

NOVEL CONDUCTING PAPER FROM BACTERIAL CELLULOSE AND POLYANILINE

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ABSTRACT

Development of new greener material for conducting paper is sought for applications such as security paper, actuators, and anti-static packaging. It is required that these materials possess low density and good mechanical integrity. For this purpose, cellulose substrates are explored. Bacterial cellulose has been shown to be a better substrate due to ultrafine microstructure and porosity. The synthesis protocol has been optimized with respect to the molar ratio of aniline monomer to oxidizer. Preliminary results with optimized synthesis protocol and bacterial cellulose as substrate has shown promising microstructure.

KEYWORDS:-Bacterial Cellulose, Filter Paper, Conducting Polymer Composite, Polyaniline

INTRODUCTION

Conducting paper constitutes a class of materials suitable for applications such as sensors, actuators, anti-static packaging, biomedicines, protective clothing and potential battery applications. For the above mentioned applications, it becomes necessary to develop materials which possess good conductivity, mechanical flexibility, along with light weight, low cost [1]. With increasing environmental concern, greener 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 [2]. Unlike other conducting polymers, PANI can be synthesized in water with an oxidizer [3]. It exists in various forms which differs in chemical and physical properties [4]. It exhibits three different oxidation states (a) leucoemeraldine-white/clear and colorless (b) emeraldine-green for the emeraldine salt and blue for emeraldine base (c) (per) nigeraniline-blue/violet [5]. The green protonated (emeraldine) state is usually preferred because it has conductivity higher than many polymers and similar to semi-conductors [6]. Its sensitivity to changes in its physicochemical

properties makes it a suitable candidate in various applications such as organic electrodes, sensors, and actuators [7-8].

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 [10]. 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 [11-14]. 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 [15-16]. Amongst them, bacterial cellulose (BC) is particularly advantageous because it is obtained as a 100% pure, highly crystallinity dilute hydrogel with above 95% water, which implies high holding capacity [18]. 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. [17]. Recently, some research groups explored the preparation of BC/PANI conducting nano-composites through the *in situ* polymerization of aniline monomers (An) in BC membrane [12-18].

It is said “there are as many polyaniline as the number of people who prepare them” [9]. Thus a major challenge is to always optimize protocol of PANI synthesis in each lab.

The proposed work aims to provide direction towards greener, flexible, light weight conducting paper from bacterial cellulose and polyaniline composite. This work reports optimization of the strategy to obtain the composite by *in situ* polymerization.

MATERIALS AND EXPERIMENT

Aniline monomer and ammonium persulfate (APS) were purchased from Sigma-Aldrich, India. Toluene and hydrochloric acid were ordered from Alfa Aesar India. Laboratory prepared bacterial cellulose was donated by Dr. Mudrika Khandelwal from her previous work for this research. FESEM was used to study the morphology of both the substrates. Filter paper and bacterial cellulose was gold coated and imaged at 10 kV. The penetration studies were performed on filter paper and bacterial cellulose in order to get an idea of absorption of toluene and HCl. In order to produce polyaniline, several synthesis chemistry protocols were tried. Two sets of experiments were conducted -

1. 0.2 M Aniline in 37% HCl and 0.2 M APS in water were used in molar ratio 5:1, 3:1, 1:1, 1:3, 1:5
2. 0.2 M Aniline in Toluene and 0.2 M APS in 37% HCl were used in molar ratio 3:1, 1:1, 1:3

The reaction was carried out at room temperature for 24 hours. The polymer was obtained by using a filter paper and washing with DI water and acetone.

Further FTIR was done in order to verify the presence of functional groups in polyaniline. Finally a composite was prepared by carrying out polymerization in presence of BC as substrate.

RESULTS AND DISCUSSION

1. Choice of substrate

a) Microstructure - Filter paper and BC

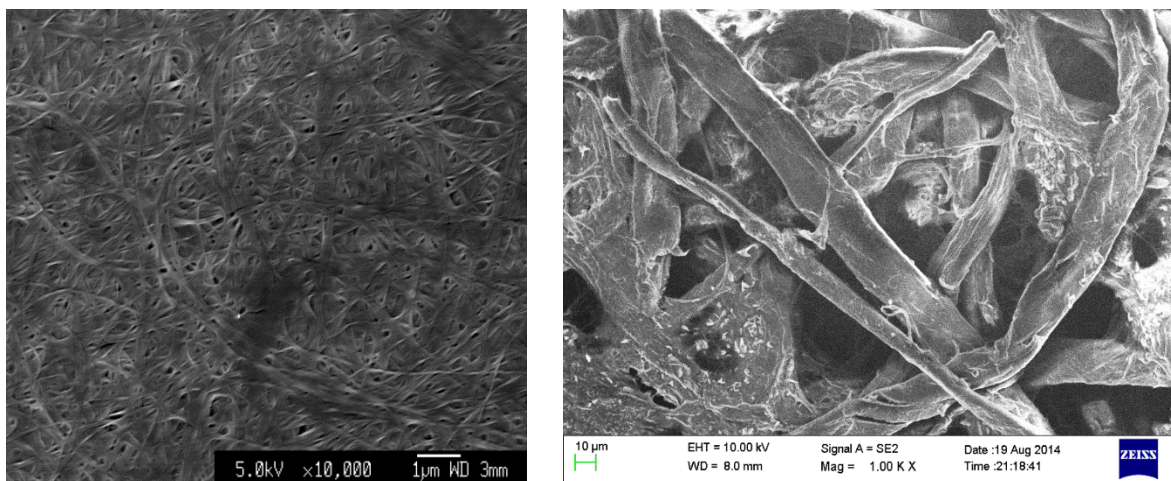


Figure 1 SEM images of (a) Bacterial Cellulose and (b) Filter Paper

Figure 1 shows fibrous structure of bacterial cellulose and filter paper. The difference lies in the dimension of fibres forming the two cellulose matrices. The bacterial cellulose fibres are in nano dimensions whereas the filter paper is composed of micro sized fibres. BC fibres are uniform while filter paper fibres have varied dimensions.

b) 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 oxidising agent should travel inside the matrix. From the literature, toluene and HCl are commonly used in polyaniline synthesis, therefore the study has been carried out on these liquids.

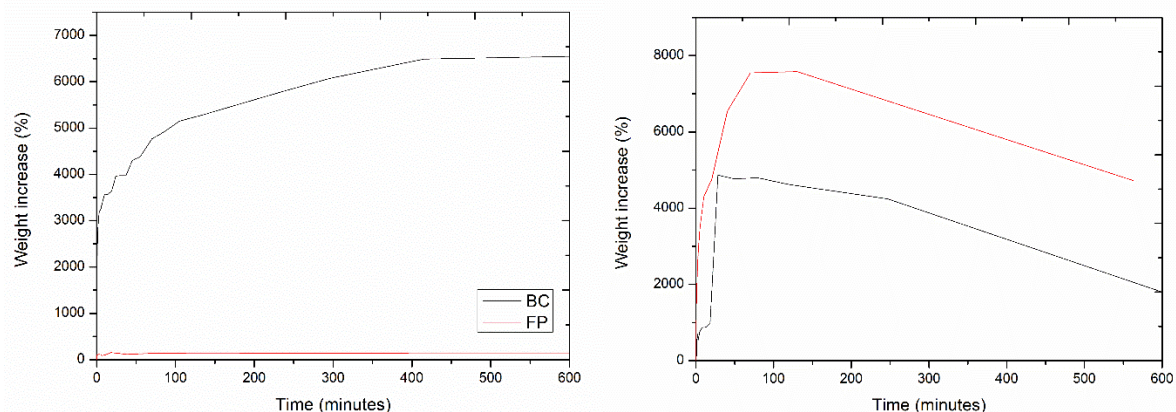


Figure 2: The gain in weight with time for BC and FP in toluene (BC=black, FP=red) and 37% HCl (FP=black, BC=red)

Figure 2 shows that the rise in weight is quicker and more for BC as compared to FP. This is because of high porosity and higher holding capacity of BC.

2. Synthesis

Two synthesis protocols have been tried as described in experiments above. The obtained results are summarized below.

Green coloured powders were obtained in most experiments, which is a signature of emeraldine polyaniline. The yield varied.

a) Experiment 1:

Aniline was dissolved in HCl and APS was dissolved in water. The molar ratio was varied. Green powders were obtained in systems with Aniline / APS molar ratio more than 1. Brown powders in the rest. Yield scaled up with volume. Table 1 below shows photos of powders obtained and weight. The yield has been quantified in terms of final weight of powder with respect to weight of reactants. Yield was higher for molar ratio more than 1.

b) Experiment 2:

Aniline was dissolved in HCl and APS was dissolved in Toluene. The molar ratio was varied. Dark green powders were obtained in all.

FTIR spectra for all the powders is discussed below. Further work was done with Aniline/ APS =1 using conditions in experiment 1.

Experiment 1





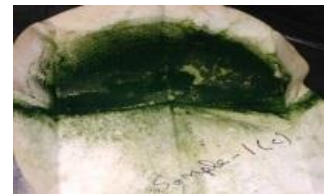
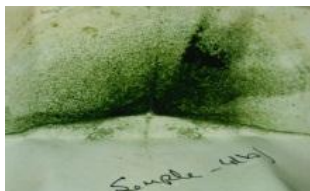
APS/Aniline molar ratio: -5:1		Polyaniline obtained - 0.0378 g Brown powder was collected
APS/Aniline molar ratio: -3:1		Polyaniline obtained - 0.0486 g Brown powder was collected
APS/Aniline molar ratio: -1:1		Polyaniline obtained - 0.0745 g Dark Green powder was collected
APS/Aniline molar ratio: -1: 3		Polyaniline obtained - 0.054 g Dark Green powder was collected
APS/Aniline molar ratio: -1: 5		Polyaniline obtained - 0.0719 g Dark Green powder was collected

Table 1: Experiment set 1: molar ratio, weight of reactants, final powders and yield

APS/Aniline molar ratio	Weight of APS+Aniline	Weight obtained	Weight obtained/Weight of APS+Aniline
5:1	1.23	0.038	0.01
3:1	0.77	0.048	0.06
1:1	0.64	0.075	0.12
1:3	0.51	0.054	0.1
1:5	0.69	0.072	0.1
1:1	0.96	0.157	0.16

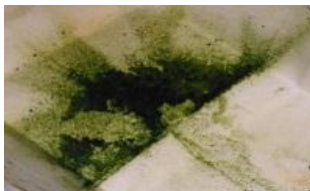
Experiment 2

APS/Aniline molar ratio: -3:1



Polyaniline obtained - 0.1106g
Dark Green powder was collected

APS/Aniline molar ratio: -1:1



Polyaniline obtained - 0.0318g
Green powder was collected

APS/Aniline molar ratio: -1: 3



Polyaniline obtained - 0.13025g
Yellowish green powder was collected

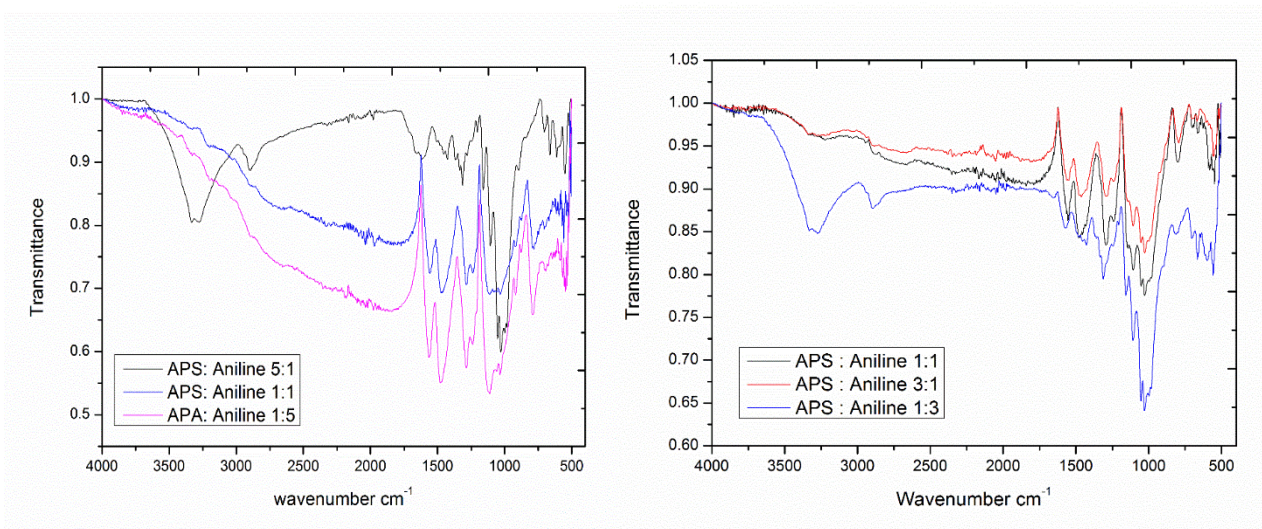


Figure 3: FTIR Spectra for experiment set 1 and 2 with indicated molar ratios

In the FTIR spectra, peaks corresponding to polyaniline can be identified. The absorption peaks observed include those corresponding to the stretching of quinone and benzene ring in PANI. The absorption band for the stretching of the C-N band and vibration of C-H in benzene are also visible. The absorption peak of N-H, C-O and C-N stretching is also seen. This confirms

formation of PANI. However, a few extra peaks may be seen for molar ratio Aniline/APS less than 1.

3. Preparation of Composite

Further BC/PANI Composite was prepared using 1:1 composition of APS/Aniline which was conducting hence can easily be studied under FESEM image without using gold coating. It may be observed that BC nanofibres are well coated with PANI.

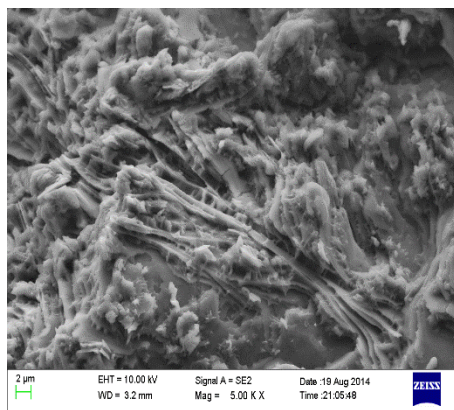


Figure 4:FE-SEM image of BC/PANI Composite

CONCLUSIONS

It has been shown that bacterial cellulose is a better substrate than filter paper due to its nanofibrous network and better porosity. Effect of Aniline to APS molar ratio on polyaniline synthesis has been studied. Ratios above 1 are favorable in terms of quality and yield. A preliminary result has been presented which shows good coating of the nanofibrous network with polyaniline. On the basis of these results, further work will be directed towards measurement of conductivity and mechanical properties and optimization of composite preparation accordingly.

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