© 2019 IJSRST | Volume 6 | Issue 4 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Science and Technology
DOI : https://doi.org/10.32628/IJSRST19643

# Synthesis and Characterization of Nanocomposite of Copolymer of N-Methyl Pyrrole (NMPy) and N, N-Dimethyl Aniline (NDMA)

**R. Rathore, Soni Sharma**
Department of Chemistry, Meerut College, Meerut, Uttar Pradesh, India

## ABSTRACT

Nanocomposite of copolymer of N-Methyl pyrrole (NMPy) and N, N-Dimethyl aniline (NDMA) 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 were demonstrated by SEM.

**Keywords :** Nanocomposite, Copolymer, XRD, TGA, SEM, Four Probe Method.

## I. 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 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], 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 N-Methyl pyrrole (NMPy) and N,N-Dimethyl aniline (NDMA) by chemical oxidative polymerization. The properties like thermal stability, surface morphology, electrical conductivity and crystallinity of synthesized nanocomposite was also discussed.

## II. METHODS AND MATERIAL

N-methyl pyrrole (NMPy); N,N-Dimethyl aniline (NDMA); 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 N,N-Dimethyl aniline (NDMA) and N-methyl pyrrole:**

4.544g (0.0375 moles) of N, N-Dimethyl 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 0°C. 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.

## III. RESULTS AND DISCUSSION

**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. N,N-Dimethyl aniline (NDMA), 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 1637 and 1467$cm^{-1}$ 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 1145$cm^{-1}$.

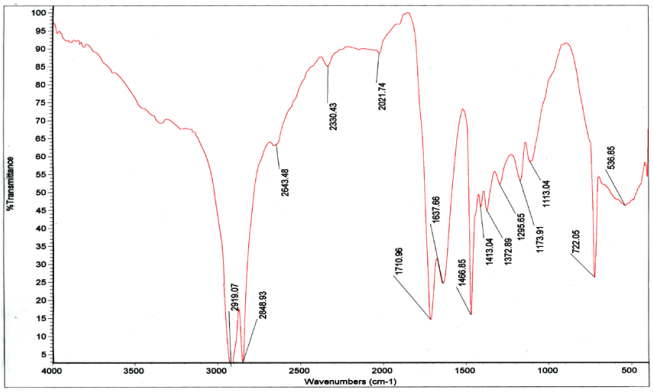
C-N stretching vibration bands appear at 1280, 1358 and 1299$cm^{-1}$ for PNMPy, PNDMA and nanocomposite material respectively. The N-H stretching vibration is absent in the spectra of PNMPy, PNDMA and nanocomposite due to the presence of $-CH_3$ group on nitrogen atom of pyrrole, aniline and nanocomposite.

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.1.1. FTIR data of homopolymer and copolymer nanocomposite of copolymer of PNMPy and PNDMA

| | N-H stretch | -$CH_3$ 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 |




Wave numbers ($cm^{-1}$)

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

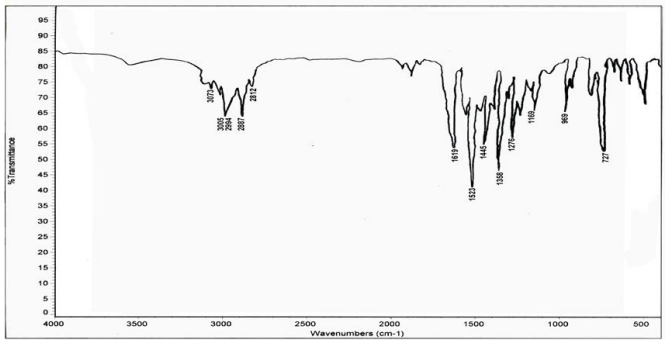



Fig.1.2. FTIR spectrum of poly- N,N-Dimethyl aniline

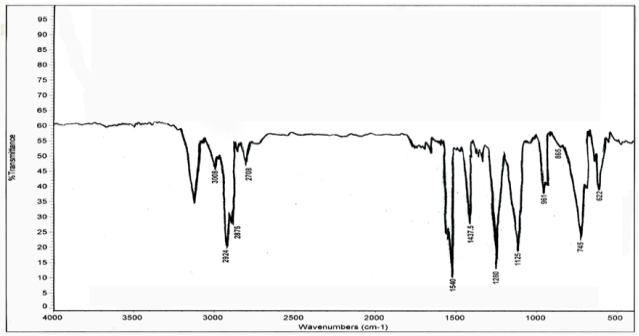



Fig.1.3. FTIR spectrum of Poly- N-methyl pyrrole

Thermal analysis: Thermogravimetric analysis measurements were carried out from room temperature to 800$^{O}$C at a heating rate of 10$^{O}$/ min under nitrogen atmosphere. Fig 2.1 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 2.1. Nanocomposite shows 7% weight loss at 125$^{O}$C, which is due to the elimination of water molecule and second weight loss of about 8% at 260$^{O}$C, which is attributed to removal of dopant. The polymer backbone degradation has been started above 400$^{O}$C and it is maximum for PNMPy and lowest for PNDMA and thus, shown good thermal stability among their homopolymers.

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

| Compounds | 1st weight loss | | 2nd weight loss | | 3rd weight loss | |
|---|---|---|---|---|---|---|
| PNMPy | 6 % | 120$^{o}$ C | 7.75 % | 280$^{o}$ C | 23.75 % | 608$^{o}$ C |
| PNDMA | 7 % | 135$^{o}$ C | 10% | 240$^{o}$ C | 55% | 462$^{o}$ C |
| Nanocomposite | 7 % | 125$^{o}$ C | 8% | 260$^{o}$ C | 45% | 469$^{o}$ C |

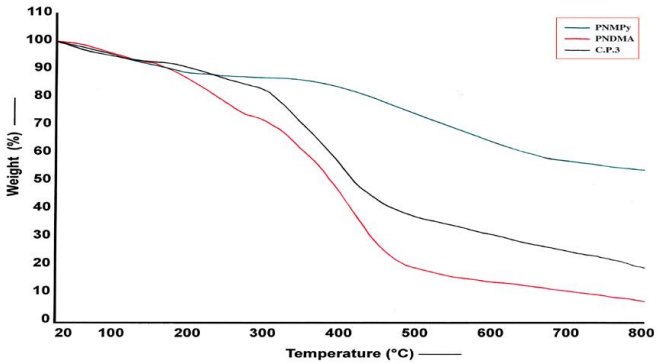



Fig.2.1. TGA curves of PNMPy, PNDMA and nanocomposite of copolymer of PNMPy and PNDMA

**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.

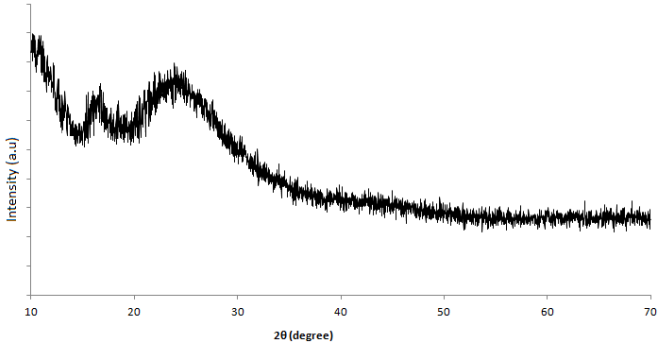



Fig.3.1. XRD spectrum of nanocomposite of copolymer of PNMPy and PNDMA.

**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 325nm size distributed over cylindrical fibers.

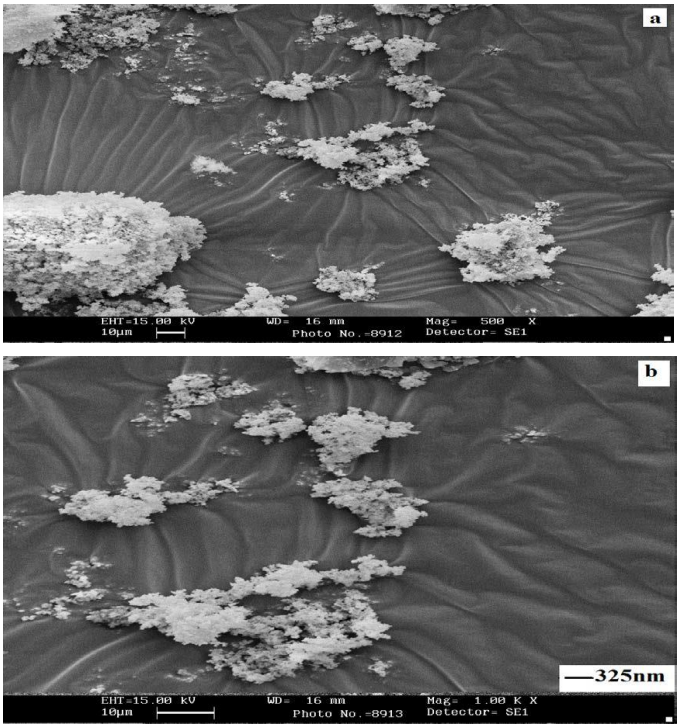



Fig4.1a and 1b.SEM images of nanocomposite of copolymer of PNMPy and PNDMA at 500X and 1000X.

**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 DMSO,

H2O2, CCl4, H2O was found to be insoluble, however the nanocomposite was sparingly soluble in NMP and gave a Dark Green Color.

## IV. CONCLUSION

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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**Cite this article as :**

R. Rathore, Soni Sharma, "Synthesis and Characterization of Nanocomposite of Copolymer of N-Methyl Pyrrole (NMPy) and N, N-Dimethyl Aniline (NDMA)", International Journal of Scientific Research in Science and Technology (IJSRST), Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 6 Issue 4, pp. 124-129, July-August 2019. Available at doi : https://doi.org/10.32628/IJSRST19643 Journal URL : http://ijsrst.com/IJSRST19643