Polyaniline: Synthesis and Natural Nanocomposites

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भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

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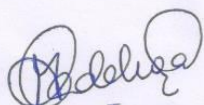
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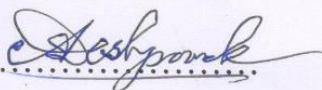**Palash Chandra Maity**

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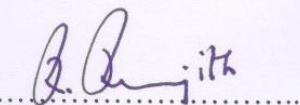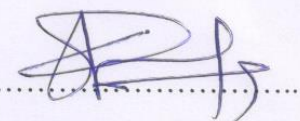
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Acknowledgement

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Abstract

Research and development in the field of conducting polymers can enable advancement in flexible electronics. Particularly polyaniline has been given importance due to stability, easy synthesis, reasonable conductivity and tunable properties by changing oxidation states.

We have presented a systematic study of effect polymerization time and temperature on polyaniline morphology and conductivity. It was noticed that with decrease in polymerization temperature and increase in polymerization duration, conductivity of polyaniline increases. It was seen that particle size of polyaniline plays an important role in determining conductivity, irrespective of crystallinity, which suggests equal probability of electron conduction along and between the polyaniline chains. The highest conductivity obtained was for 24 hours of polymerisation in temperature (-18°C).

Conducting polymers including polyaniline possess poor mechanical properties. Cellulosic materials were chosen as substrate because of abundance, bio compatibility, biodegradability, and low cost. . Polyaniline was impregnated into corn cob cover by *in situ* polymerization to prepare composite. The conductivity was measured to be 8×10^{-4} S/cm for 15 % of polyaniline in the sample. Bacterial cellulose was chosen as another substrate because of its purity, mechanical properties and tenability. Composites of polyaniline and bacterial cellulose were also made by *in situ* polymerization. Three types of bacterial celluloses with variation in microstructure and porosity were used. The best conductivity was found to be 2×10^{-3} S/cm for over 50% of polyaniline.

Chapter 1 Introduction and Aim

1.1 Background

The field of flexible electronics is gaining importance with the proven need as well as the precedent technological materials advancement, which have proven the achievability. Conducting polymers are being explored as the potential candidate to fuel the field's progress. The counterintuitive phenomena of conductivity in polymers was first observed by Shirakawa, who later received Nobel prize along with Alan J. Heeger and Alan G. Macdiarmid [1, 2]

In due course of time, several conducting polymers have been discovered [2]. This thesis deals with polyaniline which is advantageous in terms of easy synthesis, variety of oxidation states and . [3]. However, most conducting polymers including polyaniline possess poor mechanical properties which restricts their usage independently[4]. Polyaniline composites with other polymers with good mechanical properties such as strength, flexibility are seen as the way forward. In this work, cellulose produced by bacteria has been used as the substrate for making composites with polyaniline[5, 6]. The choice of using bacterial cellulose as the substrate is based on the advantages such as good mechanical properties, porosity and environment friendly[7, 8]. Three variations of bacterial cellulose have been used as the substrate.

1.2 Aim

This thesis is intended to present a strategy to produce conducting flexible composites from bacterial cellulose and polyaniline. During the course of the work, some effort was also diverted towards using corn cob cover as a potential substrate for conducting composites.

1.3 Objectives

1. Optimisation of polyaniline synthesis with respect to conductivity
2. Preparation of composites by in situ synthesis of polyaniline in bacterial cellulose and corn cob cover
3. Characterisation with respect to structure, composition and conductivity

1.4 Outline

The next chapter – chapter 2 - presents a brief literature review on polyaniline properties and synthesis followed by summary of existing literature on polyaniline composites. The original experimental work has been presented in form of papers. Chapter 4 summarises the

optimisation strategy of polyaniline with characterisation results and discussion. Chapter 5 is dedicated to composites prepared for various compositions and characterisation. Chapter 6 deals with preliminary study, where corn cob cover has been used as a substrate. Chapter 7 presents summary of the work and direction for the future research.

1.5 References

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Chapter 2 Literature Review

2.1 Introduction

Discovery of conducting polymers has incepted new age of electronics industry and technology [1-3]. The unique chemical nature, electrical properties, low weight, easy synthesis and optical properties of conducting polymers have attracted several applications. Research has shown their applicability in sensors [4], [5] actuators [6, 7], LEDs [8], organic transistors, solar cell [9], corrosion inhibitor [10] and electronic paper. In this chapter, the progress of organic electronic device in the electronic market, literature review on synthesis methods, conductivity and morphology of polyaniline, bacterial cellulose and bacterial cellulose - polyaniline composite for different electronic device fabrication has been introduced.

2.2 Organic Electronics Market

Conducting polymer are the key enabler of organic electronics. Organic electronics are growing in market size (as shown in Figure 2.1) due to advantages over conventional inorganic electronics including low cost, flexible, light weight, and biocompatibility as listed in the Table 2.1. According to market study of organic electronic devices, it was estimated that 130 million of TV set, 400 million of smart phone, 300 million of PC are made of organic electronic. The others areas of demand are medical, and security. The collection of revenue by the end of 2015 is 29.5 billion $ and the expected revenue at the end of 2021 is 79 billion $ (Figure 2.1) [11, 12]. Organic electronic device are competitors of inorganic electronic device. In some of the cases, efficiency and performance of organic electronic and cost-effectiveness is higher than that of inorganic semiconductor [13, 14]. Generally used semiconductors, Silicon, Germanium, Gallium arsenide are extremely brittle, costly, difficult to scale up and require high temperature synthesis.

One of the key materials for organic electronics is conducting polymer. Conducting polymer does not possess mechanical integrity, and therefore in order to fabricate devices, the conducting polymer need a substrate or are blended with materials which possess mechanical strength. The substrate materials used are mostly synthetic polymers or inorganic materials, according to the application reported so far. Those materials are not biodegradable and biocompatible.[15] The motivation is to find low cost, biocompatible, flexible natural organic sustainable substrate material.
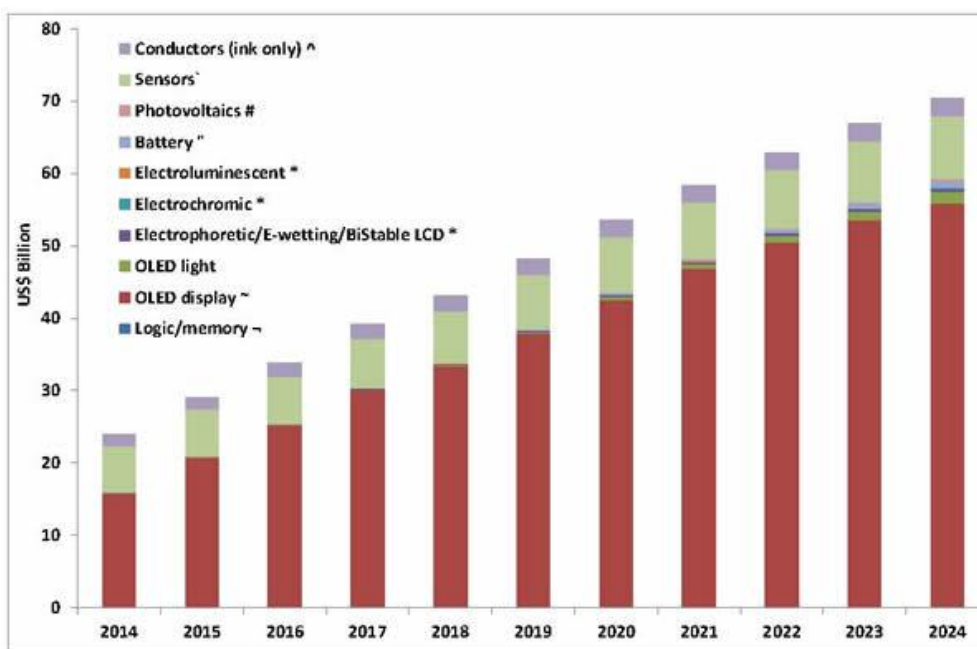
Figure 2.1 Market of organic electronics (http://www.electronics.ca/wp/wp-content/uploads/2015/02/Structural-Electronics-Market-Report.jpg)

Table 2.1 Advantages of organic semiconductors over inorganic semiconductors

	Organic Semiconductors	Inorganic Semiconductors
Product cost	Less	High
Product weight	Light weight	Heavy
Production Temperature	Room temperature	High temperature
Band gap	UV-Visible rage	Band gap can be both higher and lower the UV Visible range
Energy efficient	More	Less
Flexibility	Flexible	Not Flexible

2.3 Conducting polymers

Previously, polymers were considered as good insulator. This idea was abolished when the conducting polymer was first discovered in year 1977 by Shirakawa [[16]]. The first discovered conducting polymer was polyacetylene. Today several conducting polymers are known, for example, polythiophene, Polyaniline, polypyrrole, polyphenylene, poly (3, 4-ethylene dioxythiophene) (Figure 2.2) [17, 18] .
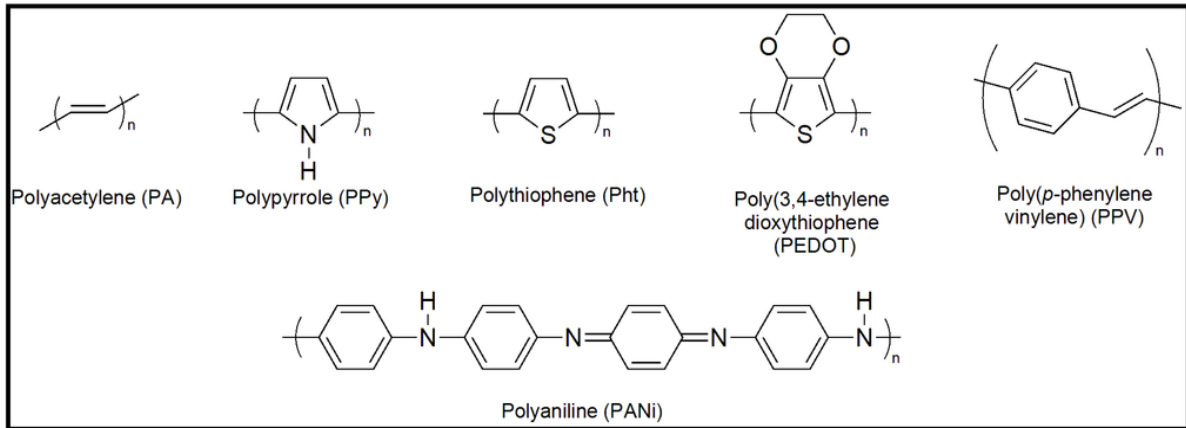
Figure 2.2 Conducting polymers and their structures [19]

The intrinsic conductivity of conducting polymers is very poor. Therefore, doping is adopted to increase the conductivity. Conductivity of doped polymers is comparable to that of semiconductor or metal (as shown in Figure 2.3). In doped condition, polyacetylene gives highest conductivity amongst the conducting polymer and its conductivity is comparable with metal but it react with air and gets oxidized. One of the main challenges with conducting polymers is the stability and processability, because only a few conducting polymers are soluble or fusible (Figure 2.4) [20].
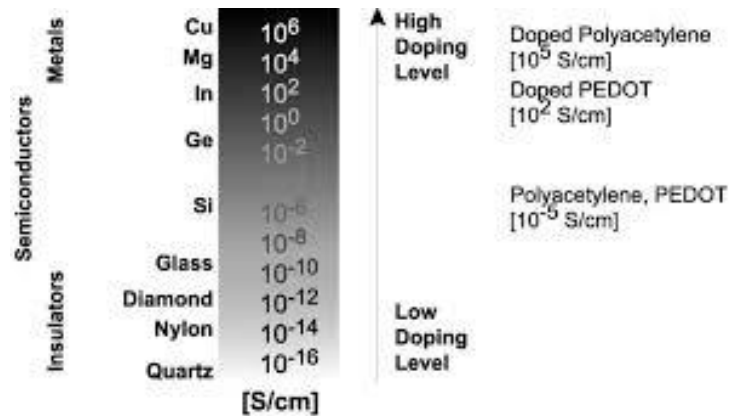
Figure 2.3 Conductivity comparison of metal and conducting polymers [image]
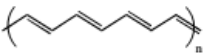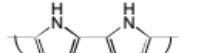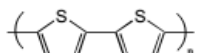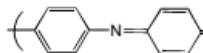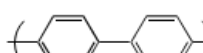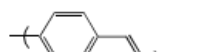
	Structure	Maximum conductivity S/cm	Stability	Processability
Polyacetylene		1.5×10^5	Reacts with air	Film not soluble or fusible
Polypyrrole		2000	Reasonably stable	Insoluble and infusible
Polythiophene		100	Stable	Insoluble and infusible
Polyaniline		10	Stable	Soluble in neutral form
Polyphenylene		1000	Stable	Insoluble and infusible
Polyphenylene-vinylene		1000	Stable undoped form	Soluble precursor route available

Figure 2.4 Processability and stability of conducting polymer [21]

The formation of band gap of a conducting polymer is similar to that of inorganic semiconductor. In organic semiconductor, when two molecular orbits overlap each other, it forms two district energy level - LUMO and HOMO. The energy difference between two outer most bands is called band gap [15]. The organic semiconductors are hydrocarbon molecule with backbone of carbon atom. The conducting polymer possess conjugate sigma (σ) and pie (π) (as shown in Figure 2.5) which is the key requirement for conduction. The sigma bond corresponds to strong covalent bond and localized electrons. For pi bond the electron are free or delocalized. Those delocalized or loosely bound electron take part in conduction. Generally, loosely bounded electron increase the electron density of conduction band.

The strong bond form sp^2 hybridisation between adjacent carbon atoms. This forms bonding and anti-bonding state of adjacent carbon atoms - σ and σ^* as shown in Figure 2.6. The remaining P_z orbital of two nearest carbon atom form bonding pie (π) and pie (π^*). This bonding and anti-bonding of pi orbitals possess lesser band gap.

The loosely bounded π electron form 1D band structure along the polymer chain. The conduction occurs by the process of hoping or tunnelling one chain to another chain.
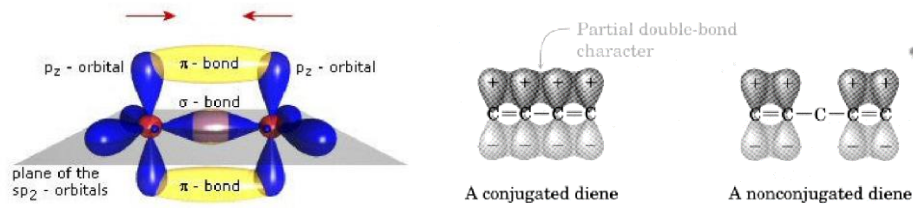
Figure 2.5 (a) over lap of P_z orbital (b) difference between conjugate overlapping and non-conjugate
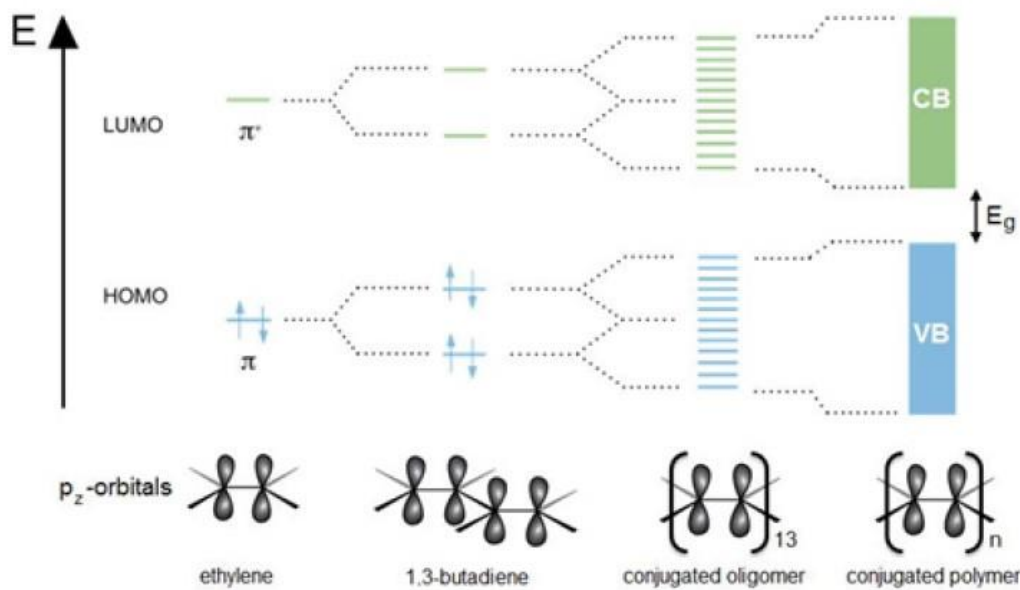
Figure 2.6 Formation of band gap of conducting polymer [15]

The conductivity of conducting polymer sum of the conductivity of three mechanisms (Figure 2.7) -

1. Inter chain conductivity 2. Intra chain conductivity and 3. Hopping.

In intra-chain conduction, electrons move along the polymer chain and is believed to be faster than other type of conduction. In the inter-chain conduction, electron move freely from one chain to another chain. The conductivity of conducting polymer depends on conjugate length (alternate pi bond and sigma bond) or chain length of molecule, interaction between molecules, carrier density, band width and mobility of the polymer. The mobility of charge carriers of a conducting polymer is very low due to defect and electron confinement.

The organic conducting polymer are amorphous and semi- crystalline in nature. This leads to random arrangement of molecule and random arrangement of molecule create dislocation. This

random arrangement creates random potential and dislocation or vacant sites creates potential well in which the charge carriers become trap. As a result of this, the mobility of the charge carriers gets reduce. So, for conduction, the trap charge needs to move from one site to another site and it is possible by hopping or tunneling (shown in Figure 2.8). The charge carriers take part in conduction are called polarons, bipolarons [22-24].

1 = undisturbed intrachain motion
2 = disturbed intrachain motion
3 = interchain motion
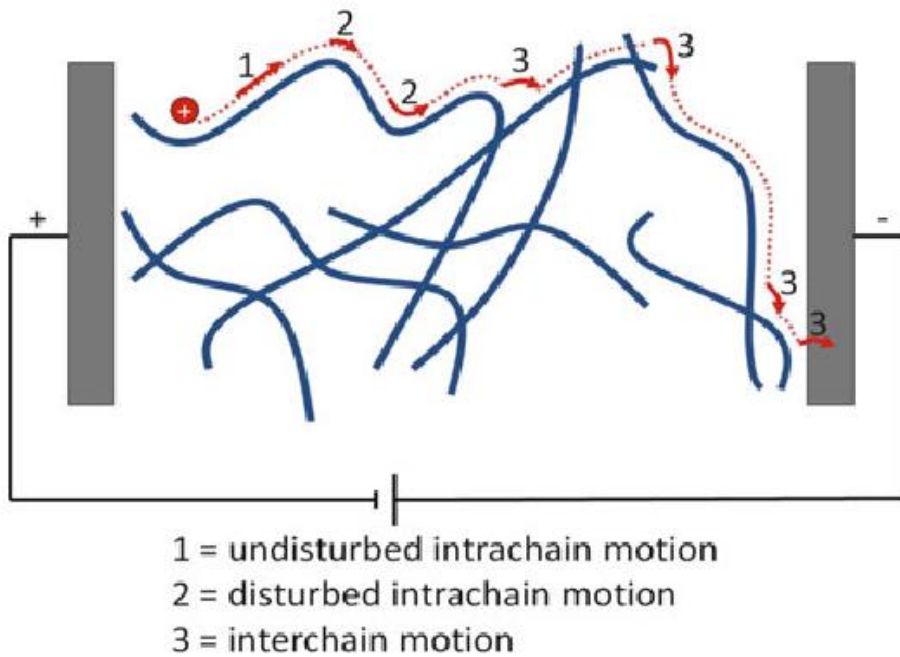
Figure 2.7 Bulk conductivity of conducting polymer
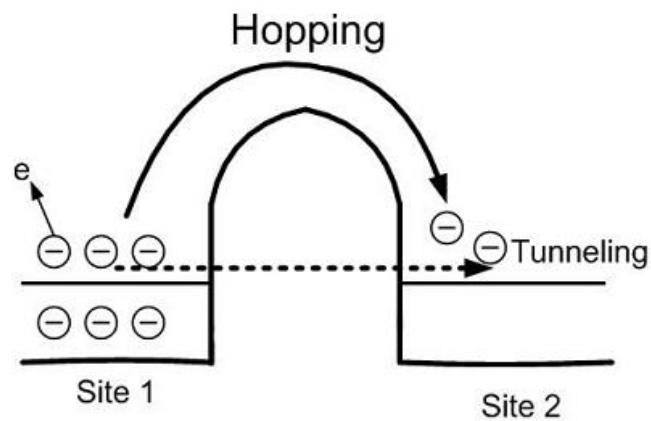
Figure 2.8 Schematic diagram for hoping and tunnelling [24]

2.4 Polyaniline

Amongst the conducting polymers polyaniline is most interesting one. It possesses good electrical conductivity, several redox states, environment stability in conducting form, non-toxicity, and easy synthesis in aqueous medium. It shows wide spectra of conductivity near insulator to semiconductor region 10^{-8} to 10 s/cm depending on doping level. It also exhibits change in colour according to its oxidation state.

Oxidation state of polyaniline:

Emberaldine Base: Stable, conducting, contains equal units of oxidized and reduced Nitrogen (Figure 2.9)

Pernigraniline: completely oxidized, low conductivity, less stable (Figure 2.10)

Leucoemeraldine state: completely reduced state, insulating (Figure 2.11)
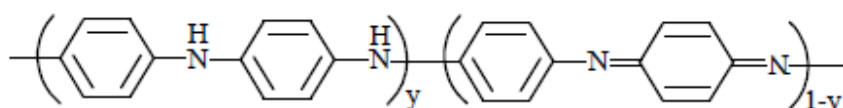
Figure 2.9 Emberaldine base y=0.5
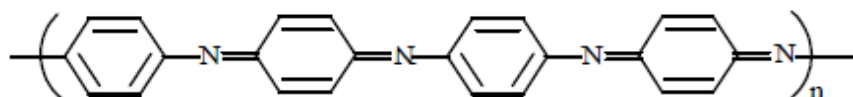
Figure 2.10 Pernigraniline
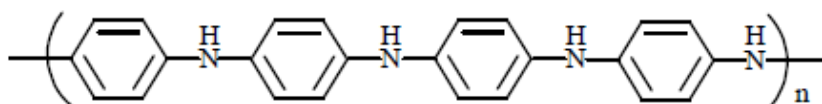
Figure 2.11 Leucoemeraldine base

2.5 Synthesis of Polyaniline

Polyaniline can be synthesized by various routes. The most common methods of polyaniline synthesis are chemical oxidative, electrochemical and enzymatic. In chemical synthesis route,

polyaniline powder is obtained, while in electrochemical synthesis, a film on a substrate is obtained. In enzyme based synthesis, a suspension of polyaniline is obtained [25].

The chemical oxidative synthesis is relatively simple and cheap, compared to electrochemical and other processes[26-28]. However, people use electrochemical synthesis due some advantages over chemical synthesis. In this method, conducting blend and composite is produced that can be modified by different condition of electrolysis. The electrochemical synthesis is a clean process. The disadvantages of this method is that the size of the film depends on the size of the electrode and appropriate conducting substrate for depositing Polyaniline has to be chosen [29, 30].

In chemical synthesis, aniline monomer solution (solvent may be acid or organic solvent) and oxidant solution are mixed together to carry out the polymerization. For preparation of solution or dispersion of aniline monomer, HCl, H_2SO_4, H_3PO_4, toluene and CH_3COOH, acetone has been used. The common oxidant which has been used for polymerization are ammonium per sulfate, potassium per sulfate, hydrogen peroxide, vanadium pent oxide [28, 31, 32].

The conductivity, yield and morphology depends of various parameters. It depends on solvent acid or organic liquid. It depends on oxidant and strength of oxidant, polymerization time, temperature and also depends on pH value of reaction medium as shown in Figures 2.12-2.15. With increasing pH of synthesis medium, the conductivity of polyaniline inceases and conductivity also increase with molcular weight.
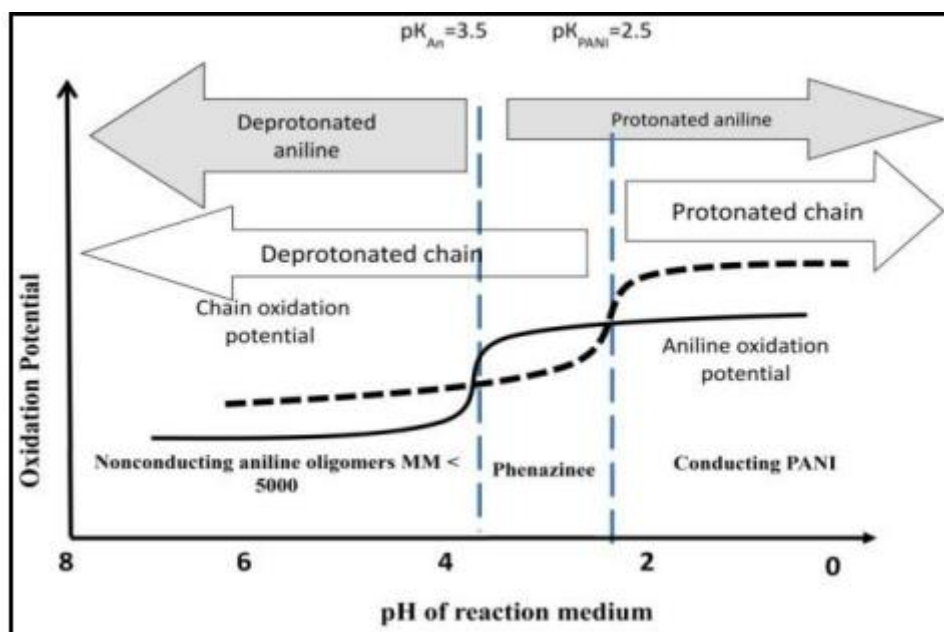
Figure 2.12 Function of pH value in polymerization medium[31]
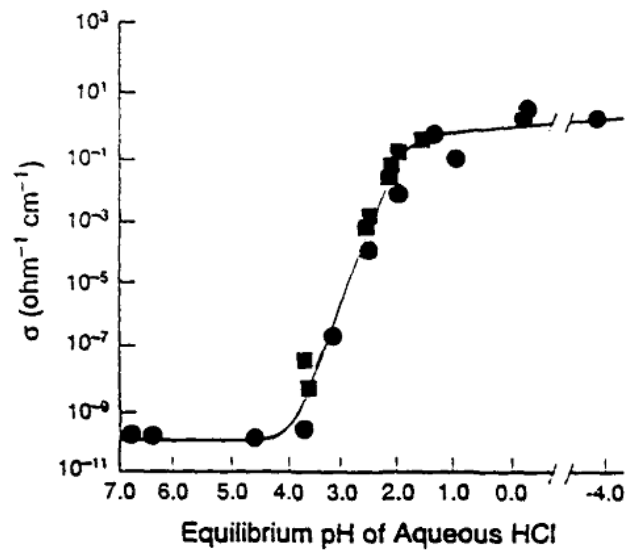
Figure 2.13 conductivity changes with respect to different pH medium[33]
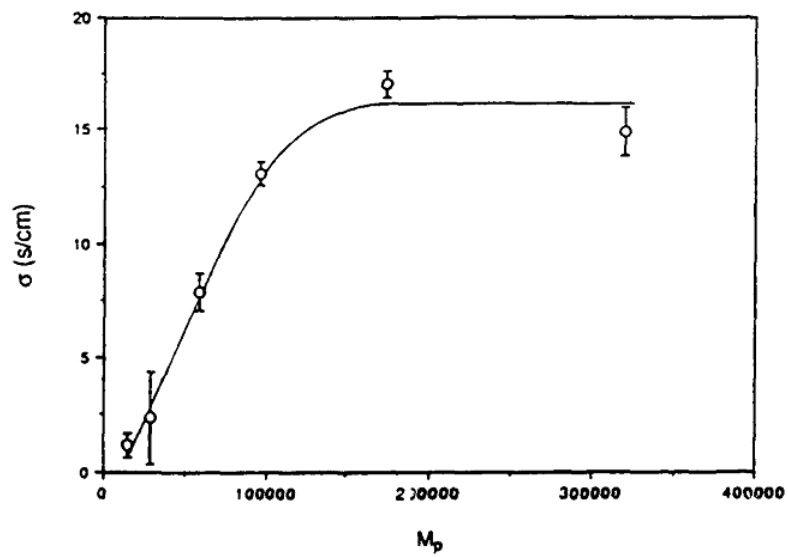
Figure 2.14 conductivity increase with increase molecular weight [33]
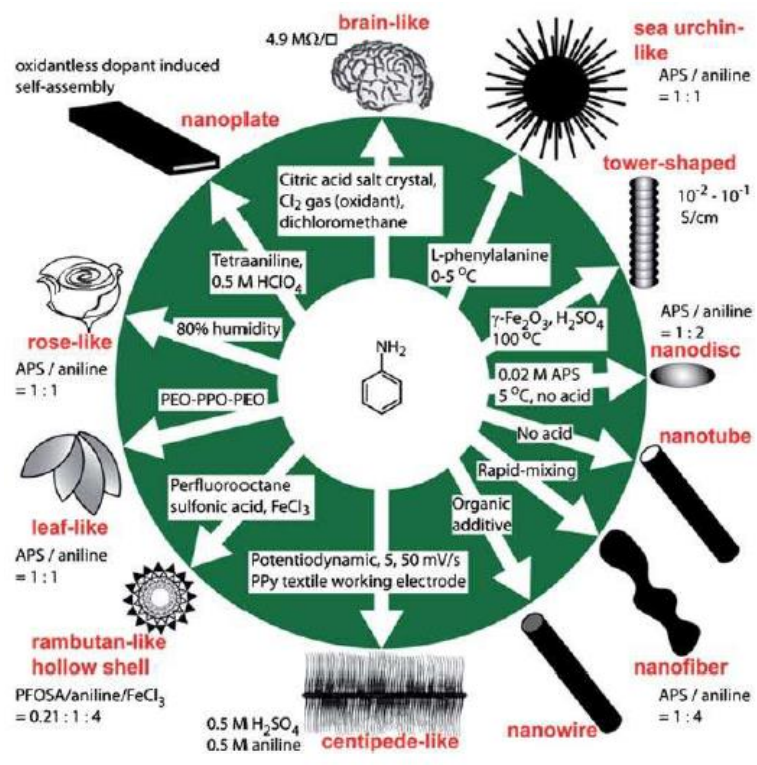
Figure 2.15 Nanostructures of polyaniline obtained under different synthesis conditions [34]

2.6 Doping of Conducting Polymers

Conducting polymer in intrinsic form or undoped form conductivity is very poor ($\sigma = 10^{-8}$ S/cm). In the process of doping, impurities are added which increase the electrical conductivity of the semiconductor. The conductivity change is of the order of 10^8 S/cm [35]. Doping is simply addition or removal of electron from the backbone polymer chain which delocalises the electron. Those delocalised electron take part in conduction.

The doping of conducting polymer is different than that of conventional inorganic semiconductor. In inorganic semiconductor for doping added dopant is ppm (parts per million) level. This dopant interacts with the lattice of the inorganic semiconductor and crystal structure get distorted after mixing of dopant. This distorted of crystal structure help to create extra electron and hole. The holes move in valance bond or electron in conduction band. The dopant are distributed in the specified position of the lattice [20].

In case organic semiconductor or polymers, the amount of dopant is high. The dopant can vary up to 50% of the polymer. Dopant is randomly distributed in polymer matrix and directly interacts with the polymer chain and the polymer chain get charged, according to nature of

dopant. The properties of organic semiconductor, optical, magnetic, crystallinity, mobility, carrier concentration and conductivity depends on doping concentration [35].

There has various doping technique to dope conducting polymer

- Gaseous doping
- Solution doping
- Electrochemical doping
- Radiation doping
- Ion exchange

Dopant can be classified such way

- Neutral dopant : Br_2, I_2 , AsF_2, Na, $H2SO4$, $FeCl3$
- Ionic dopants: LiClO4, FeClO4, CF3SO3Na, BuNClO4 etc.
- Organic dopants: CF3COOH, CF3SO3Na, p-CH3C6H4SO3H
- Polymeric dopants: PVS, PPS

The nature of doping are two type p-type and n-type. The first type (p type) is oxidative type doping and the second type (n-type) is reduction type. The dopant directly interact polymer chain and donate or accept electron according to chemical nature as shown in Figure 2.16 [16].
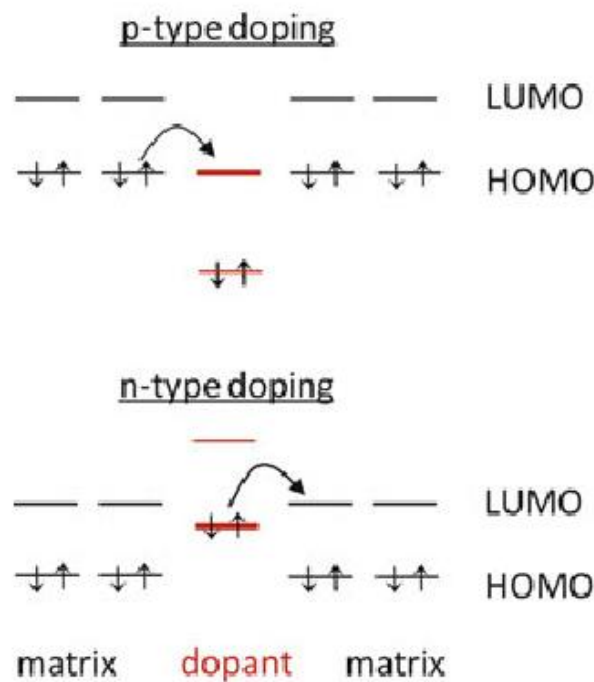
Figure 2.16 Electronic configuration of p-type and n type doping

2.7 Bacterial cellulose

The cellulose is abundant material in nature. All the plants cells are made of cellulose. Now a days, people are talked about cellulose in different area of study chemistry, textile industry, medical, pharmaceutical [36-38].

Although plants and trees are the main sources of cellulose, some microscopic organisms (bacteria, algae, a few fungi) has been reported to produce cellulose. The cellulose produced by bacteria is known as bacterial cellulose. The bacteria produce cellulose as a thick hydrogel or pellicle. The bacterial cellulose is different from the plant cellulose. The plant cellulose contains hemicellulose and lignin. Bacterial cellulose is pure, highly crystalline, posseses higher mechanical strength and toughness. Bacterial cellulose has two crystalline form I_α and I_β whereas for plant cellulose mainly I_β .[36, 39]

The structure of bacterial cellulose is polymer of glucose units linked with β-1,4 glycosidic bond (Figure 2.17). Bacterial cellulose exists in form of fibrils composed of glucan chain which interact by hydrogen bond (Figure 2.18). It has good mechanical property - UTS (about 200MPa), elongation (around 8%) and Young Modulus 7 GPa [40]

200nm
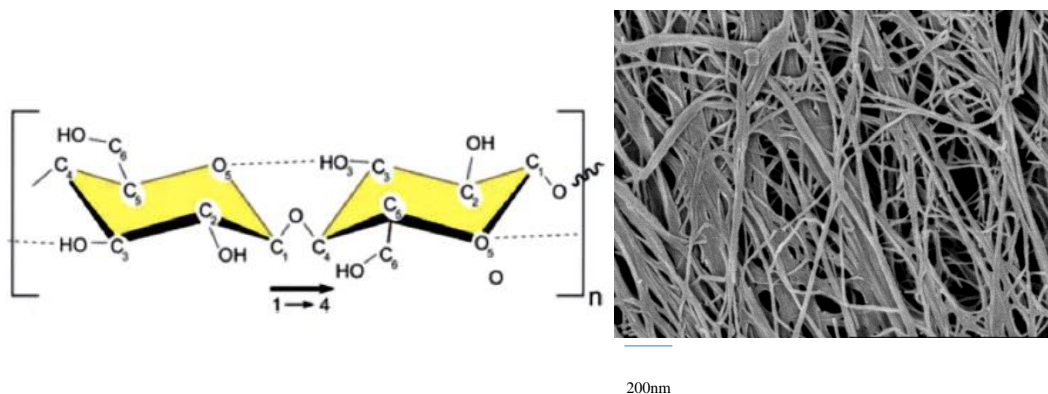
Figure 2.17 a) Schematic of bacterial cellulose monomer [41] b) Fibrillar structure bacterial cellulose [41]

2.8 Polyaniline Bacterial composite

The two major limitations of polyaniline are poor mechanical stability and that, it can't be process by conventional method. To overcome this problem, we generally prepare polymer blends and composite other material, which possesses mechanical strength. Synthetic polymer are not biocompatibility and recyclability. Cellulose has long been studied as a preferred

substrate. Another advantage is Polyaniline and cellulose strongly interact to each other by hydrogen, which facilitates the *in situ* polymerization of aniline in cellulose matrix (as shown in Figure 2.18 below). Some of the proposed applications are smart textile [42], flexible electronics, and flexible supercapacitors [43]
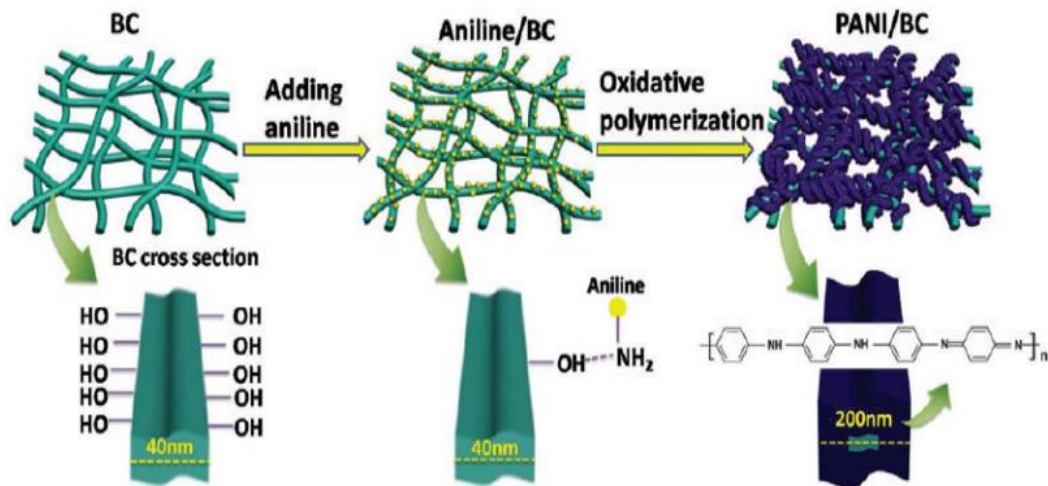
Figure 2.18 Schematic of *in situ* oxidation polymerisation of polyaniline to form polyaniline/bacterial cellulose composite [44]

Quite a few studies are available on bacterial cellulose and polyaniline composites. The composites were mostly prepared by *in situ* polymerization. In some cases, bacterial cellulose membranes were used while in other nanowhiskers derived from bacterial cellulose were used. In one of the studies, the effect mass ratio of cellulose to aniline, ratio of APS (the oxidising agent) to aniline, concentration of acid, time and temperature of polymerisation has been studied. It was found equi-molar ratio of aniline and APS was the best and the polymerisation carried out at lower temperature and longer duration yielded better conductivity. The highest conductivity achieved was 5×10^{-2} S/m and conductivity increased with twist angle[44].
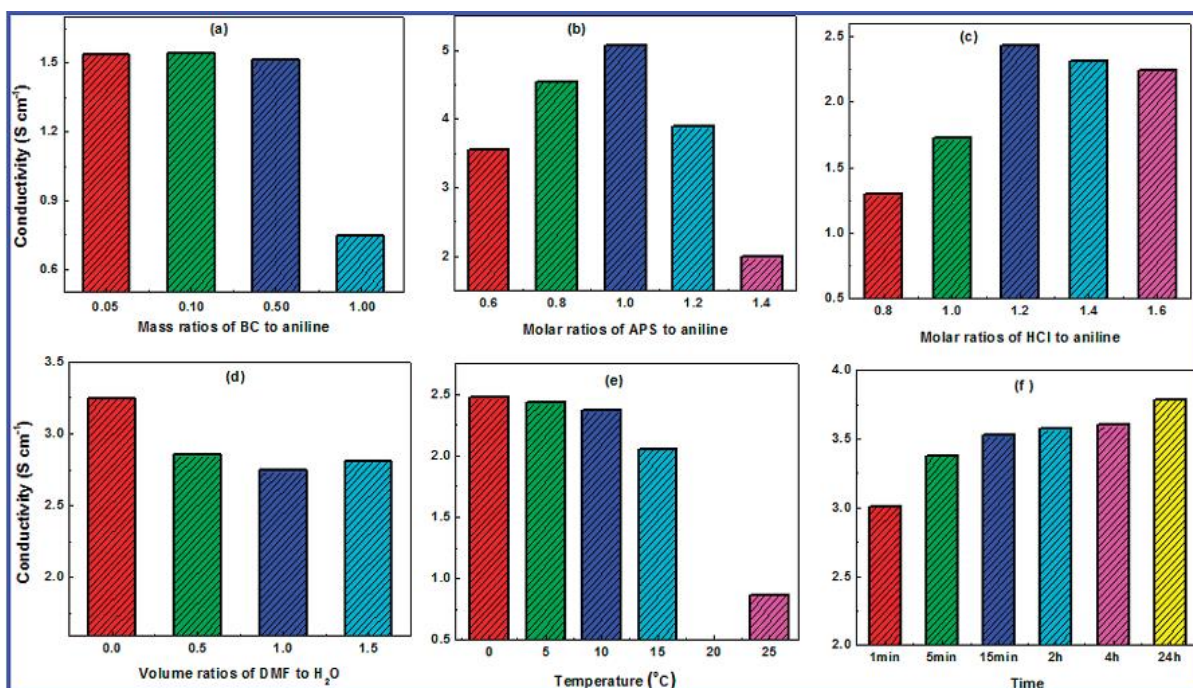
Figure 2.19 Conductivity of bacterial cellulose and polyaniline composite in different parameter [43]

In another study, at first bacterial cellulose was dipped into aniline hydrochloric solution for 48 hours at room temperature for aniline hydrochloric to fully filtrate through the bacterial cellulose. After that ammonium per sulphate was added drop by drop and the reaction was allowed to proceed for 5, 10, 20, 30, 60 and 120 min. It was found that with increase in reaction time, first conductivity increases up to 20 min then conductivity decreases from 30 to 120 min and measured conductivity range was 1.3×10^{-2} S/cm to 6.7×10^{-8} S/cm [45]

In another study, flexible Electrically Conductive Nano composite Membrane Bacterial cellulose and polyaniline composite was prepared by In situ chemical oxidative polymerization by APS in various reaction time up to 90 min and got highest value of conductivity 5×10^{-2} S/cm. Measured young modulus and tensile strength of the composite was 5 GPa and 95.7 MPa [44]

Bacterial Cellulose Nanofiber-Supported Polyaniline Nanocomposites with Flake-Shaped Morphology has also been studied for Supercapacitor Electrodes. With optimised preparation condition, the conductivity achieved was 5.1 S/cm. [43]

New Bacterial Cellulose/Polyaniline Nanocomposite Film with One Conductive Side through Constrained Interfacial Polymerization was synthesized by interfacial polymerization technique. The bacterial cellulose wet film was taken into cup and after that toluene aniline monomer solution was taken into it. After that, the cup was immersed into acidic APS solution for 10 min. The reaction was carried out at 0°C for 24 hour. Calculated minimum resistivity of the both the bacterial cellulose and polyaniline side of the composite were 1.46×10^{8} Ω.cm and 40 Ω.cm respectively and it was noticed that strength of composite decreases with incorporation of polyaniline [46].

Conducting composite membrane from bacterial cellulose and polyaniline and doped with DBSA was prepared by *in situ* oxidative polymerization. Conductivity of pure polyaniline was 1.66×10^{-4} and it was changed to 7.78×10^{-6} S/cm when it was composited with bacterial cellulose [47].

Another study presented polyaniline grafted cellulose for humidity sensor**s.** Synthesis of polyaniline grafted cellulose was done by co polymerisation method. 10 ml of polyaniline and 5g of cellulose were dissolve in 200ml water which contain 2% of HCl. After that 5 ml 1M copper sulphate solution was added. Measured conductivity of pure polyaniline and composite were 1.05 S/cm and 1.25×10^{-2} S/cm, respectively [48].

Stable lyotropic chiral nematic liquid crystalline phase was synthesized by cellulose nanocrystal. This was used an asymmetric reaction medium for *in situ* polymerization of polyaniline. The measured conductivity in different cellulose to aniline ratio varied 10^{-2} to 7×10^{-5} S/cm.[49]

Conducting composite of cellulose and polyaniline was synthesize heterogeneously by chemical oxidative polymerization and doped by various acid. Conductivity of the composite varied with consumption of polyaniline in the composite and also depends on the acid used [43, 50]

Cellulose nanofibre and polyaniline composite was made by *in situ* polymerization by using oxidant APS in HCl acidic medium. Measured resistance was 11Ω/ cm^{2} in HCl doping condition and measured tensile stress was 3.61 MPa and Young modulus was 276.6 Mpa [51].

It was found in one of the works that conductivity of composite increased from 10^{-6} S/cm to 10^{-2} S/cm with increase in polyaniline content from 10 to 20% and no further change was observed for increase in polyaniline from 20 to 30% [52].

2.9 Summary

Bacterial cellulose is a suitable substrate for making conducting composites with polyaniline. Some work has been done before but a lot of variability is observed in conductivity values. Systematic study of effect of time and temperature on conductivity of polyaniline is scattered. Moreover, effect of modification in bacterial cellulose on composite properties has not been studied.

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Chapter 3 Synthesis Time - Temperature Effect on Polyaniline Morphology and Conductivity

(reproduced as paper)

Abstract

This paper studies the effect of duration and temperature of polymerisation on morphology and conductivity of polyaniline produced by oxidative polymerisation. It has been reported that with decrease in temperature and increase in polymerisation duration, the yield and particle size increases. The polyaniline particles are rod-like at the onset of polymerisation and also at low polymerisation temperatures. The conductivity has been determined by four-point measurement with incorporation of correction factor. It was found that the electrical conductivity varies from below 0.5 S/cm to over 11 S/cm with variation in duration and temperature of polymerisation. Conductivity is proposed to be dependent on the particle size as conductivity increases with decrease in polymerisation temperature and increase in polymerisation duration, similar to the trend observed for particle size. This may be indicative of equal probability of inter- chain and intra-chain charge transport.

Keywords: Polyaniline, four-point conductivity, morphology, time temperature effect

3.1 Introduction

With technological advancement and emphasis on developing flexible and wearable electronics, light-weight conducting materials are being sought. Polymers, being light weight and flexible, are an obvious choice for such applications. Some polymers such as polyaniline, polypyrrole, polythiophene, polyphenylene, polyphenylene and polyacetelyne are known to exhibit conductivity [1, 2]. Amongst these, polyaniline offers several advantages over other conducting polymers in terms of facile synthesis, stability, morphological tunability, and control over doping level to tune conductivity [3-6].

Aniline is often produced by oxidative polymerisation, chemical or electrochemical, of aniline [7-9] . Standardisation of polyaniline synthesis to obtain unique electrical properties has always been a challenge and thus a vast range of conductivity values, varying from below 0.5 S/cm to over 300 S/cm, are reported in the literature [8, 10-14]. Several factors such as the choice of

oxidising agent and ratio of amounts of oxidising agent and aniline, doping, polymerisation temperature and so on, have been shown to affect its conductivity and yield [4, 10-12, 14-18].

These factors have been shown not only to affect yield and conductivity but also the microstructure and morphology [4, 15, 19-21]. Polyaniline has been found to exhibit several nanostructural forms, given different synthesis conditions and parameters [5, 6, 19]. Effect of parameters, such as cations, temperature of polymerisation, substrate, on polyaniline morphology and molecular weight has been discussed in the previous work, but without much reference to effect on conductivity [6, 15, 19, 20, 22]. Polyaniline nanostructures have attracted special attention in anticorrosion coatings, energy applications and sensors parameters [5, 6, 19].

Very few reports are available on the effect of polyaniline synthesis and processing parameters on properties along with its correlation with the morphology [5, 12, 15, 23, 24]. In this work, effect of polymerisation duration and temperature has been studied on morphology as well as conductivity. Polymerisation at sub-zero temperatures have shown an improvement in conductivity, be it solid state or liquid reaction medium [11, 12, 14, 21]. In a separate report morphology of polyaniline has been studied at low temperatures but the correlation between conductivity and morphology has not been well established. Here, the study has been carried out at three different polymerisation temperatures and durations. Evolution of morphology with time and temperature has been reported. Low concentration of reactants has been used to minimize the effects of concentration [10].

Another important consideration in this paper is the strategy to extract the conductivity values from four-point measurement by using correction factors. Most of the literature on the conductivity of polyaniline has produced conductivity values by four-point method, but have not accounted for correction factors.

3.2 Materials

Aniline and ammonium persulphate (APS) were used to prepare polyaniline by oxidative polymerisation. The chemicals aniline monomer (≥99.5% pure) and ammonium persulphate (APS, ≥98.0% pure) were purchased from Sigma-Aldrich, China. Hydrochloric acid was ordered from Alfa Aesar India. 0.2 M APS in water and 0.2 M aniline solution in 1M HCl were mixed in equimolar ratio. The time and temperature of polymerisation were varied as shown in the Table 1 below.

Table 3.1List of various polyaniline samples prepared by varying polymerisation time and temperature and their names

Time / Temperature	30 min	6 hour	24 hour
Room temperature (27-28˚C)	RT30m	RT06h	RT24h
normal fridge (4˚C)	NF30m	NF06h	NF24h
deep freezer (-18 ˚C)	DF30m	DF06h	DF24h

RT - room temperature (27-28˚C)

NF - normal fridge (4˚C)

DF - deep freezer (-18˚C)

Fourier transform infrared spectroscopy (FTIR) was used to confirm formation of polyaniline. FTIR was performed on powders and pellets in the range 500 cm^{-1} to 4500 cm^{-1} on TENSORS 37 Brukers. Scanning electron microscope was used to image the powders prepared. Samples were placed on a carbon tape and imaged on Zeiss Supra 40 FESEM at an accelerating voltage of 15kV.

Conductivity measurements were carried out using four probe technique by four probe set up (scientific equipment Roorkee). The change in voltage with change in current was measured. The powders were made into a pellet using 0.1-0.2 g of polyaniline powder pressed in a rectangular dice with dimension 5 mm by 10 mm by using pressure of one tonne/cm^2. The dimensions, mass and calculated density of pellets from the various powders are listed in Table 2. Since the pellet has finite dimensions, the measurements were corrected by correction factors, which is discussed here. Resistivity of the sample may be calculated by using the following equation (i) where F is the correction factor and s is the probe distance which is 2 mm in this case. The ratio of voltage to current was calculated for several values and the average was taken for calculation of the conductivity.

$$\rho = 2\pi s F \frac{V}{I} \ \ldots\ldots\ (i)$$

For the correction, three factors have been calculated for the given sample dimensions.

$F = F1 \times F2 \times F3 \ \ldots\ldots\ (ii)$

Where F1 is due to sample thickness, F2 due to lateral sample dimensions and F3 due to probe placement relative to the edges.

The values of F1 was calculated using equation (iii) and is listed in Table 3.

$$F1 = \frac{\frac{t}{s}}{2\ln[\frac{\sinh(\frac{t}{s})}{\sinh(\frac{t}{2s})}]} \quad \ldots\ldots\ldots\ldots \text{(iii)}$$

The values of F2 can be considered as 1 and F3 was found from Figure 1 [25-28]. F_{31} and F_{32} represents for non-conducting bottom sample. Considering d/s as 1, F_{31} is 1 and d/s =1 for the other dimension, F_{32} is 0.8. So, taking product of the two functions, F3 was calculated to be 0.8

Table 3.2 Dimensions, mass and calculated density of pellets from the various powders

Sample	Length (cm)	Breadth (cm)	Depth (cm)	Mass (g)	Density (g/cm^3)
RT30 m	0.99	0.40	0.16	0.08	1.26
NF30m	0.99	0.40	0.20	0.10	1.22
DF30m	0.99	0.40	0.21	0.10	1.23
RT06h	0.99	0.44	0.41	0.23	1.31
NF06h	1.00	0.40	0.19	0.10	1.24
DF06h	1.00	0.40	0.20	0.08	1.00
RT24h	0.99	0.40	0.33	0.17	1.28
NF24h	0.99	0.40	0.21	0.09	1.14
DF24h	1.00	0.41	0.22	0.10	1.13
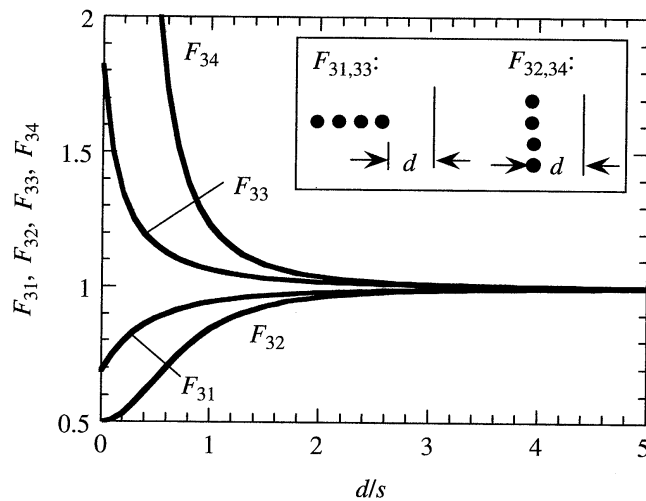
Figure 3.1 Variation in values of F3 with d/s where d is distance between probe end to sample edge and s is probe spacing [25]

Table 3.3 Values of correction factors for all samples

Sample ID	F1	F2	F3	F
RT30 m	0.53	1	0.8	0.42
NF30m	0.62	1	0.8	0.50
DF30m	0.63	1	0.8	0.50
RT06h	0.90	1	0.8	0.72
NF06h	0.60	1	0.8	0.48
DF06h	0.62	1	0.8	0.50
RT24h	0.83	1	0.8	0.66
NF24h	0.63	1	0.8	0.50
DF24h	0.65	1	0.8	0.52

3.3 Results and Discussions

3.1 Yield

Effect of time: Figure 2 (a), (b), (c) shows the powders produced at polymerisation temperatures of -18˚C, 4˚C and RT for three different durations. As the duration of polymerisation increased from 30 min to 6 hours and further to 24 hours, there is an increase in the quantity of polyaniline produced for all polymerisation temperatures. The amount of polyaniline obtained by polymerisation for 30 min at room temperature is about 0.24 g, while that for 24 hours of polymerisation, the yield is 0.32 g. The yield was 0.33 g when the polymerisation temperature was reduced to -18˚C, even with polymerisation duration of 30 min.

Effect of polymerisation temperature: Figure 2 (d), (e), (f) shows the powders produced for polymerisation duration of 30 min, 6 hours and 24 hours, for three different polymerisation temperatures. Lower polymerisation temperature leads to higher yield. Since the polymerisation reaction is exothermic, the reactions goes forward with a decrease in temperature [29]. Therefore, larger quantity is obtained for lower temperatures of polymerisation. Also, the degradation of polyaniline, due to rise in temperature during the reaction, is expected to be lesser at lower starting temperature [10].
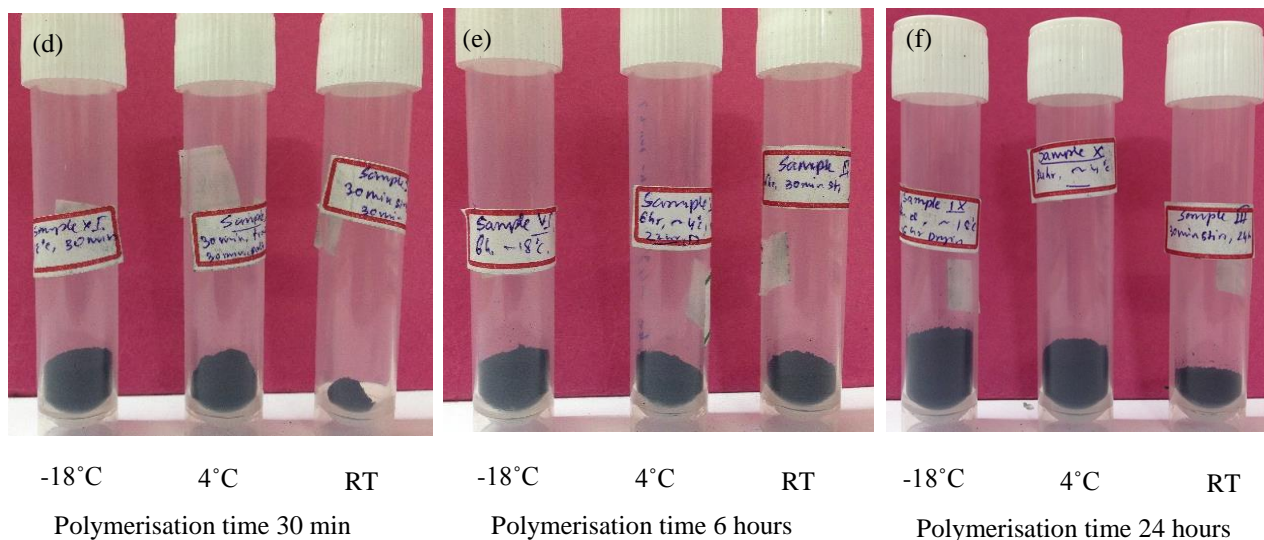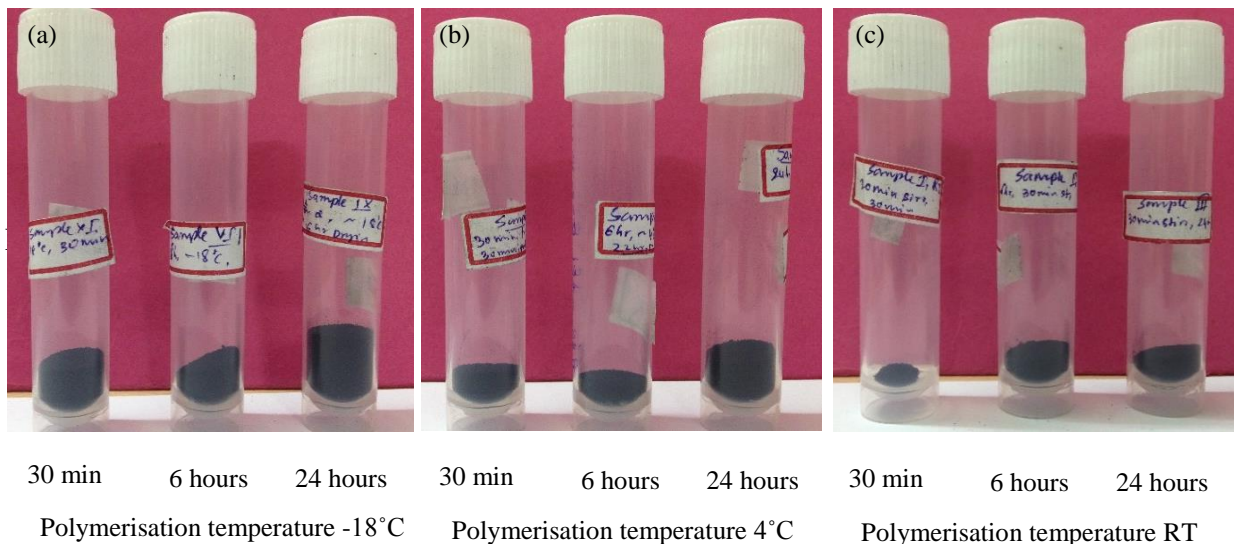
Figure 3.2 Powders produced at (a) polymerisation temperature of -18˚C (b) polymerisation temperature of 4˚C (c) polymerisation temperature of RT for 30 min, 6 hours and 24 hours at each temperature. Powders produced for (d) polymerisation time of 30 min (e) polymerisation time of 6 hours and (f) polymerisation time of 24 hours at temperatures of -18˚C, 4˚C and RT

3.2 FTIR

FTIR was performed on all samples to confirm formation of polyaniline emeraldine salt. Figure 3 shows the FTIR spectra for one of samples RT24h. FTIR analysis of polyaniline emeraldine salt, the main part of the spectra has peaks corresponding to 1546, 1482, 1283, 1218, 1143 and 764 cm⁻¹. Peaks at 1546 and 1482 cm⁻¹ are attributed to non-symmetric vibration of C-H bond in quinoid and benzenoid. C-N bond stretching in quinoid and benzenoid are observed 1283 and 1218 cm⁻¹. The peaks corresponding to C-H bending is seen at 1143 cm⁻¹. The polar

structure due to proton acid doping shows peak at 764 cm^{-1}. Those values match with the literature [30, 31]. The additional peaks for C-H stretching vibration appears at 2920 cm^{-1}, aliphatic hydrocarbon stretching vibration (C-H, CH$_2$) at 2838 cm^{-1} and that for diozonium salt at 2377 cm^{-1} [24].Therefore it can be concluded that the samples obtained are polyaniline.
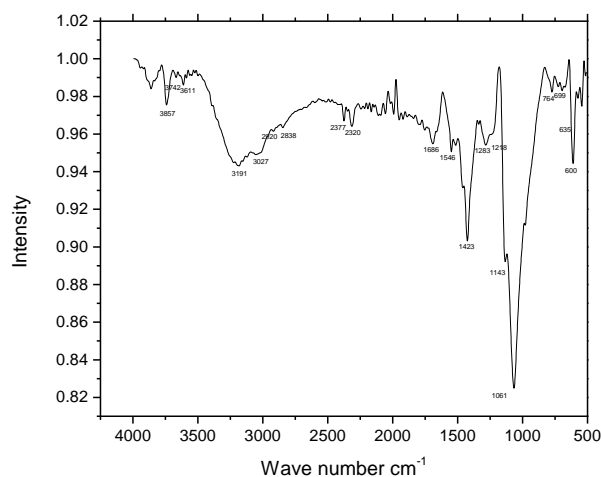
Figure 3.3 FTIR spectra of sample RT 24h with main peaks indicated

3.3 Scanning electron microscopy

Figure 4 shows the SEM images of all the powders of polyaniline prepared. The average particle sizes with variation in polymerisation time and temperature are listed below in table 4. It can be seen that with increase in polymerisation duration from 30 min to 24 hours with polymerisation carried out at room temperature, particle size increases from 151 nm to 355 nm and with decrease in the polymerization temperature from room temperature to -18˚C, particle size increases from 151 nm to 183 nm for 30 min of polymerisation. The trends are consistent for all cases studied in this paper.

It can be seen that for 30 min polymerization time, rod-like particles are present. With increase in polymerisation duration, rod-like particle become less abundant and more spherical/globular particles are seen. Similar observation can be made with increase in temperature.

The rod or fibre like morphologies are obtained by suppressing secondary growth [32, 33]. Formation of ice, for polymerisation carried out at sub-zero temperature, causes confinement of the polymerising monomer and the oxidising agent which actually increases the local concentration. This can further accelerate the polymerisation and also causes directional polymerisation. It has been shown that PANI first forms fibres [32], however, with the progress

of the polymerization, the formed fibres serve as the scaffolds for the further growth of PANI and finally develop to a particle form. Thus, a longer polymerization time favours the formation globular particles [5, 20, 33]. Several reports have claimed increase in molecular weight with decrease in polymerisation temperature [11, 34, 35].
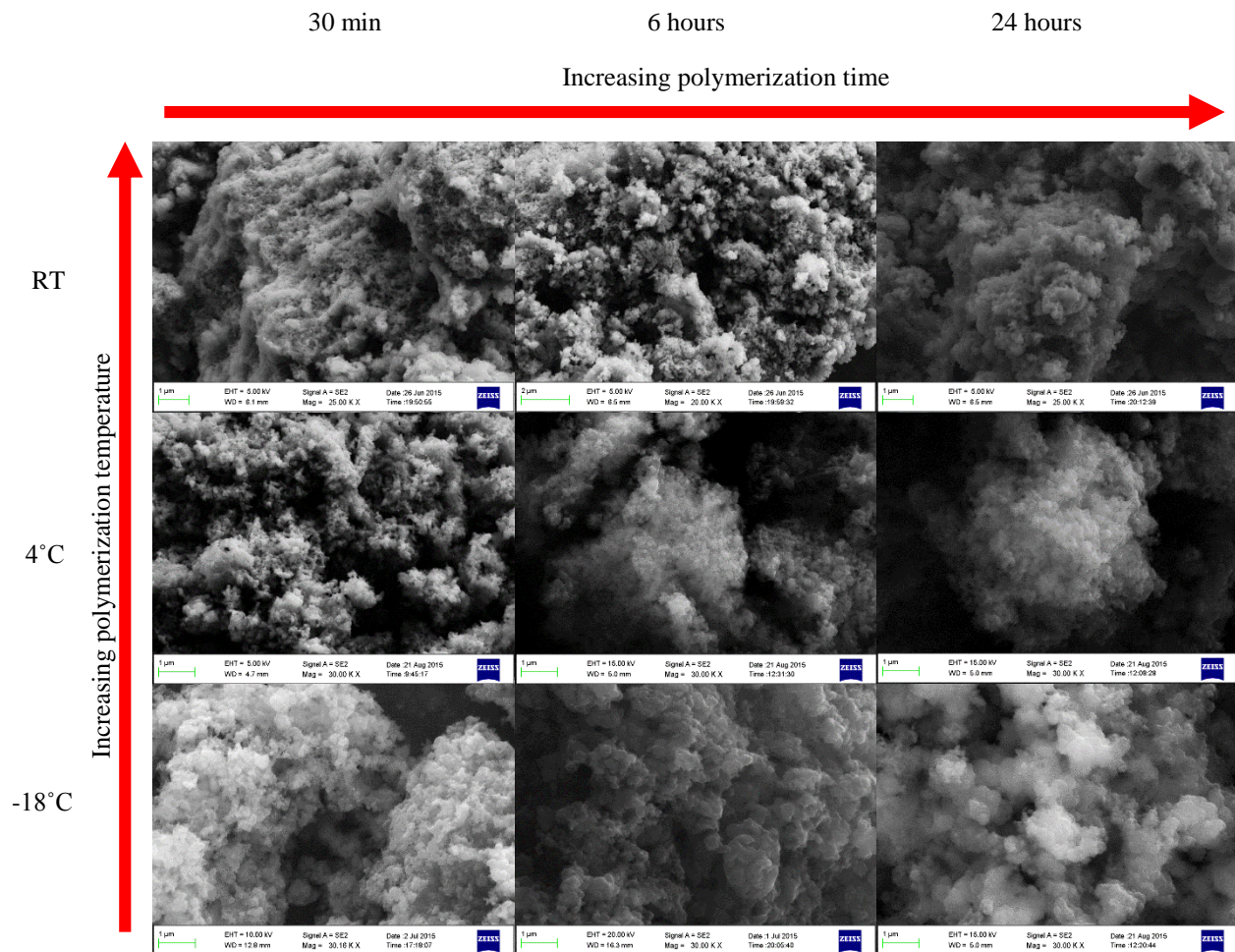
Figure 3.4 SEM images of Polyaniline powders produced at different polymerisation temperature for different time

3.4 Conductivity measurement

Conductivity measurements were done by four point measurements. However due to the limitations in the size, correction factors need to be employed to correctly estimate the value of conductivity. It must be remembered that the resistivity of the material is assumed to be uniform in the area of measurement. The corrections have been done considering a non-conducting boundary at the bottom of the pellet.

The variation in voltage with change in current for all samples was recorded at room temperature. The average values of V/I was taken for conductivity calculation below and listed in Table 5.

Table 3.4 Average particle size of polyaniline produced with variation in polymerisation time and temperature

Time / Temperature	30 min	6 hour	24 hour
Room temperature (27-28C)	RT30m 151±47 nm	RT06h 256±70 nm	RT24h 355±81 nm
normal fridge (4C)	NF30m 165± 46nm	NF06h 311±75 nm	NF24h 372± 90nm
deep freezer (-18 C)	DF30m 183±63 nm	DF06h 368± 79nm	DF24h 380±84 nm

Table 3.5 Values of correction factors, average V/I values, resistivity and conductivity

	V/I	S	F	P(Ω.cm)	σ(S/cm)
RT30 m	4.16	0.2	0.42	2.20	0.5±0.02
NF30m	0.46	0.2	0.50	0.28	3.5±0.10
DF30m	0.39	0.2	0.50	0.24	4.1±0.11
RT06h	0.27	0.2	0.72	0.24	4.2±0.12
NF06h	0.28	0.2	0.48	0.17	6.0±0.51
DF06h	0.20	0.2	0.50	0.13	7.8±0.39
RT24h	0.21	0.2	0.66	0.18	5.7±0.09
NF24h	0.22	0.2	0.50	0.14	7.1±0.14
DF24h	0.14	0.2	0.52	0.09	11.1±0.17

It can be seen from Table 6 that conductivity increases from 0.5 S/cm to 11 S/cm with increase in polymerisation time and decrease in polymerisation temperature. The increase in conductivity here may be attributed to increase in crystallinity and molecular weight. It has been indicated in the literature that with increase in polymerisation time and decrease in

polymerisation temperature, molecular weight and crystallinity increases [11, 35]. It is seen from the SEM that the particle size also increases with the increase in polymerisation time and decrease in polymerisation temperature. This suggests that the conduction pathways are enhanced with increase in particle size.

Earlier work has shown that crystallinity increases along with molecular weight as the polymerisation temperature is decreased. However, they have not reported any change in conductivity and thus suggested only a weak dependence of MW and crystallinity on conductivity [12]. This has been attributed to relative ease of inter chain charge transport as compared to intra chain. On the other hand, some reports have also suggested high conductivity along chain than across in an oriented film of polyaniline [11]. The results obtained here suggests that conductivity is directly related to particle size, which is function of crystallite size as well as aggregation. As the fibrillary morphology is the preferred polyaniline morphology and is associated to the orientation of polyaniline chains, the conductivity is significantly higher at lower temperature even with small polymerisation duration.

The conductivity values obtained are reasonably better that those report in literature [5, 14], which may further be enhanced by doping or using lower polymerisation temperatures and other factors discussed before.

Table 3.6 Variations in conductivity with polymerisation time and temperature

Time Temperature	30 min	6 hour	24 hour
Room temperature (27-28˚C)	0.5 S/cm	4.2 S/cm	5.7 S/cm
normal fridge (4˚C)	3.5 S/cm	6.0 S/cm	7.1 S/cm
deep freezer (-18 ˚C)	4.1 S/cm	7.8 S/cm	11.1 S/cm

3.4 Conclusions

This paper shows effect of polymerisation duration and temperature on yield, conductivity and morphology. It has been shown that with increase in polymerisation duration and decrease in polymerisation temperature, the yield and conductivity of polyaniline increases. Electron microscopy reveals that the morphology changes from rod-like particles to globular

morphology on increase in time and temperature. The conductivity of polyaniline varies from 0.5 S/cm to 11.1 S/cm with increase in polymerisation time and decrease in polymerisation temperature, which can be correlated to the particle size.

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Chapter 4 Polyaniline and Bacterial Cellulose Composite

Abstract

Polyaniline is a preferred conducting polymer, but lacks mechanical integrity. It is almost impossible to make free standing sheets out of purely polyaniline. Therefore, Polyaniline composites are made. Here, composite of polyaniline with bacterial cellulose has been made with three different compositions. Also modified bacterial cellulose has been used to study the effect of bacterial cellulose morphology on composite properties.

1. Introduction

In last three or four decades, people have focused on conducting polymers to substitute conductors or semiconductors. Now it is possible to replace metals and semiconductors with conducting polymers, as their conductivity is comparable with semiconductors or metal[1, 2]. Along with the conductivity, light weight, low cost, easy synthesis, tunable conductivity, tunable morphology and environmental stability put conducting polymers in a better position [3]. The example of conducting polymers are polyacetylene, polythiophene, polyphenylene, polypyrrole, polyaniline etc.[4]

Polyaniline possesses unique character of oxidation or reduction, environmental stability, tunable conductivity, tunable morphology, optical character and bio compatibility which can enable diverse applications [5]. It has been used in sensors, actuators, corrosion inhibitors[6], solar cell [7, 8] . In spite of all these properties, polyaniline does not possess mechanical integrity.

For sake of mechanical integrity, polyaniline needs to be on substrate or into the matrix or mixed with a binder. In general, for fabricating devices, synthetic polymers (polyethylene, PVC, PMMA)[9] or binders (PVA, PVDF)[10] are used. Synthetic polymer causes pollution and some of synthetic polymers are not bio compatible and are also toxic[11, 12]. So, for alternative substrate which does not create any pollution, is bio compatible, abundant and also low cost, cellulose is a better choice as a substrate[13].

Cellulose is an abundant material on earth. It is bio compatible and biodegradable. In this case, bacterial cellulose has been chosen due to some advantages over plant cellulose. Bacterial

cellulose is pure, has higher crystallinity, high strength, high porosity, high water holding capacity than other kinds of cellulose[14].

It has been reported that bacterial cellulose polyaniline composites can be used for flexible electronic devices (e.g. sensor, actuators, anti-static coatings, supercapacitors) [15-18]. The flexibility, conductivity and mechanical stability still now are questionable[19]. Here, unmodified bacterial cellulose and modified bacterial cellulose have been used as substrate. These modified bacterial celluloses have different specific surface area, porosity and crystallinity[20]. So, in this paper aim is to study the effect of bacterial celluloses porosity, crystallinity effect on incorporation of polyaniline and conductivity.

2. Material & Methods

Aniline and Ammonium Per sulphate (APS) were used to prepare polyaniline by oxidative polymerisation. The chemicals Aniline monomer (≥99.5% pure) and ammonium per sulphate (APS, ≥98.0% pure) were purchased from Sigma-Aldrich, China. Hydrochloric acid was ordered from Alfa Aesar India. Unmodified bacterial cellulose (BC_NA), bacterial cellulose modified by polyethylene glycol (BC_PEG) and bacterial cellulose modified by carboxy methyl cellulose (BC_CMC) were taken from Dr. Mudrika Khandelwal.

Three different concentration of aniline solution and APS solutions was prepared - 0.05 M, 0.1 M and 0.15 M, which were to maintain the weight ratio of bacterial cellulose to aniline as 1:1, 1:2 and 1:3, respectively.

At first, aniline solution was taken into Petridis and a piece of bacterial cellulose (2cm×1cm) was dipped into the aniline solution for 30- 45 min as shown in Figure 1. After that same volume and same concentration of APS solution was added. Then, the mixture was kept into deep freeze at -18°C for 24 hour for polymerization (Figure 2). Three different kind of celluloses were used and three different compositions were synthesised. Details of the sample are shown in the table below.

Table 4.1 Bacterial cellulose and aniline ratio before polymerization

BC: Aniline	PEG	NA	CMC
1:1	PEG1	NA1	CMC1
1:2	PEG2	NA2	CMC2
1:3	PEG3	NA3	CMC3

After the polymerization, the sample were taken out from freeze and washed 4- 5 times with DI water followed by acetone. After washing, the samples were kept into oven at 60°C for 36 hours for drying.

Figure 4.1 Synthesis image of BC and aniline before polymerization

Figure 4.2 Synthesis after 24 hour polymerization

Surface morphology of dried polyaniline bacterial cellulose composite sample were investigate by FESEM (Zeiss Supra 40 FESEM). The experiment carried out with beam energy 10keV, 30k magnification and with working distance 4-5 mm. Thermal stability or thermo gravimetric analysis of bacterial cellulose and polyaniline composite was performed by instrument. The experiment was carried out in nitrogen atmosphere in temperature range 50°C to 500°C with heating rate 5°C/min. FTIR (Fourier Transform Infrared Spectroscopy) was performed on the sample to know the chemical bond or functional group present in the sample by the instrument LINSEIS The experiment was carried out from wave number 500-4000 cm^{-1}. To measure

surface area, porosity and pore volume, BET experiment was performed by instrument Quantachrome autosorbe iO2. The sample was degassed at 120℃ at pressure of 10^{-4} Pa for 4hrs. The experiment was carried out nitrogen atmosphere.[21, 22]

Conductivity was measured by four probe method by the instrument (Roorkee). The distance between two probe was 2mm. The electrical conductivity of the samples was measured by conventional four probe method by four probe instrument.

3. Result and discussion

Composition of the composite was determined by taking difference between final dried weight of composite and starting weight of bacterial cellulose. The calculated weight percentages of the prepared composites are listed in Table 4.2 below

Table 4.2 calculation of weight percentage of polyaniline

BC: aniline		Initial mass	Final mass	mass of PANI	% of PANI	Initial mass	Final Mass	Mass of PANI	% PANI	Average % PANI
01:01	PEG1	0.0112	0.0177	0.0065	37	0.0125	0.0176	0.0051	29	33
						0.0122	0.0134	0.0012	9	9
	NIA1	0.0116	0.0163	0.0047	29	0.0121	0.0195	0.0074	38	34
01:02	PEG2	0.0137	0.0285	0.0148	52	0.0139	0.0284	0.0145	51	52
	CMC2	0.0155	0.0183	0.0028	15	0.0176	0.0225	0.0049	22	19
	NIA2	0.015	0.0338	0.0188	56	0.0132	0.032	0.0188	59	58
01:03	PEG3	0.0109	0.0279	0.017	61	0.0153	0.037	0.0217	59	60
	CMC3	0.0174	0.0216	0.0042	19	0.0193	0.0294	0.0101	34	27
	NIA3	0.013	0.0357	0.0227	64	0.0151	0.0401	0.025	62	63

It was noticed that with increase in amount of aniline, the percentage of polyaniline contained in the composite with respect to bacterial cellulose increased and however the increment is not proportional to aniline amount used. It may be speculated that because of the initial aniline entering the pore of the cellulose, the pores saturate and subsequent addition is lesser as seen in Table 3.

Table 4.3 Surface area and pore volume of composite after polymerization

Sample	% of Polyaniline	Specific surface area m^2/g	Pore size Å	Pore volume cc/g
N/A (1)	34	170.5	38	0.522
N/A (2)	58	44.82	38	0.131
N/A(3)	63	42.1	38	0.141
DF24h	100	32.2	30.5	0.559

Other point to notice is the incorporation is more in BC_NA and BC_PEG due to higher porosity as compared to BC_CMC as shown in Table 4.4.

Table 4.4 Surface area of cellulose before polymerization

Sample	Multipoint BET M^2/g	Single Point BET M^2/g
PEG	113	103
CMC	11.6	11
NIA	66	58

Morphology of the BC-PANI composite was studied by FESEM as shown in Figure 3. It is clearly observed that the fibrils of the bacterial cellulose are coated with polyaniline and distributed uniformly throughout the sample.
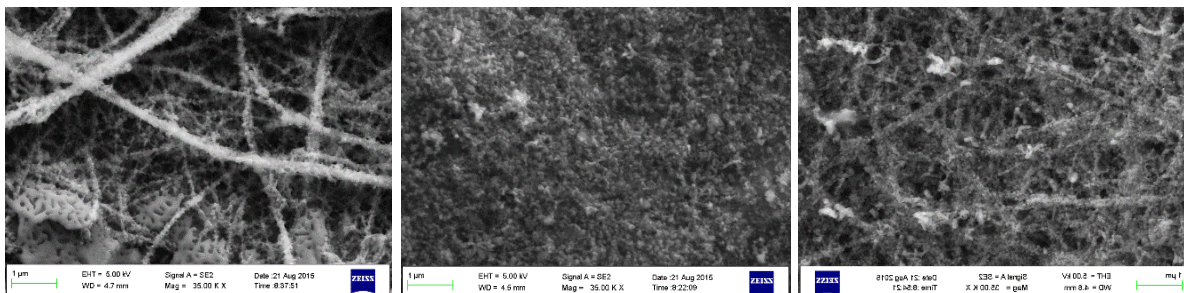
Figure 4.3 Morphology of cellulose after polymerization
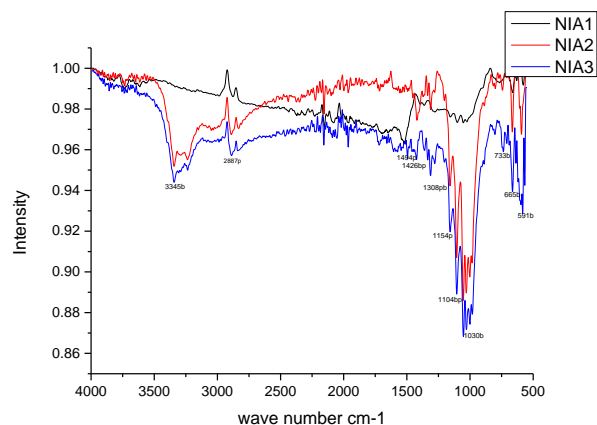
Figure 4.4 (a) FTIR spectra of NIA1, NIA2 and NIA3
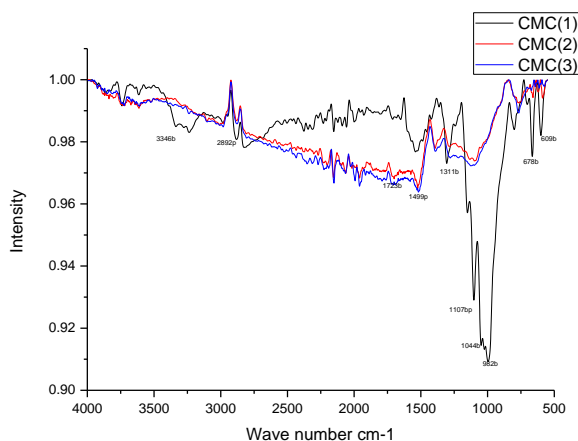
Figure 4.4 (b) FTIR spectra of CMC1, CMC2 and CMC3

Infrared spectrum of BC PANI composites are shown in Figure 4.4 The absorption spectra of BC shows main characteristic bands at 3345 cm^{-1} (due to stretching vibration of O-H bond), at 2887 cm^{-1} (due to C-H bond pyraniod stretching vibration), at 1308 cm^{-1} (CH$_2$ Wagging at C$_6$), 1030 cm^{-1} (assigned for stretching vibration of C-O bond) , 733 cm^{-1}(CH bending out of plane), 665 cm^{-1}(C-O-H group). The FTIR peaks of pure polyaniline emeraldine salt appeared at 1546, 1482, 1283, 1218, 1143 and 764 cm^{-1}. Peaks at 1546 and 1482 cm^{-1} are attributed to non-symmetric vibration of C-H bond in quinoid and benzenoid. C-N bond stretching in quinoid and benzenoid are observed 1283 and 1218 cm^{-1}. The peaks corresponding to C-H bending in N=Q=N (Q= quinod) and QN+N-B (B= benzoniod) is seen at 1143 cm^{-1}. The polar structure due to proton acid doping shows peak at 764 cm^{-1}. Those values match with the literature. The

additional peaks for C-H stretching vibration peak appeared at 2920 cm^{-1}, aliphatic hydrocarbon stretching vibration (C-H, CH$_2$) is appeared at 2838 cm^{-1} and that for diozonium salt appears 2377 cm^{-1}, whereas for BC- Pani composite, FTIR peaks appeared at 3345 cm^{-1}(OH stretching vibration), 2905 cm^{-1} (C-H stretching), 1428 cm^{-1} (CH$_2$ symmetric bending), 1160 $^{-1}$cm (C-O-C symmetric stretching), 1035 cm^{-1}(C-O stretching) [23-26].

The TGA of Polyaniline and polyaniline composite with BC_PEG is shown in the Figure 5. Up to the temperature 100°C the weight loss is due the removal water contain in emeraldine salt. In temperature range 100°C to 275°C weight loss due the removal of water from polymer chain. Those water link with Polyaniline chain as a dopant. In temperature range 275°C to 400°C weight loss is due to removal of dopant or removal of small oligomer chain. With increasing temperature of Polyaniline, the linkage is happening in the Polyaniline that's why weight loss reduce with increase temperature.[27]

For bacterial cellulose and Polyaniline composite, the first stage of weight loss is due to moisture evaporation up temperature 75 °C for PEG(1) and PEG(2). The second stage, temperature 75°- 150°C is stable. The third stage in temperature range 150°C to 275°C weight loss is due decomposition of cellulose. After the decomposition of cellulose, weight loss reduces is due cross linkage happen in polymer chain with increasing temperature 400°C [21, 28], whereas for PEG(3), the weight loss is continuous with increasing temperature.
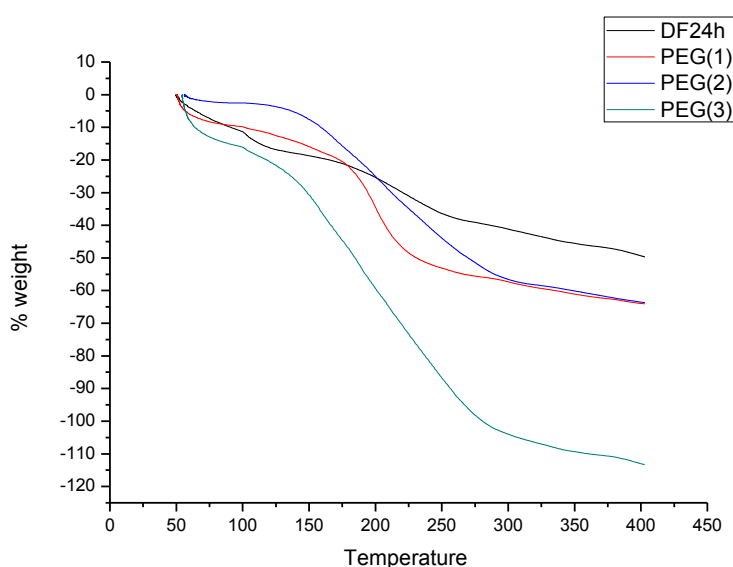

Figure 4.5 TGA of polyaniline and BC composite

The conductivity measurement was done by four probe technique. The correction factor was introduced because sample were finite dimension

$$\rho = 2\pi S F \left(\frac{V}{I}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

The resistivity (ρ) of the samples was calculated by the equation (1) and hence S= distance between two probe, F = correction factor, V = voltage difference between two internal probe and I = current between two outer probe[29].

The correction factor F can be divided in to three part

$$F = F1 \times F2 \times F3$$

Where F1 due to sample thickness, F2 due to sample lateral dimension, F3 due probe placement relative to edge.

The value of F1 calculated by the equation 2

$$F1 = \frac{t/s}{2\ln[\frac{\sinh(t/s)}{\sinh(t/2s)}]} \ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where t = thickness of the sample

Here S > 4t, so the equation 2 become

$$F1 = \frac{t/s}{2\ln 2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 3$$

Length and breadth of the sample was considered as bulk relative to probe spacing. So F2 and F3 were considered as 1. The calculated conductivity with appropriate correction factor of the samples in the table 4.5 below. It was noticed that with increase of percentage of polyaniline, conductivity of composite increased.[29, 30]

Table 4.5 Conductivity spectrum of the composite

CMC	Conductivity σ	PEG	Conductivity σ	NIA	Conductivity σ
CMC1	1.2×10^{-4} S/cm	PEG1	2.3×10^{-3} S/cm	N/A1	4×10^{-4} S/cm
CMC2	3.1×10^{-4} S/cm	PEG2	7×10^{-4} S/cm	N/A2	5×10^{-4} S/cm
CMC3	10×10^{-4} S/cm	PEG3	2×10^{-3} S/cm	N/A3	

4. Conclusion

Consumption of polyaniline depends on specific surface area and pore volume of the modified bacterial cellulose. The result shows that PEG has higher surface area and incorporation of polyaniline is higher.

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Chapter 5 Polyaniline composite with corn cob cover

(Reproduced from paper)

Abstract

Corn cob cover (CCC) is abundantly available and is rarely used for advanced applications. This papers shows a facile single pot method to make low cost, flexible, conducting and light weight composites from CCC and polyaniline. Additional advantage of using CCC is the hydrophobic nature, which is retained to some extent even on addition of polyaniline. These biodegradable composites produced are flexible, mechanically stable with a conductivity of 8×10^{-4} S.cm-1 at about 15 wt.% polyaniline. The contact angle was found to change from 135° to 110°, which suggests retention of its hydrophobic nature. The obtained properties from the composite makes it a suitable material for anti-static packaging. Further improvements in electrical properties can make it suitable for super-capacitors and battery applications.

5.1 INTRODUCTION

With increasing usage of electronic devices, materials with good conductivity, low density, low cost, water resistance and flexibility have been sought. In such a case, polymeric materials are preferred due to low density and especially biopolymers because of their low environmental impact. This paper aims to make a flexible conducting paper with the above mentioned properties using corn cob cover (CCC), which generally waste and remains un-utilised. It is hydrophobic, bio-degradable, low cost, and flexible and has good toughness. For this work, polyaniline has been used to make composites with CCC to impart conductivity. Polyaniline is an organic semiconductor [1] and its unique properties such as wide spectra of resistance in different oxidation states [2], make it suitable for applications such as sensor, actuator, organic electronics, organic LED, super capacitor, battery electrode and correction inhibitor etc. [3, 4]. However, polyaniline does not possess good mechanical properties. For enhancing mechanical

integrity, several attempts have been made to prepare composites with suitable substrates [5]. This is the first report of CCC-polyaniline composite as per the knowledge of the authors.

5.2 MATERIAL AND METHODS

The chemicals aniline monomer (≥99.5% pure) and ammonium per sulphate (APS, ≥98.0% pure) were purchased from Sigma-Aldrich, India. Hydrochloric acid was ordered from Alfa Aesar India. The corn cob cover was procured from a vegetable market and cut into small pieces and washed with DI water and followed by acetone. The process was repeated about 3 times. The washed corn cob cover was kept at 60˚C for 6 hrs in an oven for drying. The corn cob cover was dipped properly in 5 ml of 0.2M aniline solution in 1M HCl for 30 min and subsequently 5 ml of APS solution was added in it. Then the mixture was kept in deep freezer at -18˚C for 24 hours for polymerization. The sample turns green in colours. It was washed 4-5 times with DI water and followed by acetone. After that, the composite samples were put into an oven for 5 hour at 60˚C for drying. The contact angle measurement was performed by instrument telescope-goniometer (Ramehart) by using water droplet method. This experiment was performed at room temperature and atmospheric pressure. The morphologies of the CCC and composite were studied by FESEM (Zeiss Supra 40 FESEM). The samples were gold coated (if required) and imaged at accelerating voltage of 5-10 KV. The conductivity was measured by four probe method (Four scientific equipment Roorkee). The correction factors were calculated to account for finite dimension.
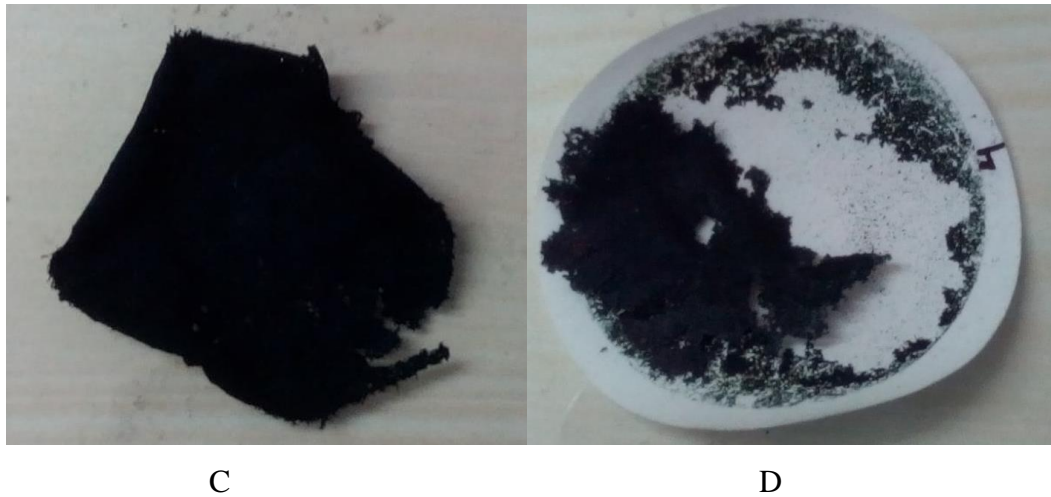

A   B

| C | D |

Figure 5.1 A, B,C,D conducting sheet from corn cob fibre nano-whiskers

5.3 RESULTS AND DISCUSSION

The percentage incorporation of polyaniline in the composite was calculated by using change in weight after polymerisation. It was found to be close to 15%   Figure 2 (a and b) shows images of the contact angle measurements performed on CCC and composite. The corn cob cover was found to be hydrophobic with a contact angle of 135° (contact angle > 90° is referred to as hydrophobic).The contact angle was reduced to 110° for CCC-polyaniline composite, probably due to the presence of polyaniline [6]. However, the contact angle still shows retention of significant hydrophobicity.
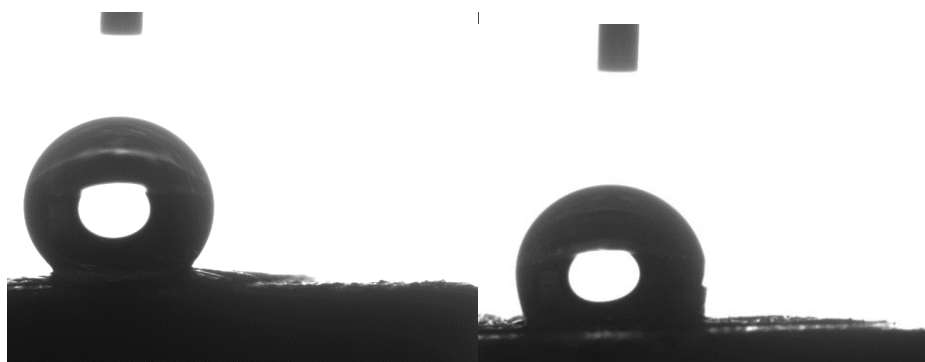

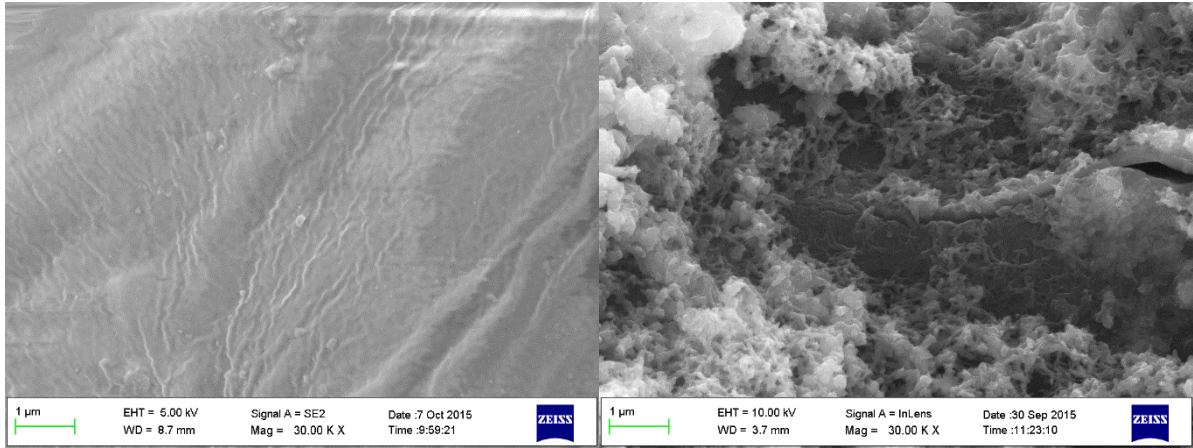Figure 5.2 Images for contact angle measurement of a) CCC and b) composite

Figure 5.3 (a and b) shows the SEM images of CCC and composite.

It can be seen that CCC surface is uniformly coated with polyaniline in a network-like structure.

The electrical resistivity of the composite was measured by four-point method at room temperature. The conductivity was calculated by the equation (1), where S is distance between the two probe, F is correction factor and (V/I) was taken average voltage and current ratio of the sample. The correction factor is important because dimensions of composite are finite [7, 8]. The equation of resistivity is written as

$$\rho = 2\pi S F \left(\frac{V}{I}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

$$F = F1 \times F2 \times F3 \ldots\ldots\ldots\ldots\ldots \text{(2)}$$

F = the correction factor

F1= correction factor due to thickness of the specimen

F2=the correction factor due lateral dimension of the sample

F3= correction factor due to probe place respect to edge

$$F1 = \frac{t/s}{2\ln\left[\frac{\sinh\frac{t}{s}}{\sinh\frac{t}{2s}}\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

For thin sheet (t<<s) above equation (2) become

$$F1 = \frac{t/s}{2\ln2} \quad \ldots\ldots\ldots \ldots\ldots\ldots\ldots \text{(4)}$$ and F2 and F3 can be considered as 1.

The conductivity of the composite was found to be 8×10^{-4} S/cm. These values are in the range of the values reported for other composites of polyaniline [9], but at lower polyaniline content. The additional advantage of this composite is the flexibility, low cost and water repellence.

5.4 CONCLUSION

In this paper, the CCC and polyaniline composite was successfully made. SEM image shows uniform coating of polyaniline on CCC. The water contact angle of CCC reduces from 135° for CCC to 110° for composite but the composite remains considerably hydrophobic. The conductivity was found to be 8×10^{-4} S/cm using appropriate correction factor in four-point measurement. A composite with the properties discussed in this paper can be used for antistatic coating application. Further improvements in electrical properties can make it suitable for super-capacitors and battery applications.

Some drawback of using corn cob cover

1. We don't know the chemical composition of Corn Cob Cover properly. Its chemical composition may be contain cellulose, hemicellulose, lignin and other. We know how aniline and polyaniline interact with the cellulose but we don't know how polyaniline interact with hemicellulose and lignin.
2. We used 1M HCL, 1M hydrochloric acid is a strong acid and that might be interact or react some functional with corn cob cover.
3. We did not a count of some functional group dissolve in 1M HCl during synthesis or acetone during wash.
4. So, it is better to study first functional group, composition and percentage of composition then polymerization
5. Hydrophobicity of material arise from different part of the material, it is due to functional group, wax on the surface and structural. We don't know which port of the material contributed that hydrophobicity. Corn cob Cover has possessed uneven surface, so it error prone to measure hydrophobicity of an uneven surface.

5.5 REFERENCES

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Conclusion

Polyaniline was synthesized in different time and temperature. It was noticed that morphology, conductivity and yield were changed with respect to time and temperature. It is found that conductivity and particle size increase with lowering synthesis temperature and increasing time of polymerization. Particle size changed from 151±47 nm to 380±84 nm where Conductivity changed from 0.5 S/cm to 11.1 S/cm. So, with increase particle size conductivity increases.

Polyaniline and bacterial cellulose composite was synthesized by Insitu polymerization. It was found that polyaniline coated on bacterial cellulose fibre and no free polyaniline sat on surface of composite. It was noticed that consumption of polyaniline depended on the surface area and pore volume of the bacterial cellulose. Measured conductivity range was from 1.2×10^{-4} S/cm to 2×10^{-3} S/cm.

Future work

Based on conductivity optimisation done in Chapter 3, we made a conclusion that increasing polymerization time and decreasing polymerization temperature, causes increase in particle size and conductivity, from 0.5 S/cm to 11.1 S/cm. We want to further correlate these properties with molecular weight, crystallinity and other parameters.

So far, conductive composites were obtained from polyaniline and bacterial cellulose *in situ* polymerization with conductivity range from 12×10^{-4} S/cm to 2×10^{-3} S/cm. Mechanical stabilities and flexibility of the film were not measured. So our future plan is to optimise the conductivity and flexibility of the composites by varying polyaniline and cellulose weight percentage. We also plan to lower the cost of device fabrication and optimise its functionality.