



## Characterization and DC Electrical Conductivity of ZnO/LDPE Nanocomposites

Manisha C. Golchha<sup>1\*</sup>, Vijaya S. Sangawar<sup>2</sup>, Amit L. Gadre<sup>3</sup> and Ganesh R. Yerawar<sup>4</sup>

<sup>1</sup> Department of Physics, Brijlal Biyani Science College, Amravati (MS), India.

<sup>2</sup> Department of Physics, G. V. I. S. H., Amravati (MS), India.

<sup>3</sup> Department of Physics, Arvindbhou Deshmukh Mahavidyayaka, Bharsingi, Dist. Nagpur (MS), India.

<sup>4</sup> Department of Physics, KES's Arts, Commerce and Science College, Arvi, Dist. Wardha (MS), India.

### Abstract

Using Low Density Polyethylene (LDPE) and Zinc Oxide Nanoparticles (ZnO NPs) in different weight percentages (0, 0.5, 1, 3, 5 wt.%), polymer inorganic nanocomposite thin films (PINCs) were prepared by solution cast technique. The X-Ray Diffraction (XRD) pattern study of the sample indicates the presence of ZnO NPs in LDPE matrix and absence of any extra peak in the pattern shows there is no new phase formation. Fourier infrared transformation (FTIR) spectra confirm the presence of ZnO NPs in LDPE thin films. The DC electrical conductivity of the thin films was also studied as a function of temperature and filler concentration. The conductivity was found to be sensitive to temperature and also increased with increase in temperature and concentration of ZnO NPs.

**Keywords:** ZnO/LDPE nanocomposite, thin films, XRD, FTIR, DC conductivity.

### Introduction

The intrinsic electrical and thermal conductivities of polymers are usually much lower than those of metals, metal oxides or ceramic materials, and hence are characterized as good insulators. An effective way of lowering the electrical or thermal resistivity of polymer composites is by adding conductive fillers (metals, metal oxides and carbon fibers) to the polymeric matrix<sup>1</sup>.

Polymers, which are reinforced with nanostructured materials dispersed at nano level, are known as polymer nanocomposites. Organic/Inorganic nanocomposites are generally organic polymer composites with inorganic nanoscale fillers. The integration of inorganic nanoparticles into polymer matrix allows both properties from inorganic nanoparticles and polymers to be combined and enhanced<sup>2</sup>. They exhibit superior properties in terms of increased strength, improved heat resistance, decreased activation energy,



increased capacitance, improved thermal behaviour at very low loadings of <5 wt% of nano-fillers as compared to the pure polymers<sup>3</sup>.

Polymer inorganic nanocomposites of LDPE and ZnO NPs were prepared with a view that they can exhibit some novel properties. In the present work, ZnO/LDPE nanocomposites were prepared by adding ZnO NPs in different weight % (0, 0.5, 1, 3, 5 wt.%) in LDPE. In this paper, the effect of doping inorganic ZnO NPs on structural and electrical properties of LDPE is reported.

## Materials and Methods

ZnO/LDPE nanocomposites thin films were prepared by solution-cast technique<sup>4</sup>. With the help of hot plate magnetic stirrer, LDPE was dissolved in Xylene at 100°C for 2 hrs. Then ZnO NPs were added to the

solution of LDPE in different wt. % (0, 0.5, 1, 3 and 5) and further stirred for 2 hrs. The sample was obtained by casting the solution on a leveled glass substrate kept in a pre-heated oven. After complete evaporation, the film was detached from the glass surface. The thickness of all samples was kept constant (~ 61.52  $\mu\text{m}$ )<sup>5</sup>.

## Result and Discussion

### X-Ray Diffraction (XRD) Analysis

The structure of the Polymer Inorganic Nanocomposites (PINCs) thin films was characterized by XRD in order to confirm the structure and the presence of ZnO NPs within the LDPE matrix. The XRD patterns using  $\text{CuK}_{\alpha}$  radiation for pure LDPE and ZnO NPs (0.5 and 5 wt. %) filled LDPE nanocomposite thin films are represented in Figures 1.1, 1.2(a) and (b) respectively.

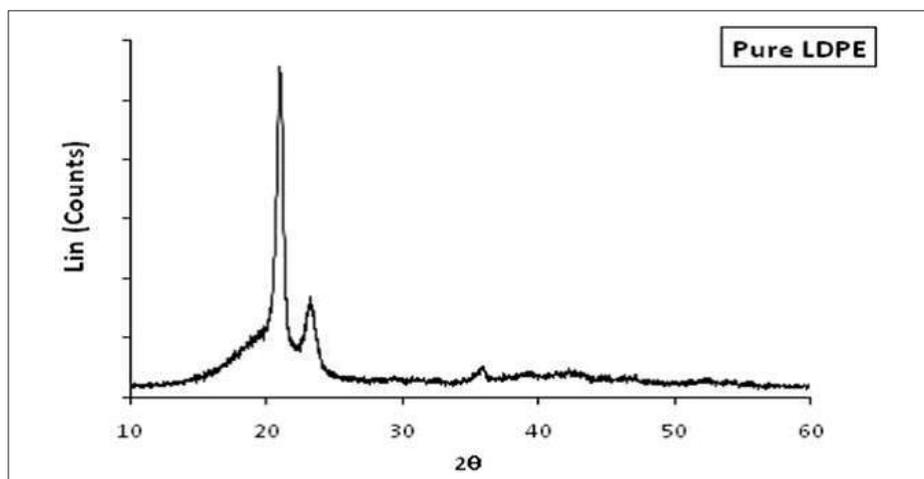


Fig. 1.1 X-ray Diffractogram of Pure LDPE Thin Film

The XRD pattern in Figures 1.1, 1.2(a) and (b) show a dominant fairly sharp peak at 21.4° and a weak broad peak at 23.7° which corresponds to LDPE. The peaks for LDPE sample appearing at 21.4° and 23.7° correspond to (110) and (200) reflections from the orthorhombic polyethylene crystals<sup>7</sup>. This dominant

peak and the small weak broad peak arise from crystalline and amorphous regions in LDPE<sup>7</sup>.

In Figures 1.2(a) and (b), the typical diffraction peaks of ZnO NPs are observed at 31.3°, 34.2° and 35.9° and all diffraction peaks are in agreement with the

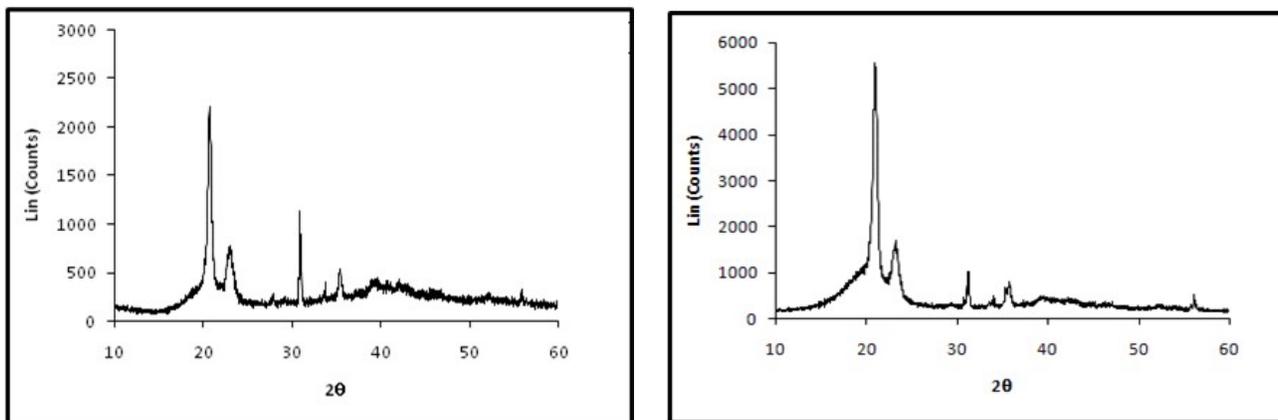


Fig. 1.2 X-ray diffractogram of (a) 0.5 wt.% and (b) 5 wt.% ZnO NPs filled LDPE thin film

hexagonal wurtzite structure<sup>8</sup>. With the increase in ZnO NPs content, the intensity of the peaks increased which proved that introducing increasing ZnO NPs content resulted in an increase in the degree of crystallization of LDPE.

Thus, an increase in the intensity and decrease in the width of ZnO/LDPE nanocomposites are observed indicating an increase in semi-crystalline structure, which leads to their good compatibility.

#### Fourier Transform Infrared (FTIR) Analysis

FTIR spectroscopy was used to reveal the incorporation of ZnO NPs in LDPE matrix. FTIR spectra of the samples were obtained in the wave number range 400–4000  $\text{cm}^{-1}$ . Fig. 2 shows the FTIR spectra of LDPE and ZnO/LDPE nanocomposite. The spectrum of the nanocomposite exhibits the characteristic absorption bands corresponding to polymeric groups and ZnO.

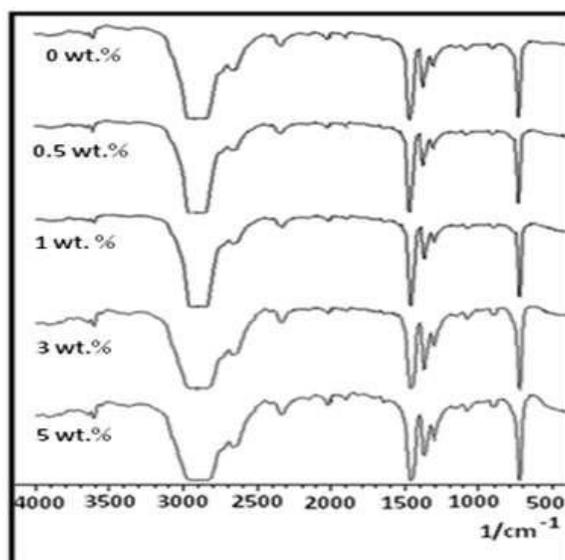


Fig. 2 Infrared Spectra of LDPE and ZnO NPs (0.5, 1, 3, 5 wt. %) filled LDPE Thin Films



The peaks in the region 3370- 3750  $\text{cm}^{-1}$  are due to O-H stretching of hydroxyl group. A strong peak observed at 3000-2800  $\text{cm}^{-1}$  corresponds to  $\text{sp}^3$  C-H stretching. The bands at 2915  $\text{cm}^{-1}$  and 2332  $\text{cm}^{-1}$  are due to aliphatic C-H and C-C respectively. The prominent bands of LDPE at 1465  $\text{cm}^{-1}$  and 1375  $\text{cm}^{-1}$  are due to the  $-\text{CH}_2-$  group in the PE chain. Other characteristic bands of LDPE are 1304  $\text{cm}^{-1}$  ( $\text{CH}_2$  wagging), 1080.14  $\text{cm}^{-1}$  (C-H bond) and 890  $\text{cm}^{-1}$  (C=CH). The peak at 723.3  $\text{cm}^{-1}$  is probably due to C-H rocking.

On comparing the FTIR spectra of unfilled and ZnO filled LDPE thin films, it is observed that ZnO filled

LDPE thin film spectra contain one additional peak at  $\sim 422 \text{ cm}^{-1}$  corresponding to ZnO bond along with all the characteristic peaks of unfilled LDPE spectra. This indicates that there is no chemical bonding between the ZnO and LDPE. There is also no significant shift in the characteristic transmittance peaks indicating that LDPE did not have strong interaction with ZnO.

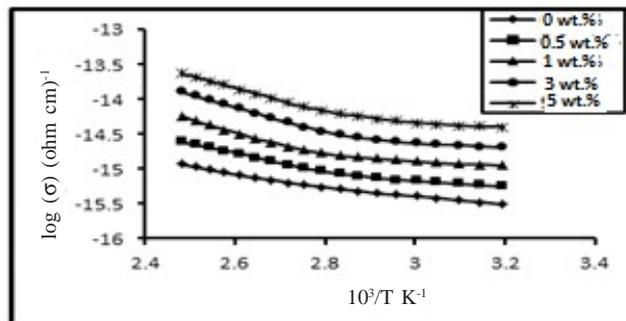
Since no noticeable change in peak positions was observed in all the FTIR spectra, the peak frequencies and their co-relation has been tabulated in a single table (Table 1). Our results are in good agreement with previous reports.<sup>9, 10</sup>

**Table 1. Frequency Correlation in LDPE and ZnO NPs (0.5, 1, 3, 5 wt. %) Filled LDPE Thin Film**

Sr. No.	Frequency ( $\text{cm}^{-1}$ )	Correlation
1	3604	O-H stretching
2	3000-2800	Strong C-H stretching
3	2915	Aliphatic C-H
4	2332	Aliphatic C-C
5	1465.9	C-H bending $\text{CH}_2$
6	1375	$-\text{CH}_2-$ group
7	1304	$\text{CH}_2$ wagging
8	1080.14	CH
9	890	C=CH
10	723.3	C-H rocking
11	422	Zn-O bond

### DC Electrical Conductivity

DC electrical conductivity measurement of thin film samples was carried out in the temperature range 319 K – 403 K. The effect of temperature and varying filler concentrations on conductivity of LDPE was studied. Fig. 3 represents DC electrical conductivity thermograms ( $\log \sigma$  vs.  $10^3/T$  plots) of samples i.e. LDPE and 0.5, 1, 3, 5 wt. % ZnO NPs filled LDPE. In all these samples, conductivity increases with increase in temperature and with ZnO NPs concentration.



**Fig. 3 DC conductivity of LDPE and ZnO NPs (0.5, 1, 3, 5 wt. %) filled LDPE Thin Films**

The thermograms reveal that conductivity increases with increasing temperature indicating the semiconducting nature of nanocomposite thin film samples. An increase in conductivity with rise in temperature obeys the equation,

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \dots \dots \dots (1)$$

where,  $\sigma$  is the conductivity,  $\sigma_0$  represents the pre-exponential factor, T is the absolute temperature and k is Boltzmann constant and  $E_a$  is the electrical activation energy.

There are two phases i.e. polymer phase and filler phase. The increase in conductivity at higher temperatures may be due to softening; the injected charge carrier can move more easily into the volume of the sample giving rise to a large current and subsequently increase in conductivity. As temperature increases, the chain of LDPE becomes more flexible. This conduction is mainly due to a direct contact with ZnO NPs particles<sup>11, 12</sup>.

The increment in temperature provides an increase in free volume and segmental mobility. These two entities then permit free charges to hop from one site to another thus increasing conductivity. The conductivity increase with temperature indicates that more ions gained kinetic energy via thermally activated hopping of charge carriers between trapped sites<sup>13</sup>.

The tunneling distance is the average distance between the two closest separated points of adjacent particles and is only a few nanometers in length. Tunneling is a characteristic of the conductivity of nanocomposites. The conductivity of the percolating network in nanocomposites appears to be the result of electron transport between the nearest neighbor connections which denote the dominating conducting elements across the inter particle tunneling distance<sup>14</sup>. Tunneling is a transport process that depends on thermal

fluctuations, and a temperature increase will reduce tunneling resistance, i.e. give rise to conductivity. It appears, however, that the tunneling conduction can compensate for the lack of particle contacts because at higher temperatures the energy barrier tends to be lower<sup>15</sup>.

The overall conduction mechanism is related to electron transfer through the ZnO NPs aggregations distributed in the polymeric matrix. The thermo-electrical conduction behavior of the composites is interpreted in the form of variable range hopping mechanism, mobility of LDPE chains and the transfer of electrons through the ZnO NPs aggregations distributed in the polymer matrix.

## Conclusions

The ZnO/LDPE nanocomposites films were prepared by solution - cast technique. The XRD pattern confirms the presence of crystalline metal oxide within the polymer matrix. The functional groups present in the samples were identified using FTIR spectroscopy for ZnO/LDPE.

The DC electrical conductivities of prepared ZnO/LDPE nanocomposites thin films were determined as a function of filler concentration and temperature. DC conductivity was found to increase with increasing filler concentration and temperature which may be due to increase of charge carriers with increasing filler concentration. The overall conduction mechanism is related to electrons transfer through the ZnO aggregations distributed in the polymeric matrix, variable range hopping mechanism and tunneling mechanism.

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