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Preparation and characterization of conductive Polyaniline/Sago/Graphene nanocomposites via ultrasonic irradiation

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Abstract. This work, which is a part of our ongoing studies on developing Polyaniline/Sago/graphene (P/S/G) nanocomposites. The nanocomposites were synthesized via ultrasonic irradiation (U.I) method in presence of hydrochloric acid and Ammonium persulfate. The quantity of PANI and Sago was kept constant and the effects of graphene nanoplatelet (GnP) dosage on their electrical conductivity and morphology was evaluated. Electrical conductivity measurements using a standard four-point probe technique and morphological analysis was carried using Transmission electron microscopy (TEM). The electrical conductivity of nanocomposites was found to be drastically increased as compared to that of PANI/Sago blend at room temperature. Further the conductivity of nanocomposites was also found to be increased with the increase in weight % of GnP. The results also showed that incorporation of less than 1 wt.% of GnP into polymeric matrix had improved electrical conductivity of the nanocomposites from 2.98×10^{-4} to 1.34×10^{-1} S cm^{-1}. The morphology of the generated P/S/G nanocomposites shows uniform dispersion of GnP.

1. Introduction

Conducting polymers, extensively conjugated molecules, have π electron delocalization along their backbone which gives them unique optical and electrical properties. This characteristic causes them to act as a semiconductor or a conductor [1]. Polyaniline (PANI) is one of the most attractive conducting polymers among the known conducting polymers due to some of its characteristics including good environmental, thermal, and chemical stability, tunable conductivity switching between insulating and semiconducting materials, low operational voltage, facile synthesis, potentiality for practical applications and low cost [2]. In recent years, considerable interest has been shown in PANI as a conducting organic polymer because of its potential applications in new technologies, such as chemical sensors, electrochromic displays, electronic devices, and secondary batteries [3-8].

Usually, two methods including chemical oxidation and electrochemical synthesis are employed for preparing PANI. Although prepared PANI via electrochemical synthesis generally has higher conductivity, this method is restricted by the size, shape and nature of the involved electrode. Therefore, this method cannot be used to prepare a large amount of PANI or to produce fine PANI

powders; thus PANI used for commercial application is normally synthesized via the chemical oxidation method [9]. However, there are certain limitation of PANI, PANI is non-biodegradable, non-flexible and non-processable, only very low amount of PANI can be and should be used for producing conductive nanocomposites [10]. In addition, the particle size of PANI should be controlled within a proper range, i.e. less than 100 nm, in order that PANI particles can be easily excreted through circulatory systems after complete degradation of polymeric matrix.

The processability of PANI may be achieved by means of several methods that were summarized by Bhadra et al. [11]. Those methods include: chemical modification of aromatic rings or alkylation of nitrogen atoms, modification of doping process using specific Broensted or Lewis acids, or synthesis of the colloidal form of PANI. The second group of processability improvements belongs to the group of PANI composites. According to that, PANI can be applied in a suitable insulating matrix as conductive filler. These types of composites can be easily processed and they show quite good mechanical properties. Today, several preparation methods of PANI composites are known. One of them is in situ polymerization. Three procedures of such method are known: simultaneous synthesis of both PANI and a matrix partner in the same medium; polymerization of aniline in a suitable counterpart polymer solution or dissolution/dispersion of PANI in an appropriate solvent, and polymerization of the matrix in the solution. Despite the fact that, all the described methods of PANI modification, lead to a new class of organic materials with interesting potential application, it is worth emphasizing, that all of them result in materials with lower electrical conductivity as compared to pure, unmodified PANI.

In case of PANI composites, hundreds of matrices have been used to prepare a desirable material. Preparation of PANI/biopolymer composites, being an interesting challenge and has been realized using several matrices that mainly include chitosan [12], cellulose/ cellulose derivatives [13], or gums [14]. On the other hand, starch, which is one of the cheapest and easiest to obtain plant biomaterials, has not been intensively investigated in this field. The only known PANI/starch composites include: chemical polymerization of PANI in aqueous suspension of taro [15] or maize [16] starches which leads to the deposition of PANI at the surface of starch granule.

The idea of obtaining composites comprising a biodegradable polymer, i.e. starch and PANI may enable various applications of these materials. It may result in new materials suitable for application in different industries including: biomedicine, paper industry, food packaging, and many others. Additionally the combination of a natural fully nontoxic, biodegradable material with a synthetic and multifunctional PANI looks as a promising new direction on the field of advanced, functional materials preparation. Starch as an abundant polysaccharide is a cheap and easily available polymer, which can be extracted and purified from natural sources. Therefore, in this study Sago starch was used as a matrix for synthesis of PANI/Sago blends. Sago starch is obtained from sago palm (metroxylon sagu) which typically found in tropical Asia. Sago starch is made of two glucosidic macromolecules; amylose and amylopectin. It has an important reserve polysaccharide which is readily available, low cost, and able to biodegrade. However, the introduction of Sago will reduce the conductivity of the blend drastically. Thus, certain conductive material needs to be introduced to PANI/Sago blend.

Among various conductive materials (such as active carbon, carbon nanotubes, graphene), graphene is the most preferred one. Graphene, a single layer of carbon atoms in a hexagonal lattice, has recently attracted much attention due to its novel electronic and mechanical properties. Therefore, this paper reports the synthesis of Polyaniline/Sago/Graphene (P/S/G) nanocomposites via ultrasonic irradiation technique. The electrical conductivity and morphology of the synthesized nanocomposites will be investigated.

2. Materials and Methods
2.1   Synthesis of P/S/G nanocomposites
Aniline (ANI) (99%) and ammonium persulfate (APS) were purchased from Sigma Aldrich and hydrochloric acid 1 M (HCl) were obtained from TOLSA and deionize water was used to synthesis polyaniline (PANI). Graphene (xGnP® Graphene Nanoplatelets Grade M) was obtained from XG sciences, USA. The PANI nanoparticles were prepared by in situ polymerization of aniline in acidic

medium under ultrasonic irradiation in an inert atmosphere. In a 250 mL three-necked flask equipped with inlet and outlet of inert gas, measured quantity of GnP was added to 4 mL (0.0439 mol) of double distilled aniline and sonicated for an hour. Then 100 mL hydrochloric acid (1.0 M) was added; followed by addition of 3 gm of sago into the above solution and kept standstill. Then, the oxidant solution was prepared by dissolving 5 g (0.022 mol) APS in 50 mL water. Both solutions were cooled to 0-4 ℃ in an ice bath. The solutions were degassed with inert gas. The oxidant solution was then added dropwise to aniline salt solution through a dropping funnel under ultrasonic irradiation with a power of 100 W and operated at 40 kHz for 1 h. The obtained solution was kept aside for 24 hrs for reaction to complete. In all reactions, the molar ratio of aniline to ammonium peroxydisulfate was kept at 1:1. In order to remove excess acids and by-products from polymerization, the as-prepared PANI nanoparticles were purified by washing with water three times followed by ethanol until pH 7 was achieved. The dark green powder was collected on a filter paper using vacuum filtration. The filtrate was dried in vacuum (50 ℃) for 12 hrs.

2.2   Characterization
Electrical conductivity was measured by using four probe Keithley meter (Model 6517 A) coupled with a resistivity chamber (Model 8009) wherein the electrodes are located in a shielded box to minimize stray electrostatic pick-up, which can cause measurement errors. The electrodes are made of stainless steel and are built to ASTM standards. The electrodes in the 8009 resistivity chamber are coated with conductive rubber for better sample electrode contact. Three specimens of each sample were taken for measurement in order to ensure the repeatability and reproducibility of result. For the measurement of electrical conductivity, the powdered conducting PANI nanocomposites of 5 g was prepared in pellet form (diameter: 13 mm, thickness: 1 mm) at pressure of 14 MPa using a Carver model C Press. Morphology of the PANI nanocomposites was studied by using Hitachi HT7700 High Resolution – Transmission Electron Microscope 120kv (HR-TEM 120 KV).

3.   Result and Discussion
3.1   Electrical Conductivity:
Electrical conductivity of P/S/G nanocomposites are illustrated in Fig. 1 and reported in Table 1. Four probe method was used for measurement of electrical conductivity of the prepared blends and nanocomposites by pelletizing them (diameter: 13 mm, thickness: 1 mm) at pressure of 14 MPa using a Carver model C Press. The conductivity of neat PANI prepared by ultrasonic irradiation was found to be 1.78 S/cm. As expected upon incorporation of sago starch the conductivity reduced to 3.11786E-4 S/cm. As part of the ongoing research it was found that the higher the polyaniline content in the blend the higher conductivity will be, will is expected and also reported by Zareh et al., [17]. However, since PANI is non-biodegradable, non-flexible and non-processable, only very low amount of PANI is preferred for producing conductive nanocomposites [10]. Therefore, this research focuses on using as low as possible quantity of PANI. The selected blend for incorporation of GnP was P/S-20/80 (20 wt% PANI and 80 wt% Sago).

Table 1. The electrical conductivity of the neat PANI and P/S/G nanocomposites.

Sample ID	GnP (wt.%)	Electrical Conductivity (S cm^{-1})
Neat PANI	-	1.78
P/S	-	3.11786E-4
P/S/G-1	0.125	2.986E-4
P/S/G-2	0.25	0.0014
P/S/G-3	0.5	0.022
P/S/G-4	1.0	0.090
P/S/G-5	1.5	0.138

The electrical conductivity of the HCl doped P/S/G nanocomposites increased with increase in GnP content, as evident from Fig. 1. The increase in the electrical conductivity after the incorporation of GnP was attributed to the additional effects of both PANI and GnP because both are conducting. This

shows that there is a π -π interaction between the GnP and the PANI backbone, which leads to a higher conjugated system, as reported by Parveen et al., [18]. This suggests that GnP had a remarkable impact on the microstructure of the resulting P/S/G nanocomposites, which might also lead to an increase in the mobility of the charge carriers in the P/S/G nanocomposites; hence, an increase in electrical conductivity.
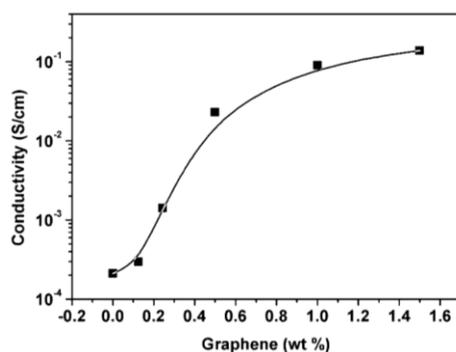
Figure 1. Conductivity value of PANI/Sago/GnP nanocomposites with different compositions of GnP

3.2   Morphology
TEM was performed to examine the inner nanostructures of P/S/G nanocomposites. The TEM image (Fig 2.a) of GnP reveals a sheet like structure with many wrinkles and scrolls [19], which is analogous to the microstructure of the individual GnP sheet. Fig 2.b shows the FE-SEM image of neat PANI, which is tubular in morphology.

Upon synthesis of P/S/G nanocomposites, TEM images shows the presence of both GnP and tubular PANI. The morphology was mostly tubular with certain flakes. The presence of flakes like strucure is attributed to the adsorption of aniline on the GnP template and its subsequent polymerization. From Fig 3, it can be clearly seen the increase in content of GnP. Fig 3 (a-c) shows uniform dispersion of GnP and also presence of tubular PANI. However, from Fig 3 (d and e) the agglomeration of GnP can be seen. This is further supported by the electrical conductivity values for subsequent nanocomposites. The increase in GnP also resulted in an increase in the diameter of P/S/G nanocomposite compared to pure PANI. The mean diameter of the PANI was measured to be 85 nm, suggesting that they are nanofibers.
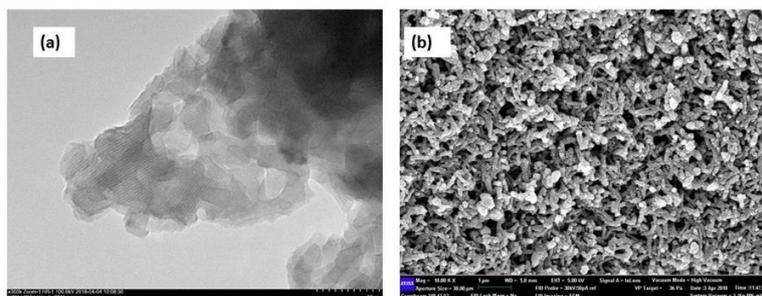
Figure 2. Morphology images of (a) TEM image of GnP dispersed in Sago Matrix, (b) FE-SEM image of Neat PANI.

4. Conclusion

P/S/G nanocomposites were successfully synthesized via ultrasonic irradiation technique. Electrical conductivity results showed that synthesized PANI had electrical conductivity of 1.78 S/cm however upon addition of sago it reduced significantly but at the same time making the PANI/Sago biodegradable, ease of handling and increasing the applications. Further upon introduction GnP to PANI/Sago and synthesising P/S/G nanocomposites the conductivity increased with increase in GnP content and reaching 0.138 S/cm for 1.5 wt% of GnP. TEM analysis confirmed the uniform dispersion of GnP and the adsorption of aniline on the GnP template. Finally, it can be concluded that the

prepared nanocomposites are appropriate candidates for different applications requiring conductive nanocomposites.
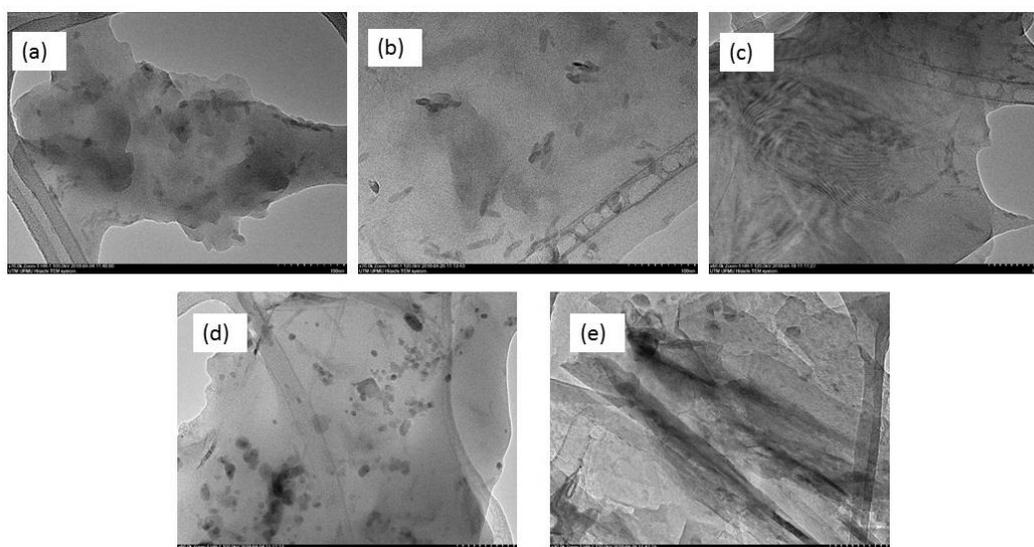
Figure 3. TEM images of P/S/G nanocomposites with varying quantity of GnP (a) 0.125 wt.% GnP (b) 0.25 wt.% GnP (c) 0.5 wt.% GnP (d) 1 wt.% GnP (e) 1.5 wt.% GnP.

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