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Study of AC Electrical Conductivity and Dielectric Properties of Polypyrrole Based zno Nanocomposites

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Abstract:

Polypyrrole based Zinc Oxide (PPy-ZnO) nanocomposites are synthesized by in-situ polymerization in different weight percentages using oxidation method. The surface Morphology and structural properties of prepared sample was studied by using X-ray diffraction and field emission scanning electron micrograph (FE-SEM).The AC electrical conductivity and Dielectric properties of Polymer based nanocomposite of various composites materials were investigated at different temperatures and frequencies from 100Hz to 1MHz. In this the dielectric constant decreased with increase in frequency and temperature. As ZnO concentration increases the AC conductivity increased with frequency. The Activation energy of PZ2 (70%ppy+30%ZnO) was maximum among the samples and it is found to be 0.1106 eV.

Keywords: Polypyrrole, ZnO; Dielectric constant, AC conductivity.

Introduction:

Recently, the conductive polymer like polypyrrole, polythiophene, polyaniline, etc.[1].received a great deal of attention because of its good environmental stability, facile synthesis and significant electrical conducting characteristics [2]. To improve the characteristics of polymer for commercial application, ZnO nanoparticles have also attracted considerable attention in the polymer community as fillers for polymer composites because of wide band gap energy of 3.37 eV and large excitation binding energy of 60 meV at room temperature [3-6]. ZnO nanoparticles into polymers can improve the optical and electrical properties of polymers due to a strong interfacial relations between the organic polymer and the inorganic nanoparticles [7]. In present work, pure PPy and ZnO doped PPy nanocomposites were synthesized by Sit tu polymerization method in a batch process and then characterized by XRD and SEM. The A C conductivities and dielectric properties of polypyrrole and its nanocomposites were measured by using two probe method.

Experimental

Zinc oxide (ZnO):

In preparation ZnO, 0.2M Zinc Acetate dehydrates dissolved in 100 ml de-ionized water was ground for 15 min and then mixed with 0.02 M solution of NaOH with the help of glass rod. After the mixing the solution was kept under constant magnetic stirring for 15 min. and then again it was grinded for 30 min. The white precipitate product was formed at the bottom. The obtained product was washed many times with the deionized water and methanol. The final product was then filtered and precipitate is obtained in the form of white paste. The paste was kept in a vacuum oven at $80^{o}C$ for 4 hrs. So the moisture will be removed from the final product

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and we will get dry product. Then this dry product was crushed into a fine powder by using grinding machine and finally this fine nano-powder of ZnO was calcinated at temperature 800 ^{o}C for 6 hrs. in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from product will be completely removed and got a final product of ZnO nanoparticles [8].

Synthesis of Polypyrole (PPy):

The Py monomer, anhydrous iron (III) chloride ($FeCl_3$) and methanol were used as received for synthesis of PPy. The solution of 7 ml methanol and 1.892 g $FeCl_3$ was first prepared in round bottom flask. Then 8.4 ml Py monomer was added to ($FeCl_3$ + methanol) solution with constant stirring in absence of light. The amount of Py monomer added to the solution (1/2.33 times of $FeCl_3$) was in such a way to get maximum yield. The ensuing black precipitates are filtered and washed several times with distilled water until clear product is Polypyrole is obtained. The obtained product is dried in oven at 600^{o}C for 4 h. The synthesized materials were characterized by using XRD, SEM.

Preparation of Pellets:

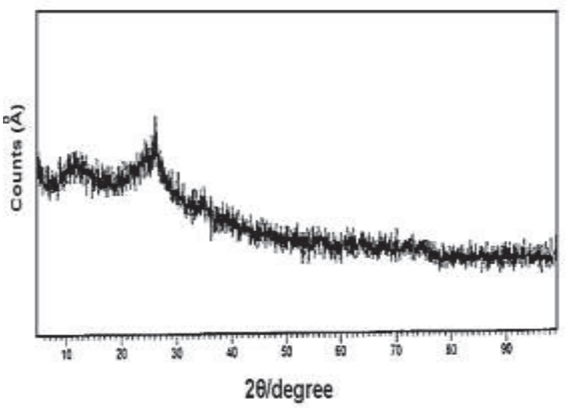
Initially, for the preparation of pellets the synthesized material ZnO and PPy were mixed with different weight percentage in pure and composite form. The pellets of different series of composition of ZnO-PPy nanopowder were prepared by using electrically operated automatic press machine (KBr Press) at load of 5 tons / cm^2 for half an hour. All the pellets were sintered at 150^{o}C for half an hour. The sintered pellets were polished and the electrodes were formed by painting conductive silver paint on the opposite faces. Again pellets were sintered for the drying the silver paint at 100 ^{o}C for half an hour. The different series of composition were listed in the table (1). Table 1

S.No	Nano composites	Sample Code
1	Pure Polypyrrole	P
2	80 % ppy + 20 % ZnO	PZ1
3	70 % ppy + 30 % ZnO	PZ2
4	60 % ppy + 40 % ZnO	PZ3
5	50 % ppy + 50 % ZnO	PZ4
7	40 % ppy + 60 % ZnO	PZ5
8	30 % ppy + 70 % ZnO	PZ6
9	20 % ppy + 80 % ZnO	PZ7
10	Pure ZnO	Z

1. Results and Discussion

1.1. X-ray Diffraction (XRD):

Fig.1. XRD of pure PPy



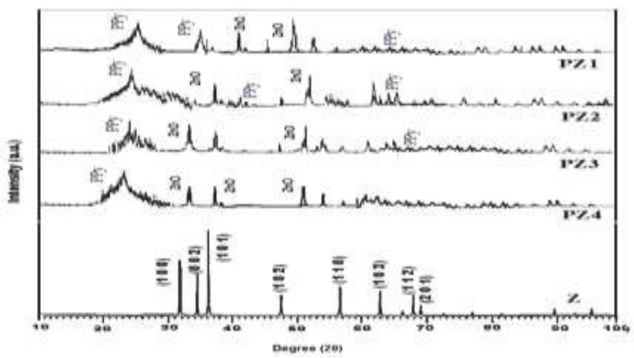


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Fig.2. XRD of all composites sample

The X-Ray diffraction pattern of pure polypyrrole (PPy) and there composites are as shown in figure (1 and 2). It is recorded in terms of 2θ in the range 10 to 100^{o}.n The pure Ppy exhibited that, it is amorphous in nature. The broad peak occurred at 24^{0} and it is characteristics of amorphous nature of polypyrrole. The broad peak occurs due to the scattering of X-rays from polymer chains at the interplaner spacing. The maximum intensity position of amorphous also depends on monomer to oxidant ratio. The X-ray diffraction patters of composites of PPy, ZnO and pure ZnO, calcinated at 200^{0}C. All the peaks match well the standard hexagonal wurtize structure of zinc oxide (ZnO) with lattice constants a = b = 0.3249 nm and c = 0.5206 nm [JCPDS card no. 36-1451]. with 100% intensity and the average crystalline size by using Scherer's formula was found to be 99.40nm [9]. All the peaks are for the composites materials. it is observed that average crystallite size of 70PPy:30 ZnO composition is least as compared to other compositions and pure material and hence 70PPy:30 ZnO composition has large active region which tends to increase the conductivity of the composition.

Scanning Electron Microscope (SEM)

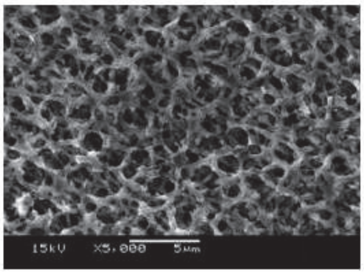

Fig. 3: SEM of Pure PPy

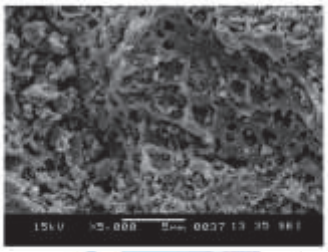

Fig. 4: SEM of PZ2 (70 PPy + 30 ZnO)

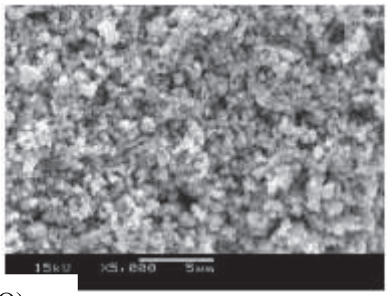

Fig. 5: SEM of Pure ZnO

From the SEM photos, it is observed that in every inch of the region, number of pores was different and an average number of pores was taken for comparative study. From every photo, porosity was calculated for one inch region and listed in the tabular form. From above figures, it is found that number of porosity of 70PPy:30ZnO composition is more and that among the prepared and pure samples. Due to high porosity, available area for the flow of ions and charges is more and conductivity enhances . High porosity reduces the obstacle to the flow of charges and ions as collisions reduce (relaxation time increases) and charges mobility increases. This tends to high electrical conductivity.

Result and Discurssion

AC Conductivity

Figure (6) show the variations of ln(ac □) with ln (frequency) at constant temperature at 300K. From these it is observed that as frequency increases, ac conductivity (ac □) increases continuously. With increase in frequency, more and more polarization of the sample takes place and it results in increase in conductivity. The Maximum conductivity was found to be for sample PZ2 (70% PPy + 30% ZnO) and its value is ln (ac □) = - 3.28 i.e. ac □ = 5.248×10^{-4} S/cm with increase in temperature, ac conductivity (ac □) increases continuously. As there is increase in temperature more and more charges become free with increasing mobility and they contribute to the net electrical conductivity enhancement. As doping percentage of ZnO in PPy increases, conductivity increases and becomes maximum for PZ2 sample and then with further increase in doping percentage of ZnO in PPy, conductivity decreases.

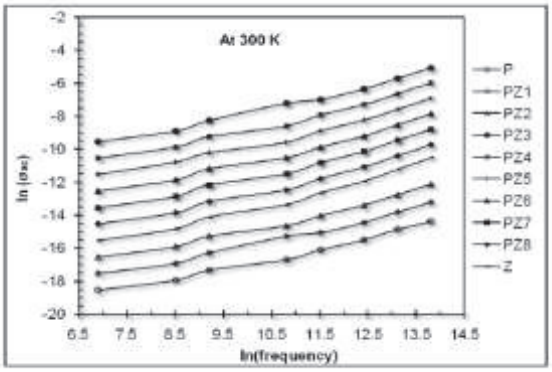

Figure 6 AC conduvtivity of Samples

Dielectric Constant

Figure (7) shows the variation of dielectric constant(**□r**) with temperature at constant frequency, with increase in temperature and increase in doping percentage of ZnO in PPy, in these dielectric constant increases and becomes maximum for 70 % PPy + 30 % ZnO sample (PZ2 sample). With further increase in doping of ZnO in PPy, dielectric constant decreases and becomes minimum for pure ZnO i.e. for Z sample. This is because PZ2 sample may have large number of free charges as compared to other compositions and their more collisions with vibrating atoms results in the increase of refractive index of the PZ2 sample and hence dielectric constant is high among the other compositions.

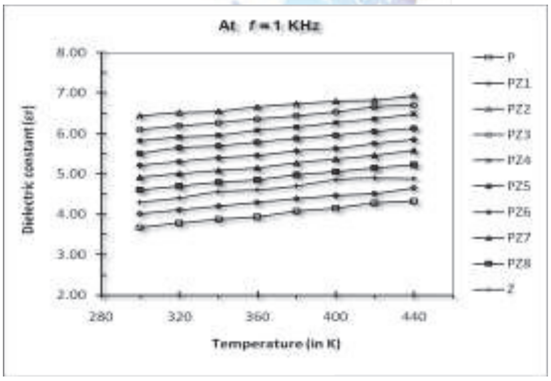

Figure 7: Graph between dielectric constant (□r) and temperature at constant frequency

Ultraviolet (UV) Spectra

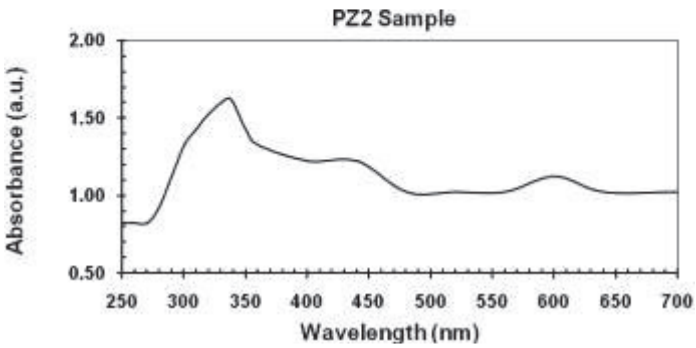

Fig. 8 Variations of absorbance (a.u.) with wavelength (nm)

As percentage of doping of ZnO in PPy increases, band gap energy decreases and becomes minimum (3.7108 eV) for PZ2 sample and with further increase in doping of ZnO, band gap energy increases and becomes maximum for Z sample. It is depicted that band gap energy for above prepared series varies from 3.7108 eV to 3.9215 eV. Minimum value of Eg for PZ2 sample shows that minimum amount of energy required to move the charges to conduction band from lower energy band and hence this sample is best among the remaining samples of the series as it requires lower energy for conduction.

Conclusion

The X-ray diffraction patterns of composites of PPy, ZnO and pure ZnO, and it shows hexagonal wurtize structure and the average crystalline size is found to be 99.40 nm . The series of sample of pure and composite form of PPy and ZnO were prepared in the form of pellet. It was observed that , frequency increases, ac conductivity (ac □) increases continuously. With increase in frequency, more and more polarization of the sample takes place and the maximum conductivity was found to be for sample PZ2. The dielectric constant increases and becomes maximum for 70 % PPy + 30 % ZnO sample (PZ2) than other prepared sample. The study of UV radiation shows UV radiation minimum band gap energy for sample PZ2 i.e. 3.7108 eV.

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