Synthesis of Novel Composites of HCl-Doped Polyaniline with Maize, Rice and Wheat Flour

FARAH KANWAL[1,*], RABIA REHMAN[1], AISHA BATOOL[2] and MUHAMMAD SAEED[1]

[1]Institute of Chemistry, University of the Punjab, Lahore, Pakistan
[2]Centre of Excellence in Solid State Physics, University of the Punjab, Lahore, Pakistan

*Corresponding author: Fax: +92 42 99231269; E-mail: farahkchem@yahoo.com

Polyaniline and its composites with rice, maize and wheat flour were prepared at 0 and -5 ℃ by oxidative polymerization of aniline in the presence of potassium dichromate as an oxidizing agent. The prepared composites were characterized by fourier transform infrared spectroscopy, UV-visible spectroscopy and standard four probe method. The UV-visible spectroscopy of the polyaniline composites show absorption maxima due to π-π* transition of the benzenoid ring and charge transfer excitations of the quinonoid structure, which are characteristics of emeraldine base. FT-IR spectra of the polyaniline composites is similar to that of pure polyaniline but with the shifts of bands to higher wave numbers due to strong interaction of dopants and polyaniline matrix. The conductivity measurements revealed that the conductance of polyaniline-maize composites offer better conducting properties among all samples.

Key Words: Polyaniline, Composites, UV, FT-IR, D.C. Conductivity.

INTRODUCTION

Polymers offer wide range of applications due to their low cost, light weight and mechanical properties. One the main property for electrical and optical phenomena to occur in polymers depends on the conjugated backbone structure[1]. Polymers with conjugated backbone in undoped state possess energy gap of Peierls-Mott origin and has been explored as an alternative to metals or organic semiconductors such as polyacetylene, polyaniline (PANI) and polypyrrole[2]. Among conducting polymers, polyaniline is specially promising because of its facile processibility, environmentally stability, outstanding properties from semi-conductors to metals and numerous applications in variety of electrical and electronic devices such as sensors, biosensors, electro-chromic materials and substrate catalyst[3,4]. Polyaniline can be synthesized by chemical and electrochemical method of polymerization by oxidation or reduction[5]. Polyaniline can combine with some filler to produce polymer composites that yield infinite density of states at the Fermi level for hopping of electrons to enhance D.C. conductivity approaching to metals.

Over recent years, many authors have pointed out that rice, maize and wheat are being natural dielectric materials appear as alternative of organic/metal oxide composites with several advantages such as low densities, low cost, non-abrasive nature[6,7], possibility of high filling levels, low energy consumption, high specific properties, biodegradability, availability of a wide variety of fibers throughout the world and generation of agricultural-based economy[8]. The interaction of polyaniline with the main components of cellulose and lignin is the subject of recent studies. In addition the utilization of waste biodegradable materials also in the manufacturing of such composites that may help the environment by reducing the land filling and promoting the recycling[9,10].

In this paper, we describe the fabrication of polyaniline composites with biodegradable materials such as maize, rice and wheat flour at two different working temperatures of 0 and -5 ℃ to explore their structural, optical and conducting properties.

EXPERIMENTAL

Aniline (Reagent grade) was doubly distilled prior to use to eliminate the oxidation impurities. Potassium dichromate, hydrochloric acid, dimethyl formaldehyde and acetone were purchased from Merck (Germany). Locally purchased maize, wheat and rice flour were used in this research work.

Synthesis of polyaniline: Polyaniline was synthesized by chemical oxidative polymerization of aniline using potassium dichromate as an oxidant. 100 mL of 2 M HCl was added in 10 mL of polyaniline at 0 ℃. 20 mL of 1 M potassium dichromate was added drop wise in acidic solution to initialize polymerization under constant magnetic stirring and nitrogen

flow for 45-50 min. As $K_2Cr_2O_7$ was added in the acidic solution it turns into dark green colour to confirm the polymerization of aniline monomer. This reaction was allowed to proceed for 24 h and after that it was collected on filter paper by using Buckner funnel and then washed with 2.0 M HCl, acetone and deionized water to remove the unreacted species and impurities. The precipitates were dried in vacuum oven at 50 ºC for 48 h and named as P-1. The same procedure was followed at -5 ºC to get P-2.

Synthesis of composites of polyaniline with maize, rice and wheat flour at 0 and -5 ºC: The above procedure was adopted to synthesize biodegradable composites of polyaniline with this modification. 2 g of maize flour was added in the polymerization solution at 0 ºC during polymerization of aniline monomer to get MPC-1. Same procedure is repeated at -5 ºC to prepare MPC-2. Other composites of polyaniline with rice and wheat flour were synthesized at these two reaction temperatures of 0 and -5 ºC *via* adopting same methodology by replacing maize with rice and wheat flour to get RPC-1, RPC-2, WPC-1 and WPC-2, respectively.

FT-IR spectra of polyaniline and its composites were characterized as KBr disc at room temperature using IR-Prestige-21 at a resolution of 4.0 cm⁻¹ over the wave number range of 4000-650 cm⁻¹ [11]. UV-visible spectra of polyaniline hydrochloride solutions in dimethyl formaldehyde (DMF) and *m*-cresol have been taken using Jasco-V530 UV-visible spectrophotometer. UV-visible spectra of samples were recorded on a spectrophotometer in the range 200-800 nm. Very small amount of each sample (0.01 g) was dispersed in 20 mL of DMF and *m*-cresol to make a very dilute solution.

D.C. electrical conductivity: Standard four probe method was used to measure the D.C electrical conductivity at room temperature (25 ºC) by adopting standard method as described earlier[12].

RESULTS AND DISCUSSION

Fig. 1a-b show the FT-IR spectra of polyaniline and its composites at 0 and -5 ºC having characteristic absorptions at 3312, 1633, 1508, 1304, 1145 and 831 cm⁻¹. The broad peak at 3312 cm⁻¹ belongs to the hydrogen bonded N-H. The peaks about 1590 and 1508 cm⁻¹ are associated with aromatic ring stretching vibrations of N-B-N and N=Q=N structures, respectively. The quinonoid band is more intense than benzenoid band in polyaniline. Absorption bands at 1590 and 1508 cm⁻¹ indicated the oxidation state of emeraldine base polyaniline[13]. The band at 1304 cm⁻¹ corresponds to the C-N stretching of
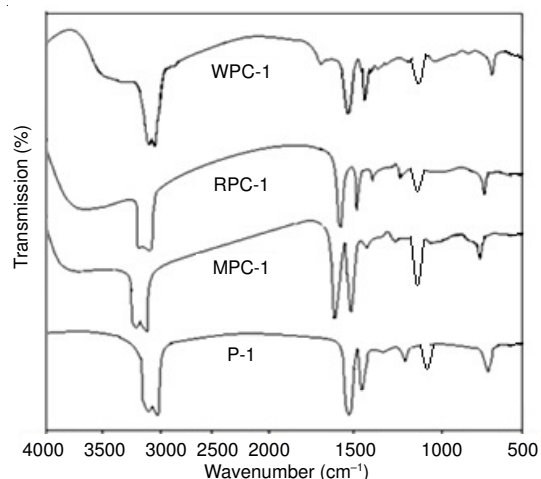

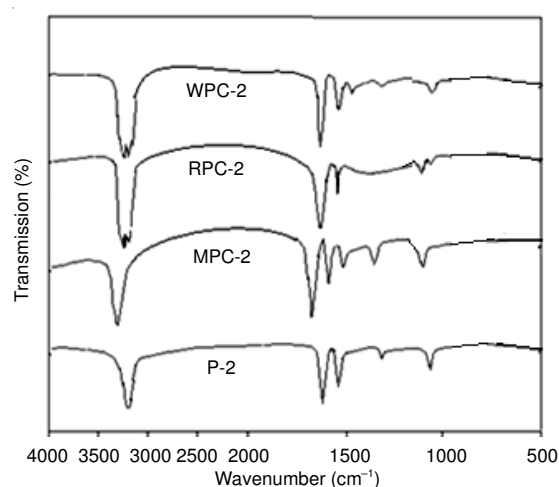Fig. 1. (a) FT-IR Spectra of polyaniline and its composites at 0 ºC

Fig. 1. (b) FT-IR spectra of polyaniline and its composites at -5 ºC

quinonoid band and at 1145 cm⁻¹ is the characteristic band of polyaniline conductivity and considered to be a measure of degree of delocalization of electrons[14]. The peak corresponding to out-of-plane bending vibration of C-H band of benzene ring appears at 797 cm⁻¹ [15]. The FT-IR spectra of the polyaniline composites contain the same characteristics peaks as polyaniline with the clear shifts of bands towards higher wave number for MPC as compared to other composites with rice and wheat flour (Table-1). There is also an increase in the intensity of quinonoid band and electronic-like band to reflect the stabilization of quinoid to a great extent after doping to enhance their D.C conductivity.

Sample	Hydrogen bonded N-H	Benzoid ring stretching	Quionoid ring stretching	C-N stretching band of Quinoid	Electronic band	C-H out-of-plane bending
			cm⁻¹			
P-1	3322	1508	1633	1304	1145	831
MPC-1	3362	1415	1584	1208	1039	830
RPC-1	3315	1453	1611	1247	1133	831
WPC-1	3306	1442	1592	1284	1130	833
P-2	3302	1500	1628	1301	1133	829
MPC-2	3356	1551	1636	1300	1123	832
RPC-2	3308	1513	1634	1309	1131	831
WPC-2	3301	1426	1515	1253	1145	831

TABLE-1
FT-IR SPECTRA OF POLYANILINE AND ITS COMPOSITES AT 0 AND -5 ºC

The UV-visible spectra of the HCl-doped polyaniline (P-1 and P-2) has two broad peaks around 340 and 595 nm, which are attributed to the characteristic band for π-π* and π-π* transitions to show that the resulting polyaniline emeraldine salt was in the doped state[16,17,6]. The difference of energy value between these two orbitals determines the electrical properties of polyaniline. Fig. 2a and b indicating that the intensity of π-π* transitions and excitonic peaks are increased in composites of polyaniline with powered maize, rice and wheat as compared to pure polyaniline with the shift of peaks towards higher wave numbers. Transition absorption peaks correspond to MPC-1 and MCP-2 showed highest values of $\lambda_{max\ 1}$ and $\lambda_{max\ 2}$ (Table-2). These results revealed that the addition of dopant cause interactions with polymer molecules to reduce the band gap of π-π* transitions and facilitate the electronic transitions at lower energy. Excitonic transitions peaks for RPC and WPC are shifted to lower wave numbers which tends to increase the band gap of excitonic transition for electronic transitions occurs at higher energy[12,18].
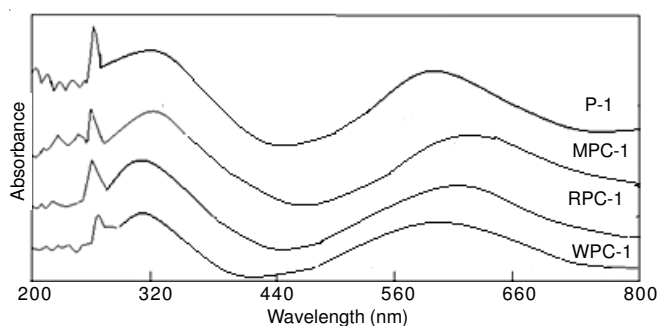

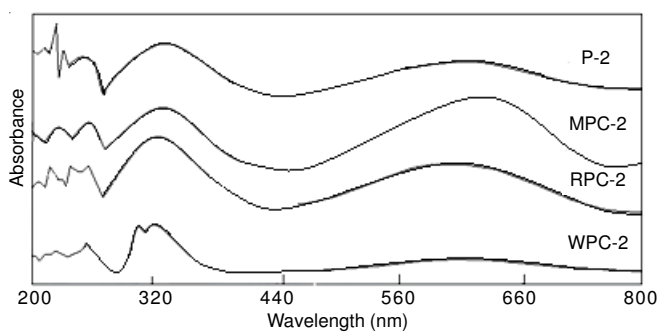Fig. 2. (a) UV-visible spectra of polyaniline and its composites at 0 ºC

Fig. 2. (b) UV-visible spectra of polyaniline and its composites at -5 ºC

TABLE-2
UV-VISIBLE ABSORPTIONS IN POLYANILINE
AND ITS COMPOSITES

Sample	Absorption at $\lambda_{max\ 1}$ (nm)	Absorption at $\lambda_{max\ 2}$ (nm)
P-1	340	595
P-2	350	630
MPC-1	365	645
MPC-2	380	630
RPC-1	330	585
RPC-2	335	590
WPC-1	305	565
WPC-2	325	585

Conductivity measurement: Room temperature D.C. conductivities of pure polyaniline at 0 and -5 ºC and their respective composites with maize, rice and wheat are shown in Fig. 4. Electrical measurements concluded that their

conductivity vary between 0.18-6 S cm⁻¹ for P-1 composites and 2.12-18.0 S cm⁻¹ for P-2 composites. The successful formation of polyaniline-maize composites is further confirmed by the significant increase in its conductivity among all prepared composites. Samples prepared at low temperature of -5 ºC exhibited good ohmic behaviour over a wide range of applied current and higher conductivity than that prepared at 0 ºC as shown in Fig. 3a-d. Table-3 showed electrical conductivity of polyaniline augment nearly three times as we doped polyaniline with maize (6 S cm⁻¹ for MPC-1 and 18 S cm⁻¹ for MPC-2). This value is many orders of magnitude higher than that of conventional polymers, 10⁻⁹ S cm⁻¹. The reason for the enhanced conductivity may be due to the facts that samples prepared at low temperature of -5 ºC cause decrease in resistance within the polymer surface which facilitate the hopping of electrons, orderings and evenness of dopant with polyaniline molecules and due to extended chains or better conjugation as confirmed from UV-visible and FT-IR analysis, respectively. Composites of polyaniline with wheat exhibited lowest value of conductivity (0.18 S cm⁻¹ for WPC-1 and 2.12 S cm⁻¹ for WPC-2) even less than bare polyaniline samples due to poor compactness, crystallinity and random orientation of particles in the polyaniline matrix to resist the hopping of electrons to conduct electricity.
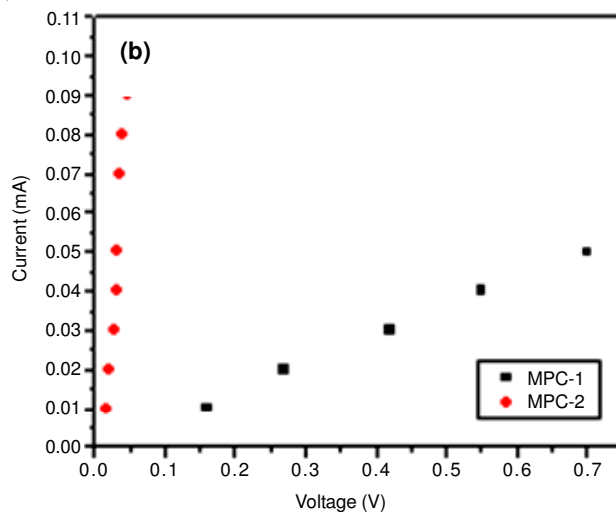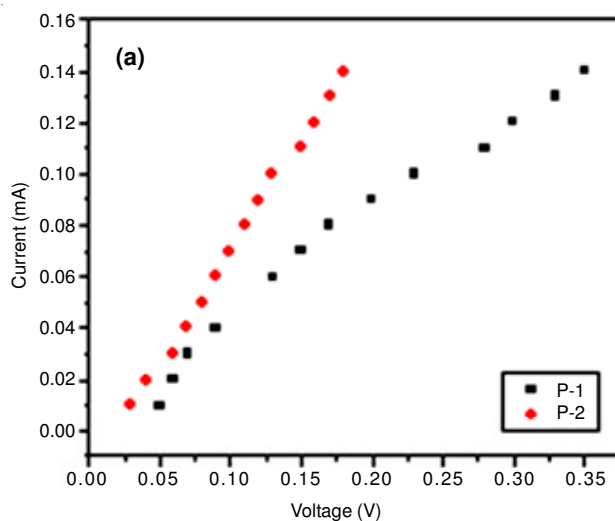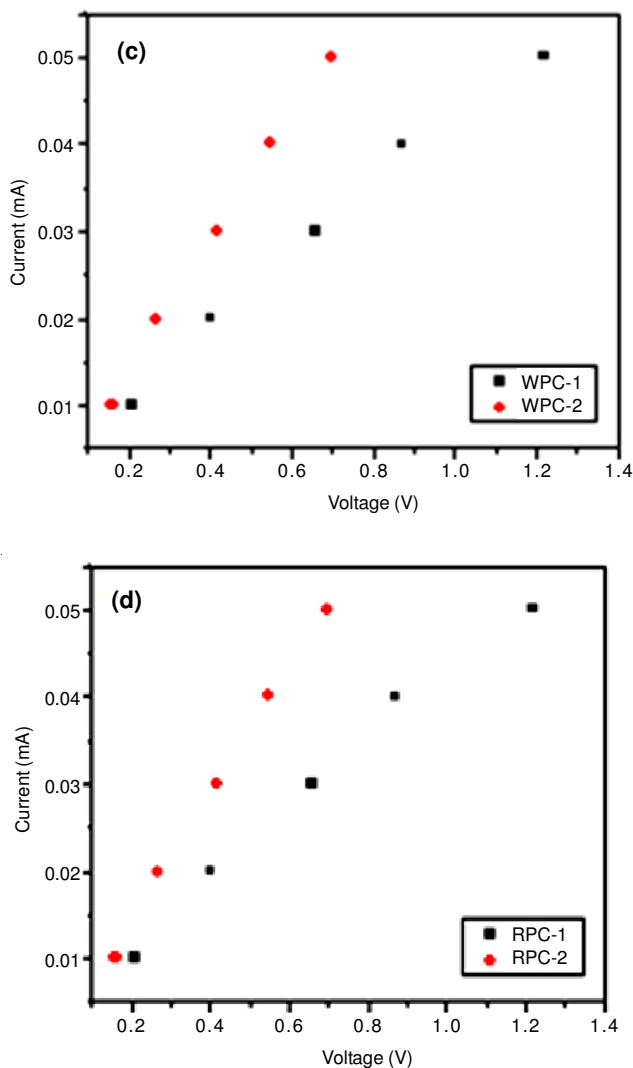
Fig. 3. Comparison of I-V characteristic curves for (a) HCl-doped polyaniline, (b) maize flour polyaniline composites, (c) wheat flour polyaniline composites at 0 and -5 ºC and (d) rice flour polyaniline composites at 0 and -5 ºC
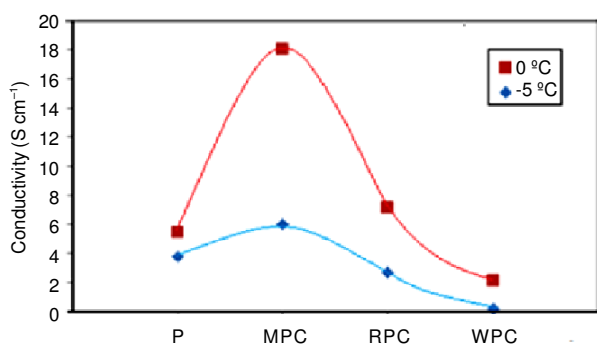

Fig. 4. D.C conductivity of P-1, P-2 and their respective composites with maize, rice and wheat flour

TABLE-3
CONDUCTIVITY OF POLYANILINE AND ITS
COMPOSITES AT 0 AND -5 ºC

Reaction temperature (ºC)	Sample	D.C conductivity (S cm^{-1})
0	P-1	3.8
	MPC-1	6.0
	RPC-1	2.7
	WPC-1	0.18
-5	P-2	5.4
	MPC-2	18.0
	RPC-2	7.2
	WPC-2	2.12

Conclusion

HCl-doped polyaniline and its composites with powdered maize, rice and wheat are synthesized by chemical oxidation method at 0 and -5 ºC. FT-IR analysis confirmed the successful formation of composites and strong interactions between dopant and backbone of polyaniline by the appreciable shift of peaks. Conductivity was found to be dependent upon nature of dopant, reaction temperature, better conjugation and band gap energy. The outstanding enhanced conductivity of polyaniline-maize composites among all samples is due to its interaction with polymer backbone to reduce the band gap of π-π* and to facilitate the electronic transition at lower energy.

REFERENCES

1. H. Eisazadeh, *World Appl. Sci. J.*, **3**, 14 (2008).
2. A.J. Epstein, W.P. Lee and V.N. Prigodin, *Synth. Met.*, **117**, 9 (2001).
3. Y. Wang and X. Jing, *Polym. Adv. Technol.*, **15**, 481 (2004).
4. R. Khan, P. Khare, B.P. Baruah, A.K. Hazarika and N.C. Dey, *J. Adv. Chem. Eng. Sci.*, **1**, 37 (2011).
5. F. Kanwal, S.A. Siddiqi, S. Tasleem, G. Sakina and T. Jamil, *J. Chem. Soc. Pak.*, **31**, 882 (2009).
6. B. Gross, *J. Chem. Phys.*, **17**, 866 (1946).
7. F. Mengeloglu, L.M. Matuana and J.A. King, *J. Vinyl Additive Technol.*, **6**, 153 (2000).
8. L.M. Matuana, C.P. Park and J.J. Balatinecz, *Polym. Eng. Sci.*, **38**, 1862 (1998).
9. F. Mengeloglu and L.M. Matuana, *J. Vinyl Additive Technol.*, **9**, 26 (2003).
10. Y. Geng and K. Li, *J. Appl. Polym. Sci.*, **91**, 3667 (2004).
11. P.S. Kalsi, Spectroscopy of Organic Compounds, Wiley Eastern Limited, New Dehli, edn. 6 (2006).
12. F. Kanwal, S.A. Siddiqi, A. Batool, M. Imran, W. Mushtaq and T. Jamil, *Synt. Met.*, **161**, 335 (2011).
13. D.C. Tiwari, R. Jain and S. Sharma, *J. Appl. Polym. Sci.*, **110**, 2328 (2008).
14. X. Chen, Z. Zhou, W. Lv, T. Huang and S. Hu, *J. Mater. Chem. Phys.*, **115**, 258 (2009).
15. A. Reung-u-Rai, A. Prom-Jun, W. Prissanroon-Ouajai and S. Ouajai, *J. Miner. Met. Mater.*, **18**, 27 (2008).
16. K. Dutta and S.K. Dc, *Phys. Lett. A*, **361**, 141 (2007).
17. S. Shadra, D. Khastgir, N.K. Singh and J.H. Lee, *Prog. Polym. Sci.*, **34**, 783 (2009).
18. H. Zengin and B. Erkan, *Polym. Adv. Technol.*, **21**, 261 (2010).