

Structural and Dielectric Properties of PPy/ZnO Composites

Tanveer Fatima, T. Sankarappa*, J.S.Ashwajeet and R.Ramanna

Department of Physics, Gulbarga University, Gulbarga, Karnataka – 585106, India

ABSTRACT

Polypyrrole-ZnO composites have been synthesized by chemical oxidation method using an anhydrous ferric chloride (FeCl_3) as an oxidizing agent for different weight percentages of ZnO. The surface morphology has been studied by scanning electron micrograph (SEM) and structure by X-ray diffraction technique. The SEM images of composites showed agglomeration of particles. The XRD pattern of the composites revealed the composites to be largely noncrystalline. The dielectric properties were measured at room temperature for the frequency range from 100Hz to 1MHz. Dielectric constant and loss decreased with increase in frequency. AC conductivity increased with frequency and ZnO concentration. Conductivity contains both frequency dependent and independent contributions, Conduction in these composites can be attributed to free as well as trapped charges.

Keywords: Conducting polymer; Polypyrrole; Zinc Oxide; Dielectric constant.

1. INTRODUCTION

Polymers were generally considered to be electrically non-conducting. However, conjugated polymers, which contain double bonds shows semiconducting nature. Among them, Polypyrrole (PPy) has attracted much attention owing to its unique electrical conductivity, excellent environment stability and the ease with which it can be prepared [1]. PPy can be made to give conductivities up to 1000 S cm^{-1} , which is nearer to conductivity of metals. This lead to applications in batteries, functional electrodes, electro-chromic devices, optical switching devices, sensors and so on [2].

Neutral polypyrrole is a dielectric with a band gap of about 4 eV. This polymer can be made conductive by chemical doping, which results in the removal of electrons from the polymer chain and the formation of positive charges and structural defects called polarons. These

defects are stabilized by the dopant anions and by the system of conjugated double bonds. At a high doping level, the distance between polarons in a chain decreases, leading to coupling of their spins and the formation of dications and bipolarons with the zero spin. The energy levels of polarons and bipolarons are in the band gap of the polymer. Therefore the conductive polymers can be considered to be semiconductors with the acceptor type conductivity [3].

Transition metal oxides (TMO) are the most fascinating class of materials. Composites of conducting polymers and TMO nano particles are important in modern science and technology due to their potential applications and important physical properties. Numerous attempts are going on to refine the methods of mixing organic polymers with TMOs. In almost all the cases some specific nature of association between the two components has been observed [4-10].

Among the transition metal oxides, zinc oxide (ZnO) is an important wurtzite-type versatile semiconducting material with a direct energy gap of 3.4 eV. Thermal stability, irradiation resistance and flexibility to form different nanostructures are the advantages that expedite its potential applications in photo detectors surface acoustic wave devices, ultraviolet nanolaser, solar cells, gas sensors, biosensors, nanogenerator etc [11]. There are no articles reporting on electrical studies on ZnO doped PPy system.

Moreover, ZnO is cheaper than other TMOs and is compatible with biomaterials. It is known that metal oxides do not easily mix up with conducting polymers but they get encapsulated in polymers thereby improving physical properties of polymers and thus making them suitable for diverse applications. Keeping in view of these, PPy-ZnO composites have been prepared and structural and dielectric studies were carried out. The same are reported in this paper.

2. EXPERIMENTAL

AR grade Pyrrole, Zinc oxide and ferric chloride have been used to prepare composites. Pyrrole solution of 0.1M was prepared by dissolving 5ml of Pyrrole in 100 ml of double distilled water. This solution was taken in a beaker and placed in an ice tray mounted on magnetic stirrer. Pre-cooled 0.3 M Ferric chloride anhydrous (oxidizing agent) solution was added drop-wise to pyrrole solution. The mixture was stirred continuously for 5 hours by

maintaining temperature of solution to be below 276K. The Greenish black precipitate Polypyrrole was filtered and dried in furnace maintained at 373K. The yield of the polypyrrole was 5g [12].

PPy-ZnO composites were prepared by mixing different weight percentages of ZnO with polypyrrole powder. The weight percentages of ZnO considered for making the present composites were 10%, 20%, 30%, 40% and 50% and were labelled as PZ1, PZ2, PZ3, PZ4 and PZ5 respectively. Pure PPy and PPy-ZnO powder were pressed in the form of pellets of 1 cm diameter and 3mm thickness by applying 3 tones a pressure using hydraulic press. The conducting silver paste was applied on two large surfaces of pellets to act as electrodes.

The SEM images of pure PPy and PPy-Zno composites were recorded using Scanning Electron Microscope (Jeol 6390LV). The XRD patterns were recorded in a X-ray Diffractometer (Bruker AXS D8 Advance) using Cu $k\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) 2θ in the range from 10° to 80° . The frequency dependent dielectric properties were studied at room temperature in the frequency range 100Hz-1MHz using (Hioki 3532-50) LCR meter. LCR meter gave the data on Complex impedance Z , Phase angle ϕ , equivalent parallel capacitance C_p and dissipation factor D . Using these measured quantities, dielectric constant and dielectric loss were estimated.

4. RESULTS AND DISCUSSION

4.1 SEM Analysis

Fig.1 depicts SEM micrographs of pure PPy and PPy-ZnO nano composites powders. PPy grains appear spherical and grains of ZnO are shapeless. The primary particles got clustered into agglomerates of different sizes in composites. Grain sizes for PPy are determined to be in the range of 250 nm to 290 nm. Particle sizes for ZnO are in the range of 150 nm to 165 nm.

Fig.1(c) shows SEM micrograph of PZ1 in which only PPy particles is visible. Absence of ZnO particles may be due to the fact that PPy encapsulated completely the small number of ZnO particles. Similar observation was made in [13]. The average particles measured in this case was about 285 nm. Fig 1(d) represents the SEM micrograph of the PZ5. Here, both PPy and ZnO phases are visible. Average size of particle is 311 nm. Also it can be seen that in Fig

1(d), porosity is much less compared to that observed in Fig 1(c). This makes it clear that there is uniform distribution of ZnO particles in PPy matrix. ZnO particles embedded in PPy formed multiple phases. This is probably due to an increased inter-chain interaction compared to its stabilized particles [14].

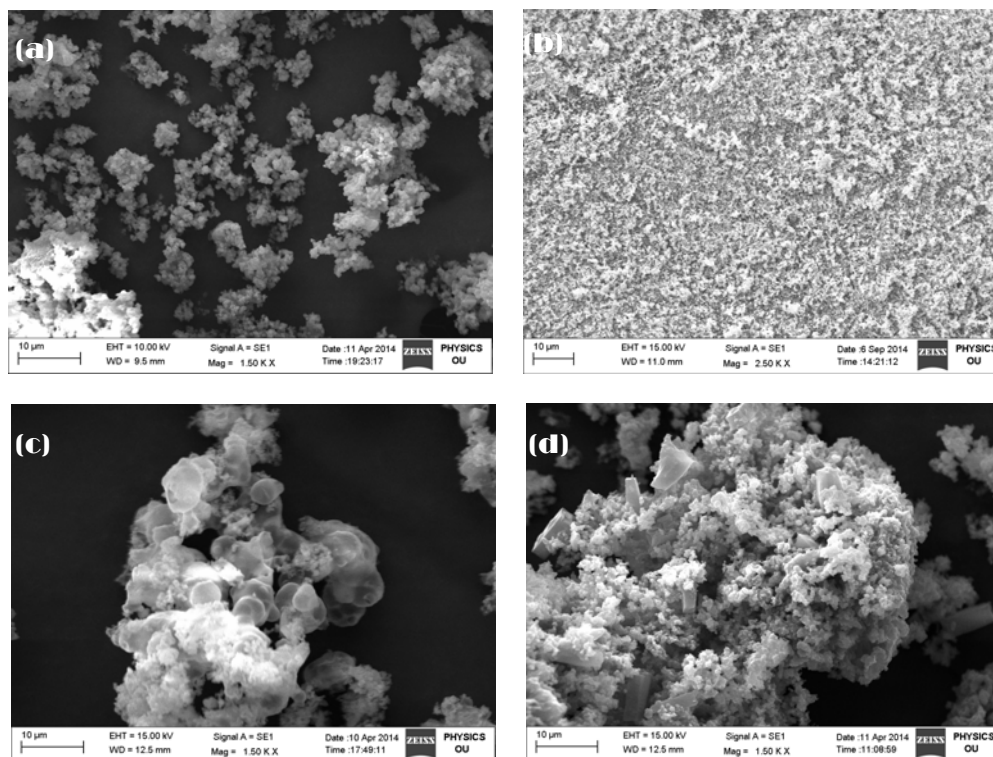


Fig.1. SEM micrograph of (a) pure PPy.(b) pure ZnO. (c) PZ1. (d) PZ5.

4.2 EDX

EDX analysis was performed to confirm the incorporation of ZnO particles in PPy. The elements analyzed were Zn, C, O and Cl. Zn was detected in all PPy/ZnO samples which confirms that TMO (ZnO) is located inside the composites and not on the surface [15]. In Fig 2(a) The elements C and O is associated with PPy. In Fig 2(b) and 2(c) an additional peak represent elements C and O is associated with PPy. In Fig 2(b) and 2(c) an additional peak representing Zn is present indicating that Zn and O are distributed uniformly throughout the samples.

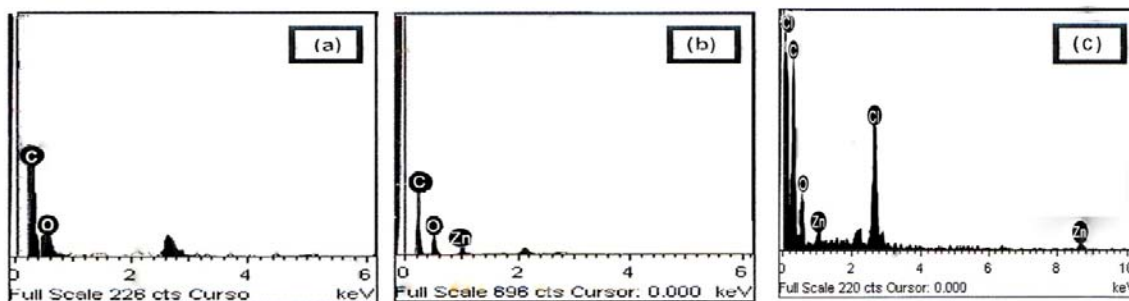


Fig. 2. EDX of (a) Pure PPy. (b) PZ1. (c) PZ5

4.3 XRD

XRD patterns of pure PPy, pure ZnO and PPy/ZnO composites are shown in Fig 3(a-c). Fig 3(a) represents XRD pattern of pure PPy. Here first broad peak centered at $2\theta = 25^\circ$ is a typical hump for conducting polymer polypyrrole. This is in agreement with earlier studies [16]. Fig 3(b) represents XRD pattern of pure ZnO. There are about 11 sharp peaks observed here. These are well known peaks for ZnO. The d-spacing and hkl values are tabulated in table 1.

Fig 3(c) represents XRD pattern of PZ2. Here there is only one small peak at 34.9° . The same peak was observed in all five composites the size of peak is small and is not sharp like in pure ZnO. The peak position is not matching with any of peaks of ZnO. Non appearance of ZnO peaks in the XRD patterns of PPy/ZnO composites indicate complete encapsulation of ZnO particles by polymer [17]. So the XRD patterns of the present composites reveal the non-crystalline nature of them.

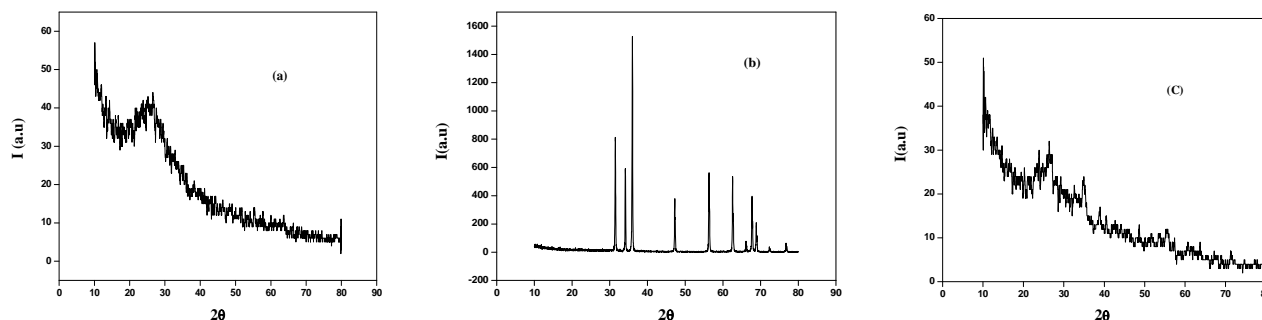


Table 1: XRD Results of PPy/ZnO composites

Sample	2θ	d (Å ⁰)	<hkl>
PZ2	34.9433	2.56779	110
ZnO	31.4586	2.84381	100
	34.1205	2.62780	002
	35.9601	2.49748	101
	47.2684	1.92304	102
	56.3470	1.63285	110
	62.6394	1.48311	103
	66.1716	1.41225	200
	67.7468	1.38319	112
	68.8894	1.36302	201
	72.3839	1.30558	004
	76.7830	1.24035	202

4.3 Dielectric properties

The dielectric constant (ϵ'), dielectric loss (ϵ'') and a.c conductivity σ_{ac} of the samples are calculated using the relations [18].

$$\epsilon' = (d/\epsilon_0 A) C \quad (1)$$

$$\epsilon'' = \epsilon' (\tan \delta) \quad (2)$$

$$\sigma_{ac} = \omega \epsilon_0 \epsilon'' \quad (3)$$

Where C is the capacitance, d the thickness and A area of the sample.

Frequency and compositional dependence of dielectric properties for composites are shown in Fig 4(a-d). Fig 4(a) and Fig 4(b) illustrates variation of ϵ' and ϵ'' respectively with frequency for pure PPy and all five composites.

In these, it can be observed that ϵ' and ϵ'' decreases fast with increase in frequency from their initial values. Above 10 KHz both the parameters show slow variation with frequency. At different frequencies, ϵ' and ϵ'' were found to increase up to certain amount of ZnO and decreases for further increase in ZnO for composites.

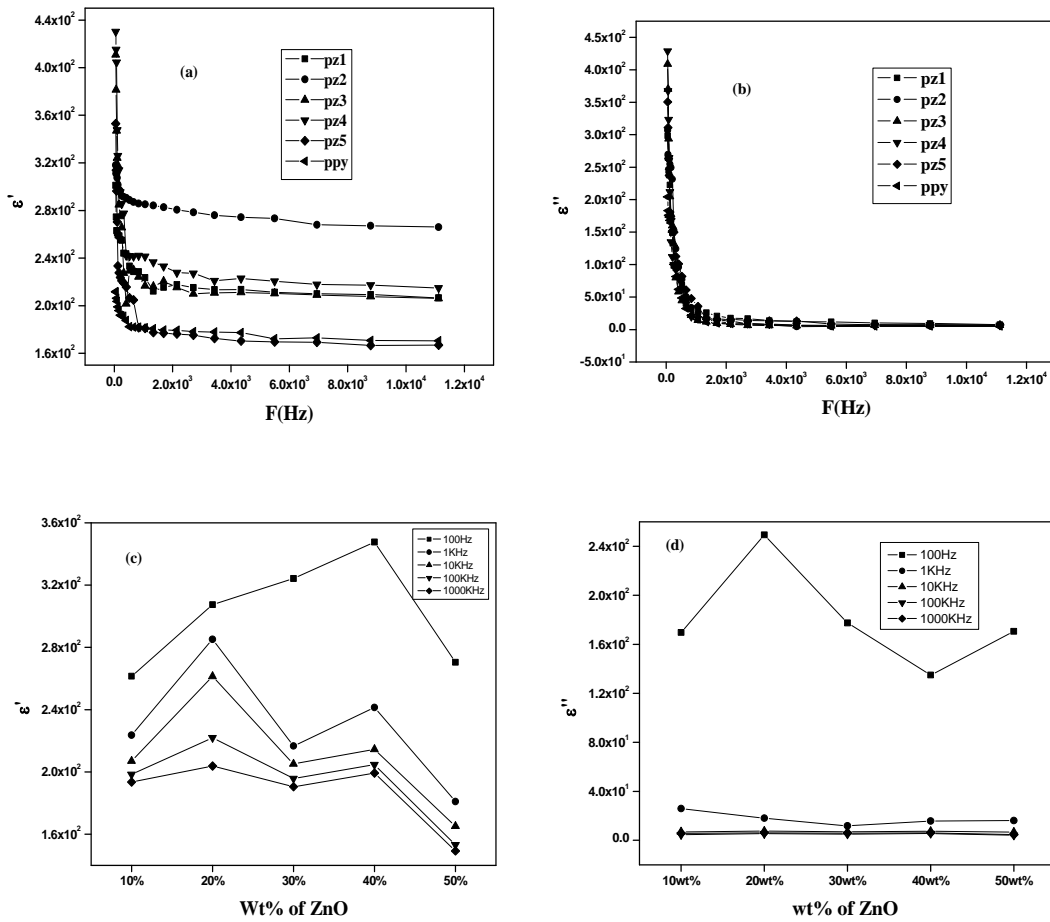


Fig. 4. (a) ϵ' versus frequency. (b) ϵ'' versus frequency. (c) ϵ' versus wt% of ZnO (d) ϵ'' versus wt% of ZnO.

At lower frequency, the dipoles can respond to rapid variation in field and dipole polarization has its maximum value. At higher frequencies dipole polarizability will be minimum as the field cannot induce the dipole moment, so dielectric values are minimum [19]. The higher values of the dielectric constant observed at lower frequencies are because of accumulation of charges at the boundaries, pores and defects [20].

4.3 AC conductivity

The total conductivity, σ is the sum of dc and ac components as described below

$$\sigma_{\text{total}} = \sigma(0) + \sigma_{ac}(\omega) \quad (1)$$

Here, $\sigma(0)$ is dc conductivity, which is frequency independent and temperature dependent and

σ_{ac} is the ac conductivity which is both frequency and temperature dependent. The σ_{ac} obeys the Almond-West universal power law, $\sigma_{ac}(\omega) = A \omega^s$ with $\omega = 2\pi f$ the angular frequency and s the frequency exponent, $0 < s < 1$ [21].

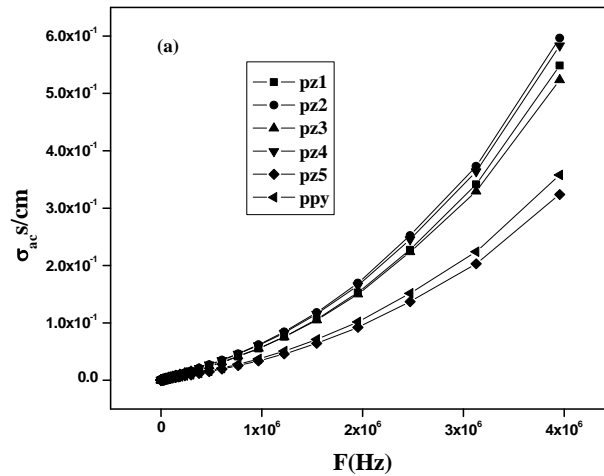


Fig. 5. Variation of σ as a function of frequency F , for PPy and PZ composites.

Variation of σ as a function of frequency is shown in Fig 5. In this figure it can observe that conductivity increases with frequency, for higher frequency and become constant at lower frequency. This makes it clear that there are dc and ac components in σ_{total} . The frequency independent part can be attributed largely to free charges. Frequency dependent conductivity is due to trapped charges, which is only active at higher frequency region. The observed nonlinear variations of σ with frequency indicate power law type of variation.

The conductivity of the composites can be split into microscopic and macroscopic parts. The microscopic conductivity depends upon the doping level, chain length etc, whereas the macroscopic conductivity depends on the inhomogeneities in the composites, compactness of pellets, orientation of micro particles etc [22]. The present PZ composites can be considered to be inhomogeneous because of doping of ZnO into them. This means that both micro and macro contributions will be there to the total conductivity. Micro contribution can be expected to increase with increasing ZnO content, as increase in ZnO content increases

inhomogeneities in the composites. Macro contribution mainly depends on particle size as it has direct link to compactness of pellets and orientation of particles.

CONCLUSIONS

The PPy/ZnO composites were synthesized chemically. Structural characterizations of the composites were carried out using SEM, XRD.

(i) SEM images of PPy/ZnO composites show agglomeration of particles. The presence of ZnO influences the morphology of the composites.

(ii) XRD spectra revealed the present composites to be largely non-crystalline. It can therefore be concluded that ZnO particles completely encapsulated by PPy.

(iii) The dielectric studies were investigated for the frequency range from 100Hz to 1MHz. Both dielectric constant and loss decreased drastically from their initial values with increase in frequency. For higher frequencies they decreased slowly.

(iv) Conductivity increased with increase in frequency and ZnO. As expected, conductivity is found to contain frequency dependent and independent parts. Both micro and macroscopic contributions may be there to the total conductivity. Both free as well as trapped charges may be responsible for conduction in these composites.

REFERENCES

1. N. Z. I. Bohari, Z. A. Talib, M. Amirul, S. M. Yunus, A. Kassim, *Int. J. Phys Sci.* 7, 10, 1670 (2012).
2. Z. Guo, K. Shin, A. B. Karki, D. P. Young, R. B. Kaner, H. T. Hahn, *J Nanopart Res.* 11, 1441, (2009).
3. O. A. Andreeva, L. A. Burkova, M. A. Smirnov, G. K. El'yashevich, *Polym. Sci. Ser. B.* 48, 11, 331 (2006).
4. E. Ozkazanc, S. Zor, H. Ozkazanc, S. Gumus, *Polym. Eng. sci.* 53, 1131 (2013).

5. C. H. Chang, P. S. Son, J. Yang, S. Choi, J. Korean Chemical Society. 53, 2,111 (2009).
6. L. Jiang, H. Jun, Y. Hohb, J. Limc, D. Lee, J. S. Huh, Sensors and Actuators B. 105, 132 (2005).
7. C. A. Ferreira, S. C. Domenech, P. C. Lacaze, J. Appl. Electrochem. 31, 49 (2001).
8. M. Li, Y. Zhang, L. Yang, Y. Liu, J. Ma, J Mater Sci: Mater Electron. 10, 1007, 2425 (2014).
9. D. P. Almond, C. R. Bowen, D. A. S. Rees, J. Phys. D: Appl. Phys. 39, 1295 (2006).
10. H. Eisazadeh, World J. Chem. 2, 2, 67 (2007).
11. E. Dalas, P. Mougoyanni, S. Sakkopoulos, Rom. Journ. Phys. 58, 3, 354 (2013).
12. M. V. Murugendrappa, M.V.N. Ambika Prasad, J. App. Poly. Sci. 103, 2797 (2007).
13. X. Gao, W. Luo, C. Zhong, D. Wexler, S. Chou, H. Liu, Z. Shi, G. Chen, K. Ozawa, J. Wang. Scientific reports. 4, 6095, 1 (2014).
14. C.A. Ferreira, S. C. Domenech and P.C. Lacaze, J. Appl. Electrochem. 31, 49 (2001).
15. A. Singh, A. Chandra, J. Appl Electrochem. 43, 773 (2013).
16. H. K. Chitte, N. V. Bhat, V. E. Walunj, G. N. Shinde, J. Sensor Technology. 1, 47 (2011).
17. A. Imani, G. Farzi, A. Ltaief, International Nano Letters. 3, 52, 1 (2013).
18. T. K. Vishnuvardhan, V. R. kulkarni, C. Basavaraja, S. C. Raghavendra. Bull.Mater. Sci. 29, 1,77 (2006).
19. T. M. Meaz, S. A. Saafan, E. H. El-Ghazzawy, M. M. Ayad, M. K. El Nimr, J. Am. Sci ,8, 1035 (2012).
20. G. M. Nasr, H. M. Osman, M. M. Omar, A. M. Abdelbary, J. Life Sci. 11, 4, 127 (2014).
21. A. N. Papathanassiou, J. Grammatikakis, I. Sakellis, S. Sakkopoulos, E. Vitoratos, E. Dalas, J. Appl. Phys. 96, 7, 3883 (2004).
22. T. Z. Rizvi, A. Shakoor, J. Phys. D: Appl. Phys. 42, 095415, 1 (2009).