Abstract

Material science in the last few decades has gained immense importance as it involves interdisciplinary activities. From materials perspective, nanoscience and nanotechnology is an emerging technology and is currently being harnessed for various applications in different domains such as electronics, optics, mechanics, biology and environment etc.

Nanocomposites are a new class of materials that have been developed in the recent past. A composite material is a combination of two or more materials having entirely different and unique physical and chemical properties that are distinguished at the interface of the materials. Polymer nanocomposites are defined as materials in which nanoparticles in the size range of 1 -100 nm with wide variety of morphology viz. nanoplates, nanotubes or nanoclusters are dispersed in the polymer matrix.The presence of few weight percent of these nanoparticles have remarkable impact on the physical, chemical, mechanical, thermal, magnetic and electrical properties of the resultant nanocomposites.

The main objective of this thesis work is to synthesize transition metal sulphide based nanocomposites in thermally stable polyphenylenesulphide (PPS) polymer matrix and to study these nanocomposites for crystallographic, morphological, optical, thermal and magnetic properties by various characterization techniques.

In this work, environmentally benign solid -solid route has been explored for synthesis of transition metal sulphides viz. zinc, cobalt and manganese based polymer nanocomposites. Throughout this study, we have intentionally chosen PPS as the polymer as it has got certain inherent characteristics. The material is thermoplastic in nature and can be moulded in any shape; it is thermally stable, chemically resistant and not soluble in any of the solvents at room temperature. These inherent characteristics when coupled with embedded semiconductor nanoparticles can be potentially used for device fabrication which can withstand very harsh and demanding environmental conditions.

The thesis work is presented in the form of six chapters. Following is the brief outline of thesis:

Chapter 1 elaborates the general introduction and the literature survey conducted during the course of this work. Nanocomposites containing

semiconductor nanoparticles embedded in the polymer matrix exhibit unique properties and are explored as an alternative option for possible applications in emerging technologies for sensors, magnetic devices, optoelectronics and catalysis. It is possible to combine the characteristics of materials that are profoundly different from one another by synthesizing nanocomposite systems. The transition metal sulphides are promising materials due to their wide range of applications in optoelectronics, display panels, light emitting diodes, lasers, photovoltaic devices, biological labelling and diagnostics etc.The metal sulfides exhibit a vast range of electrical and magnetic properties and are potential materials from the standpoint of both scientific interest and practical applications.
This chapter also deals, in brief, the different methods available for the synthesis of metal sulphide nanoparticles and their polymer nanocomposites. Moreover, it describes in short the significance of the numerous techniques used for characterizing the resultant nanocomposites. The different characterisation techniques used for this research work are summarised in this chapter. X-ray diffraction (XRD) was used for crystallographic studies and to ascertain the phase of material formed. For morphological and microstructural analysis, Field Emission Scanning Electron Microscopy (FESEM) and High Resolution Transmission Electron Microscopy (HRTEM) were employed. UV–visible spectrophotometry (UV-Vis) and UV-diffuse reflectance (UV-DRS) were used for optical band gap determination. Photoluminescence spectroscopy (PL) was used for study of emission characteristics. Thermal changes in the nanocomposites were studied using Differential scanning calorimetry (DSC) and Thermo gravimetric analysis (TGA). Vibrating sample magnetometer (VSM) was utilised to determine the magnetic behaviour of the synthesized cobalt based nanocomposites.

Chapter 2 presents the work related to synthesis of Zinc sulphide (ZnS) quantum dots in polyphenylenesulphide matrix. A series of experiments were carried out using two different schemes. In the first one, the zinc metal precursors viz. zinc nitrate and zinc acetate were directly heated with the PPS by varying the molar ratio of the polymer (1:1,1:5,1:10,1:15) to see whether the sulphur from the polymer reacts with the zinc from the metal precursor to obtain the resultant sulphide containing nanocomposite. In the other scheme, zinc acetate was used as the metal precursor and thiourea was used as an external chalcogen source along with polymer. All the reactions were carried out at the melting temperature of PPS i.e.285°C under normal atmospheric conditions. The resultant nanocomposites obtained were then characterized by the techniques such as XRD, FESEM, TEM, UV-DRS, PL, DSC, TGA etc. From the results, it was evident that under the given reaction conditions the sulphur from the polymer did not react with the metal precursor and the product obtained was zinc oxide embedded in the polymer matrix, whereas, with the chalcogen enriched reaction, (using thiourea) it was possible to obtain zinc sulphide quantum dots (QDs) in the range of 3-5nm. The zinc sulphide formed was cubic in shape in the resultant nanocomposites.

Chapter 3 explains the work pertaining to synthesis of mixed phase of cobalt sulphide-oxide in polymer matrix. The mixed phase of cobalt sulphide oxide was obtained by carrying out the reaction between the sulphur moieties from the polymer with the metal precursor. Cobalt nitrate and PPS were reacted in varying molar ratio viz.1:1, 1:5, 1:10 and 1:15 and the admixtures obtained were then heated at the melting temperature of the polymer (285ºC) for six hours. The resultant products were characterized by techniques such as XRD, FESEM, TGA, DSC, DRS and HRTEM. From the results, it was inferred that with 1:1 and 1:5 ratios, the material formed was cobalt oxide having mainly Co_3O_4 phase, whereas, for the 1:10 and 1:15 ratio mixed phase of cobalt oxide (Co_3O_4) and cobalt sulphide (Co_3S_4) was obtained. The DSC analysis indicated a characteristic lowering in the melting temperature of the resultant nanocomposites. For the 1:10 and 1:15 ratio, the sulphur from the polymer partially reacted with the metal precursor and as a result corresponding metal sulphide was formed along with the metal oxide in the polymer matrix.

Chapter 4 describes single phase synthesis of cobalt sulphide (CoS) in the polymer matrix. On the basis of the results obtained from the earlier work (chapter no.2), the reactions were carried out by using cobalt acetate as a metal precursor, PPS as the polymer and thiourea as a chalcogen source. The molar ratio of the chalcogen was varied for all the reactions.

The resultant nanocomposites were characterized using different physico-chemical techniques**.** As cobalt sulphides are dilute magnetic materials and single phase (CoS) was obtained, the resultant nanocomposites were subjected to magnetic studies by Vibrating Sample Magnetometer (VSM). The results showed the magnetic nature of the material formed for all the experiments. The phase pure cobalt sulphide synthesized for comparative study by this technique showed superparamagnetism, whereas, the nanocomposites showed paramagnetic and ferromagnetic behaviour. Lowering in melting temperature was observed for the resultant nanocomposites as compared to the virgin polymer.

Chapter 5 covers the synthesis and characterization of manganese sulphide based nanocomposites. Based on the results from chapter 2 and 4, chalcogen enriched reactions were carried out using manganese acetate as a metal precursor, PPS as polymer and thiourea as a chalcogen source for *in-situ* synthesis of manganese sulphide nanoparticles in thermally stable polyphenylene sulphide (PPS) matrix. X-ray diffraction revealed the formation of mixed phases of α- MnS and γ- MnS. FESEM and HRTEM images showed the formation of cubic as well as spherical nanoscale morphology depending upon the reaction conditions.

Chapter 6 describes the summary of the work conducted. The outcome of the thesis and future scope of the work have been also discussed. The studies revealed that incorporation of semiconductor nanoparticles in the polymer matrix leads to entirely different set of properties as compared to the virgin polymer. This solid-solid method being relatively simple can be explored in future using other thermoplastic polymers as matrix.