SYNTHESIS AND CHARACTERIZATION OF NANOCOMPOSITE OF COPOLYMER OF 3,4-DIMETHYL PYRROLE (DMPY) AND 2,5-DIMETHOXY ANILINE (DMOA)

Chemistry

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ABSTRACT
Nanocomposite of copolymer of 3,4-Dimethyl pyrrole (DMPy) and 2,5-Dimethoxy aniline (DMOA) doped with HCl was synthesized by chemical oxidative polymerization. APS was used as oxidant. The sample was characterized by FTIR, TGA, XRD and four probe method. FTIR confirms the formation of copolymer and its structure. XRD analysis shows the amorphous nature of polymer nanocomposite. The electrical conductivity of sample was measured by using four probe method. Size and surface morphology was demonstrated by SEM.

KEYWORDS
Nanocomposite, copolymer, XRD, TGA, SEM, Four probe method.

1. INTRODUCTION
Tremendous interest have being shown in nanostructured materials, amongst the scientific community predominantly due to their peculiar and fascinating properties as well as their unique applications.

Amongst the wide variety of nanostructured materials, conducting polymer and copolymer based nanostructured materials justify the special attention due to their edge over others as they combine the advantage of organic conductor with that of low dimensional materials. These nanostructured materials possess some unique properties such as π-conjugated polymeric chains, metal/ semico nductor like conductivity, reversible physical properties by novel doping/de-doping process. Since their discovery, the conjugated polymers can be made to conduct electricity through doping [1].

Further, even among innumerable conducting polymers, polyaniline and polypyrrole have gathered special attention. Due to the excellent redox recyclability, Polyaniline and its derivatives are deliberated to be one of the most promising class of organic conducting polymer [2], good environmental stability [3], and ease of doping [4]. Polypyrrole, because of good environmental stability and ease of synthesis is another important and most studied conducting polymer [5, 6]. It's an integral biocompatible polymer [7]. Due to their exceptional properties they can be used in various applications such as biosensors [8, 9], gas sensors [10], antielectrostatic coating [11], solid electrolytic capacitors [12, 13], light weight batteries and anticorrosive devices [14] etc.

In this study we reported the synthesis of nanocomposite of copolymer of 3,4-Dimethyl pyrrole (DMPy) and 2,5-Dimethoxy aniline (DMOA) by chemical oxidative polymerization. The properties like thermal stability, surface morphology, electrical conductivity and crystallinity of synthesized nanocomposite was also discussed.

Materials and methods
3, 4-dimethyl pyrrole (DMPy); 2,5-Dimethoxy aniline (DMOA); ammonium persulphate (APS); hydrochloric acid (HCl) were obtained from across organic (USA). All chemicals were of analytical grade. Solutions were prepared in double distilled water.

Among other polymerization techniques, chemical oxidative method [15-17] is a very versatile and easy route to synthesize large amount of conducting polymers. Chemical oxidative polymerization [18] is followed by oxidation of comonomer to cation radical and their coupling to form dication and repetition of this process generates a polymer.

Synthesis of nanocomposite of copolymer of 2, 3-dimethyl aniline and 3, 4-dimethyl pyrrole:
1.436g (0.009375moles) of 2, 5-dimethoxy aniline and 0.892g (0.009375 moles) of 2, 4-dimethyl pyrrole were mixed with 1M 100 ml HCl with continuous stirring for 30 minutes in a reactor. The APS solution was prepared by using 0.01875 mole i.e.4.27g, with 50ml of 1M HCl. Then APS solution was dropped (by stirring for 30 minutes) into a reactor which contained aniline and pyrrole solution at 0oC. Further, agitation was applied for 12 hour after dropping process, and brownish black compound was obtained.

Characterization:
Fourier transform infrared spectrophotometer (Perkin Elmer) was used to determine the chemical structure of the nanocomposite. Surface morphology of the prepared nanocomposite was characterized by scanning electron microscopy (SEM.LEO 435 VP). The ordered structure and crystallinity of the composites were obtained by X-ray diffraction method (XRD). Thermal analysis was done by using Thermogravimetric analyzer.

Results and discussions:
FTIR spectrum: The spectrum of nanocomposite of copolymerized pyrrole and aniline has being shown in fig.1.1.and the spectra of their homopolymers i.e. poly-2, 5-dimethoxy aniline (PDMOA), poly-3, 4-dimethyl pyrrole (PDMPy) have shown in fig 1.2 and 1.3, respectively. The characteristic bands observed in the IR region have been recorded in table 1.1.

The bonds at 1560 and 1450cm^{-1} in the spectrum of nanocomposite are attributed to C=C stretching frequencies of quinoid and benzenoid ring respectively. These bonds appear at 1610 and 1475 cm^{-1} in the spectrum of PDMOA. C-N stretching vibrations appear at 1273, 1300 and 1206 cm^{-1} for PDMPy, PDMOA and nanocomposite respectively.

The peaks corresponding to C=O group in the spectrum of PDMOA appears at 1740cm^{-1}, the same peak is also observed in the spectrum of the nanocomposite.

All characteristic peaks of PDMPy and PDMA also exist in the spectrum of nanocomposite confirming the presence of aniline and pyrrole unit in prepared nanocomposite.

Table.1.1. FTIR data of homopolymer and copolymer nanocomposite of copolymer of PDMPy and PDMA

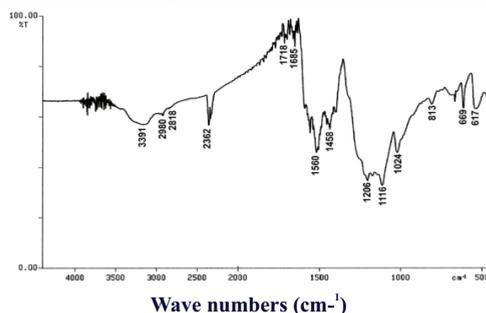|	N-H stretch	-CH₃ stretch	C-N	C-H in plane	C-H out of plane
PDMPy	3448	2996,2912	1273	1020	750
PDMOA	3431.26	…………	1300	1100	815
Nanocomposite	3391.42	2980,2818	1206	1116	813

Wave numbers (cm⁻¹)

Fig.1.1. FTIR spectrum of nanocomposite of copolymer of PDMPy and PDMOA
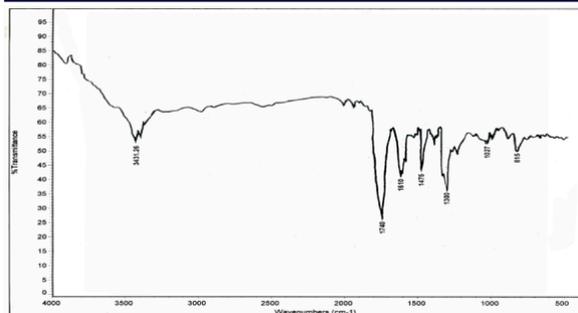
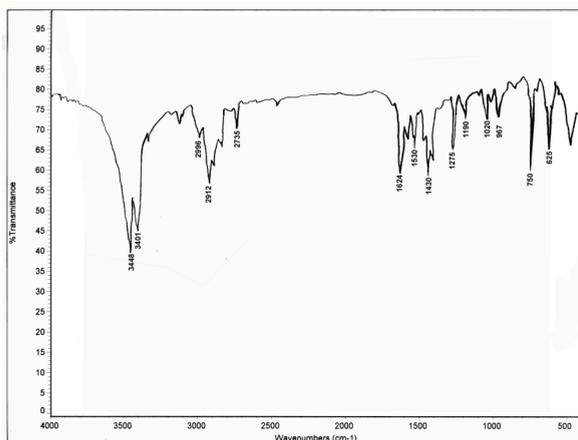**Fig.1.2. FTIR spectrum of poly-2, 3-dimethyl aniline**

Fig.1.3. FTIR spectrum of Poly-3, 4-dimethyl pyrrole

Thermal analysis: Thermogravimetric analysis measurements were carried out from room temperature to 800°C at a heating rate of 10°/ min under nitrogen atmosphere. Fig 2.1 shows the comparative TGA curves of nanocomposite (C.P.8), poly3, 4-dimethyl pyrrole (PDMPy) and poly-2, 5-dimethoxy aniline (PDMOA).

Thermogram of nanocomposite (C.P.8) shows three distinct regions of weight loss. All results were tabulated in table 2.1.which shows the initial loss in weight of about 7% weight loss occurs at 60°C-160°C for nanocomposite, featuring due to water deprivation. Further 10% weight loss took place in the range of 160°C-270°C corresponding to doping acid deprivation. From 250°C polymer chain began to degrade until 600°C. The decomposition temperature for prepared nanocomposite was 520°C and shown good thermal stability among their homopolymers.

Table.2.1. TGA curves of PDMPy, PDMOA and nanocomposite of copolymer of PDMPy and PDMOA.

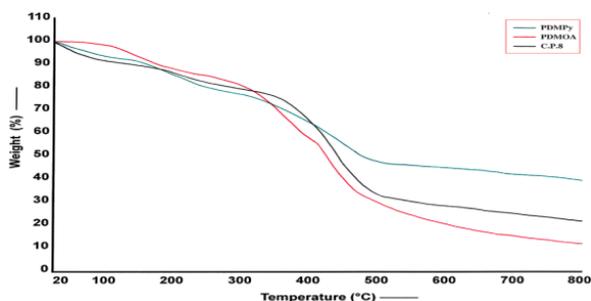| Compounds	1st weight loss		2nd weight loss		3rd weight loss	
PDMPy	7.5%	113°C	14%	255°C	30.5%	482°C
PDMOA	9%	163°C	7.5%	262.5°C	49.75%	465°C
Nanocomposite	6.5%	143.5°C	9.5%	275°C	52%	520°C

Fig.2.1. TGA curves of PDMPy, PDMOA and nanocomposite of copolymer of PDMPy and PDMOA

X-Ray Diffraction: XRD pattern of these nanocomposite exhibits broad peak at 2θ= 20° -30° and these peaks are indicative of an amorphous behavior. The broad peak is characteristic of amorphous polypyrrole at 2θ=24° [19] and it is due to the scattering from PPy chains at the interplanar spacing [20]. The copolymer of poly-2, 5-dimethoxy aniline and polypyrrole has shown broad characteristic peaks for their amorphous nature [21-22]. So on the behalf of earlier reported XRD graphs of poly aniline, polypyrrole and copolymer of aniline and pyrrole we can predict the formation of nanocomposites of substituted aniline and pyrrole and broadness of peak around at 2θ= 20° -30° is due to their amorphous nature.
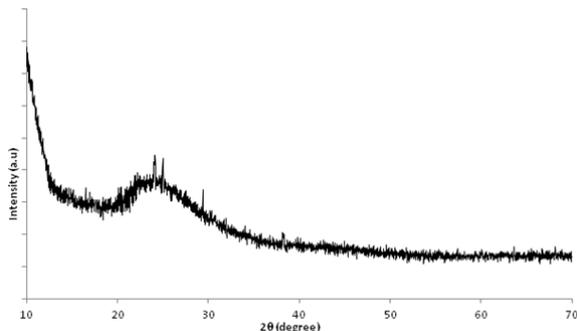

Fig.3.1. XRD spectrum of nanocomposite of copolymer of PDMPy and PDMOA.

Surface morphology:
Surface morphology of the nanocomposite was studied by scanning electron microscopy (SEM). Fig 4.1a and 4b shows the SEM micrographs at 500X and 1000X magnifications. It shows two different types of structure. One is cylindrical fiber type and other granular forms. Micrograph displays those granular particles of 250nm size distributed over cylindrical fibers.
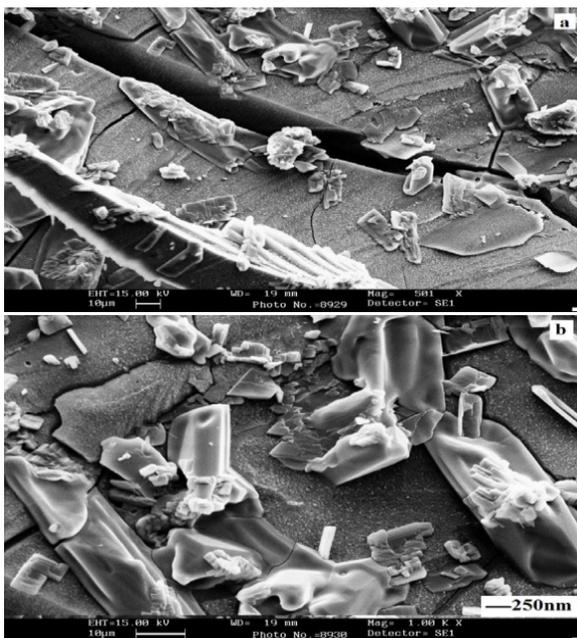

Fig4.1a and 1b.SEM images of nanocomposite of copolymer of PDMPy and PDMA at 500X and 1000X.

Electrical conductivity measurement:
Electrical conductivity of prepared nanocomposite was measured by Four Probe method. It is observed that the conductivity decreases from 10-2 to 10-5 when aniline was polymerized with pyrrole. The conductivity of prepared nanocomposite was 2.5x10-5s/cm.

Solubility test:
The nanocomposite of copolymer of substituted aniline and pyrrole, on trying to dissolve in NMP, H2O2, CCl4, H2O was found to be insoluble, however the nanocomposite was sparingly soluble in DMSO and gave a Brownish black color.

Conclusions:

The nanocomposite of copolymer of 3, 4-dimethyl pyrrole and 2, 5-dimethoxy aniline was successfully synthesized via chemical oxidative polymerization using APS as dopant. The particle size of nanocomposite was 250nm. Prepared nanocomposite has shown good thermal stability, electrical conductivity, and was almost insoluble, except in DMSO.

REFERENCES

1. Shirakawa, H., E.J. Louis, A.G. MacDiarmid, C.K. Chiang, and A.J. Heeger. Synthesis of electrically conducting organic polymers- Halogen derivatives of polyacetylene, (CH) x. Chem Commun 16:578-850 (1977).
2. Wu M.S, Wen T.C, Gopalan A. Mater Chem Phys; 74:58 (2002).
3. Camalet JL, Lacroix JC, Aeiyach S, Chane-ching K,Lacaze PC. Synth Metal;93:133 (1998).
4. Paul EW, Ricco AJ, Wrighton WS. J Phys Chem; 89:1441(1985).
5. Wu T-M., Lin S-H.: Synthesis, characterization, and electrical properties of polypyrrole/multiwalled carbon nanotube composites. Journal of Polymer Science Part A: Polymer Chemistry, 44, 6449–6457 (2006). DOI: 10.1002/pola.21724
6. Carrasco P. M., Grande H. J., Cortazar M., Alberdi J. M., Areizaga J., Pomposo J. A.: Structure–conductivity relationships in chemical polypyrroles of low, medium and high conductivity. Synthetic Metals, 156, 420–425 (2006). DOI: 10.1016/ j.synthmet. 2006.01.005
7. A. Ramanavicius et al, Electrochemical sensors based on conducting polymer-polypyrrole Electrochim. Acta 51, 2006, pp. 6025-6037
8. J. C. Vidal, E. Garcia and J. R. Castillo, "In situ Preparation of a Cholesterol Biosensor: Entrapment of Cholesterol Oxidase in an Overoxidized Polypyrrole Film Electrodeposited in a Flow System: Determination of Total Cholesterol in Serum," Analytica Chimica Acta, Vol. 385, No. 1-3, 1999, pp. 213-222. doi:10.1016/S0003-2670(98)00838-1
9. T. E. Campbell, A. J. Hodgson and G. G. Wallace, "Incorporation of Erythrocytes into Polypyrrole to Form the Basis of a Biosensor to Screen for Rhesus (D) Blood Groups and Rhesus (D) Antibodies," Electroanalysis, Vol. 11, No. 4, 1999, pp. 215-222.
10. D. Kincal, A. Kamer, A. D. Child and J. R. Reynold, "Conductivity Switching in Polypyrrole-Coated Textile Fabrics as Gas Sensors," Synthetic Metals, 92, 1998, pp. 53 55. doi:10.1016/S0379-6779(98)80022-2
11. S. C. Yang, H. Liu, R. L. Clark, PCT Int. Application, WO 99 22, 380 (Cl.H01 B1/00).
12. T. Takamatsu, Y. Taketani, Jpn. Kokai. Tokyo Koho JP11 121, 279 [99 121,279]
13. Y Kojima, H. Kamikawa, T. Takamatsu, Jpn. Kokai. Tokyo Koho JP11 121, 280[99 121,280]
14. Fahlman, M., S. Jasty, and A.J. Epstein. Corrosion protection of iron/steel by emeraldine base polyaniline: An x-ray photoelectron spectroscopy study. Synth Met 85 (1-3): 1323-1326 (1997).
15. S. A. Chen and C.C. Tsai, Macromolecules, 2, 2234(1993)
16. Y. Wei, J. Tan, A.G.MacDiarmid, J.G.Masters, A.L.Smith and D.Li, JCSCC, 7, 552(1994)
17. Somanathan and G.Wehner, Ind.J.Chem., 33A, 572(1994)
18. A. Obtani and T. shimadzu, Bull. Chem. Soc.Jpn., 2,234(1989)
19. R.E. Partch, S.G. Gangoli, E. Matijevic, W. Cai and S. Arajs, "Conducting Polymer composites I: Surface- induced polymerization of pyrrole on Iron (III) and cerium (IV) oxide particles", Journal of colloid and interface science, vol. 144, No.1, pp 27-35 (1991)
20. R.E. Partch, S.G. Gangoli, E. Matijevic, W. Cai and S. Arajs, "Conducting Polymer composites I: Surface- induced polymerization of pyrrole on Iron (III) and cerium (IV) oxide particles", Journal of colloid and interface science, vol. 144, No.1, pp 27-35 (1991)
21. S.E. Mavundla. G.F.Malgas, E.Iwuoha and D. Motaung,"Physiochemical and morphological properties of poly (aniline-co-pyrrole)" Journal of material science 45, 3325-3330 (2010).
22. S.E. Mavundla. G.F.Malgas, E.Iwuoha and P. Baker,Synthesis and electrochemistry of novel nanophase hexagonal poly (2, 5-dimethoxy aniline)" Electroanalysis 20, 2347 (2008).