3.1 Introduction

Nanocrystalline materials may be considered as the challenge of this age. Intensive investigations were stimulated for several applications for these new classes of materials. Zinc oxides of particle size in nanometer range have been paid more attention for their unique properties. They are widely used for solar energy conversion, non-linear optics, catalysis, varistors, pigments, gas sensors, cosmetics etc.\textsuperscript{1-10} As a wide band gap semiconductor, ZnO has been widely studied in varistors, transparent conductors, transparent U.V. protection films, chemical sensors and so on.\textsuperscript{11-14}

Zinc oxide in combination with stearic acid is used as activator for sulphur-vulcanization of elastomers. In addition to its role as an activator, there are also evidences that the inclusion of ZnO in the compound brings also other benefits such as reduction in heat build-up, improvement of abrasion resistance and heat resistance of the vulcanizates and their resistance to dynamic loading\textsuperscript{15} helps to dissipate local heat concentrations in rubber products. Zinc oxide is a necessary ingredient in rubber compounds for bonding rubber to the reinforcing steel cord etc.
Besides improving the properties of vulcanized rubbers, ZnO also assists in the processing of uncured rubbers. ZnO is added to rubber formulation to reduce shrinkage of moulded rubber products and maintain the cleanliness of moulds. Although zinc is generally considered as one of the least harmful among heavy metals, there is an increased concern about its environmental effects. Diffuse emissions of zinc from rubber products, such as the wear of tyres may enter into the environment. In view of the upcoming legislation and ecolabelling requirements for tyres for instance, it can be stated that it is desirable to keep the ZnO content in rubber compounds as low as possible, not only for environmental but also for economical reasons.

The efficiency of ZnO during vulcanization can be enhanced by the maximization of the contact between the ZnO particles and the accelerators in the compound. This contact is dependent on the size of the particles, their shape and the specific surface area. Zinc oxides of particle size in nanometer range have been paid more attention for their unique properties. Various methods have been employed for the synthesis of nano ZnO which include precipitation from an alcoholic solution of zinc acetyl acetonate by alkali, hydrolysis of zinc acetate in polyol medium and a modified sol-gel procedure where in an alkylzinc reacts with tert-butyl alcohol to form alkylzinc alkoxide, which then reacts with aqueous ethanol. Despite recent advances, commercial exploitation of ZnO nanoparticles is currently limited by the high synthesis costs. In this chapter, we describe the preparation and characterization of nano zinc oxide by precipitation and solid state pyrolytic method which is simple, rapid and low cost.

3.2 Experimental

3.2.1 Materials

Zinc sulfate, ammonium bicarbonate, zinc acetate and sodium bicarbonate were supplied by Sd. fine chem. Ltd., Mumbai, India
3.2.2 Method I- Precipitation method

Zinc sulfate (1.5 mol/l) and ammonium bicarbonate (2.5 mol/l) were prepared in distilled water and 100 ml ZnSO₄ solution was added to 126ml NH₄HCO₃ solution while stirring and the reaction mixture was kept at 45°C. The slurry of basic zinc carbonate (BZC) in the form of a white precipitate was obtained. It was then filtered, washed and dried. Finally zinc oxide nanoparticle was prepared by calcining the precipitate at 500°C for 1 hour.

In this process, the reaction of Zn ions and ammonium acid carbonate proceeds according to the equation 3.1.

\[ 5\text{ZnSO}_4 + 10\text{NH}_4\text{HCO}_3 \rightleftharpoons \text{Zn}_5(\text{OH})_6(\text{CO}_3)_2(s) + 5(\text{NH}_4)_2\text{SO}_4 + 8\text{CO}_2↑ + 2\text{H}_2\text{O} \]

……………….. (3.1)

The complex formed decomposes upon calcining to ZnO according to the equation 3.2.

\[ \text{Zn}_5(\text{OH})_6(\text{CO}_3)_2 \rightleftharpoons 5\text{ZnO} + 2\text{CO}_2↑ + 3\text{H}_2\text{O}↑ \]

……………….. (3.2)

3.2.3 Method II– Solid-state pyrolytic method:

Zn(CH₃COO)₂.2H₂O (2.2g, 10mmol) and NaHCO₃ (2g, 23.8mmol) are mixed at room temperature. The mixture is pyrolysed at 300°C for 3 hours. The Zn(CH₃COO)₂.2H₂O is changed into ZnO nanoparticles, while the NaHCO₃ is changed into CH₃COONa and eventually washed away with deionized water. Consequently, white ZnO nanoparticles are obtained through the thermal decomposition process.

3.3 Characterization of ZnO

Bulk density (ASTM D 1895)

Bulk density is defined as the weight per unit volume of a material. It is primarily used for powders or pellets. The test can provide a gross measure
of particle size and dispersion, which can affect material flow consistency and
reflect packaging quantity.

**Procedure**

The small end of the funnel was closed with hand or a suitable flat
strip and pour 115 ± 5 cm³ samples into the funnel. The bottom of the funnel
was opened quickly and the material was allowed to flow freely into the cup.
If caking occurs in the funnel, the material may be loosened with a glass rod.
After the material has passed through the funnel immediately scrap off the
excess on the top of the cup with a straight edge without shaking the cup.

Bulk density= $M/V$ where, $M$ is mass of the sample and $V$ is the volume of
the container.

**Purity of zinc oxide**

Weighed accurately about 1.5g of the material and 2.5g of ammonium
chloride. Dissolved in 50 ml of standard hydrochloric acid (1N) and titrated
the excess of acid with standard sodium hydroxide solution (1N) using
methyl orange as indicator. Carried out a blank determination without using
the material. Purity of zinc oxide is calculated using equation 3.3.

Zinc oxide, percent by mass = $4.07 \frac{(B-A)}{M}$ .................. (3.3)

Where, $B = \text{Volume in ml of standard sodium hydroxide solution used in the}$
blank determination.

$A = \text{Volume in ml of standard sodium hydroxide solution used in the}$
titration with the material

$M = \text{mass in gm of the material taken for the test}$
Energy dispersive X-ray spectrometry

The chemical stoichiometry of ZnO nanoparticle is investigated with EDX, (EDS, HITACHI, and S-2400).

Transmission Electron Microscopy (TEM)

The morphology and particle size of zinc oxide were observed using transmission electron microscope (TEM). The transmission electron microscope (TEM) images were taken on a JEOL GEM 3010 Transmission Electron Microscope operating at 300kv.

XRD

X-ray powder diffraction (XRD) was used to characterize the zinc oxide powders. Particle size of the samples was determined using X-ray diffraction technique. XRD patterns were collected using Bruker, D8 advance rotaflex diffraction meter using CuK radiation and $\lambda = 1.5406\text{Å}$. Crystallite size is calculated using Scherrer equation 3.4.

$$\text{CS} = 0.9\lambda / \beta \cos \theta$$

Where, CS is the crystallite size, $\beta$ is full width at half maximum (FWHM) of an hkl peak at $\theta$ value.\(^{25}\)

Surface area

Surface area of the zinc oxide nanoparticles and conventional zinc oxide were measured using BET method. Surface area analysis was done using Micromeritics BJH surface analyzer tristar 3000. Measurements were carried out by nitrogen adsorption at liquid nitrogen temperature.

Fourier transform infrared spectroscopy

Fourier transform infrared spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm\(^{-1}\). Different functional groups and structural features in the molecule absorb at
characteristic frequencies. The frequency and intensity of absorption are the
indication of the band structures and structural geometry of the molecule.
FTIR spectra were taken using Thermo Avtar 370 spectrometer.

Thermogravimetric analysis

Thermogravimetric analyzer (TGA, Q-50, and TA Instruments) was
used to study the thermal stability of ZnO. Approximately 5 mg of the
samples were heated at the rate of 20°C/min to 800°C.

Differential scanning calorimetric analysis

The differential scanning calorimetry of natural rubber with ZnO is
recorded with a differential scanning calorimeter Q-100, TA instruments. The
energy changes associated with transitions were recorded in a temperature
range of -60 to 100°C. Samples of known weight encapsulated in standard
aluminium pans placed in the sample holder were subjected to the analysis.

3.4. Results and discussion
ZnO Characterization
3.4.1 Bulk density

The different types of ZnO prepared in the laboratory are
characterized by determining the bulk density. Determination of the bulk
density of the sample is the primary identification. The bulk density of the
prepared samples is shown in Table 3.1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Bulk density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO(c)</td>
<td>0.538</td>
</tr>
<tr>
<td>ZnO(p)</td>
<td>0.655</td>
</tr>
<tr>
<td>ZnO(s)</td>
<td>0.596</td>
</tr>
</tbody>
</table>
From the bulk density results, it is seen that ZnO prepared in the laboratory has high values when compared with those of the conventional ZnO. This may be due to reduction in particle size and difference in structure. It is observed that particle size is lower for ZnO(p) and ZnO(s) than that of ZnO(c).

### 3.4.2 Purity of zinc oxide

Purity of ZnO are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Purity of ZnO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO(p)</td>
<td>99.8</td>
</tr>
<tr>
<td>ZnO(s)</td>
<td>99.9</td>
</tr>
<tr>
<td>ZnO(c)</td>
<td>99.8</td>
</tr>
</tbody>
</table>

The purity of nano zinc oxide prepared from precipitation and solid state pyrolytic method is not less than 99.0 percent. This indicates the high purity of prepared nano zinc oxide and conventional zinc oxide.

### 3.4.3. Energy dispersive X-ray spectrometry

The chemical stoichiometry of ZnO nanoparticle was investigated with EDX (Figure 3.1 a, b), which affirmed an atomic ratio of Zn: O \(\cong 1:1\).

<table>
<thead>
<tr>
<th>Element</th>
<th>Element %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>19.66</td>
<td>24.21</td>
</tr>
<tr>
<td>Zn</td>
<td>80.34</td>
<td>75.79</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**Figure 3.1 a:** EDX patterns of ZnO(p) nanoparticles
3.4.4 Transmission electron microscopy studies

![TEM image of ZnO nanoparticles: precipitation method](image)

![TEM image of ZnO nanoparticles: solid-state pyrolytic method](image)

Figure 3.2a and Figure 3.2b show TEM images of zinc oxide prepared by precipitation method and solid state pyrolytic method. It shows that ZnO particle size prepared by precipitation method is having an average particle size of 20 nm and that prepared by pyrolytic technique have an average particle size of 30 nm.

3.4.5 X-ray powder diffraction studies

![XRD patterns of ZnO](image)

Figure 3.3 XRD patterns of ZnO prepared by (a) method 1 (b) method 2 (c) Conventional ZnO

<table>
<thead>
<tr>
<th>Element</th>
<th>Element %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>19.66</td>
<td>24.57</td>
</tr>
<tr>
<td>Zn</td>
<td>80.34</td>
<td>75.43</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 3.1.b: EDX patterns of ZnO(s) nanoparticles
Figure 3.3 shows the XRD patterns of ZnO samples. It is very clear from the above figures that the major reflections between 30° and 40° (2θ values) indicate more crystalline regions in the zinc oxide sample. Also the less intense peaks at 48°, 57°, 63° and 70° (2θ values) indicate the high crystallinity of ZnO samples. The detailed analysis of the XRD and the assignments of various reflections are given in the Table 3.3.

**Table 3.3 Analysis of XRD and the assignments of various reflections of ZnO**

<table>
<thead>
<tr>
<th>Sample</th>
<th>d (Obs)</th>
<th>FWHM</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO(p)</td>
<td>2.455</td>
<td>0.471</td>
<td>19.36</td>
</tr>
<tr>
<td>ZnO(s)</td>
<td>2.463</td>
<td>0.444</td>
<td>20.52</td>
</tr>
<tr>
<td>ZnO(c)</td>
<td>2.451</td>
<td>0.236</td>
<td>38.66</td>
</tr>
</tbody>
</table>

Crystallite size of the ZnO samples was calculated using Scherrer’s formula. The crystallite size for zinc oxide prepared from method 1 and 2 ranges from 15 nm–30 nm and the crystallite size for conventional zinc oxide range from 40 nm to 60 nm.

**3.4.6. Surface area**

**Table 3.4 Surface area of zinc oxide**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Samples</th>
<th>Surface area (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Conventional zinc oxide</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Zinc oxide from method 1</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>Zinc oxide from method 2</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 3.4 shows the surface area for conventional zinc oxide and zinc oxide nanoparticle prepared from method 1 and 2 respectively. The surface area is found to be about 8 times high for ZnO from precipitation method and about 3 times high for ZnO from pyrolysis method compared to conventional zinc oxide.
3.4.7. Fourier transform infrared spectroscopy

Figure 3.4 FTIR spectrum of ZnO sample prepared by (a) method 1 (b) method 2 (c) Conventional ZnO

Figure 3.4 shows the IR spectra of ZnO samples. The peak at 450 cm\(^{-1}\) shows the distinct stretching vibration of zinc oxide.

3.4.8. Thermogravimetric analysis

Figure 3.5 Thermogravimetric analysis of zinc oxides (a) ZnO(p) (b) ZnO(s)

From the figure it is seen that TGA curve for the nano ZnO from pyrolytic method shows the absence of any actual loss in weight. This indicates the thermal stability and high purity of nano ZnO(s). The TGA curve for the nano ZnO from precipitation method shows a very small decrease in weight percentage at around 190°C-250°C. As reported by Morishige et al.\(^{26}\) the peaks at around 250°C may be caused by the decomposition of the condensation dehydration of the hydroxyls.
3.4.9 Differential scanning calorimetry

![DSC thermograms](image)

**Figure 3.6** DSC thermogram of natural rubber with (a) ZnO(p) (b) ZnO(s) and (c) ZnO(c)

The differential scanning calorimetric study of the natural rubber with prepared nano zinc oxides and with conventional ZnO were done at low temperatures to study the change in glass transition temperature (Tg) during the zinc oxide incorporation. The DSC thermogram of natural rubber with ZnO(p), ZnO(s) and ZnO(c) are shown in the figure 3.6(a),(b),(c) respectively. It is clear from the thermograms that there is no change in the glass transition temperature after the ZnO incorporation, which indicates that the incorporation of zinc oxides will not affect the glass transition temperature of natural rubber.
3.5 Conclusions

1. Nano zinc oxides could be successfully prepared by precipitation and pyrolytic methods and their yield is high.

2. Bulk density of prepared zinc oxides is greater than that of conventional zinc oxide.

3. Surface area of prepared zinc oxides is greater than that of conventional zinc oxide.

4. Zinc oxides prepared in the laboratory are highly pure.
3.6 References


Chapter 3


