

Characterization of copolymer nanocomposite of 3,4-dimethyl pyrrole and 4-methoxy-2-methyl aniline

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Nanocomposites copolymer of 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA) is synthesized using chemical oxidative polymerization doped with HCl and Ammonium persulfate (APS) used as an oxidant. Nanocomposite obtained is characterized for structural configurations by UV-Vis and FTIR spectrophotometer, TGA, XRD. Four probe method is adopted for the measurement of electrical conductivity. Spectral study confirms the π - π^ transition in nanocomposite copolymer. The formation of copolymer and its structure is confirmed by FTIR. The amorphous nature of polymer nanocomposite is established by the XRD. The electrical conductivity of sample was comparable to the intrinsic conductive polymers used. SEM micrographs are used to study the size and surface morphology of copolymer nanocomposite.*

Key words: Copolymer, nanocomposite, UV-VIS, XRD, SEM, FTIR.

1. INTRODUCTION

Organic polymers have electric conduction in the range from high metallic conductivity to semiconductive, thus, referred to as intrinsically conductive polymers (ICP) [1]. ICPs are highly advantageous in terms of their processability, especially in dispersions [2]. Conducting polymer nanocomposites of polyaniline have gathered special attention due to the excellent redox recyclability [3] and their derivatives are deliberated to be one of the most promising classes of organic conducting polymers [4] owning good environmental stability [5], ease of doping [6]. Polypyrrole, because of good environmental stability and ease of synthesis is another important and most studied conducting polymer [7,8]. It's an integral biocompatible polymer [9]. Due to their exceptional properties, they are likely to be used in various applications such as biosensors [10,11], gas sensors [12], anti-electrostatic coating [13], solid electrolytic capacitors [14,15], light weight batteries and anticorrosive devices [16] etc. Inorganic nanoparticles of different nature and size can be combined with the conducting polymers, giving rise to a host of nanocomposites with interesting physical properties and important application potential [17]. Nanocomposite copolymer 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA) exhibits fair thermal stability [18].

The present study reports the synthesis of nanocomposite of copolymer of 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA) by chemical oxidative

polymerization. Synthesized nanocomposite is evaluated for various physical properties like optical, thermal stability, surface morphology, electrical conductivity, crystallinity and solubility. Results obtain are compared and discussed based on previous literature.

2. MATERIALS AND METHODS

Analytical grade chemical 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA) was obtained from Acros Organics, USA while ammonium persulphate (APS) and hydrochloric acid (HCl) were obtained from Qualigens, India. All the solutions were prepared in double distilled water. Among various prominent polymerization techniques, chemical oxidative method [19-21] is the most versatile and easy route-to-synthesize, even in scale up arrangement for obtaining the conducting polymers, hence been adopted to synthesize the nanocomposite of the copolymer of 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA). Chemical oxidative polymerization [22] 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 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA)

0.6430g (0.004687 moles) of 4-methoxy-2-methyl aniline and 0.446g (0.004687 moles) of 3, 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 0.009375 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 melting ice temperature (4°C). Further agitation was applied for 36 hours after dropping process and left as such for 6 days till brown coloured compound was obtained.

2.2 Characterization

Absorption spectra is obtained using UV-Vis (Shimadzu 1900) double beam spectrometer to characterize the structures of intrinsically conducting polymers (ICPs) and to determine the conjugation in polymer backbone. The 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 UV-VIS Spectrum

UV-VIS absorption spectral analysis of the synthesized copolymer nanocomposite of 3,4-dimethyl pyrrole and 4-methoxy-2-methyl aniline is shown in Fig. 1. Absorption peaks are observed at around 313 nm and 607 nm. First peak around 313 nm is due to the $\pi-\pi^*$

transition (band gap) and is directly related to the extent of conjugation. The other peak near 607 nm is due to molecular exciton associated with the quinone-diamine structure [23] i.e. transition between HOMO orbital of benzenoid rings and LUMO of the quinoid rings. UV-VIS spectra of aniline and pyrrole cannot be obtained as a linear combination of the spectra of the constituent homopolymer [24]. The copolymer exhibits roughly uniform absorption throughout the whole visible region. While both polyaniline and polypyrrole show a pronounced absorption above 800 nm corresponding to the presence of localized polaron responsible for the electrical conduction, the absorption of a copolymer in the region is reduced. This is in accordance with the low conductivity observed for copolymer prepared at equimolar proportion of comonomer.

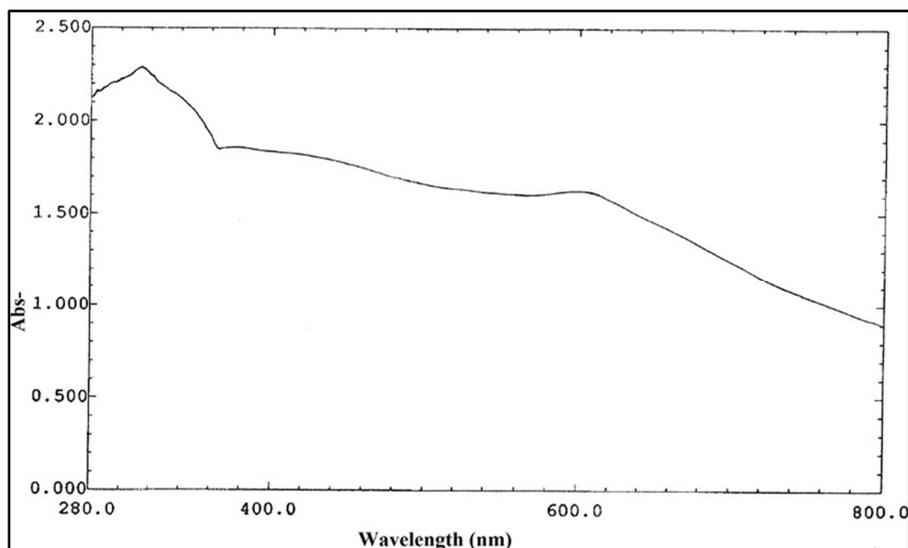


Fig. 1: UV-Vis absorption spectra of copolymer nanocomposite of 3,4-dimethyl pyrrole and 4-methoxy-2-methyl aniline (MMA).

3.2. FTIR Spectrum

The FTIR spectra of doped form of 3,4-dimethyl pyrrole (DMPy), 4-methoxy-2-methyl aniline (MMA) and nanocomposite of the two materials, in the range 400-4000 cm^{-1} is shown in Fig. 2, Fig. 3 and Fig. 4. respectively. The main characteristic bands observed in the IR region have been recorded in Table 1. The spectrum for MMA shows peaks at 1596 cm^{-1} and 1500 cm^{-1} which are due to the stretching vibrations of quinoid and benzenoid structure respectively [25-27]. These peaks also appear in the spectrum of nanocomposite at 1458 cm^{-1} and 1510 cm^{-1} . C- N stretching vibration occurs at 1275 cm^{-1} , 1350 cm^{-1} and 1378 cm^{-1} in DMPy, MMA and nanocomposite respectively. All characteristic peaks of DMPy and MMA also exist in the spectrum of nanocomposite confirming the presence of aniline and pyrrole unit in it. The spectrum of nanocomposite reveals all characteristic peaks of homopolymers. It correlates to be observed for nanocomposite copolymer of N-

methyl Pyrrole and 2,5-Dimethoxy Aniline composite [28]. It is observed that the peaks shifted towards lower wave number and it confirms the presence of copolymer unit in composite material.

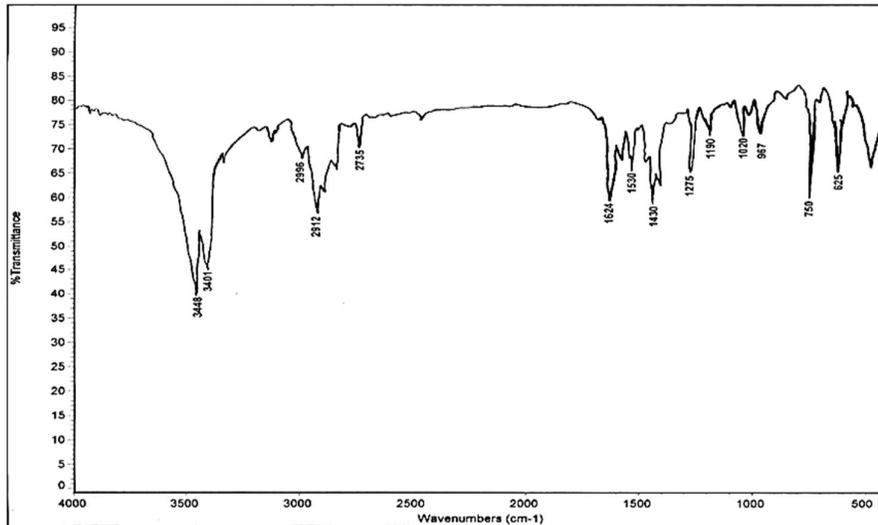


Fig. 2: FTIR of homopolymer of 3,4-dimethyl pyrrole (DMPy).

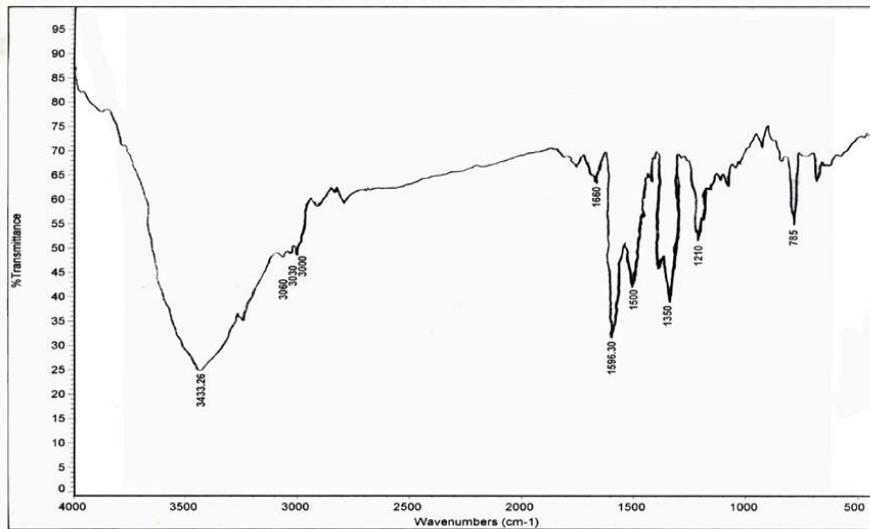


Fig. 3: FTIR of homopolymer of 4-methoxy-2-methyl aniline (MMA).

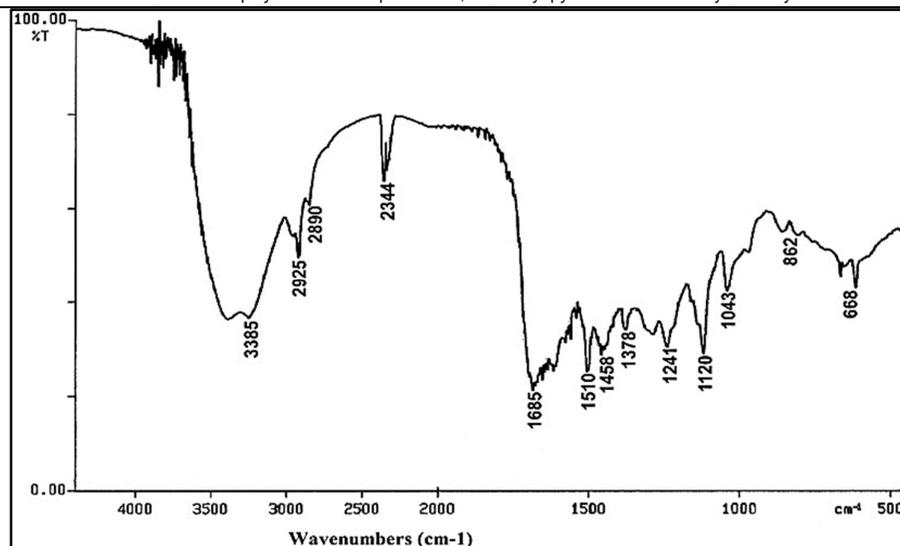


Fig. 4: FTIR of copolymer of 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA).

Table 1: FTIR data of homopolymers and copolymer nanocomposite of 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA) (All units cm^{-1}).

	N – H stretch	- CH ₃ stretch	C – N stretch	C – H in plane	C – H out of plane
DMPy homopolymer	3448	2996, 2916	1275	1020	750
MMA homopolymer	3433	3060, 3030, 3000	1350	1096	785
Copolymer nanocomposite	3385	2925, 2890	1241	1043	862

3.3. Thermal Analysis

Thermogravimetric analysis measurements were carried out from room temperature to 800° C at a heating rate of 10° per minute under nitrogenous atmosphere. The comparative TGA curves of homopolymers of ICP and the copolymer nanocomposite (CP - 9) of 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA) is shown in Fig.5. Thermogram of nanocomposite shows three distinct regions of weight loss. All results are tabulated in Table 2.

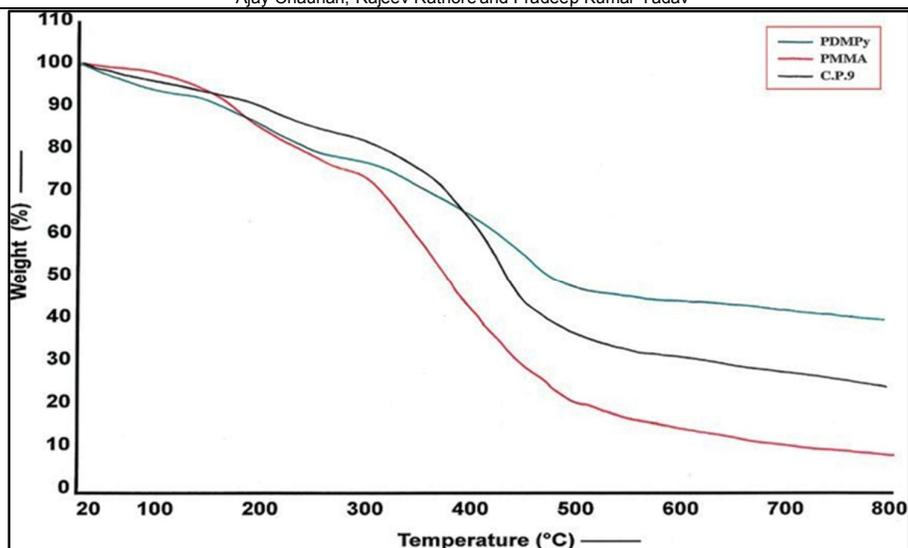


Fig. 5: TGA curves of DMPy, MMA and nanocomposite of copolymer of DMPy and MMA.

The TGA curves shows loss of moisture in the first step of decomposition after 100° C. Second weight loss occurs at around 250° C due the removal of dopant. The highest percentage weight loss is observed at decomposition temperature between 250° C to 600° C.

From this table and figure, it can be inferred that nanocomposite has shown good thermal stability. It shows three stages of decomposition. Initial step decomposition occurs near 150°C, due to evaporation of water molecule. Decomposition took place at 263°C due to dopant removal and final decomposition is due to polymer backbone decomposition. TGA curve of nanocomposite shows 41% weight loss at 487°C. Thus, synthesized copolymer nanocomposite exhibits significant thermal stability from normal room temperature to 250°C.

Table 2.1: TGA weight loss in DMPy, MMA and nanocomposite of copolymer of DMPy and MMA.

	1 st weight loss		2 nd weight loss		3 rd weight loss	
DMPy	7.5%	113°C	14%	255°C	30.5%	482°C
MMA	3%	112°C	17%	237.5°C	59%	498°C
Nanocomposite	11%	150°C	10%	263°C	41%	487°C

3.4. X-Ray Diffraction

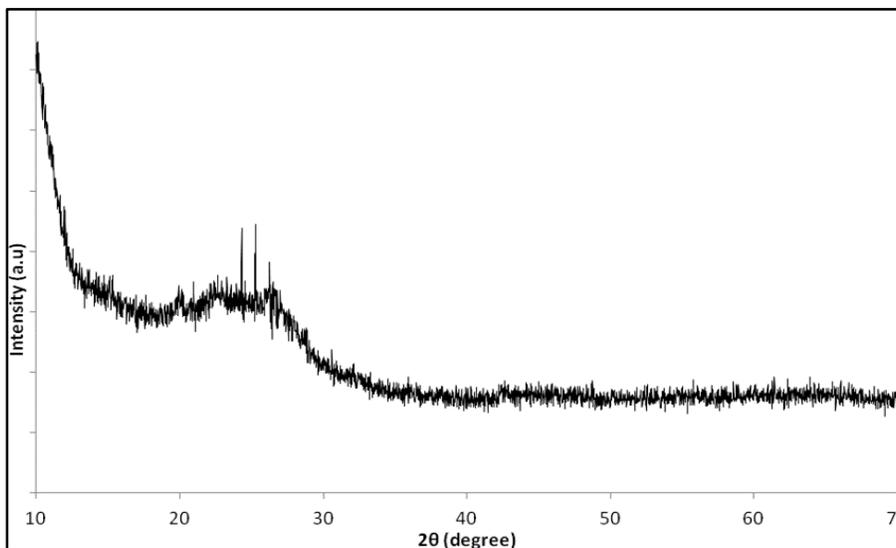


Fig. 6: XRD spectrum of nanocomposite of copolymer of DMPy and MMA.

XRD pattern shown in Fig.6 for the nanocomposite exhibits broad peak at $2\theta = 20^\circ$ to 30° and these peaks are indicative of an amorphous behavior. The broad peak is characteristic of amorphous polypyrrole at $2\theta = 24^\circ$ [24] and it is due to the scattering from PPy chains at the interplanar spacing [25]. The copolymer of poly-2, 5-dimethoxy aniline and polypyrrole has shown broad characteristic peaks for their amorphous nature [26,27]. Thus, on the basis 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 in the range of 20° to 30° is due to their amorphous nature.

3.5. Surface Morphology

Surface morphology of the nanocomposite was studied by scanning electron microscopy (SEM). Fig. 7a and 7b shows the SEM micrographs at 500X and 1000X magnifications. The micrograph shows a mixed morphology of small flakey particles and network of large fibers. At 1000X (9b), micrograph shows that small flakey particles (thickness 280nm) are randomly distributed over the network of long fibers. It shows some side branches, may be due to presence of many alkyl groups [29] present in copolymer of DMPy and MMA.

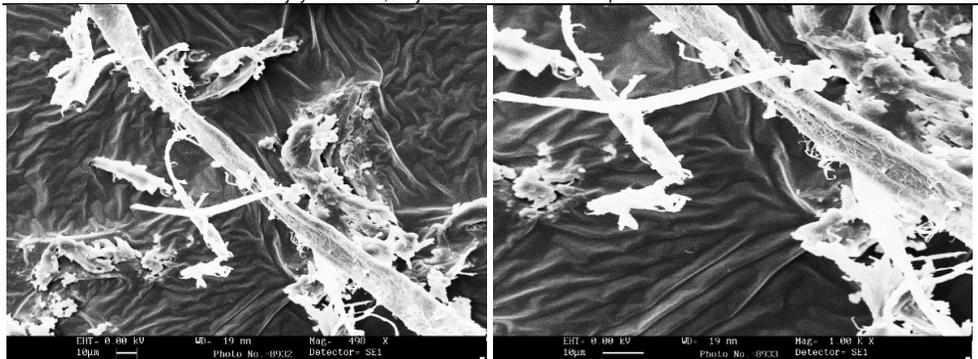


Fig. 7: SEM images of nanocomposite copolymer of DMPy and MMA at (a) 500X and (b) 1000X magnification.

3.6. Electrical Conductivity Measurement

Electrical conductivity of prepared nanocomposite was measured by Four Probe method using cross bridge arrangements [30]. It is observed that the conductivity decreases from 10^{-2} to 10^{-5} when aniline was polymerized with pyrrole. The conductivity of prepared DMPy and MMA nanocomposite was 5.2×10^{-5} s/cm. The lowering of conductivity for copolymer than Polyaniline is expected to arise from the steric effect of the bulky substituent ($-\text{OCH}_3$, $-\text{C}_2\text{H}_5$ etc.) may provide torsional twist in the polymer backbone, reducing the coplanarity and average electron delocalization length. Such type of observation has been noted for substituted polyaniline and copolymers of aniline with substituted aniline. The results indicate that when polymerizing aniline with pyrrole. The conductivity decreases for polyaniline and improve for polypyrrole. This means copolymerization can increase the conductivity of polypyrrole. This is evidence that the copolymer formed is not just the combination of polypyrrole and polyaniline but completely new material with new properties.

The presence of longer alkyl chain would reduce the conjugation length in copolymer backbone which in turn lower the concentration of charge carrier/conductivity.

3.7. Solubility Test

The dark brown nanocomposite of DMPy and MMA copolymer of substituted aniline and pyrrole was tested for solubility in preferred solvents for ICPs such as DMSO, NMP, H_2O_2 , CCl_4 , and H_2O . Solubility for the synthesized nanocomposite was found to be insoluble in H_2O_2 , CCl_4 , and H_2O solvents except for DMSO and NMP which showed sparingly solubility forming a dark brown-green coloured solution similar to earlier reported nanocomposite copolymer [31,32]

4. CONCLUSIONS

The nanocomposite of copolymer of 3,4-dimethyl pyrrole (DMPy) and 4-methoxy-2-methyl aniline (MMA) was successfully synthesized via chemical oxidative polymerization using APS as dopant. The nanocomposite of copolymer had a fibrous structure. Prepared nanocomposite has shown good thermal stability, electrical conductivity, and was almost insoluble in common solvent except for specific DMSO and NMP.

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