

Synthesis and Dielectric Properties of Poly Benzyl Bis (Thiosemicarbazone)/Nano Cerium Oxide Nanocomposites

Mojtaba Arianfar*

Faculty of Science, Department of Chemistry, Golestan University, Gorgan, 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 dielectric properties in presence of metal oxide, were investigated. Prepared samples were characterized by Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction (XRD), Structure and morphology of prepared nanocomposites were evaluated by Scanning Electron Microscopy (SEM) and XRD techniques. The dielectric properties were investigated in the frequency range 50 Hz - 20 MHz and the temperature range between 40°C to 150°C. The dielectric constant (ϵ) and dielectric loss ($\tan \delta$) is measured for different compositions of nanocomposites. Particle sizes of CeO₂ were calculated to be 10 nm from Debye-Scherrer equation. FT-IR verified polymerization of monomers. The dielectric properties of cerium oxide nanocomposite were studied for different frequencies at different temperatures. The dielectric constant and the dielectric loss of the cerium oxide nanocomposite decreased with increase in frequency. The AC electrical conductivity study revealed that the conduction depended on both the frequency and the temperature.

Keywords: Dielectric; Nanocomposites; Monomers; Polymer matrix

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 researcher's 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].

CeO₂ is one of the most attractive rare earth metal oxides. It has several applications in the field of corrosion prevention, electrochemical cells, electromagnetic shielding, thermal coatings, optical and photoelectrical properties [3]. Mostly the rare-earth elements exist in trivalent state, but cerium exists in both trivalent (+3) as well as tetravalent (+4) state. Because of its ability to alter oxidation state it has the several applications such as catalytic converters and solid oxide fuel cells. Also, CeO₂ has great attention because of its unique features like non-toxicity, biocompatibility, oxygen storage capability, optical, and thermal properties, which have significant applications in solar cells, gas sensors and biosensors [4,5]. There are different methods for synthesis of CeO₂, like coprecipitation, hydrothermal, and sol-gel method.

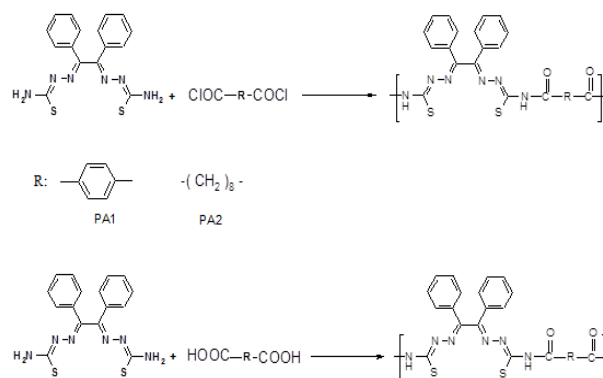
Polyimide, as a well-known high-performance polymer, has been one of the most promising candidates for preparing polymer/inorganic

composite materials due to its excellent mechanical strength, high thermal stability, preferable chemical resistance and easy film casting [6,7].

Materials Preparation

Synthesis of benzyl bis (thiosemicarbazone) ligand

20 mmol benzyl was dissolved in 20 ml ethanol and 1 ml 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].



*Corresponding author: Mojtaba Arianfar, Faculty of Science, Department of Chemistry, Golestan University, Gorgan, Iran, Tel: +981712231801; Fax: +981712235006; E-mail: aryanfar.mojtaba@gmail.com

Received November 16, 2016; Accepted November 24, 2016; Published November 28, 2016

Citation: Arianfar M (2016) Synthesis and Dielectric Properties of Poly Benzyl Bis (Thiosemicarbazone)/Nano Cerium Oxide Nanocomposites. Chem Sci J 7: 143. doi: 10.4172/2150-3494.1000143

Copyright: © 2016 Arianfar M. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

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 1 h 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 colour 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.

Results and Discussion

Monomer characterization

Elemental analysis of synthesized monomer presented in Table 1 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 (Spectrums 1-3). 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.

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 (Spectrum 4).

Comparison of IR peaks between polymer and nanocomposites shows that CeO₂ nanoparticles cause shift of carbonyl peak toward low frequencies. Spectrums 5 and 6 shows nanocomposite and CeO₂ nanoparticles XRD. Crystallite sizes were calculated by debye scherrer equation:

$$D = k\lambda / \beta \cos\theta$$

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:

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

Network internal strain can be obtained by plotting (ε) sinθ against βcosθ. 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. The Figure 1 shows SEM images of CeO₂ nanoparticles and nanocomposite. According to SEM image, it is seen that CeO₂ nanoparticles are at nanocomposite surface.

Dielectric studies

Spectrum 7a-7c shows the plots of dielectric constant of PBTC/CeO₂ nanocomposite films in the frequency range 50 Hz to 20 MHz. For all the frequency and temperature range dielectric constant have been calculated. Dielectric constant is a frequency dependent parameter in the polymer systems. The dielectric constant for the PBTC blend shows maximum value of 110 at 50 Hz and at 160°C. By increasing the frequency gradually, the dielectric constant value decreases at 10 KHz for all the temperatures. For 5 wt% of CeO₂ loading in the nanocomposite, the similar changes were observed. When the wt% of CeO₂ increases the dielectric constant value decreases. The decrease in the dielectric constant values with increasing frequency is due to interfacial polarization effect. It can be explained on the basis that the dipole of the composites does not get enough time to re-orient themselves in the direction of applied electric field [9,10].

Spectrum 8a-8c shows the plots of dielectric loss (Tan δ) of PBTC/CeO₂ nanocomposites in the frequency range of 50 Hz to 20 MHz and the temperature in the range 40-160°C. For nanocomposites, the tangent loss value shows 3 at 70°C. The dielectric loss decreases from to 3.9 at 50 Hz and at 80°C for 3% of CeO₂ loading to 2.4 at 50 Hz and at 160°C for 5% of CeO₂ loading. For all tangent loss plots beyond 500 KHz shows very low value. Dielectric loss values decrease on increasing frequency. As compared to dielectric constant values of all nanocomposites shows low dielectric loss values which is highly attractive for high-k capacitor applications.

Conclusion

PBTC nanocomposites were successfully prepared by in situ polymerization. FTIR and XRD spectra revealed the successful

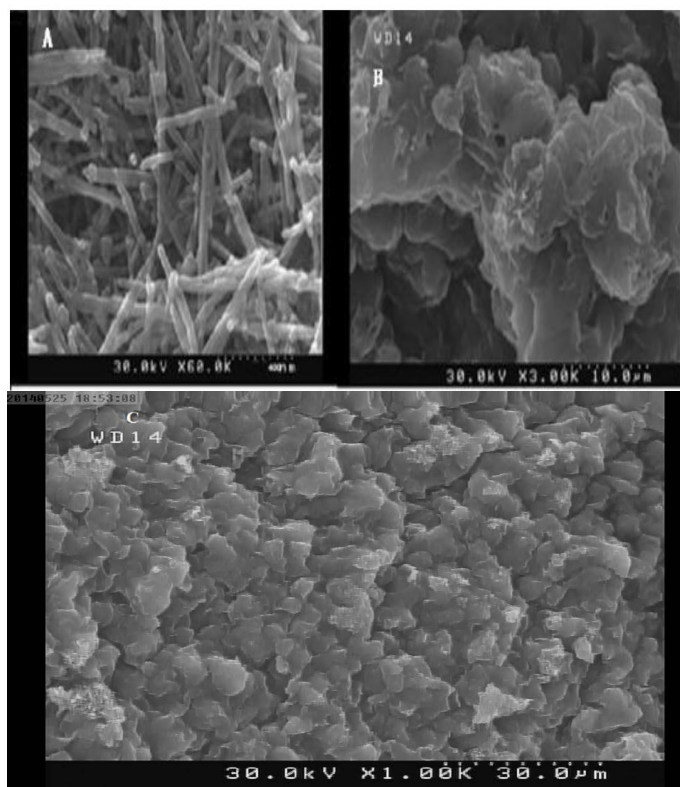
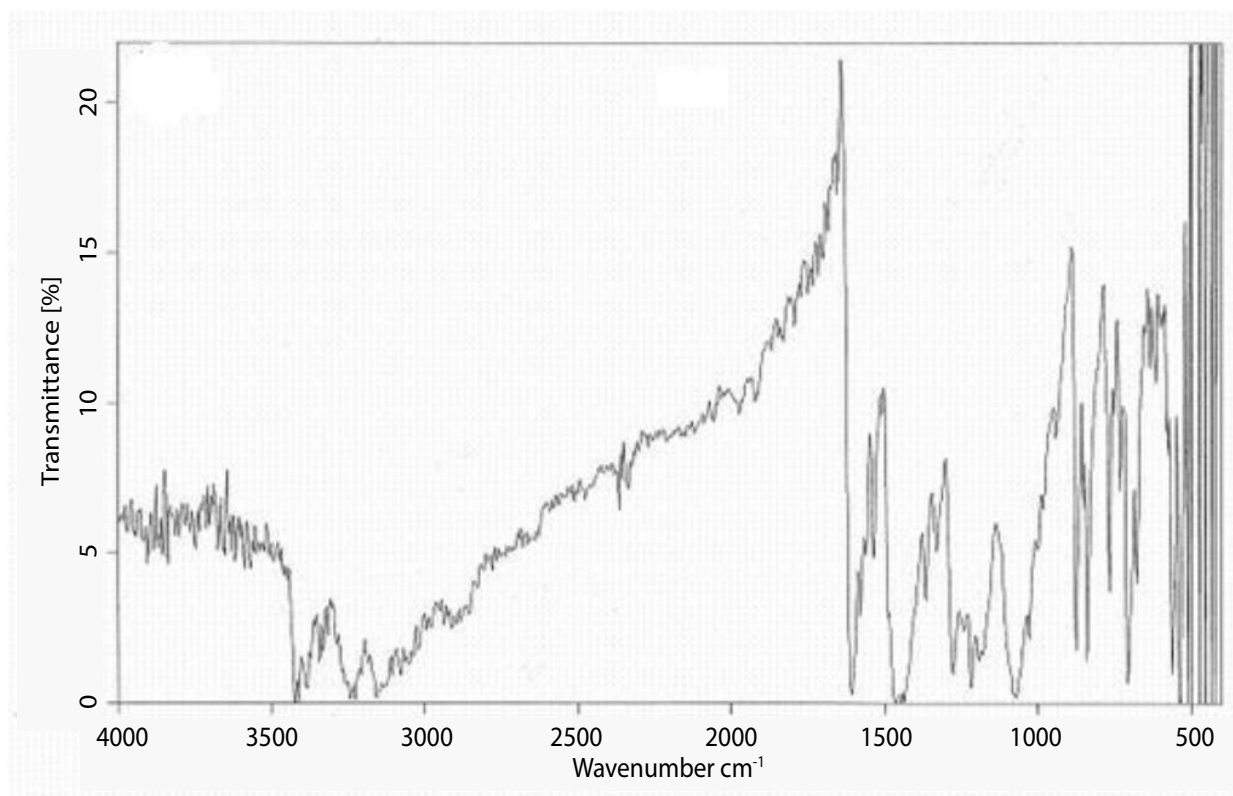
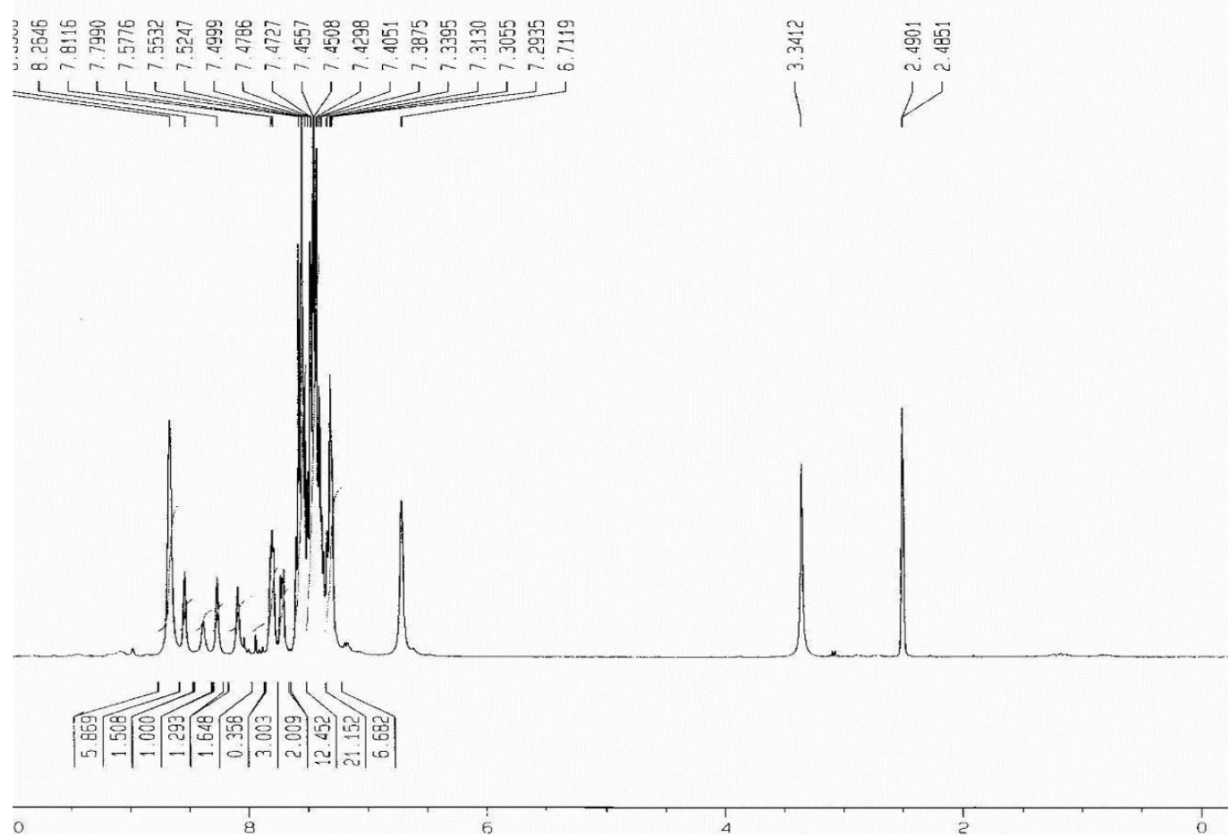


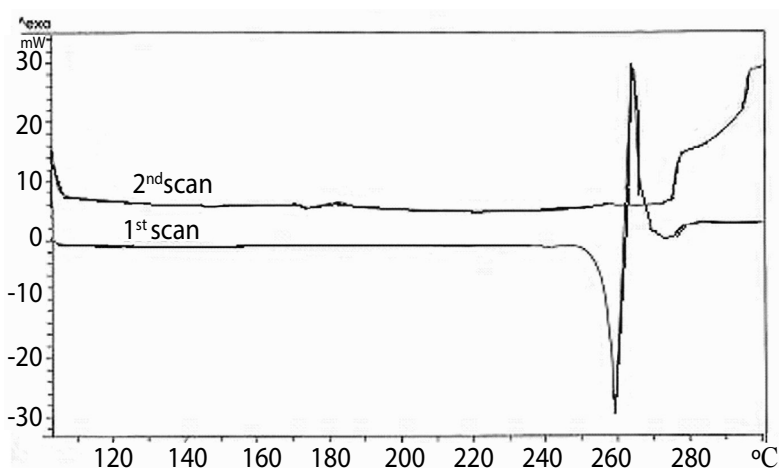
Figure 1: SEM image of A: nano oxide Ceria and B, C: nanocomposite.



Spectrum 1: Benzyl bithiosemicarbazone FT-IR.



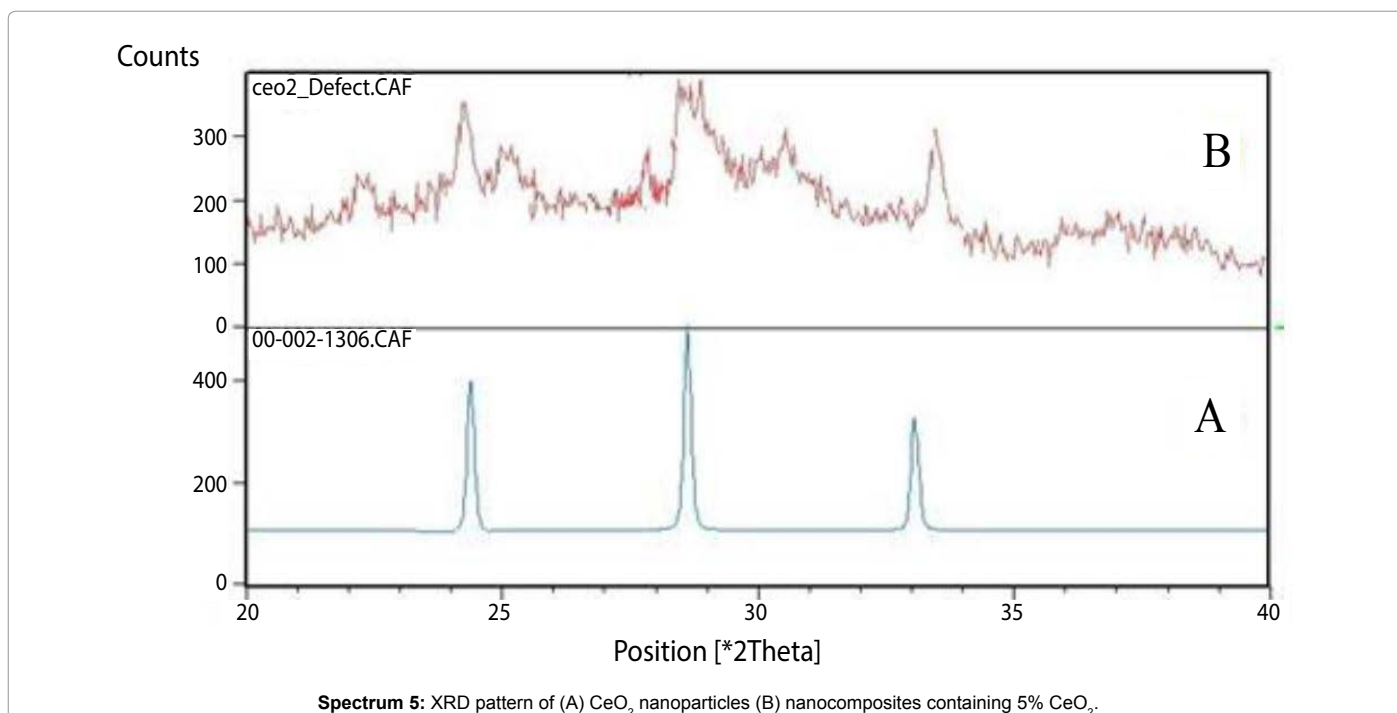
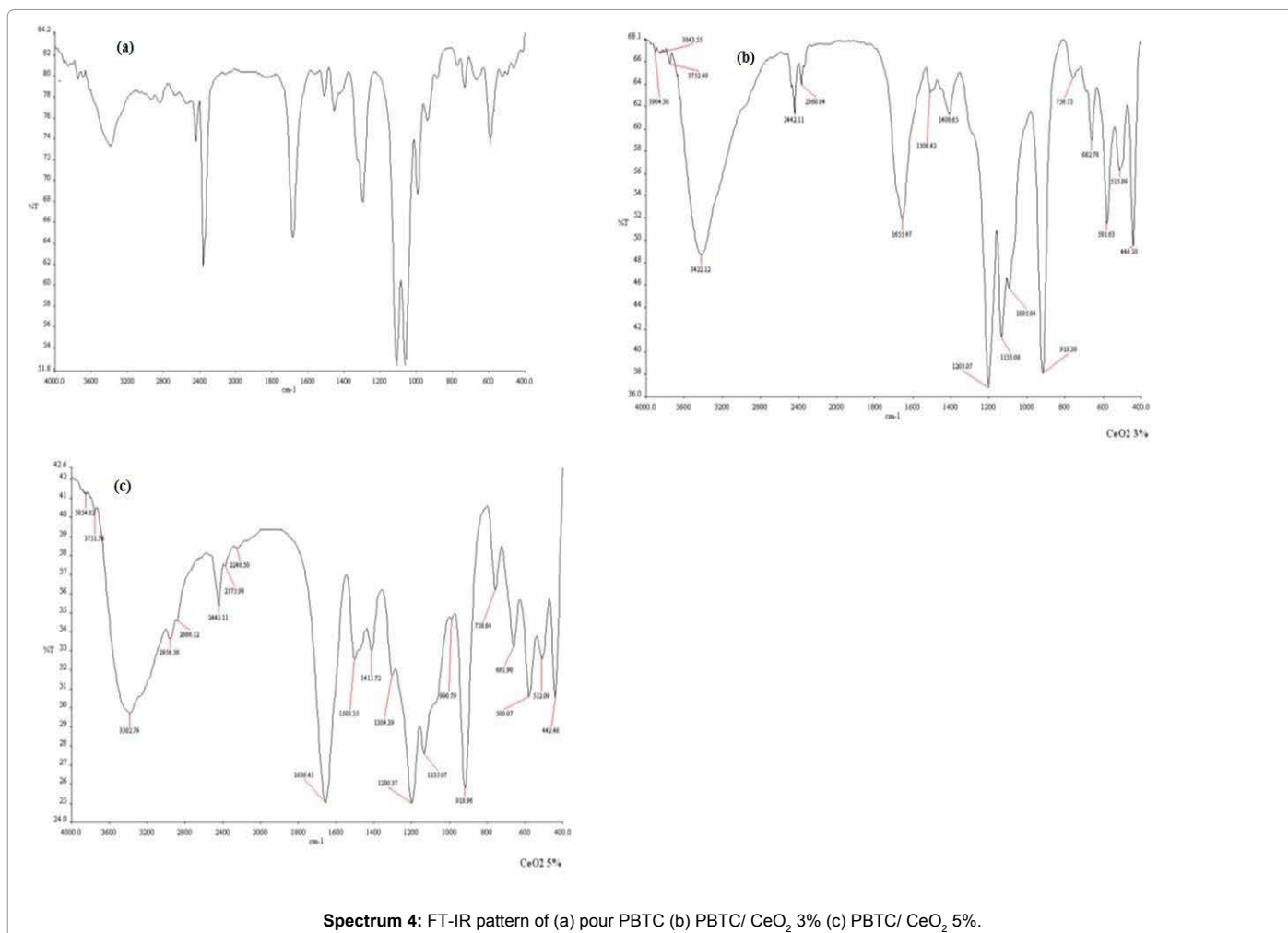
Spectrum 2: ^1H NMR of benzyl bis thiosemi carbazone in DMSO.

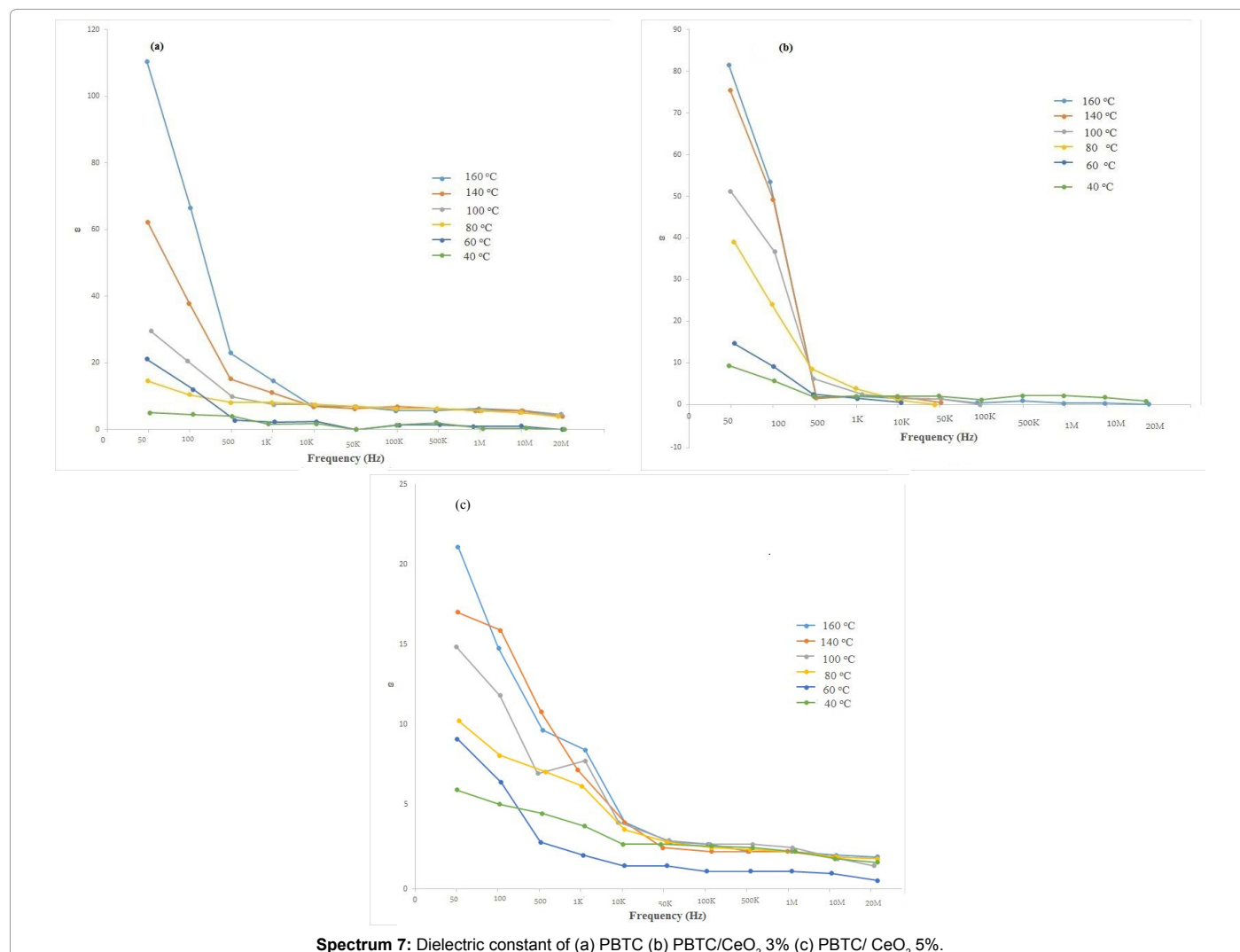
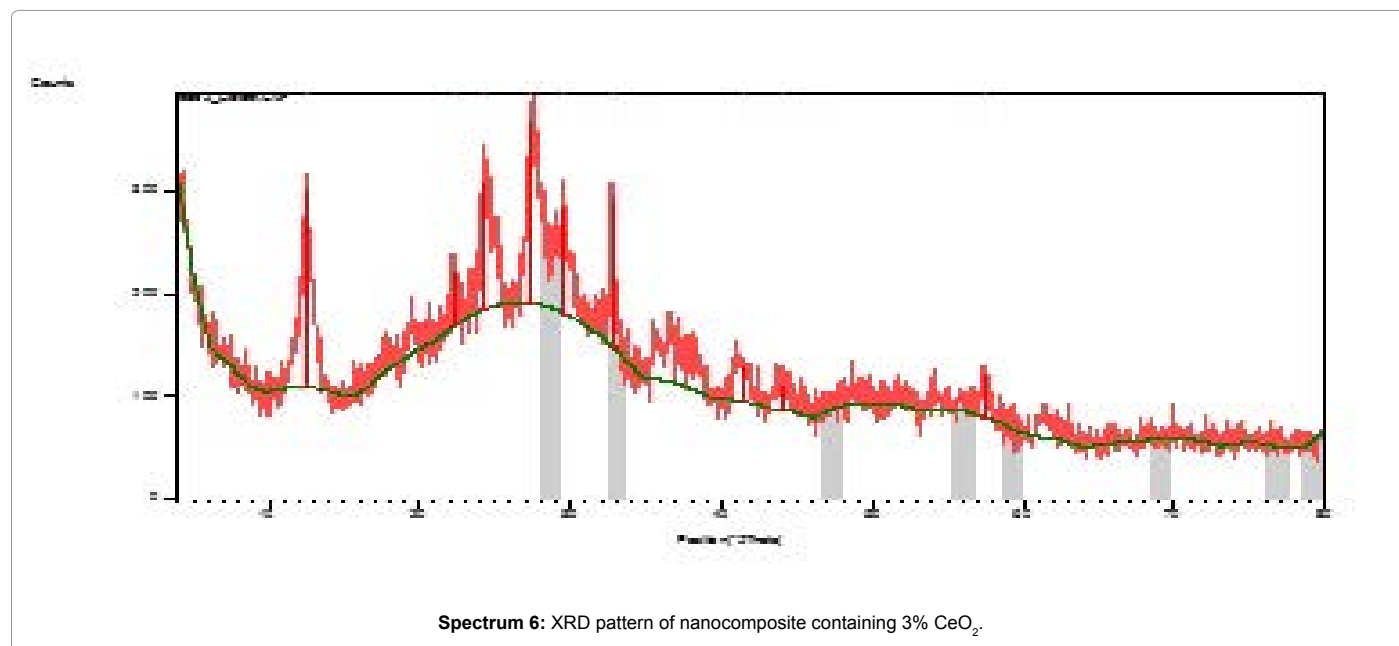


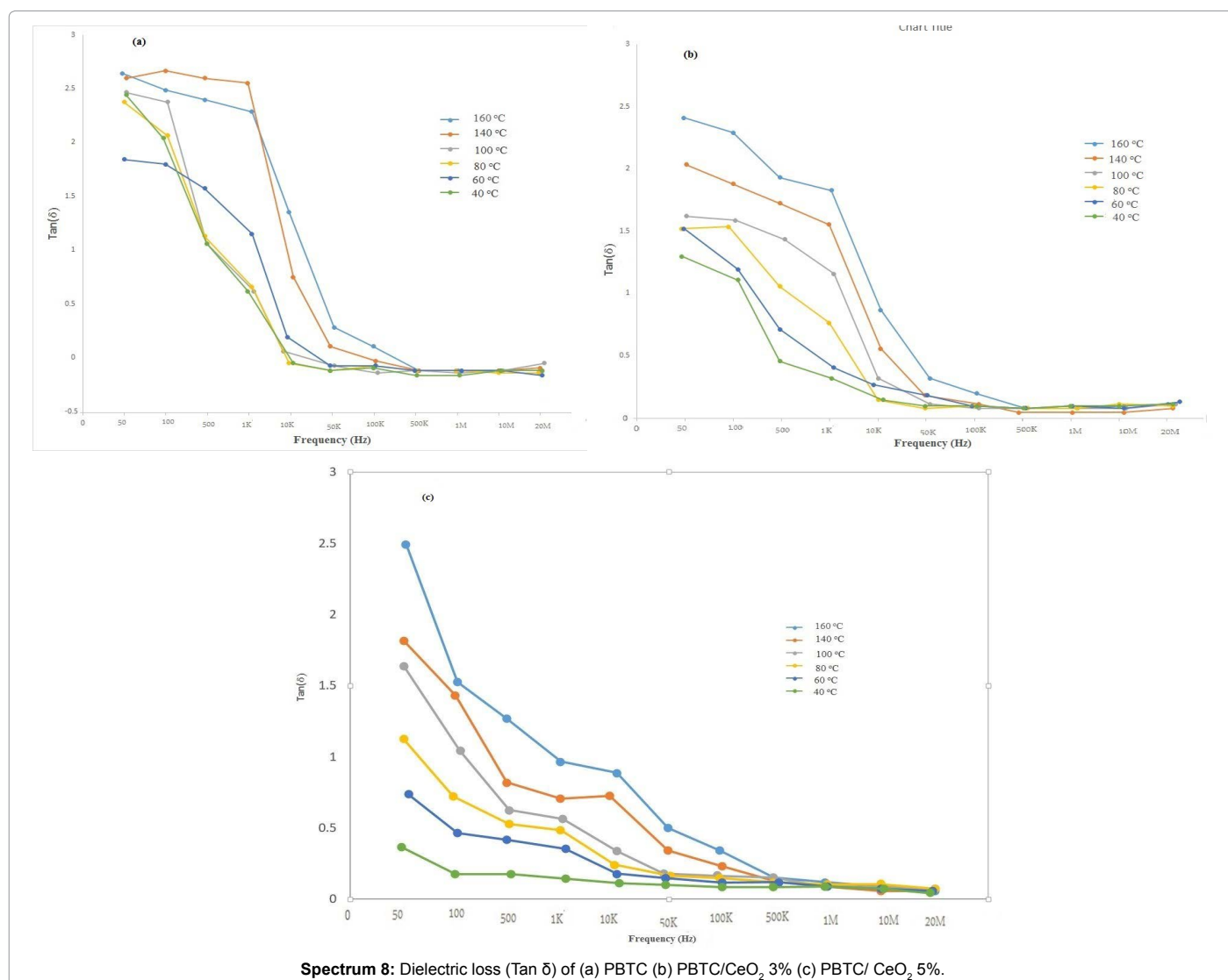
Spectrum 3: DSC profile of benzyl bis (thiosemicarbazone).

Substrate	IR (KBr, cm^{-1})	^1H NMR (DMSO- d_6 , δ , ppm)	Elemental analysis							
			Calc.				Found			
			C	H	N	S	C	H	N	S
$^a\text{LH6}$	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	4.49	23.59	17.97	54.15	4.49	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	5.05	17.28	13.17	59.45	4.95	17.18	13.32

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







Spectrum 8: Dielectric loss (Tan δ) of (a) PBTC (b) PBTC/CeO₂ 3% (c) PBTC/ CeO₂ 5%.

incorporation of CeO₂ in to the PBTC matrix. From the SEM results we confirm the homogeneous dispersion of the CeO₂ with the polymer matrix. From the dielectric measurements, it was observed that the nanocomposites have significantly high dielectric constant and comparatively low dielectric loss facilitating the applications of nanocomposites as a high-k dielectric material for embedded capacitor applications.

References

1. Qiu K, Netravali A (2013) Halloysite nanotube reinforced biodegradable nanocomposites using noncrosslinked and malonic acid crosslinked polyvinyl alcohol. *Polym Compos* 34: 799-809.
2. Chatterjee U, Jewrajka SK, Guha S (2009) Dispersion of functionalized silver nanoparticles in polymer matrices: Stability, characterization, and physical properties. *Polym Compos* 30: 827-834.
3. Ansari AA, Solanki PR, Malhotra BD (2009) Hydrogen peroxide sensor based on horseradish peroxidase immobilized nanostructured cerium oxide film. *J Biotech* 142: 179-184.
4. Ansari AA, Kaushik A, Solanki PR, Malhotra BD (2008) Sol-gel derived nanoporous cerium oxide film for application to cholesterol biosensor. *Electrochem Commun* 10: 1246-1249.
5. Pawde SM, Deshmukh K, Parab S (2008) Preparation and characterization of poly (vinyl alcohol) and gelatin blend films. *J Appl Polym Sci* 109: 1328-1337.
6. Li HY, Ning SF, Hu HB, Liu B, Chen W, et al. (2007) *Chinese J Polym Sci* 25: 49.
7. Dang Z, Lin Y, Xu H, Shi C, Yao S, et al. (2008) Fabrication and Dielectric Characterization of Advanced BaTiO₃/Polyimide Nanocomposite Films with High Thermal Stability. *Adv Funct Mater* 18: 1509-1517.
8. Chang CM, Chang CC (2007) Preparation and characterization of polyimide-nanogold nanocomposites from 3-mercaptopropyltrimethoxysilane encapsulated gold nanoparticles. *Polym Degrad Stab* 93: 109-116.
9. Livi A, Levita V, Rolla PA (1993) Dielectric behaviour at microwave frequencies of an epoxy resin during crosslinking. *J Appl Poly Sci* 50: 1583-1590.
10. Deshmukh K, Ahamed MB, Pasha SKK, Deshmukh RR, Bhagat PR (2015) Highly dispersible graphene oxide reinforced polypyrrole/polyvinyl alcohol blend nanocomposites with high dielectric constant and low dielectric loss. *RSC Advances* 5: 61933-61945.