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In-situ fabrication of cobalt oxide / sulphide mixed phase nanoparticles in Polyphenylenesulphide matrix

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A novel approach for the in-situ fabrication of combined cobalt oxide / sulphide nanoparticles in sulphur containing polymer polyphenylenesulphide (PPS) by polymer inorganic solid-solid reaction technique is reported here. At present, there is considerable interest in polymer-metal chalcogenides / oxides based nano-composites on account of their optical, magnetic, electronic and catalytic properties. We have demonstrated the suitability of solid-solid reaction methodology by reacting commonly available cobalt precursors with engineering thermoplastic PPS. The cobalt precursor was reacted with PPS in 1:1, 1:5, 1:10, and 1:15 molar ratios, respectively, by heating the mixture at the melting temperature of the polymer (285 °C) for six hours. The resultant products were characterized by X-ray diffractometry (XRD), Field-emission scanning electron microscopy (FESEM), Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), Diffuse reflectance spectroscopy (DRS) techniques and High resolution transmission electron microscope (HRTEM). The shift in melting temperature of PPS was observed. Increase in absorption peak is observed in the range of 320 to 370 nm with the increase in PPS concentration. Resultant nanoparticles of cobalt sulphide and cobalt oxide embedded in the PPS matrix showed spherical and distorted rod like morphology.

Keywords : Polymers, nanocomposites, cobalt sulphide /oxide, solid-solid reaction.

1. Introduction : Polymer nanocomposites are material wherein small amounts of nanofillers are dispersed in the polymer matrix. The presence of nanoparticles in the polymer matrix has a significant impact on the properties of the polymer and profound changes are observed in the physical, chemical, mechanical and electrical properties of the polymer. Currently polymer nanocomposites have emerged as a new category of materials with diversified application in optoelectronics, semiconductor, photovoltaic and other applications [1]. The transition metal sulfides nanomaterials have been the focus of considerable interest due to their unique optical and electrical properties and their wide variety of potential applications in nanoscale devices such as electroluminescence and nonlinear optical devices

[2]. Cobalt sulphide / oxides are one of the important class of material which have found direct applications in solar selective coatings, photo detectors, solar cells, biological labeling, Li- Ion battery, and magnetic devices etc. [3 - 4]. Cobalt sulphide / oxides are present in various different stable phases such as CoS, Co₃S₄, CoS₂, Co₉S₈, CoO, Co₃O₄ etc. Till date numerous techniques have been used for the synthesis of nanoscale cobalt sulphide and oxide nanoparticles separately such as anodized alumina films for growth of cobalt disulphide nanowires by application of two electrical fields [5], colloidal synthesis of hollow nanocobaltsulphide spheres [6], hollow metal oxides and sulphides by laser ablation in liquid [7], hydrothermal technique [8], biomolecule-assisted hydrothermal process [9], slow formation of cobalt sulfide in montmorillonite by solid- solid reaction [10], coprecipitation method for generation of cobalt oxide nanoparticles [11 - 12], chemical bath deposition of thin films [13], Co₃O₄ nanowalls by direct heating of cobalt foil on hot plate [14], ring opening metathesis polymerization (ROMP) to synthesize cobalt di-block copolymer etc. [15].

Herein, we present a single step and relatively rapid inorganic-polymer solid-solid reaction route for in-situ fabrication of nanoscale cobalt sulphide / oxide nanoparticles in the polymer matrix of Polyphenylenesulphide [PPS]. We have been able to extract the sulphur moiety from the polymer and react it with the metal precursor by increasing the ratio of the polymer. Till date, use of this technique has been reported for the synthesis of other metal chalcogenides (Ag₂S, PbS) [16 - 17]. However, no attempts have been reported for cobalt oxide/sulfide nanostructures. The polymer PPS, has been intentionally chosen as it is a semi-crystalline material with a low glass transition temperature and inherently it possess excellent blend of characteristics such as high temperature resistance, chemical resistance and dimensional stability.

2. Experimental Work :

2.1 Materials : Polyphenylenesulphide (PPS) with number average molecular weight 10,000 having glass transition temperature (T_g) 88 °C with melting temperature of 285 °C was obtained from Sigma Aldrich, while, cobalt nitrate was obtained from Merck and was used as received.

2.2 Synthesis of cobalt sulphide/ oxide in PPS matrix : The material was synthesized by reacting the precursors in the molar ratio of 1:1, 1:5, 1:10, 1:15 respectively, for cobalt nitrate and PPS. The materials for each molar ratio were mixed in agate mortar and pastel and a few drops of acetone were added for proper wetting of the reactants. The admixtures thus formed were then heated at the melting temperature of the polymer at 285 °C for six hours in a muffle furnace under normal atmospheric conditions.

2.3 Characterisation : The phase identification of the resultant powder products was conducted using X-ray diffractometer (Bruker D5005), using CuK α radiation. Material in powdered form was used for such analysis. The particle size and the surface morphology of the samples were investigated by HRTEM with FEI Tecnai G², at an acceleration voltage of 200KV. The samples for HRTEM were prepared by dispersing fine powder of the resultant product in isopropyl alcohol. The dispersion was then coated on carbon coated grid for further analysis. The surface morphology was determined using FESEM, Hitachi S-4800, the solid samples were used as such for determination. In order to prevent the charging effect associated with FESEM, the samples were taken on carbon tape and coated with thin Au film. The DSC analysis was carried out using Mettler Toledo Model 822 at the heating rate 10 °C/min, under nitrogen atmosphere. Thermogravimetric analysis was done on Mettler Toledo TGA/SDTA 851 at the heating rate of 10 °C/ min. The UV-DRS spectra were recorded on UV 3600, Shimadzu UV-VIS-NIR spectrophotometer for solid powder samples.

3. Results and Discussions :

3.1 X-Ray Diffraction Analysis [XRD] : The XRD pattern obtained for the resultant products are depicted in Figure (1). The patterns in Figure 1.a and b correspond to the 1:1 and 1:5 ratio of cobalt nitrate to PPS indicating the formation of Co_3O_4 . The diffraction peak at 2θ value of 36.8, 44.8, 59.3 and 65.2 respectively corresponds to the (hkl) planes of (311), (400), (511) and (440) indicating the formation of cubic Co_3O_4 [JCPDS no.42-1467]. For samples corresponding to 1:10 and 1:15 precursor to PPS ratio, mixed phases of Co_3S_4 and Co_3O_4 were obtained with dominance of Co_3O_4 phase. This substantiates our observation that the sulphur moiety from the polymer has reacted with the metal precursor. The diffraction peak at 26.7, 31.4, 38.1, 55.1 correspond to cubic Co_3S_4 , [JCPDS no.47-1738] whereas the peak at 36.8 corresponds to Co_3O_4 . The peak observed at 2θ value of 20.5 °C in Figure 1. (b), (c) and (d) matches with the peaks for PPS.

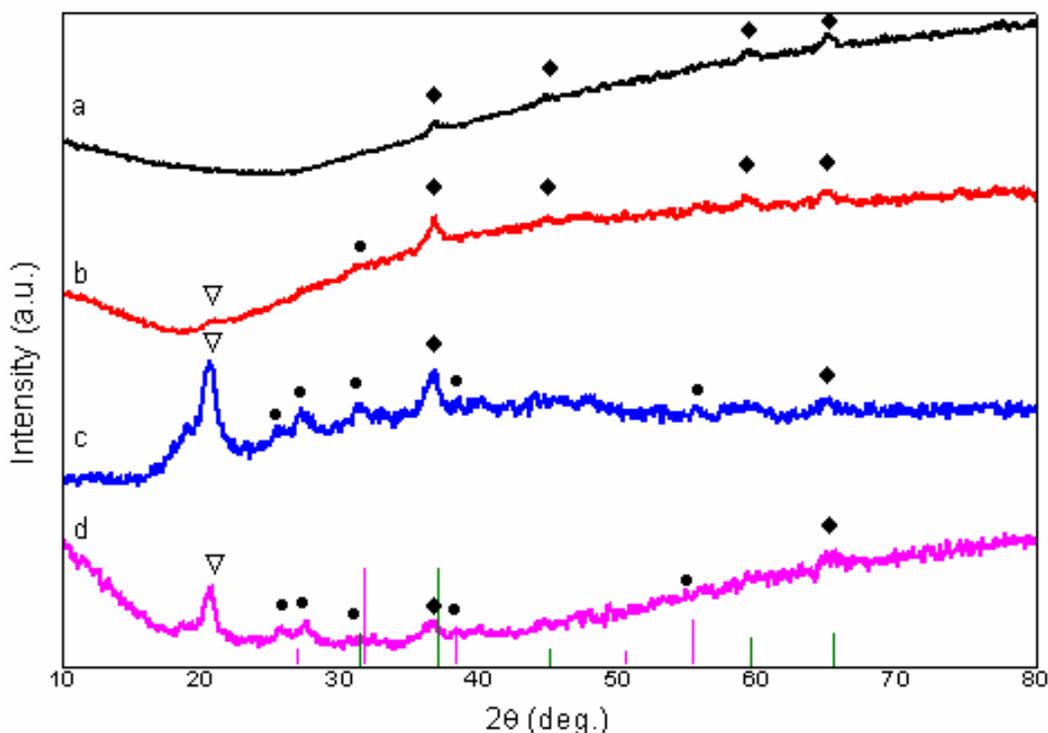


Figure (1) : XRD patterns of Co_3O_4 and Co_3S_4 , samples of Cobalt to PPS ratios where a) 1:1, b) 1:5, c) 1:10, d) 1:15 (♦) indicates oxide peaks, (●) indicates sulphide peaks and (▽) corresponds to PPS peak. Pink line indicates the JCPDS No. (47-1738) corresponding to Co_3S_4 and green line indicates the JCPDS No. (42-1467) corresponding to Co_3O_4 .

3.2 Field Emission Scanning Electron Microscopy [FESEM] : The FESEM for the various ratios of cobalt precursor to polymer for the resultant nanocomposites are depicted in Figure (2). Formation of irregular shape morphology having size in the range of 30 nm to 100 nm is observed for the 1:1 ratio (Figure 2a). Uniform distribution of the Co_3S_4 and Co_3O_4 is observed for the higher proportion of PPS (Figure 2c and d). In comparison to all the other prepared compositions, the composition with 1:10 cobalt to polymer shows uniform distribution with the average particle size of 30 nm.

3.3 High Resolution Transmission Electron Microscope [HRTEM] : The HRTEM analysis is shown in Figure (3). The formation of nanoparticles embedded in the PPS matrix is observed for the Co_3O_4 prepared using 1:1 ratio. The average particle size for the resultant composition was found to be in between 5 to 10 nm (Figure 3a,3b). The SAED pattern indicates the formation of cubic Co_3O_4 , which is also evident from the XRD analysis for the resultant nanocomposites (Figure 3c). The interplanar

spacing of 0.24 and 0.28 corresponds to [311] and [220] planes, respectively, thereby indicating the formation of crystalline Co_3O_4 . HRTEM analysis of nanocomposites prepared using 1:5 ratio also indicates formation nano sized Co_3O_4 having size in the range of 5 to 10 nm (Figure 3d, 3e). Slight agglomerations of nano particles are observed. The SAED pattern and the lattice spacing (Figure 3f) also confirms the formation of cubic Co_3O_4 and also supports the XRD analysis. For higher ratio (1:10 and 1:15) the formation of distorted rod like morphology was observed (Figure 3g, 3j). The SAED pattern and lattice spacing indicates the formation of Co_3S_4 (Figure 3h, i and 3k, l) with lattice spacing of 0.2855 matching well with [311] plane of Co_3S_4 .

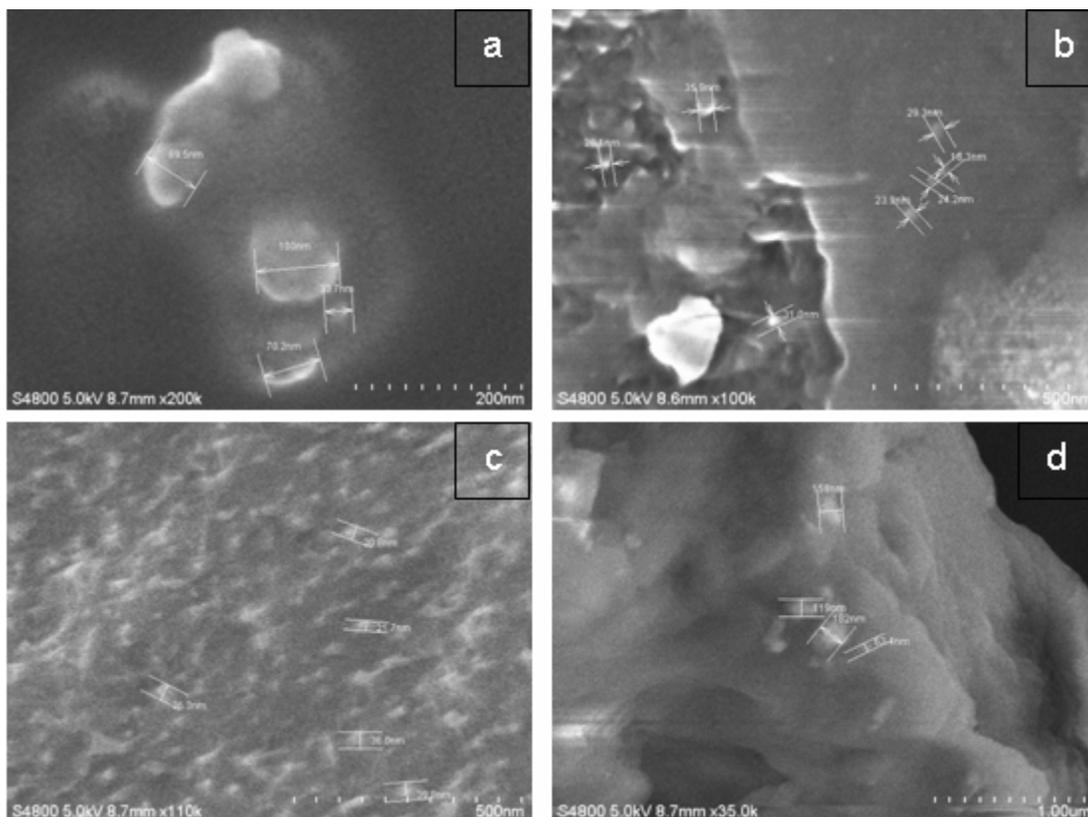


Figure (2) : FESEM images for the resultant products for different ratios of Cobalt Nitrate precursor to PPS where a) 1:1, b) 1:5, c)1:10 and d)1:15.

3.4 Differential Scanning Calorimeter (DSC) Analysis : The changes in the polymer structure were studied by carrying out the DSC analysis for the resultant nanocomposites. The DSC patterns are shown in Figure (4) for all the compositions. A shift is observed in the melting temperature of the polymer on incorporation of the nanoparticles. The neat PPS showed the melting temperature as a doublet with major endothermic peak at 280 °C and the other smaller peak at 310 °C [Figure 5e], whereas for 1:1 ratio there is a small endothermic peak at 191 °C, this can be attributed to the cyclisation of PPS, which is also evident from the XRD [Figure 1a] and indicates that the polymer matrix is altered. The melting temperature for the 1:5 is observed in the form of a doublet with the peaks at 260 °C and 290 °C, [Figure 4b] and the same phenomenon is observed for the 1:15 ratio with the melting temperature at 270 °C and 290 °C [Figure 4d]. Broadening in the melting peak is also observed. This may be due to the large difference in the glass transition and the melting temperature of PPS. For the 1:10 ratio a single endothermic peak is observed at 270 °C [18].

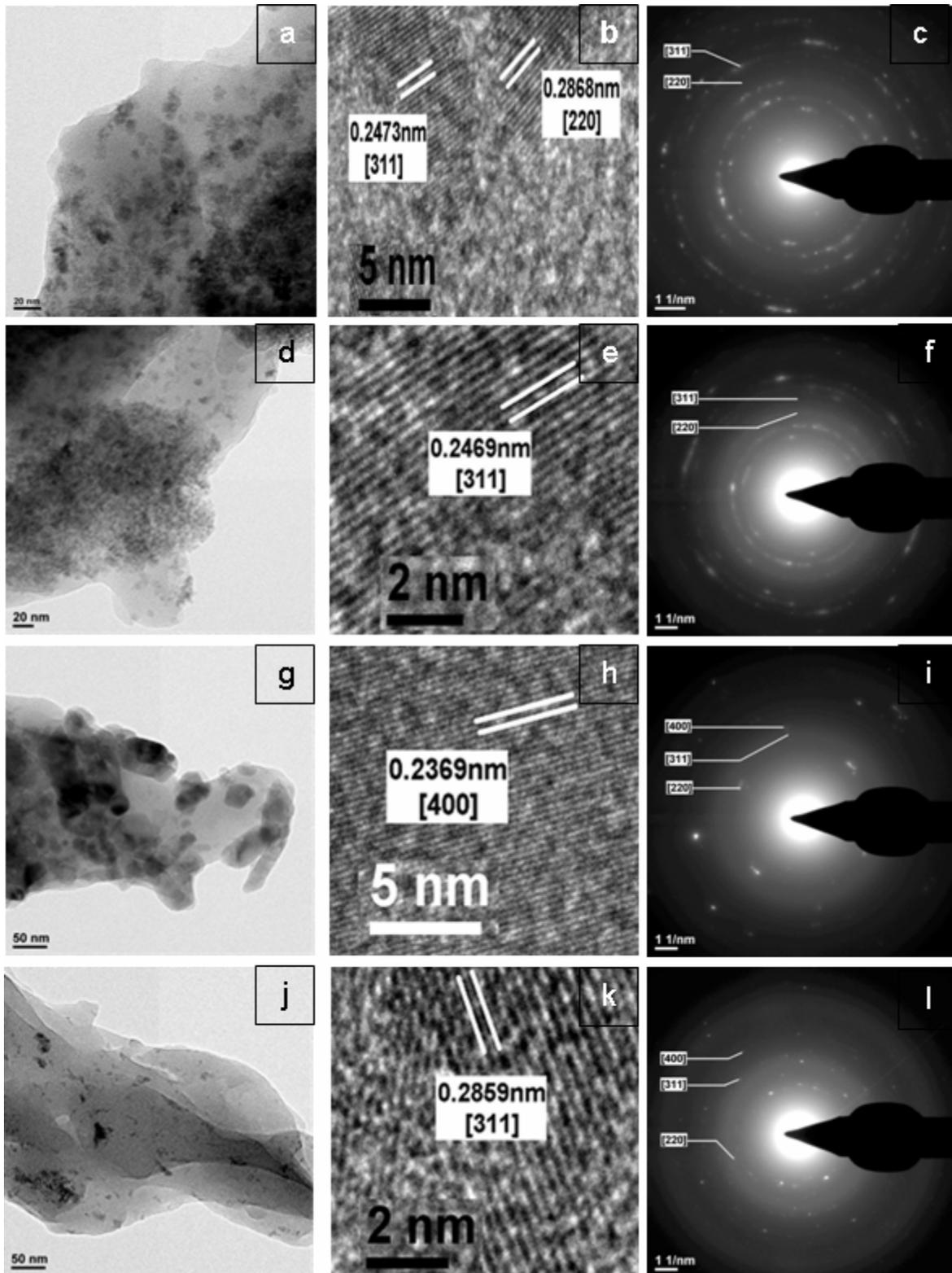


Figure (3) : HRTEM images for the material for different ratios of Cobalt Nitrate precursor to PPS where a) 1:1, b) 1:5, c)1:10 and d)1:15.

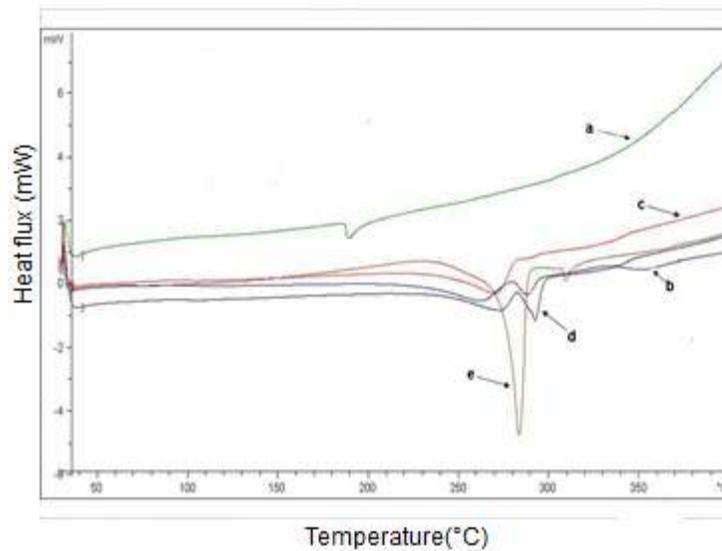


Figure (4) : DSC for the materials for different ratios of Cobalt Nitrate precursor to PPS where a) 1:1, b) 1:5, c) 1:10, d)1:15 and e) pure PPS.

3.5 Thermogravimetric Analysis [TGA]

The TGA data for the prepared nanocomposites is depicted in Figure (5). The polymer as such shows a higher weight loss as compared to the prepared nanocomposites Figure (5e). At 605°C, 40% weight loss is observed for the neat PPS, whereas for the 1:1, 1:5, 1:10 & 1:15 [Figure 5 a, b, c, d] cobalt to precursor ratio, the weight loss observed is 26, 32, 37 and 34 % respectively. The lower weight loss for the 1:1 and 1:5 ratio can be attributed to the formation of Co_3O_4 , whereas slightly higher weight loss observed for 1:10 and 1:15 can be assigned to the formation of mixed phases of Co_3S_4 and Co_3O_4 . The overall thermal stability of the polymer has increased due to presence of nanoparticles in the matrix.

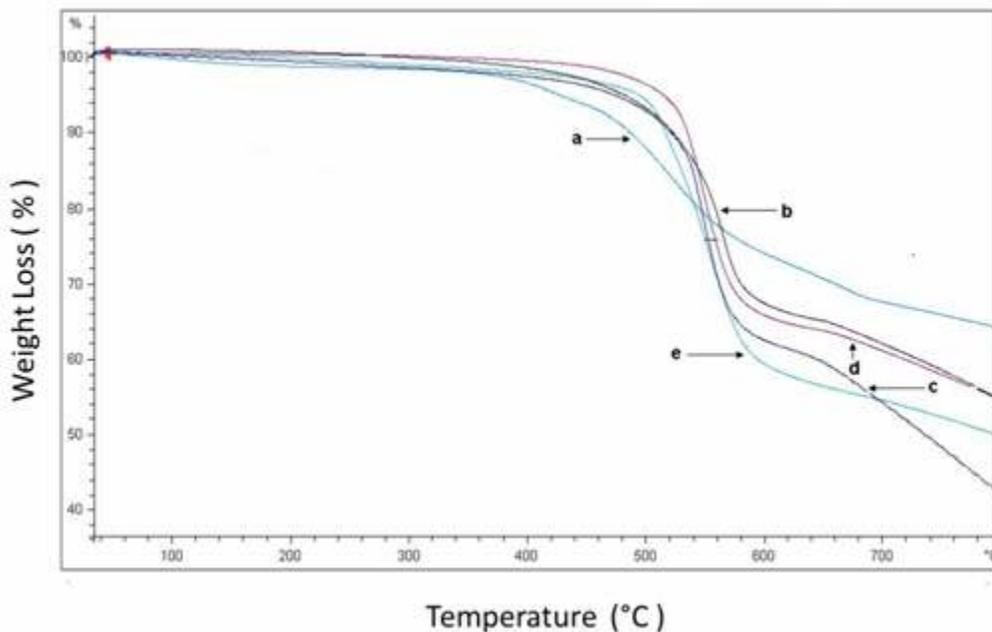


Figure (5) : TGA for the materials for different ratios of Cobalt Nitrate precursor to PPS where a) 1:1, b) 1:5, c) 1:10, d)1:15 and e) pure PPS.

3.6 Ultraviolet Diffuse Reflectance Spectra (UV-DRS) : DRS spectra of prepared nanocomposites are depicted in Figure (6). PPS indicates the absorption edge at 390 nm. The band edge of the nanocomposites was located at ~ 790 nm (1.5 eV), had a blue shift of approximately 288 nm with respect to the band gap of 1078 nm (1.15 eV) for bulk Co_3S_4 . The hump centered at 750 nm indicates the band gap of Co_3O_4 and Co_3S_4 which are almost in the same range [19 - 20].

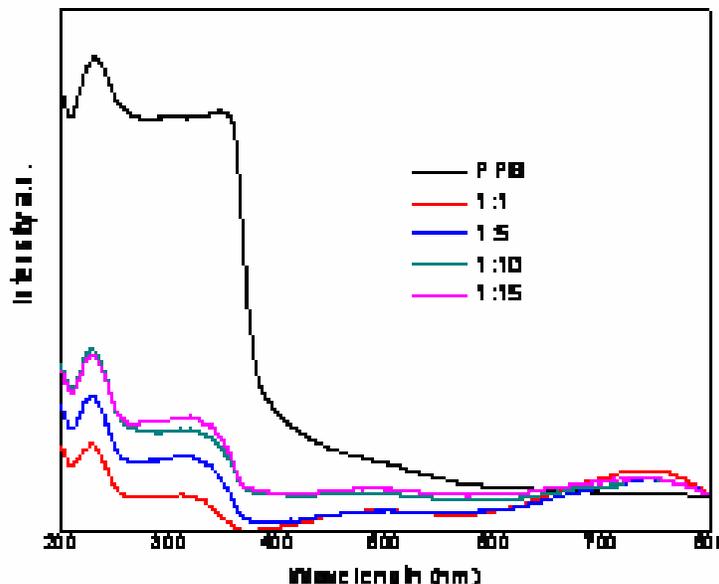


Figure 6: DRS of Cobalt to PPS ratios 1:1, 1:5, 1:10, 1:15 and PPS.

4. Conclusions : To summarize, we have been successfully able to synthesize cobalt sulphide / oxide nanoparticles in polymer matrix by facile solid-solid reaction technique. The formation of cubic structure Co_3O_4 and Co_3S_4 was confirmed by XRD and HRTEM. The polymer nanocomposites formed were studied for thermal characteristics and shift in melting temperature T_m was observed as compared to the virgin polymer. Also, the thermal stability of the polymer has increased due to presence of nanoparticles. The polymer PPS being an engineering thermoplastic with inherent flame retardant characteristics can be moulded as desired for advanced device fabrication. The oxides/ sulphides of cobalt being magnetic in nature and their potential for synthesis at nanoscale levels in the form of nanocomposites can be explored further for spintronics application in solid state device fabrication. This technique being quite simple can be used for preparation of nanocomposites for future generation smart materials.

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