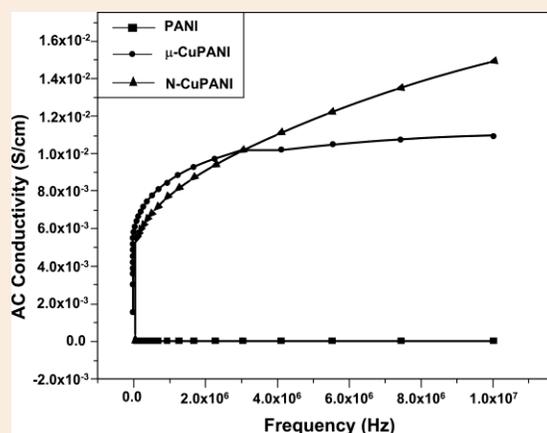


Research Article

Studies on Structural and Electrical conducting properties of Micro and Nano Copper Doped Polyaniline

C. Shanmugapriya*¹ and G. Velraj²¹Department of Science (Physics), Sona College of Technology, Salem-636005, Tamilnadu, India²Department of Physics, Periyar University, Salem-636011, Tamilnadu, India**Abstract**

Polyaniline (PANI) based metal composites are a special class of hybrid materials which combine the property of soft conducting polymer and hard inorganic materials to develop complementary behaviors such as high performance of electrical conductivity. This study is based on the system consisting of conducting polymer PANI doped with micro and nano copper particles which were prepared by the chemical oxidation polymerization method separately. The structural and electrical conducting properties of PANI, micro copper doped polyaniline (μ -CuPANI) and nano copper doped polyaniline (n-CuPANI) have been investigated by FT-IR, X-Ray diffraction (XRD) and conductivity measurements. The surface morphology of the samples was investigated by SEM. The conductivities of PANI and its composites after doping have been compared. The results revealed that nanocomposite (1.49×10^{-2} S/cm) and microcomposite (1.09×10^{-2} S/cm) have an increased electrical conductivity than PANI (5.03×10^{-5} S/cm) at room temperature.

***Correspondence**C. Shanmugapriya,
Email: cspriyais@gmail.com**Keywords:** FT-IR, XRD, Micro composite, Nano composite, Polyaniline, Conductivity**Introduction**

In recent years the conducting polymer PANI has been extensively studied due to ease synthesis, good environmental stability, high conductivity in doped state, special electronic, optical, magnetic and mechanical properties. So PANI is a promising material for various techno-commercial applications such as solar cells, sensors and organic electrodes [1-3]. PANI can be synthesized by chemical oxidative polymerization [4,5] and electrochemical polymerization [6,7]. Chemical oxidative polymerization method for preparing PANI has been used since it allows mass production in a short duration. Various physical and chemical properties can be enhanced by making blends or composite with metal particles [8,9]. Thus the combination of organic-inorganic hybrid materials possesses the properties of both the constituents.

This new kind of composite materials with synergistic performance can be utilized in various fields such as rechargeable batteries, nanoelectronic devices and biological sensors [10-13] etc. They can be synthesized either by electrochemical or by chemical oxidation polymerization. The possibility of synthesizing and making a composite of conducting polymer with metal particles provides a versatile class of polymers. This metal particle which is an additive increases the electrical conductivity of conducting polymer [14,15]. In the present work we report the synthesis of PANI, μ -CuPANI and n-CuPANI by chemical oxidation polymerization method separately. We present

the structural and electrical properties of pure PANI, micro and nanocomposite. The structural properties were analyzed by FT-IR and XRD. The conductivity measurements were studied using two probe methods.

Experimental

Materials

Aniline (C_6H_7N) monomer, sulphuric acid (H_2SO_4), potassium dichromate ($K_2Cr_2O_7$), micro copper particles (sigma Aldrich, 99%) and nano copper particles (nanoshell LLC, USA) were obtained and used as received.

Synthesis of Polyaniline

PANI was prepared by the chemical oxidation polymerization method. $K_2Cr_2O_7$ is used as an oxidant. H_2SO_4 is used as a dopant. 1M of H_2SO_4 was added drop wise into 1M of the aniline monomer solution. This reaction mixture was placed on a magnetic stirrer for 1hour at constant RPM value. The solution of 0.5M of $K_2Cr_2O_7$ was added drop wise into the mixture. This reaction mixture was stirred continuously at constant RPM value for 24 hours under ice cold temperature. The precipitate was separated out by filtering. The final suspension was dried in oven at $100^\circ C$ for 90 minutes. The final product was grounded into a fine powder.

Synthesis of Micro/Nano Composite

100 mg of PANI powder was mixed with 100 ml of distilled water. 100 mg of micro/nano copper particles was added to this mixture and stirred for 12 hours continuously. Then the precipitate was separated out by filtering. The final product was dried in oven at $100^\circ C$ for 60 minutes.

Instrument

FT-IR spectrum was recorded on a bruker optic GmbH Tensor 27/ FT-IR spectrometer in the range of $4000cm^{-1}$ - $400cm^{-1}$ using KBr pellet method. XRD was carried out by a diffractometer, using Cu-K α radiations ($\lambda = 1.54064 \text{ \AA}$) operated at 40 KV and 30 mA. The conductivity measurements were performed by a typical two probe method with PSM 1735 Frequency response analyzer employing the pressed pellet method over the frequency range from 1KHz to 10MHz at room temperature.

Results and Discussion

FT-IR Spectroscopy

The FT-IR spectra of undoped PANI and their composites μ -CuPANI and n-CuPANI were recorded and shown in the figure 1a,b&c. The figure 1a reveals all the characteristics peak of PANI i.e., the band at $1565cm^{-1}$ and $1480cm^{-1}$ are attributed to C=N quinonoid stretching mode of vibration and C=C benzenoid stretching mode of vibration. The peak at $1300cm^{-1}$ is due to the C-N stretching mode of the polymer. The band at $1117cm^{-1}$ is attributed to C-H in plane bending. The peak at $876cm^{-1}$ is due to C-H out of plane bending. The peak observed at $803cm^{-1}$ is due to the N-H out of plane bending absorption.

The peaks observed in the present work matches well with the literature [16, 17] confirming the formation of PANI. The similar intensity pattern was also observed in micro and nanocomposites which are shown in figure 1b&c except with some slight differences. These spectral differences between pure PANI and micro and nanocomposites are due to the strong physio chemical interactions between the micro and nano copper particles with PANI.

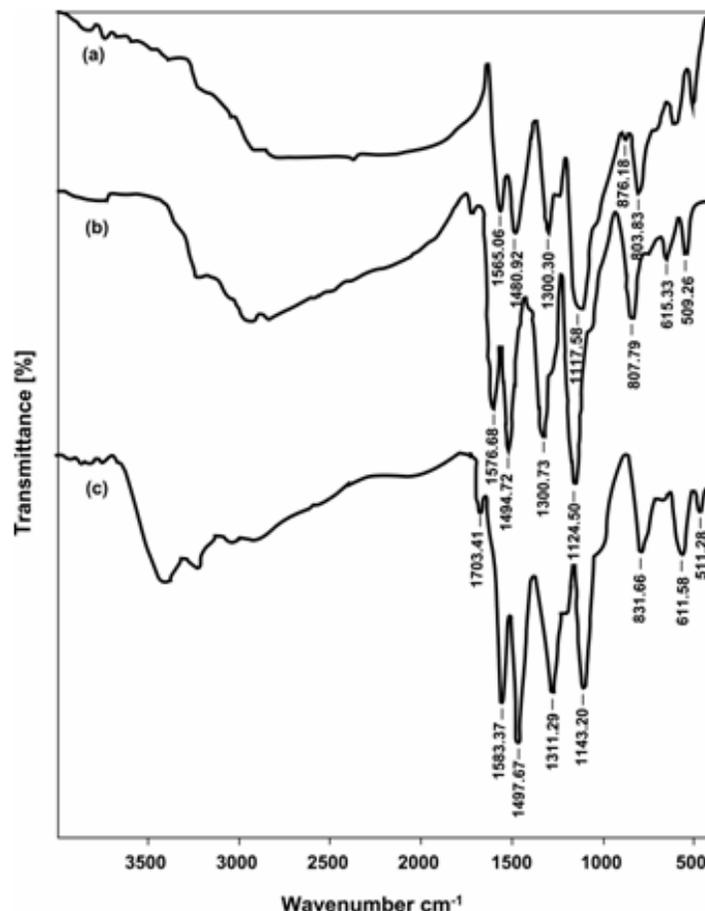


Figure 1 FT-IR spectra of (a) PANI (b) μ -Cu PANI (c) n-Cu PANI

XRD Measurements

XRD studies showed that PANI is amorphous in nature as shown in the **figure 2a**. The broad diffraction peak at $2\theta = 25.27^\circ$ is characteristic peak for PANI [18]. XRD patterns of micro and nanocomposite were shown in the figure 2b&c.

After doping the samples showed crystalline nature which was confirmed by the peaks at about $2\theta = 43.47^\circ$ and 50.43° for μ -CuPANI and $2\theta = 43.40^\circ$ and 50.49° and for n-CuPANI. These peaks were matched with JCPDS data of Copper file no. 04-0836. The variation in the diffraction intensity between the pure and its composite samples indicates that there is an existence and interaction Cu particles with PANI network. The average crystalline sizes have been estimated using the Scherrer's formula [19]

$$D = K\lambda/\beta\cos\theta \quad (1)$$

Where, D is the crystalline size, K is the shape factor which can be assigned a value of 0.89, if the shape is unknown, and β is the full width at half maximum of the diffraction angle in radians.

When applied to the sharp peak equation (1) leads to the average crystallite sizes of about 98 nm, 30 nm and 23 nm for PANI, μ -CuPANI and n- CuPANI respectively.

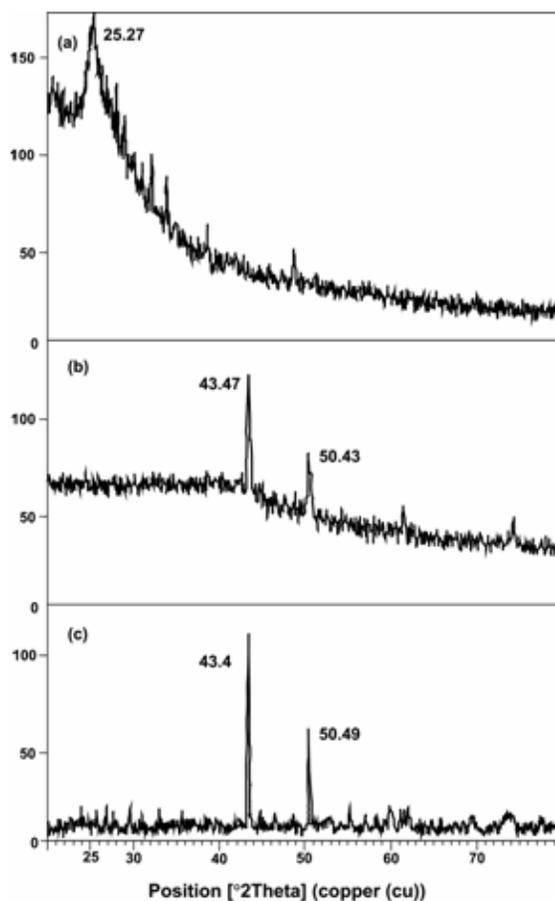


Figure 2 XRD pattern for (a) PANI (b) μ -Cu PANI (c) n-Cu PANI

Electrical conductivity Measurements

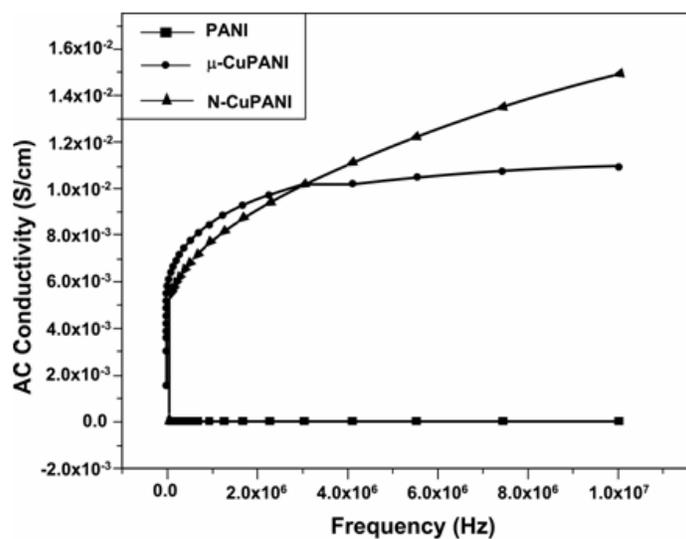


Figure 3 A.C conductivity Vs frequency

Conductivity measurements have been performed by a typical two probe technique using PSM 1735 Frequency Response Analyser. The frequency dependent electrical conductivities of pure PANI, μ -CuPANI and n- CuPANI are given in **Figure 3(a, b& c)**.

Conducting sample of pure PANI, μ -CuPANI and n- CuPANI was formed as pellet by pressing the powder in a pelletizer. Now disc shaped specimens of 13 mm in diameter and about 93 mm thickness was formed for these samples. These samples were placed in between the probes in a sample holder and the resistance is measured varying the frequency from 1KHz to 10 MHz at room temperature. The A.C conductivities of pure PANI, μ -CuPANI and n-CuPANI was calculated using the formula, [20]

$$\sigma_{A.C} = \epsilon_0 \epsilon_r \omega \tan \delta \quad (2)$$

Where, ϵ_0 is the permittivity of free space, ϵ_r is the dielectric constant and $\omega = 2\pi f$, where f is the frequency and $\tan \delta$ is the dielectric loss.

The room temperature A.C electrical conductivities of PANI, μ -CuPANI and n- CuPANI were 5.03×10^{-5} S/cm, 1.09×10^{-2} S/cm and 1.49×10^{-2} S/cm. When we compare the A.C conductivities of n-CuPANI and μ -CuPANI with pure PANI, the conductivity have been increased by three orders. The result shows that micro and nanocomposite posses better electrical conductivity than PANI. This enhanced conductivity of n-CuPANI and μ -CuPANI is due to the incorporation of metal particles into the polymer matrix which favors electronic transport and due to the crystallinity in the composites as observed from XRD results.

Conclusions

In this communication PANI, μ -CuPANI and n-CuPANI were successfully synthesized by chemical oxidation polymerization process. The structure of PANI and its composites have been confirmed by FT-IR and showed that there exist a strong interaction between PANI and micro/nano copper. The XRD pattern of PANI show amorphous nature and its composites show the presence of copper particle and exhibits crystalline nature. A.C conductivity results indicate a significant increase in electrical conductivity in the micro and nanocomposites compared to pure PANI. This may be due to the influence of copper particles on the PANI and it acts as inter crystallite networks and facilitate the conduction path for the flow of current.

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