) AFM of Nanowhiskers

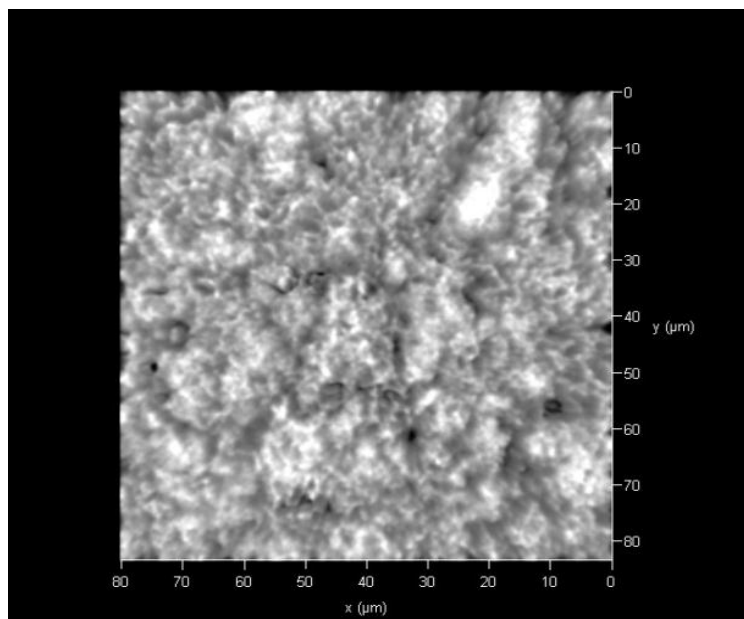
The AFM images was obtained from Dr. Mudrika Khandelwal's doctoral thesis. It can be seen from Figure 4.7 that these nanowhiskers are finite in length while the un-hydrolysed material comprised of endless microfibrils. The heights of the BC nanowhiskers are in the range of 6-10 nm and length in the range of 1-3 micron. Similar observation is expected for FP; however the dimensions will be different [84].



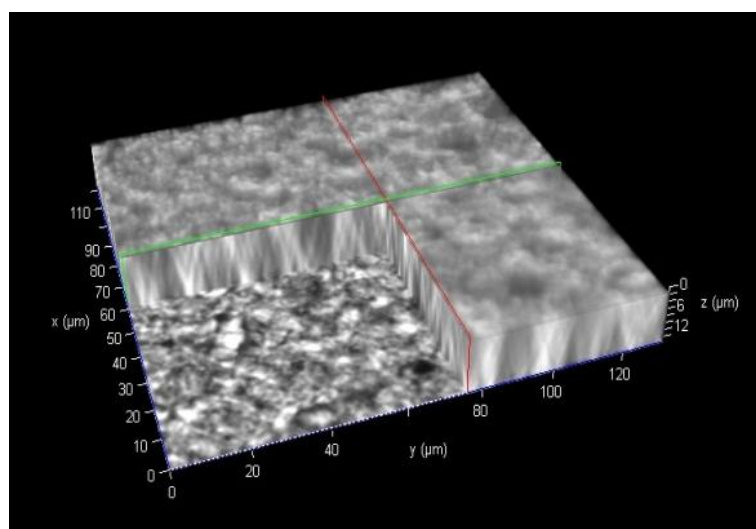
**Figure 4.7. AFM image of nanowhiskers**

### d) Films Confocal Laser scanning microscope

The Confocal Laser scanning microscope helps in obtaining a high resolution image of our partially transparent films or rather to acquire in-focus images from selected depths . Figure 4.8 shows the porosity in the material and thickness of the sample from side view. The thickness of the film calculated using this instrument is 14  $\mu\text{m}$ .



(a)

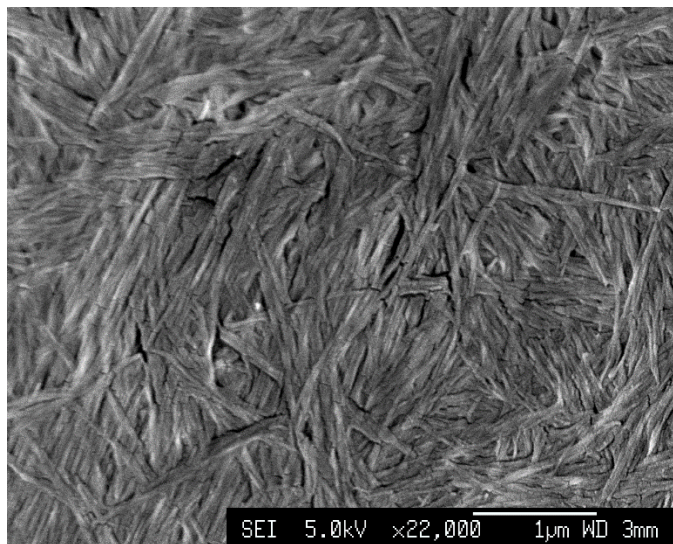


(b)

**Figure 4.8. Confocal microscopy images of nanowiskers film showing (a) pores in the film (b) thickness through side view**

### e) Films SEM

Figure 4.9 shows the SEM image of BC nanowiskers sheet. It indicates the entanglement and association of cellulose nanowiskers leading to sheet formation. Locally organized domains of nanowiskers may be observed.



**Figure 4.9. SEM of BC nanowhiskers sheet**

#### **4.6 SUMMARY**

1. Comparative study of BC and FP has been presented.
2. BC was found to be more suitable because of its higher porosity and uniform nanofibrous network.
3. FTIR shows similarity in the chemical structure of both-bacterial cellulose and filter paper.
4. Acid hydrolysis produced nanowhiskers which have much shorter length than the fibrils present in FP and BC.
5. Nanowhisiker can produce flexible film. Characterization of the films by confocal microscopy and SEM are presented.

# Chapter 5

## Polyaniline Synthesis and Characterization

It is said “there are as many polyaniline as the number of people who prepare them” [8]. So, it is important to optimize the synthesis of polyaniline in laboratories individually. Moreover the property of polyaniline varies with slight variations in synthesis chemistry, synthesis conditions, and morphology. It is evident from the literature that several factors such as acid, oxidant, solvent, temperature etc. play role in properties of polyaniline [19,21,22,26,36,38,66,74-76]. Therefore, in this work, a few of the factors have been optimized –oxidizing agent to Aniline ratio, solvent systems, time, and temperature.

### 5.1 SYNTHESIS AND CHEMICAL CHARACTERIZATION

Aniline is insoluble in water, but soluble in toluene. Also its salt with hydrogen chloride is soluble in water. In the effort to obtain an optimal strategy for polyaniline synthesis, both the ways have been tried. Ammonium persulphate is soluble in water and this aqueous solution was used for synthesis. An additional variation was created by adding HCl to APS solution. HCl has been used as the doping agent. The 0.2 M of APS solutions and 0.2 M of Aniline solution have been used in all cases. A list of solvent variations is presented in Table 5.1.

**Table 5.1. Variation in reactants for polyaniline synthesis**

Experiment	Solvent for Aniline	Solvent for APS
1	50% HCl (6 M )	Water
2	Toluene	Water
3	50% HCl (6 M )	50% HCl (6 M )
4	Toluene	50% HCl (6 M )



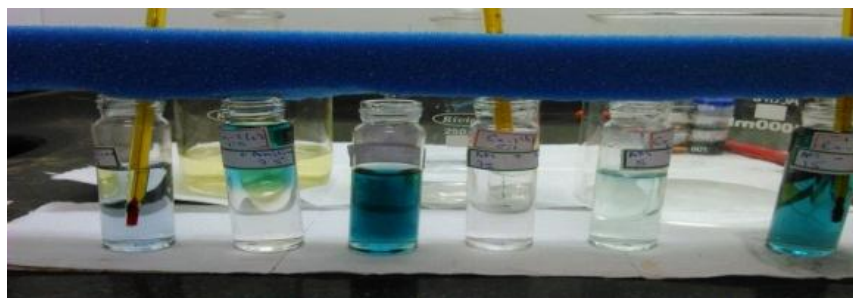
### 5.1.1 0.2 M APS in water and 0.2M Aniline in 50% HCl (6 M )

0.2M APS in water and 0.2M Aniline in 50% HCl were mixed in 6 different ratios of volume to vary the APS to aniline molar ratio as listed in table 5.2. The reaction between APS solution and aniline solution proceeds by showing colour changes as shown in Figure 5.1. Experiment 1\_1 and 1\_6 corresponded to the molar ratio of aniline to APS (1:1) but the total volumes were different. This was done to see the effect of volume on synthesis and yield.

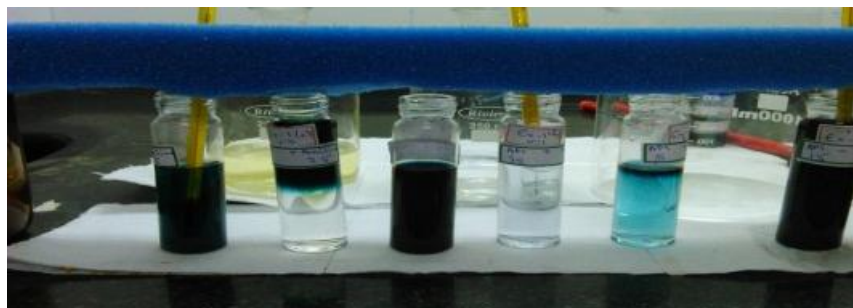
**Table 5.2. Variation in the concentration of 0.2 M APS in water and 0.2M Aniline in 50% HCl (6 M )**

Sr. no.	Milimolar ratio of APS to Aniline	Volume of the system	APS (ml)	Aniline (ml)
1_1	5:1	30	25	5
1_2	3:1	20	15	5
1_3	1:1	20	10	10
1_4	1:1	30	15	15
1_5	1:3	20	5	15
1_6	1:5	30	5	25

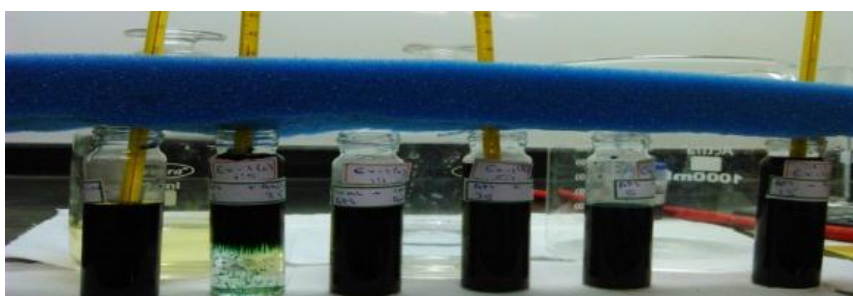
Figure 5.2 shows the powders obtained from all six variations in experiment 1. Powders from experiment with excess APS were violet to purple in colour. On the other hand, powders obtained (1\_3 to 1\_6) from synthesis with APS to aniline milimolar ratio 1:1, 1:3 and 1:5 showed the characteristic green colour of the conducting oxidation state of polyaniline – emeraldine. The powders prepared (1\_1 to 1\_6) were characterized by FTIR. The FTIR spectra obtained from 1\_1 and 1\_2 were similar and is represented in Figure 5.3. The FTIR spectra for other samples which yielded green powder were also same but different from that for brown powder. The spectra for green powder matched well with polyaniline spectra.



(a)



(b)




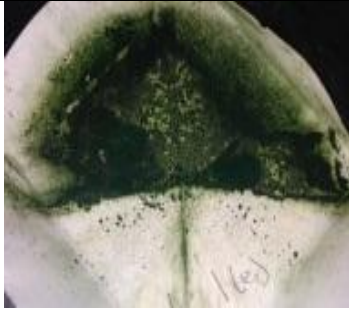




(c)

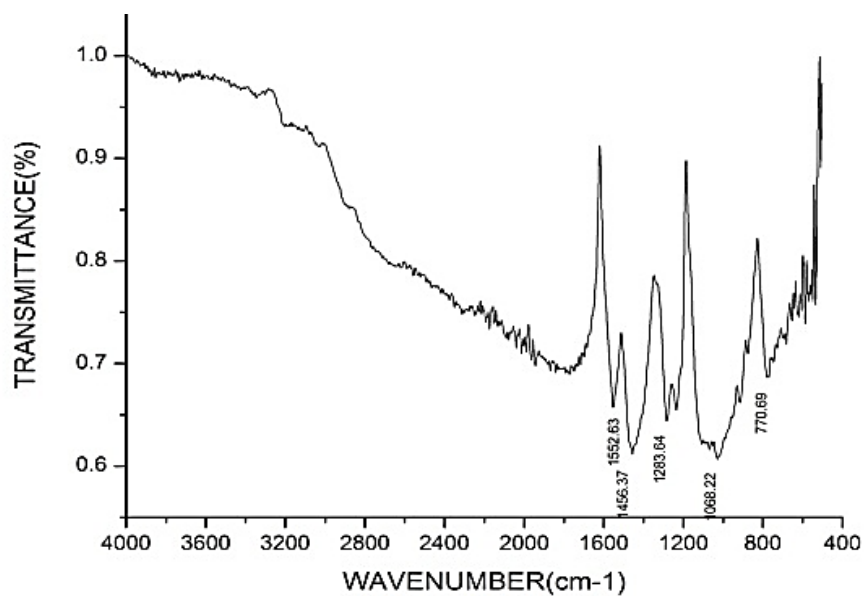
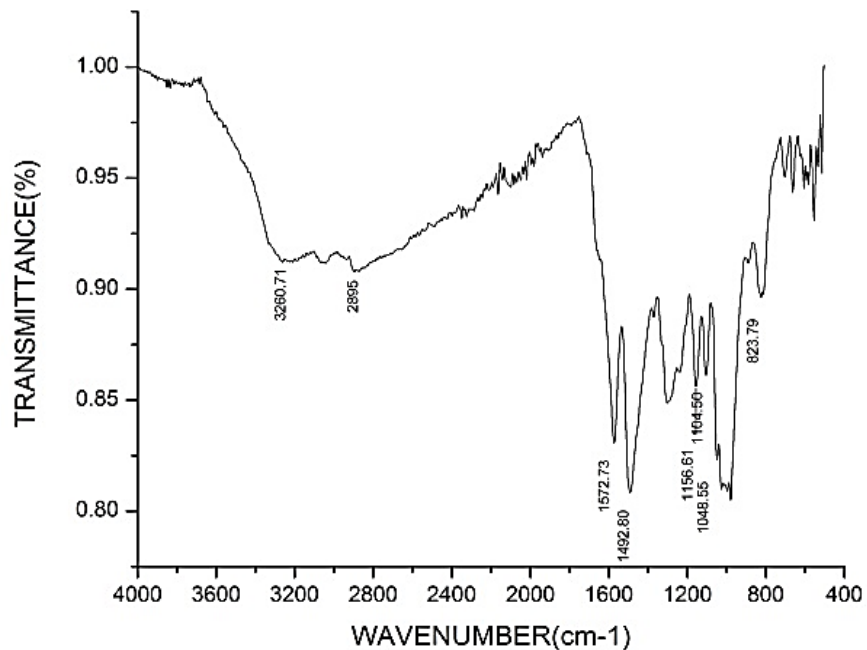


(d)

**Figure 5.1. Time snapshot of the sample showing reaction progression with (a) 2 min (b)10 min (c) 30 min and (d) 24 hours from left to right 1\_1, 1\_2, 1\_3, 1\_4, 1\_5 and 1\_6.**

Sample/APS:Aniline	Photograph and observations	Sample/APS:Aniline	Photograph and observations
1_1 5:1	 <p>Brown in colour Small quantity obtained</p>	1_4 1:1	 <p>Green in colour Moderate quantity obtained</p>
1_2 3:1	 <p>Brown in colour Moderate quantity obtained</p>	1_5 1:3	 <p>Green in colour Moderate quantity obtained</p>
1_3 1:1	 <p>Green in colour Moderate quantity obtained</p>	1_6 1:5	 <p>Green in colour Moderate quantity obtained</p>

**Figure 5.2. Photographs and observations for the samples of experiment 5.1.1.**



**Figure 5.3. FTIR spectra of a) brown powders from 1\_1 and 1\_2 b) green powders from 1\_3, 1\_4, 1\_5 and 1\_6.**

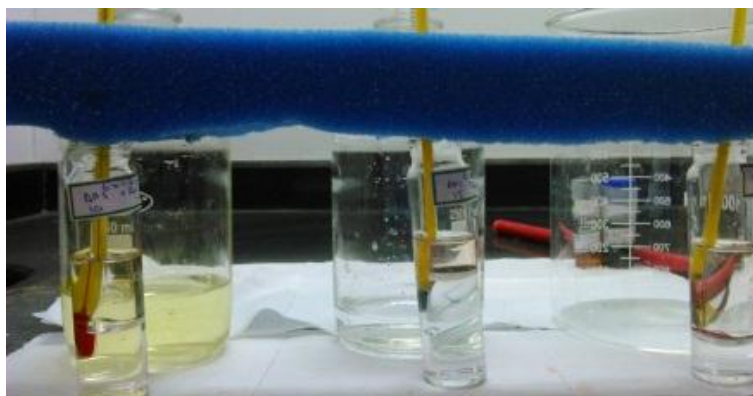
### 5.1.2 0.2 M APS in water and 0.2M Aniline in Toluene

0.2 M APS in water and 0.2M Aniline in Toluene were mixed in different ratio to obtain various molar ratios as listed in table 5.1.2. The colour change as seen with the progress of reaction as shown in Figure 5.4.

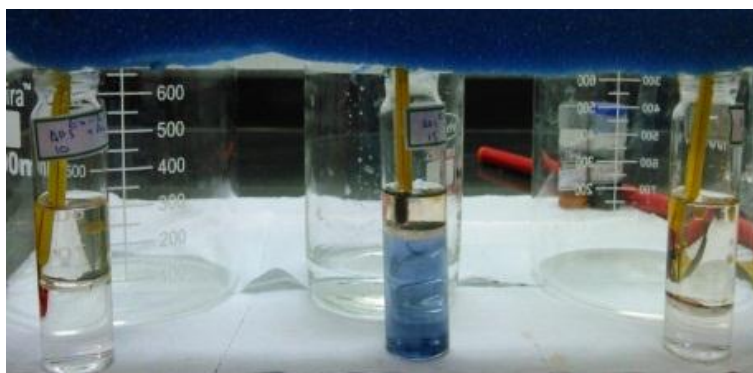
Green powders were obtained in 2\_1 and 2\_3 after filtration and drying. The FTIR spectra shown in Figure 5.5 confirms the formation of polyaniline in all. The quantity of powders obtained from the samples 2\_2 and 2\_3 was more than 2\_1.

**Table 5.1.2. Variation in the concentration of 0.2 M APS in water and 0.2M Aniline in Toluene**

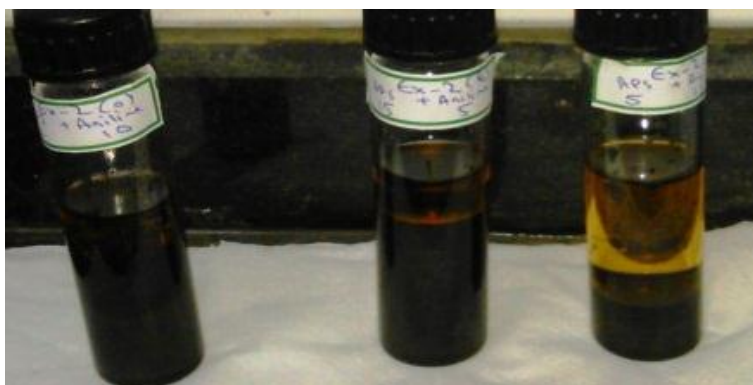
Sr. no.	APS/Aniline Mili molar ratio	APS(ml)	Aniline(ml)
2_1	3:1	15	5
2_2	1:1	10	10
2_3	1:3	5	15



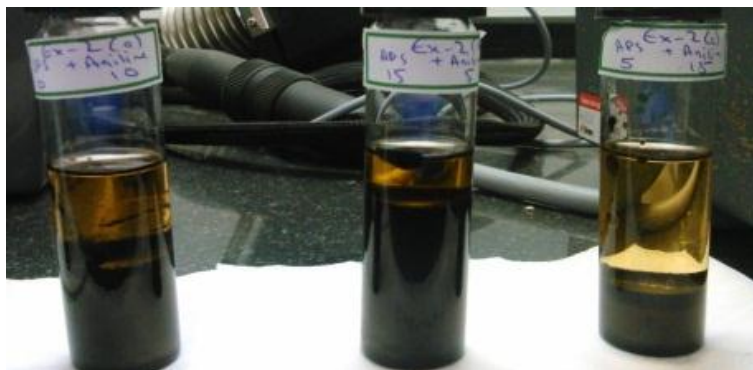
**(a)**



(b)



(c)

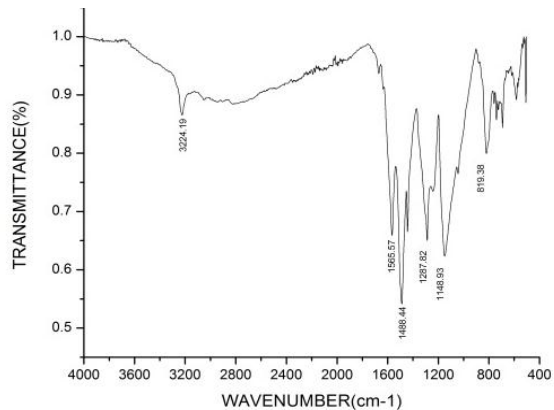


(d)

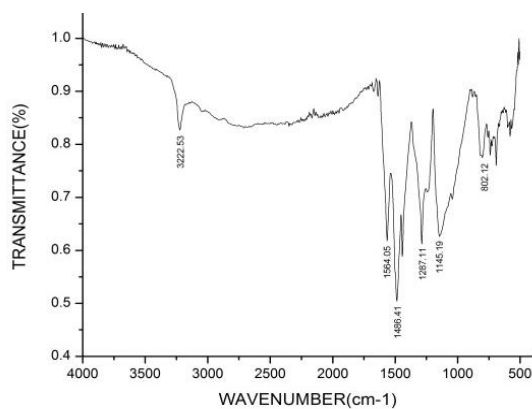
**Figure 5.4. Time snapshots of the sample showing reaction progression with (a) 2 min (b) 10 min (c) 30 min and (d) 24 hours from left to right 1\_2, 1\_1 and 1\_3.**



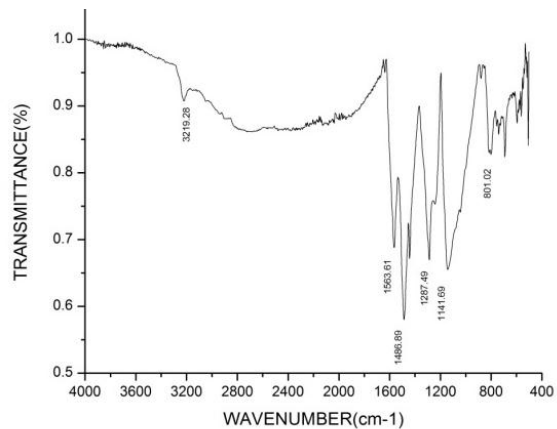
APS/Aniline molar ratio- 3:1



APS/Aniline molar ratio- 1:1



APS/Aniline molar ratio- 1:3



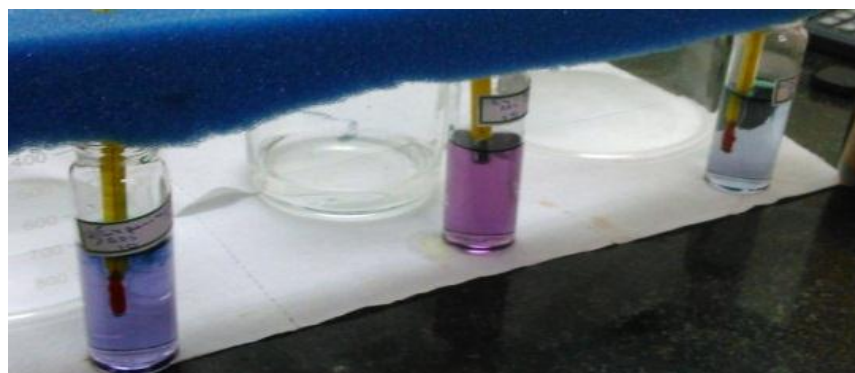
**Figure 5.5. Photograph and FTIR spectra of a) pinkish black powders from 2\_1 b) green powders from 2\_2, and c) bluish green from 2\_3.**

### 5.1.3 0.2M APS in HCl and 0.2M Aniline in 50%HCl

0.2 M APS in HCl and 0.2 M Aniline in 50%HCl were mixed in different ratios to obtain various molar ratios as listed in table 5.1.3. The colour change as seen with the progress of reaction as shown in Figure 5.6. Green yellow powders were obtained in 3\_2 and yellowish green in 3\_3 after filtration and drying. The FTIR spectra shown in Figure 5.7 confirms the formation of polyaniline in 3\_2 and 3\_3. The quantity of powders obtained from the samples 3\_2 was more than 3\_3.

**Table 5.1.3. Variation in the concentration of APS and Aniline**

<b>Sr. no.</b>	<b>APS/Aniline Mili molar ratio</b>	<b>APS(ml)</b>	<b>Aniline(ml)</b>
<b>3_1</b>	<b>3:1</b>	<b>15</b>	<b>5</b>
<b>3_2</b>	<b>1:1</b>	<b>10</b>	<b>10</b>
<b>3_3</b>	<b>1:3</b>	<b>5</b>	<b>15</b>



**(a)**





(b)

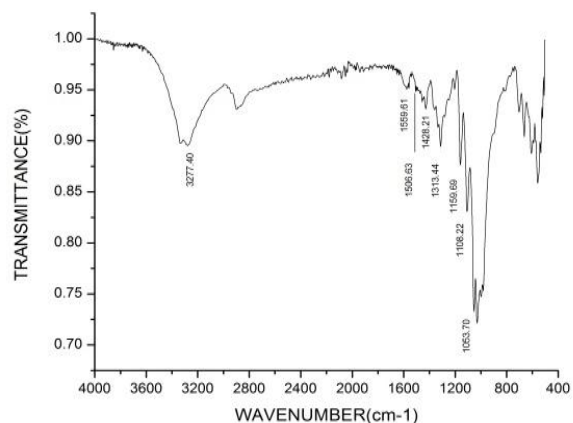


(c)

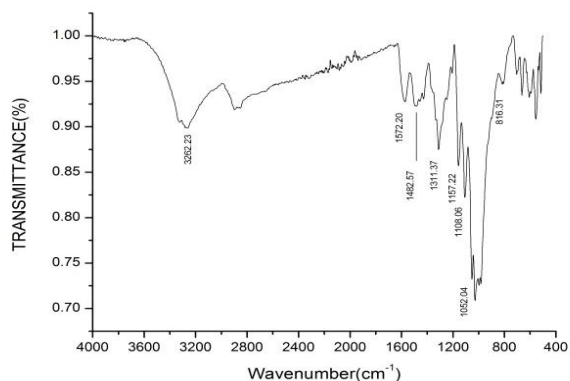


(d)

**Figure 5.6. Time snapshot of the sample showing reaction progression with (a) 2 min (b) 10 min (c) 15 min and (d) 24 hours from left to right 3\_2, 3\_1 and 3\_3.**



APS/Aniline molar ratio- 1:1



APS/Aniline molar ratio- 1:3

**Figure 5.7. Photograph and FTIR spectra of a) greenish yellow powders from 3\_2 b) green powders from 3\_3.**

#### 5.1.4 0.2M APS in HCl and 0.2M Aniline in Toluene

0.2 M APS in HCl and 0.2 M Aniline in Toluene were mixed in different ratios to obtain various molar ratios as listed in table 5.1.4. The colour change as seen with the progress of reaction as shown in Figure 5.8.

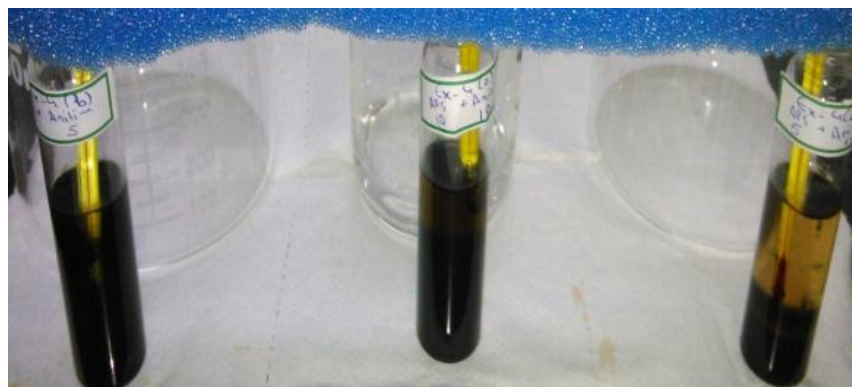
Green powders were obtained in 4\_1 and 4\_2 while yellowish green in 4\_3 after filtration and drying. The FTIR spectra shown in Figure 5.9 confirms the formation of polyaniline in all. The quantity of powders obtained from the samples 4\_2 and 4\_3 was more than 4\_1.

**Table 5.1.4. Variation in the concentration of 0.2M APS in HCl and 0.2M Aniline in Toluene**

<b>Sr. no.</b>	<b>APS/Aniline Mili molar ratio</b>	<b>APS</b>	<b>Aniline</b>
<b>4_1</b>	<b>3:1</b>	<b>15</b>	<b>15</b>
<b>4_2</b>	<b>1:1</b>	<b>10</b>	<b>10</b>
<b>4_3</b>	<b>1:3</b>	<b>5</b>	<b>15</b>



**(a)**



**(b)**



(c)

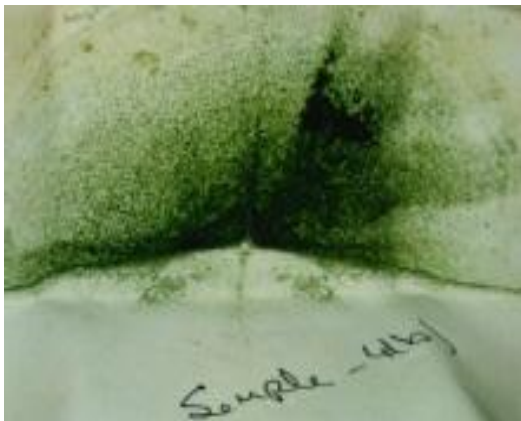


(d)

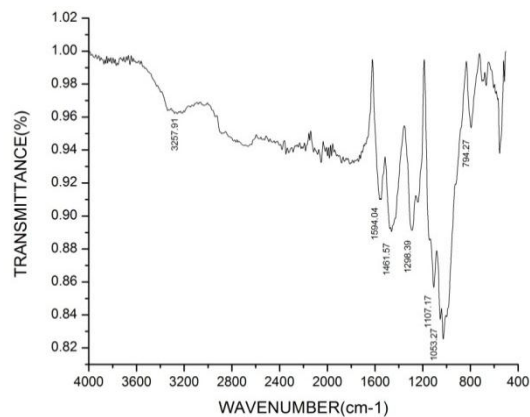
**Figure 5.8. Snapshot of the sample showing reaction progression with (a) 2 min (b) 5 min (c) 15 min and (d) 24 hours from left to right 3\_2, 3\_2 and 3\_3.**

### 5.1.3 Summary of variations

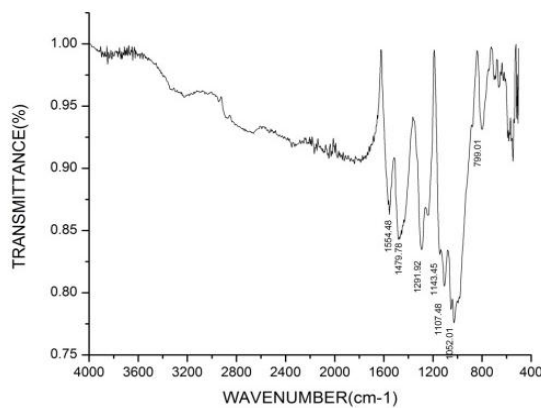
From the observations above for the set of experiments, it is evident that 1:1 molar ratio of APS to aniline is best suited for the formation of polyaniline. Also aqueous solutions are preferred from environmental perspective. Hence polyaniline obtained from experiment 1\_3 and 1\_4 were further tested for conductivity, which is discussed below.



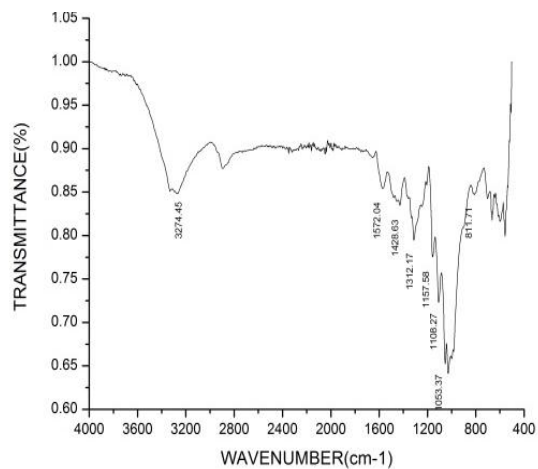
APS/Aniline molar ratio- 3:1



APS/Aniline molar ratio- 1:1



APS/Aniline molar ratio- 1:3



**Figure 5.9. Photograph and FTIR spectra of a) greenish powders from 4\_1 and 4\_2 and b) yellowish green powders from 4\_3.**

## 5.2 PPMS MEASUREMENTS

The variation in resistance with temperature was measured and used to obtain conductivity and activation energy. The details of the protocol are included in chapter 3. The resistance was measured both with increasing and decreasing temperature. The results are only included for sample 1\_1 where the polyaniline was prepared from equimolar 0.2 M aqueous APS and Aniline in 50% HCl.

Figure 5.10 shows that with increase in temperature, resistance of the sample decreases. This suggests that polyaniline shows a semi-conductor behavior as also reported in literature [1,2,8,10,25,27,41,54,66,75]. With increase in temperature, resistance decreases i.e. resistivity decreases (directly proportional) and conductivity increases (inversely proportional). The conductivity obtained from sample is 1.48 S/cm at room temperature, which is approximately equal to the one reported in literature [4,5,35,54]. The Activation energy thus obtained from the slope of  $\ln \sigma$  vs  $1/T$  graph, using Arrhenius equation was found to be 0.35 eV which is similar to the reported value [77].

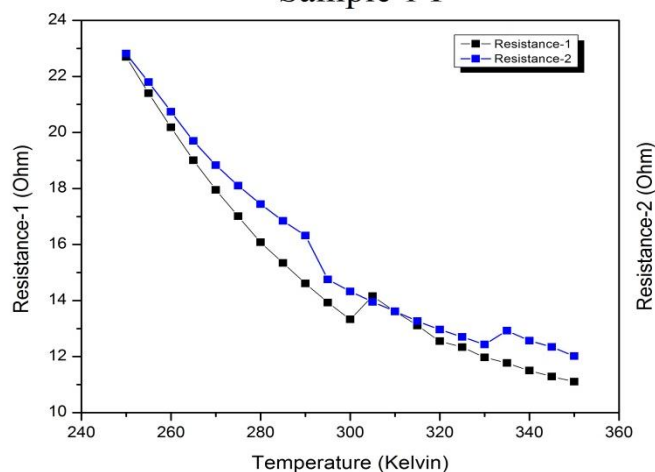


Figure 5.10. Graph showing Resistance vs temperature

## 5.3 SUMMARY

- The conductivity obtained from sample 1\_6 is 1.48 S/cm at room temperature (300 K) which is approximately equal to the one reported in literature.
- The formation of emeraldine state of PANI has been confirmed. The molar ratio of APS to Aniline 1:1 has been found to be the suitable combination for desirable results.

# Chapter 6

## Composite Preparation

The main objective of the project is to prepare conducting composites from polyaniline (PANI) and bacterial cellulose. Several strategies have been thought and tested. The focus of all the strategies is to perform *in situ* polymerization of aniline in the cellulosic matrix. Conducting PANI is produced as insoluble particles, therefore it results in non-uniformity in the film when incorporated later. In order to resolve this problem, *in situ* polymerization was done using PANI.

In this work, two kinds of matrices have been used - bacterial cellulose and filter paper. Another variation has been created by producing nanowhiskers which has been discussed in chapter 4 section 4.5. The first section briefly discusses various strategies for composite preparation. The subsequent sections are dedicated to the most encouraging strategy and characterisation of the composites produced by this strategy.

### 6.1 COMPOSITE PREPARATION STRATEGIES

The following 5 strategies have been used-

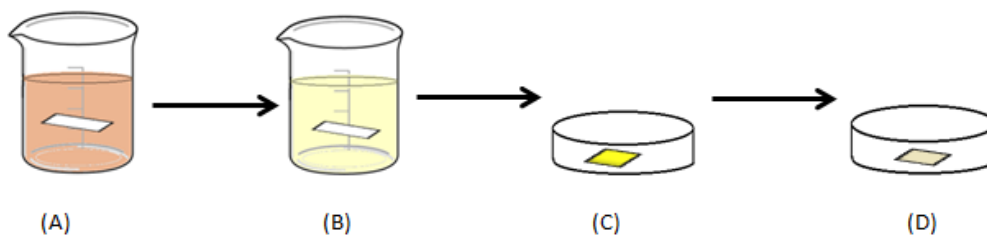
- a) dip process
- b) drop process
- c) both solution mixed together
- d) matrix assembly post polymerization
- e) polymerization after sheet formation

On the basis of the literature, several solvents can be used in synthesis of PANI, but preference has been given to aqueous based systems. Also composites have been made from both BC and FP only by the first two strategies. Later only bacterial cellulose has been used as a substrate, because preliminary results in this chapter and the previous ones, suggest better potential with BC.

### 6.1.1 DIP PROCESS

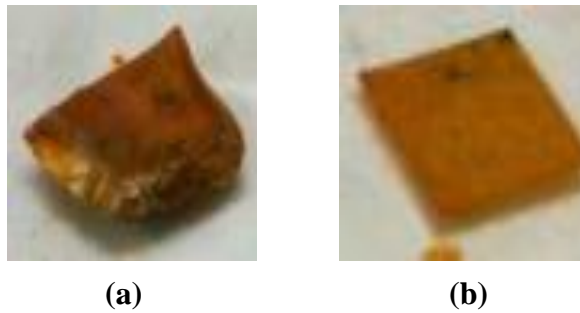
Bacterial cellulose is in form of porous membranes. Taking the advantage of porosity, bacterial cellulose samples were dipped in APS solution followed by dipping in Aniline solution. The oxidizing agent APS would be incorporated in the BC matrix and then when aniline monomer is allowed to enter the matrix, polymerization starts within the matrix. The time allowed for the oxidizing agent and the monomers plays an important role. The required time to dip can be estimated from the penetration/swelling studies shown in chapter 4. Similar process was followed for filter paper.

15 mL each of APS solution (0.05M APS in 6M HCl) and aniline solution (0.1M of Aniline in 6 M HCl) were prepared. First, the sample was dipped in APS solution for 5 min and then was carefully transferred into aniline solution and kept for approximately 10 min. The sample was then removed and kept in refrigerator for 24 hours for polymerization and then washed with acetone and DI-water several times and finally kept for drying for 24 hours. The obtained samples just before drying are shown in Figure 6.2. It appears yellowish in colour due to excess amount of acid (i.e., HCl). Acid content was found to be too high, which led to degradation of cellulose even before drying.



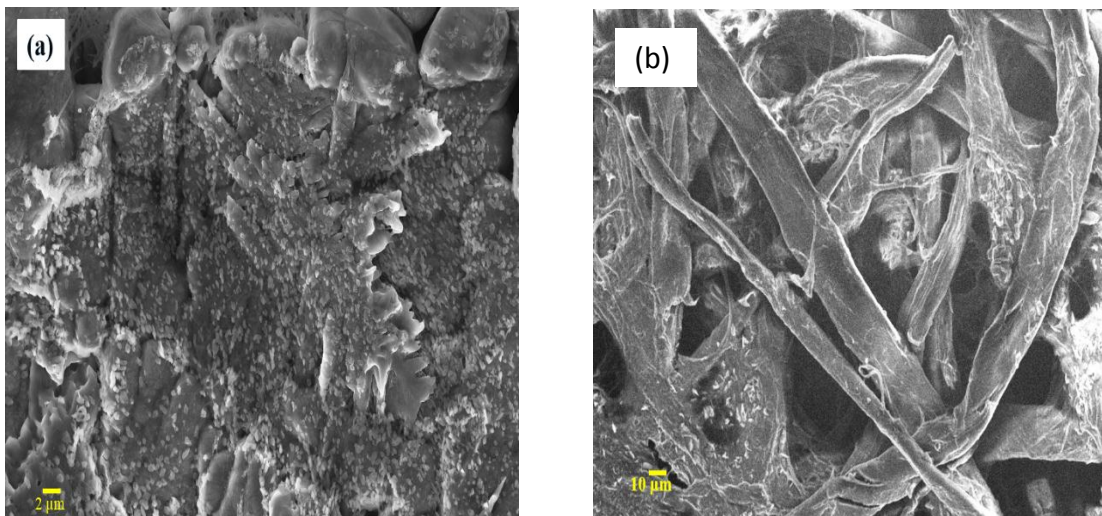
**Figure 6.1. Stages in dipping process for a substrate, (A) sample is placed in APS solution (B) then sample is placed in Aniline solution (C) sample is taken out in a petridish and kept at low temperature (D) finally dried using oven.**





**Figure 6.2. Samples obtained just before drying for dipping process (a) BC (b) FP**

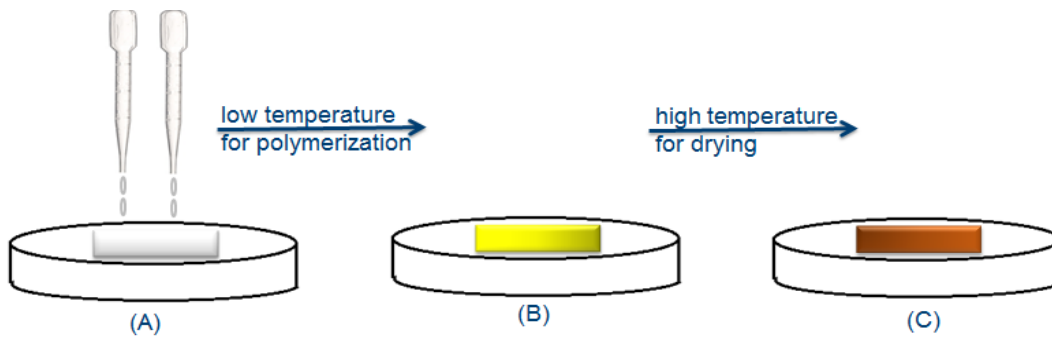
Figure 6.3 shows the SEM images for composite prepared from BC as well as filter paper. It can be seen that thin, continuous and uniform fibrils are present in BC unlike that in filter paper. SEM images reveal that the PANI deposition was not uniform in both cases. Another thing to note is that the signature of emeraldine polyaniline formation is green colour, which was not observed here. Also, it is very difficult to estimate the molar ratio of APS and aniline actually participating in the current method, as the amount of APS and aniline absorbed cannot be directly determined.



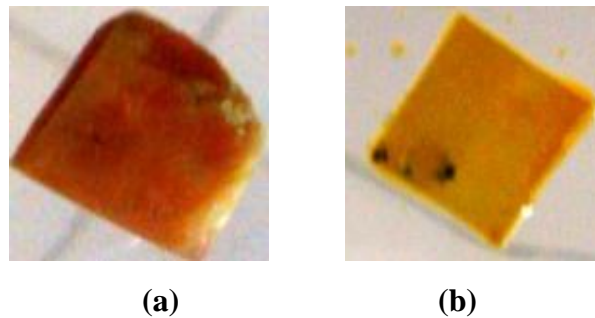
**Figure 6.3. SEM image of the composite with (a) BC and (b) FP**

### 6.1.2 DROP BY DROP PROCESS

In this process, instead of dipping matrix in solution, solutions were poured drop by drop. First APS solution was poured, followed by aniline. APS is used first and then aniline for the ease of creating sites on BC to have better uniform deposition of PANI on BC[5]. For sake of comparisons, concentrations of APS and aniline solutions were kept the same. The APS solution (0.05M APS in 6M HCl) and then aniline solution (0.1M of Aniline in 6M HCl) were dropped on the sample as shown in Figure 6.4. The sample was then removed and kept at a 4°C for 24 hours for polymerization and then washed with acetone and DI-water 5 to 10 times and finally kept for drying 24 hours and Figure 6.5 shows a photograph of the sample just before drying.

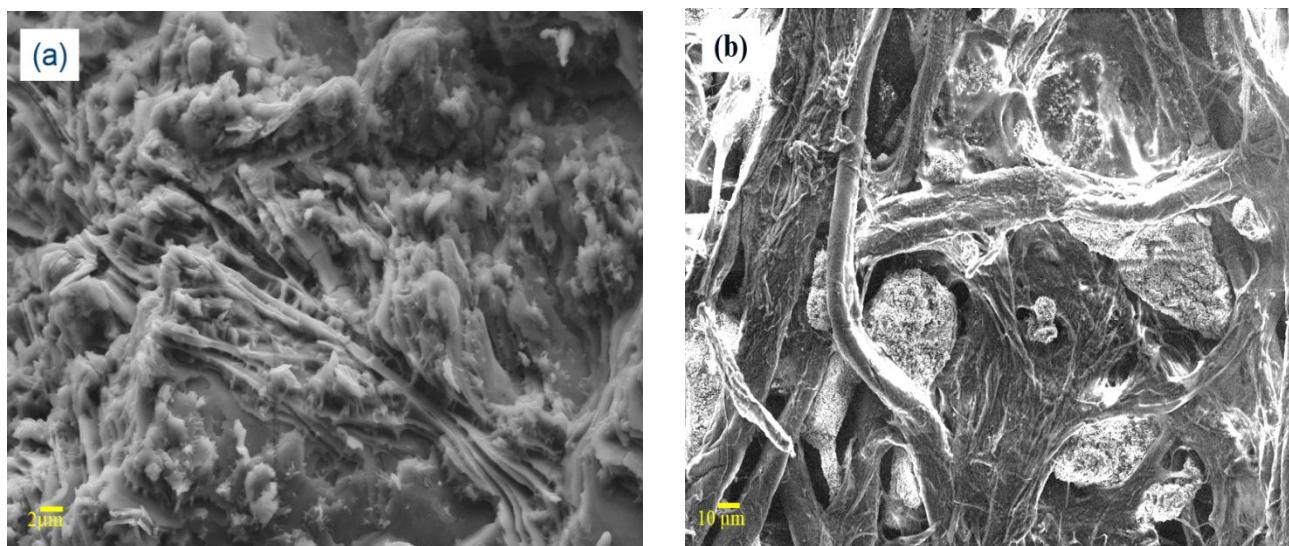


**Figure 6.4.**



**Figure 6.5. Sample obtained after drop process (a) BC b) FP just before drying**

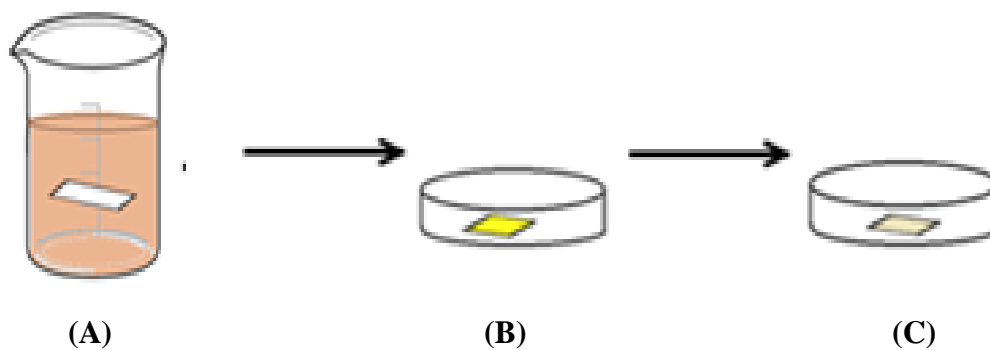
Figure 6.6 shows the SEM images of composites of PANI with BC and filter paper. It shows that BC is better and uniformly coated with PANI than Filter Paper. It also shows finer morphology of bacterial cellulose as compared to filter paper. Acid content was found to be too high, which led to degradation of cellulose even before drying. Similar to the methods discussed above, the signature green colour of emeraldine polyaniline was not observed here. Also, again it is very difficult to estimate the molar ratio of APS and aniline in the current method, as the amount of APS and aniline absorbed cannot be directly determined.



**Figure 6.6. SEM image of the composite (a) BC and (b) FP**

### **6.1.3. BOTH SOLUTIONS MIXED TOGETHER**

Matrix was placed inside the mixture of 0.2M of Aniline solution in 1M HCl (15 ml) and 0.2M of APS solution in aqueous medium (15ml) in a beaker for 6 to 7 hours then it was taken out and kept in freeze for a day to polymerize and then finally dried at room temperature as shown in Figure 6.7.



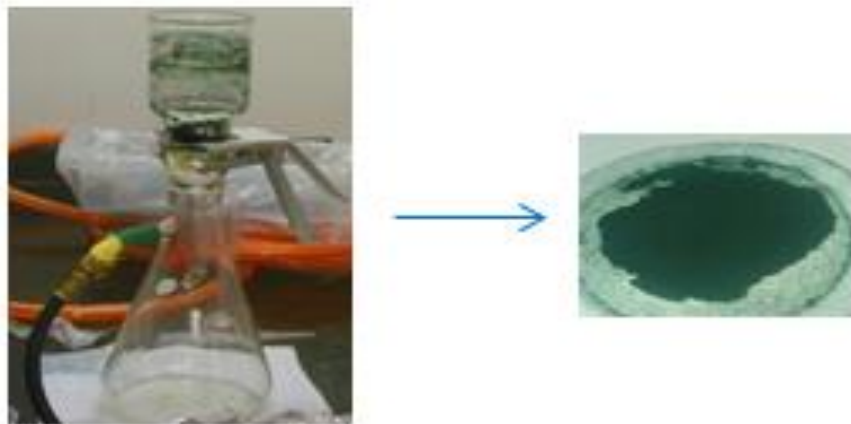
**Figure 6.7. Process of (A) APS and Aniline solution having filter paper/BC (B) Sample was kept for polymerizing and finally(C) dried at room temperature**

#### **6.1.4. MATRIX ASSEMBLY POST POLYMERIZATION**

This method is similar to the above, except that in this case BC nanowhiskers were used instead of BC sheet and matrix assembly was carried out after polymerization. This method was believed to allow uniform PANI formation over individual cellulose fibrils (converted to nanowhiskers). BC nanowhiskers were prepared as discussed in chapter 4 section 4.5. The nanowhiskers were mixed with 0.2 M of APS solution in aqueous medium and 0.2M of Aniline solution in 1M HCl and kept for stirring for a day. The suspension was filtered and washed with DI-water and acetone using filtration assembly to wash away excess acid and to obtain sheet as shown in Figure 6.8. It must be noted that care was taken to control HCl content. Similar synthesis was carried out with APS in water and Aniline in toluene. The sheets obtained are shown in Figure 6.9. The sheets were found to possess the signature green colour of emeraldine state of polyaniline.

#### **6.1.5. POLYMERIZATION AFTER SHEET FORMATION**

In this the sheet was prepared from BC nanowhiskers as discussed in Chapter 4. The APS solution (0.2M APS in aqueous medium) and aniline solution (0.2M of Aniline in 1M HCl) were mixed and then the substrate/sheet was placed inside for 24 hours to polymerize. It was then taken out of that petridish, washed with acetone and DI water, then finally dried at room temperature. Polymerisation was carried out at two temperatures 3 to 4°C and -4°C. The results are discussed in section 6.2.2.



**Figure 6.8. (a) Nanowhiskers and PANI/APS in filtration assembly after polymerization and (b) dried sheet**



**(A)**



**(B)**

**Figure 6.9. Photographs of composite with BC nanowhiskers and (A) APS in water and aniline in 6M HCl and (B) APS in water and aniline in toluene**

## **6.2 EFFECT OF VARIOUS FACTORS ON COMPOSITE PROPERTIES**

The following sections discuss the composites formation by matrix assembly post polymerization and polymerization after sheet formation methods which are already discussed above. Some of the important factors which affect composite properties include temperature and time provided for polymerization, relative content of BC and PANI, and over all weight of the system. Effect of some of these factors are discussed below:

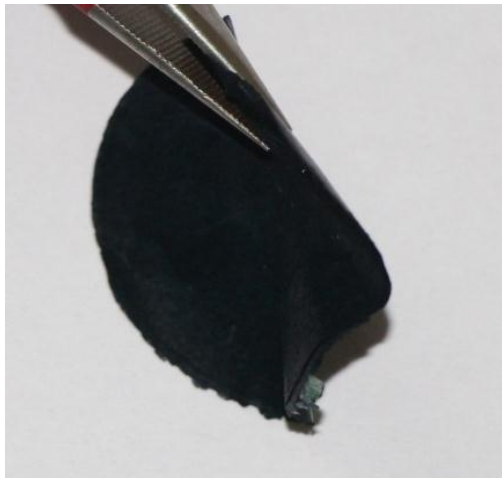
### **6.2.1 EFFECT OF TIME**

0.2 M of APS in DI-water and 0.2 M Aniline in 1M HCl solution are mixed together in a beaker and BC nanowhiskers were then added in it drop by drop .The mixture was stirred for 90 minutes and then kept for polymerization at different time duration i.e., 2.5 hours and 2 hours respectively. Once uniform suspension is obtained, it was washed using DI-water and acetone using filtration assembly to obtain sheet of the same composite. The two sheets prepared from the process are shown in Figure 6.15. It shows that flexibility of the composite with 24 hours of polymerization showed better flexibility than that with 2.5 hours of polymerization time.

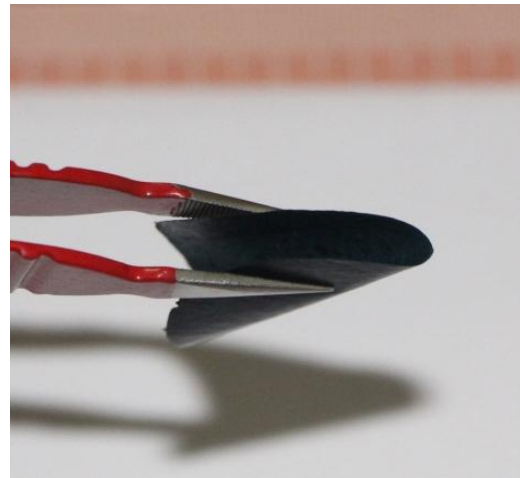
### **6.2.2 EFFECT OF TEMPERATURE**

The composite sheet was prepared through polymerization after sheet formation process were kept for polymerization at different temperatures 3°C and -4°C. The photographs of these two samples are shown in Figure 6.11 below. Figure 6.12 shows the SEM images of composites formed by polymerization of PANI on nanowhiskers sheet. Figure 6.12.a and 6.12.b represents the morphology of composite prepared at temperature of 4 °C and -4 °C respectively. As can be seen, the polymerization of PANI at lower temperature i.e., -4 °C was uniform on nanowhiskers sheet.

Preliminary resistance measurements by multimeter showed that the composite sheet prepared by this process had resistance of about 800 Ω and 80 kΩ for samples prepared at 4°C and -4°C, respectively.



(a)



(b)

**Figure 6.10. Image of composite sheets with 3 ml BC nanowhiskers and 1 ml of PANI suspension at (a) 2.5 hours and (b) 24 hours of polymerization**

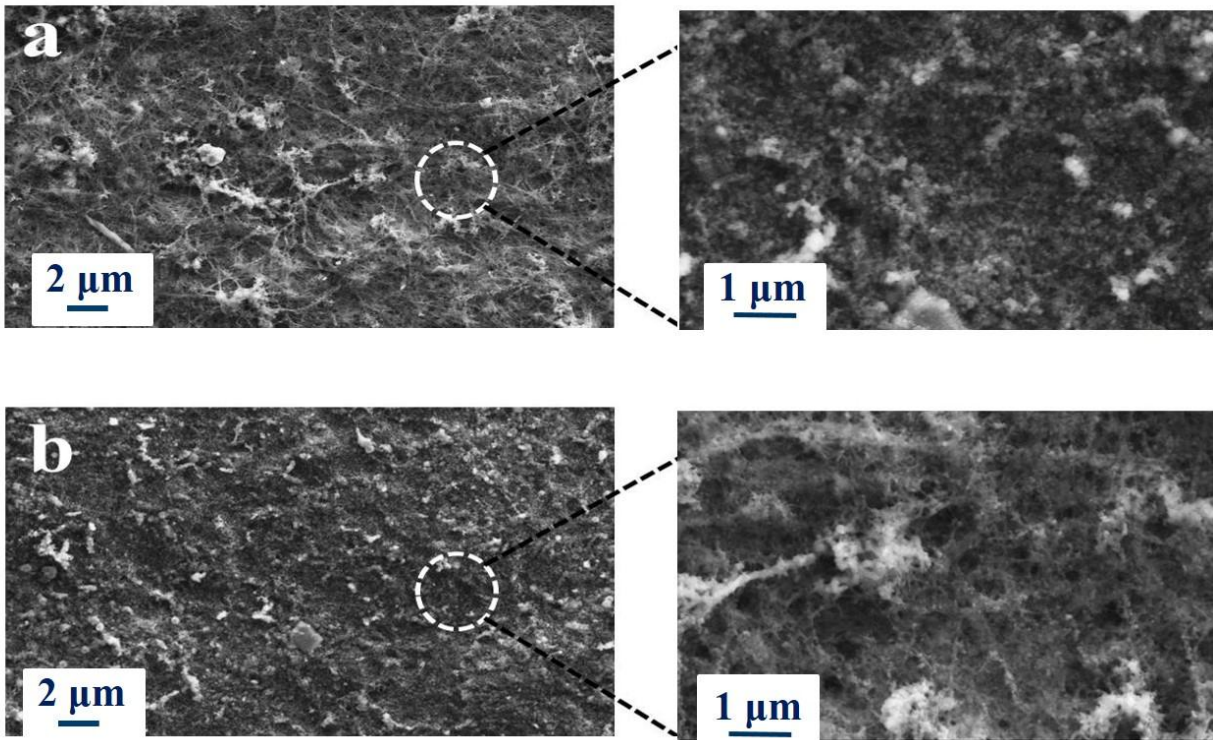


(A)



(B)

**Figure 6.11. Photograph of composite with difference in polymerization temperature (A) at 3 to 4°C and (B) at -4°C**



**Figure 6.12. SEM image of composite with difference in polymerization temperature (a) at 3 to 4°C and (b) at -4 °C**

### **6.2.3 Effect of Ratio of Weight**

In order to prepare conducting sheets of the composite, the relative ratio of weight of aniline to BC was varied. Several batches of bacterial cellulose were studied, which varied in actual BC nanowhisker content (wt%). The results for different batches are separately discussed, as variability in terms of surface charge, aspect ratio nanowhiskers is expected, between batches.

#### **1) Batch 1**

The batch 1 was 0.7 wt. % of BC nanowhiskers in water. The nanowhiskers were mixed with 0.2M APS aqueous solution and 0.2M Aniline solution in 1M HCl and kept for stirring followed by polymerization at 3°C for 24 hour. Once uniform suspension is obtained, it was washed with DI-water and acetone using filtration assembly to wash away excess acid and to obtain sheet as



shown in Figure 6.9. Three samples with different BC: PANI ratios were prepared as listed in table 6.1 below.

**Table 6.1: Variations in BC and PANI wt. ratios**

Sample no.	Aniline (mg)	Aniline (ml)	BC (mg)	BC (ml)	BC:PANI	Time for polymerization
1	67.06	3.5	35	5	0.5	24 hr
2	47.9	2.5	35	5	0.7	24 hr
3	28.74	1.5	35	5	1.2	24 hr

Figure 6.13 shows photographs of the samples discussed above in table 6.1. It shows that fragile and brittle sheet were obtained in samples with lower BC:PANI ratio, however reasonably flexible sheets were obtained for BC:PANI weight ratio of 1.2. The third sample has the best flexibility among the three samples because of higher relative BC to PANI content, BC provides mechanical integrity to the sample.

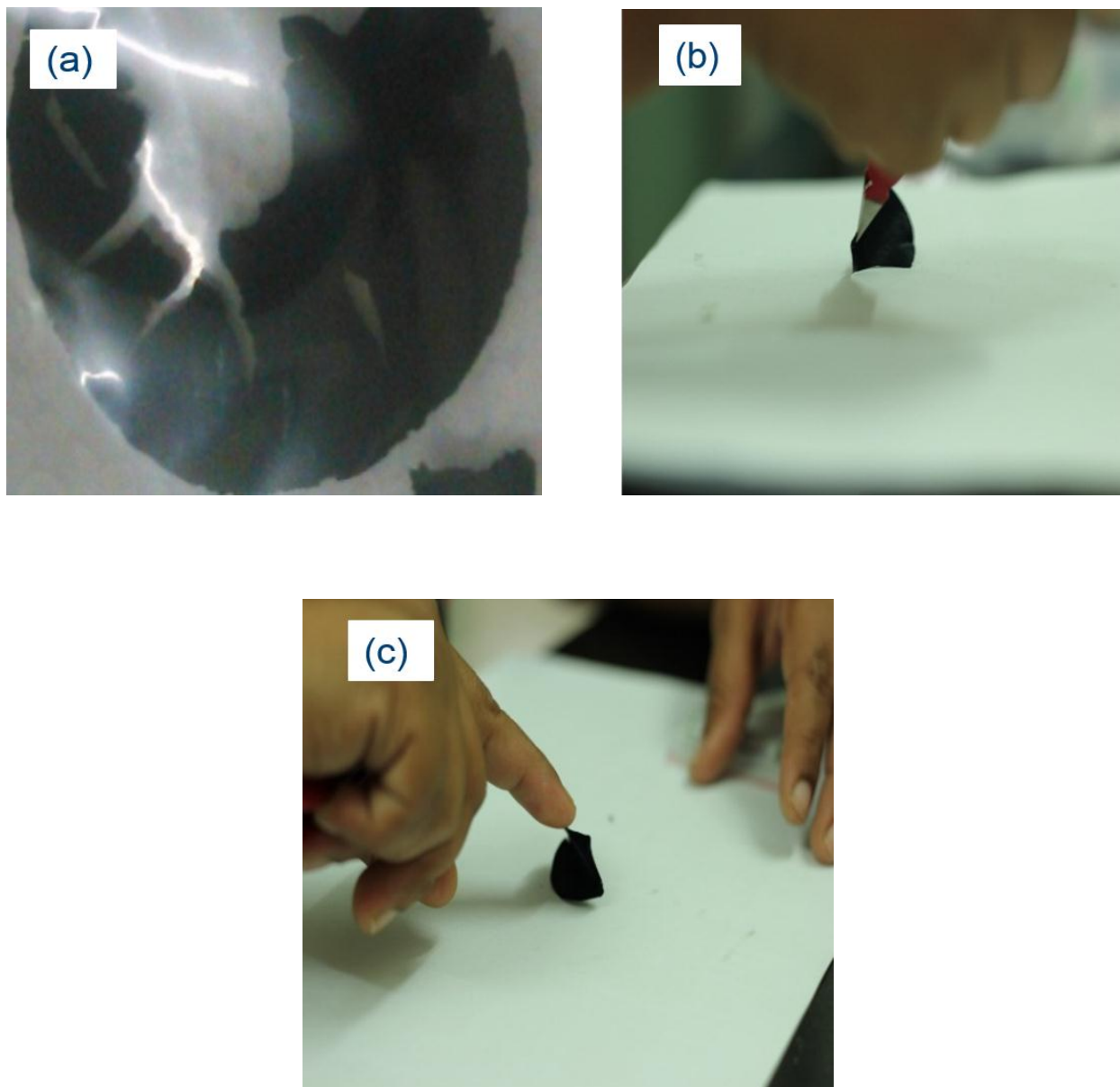
Another important factor to consider is the total weight of the system that is total weight of aniline and cellulose. It has been shown before that a minimum amount of BC is required to form a sheet with mechanical integrity but at the same time, increase in the total weight of the system would compromise the sheet flexibility. Therefore, the third sample has also advantage in terms of total weight of the system. The flexibility of the composite is related to both relative cellulose and PANI content and the total weight of cellulose and PANI together.

Figure 6.14 shows the SEM images of composites of PANI with BC. They show uniform coating of PANI on BC nanowhiskers in all cases.

## 2) Batch 2

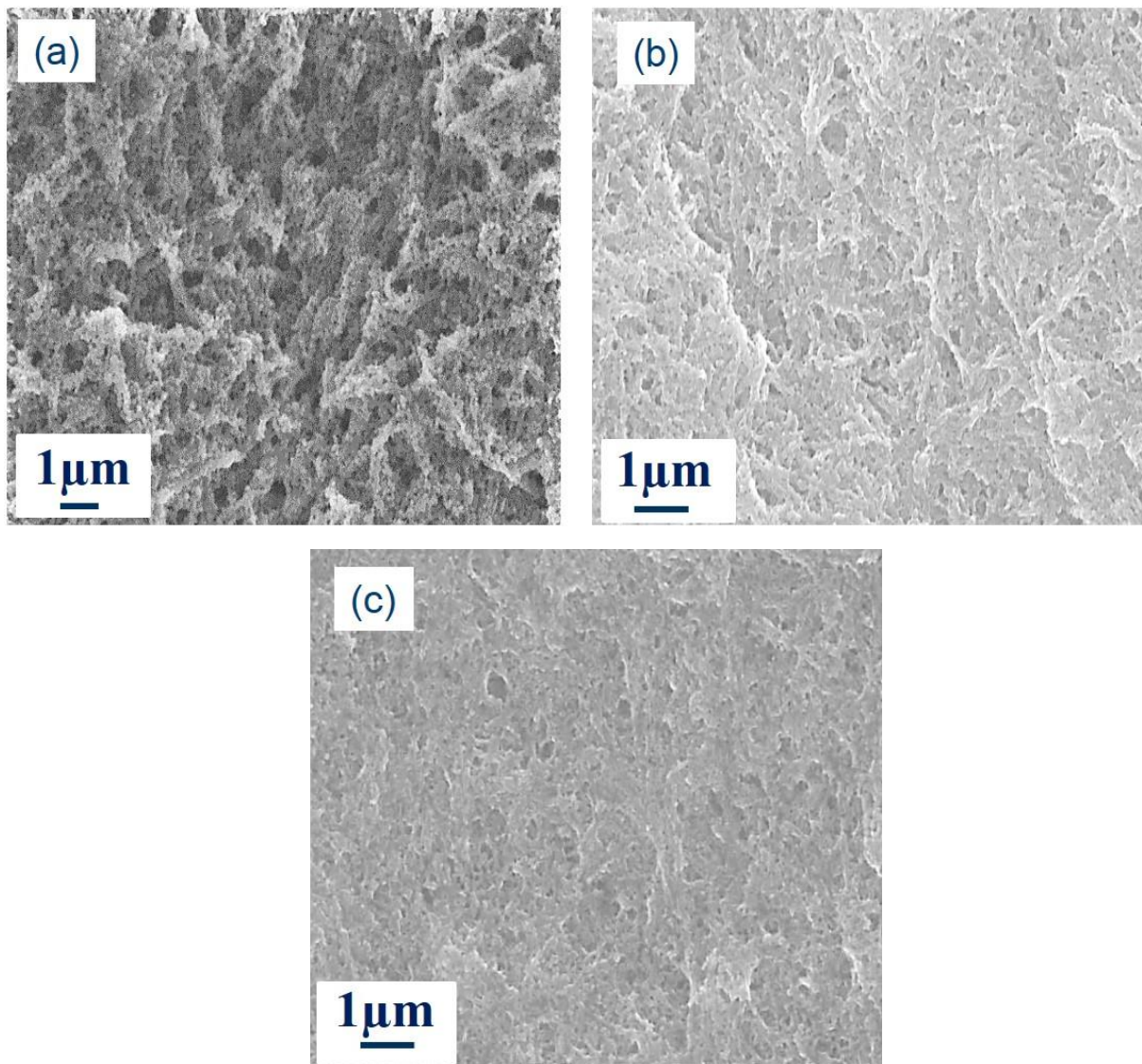
The batch 2 was 0.9 wt% of BC nanowhiskers aqueous suspension. The nanowhiskers were mixed with 0.2 M of APS solution in aqueous medium and 0.2M of Aniline solution in 1M HCl and kept for stirring followed by polymerization at 3°C (controlled temperature) for 24 hours.

Once uniform suspension was obtained and washed with DI water and acetone using filtration assembly to wash away excess acid, residual APS, aniline and other by-products and to obtain sheet. Three samples with different BC: PANI ratios were prepared and listed table 6.2.



**Figure 6.13. Photographs of composite with 5 ml BC nanowhiskers and (a) 7 ml (b) 5 ml (c) 3 ml of PANI suspension i.e., BC:PANI ratio of 0.5, 0.7 and 1.2 respectively**

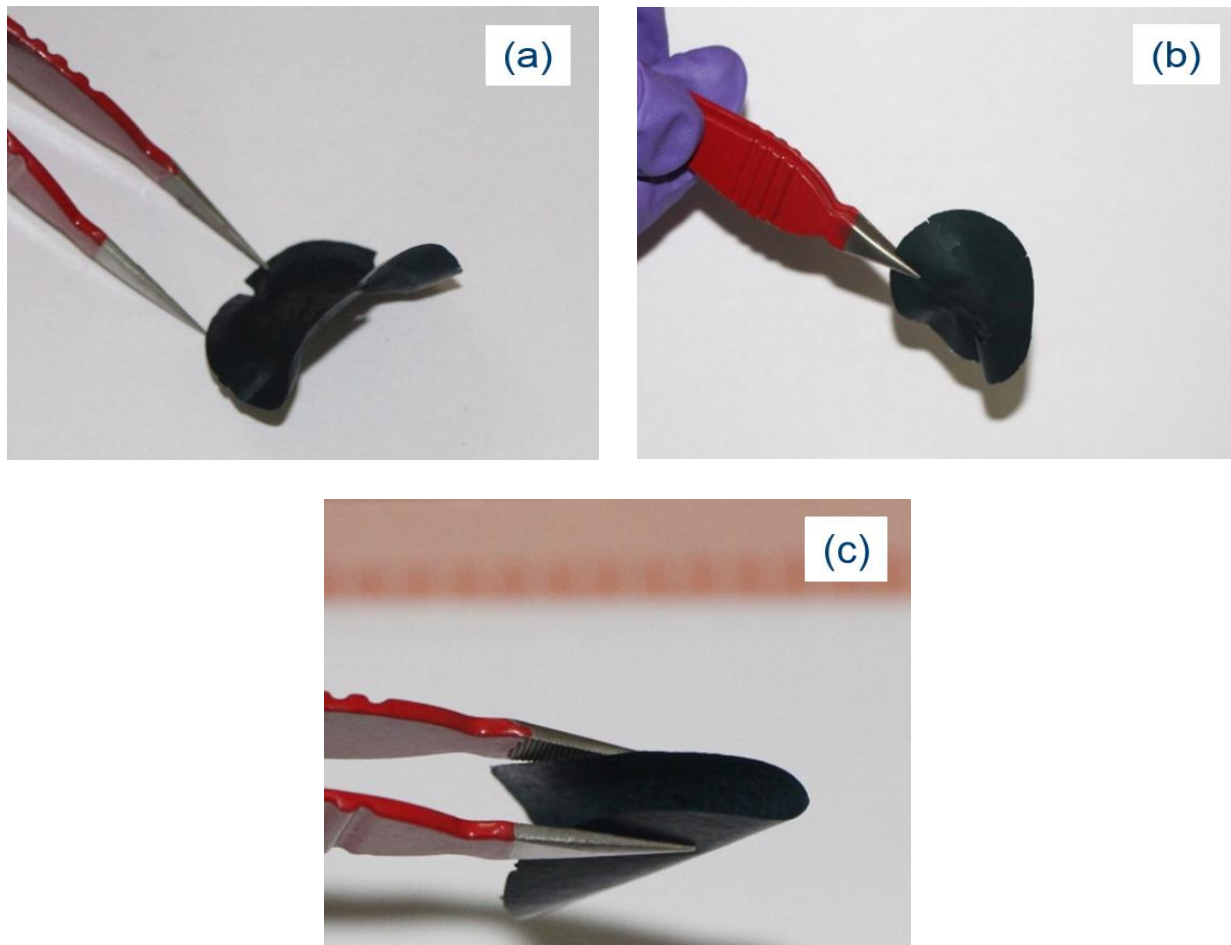
Figure 6.15 shows photographs of the samples discussed above in table 6.2. It shows that reasonably flexible sheets were obtained in all the three samples. It shows again a similar trend as seen in Figure 6.13 that is the flexibility of the composite is inversely related to the amount of PANI and total weight of the composite. Figure 6.15 (c) shows best flexibility and can be rolled actually like paper without breaking. Figure 6.16 shows the SEM images of composites of PANI with BC. They show uniform coating of PANI on BC nanowhiskers in all cases.



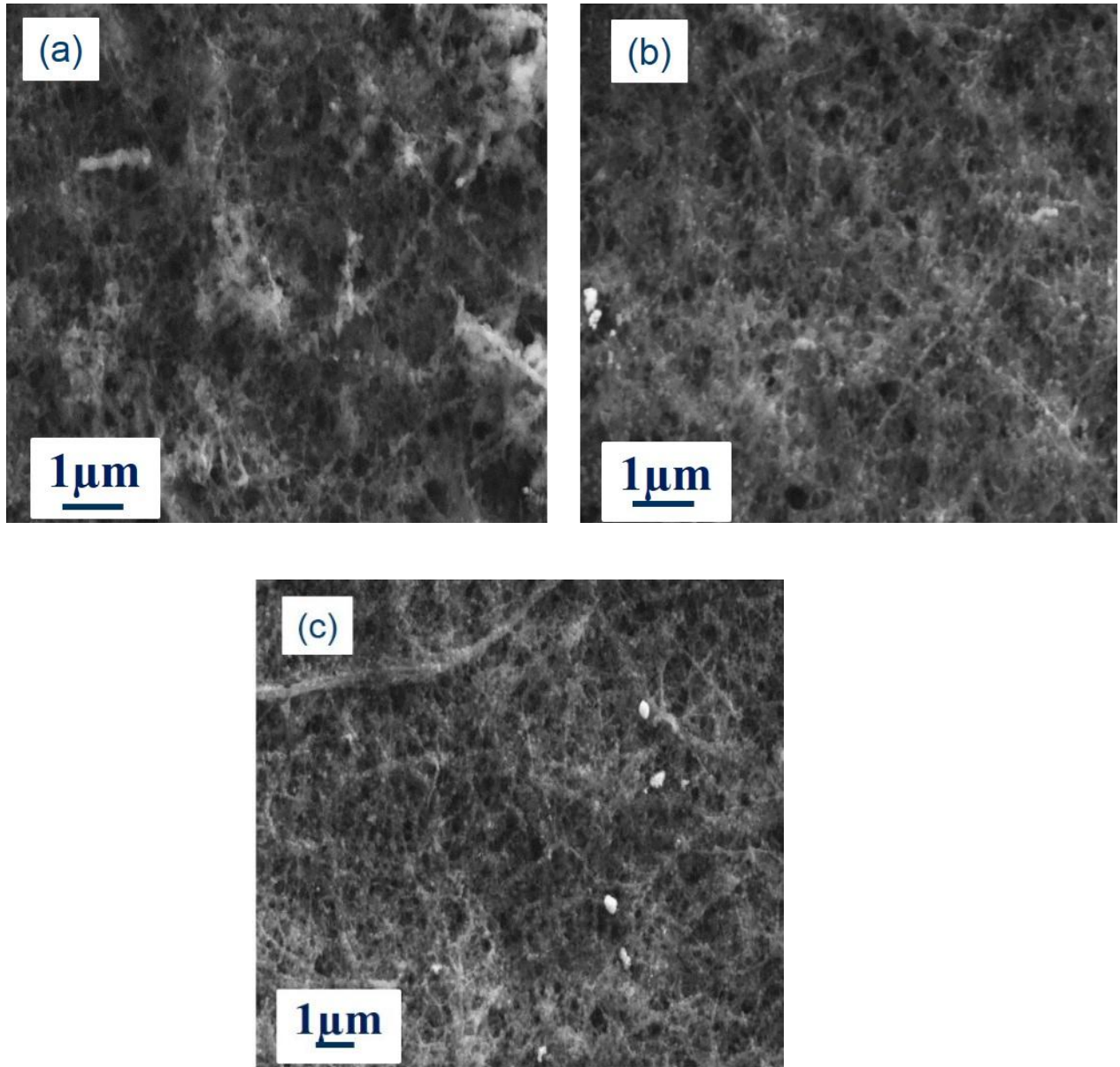
**Figure 6.14. SEM image of the composite with 5 ml BC nanowhiskers and (a) 7 ml (b) 5 ml and (c) 3 ml of PANI suspension i.e., BC:PANI ratio of 0.5, 0.7 and 1.2 respectively.**

**Table 6.2:-Variations in BC:PANI wt. ratio used for composite preparation**

Sample no.	Aniline(mg)	Aniline + HCl (ml)	BC(mg)	BC(ml)	BC:PANI	Time for polymerization(hours)
1	28.74	1.5	27	3	0.9	24
2	19.16	1	27	3	1.4	24
3	9.58	0.5	27	3	2.8	24



**Figure 6.15. Photographs of composite with 3 ml BC nanowhiskers and (a) 3 ml (b) 2 ml (c) 1 ml of PANI suspension i.e., BC:PANI ratio of 0.9, 1.4 and 2.8 respectively**



**Figure 6.16. SEM image of the composite with 5 ml BC nanowhiskers and (a) 3 ml (b) 2 ml (c) 1 ml of PANI suspension i.e., BC:PANI ratio of 0.9, 1.4 and 2.8 respectively.**

### **6.3 CONDUCTIVITY MEASUREMENTS**

#### **(a) Multimeter measurements**

The preliminary resistance measurements through the multimeter for the above samples are listed in Table 6.3. In Batch 1 and 2, the amount of BC: PANI was varied. As the amount of PANI

decreases from sample 1-3 (table 6.3), the resistance of composite increases. It can be further studied using 2 probe conductivity instrument.

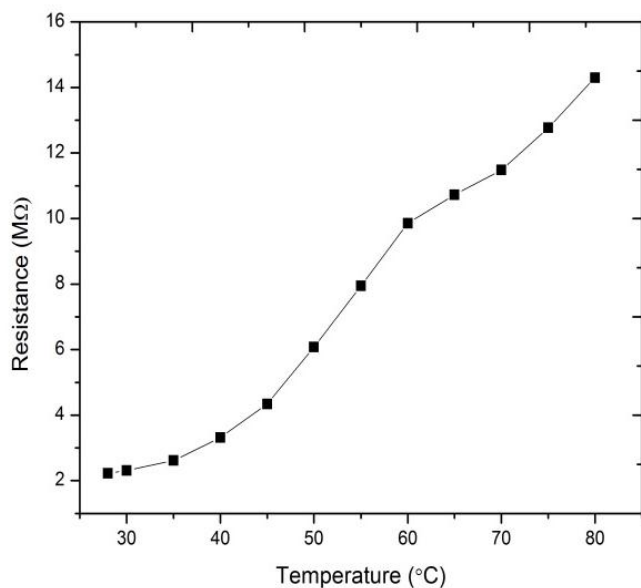
**(b) 2 probe measurement**

Figure 6.17 illustrates the 2 probe measurement of studying the effect of temperature change on the resistance of the composite (batch-II sample 3). Loading and unloading cycles were represented by Figure 6.17.a and 6.17.b respectively. PANI is known intrinsic semiconductor, and the bacterial cellulose is well known insulator. Therefore, the conductivity of the composite is mainly attributed by the presence of PANI. However, from Figure 6.17, the resistance increases with increase in temperature, which is different from expected trend. This deviation can be the result of the following,

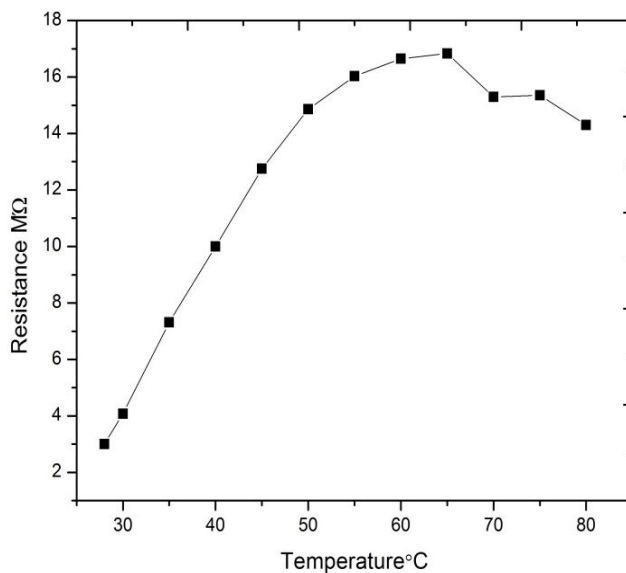
1. Crack propagation within the sample
2. Contact resistance
3. Distance between the two probes
4. Low work function of silver
5. Porosity within the sample
6. Insufficient doping

**Table 6.3: Multimeter reading for the samples from batch 1 and 2**

Batch	Sample	Resistance range
Batch 1	1	60-120 kΩ
	2	70-110 kΩ
	3	80-190 kΩ
Batch 2	1	2-12 kΩ
	2	54-104 kΩ
	3	80-240 MΩ



(a)



(b)

**Figure 6.17. Resistance vs. Temperature curve of sample 3 batch 2 while (a) increasing and (b) decreasing temperature**

## SUMMARY

1. The best protocol for composite formation is matrix assembly post polymerization.
2. Time of polymerization plays an important role in deciding the flexibility of the composite. Sheets with polymerization time of 24 hours showed better flexibility than that for 2.5 hours.
3. Temperature also has a role on composite properties. Lower the temperature better was the conductivity but further optimization is required.
4. Weight ratio of BC to PANI was optimized to be greater than 1 for a flexible sheet formation.
5. Weight of the composite sheet is also important in determining sheet flexibility.

# Chapter 7

## Life Cycle, Cost and Scalability – the other engineering angle

Any research from engineering perspective is incomplete without a perspective on scalability, cost of production, comparison to the existing products and most importantly effect on the environment.

**Product proposed:** conducting paper from polyaniline and bacterial cellulose

**Target applications:** sensors, anti-static packaging, actuators

**Similar products:** metal sheets

**Advantages:** It is lighter in weight compared to conventional metals and semiconductors and possesses conductivity in a similar range. Polyaniline provides huge opportunity to tailor its properties during synthesis.

### 1. CRADLE TO GRAVE ASSESSMENT

- There are concerns about aniline with regards to its toxicity. However, the polymerized form of aniline- polyaniline- is non-toxic and thus benign to the environment.
- Environmental impact while the starting chemical are produced should be considered.
- The substrate material - bacterial cellulose - used in the proposed composite is a naturally produced material which is produced in pure form by bacteria, hence no chemical treatments for extraction and no deforestation.
- The waste generated are non-toxic, however a dedicated analysis would be useful.
- Disposal of material also needs to be studied. It may be mentioned that since one of two component system is natural, impact of disposal or recycling may not be too much.

### 2. PRODUCT LIFE

Polyaniline properties are sensitive to moisture and air. Therefore a dedicated research on this is required to assess durability of the product. The degradation behavior of the proposed BC/PANI composite still needs to be studied.



### 3. COST AND SCALABILITY

A further detailed research on BC/PANI composites from various aspects including procuring raw material to producing the product and scaling up, is required to bring it as a suitable material in the market. The method used in this work is batch process. The cost estimation of producing a single film of the composite requires the following-

#### a) Chemicals –

Starting materials	Amount	Cost
Aniline	9.58mg	
APS	22.8mg	
Bacterial cellulose	27mg	Not available
HCl	1.5ml	
DI water	150 ml	Not available
Acetone	150ml	

#### b) Energy cost –

	Power(Watts)	Time(hours)
Vacuum pump for filtration for nanowhiskers preparation as well as sheet formation	Not available	4-5
Refrigerator	150	24
Centrifuge for nanowhiskers preparation	Not available	1
Magnetic Stirring	Not available	2-3
Oven for drying	2400	4

A continuous production method is required for better scalability. Methods for quality control also need attention.

# Chapter 8

## Conclusions and Future Work

This work was intended to develop a conducting paper based on bacterial cellulose and polyaniline composite, which may be used in flexible electronics application such as actuators, sensors, anti- static packaging. The focus was to exploit the conducting nature of PANI to obtain flexible conducting sheets along with a suitable substrate (i.e., bacterial cellulose) because PANI lacks in mechanical integrity. This chapter presents the main conclusions of the thesis and comprehensively elaborates on the new challenges for future work.

### 8.1 CONCLUSIONS

The main objectives of this work were -

1. Study of Substrates : bacterial cellulose vs. filter paper
2. Polyaniline synthesis and characterization
3. Composite preparation and conductivity measurements

The main accomplishments in each of these aspects are summarized below.

#### 8.1.1 STUDY OF SUBSTRATES: BACTERIAL CELLULOSE TO FILTER PAPER

Since PANI alone cannot form a flexible sheet, a suitable material is required. The pre-requisite substrate properties are good mechanical strength, light weight, cost effective, environment friendly, and so on. Cellulose is a versatile gift of nature [78] and fulfills all the above mentioned requirements but property of cellulose varies as per the source. Therefore, initially a comparative study of BC and FP was carried out. They were compared in terms of morphology, microstructure, surface area and porosity. BC was found to be more suitable because of its higher porosity and uniform nanofibrous network. FTIR showed similarity in the chemical structure of both.

Bacterial cellulose was acid hydrolysed to produce nanowhiskers with shorter length than the fibrils present in unhydrolysed or as-produced BC. Then BC nanowhiskers sheets were prepared whose flexibility can be changed by varying the amount of cellulose used.

### **8.1.2 POLYANILINE SYNTHESIS AND CHARACTERIZATION**

In order to obtain conducting PANI, synthesis parameters such as molar ratio of APS to Aniline, time and temperature of polymerization, washing and drying time and solvent were varied. The solutions used for synthesis were 0.2 M Aniline in 1M HCl and 0.2 M APS in DI-water. It was found that 1:1 molar ratio of APS to Aniline gives best yield and the desirable PANI properties.

### **8.1.3 COMPOSITE PREPARATION AND CHARACTERIZATION**

The composite were prepared using dip process, drop process, both solution mixed together, matrix assembly post polymerization and polymerization after sheet formation. The best protocol for composite formation was found to be matrix assembly post polymerization. The weight ratio of cellulose to PANI was optimized to be above 1.2 for a flexible sheet formation. It was found that time and temperature plays a crucial role in deciding the flexibility and conductive nature of the composite sheet. It was seen that sheets with better flexibility were obtained when polymerization was carried out for 24 hours and at  $-4^{\circ}\text{C}$  as compared to those obtained at 2.5 hours and  $3^{\circ}\text{C}$ .

## **8.2 NEW CHALLENGES FOR FUTURE WORK**

During the course of this study, some interesting challenges in field of conducting cellulose composites have been unraveled, some of which are discussed below.

### **8.2.1 DOUBLE DISTILLATION OF POLYANILINE**

Since aniline is hygroscopic in nature, double distillation process must be followed before getting it polymerized to polyaniline. It has been studied that distilled PANI shows better result in some of the studies [79-81].

### **8.2.2 VARIATION OF BC TO PANI, WHILE KEEPING THE OVERALL WEIGHT OF THE SYSTEM AS CONSTANT AND USE OF SECONDARY DOPING**

In this work, BC to PANI weight variation has been explained for composite sheet formation. But overall weight of the system should be kept constant while varying the BC to PANI weight ratios as flexibility of the composite sheet is inversely proportional to overall weight of the composite. Also it has been reported in literature that secondary doping can enhance the conductivity [83].

### **8.2.3 OPTIMIZATION OF POLYMERIZATION TEMPERATURE AND TIME OF THE COMPOSITE**

For chapter 6 section 2(A &B), it can be summarized that time and temperature plays a crucial role in deciding the flexibility and conductive nature of the composite sheet. Further optimisation can be carried out to make highly conductive film.

### **8.2.4 EFFECT OF STIRRING ON COMPOSITE UNIFORMITY AND OPTIMISATION WITH RESPECT TO TIME**

Stirring helps in proper mixing of two components in the composite. Therefore proper study on optimizing the speed and time of stirring is required during *in situ* polymerization of the composite as it may lead to more uniform and better conductive sample.

### **8.2.5 STUDY OF DIFFERENT MODELS EXPLAINING CONDUCTIVITY VALUES WITHIN THE COMPOSITE**

Conductivity in the sample can be due to various mechanism. Conductivity data can be analyzed by fitting the best model.

### **8.2.6 MORPHOLOGY OF THE COMPOSITE WITH RESPECT TO DIFFERENT REACTION CONDITIONS**

The oxidation of aniline and substituted anilines can produce an almost limitless number of micro- and nano-structures of different sizes and shapes including nano fibers, nanowires, nanotubes, hollow spheres, helices, flowers, and many more.[36]

Modifying a wide variety of synthesis parameters such as reagent concentration, pH, homogeneous or heterogeneous polymerization, addition rate of reagents, or even the amount of

stirring during polymerization can have a profound impact on the polymer morphology, which would further affect conductivity and mechanical properties.

### **8.3 CONCLUDING REMARKS**

Conducting and flexible PANI sheets were prepared using vacuum aided solution casting technique. In this work, parameters for substrate selection, suitable molar ratio of APS to aniline and strategies for composite preparation have been studied. Therefore, this work has established a basic ground work in field of conducting paper from bacterial cellulose and polyaniline. Further work is needed to optimize and produce a product useful for the society.

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