Synthesis and Characterization of Nanocomposite of Copolymer of N-Methyl Pyrrole (NMPy) and 2-Ethyl Aniline (EA)

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Abstract

Nanocomposite copolymer of N-Methyl Pyrrole (NMPy) and 2-Ethyl Aniline (EA) doped with HCl was synthesized by chemical oxidative polymerization. APS was used as oxidant. The synthesized composite 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 composite was measured using four probe method. Size and surface morphology was reviled by SEM.

Keywords

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

Introduction

Nanostructured materials have attracted an incredible curiosity amid the scientific community predominantly due to their unusual yet peculiar and fascinating properties as well as their exceptional solicitations.

The slight advantage of conducting polymers and copolymers have over the other nanostructured materials is justified, as they associate the pro of organic conductor with that of low dimensional materials. The exceptional properties, such as ð-conjugated polymeric chains, metal/ semiconductor like conductivity, reversible physical properties by novel doping/de-doping process, possessed by these nanostructured materials. By doping these conjugated polymers can conduct electricity since their inception [1].

Additionally, even among numerous 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], 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], anti-electrostatic 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 N-Methyl pyrrole (NMPy) and 2-Ethyl aniline (EA) by chemical oxidative polymerization. The properties like thermal stability, surface morphology, electrical conductivity and crystallinity of synthesized nanocomposite was also discussed.

Materials and Methods

N-methyl pyrrole (NMPy); 2-Ethyl aniline (EA); 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-Ethyl Aniline and N-Methyl Pyrrole

4.544g (0.0375moles) of 2-ethyl aniline and 3.042g (0.0375 moles) of N-methyl pyrrole were mixed with 1M 100 ml HCl with continuous stirring for 30 minutes in a reactor. The APS solution was prepared by using 0.075 mole i.e.17.115g, 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 0îC. Further agitation was applied for 12 hour after dropping process, and dark green 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-ethyl aniline (PEA), poly-N-methyl pyrrole (PNMPy) 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 bands at 1634 and 1466cm^{-1} in the spectrum of nanocomposite are characteristic band of nitrogen quinoid (N=Q=N) and benzenoid (N-B-N). The spectrum of PEA shows these bands at 1540 and 14300cm^{-1}.

The bonds around 1376, 1251cm^{-1} are assigned to the bending vibration of N-H and asymmetric C-N stretching mode of benzenoid rings respectively in the spectrum of PEA. This band appears at 1280 and 1286cm^{-1} for PNMPy and nanocomposite respectively.

The bands at 1540 and 1437cm^{-1} are characteristic band for PNMPy. C-H in plane and out of plane deformations are shown in table 3.2.2.for polymer and copolymer. N-H stretch occurs at 3377, 3380cm^{-1} for PEA and nanocomposite respectively. This peak is absent in the spectrum of PNMPy. Presence of all peaks in spectrum of nanocomposite confirms the presence of polypyrrole and polyaniline units in composite.

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

	N-H stretch	-CH_3 stretch	C-N	C-H in plane	C-H out of plane
PNMPy	……..	2924,3008,2875	1280	1125	868
PEA	3380	3040,2930,2876	1251	1121	768
Nanocomposite	3377	2918,2849	1286	1166	886

Table 1.1 FTIR data of homopolymer and copolymer nanocomposite of copolymer of PNMPy and PEA

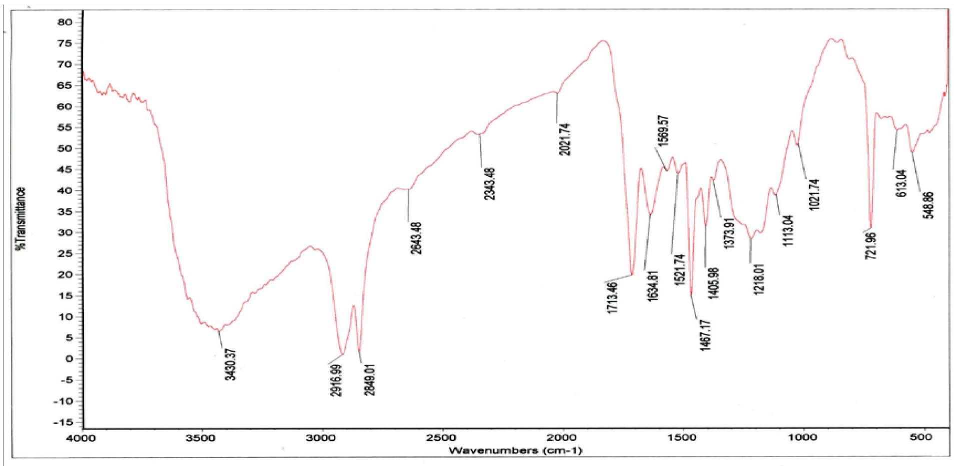

Fig.1.1. FTIR spectrum of nanocomposite of copolymer of PNMPy and PEA

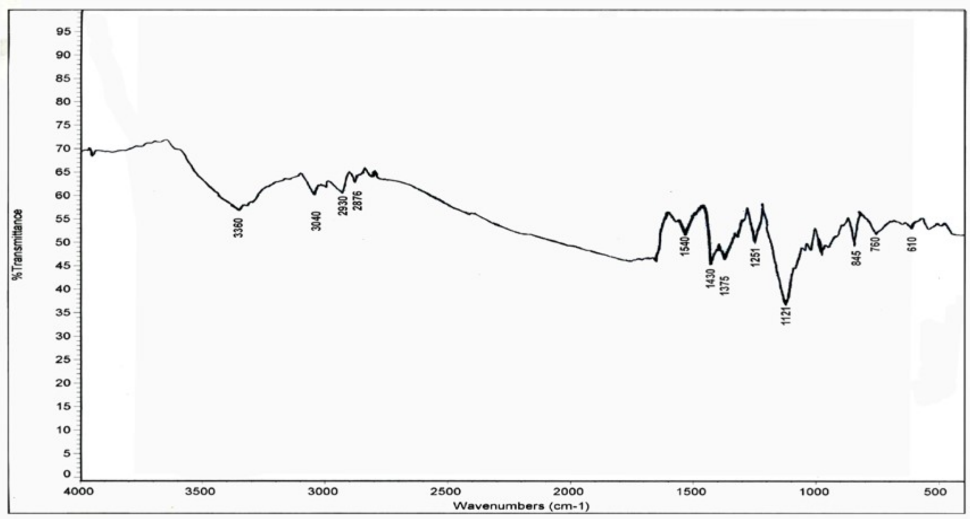

Fig.1.2. FTIR spectrum of poly-2-ethyl aniline

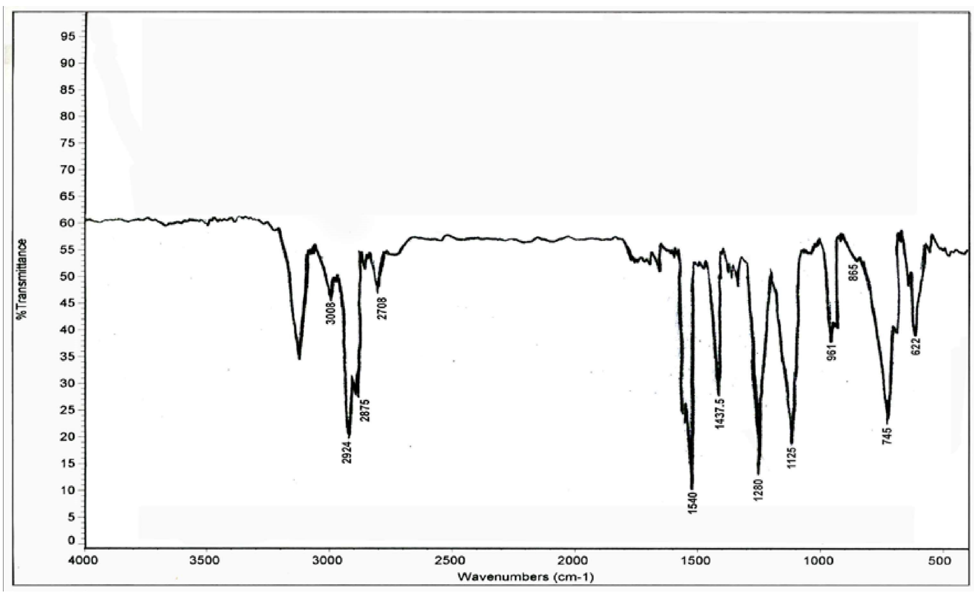

Fig.1.3. FTIR spectrum of Poly- N-methyl pyrrole

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.1), poly N-methyl pyrrole (PNMPy) and poly-2-ethyl aniline (PEA).

Thermogram of nanocomposite (C.P.1) shows three distinct regions of weight loss. All results were tabulated in table 2.1. Nanocomposite shows initial weight loss of 6.25% by 118<"C and it is attributed to the loss of water molecule and other volatile compounds. The loss of dopant (HCl) started around 118<"C and completed near 270<"C. Afterward degradation of polymer backbone has been started and maximum at 481<"C. PNMPy and PEA show polymer degradation maximum at 608<"C and 519<"C respectively and thus, shown good thermal stability among their homopolymers.

Compounds	1st weight loss		2nd weight loss		3rd weight loss	
PNMPy	6%	120°C	7.75%	280°C	23.75%	608°C
PEA	10.3%	110°C	6.7%	230°C	33.5%	519°C
Nanocomposite	6.25%	118°C	9.75%	270°C	30%	481°C

Table.2.1. TGA curves of PNMPy, PEA and nanocomposite of copolymer of PNMPy and PEA.

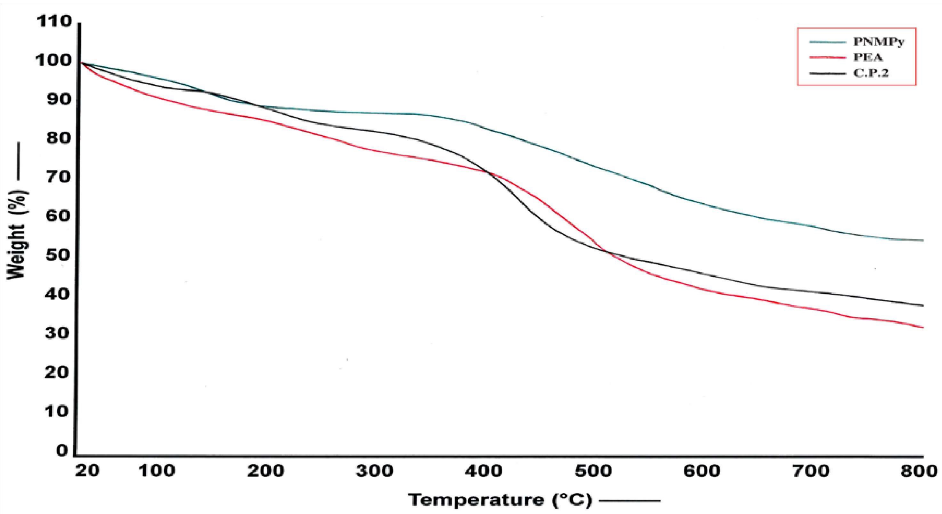

Fig.2.1. TGA curves of PNMPy, PEA and nanocomposite of copolymer of PNMPy and PEA

X-Ray Diffraction: XRD pattern of these nanocomposite exhibits broad peak at 2è= 20ᵖ - 30ᵖ and these peaks are indicative of an amorphous behavior. The broad peak is characteristic of amorphous polypyrrole at 2è=24ᵖ [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 [21-26]. 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 2è= 20ᵖ -30ᵖ is due to their amorphous nature.

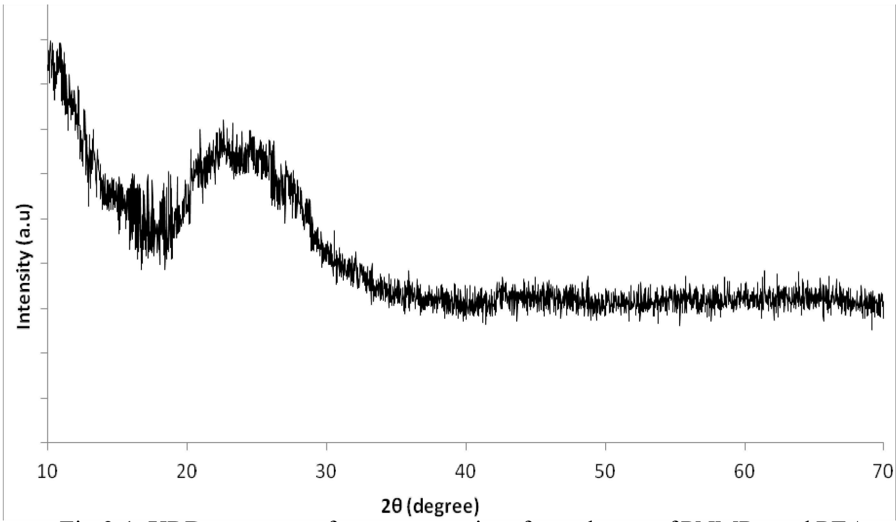

Fig.3.1. XRD spectrum of nanocomposite of copolymer of PNMPy and PEA.

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 300nm size distributed over cylindrical fibers.

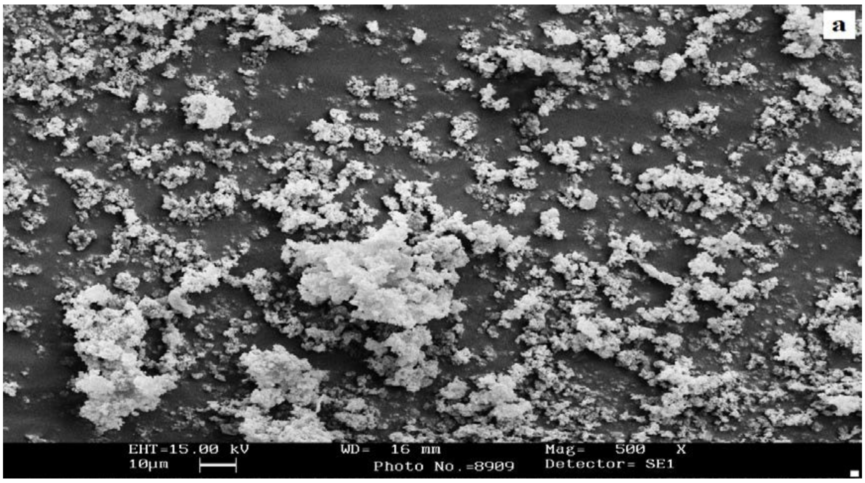

Fig. 4.1a

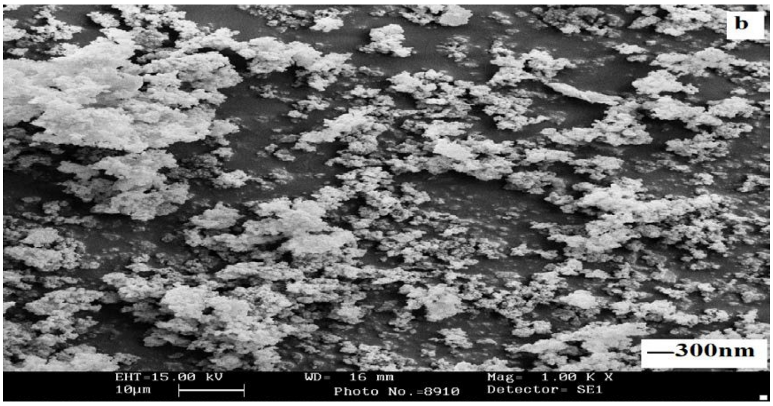

Fig. 4.1b

SEM images of nanocomposite of copolymer of PNMPy and PEA 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 $2.5x10^{-5}$ s/cm.

Solubility Test

The nanocomposite of copolymer of substituted aniline and pyrrole, on trying to dissolve in H_2O_2, CCl_4, H_2O was found to be insoluble, however the nanocomposite was sparingly soluble in DMSO and NMP, giving a Dark Green color.

Conclusions

The nanocomposite of copolymer of 2-ethyl aniline and N-methyl pyrrole was successfully synthesized via chemical oxidative polymerization using APS as dopant. The particle size of nanocomposite was 300 nm. Prepared nanocomposite has shown good thermal stability, electrical conductivity, and was almost insoluble, except in DMSO and NMP.

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