Synthesis and Characterization of Copolymer Nanocomposite N-Methyl Pyrrole (NMPy) and Aniline-2-Sulphonic Acid (ASA)

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Copolymer nanocomposite of N-Methyl pyrrole (NMPy) and Aniline-2-Sulphonic acid (ASA) doped with HCl was synthesized using chemical oxidative polymerization. Ammonium persulfate (APS) was used as an oxidant. The nanocomposite samples were characterized for structural configurations by FTIR, TGA and XRD. Four probe method was adopted for the measurement of electrical conductivity. 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.

Key words: Nanocomposite, copolymer, XRD, TGA, SEM, four probe method.

1. 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 π -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 classes 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 Aniline-2-Sulphonic acid (ASA) by chemical oxidative polymerization. The

properties like thermal stability, surface morphology, electrical conductivity and crystallinity of synthesized nanocomposite was also discussed.

2. MATERIALS AND METHODS

N-methyl pyrrole (NMPy); Aniline-2-Sulphonic acid (ASA); ammonium persulphate (APS); hydrochloric acid (HCI) were obtained from Acros Organics, 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 di-cation and repetition of this process generates a polymer.

2.1. Synthesis of Nanocomposite of Copolymer of Aniline-2-Sulphonic Acid (ASA) and N-methyl Pyrrole

1.62g (0.009375moles) of aniline-2-sulphonic acid and 0.7605g (0.009375 moles) of Nmethyl pyrrole were mixed with 1M 100 ml HCl with continuous stirring for 30 minutes in a reactor. The APS solution was prepared by using 0.00937 mole i.e., 2.139g, 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 0°C. Further agitation was applied for 12 hours after dropping process, and brown compound was obtained.

2.2. 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. Electrical conductivity was measured by Four Probe method.

3. RESULTS AND DISCUSSIONS

3.1. FTIR Spectrum

The spectrum of nanocomposite of copolymerized pyrrole and aniline has been shown in Figure 1 and the spectra of their homopolymers i.e., N, N-Dimethyl aniline (NDMA), poly-N-methyl pyrrole (PNMPy) have shown in Figure 2 and 3, respectively. The characteristic bands observed in the IR region have been recorded in Table 1.

The bands at 1637 and 1467cm⁻¹ in the spectrum of nanocomposite are attributed to C=C stretching frequencies of quinoid and benzenoid ring respectively. These peaks also appear in spectrum of PNDMA at 1523 and 1145cm⁻¹.

C-N stretching vibration bands appear at 1280, 1358 and 1299cm⁻¹ for PNMPy, PNDMA and nanocomposite material respectively. The N-H stretching vibration is absent in the

spectra of PNMPy, PNDMA and nanocomposite due to the presence of $-CH_3$ group on nitrogen atom of pyrrole, aniline and nanocomposite.

The characteristics band of polymer of aniline and pyrrole were also present in the spectrum of nanocomposite. The band of the homopolymer were not retained as such and undergone a slight shift in the spectrum of prepared nanocomposite.

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

 Table 1: FTIR data of homopolymer and copolymer nanocomposite of copolymer of PNMPy and PNDMA.

	N-H stretch	-CH₃ stretch	C-N	C-H in plane	C-H out of plane
PNMPy		2875, 2924, 3008	1280	1125	868
PEA		3073, 3005, 2994, 2887	1358	1169	727
Nanocomposite		2919, 2848	1299	1173	722



Fig. 1: FTIR spectrum of nanocomposite of copolymer of PNMPy and PNDMA.



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3.2. Thermal Analysis

Thermogravimetric analysis measurements were carried out from room temperature to 800°C at a heating rate of 10°/ min under nitrogen atmosphere. Figure 2 shows the comparative TGA curves of nanocomposite (C.P.1), poly N-methyl pyrrole (PNMPy) and poly-N, N-Dimethyl aniline (NDMA).

Thermogram of nanocomposite (C.P.1) shows three distinct regions of weight loss. All results were tabulated in Table 2. Nanocomposite shows 7% weight loss at 125°C, which is due to the elimination of water molecule and second weight loss of about 8% at 260°C, which is attributed to removal of dopant. The polymer backbone degradation has been started above 400°C and it is maximum for PNMPy and lowest for PNDMA and thus, shown good thermal stability among their homopolymers.

Table 2: TGA	curves of PNMP	, PEA and	nanocomposite	of copolymer	of PNMPy a	and
		PN	DMA.		-	

Compounds	1 st weight loss		2 nd weight loss		3 rd weight loss	
PNMPy	6%	120°C	7.75%	280°C	23.75%	608°C
PNDMA	7%	135°C	10%	240°C	55%	462°C
Nanocomposite	7%	125°C	8%	260°C	45%	469°C



Fig. 2: TGA curves of PNMPy, PNDMA and nanocomposite of copolymer of PNMPy and PNDMA.

3.3. X-Ray Diffraction

XRD pattern of these nanocomposite as in Figure 3 exhibits broad peak at $2\theta = 20^{\circ} - 30^{\circ}$ and these peaks are indicative of an amorphous behavior. The broad peak is characteristic of amorphous polypyrrole at $2\theta = 24^{\circ}$ [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]. Thus, 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 $2\theta = 20^{\circ} - 30^{\circ}$ is due to their amorphous nature.



Fig. 3: XRD spectrum of nanocomposite of copolymer of PNMPy and PNDMA.

3.4. Surface Morphology

Surface morphology of the nanocomposite was studied by scanning electron microscopy (SEM). Figure 4(a) and 4(b) shows the SEM micrographs at 500X and 1000X magnifications respectively. It shows two different types of structure. One is cylindrical fiber type and other granular forms. Micrograph displays those granular particles of 325nm size distributed over cylindrical fibers.

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Fig. 4: (a) SEM images of nanocomposite of copolymer of PNMPy and PNDMA at 500X.



Fig. 4: (b) SEM images of nanocomposite of copolymer of PNMPy and PNDMA at 1000X.

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3.5. 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 2.5×10^{-5} s/cm.

3.6. Solubility Test

The nanocomposite of copolymer of substituted aniline and pyrrole, on trying to dissolve in DMSO, H_2O_2 , CCI_4 , H_2O was found to be insoluble, however the nanocomposite was sparingly soluble in NMP and gave a Dark Green Color.

4. CONCLUSIONS

The nanocomposite of copolymer of N,N-Dimethyl aniline (NDMA) and N-methyl pyrrole was successfully synthesized via chemical oxidative polymerization using APS as dopant. The particle size of nanocomposite was 325 nm. Prepared nanocomposite has shown good thermal stability, electrical conductivity, and was almost insoluble, except in NMP.

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