DC ELECTRICAL CONDUCTIVITY AND THERMAL ANALYSIS OF LOW DENSITY POLYETHYLENE FILLED WITH ZINC OXIDE NANOPARTICLES

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A B S T R A C T

This paper describes the studies related to Zinc Oxide nanoparticles (0, 0.5, 1, 3 and 5 wt. %) filled Low Density Polyethylene thin films prepared by solution casting technique. The DC electrical conductivity of ZnO/LDPE nanocomposite thin films was studied as a function of temperature and filler concentration. The conductivity was found to be sensitive to the temperature and also increased with increase in temperature and concentration of ZnO NPs. The activation energy, Ea, was calculated from the graph of log σ vs 103/T plot within low and high temperature regions. The thermal transition of the nanocomposites was evaluated using DSC analysis

Keywords: ZnO NPs, LDPE, Polymer Nanocomposites, DC conductivity, DSC.

1. Introduction

Recently nanocomposite materials have become one of the most extensively studied material all over the world. The area of polymer nanocomposites has grown to represent one of the largest classes within the scope of materials science, becoming a key area in nanoscience and nanotechnology offering significant potential in the development of advanced materials in numerous and diverse application areas (Ajayan P M , 2000; Thostenson E T, 2001; Ray S S and Okamoto, 2003).

Organic/inorganic nanocomposites are generally organic polymer composites with inorganic nanoscale fillers. The integration of inorganic nanoparticles into a polymer matrix allows both properties from inorganic nanoparticles and polymer to be combined/ enhanced. (Li S et al, 2010). Generally, these nanocomposites are endowed with the special properties of the nanofillers, leading to materials with quite innovative characteristics.

Polymer Inorganic Nanocomposite of LDPE and ZnO NPs were prepared with the view that they can exhibits some novel properties. Thus in the present work, ZnO/ LDPE nanocomposites were prepared by adding the ZnO NPOs in different weight % (0, 0.5, 1,3 and 5) in LDPE. In this paper the effect of doping inorganic ZnO NPs on the electrical and thermal properties of LDPE is enclosed.

2. Experimental

Commercial grade granular LDPE provided by Indothene (24FS040) was used as it is and Xylene (AR Grade, E Merck) as a solvent. The hexagonal Wurtzite structured Zinc oxide nanoparticles (ZnO NPs) with average crystalline size about 80 nm, synthesized by a simple chemical solution method followed by combustion (Golchha M C et al, 2011), and used as filler.

Thin films of ZnO/LDPE nanocomposites were prepared by using solution - cast technique (Sangawar V S et al, 2006). LDPE was dissolved in Xylene using hot plate magnetic stirrer at 100^0C for 2 hrs. Then ZnO NPs were added to the solution of

LDPE in different weight % (0, 0.5, 1, 3 and 5) and was further stirred for 2 hrs at temperature constant. The melt was then poured on clean optically plane glass plate kept in pre-heated oven. After complete evaporation the film was detached from the glass surface. The thickness of all samples was kept constant and it is of the order of ≈ 61.52 μm(Golchha M C et al, 2013).

## 3. Result and Discussion
3.1. DC Electrical Conductivity

The present study is carried out to understand the temperature dependence of electrical conduction in unfilled and ZnO NPs filled LDPE thin films. It was also decided to study the role of filler molecules when added in varying concentrations to LDPE. Electrical DC conductivity measurement of thin film samples has been carried out in the temperature range 319 K to 403 K.

Fig.1 (a) represents DC electrical conductivity thermograms (log σ vs. $10^3/T$ plots) of samples i.e. unfilled LDPE and 0.5, 1, 3, 5 wt. % ZnO NPs filled LDPE. In all these samples, conductivity increases with increase in temperature and with the ZnO NPs concentration.

The variation of D.C. electrical conductivity as a function of ZnO NPs concentration at room temperature is shown in fig.1 (b). The conductivity increases with increases ZnO filler concentration. The increase of conductivity with increasing concentration of ZnO NPs is due to increase of charge carriers with increasing filler concentration Shrivastava et al, 2009).
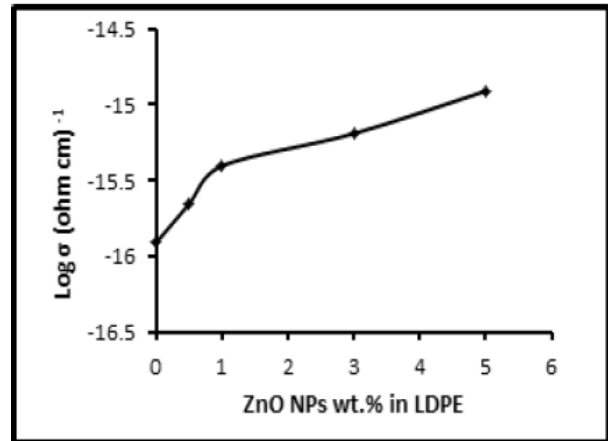
(a)
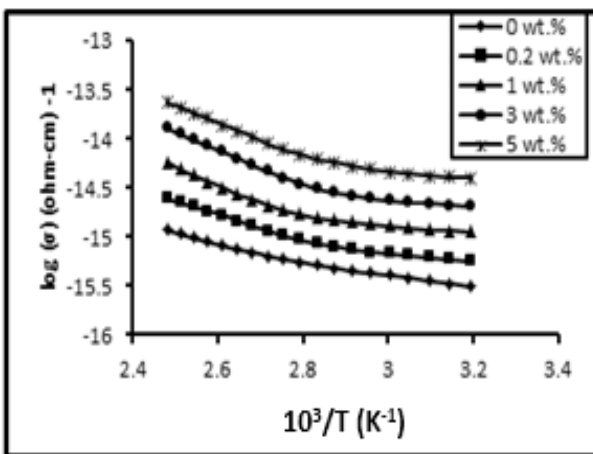
(b)

Fig.1- (a) DC conductivity of LDPE and ZnO/LDPE; (b) DC conductivity versus wt. % of ZnO NPs

Activation energy values are calculated from the slope of the thermograms and are enclosed in table 1. Ea values for ZnO NPs (0, 0.5, 1, 3 and 5 wt. %) filled LDPE nanocomposite thin films are found to be change with temperature, in LTR decreases with increase in filler concentration. While Ea values are found to be higher in HTR as compared to LTR and increases with increase in filler concentration with slight discrepancies.

Table 1: Activation Energy values for unfilled and ZnO/LDPE nanocomposites in LTR and HTR

Filler Concentration (In Wt. %)	Ea values in eV	
	LTR	HTR
0	0.120	0.131
0.5	0.109	0.299
1	0.099	0.321
3	0.090	0.328
5	0.087	0.325

All the observations from the graphs can be explained as follows. The thermograms reveal that conductivity increases with increasing temperature i.e. semiconducting nature of nanocomposite thin film samples. An increase in conductivity with rise in temperature obeys the equation,

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

Where, σ is the conductivity, σ0 represents the pre-exponential factor, T is the

absolute temperature and k is Boltzmann's constant and Ea is the electrical activation energy. The activation energy Ea was calculated from log σ vs.10^3/T plots. Table shows Ea values in low and high temperature regions for each sample. Thus addition of ZnO NPs increases the conductivity of LDPE.

There are two phases i.e. polymer phase and filler phase. The increase in conductivity at higher temperature 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 increase in conductivity at higher temperature. As temperature increases, the chain of LDPE becomes more and more flexible. This conduction is mainly due to a direct contact with ZnO NPs particles as explained by Twainsi A et al, 1999 and Saq-an S A et al, 2004.

The increment in temperature provides an increase in free volume and segmental mobility. These two entities then permits free charges to hop from one site to another thus increase conductivity. The conductivity increases so as temperature indicates more ions gained kinetic energy via thermally activated hopping of charge carriers between trapped sites, which is temperature dependence (Tominaga Y et al, 2005). A conductivity increase is generally seen in the vicinity of the polymer melting point and has been termed the positive temperature coefficient (PTC) effect of resistivity (Modine F A et al, 1996). The PTC effect is most often explained in terms of a reduction in intergranular electron transport that accompanies a change in the tunneling length at the melting transition (Sarychev et al, 1994).

The tunneling distance is the average distance between the two closest separated points of adjacent particles and is only a few nanometers. Tunneling is manifested characteristics 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 (Balberg I, 2002).

The conductivity of the polymer/metal oxide composites strongly depends on the particles' interfacial resistance, which has two major contributions: contact resistance" and so-called tunneling resistances. The former dominates in highly filled composites, when physical contact between the particles is present, while the latter is related to the presence of an insulating polymer film on the particle surfaces.

Tunneling is a transport process that depends on thermal fluctuations, and a temperature increase will reduce tunneling resistances, i.e. give rise to conductivity, it is probably the result of the separation of the particles due to softening of the LDPE matrix. 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 (Shang P et al, 1978).

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

3.2. Differential Scanning Calorimetry (DSC) Analysis

The thermal transition of the nanocomposites was evaluated using DSC analysis. The thermograms of ZnO/LDPE nanocomposite thin films were recorded using Netzsch DSC 200F3 PC instrument. The PINCs samples were tested in lid pierced and sealed aluminum pan at a heating rate of 10 K/min under dry N2 gas (60 mL/min) over a temperature range from 0 to 450^0C. The as-prepared samples were used to investigate the melting behavior. The endothermic curves for 0.5 wt. % and 5wt. % ZnO NPs filled LDPE are recorded as a function of temperature and are shown in fig. 2 (a) and (b) respectively.
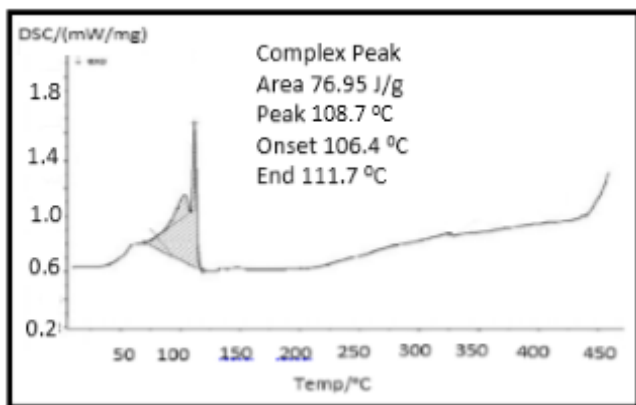
(a)
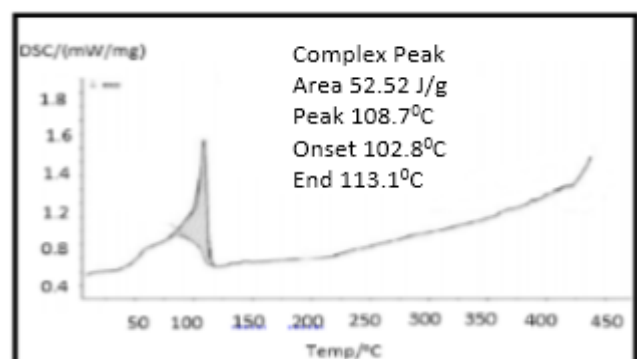
(b)

Fig. 2- DSC spectra of ZnO/LDPE nanocomposites (a) 0.5 wt. % ZnO NPs; (b) 5 wt. % ZnO NPs.

Pure LDPE is known to have melting temperature at $Tm \approx 110°C$. In DSC curves (fig. 2 (a) and (b)) of 0.5 and 5 wt. % of ZnO NPs filled LDPE samples the melting endotherm is observed at 108.7 ^{0}C for both 0.5 and 5 wt. % of ZnO/LDPE samples representing loading of ZnO NPs in LDPE does not affect the melting temperature though the addition of ZnO NPs in LDPE has reduced the melting point of LDPE by 1.3 ^{0}C. Overall, ZnO NPs loading have no appreciable effect on melting temperature of LDPE (Huang X et al, 2008).

The multiple melting behavior of the semicrystalline polymers may be designated as being the result of one of the following reasons: (1) melting, re-crystallization and re-melting during the DSC heating process, (2) the presence of more than one crystal modifications (polymorphism), (3) variation in morphology (such as lamellar thickness, distribution, perfection or stability), (4) physical aging or/and relaxation of the rigid amorphous fraction, (5) different molecular weight species and so on. (Qiu Z et al, 2003, Supaphol P, 2001).

A complicated melting behaviour in the case of 5 wt. % ZnO/LDPE (fig.2 (b)) nanocomposites was observed. Melting endotherm with one shoulder was found in the DSC traces. The shoulder was considered to be the melting endotherm of the crystallites with high thermal stability, while the final melting endotherm was ascribed to the melting of the crystallites formed through the reorganization of the crystallites with high thermal stability during the DSC heating process (Qiu Z et al,

2003, Liu T, 2003).

The enthalpy of fusion for nanocomposites was determined from the areas under the peak. It is observed that the ΔH values are consistently increased with the loading % ZnO NPs. The DSC curves shows lower enthalpies for the nanocomposites at low ZnO NPs contents (0.5 wt. %) fig.2 (a), but at higher concentrations (5 wt. %) fig.2 (b) the experimentally observed enthalpies are higher. This behavior may be explained by the fact that the particles are not agglomerated at lower % of ZnO NPs, and therefore there are large interfacial areas between the nanoparticles and the polymer. This will result in immobilization of the polymer chains and accompanying decrease in crystallinity. At higher ZnO NPs contents there is particle agglomeration, which probably gives rise to epitaxial crystallization of LDPE on the ZnO surfaces. Our results are in good agreement with Bem D B et al, 2010.

4. Conclusion

The DC electrical conductivities of prepared ZnO/LDPE nanocomposites thin films were studied as the function of filler concentration and temperature. DC conductivity was found to be increased with increasing filler concentration and temperature likely due to increase of charge carriers with increasing filler concentration. This increase in conductivity with increasing temperature reveals the semiconducting nature of nanocomposite thin film samples. 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.

DSC analysis of ZnO NPs filled LDPE revealed the endothermic curves. No glass transition temperature is observed in ZnO/LDPE DSC thermograms since it is semi-crystalline polymer. A complicated melting behaviour in the case of 5 wt. % ZnO NPs filled LDPE nanocomposites is observed attributed to melting, re-crystallization and re-melting during the DSC heating process. The increase in ΔH values for for ZnO/LDPE might be due to epitaxial crystallization of LDPE on the ZnO surfaces.

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