

# Study of Chemically Synthesized Nanocomposite Copolymer of 3,4-dimethyl Pyrrole and 2-ethyl Aniline

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*Chemically synthesized Copolymer nanocomposite of 3,4-dimethyl pyrrole (DMPy) and 2-ethyl aniline (EA) using chemical oxidative polymerization doped with HCl and Ammonium persulfate (APS) used as an oxidant was characterized for structural configurations by UV-Vis, FTIR, TGA and XRD. Four probe method was adopted for the measurement of electrical conductivity. Spectroscopy confirms the  $\pi$ - $\pi^*$  transition in nanocomposite copolymer. FTIR confirms the formation of copolymer and its structure. XRD analysis shows the amorphous nature of polymer nanocomposite. The electrical conductivity of sample was comparable to the intrinsic conductive polymers used. Size and surface morphology was demonstrated by SEM.*

**Key words:** Nanocomposite, Copolymer, XRD, TGA, SEM, Four probe method.

## 1. INTRODUCTION

Organic polymers capable of electric conduction having high metallic conductivity to semiconductor, 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 class 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 2-ethyl aniline (EA) exhibits fair thermal stability [18].

The present study reports the synthesis of nanocomposite of copolymer of 3,4-dimethyl pyrrole (DMPy) and 2-ethyl aniline (EA) 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 reported findings.

## 2. MATERIALS AND METHODS

Analytical grade chemical 3,4-dimethyl pyrrole (DMPy) and 2-ethyl aniline (EA) 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 2-ethyl aniline (EA). 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 2-ethyl aniline (EA)

0.892g (0.009375 moles) of 3, 4-dimethyl pyrrole and 1.136g (0.009375 moles) of 2-ethyl aniline were mixed with 1M 100 ml HCl with continuous stirring for 30 minutes in a reactor. The APS solution was prepared using 4.27g (0.01875 moles) in 50ml of 1M HCl. Then APS solution was dropped-mixed by continuous stirring for 30 minutes into a reactor with aniline and pyrrole, kept in melting ice bath at 0°C. Further agitation was applied for 12 hours to the obtained solution after dropping process for thorough and complete reaction till brown precipitates of copolymer was obtained.

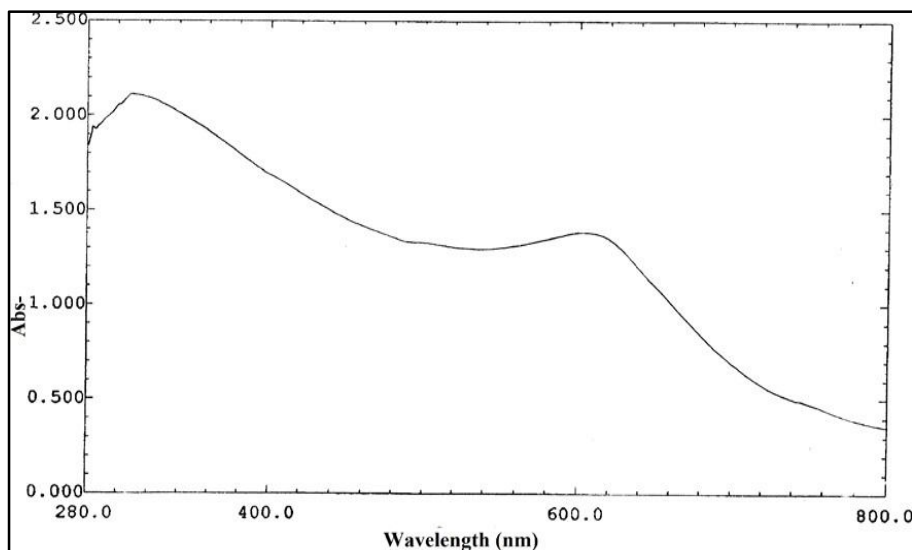
### 2.2. Characterization

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 2-ethyl aniline is shown in Figure 1. Absorption peaks are observed at around 302 nm and 605 nm. First peak around 302 nm is due to the  $\pi-\pi^*$  transition (band gap) and is directly related to the extent of conjugation. The other peak near 605 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.



**Fig. 1:** UV-Vis absorption spectra of copolymer nanocomposite of 3,4-dimethyl pyrrole and 2-ethyl aniline.

### 3.2. FTIR Spectrum

The FTIR spectra of doped form of 3,4-dimethyl pyrrole and 2-ethyl aniline and nanocomposite material respectively in the range  $400\text{--}4000\text{ cm}^{-1}$  is shown in Figure 2, Figure 3 and Figure 4 respectively. The main characteristic bands observed in IR region have been recorded in Table 1. The spectrum for EA shows peaks at  $1590\text{ cm}^{-1}$  and  $1430\text{ cm}^{-1}$  which are due to the stretching vibrations of quinoid and benzenoid structure respectively [24-26]. These peaks also appear in the spectrum of nanocomposite at  $1618\text{ cm}^{-1}$  and  $1560\text{ cm}^{-1}$ . C- N stretching vibration occurs at  $1273\text{ cm}^{-1}$ ,  $1251\text{ cm}^{-1}$  and  $1306\text{ cm}^{-1}$  in DMPy, EA and nanocomposite respectively. All characteristics peaks of DMPy and EA 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 is observed that the peaks shifted towards lower wave number and it confirms the presence of copolymer unit in composite material.

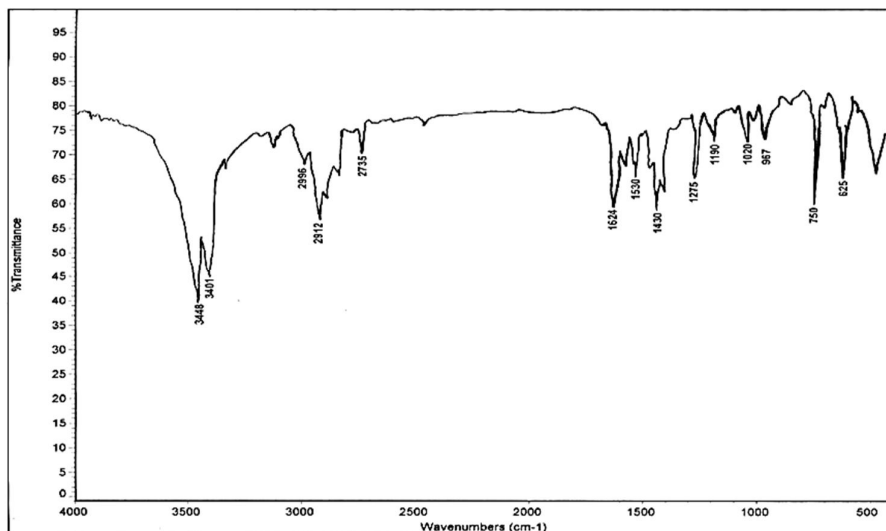


Fig. 2: FTIR of homopolymer of 3,4-dimethyl pyrrole (DMPy).

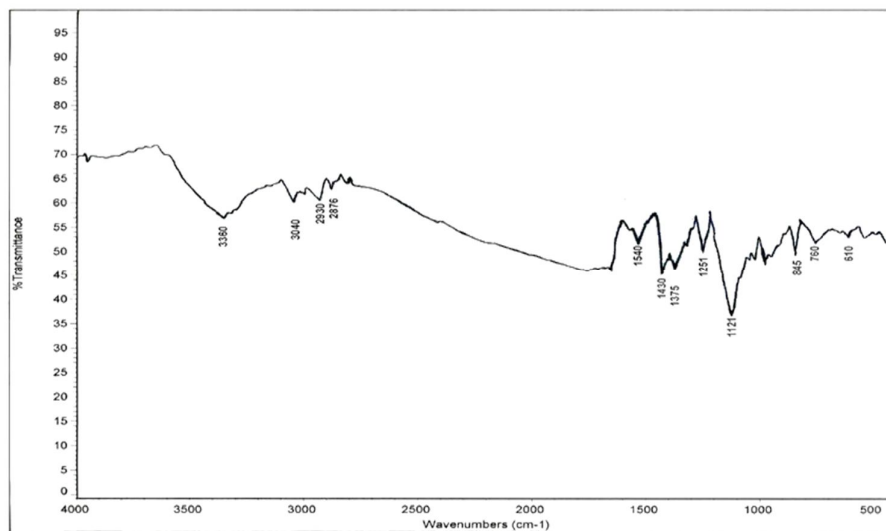
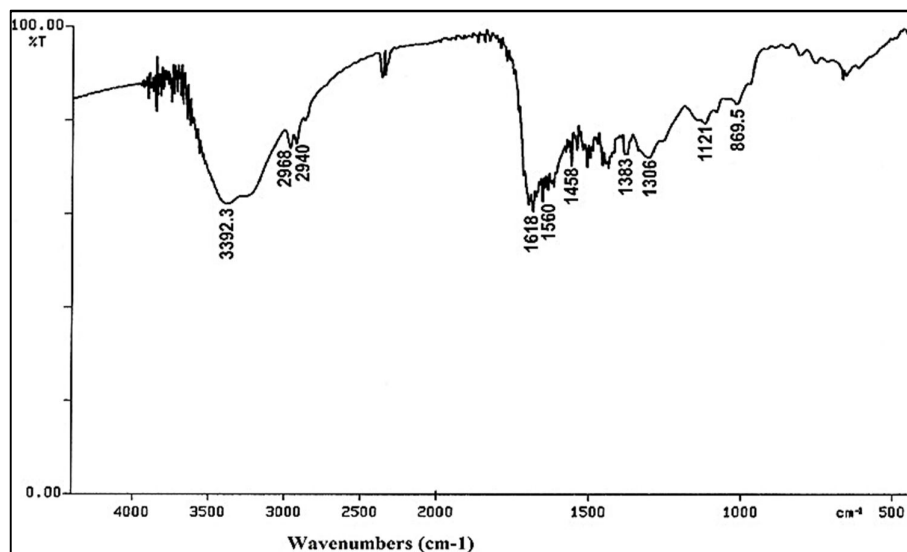


Fig. 3: FTIR of homopolymer of 2-ethyl aniline (EA).



**Fig. 4:** FTIR of copolymer of 3,4-dimethyl pyrrole (DMPy) and 2-ethyl aniline (EA).

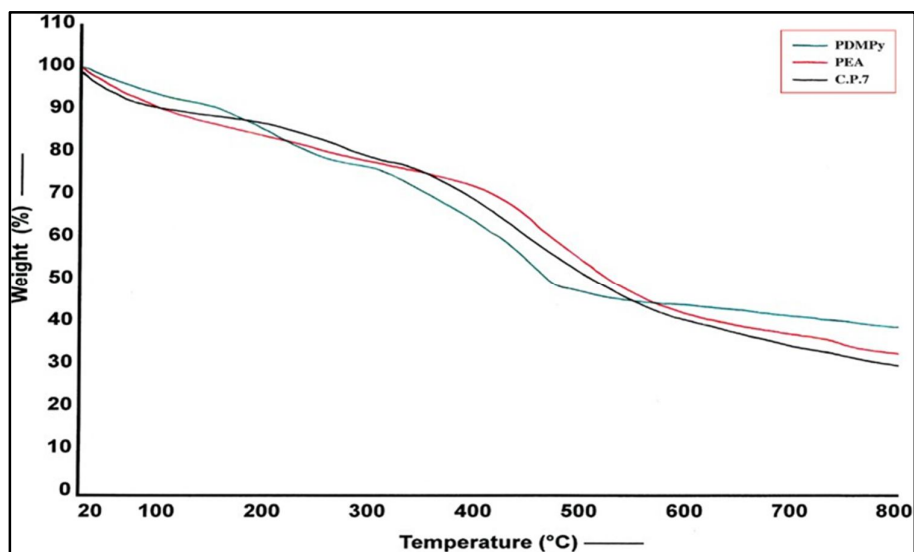
**Table 1:** FTIR data of homopolymers and copolymer nanocomposite of 3,4-dimethyl pyrrole (DMPy) and 2-ethyl aniline (EA)

	<b>N – H stretch</b>	<b>- CH<sub>3</sub> stretch</b>	<b>C – N stretch</b>	<b>C – H in plane</b>	<b>C – H out of plane</b>
<b>DMPy homopolymer</b>	3448	2996, 2912	1273	1020	750
<b>EA homopolymer</b>	3380	3040, 2930, 2816	1251	1121	760
<b>Copolymer nanocomposite</b>	3392.3	2968, 2940	1306	1121	869

### 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 nitrogen atmosphere. The comparative TGA curves of homopolymers of ICP and the copolymer nanocomposite (CP - 4) of 3,4-dimethyl pyrrole (DMPy) and ethyl aniline (EA) is shown in Figure 5. Thermogram of

nanocomposite shows three distinct regions of weight loss. All results were tabulated in Table 2.



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

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

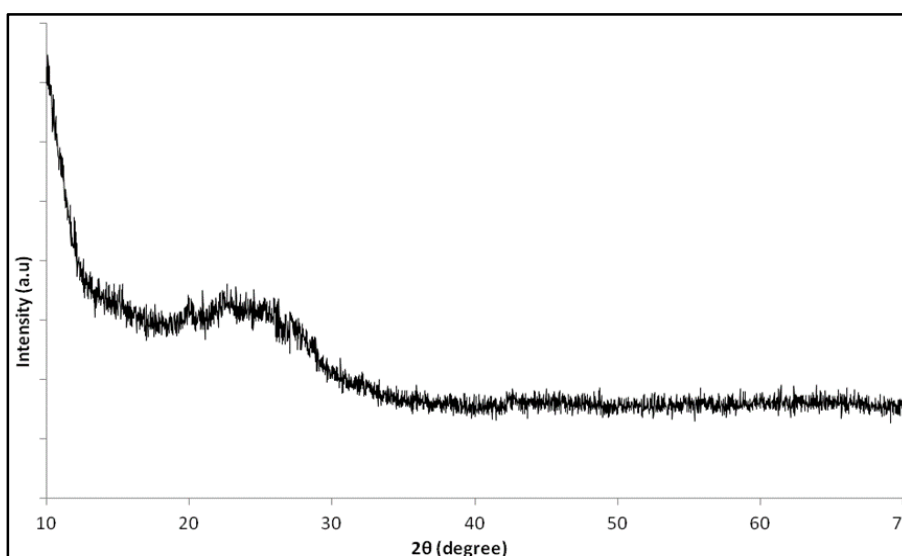
From this table, it can be inferred that nanocomposite has shown good thermal stability. It shows three stages of decomposition. Initial step decomposition occurs at 150°C, due to evaporation of water molecule. Decomposition took place at 276°C due to dopant removal and final decomposition is due to polymer backbone decomposition. TGA curve of nanocomposite shows 35.75% weight loss at 580°C. Thus, synthesized copolymer nanocomposite exhibits significant thermal stability at normal room temperature to 250°C.

**Table 2:** TGA weight loss in DMPy, EA and nanocomposite of copolymer of DMPy and EA.

	1 <sup>st</sup> weight loss		2 <sup>nd</sup> weight loss		3 <sup>rd</sup> weight loss	
<b>DMPy</b>	7.5%	113°C	14%	255°C	30.5%	482°C
<b>EA</b>	10.3%	110°C	6.7%	230°C	33.5%	519°C
<b>Nanocomposite</b>	11.25%	150°C	7.5%	276°C	35.75%	580°C

### 3.4. X-Ray Diffraction

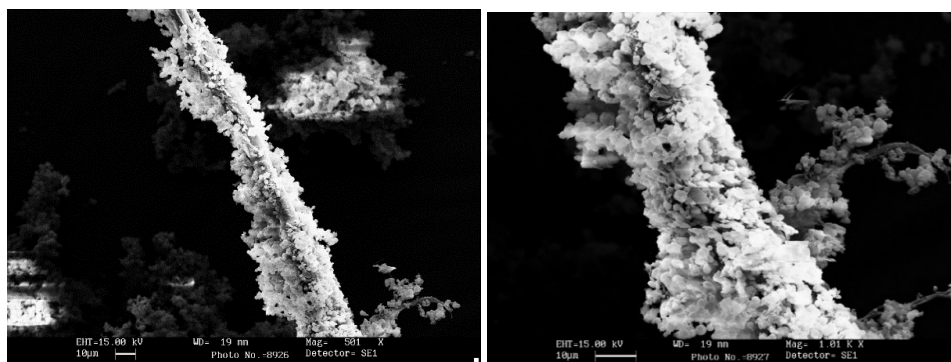
XRD pattern shown in Figure 6 for the nanocomposite exhibits broad peak at  $2\theta = 20^\circ$  to  $30^\circ$  and these peaks are indicative of an amorphous behavior. The broad peak is characteristic of amorphous polypyrrole at  $2\theta = 24^\circ$  [24] and it is due to the scattering from PPy 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 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 in the range of  $20^\circ$  to  $30^\circ$  is due to their amorphous nature.



**Fig. 6:** XRD spectrum of nanocomposite of copolymer of DMPy and EA.

### 3.5. Surface Morphology

Surface morphology of the nanocomposite was studied by scanning electron microscopy (SEM). Figure 7a and 7b 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 indicates formation of granular particles of 325nm size distributed over cylindrical fibers for the nanocomposite copolymer of DMPy and EA.



**Fig. 7:** SEM images of nanocomposite copolymer of DMPy and EA 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 [28]. 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 EA nanocomposite was  $2.9 \times 10^{-5}$  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. Though the conductivity of polymerized polyaniline is lower than the polymerized polypyrrole but the composite of copolymerized polyaniline and polypyrrole have enhanced conductivity. Thus, indicating that the copolymer formed is not just the physical combination of polypyrrole and polyaniline but a completely new material with altered 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 EA copolymer of substituted aniline and pyrrole was tested for solubility in preferred solvents for ICPs such as DMSO, NMP,  $\text{H}_2\text{O}_2$ ,  $\text{CCl}_4$ , and  $\text{H}_2\text{O}$ . Solubility for the synthesized nanocomposite was found to be insoluble in  $\text{H}_2\text{O}_2$ ,  $\text{CCl}_4$ , and  $\text{H}_2\text{O}$  solvents except for DMSO and NMP which showed sparingly solubility forming a dark brown-green coloured solution similar to DMPy and DMSO nanocomposite copolymer [29,30].



#### 4. CONCLUSIONS

The nanocomposite of copolymer of 3,4-dimethyl pyrrole (DMPy) and 2-ethyl aniline (EA) 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 DMSO and NMP.

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