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Effect of crystallite size of zinc oxide on the mechanical, thermal and flow properties of polypropylene/zinc oxide nanocomposites

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ABSTRACT

ZnO nanoparticles were prepared using zinc chloride and sodium hydroxide in chitosan medium. Prepared ZnO (NZO) and commercial ZnO (CZO) was characterized by scanning electron microscopic and X-ray diffraction studies. PP/ZnO nanocomposites were prepared using 0–5 wt% of zinc oxide by melt mixing. It was then compression moulded into films. Transparency of the composite films were improved by reducing the crystallite size of ZnO. Melt flow index studies revealed that NZO increased the flow characteristics of PP while CZO decreased. X-ray diffraction studies indicated α-form of isotactic polypropylene. An increase in mechanical properties, dynamic mechanical properties and thermal stability of the composites were observed by the addition of ZnO. Uniform dispersion of the ZnO was observed in the scanning electron micrographs of the tensile fractured surface of composites.

1. Introduction

Polymer nanocomposites have attracted great attention due to their enhanced mechanical strength and thermal properties at low filler loadings [1–3]. Now a days, nanostructured versions of conventional inorganic fillers are used in plastic composites. There are many reports on the enhancement of properties of polymer by adding inorganic nanofillers [4–7]. Recently, nanocomposites based on PP matrix constitute a major challenge for industry as they represent the route to substantially improve the mechanical and physical properties of PP. PP is one of the most widely used thermoplastic polymers due to its good physical and mechanical properties as well as the ease of processing at a relatively low cost. There are a number of investigations on the PP nanocomposites filled with different types of fillers such as carbon nanotubes [8–10], nanoclay [11,12], talc, mica and fibrous fillers.

The enhanced properties are due to the synergistic effects of nanoscale structure and interaction of fillers with polymers. The size and structure of the dispersed phase significantly influence the properties of polymer nanocomposites [13]. Recently, there are some studies on the influence of micro- and nano-sized ZnO on the properties of PP [14,15]. Morphology of the filler also plays a major role on the properties of a polymer.

In this work, we investigated the effect of crystallite size and morphology of ZnO on mechanical, dynamic mechanical, transparency, morphology, thermal and flow properties of the PP/ZnO composites prepared by melt mixing.

2. Experimental

2.1. Materials

Isotactic PP homopolymer (REPOL H200MA) with melt flow index of 25 g/min was supplied by M/s. Reliance Industries limited.

2.2. Methods

2.2.1. Preparation of zinc oxide

Zinc oxide nanoparticles were prepared by reacting zinc chloride and sodium hydroxide in chitosan medium. In this method zinc chloride (5 g in 500 ml 1% acetic acid in water) was added to chitosan (5 g in 500 ml 1% acetic acid in water) with vigorous stirring using mechanical stirrer. This was allowed to react for 24 h. During this period, stabilization of the complex take place. Then sodium hydroxide (25 g in 500 ml 1% acetic acid in water) was added drop wise from burette to the above solution with stirring using mechanical stirrer. The whole mixture was allowed to digest for 12 h at room temperature. This was to obtain homogeneous diffusion of OH^- and Cl^- to the matrix. The precipitate formed was washed several times with distiled water until complete removal

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of sodium chloride and dried at 100 °C. Then it was calcined at 550 °C for 4 h.

2.2.2. Preparation of PP/ZnO composites: compression moulding

The melt compounding was performed using a Thermo Haake Polylab system operating with counter rotating screws at 40 rpm for 8 min at 170 °C with a capacity of 60 cm^3. Composites of different concentrations (0–5 wt%) of ZnO were prepared. The hot mix immediately pressed after mixing using a hydraulic press. The samples were then made into films using compression moulding at 180 °C for 6 min in an electrically heated hydraulic press.

2.2.3. Mechanical properties of PP/ZnO composites

Mechanical properties of the compression moulded samples of PP and PP/ZnO composites were studied using a Universal testing machine (UTM, Shimadzu, model-AG1) with a load cell of 10 kN capacity. The specimens used were rectangular strips of dimensions 10 × 1 cm. The gauge length between the jaws at the start of each test was adjusted to 40 mm and the measurements were carried out at a cross-head speed of 50 mm/min (ASTM D 882).

2.2.4. Dynamic mechanical analysis (DMA)

DMA studies were carried out on rectangular shaped specimens of dimensions 3 × 1 cm by temperature sweep (temperature ramp from 30 °C to 150 °C at 3 °C/min) method at a constant frequency of 1 Hz. The dynamic storage modulus, loss modulus and tanδ were measured.

2.2.5. Scanning electron microscopy

The morphology of the tensile fractured surface of PP and composites was studied using scanning electron microscope (JOEL model JSM 6390 LV).

2.2.6. Thermogravimetric analysis

Thermogravimetric analyzer (TGA Q-50, TA instruments) was used to study the effect of ZnO on the thermal stability of PP. Approximately 10 mg of the samples were heated at the rate of 20 °C/min from ambient to 800 °C in nitrogen atmosphere.

2.2.7. Melt flow index (MFI) measurements

MFI of the composites were studied using CEAST melt flow modular line indexer (ITALY) at 190 °C and 2.16 and 5 kg wt. A preheating time of 6 min is given before each experiment. The weight of the substance extruded in 10 min in grams is then measured.

2.2.8. X-ray diffraction studies

X-ray diffraction studies were carried out using Rigaku Geigerflex at wavelength Cu Ka = 1.54 Å. Crystallite size of ZnO was calculated using Debye Sherrer equation:

$$CS = 0.9\lambda/\beta\cos\theta$$

where CS is the crystallite size, β is the full width at half-maximum of an hkl peak at θ value, θ is the half of the scattering angle.

3. Results and discussion

3.1. X-ray diffraction studies of zinc oxide

XDD pattern of NZO and CZO is shown in Figs. 1a and 1b respectively. The figures show the characteristics peaks of hexagonal crystal structure. The peaks obtained correspond to (100), (002), (101), (102), (110), (103), (112), (201), (004), (202), (104) planes. The (101) plane is most prominent. The crystallite size of ZnO are calculated using Debye Sherrer equation is 13.4 nm for NZO and 29.2 nm for CZO.

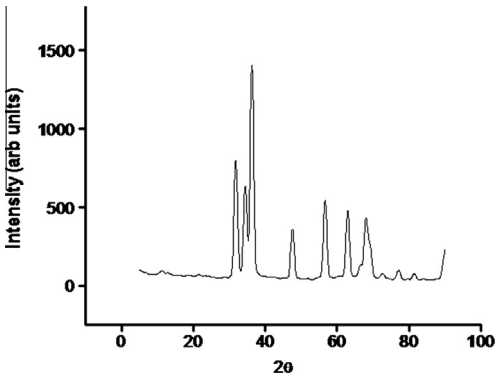

Fig. 1a. XRD pattern of ZnO prepared in chitosan medium.

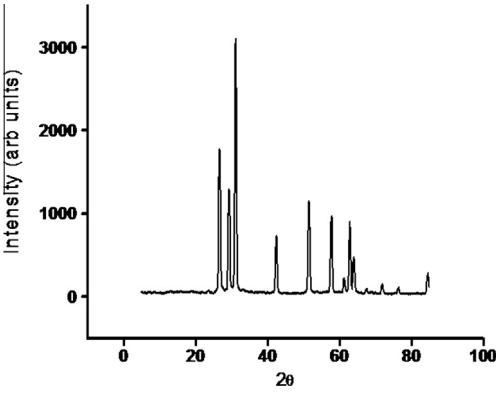

Fig. 1b. XRD pattern of commercial ZnO.

3.2. Scanning electron micrographs of zinc oxide

Scanning electron micrographs of two ZnO which is taken for the study are shown in Fig. 2. Similar morphologies and different particle sizes are seen in SEM. ZnO shown in Fig. 2a depicted as NZO and Fig. 2b is denoted as CZO. Both show sphere like morphology and small particles are observed in the scanning electron micrographs of NZO when compared to CZO.

3.3. Mechanical properties of PP/ZnO composites

Figs. 3 and 4 show variation in tensile strength and modulus of PP with ZnO content. The incorporation of ZnO in the PP matrix result in an increase in the tensile strength and modulus. It reaches maximum at 1.5 wt% concentration of ZnO and then decreases. In the case of PP with NZO the tensile strength gets increased from 31.75 to 44.37 N/mm^2 and tensile modulus from 1105.35 to 1897.02 N/mm^2 at 1.5 wt% NZO. CZO filled PP shows an increase in tensile strength from 31.8 to 41.2 N/mm^2 at 1.5 wt% CZO and tensile modulus from 1105.75 to 1422.9 N/mm^2 at 0.5 wt% of CZO. The increase in properties may be due to the interface interaction between nanoparticles and a polymer matrix that can transfer stress, which is beneficial for the improvement of the tensile strength of composite films. However, with increasing content of nanoparticles, aggregation occurs, which leads to a decrease in the contact area between the nanoparticles and polymer matrix and results in the formation of defects in the composites.