

**BIOCOMATIBLE COPOLYMER FROM CHITOSAN-SUBSTITUTED  
POLYANILINE: GRAFT COPOLYMERIZATION OF POLY  
(ORTHOPHENYLE DIAMINE) ONTO CHITOSAN****<sup>1</sup>PRADYUMNA KUMAR SWAIN, <sup>2</sup>MIRA DASH AND <sup>1</sup>P.L. NAYAK***<sup>1</sup>P.L.Nayak Research Foundation, Manorama Bhavan, Cuttack**<sup>2</sup>Departments of Chemistry, SOA University, Bhubaneswar***ABSTRACT**

Chitosan, a natural polysaccharide was grafted with poly (Orthophenylene diamine) through radical copolymerization using ammonium persulfate as the initiator in acidic medium. The chitosan– poly (orthophenylenediamine) was characterized using FTIR, Scanning Electron Microscopy, TGA and UV-visible spectroscopy taking chitosan as reference. Chitosan exhibited electrical conductivity, which increases with the extent of grafting onto chitosan. The application of conducting biomaterial such as Chitosan in the electronic devices especially for the fabrication of sensor devices would be attractive not only in terms of product cost and environmental safety but also from a materials science point of view. A plausible mechanism for grafting has been suggested.

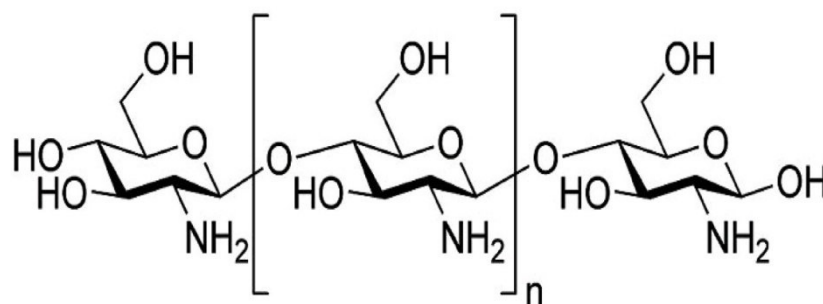
**KEY WORDS:** Biocompatible polymer, grafting, orthophenylenediamine, characterization.**P.L. NAYAK**

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## 1. INTRODUCTION

Chitosan, a polysaccharide is obtained from the deacetalization of chitin obtained from prawn and crab shells. Chitosan is used in a wide range of applications such as wastewater treatment, separation membranes food packaging, drug delivery systems and biosensors. However, in sensor applications, the poor electrical conductivity of hydrogels

results in a poor response and a high operational voltage limits its applicability in devices. Hence, composites have been attempted by incorporating a rigid conducting polymer (such as paraphenylene) into a flexible matrix (such as chitosan) to combine the good processability of the matrix and the electrical conductivity of the conductive polymer. It has amino groups which are very reactive<sup>1-2</sup>.



**Figure 1**  
**Structure of Chitosan**

Polyaniline is one of the most extensively studied conductive polymers. Potential applications include uses in rechargeable batteries, sensors, switchable membranes, anticorrosive coatings, and electronic devices<sup>3-4</sup>. Polyaniline is commercially attractive owing to its easy synthesis, either through chemical or electrochemical methods, good environmental stability, ease to control conductivity and inexpensive production in large quantities. An important characteristic of polyaniline is that it undergoes two distinct redox processes as well as pH switching between unprotonated and protonated states<sup>5</sup>. Polyaniline can be rapidly switched by the addition of bases and acids that unprotonate and protonate the base sites within the polymer. However, the major disadvantage of polyaniline is its insolubility in common solvents and its infusibility<sup>6</sup>. In an attempt to overcome these problems, we have chemically grafted polyaniline on to the chitosan. The highly conjugated polymeric structure of polyaniline produces new nano scale phenomena that are not accessible with current inorganic systems. Conducting polymers find applications in the fields like sensors, electrocatalysts, microelectronics, electromagnetic shielding, rechargeable batteries, and controlling systems. Because of

these problems, many methods are reported. Grafting with other polymers having good mechanical and physical properties is one of them. Many potential applications of polyaniline are demonstrated recently. The polymers should be insoluble in the whole range of pH to gain some of the applications<sup>7-12</sup>. In the present research program we wish to report the graft copolymerization of poly (o-phenylenediamine) onto chitosan, the physico chemical studies of the biocomposites have been investigated.

## 2. EXPERIMENTAL

### 2.1. Materials

Orthophenylenediamine aniline (OPA) from Aldrich and the monomers were under nitrogen prior to use. Chitosan (Ch) with medium molecular weight was also purchased from Aldrich. Ammonium peroxydisulfate, hydrochloric acid, and acetic acid, (Fluka) were used as received<sup>13,14</sup>

### 2.2. Synthesis of OPA/Ch composites

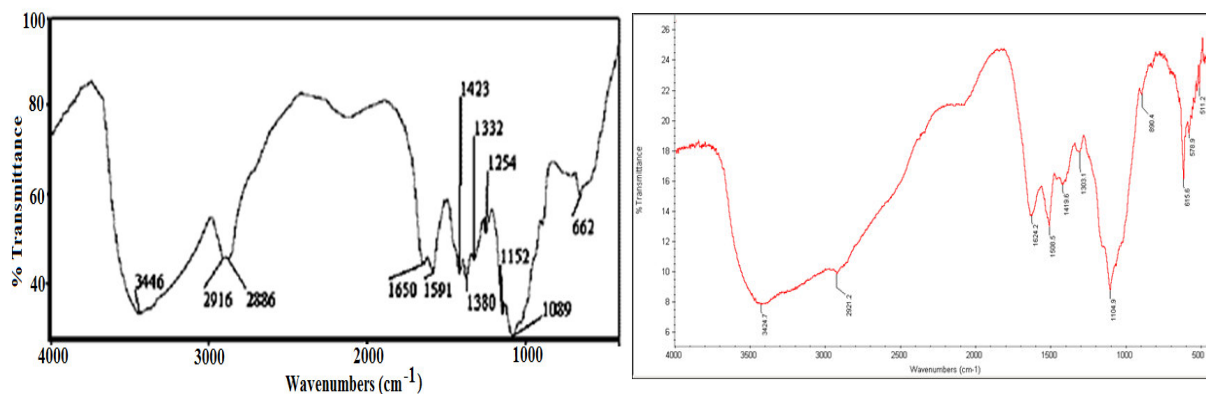
In a typical procedure, an aqueous solution of chitosan (0.2g) was prepared by dissolving chitosan in 40 ml of aqueous acetic acid (2 wt%) for 24 h and then adding 8.25 mol

orthophenylenediamine monomer in 40 ml 1 M HCl to form a homogeneous solution. Ammonium peroxydisulfate (APS, 0.0099mol) solution in 1 M HCl was dropped into the above solution with vigorous stirring under N<sub>2</sub> atmosphere. The molar ratio of oxidant/monomer was 1:2. The polymerization was carried out for 24 h at room temperature.

After that, the solution was centrifuged for 10 min at 8000 rpm and precipitation was then re-dispersed in 2 wt% of acetic acid and then washed with deionized water and centrifuged again. The washing procedure was repeated four times. The final composite was dried at 50<sup>0</sup>C for 24 h.

### 3. RESULTS AND DISCUSSION

#### 3.1. FTIR of OPA and OPA/Ch copolymer



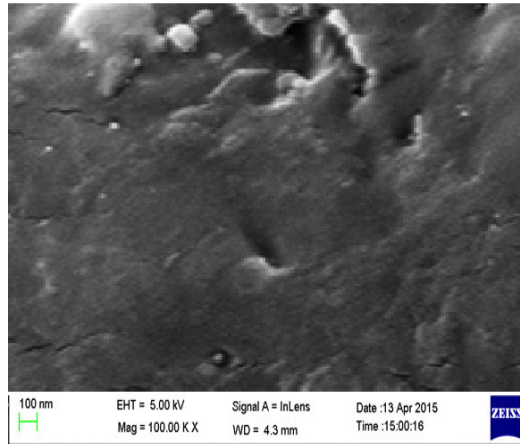
**Figure 2**  
**FTIR Spectra of Chitosan (a) and (b) grafted OPA/Ch**

The FTIR spectrum of Chitosan is shown in Figure 2 (a). The characteristic peaks of chitosan are located at 3446 cm<sup>-1</sup> for the hydroxyl group and 1591 cm<sup>-1</sup> for the amino group. The peak at 1650 cm<sup>-1</sup> is due to carbonyl stretching vibration of remaining acetamide group in chitosan. The wide peak (Figure 2 b) is observed in the area of 3,200 to 3,500 cm<sup>-1</sup> is due to the overlapping between O-H stretching vibrations in chitosan and N-H stretching vibrations in OPA. Also, there are peaks at the areas of 2,858 and 2,925 cm<sup>-1</sup> which are due to CH stretching vibrations, and the peak at 1,624 cm<sup>-1</sup> is due to C=O stretching vibrations of chitosan. The area at 1104 cm<sup>-1</sup> belongs to the C=C and C=N is

stretching vibrations in benzoic rings of OPA. Stretching vibrations of the aromatics is approximately at 1,303 cm<sup>-1</sup>.

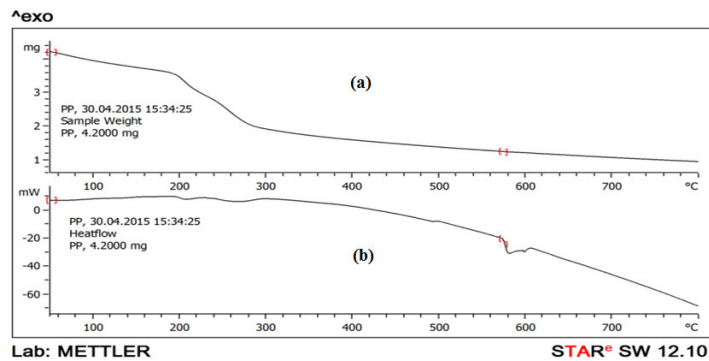
#### 3.2. SEM

Figures 3 shows SEM of OPA/Ch. As it is shown in picture, OPA is in the form of needle and homogeneous particles. Homogeneity and single-phase films are the implications of successful graft copolymer. Figure 3 is the cross cut of the same film which shows well the homogeneity and preparation of graft copolymer as well. The development of OPA chain length is sufficient on the base polymer.



**Figure 3**  
**SEM of the Grafted OPA/Ch**

### 3.3. TGA

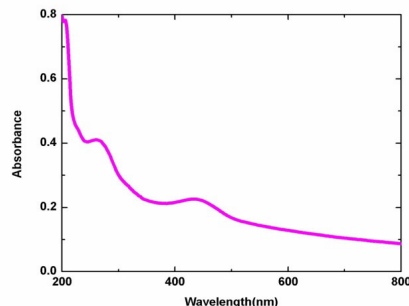


**Figure 4**  
**Thermogravimetric analysis of (a)Chitosan and (b) OPA/Ch**

In case of OPA/Ch (Figure 4 b) a total weight loss of about 50% at 600°C can be seen due to the creation of more defect sites, it is therefore not too surprising that the total weight loss of 100% at 800°C is observed. The thermal analysis of pure chitosan (Figure 2a) shows two distinct weight losses, below

250°C, a 20% weight loss observed can be attributed to amine side or N-acetyl side groups presence in chitosan. The second weight loss occurred between 300 °C and may be attributed to oxidative removal of the glycosidic linkage.

### 3.4. UV-visible spectroscopy



**Figure 5**  
**Uv-visible spectra of OPA/Ch**

The OPA/Ch Composites have a conjugate system of double bonds on their backbone. The conductive polymers have some of the conventional transfers in the UV region, such as  $n-\pi^*$ ,  $\pi-\pi^*$ , etc. The  $\pi-\pi^*$  transfers of conjugated double bonds were related to near visible regions, associated to polaron and bipolaron status as well as solution of conductive polymers. Figure-5 shows UV-visible spectrum data for OPA/Ch composites. The polymer (with aniline pattern) is expected to have two peaks in 220 nm and 430 nm with intensities of 3.5 and 1.8, respectively. The first transfer may be due to the  $n-\pi^*$  transfer and the second one due to the  $\pi-\pi^*$  of benzoic system. As we know, an increase in the chain length and subsequently, an increase in conjugated double bonds, a decrease in energy difference  $\pi-\pi^*$  occurs that causes an increase in the wavelength. UV-visible spectra data shows that spectrum of 320 nm region is for the second peak of aniline groups.

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## 4. CONCLUSION

Chitosan-poly (orthophenylene diamine) composites were synthesized by in-situ chemical oxidation using ammonium persulfate as an oxidant in HCl and CH<sub>3</sub>COOH acid medium. The synthesized copolymer was characterized using Fourier transform infrared spectroscopy (FTIR), UV-Visible, scanning electron microscopy (SEM). The FTIR results confirmed that there is a strong interaction between orthophenylene diamine and chitosan. The OPA/Ch composites exhibited a better final degradation temperature than chitosan. SEM analysis suggests OPA/Ch composite has unique and homogenous structure. This smooth morphology can be a reason for its higher conductivity. These OPA/Ch composites are promising candidates for glucose biosensor applications.

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