

Synthesis and Characterization of Poly Benzyl bis (Thiosemicarbazone)/Nano CeO₂ Nanocomposites

¹Mojtaba Aryanfar, ²Alireza Shakeri, ³Vahid Saadattalab, ⁴Hossein Mighani

^{1,4} Faculty of science, Department of chemistry, Golestan University, Gorgan, iran

^{2,3} School of chemistry, college of science, Tehran University, Tehran, iran

Abstract: In this study, benzyl bis (thiosemicarbazole) monomer, polymer and poly benzyl bis (thiosemicarbazone) (PBTC) /CeO₂ nanocomposites were synthesized through in situ polymerization and their thermal properties in presence of metal oxide, were investigated. Prepared samples were characterized by Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) and thermal gravimetric analysis (TGA). Structure and morphology of prepared nanocomposites were evaluated by Scanning Electron Microscopy (SEM) and XRD techniques. Particle sizes of CeO₂ were calculated to be 10 nm from Debye-Scherrer equation. FT-IR verified polymerization of monomers. With more attention to TGA and DTA analyses, effect of nanosized particles on thermal properties of polymers can be easily observed.

Keywords: Nano Composites, Nano oxide ceria, Aromatic polyamides, Benzyl bis (thiosemicarbazone), poly carbazole.

1. INTRODUCTION

Since the ancient times, human being has been using composites by mixing materials to improve their physical and mechanical properties in order to apply them in their life. Building stronger tools, water resistive ceilings, etc. With the introduction of nano materials to the world, nanocomposites found their way through the industries. There are several reasons why nanoparticles with nanometer scale dimensions (10²⁹ m) are of interest. Nanoparticles with such small dimensions have been shown to improve not only the mechanical properties of polymers but also, in many cases, their functionalities as well [1]. Among them, polymer nanocomposites are subject of many researchers interest. Polymer/metal nanocomposites with enhanced thermal, mechanical and physical properties are under research. Preparation of polymer/metal nanocomposites are based on three different approaches. One approach consists of the in situ preparation of nanoparticles in the matrix either by the reduction of metal salts dissolved in the polymer matrix or by the evaporation of metals on the heated polymer surface. Another approach is the polymerization of the matrix around the nanoparticles. A third approach is the blending of pre-made metal nanoparticles with premade polymers since this technique provides full synthetic control over both the nanoparticle and the polymer matrix [2]. Cerium oxide (CeO₂) is a ceramic with fluorite structure having 2700 °C melting point in which no crystallographic changes occur from room temperature to its melting point during heating. CeO₂ has different applications in several areas such as filters, UV light absorbent, gas sensors, fuel cells, catalysts, ceramic pigments and etc. Thermo-resistivity may be explained by a physical cross-linking between polymer chains and nanoparticles. These linkages confine thermal motions of chains. Polyurethane/TiO₂ [1] and polyacrylate/ZnO [2] are of related examples. On the contrary, most reports claim that presence of metal oxide causes thermo-resistivity decrease of hybrid films and decrease in thermal stability is likely due to catalytic oxidative properties of metal in hybrid films [3-4]. Recently, several reports have shown that gold nanoparticles accelerate the thermal

decomposition of polymers [5-7]. Presumably, in nanocomposites containing metal particles, metal particles enhance thermo-resistivity against the pyrolytic decomposition while in atmospheric conditions accelerate oxidative destruction due to their catalytic natures.

2. MATERIAL PREPARATION

Synthesis of benzyl bis (thiosemicarbazone) ligand:

20 mmol benzyl was dissolved in 20 ml ethanol and 1ml concentrated hydrochloric acid by heating. The prepared mixture was added to the boiling mixture of 40 mmol thiosemicarbazide in 20 ml ethanol. After adding 5 ml water, the final mixture was refluxed for 6 h. Finally, the precipitate was filtered and washed with mixture of 50/50 water- ethanol and dried [8].

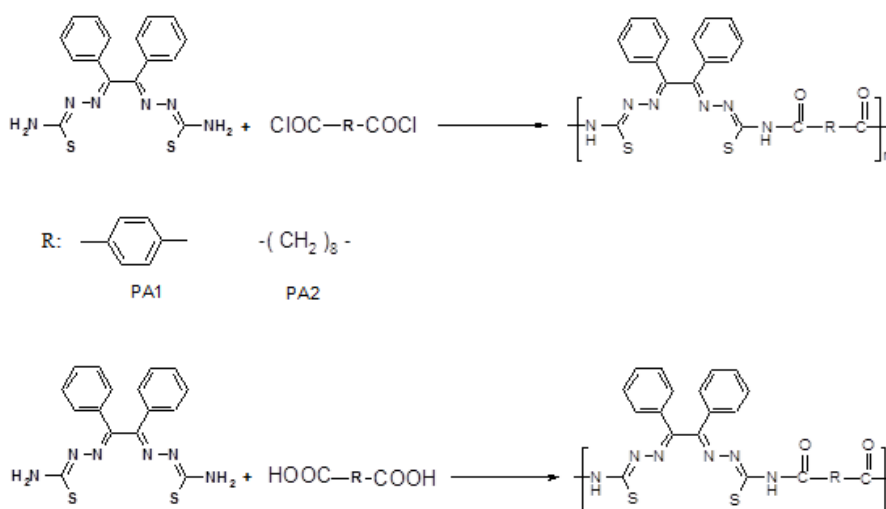


Figure 1: Synthesis of bithiosemicarbazide poly amide

Synthesis of benzyl bis (thiosemicarbazone) poly amides:

For preparation of these poly amides two different routes were employed.

a) 0.7 ml ethylenediamine (en) was introduced to 2 mmol diamine dissolved in 20 ml dimethylformamide (DMF) in a 100 ml balloon at 0 °C under nitrogen atmosphere. Then 2 mmol Acyl chloride dissolved in 10 ml DMF was added to the solution drop by drop. The solution was under stirring for 3 h at room temperature. After adding the solution to cold water, the polymer was filtered and washed with sodium bicarbonate and water and dried in 70 °C.

b) In a 100 ml balloon equipped with condenser and under nitrogen atmosphere, 2 mmol diamine and 2 mmol diacid together with 1.3 ml triphenyl phosphite were added to a solvent containing 30 ml N-methylpyrrolidone and 6 ml pyridine in which 0.6 gr lithium chloride and 1.8 gr calcium chloride have been dissolved while stirred at 110 °C for 10 h. At next step, the solution was mixed with methanol and the precipitate was separated, washed and refluxed for 1h with methanol and finally dried at 120 °C in vacuum.

Synthesis of benzyl bis (thiosemicarbazone)/3% nanosized CeO₂ poly amide ligands:

At the first, 0.028 gr nanosized CeO₂ (3% wt compared to the dry monomers) was added to solvent N-methyl pyrrolidone. Dispersion of nanosized CeO₂ was carried out in N-methyl pyrrolidone under stirring for 24 h. To ensure well dispersion of nanoparticles, dispersing under sonication for 10 min was utilized. For synthesis of nanocomposites, in a 100 ml balloon equipped with condenser and under nitrogen atmosphere, 2 mmol diamine and 2 mmol terephthalic acid along with 1.3 ml triphenyl phosphite were added to a solvent containing 30 ml N-methylpyrrolidone and 6 ml pyridine in which 0.6 gr lithium chloride and 1.8 gr calcium chloride have been dissolved. Refluxing of mixture was performed for 3 hr at 110 °C until oligomers formed. The color of solution turns into the dark brown indicating oligomers formation. At

the next step, solution of well dispersed CeO₂ was added to the reaction balloon and after enhancing temperature to 140 °C, final solution was refluxed for 10 h. Resultant precipitate was filtered and dried at 100 °C.

Synthesis of benzyl bis (thiosemicarbazone) /5% nanosized CeO₂ poly amide ligands:

This synthesis is exactly the same as the previous method except that instead of 0.028 g CeO₂, 0.047 gr CeO₂, 10 g was used.

3. RESULTS AND DISCUSSION

Monomer characterization:

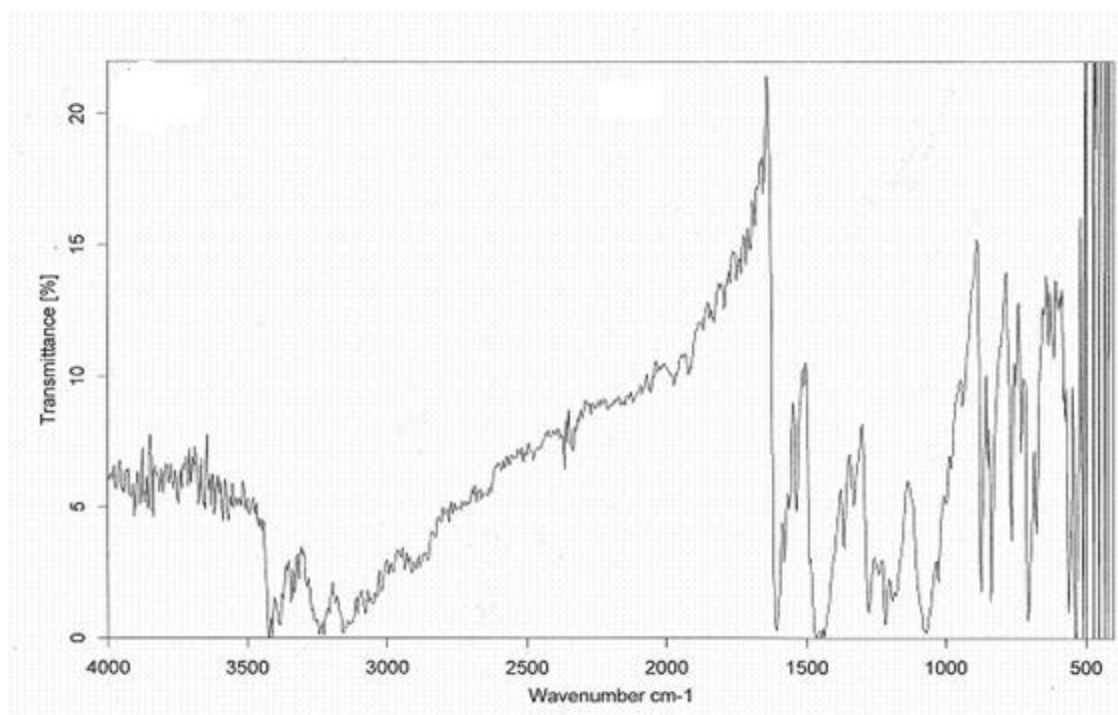
Elemental analysis of synthesized monomer presented in table 1-3 confirmed the structure of monomer. Functional groups were identified by IR spectroscopy. Characteristic peaks at 3100-13400 cm⁻¹ are related to NH and NH₂ and peaks in the region of 11200 cm⁻¹ and 1610 cm⁻¹ confirm C=S and C=N functional groups respectively(spectrum 1). To determination of proton types, ¹H NMR was used.

¹H NMR (CDCl₃): δ (ppm) 8.8(2H, s), 7.6(6H, m), 7.4(4H, m), 6.7(4H, s1)

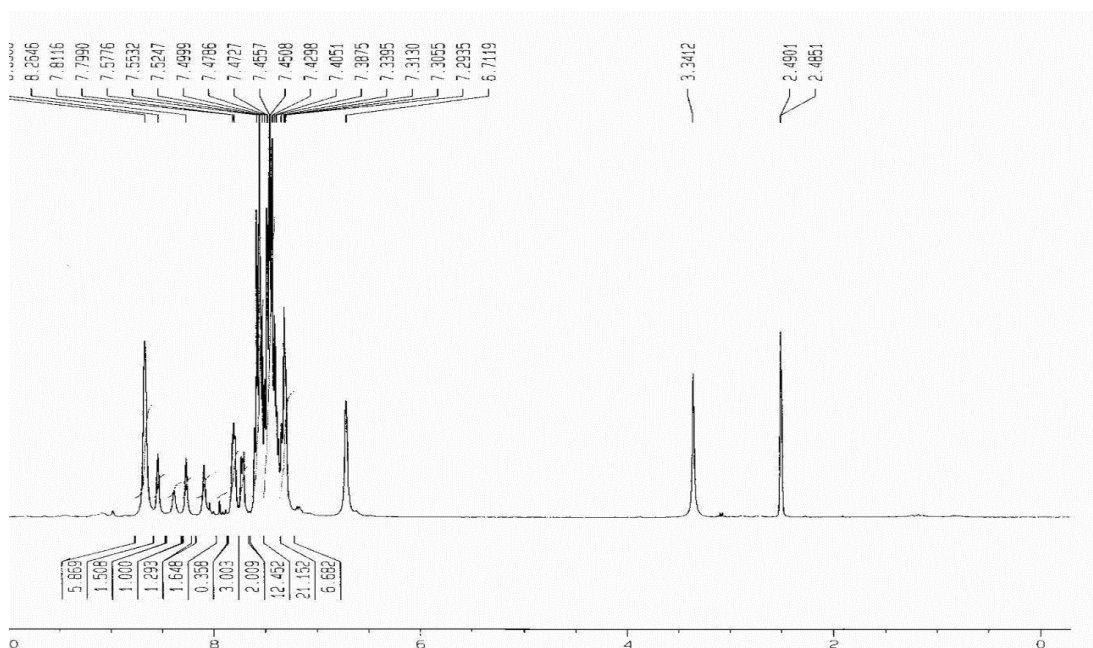
DSC profile of monomer at first scan shows that the monomer melts at 260 °C. Endothermic peak at 270°C is related to decomposition of monomer.

Table 1: Elemental and spectroscopic data of prepared poly amides synthesized by benzyl bithiosemicaebazone

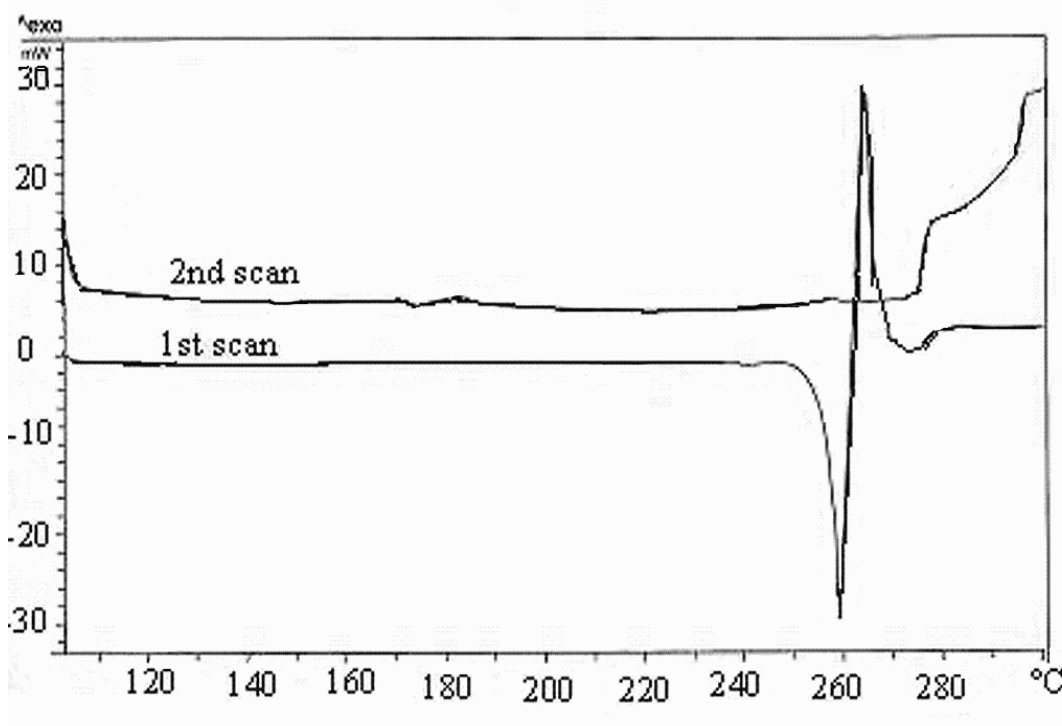
Subst rate	IR (KBr, cm ₋₁)	¹ HNMR (DMSO-d ₆ , δ, ppm)	Elemental analysis							
			Calc.				Found			
			C	H	N	S	C	H	N	S
^a LH6	3420, 3250, 3150(NH, NH ₂), 1610(C=N), 1585(NH ₂), 848(C=S).	8.8(2H), 7.6(6H), 7.4(4H), 7.3 (4H).	53.93	4.4 9	23. 59	17. 97	54.1 5	4.4 9	23.29	17.82
PA1	3389(NH), 1684(C=O), 1608(C=N), 872(C=S).	11.02(4H, NH), 8.2-8.5(4H, phenyl), 7.29-7.57(10H, phenyl).	59.26	5.0 5	17. 28	13. 17	59.4 5	4.9 5	17.18	13.32



Spectrum 1: benzyl bithiosemicarbazone FT-IR



Spectrum 2: ¹H NMR of benzyl bis thiosemi carbazone in DMSO

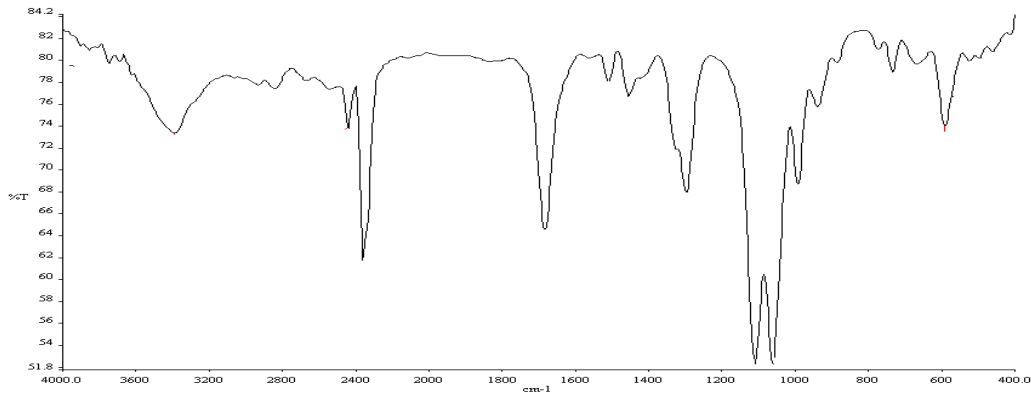


Spectrum 3: DSC profile of benzyl bis (thiosemicarbazone)

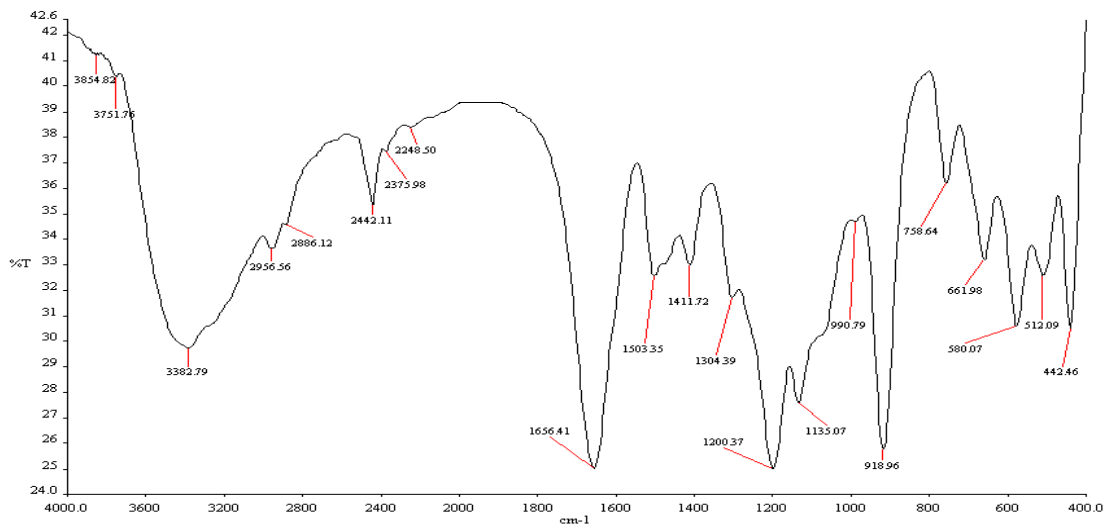
4. POLYMER AND NANOCOMPOSITE CHARACTERIZATION

IR spectra:

Characteristic peaks in the region of 3389, 1684 and 872 cm^{-1} correspond to NH, C=O and C=S groups respectively. Presence of nanoparticles and their interactions with polymer chain functional groups led to increase peak intensities in the region of 400-800 cm^{-1} .

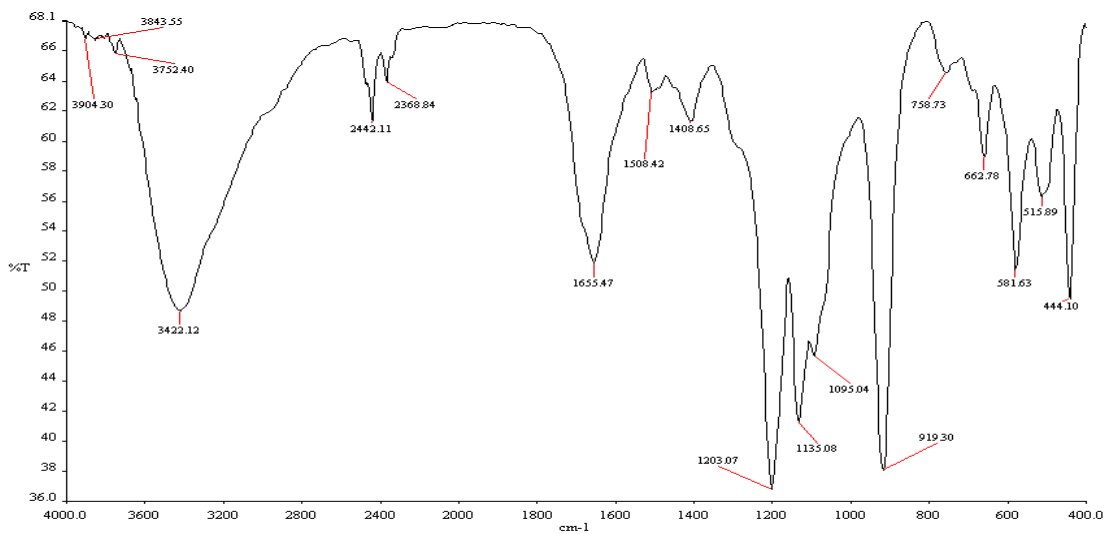


Spectrum4: poly benzyl bis (thiosemicarbazone) FT-IR



CeO₂ 5%

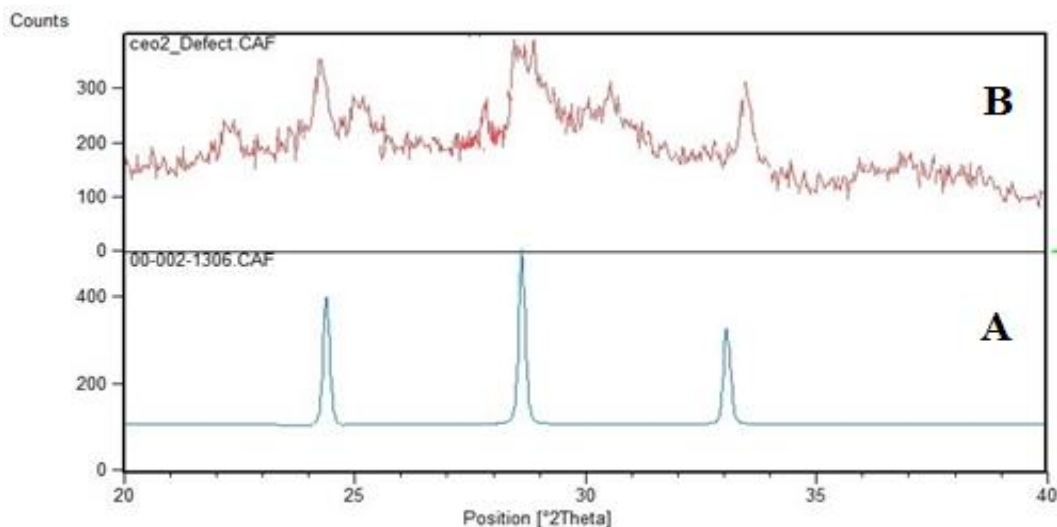
Spectrum5: FT-IR of nanocomposite containing 3% CeO₂



CeO₂ 3%

Spectrum 6: FT-IR of nanocomposite containing 5% CeO₂

Comparison of IR peaks between polymer and nanocomposites shows that CeO₂ nanoparticles cause shift of carbonyl peak toward low frequencies.



Spectrum7: XRD pattern of (A) CeO₂ nanoparticles (B) nanocomposites containing 5% CeO₂

Fig 2 shows nanocomposite and CeO₂ nanoparticles XRD. Crystallite sizes were calculated by debye scherrer equation:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

In which D stands for crystal size, k is a constant (equal 0.9 with assumption of spherical shape of nanoparticles), λ is incidence light wavelength and β is the peak width at half maximum. Micro-strain is obtained by williamson-hall equation:

$$B\cos\theta = K\lambda d + (\epsilon) \sin\theta$$

Network internal strain can be obtained by plotting (ε) sinθ against Bcosθ. Crystal size was determined about 10 nm from scherrer equation and internal strain was -63 indicating negative slope in williamson stress diagram.

Scanning Electron Microscopy (SEM):

Morphology of prepared sample was investigated by SEM. Fig 1 shows SEM images of CeO₂ nanoparticles and nanocomposite. According to SEM image, it is seen that CeO₂ nanoparticles are at nanocomposite surface.

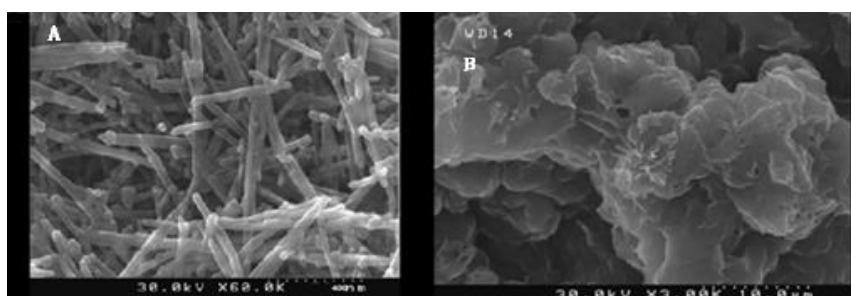
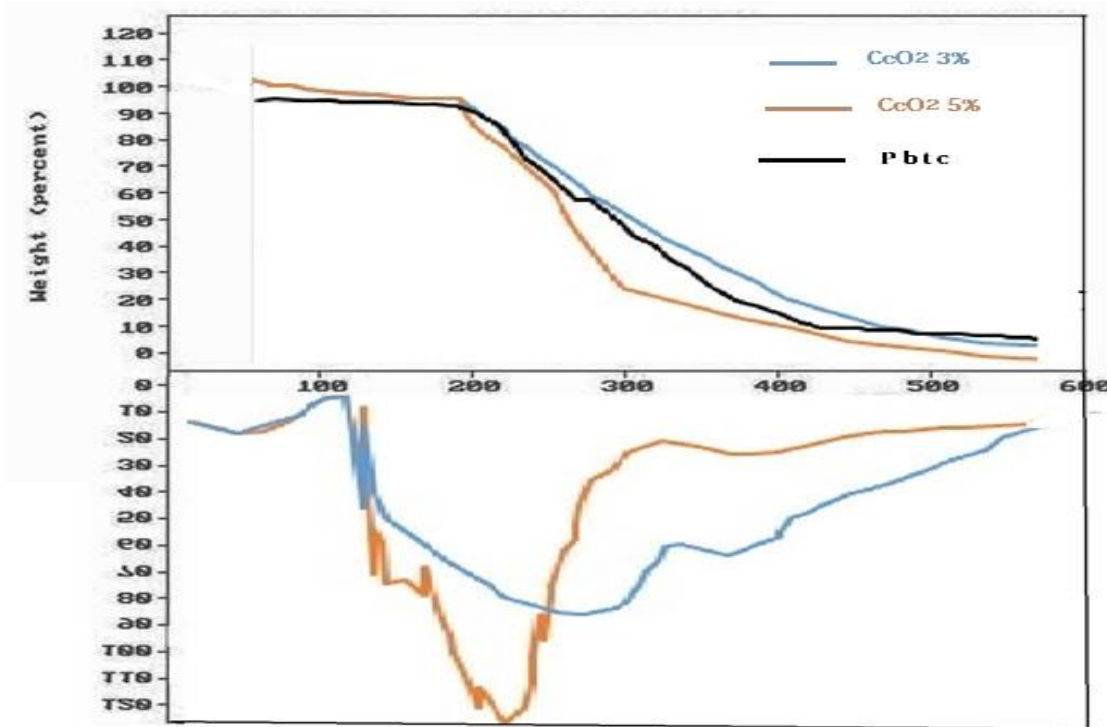


Fig 1: SEM image of A:nano oxide Ceria and B: nanocomposite

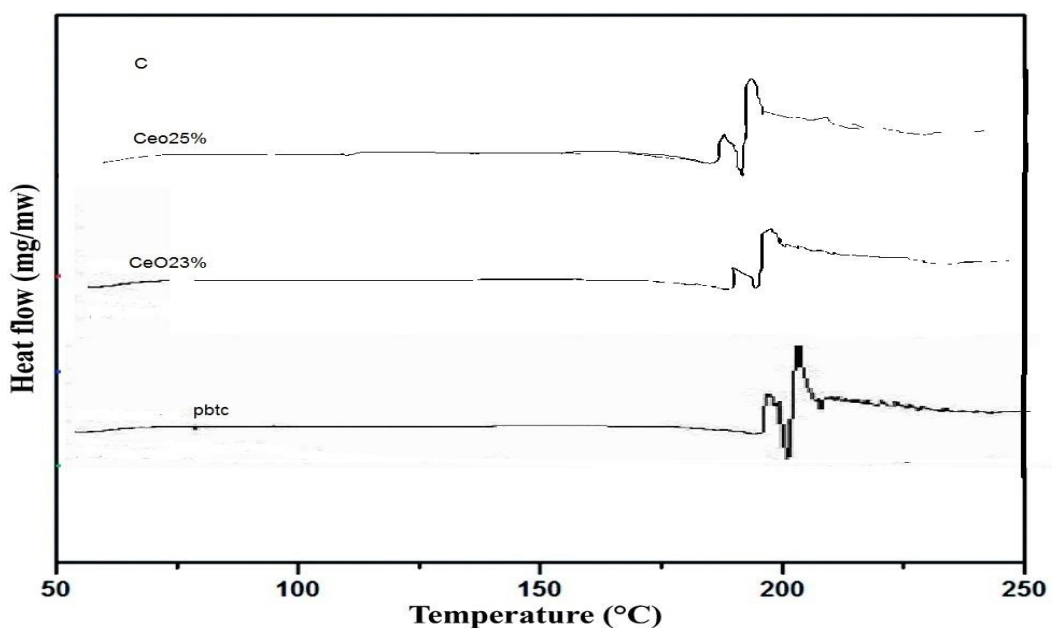
Calorimetry:

Thermal stability of polymers was investigated under nitrogen atmosphere with heating rate of 10 $\frac{^{\circ}C}{min}$ via thermal gravimetric analysis (TGA). Depend on polymer structure, initial weight loss (T₀) due to thermal degradation usually

begins from 200 °C and about this polymer weight loss (T_{10}) by 10% (usually considered as thermal resistance index) was recorded in the range of 220-290°C. Weight loss by 50% and the rest of poly amides were evaluated at 600 °C. In thermal analysis of CeO₂ nanocomposites, thermal analysis was initiated from 25 °C and terminated at 600 °C. A differential thermal analysis was performed from 0°C to 300°C under nitrogen atmosphere. Thermal analysis data showed that addition of 3% CeO₂ enhances thermal stability and decreases degradation rate of nanocomposite while in the case of 5% thermal stability was dropped and degradation rate was accelerated and this is due to sponge structure formation in polymer. DTA and DSC determine the effect of CeO₂ on thermal properties of nanocomposite.



Spectrum8: polymer and nanocomposites TGA and DTA



Spectrum9: polymer and nanocomposites DSC

5. CONCLUSION

In summary, CeO₂/ PBTC nanocomposite has been prepared by in situ approach. The resultant nanocomposite consists of dispersed CeO₂ NPs and PBTC matrix, exhibits decreased thermal stability.

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