

Recent Advances In Nano Science And Technology 2015 (RAINSAT2015)

## Influence of Cerium Oxide ( $\text{CeO}_2$ ) Nanoparticles on the Structural, Morphological, Mechanical and Dielectric Properties of PVA/PPy Blend Nanocomposites

M. K. Mohanapriya<sup>a</sup>, Kalim Deshmukh<sup>b</sup>, M. Basheer Ahamed<sup>b</sup>, K. Chidambaram<sup>a</sup>,  
S.K. Khadheer Pasha<sup>a\*</sup>

<sup>a</sup>Sensors Laboratory, Material Physics Division, School of Advanced Sciences, VIT University, Vellore-632014, TN, India

<sup>b</sup>Department of Physics, B. S. Abdur Rahman University, Chennai-600048, TN, India

### Abstract

Polyvinyl alcohol (PVA) and water soluble polypyrrole (PPy) based Cerium oxide ( $\text{CeO}_2$ ) nanocomposite films with different wt% were prepared by solution casting method. The effects of  $\text{CeO}_2$  nanoparticles on the properties of PVA/PPy nanocomposite were investigated. The structural characteristic of nanocomposites was analyzed by using FTIR and X-ray diffraction (XRD). The morphological study of PVA/PPy/ $\text{CeO}_2$  nanocomposites was examined by Scanning Electron Microscopy (SEM). The tensile strength of the nanocomposite film was measured for different wt% of  $\text{CeO}_2$  loading. The mechanical properties of nanocomposites were also investigated and it was observed that the tensile strength has significantly changed due to incorporation of  $\text{CeO}_2$  nanoparticles in PVA/PPy blend. 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 ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) is measured for different compositions of nanocomposites. The nanocomposite shows high dielectric constant with low dielectric loss which can be used for high-k capacitor or embedded capacitor applications.

© 2015 Elsevier Ltd. All rights reserved.

Selection and Peer-review under responsibility of [Conference Committee Members of Recent Advances In Nano Science and Technology 2015].

**Keywords:** Cerium oxide; FTIR; mechanical property; dielectric studies;

---

\* Corresponding author: Dr. S K Khadheer Pasha, Tel.: +91 9894665388;  
E-mail address: [skkhadheerpasha@vit.ac.in](mailto:skkhadheerpasha@vit.ac.in)

## 1. Introduction

Polyvinyl alcohol (PVA) is a water soluble semi crystalline polymer which has been used extensively for the synthesis of polymer nanocomposites. It has various properties such as glossy nature, adhesive and easy film forming ability [1-3]. In PVA, presence of hydrogen bonding between hydroxyl groups is very important for its high water solubility and high crystal modulus [4]. Normally PVA is a poor electrical conductor it can become conductive when it is added with other polymer. Polymer composites are the materials in which different systems are combined to achieve a system with improved functional properties such as physical, optical, thermal, and electrical properties. The improvement in these properties depends on the chemical nature of the nano material and the way in which it interacts with the polymer. PPy has been used in biomedical devices and photo electronic sensors because of its good conductivity, optical stability and simple synthesis [5–8]. With this interest, organic conducting Polypyrrole (PPy) is used in the present study.

CeO<sub>2</sub> 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 [9]. 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, CeO<sub>2</sub> 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 [10, 11]. There are different methods for synthesis of CeO<sub>2</sub>, like co-precipitation, hydrothermal, and sol-gel method.

In this work, polyvinyl alcohol and polypyrrole were mixed with CeO<sub>2</sub> to get the polymer nanocomposite by solution casting method. Solution casting method is one of the most frequently used methods for the preparation of polymer nanocomposites because it is cost effective. Hence with this interest, PVA/PPy/CeO<sub>2</sub> blend nanocomposites were prepared. The nanocomposite films were characterized using FTIR, XRD, SEM, Mechanical and Dielectric properties to evaluate the structure property relationship.

## 2. Experimental

### 2.1 Materials

Polyvinyl alcohol (PVA) powder was purchased from Merck Schuchart, Germany. The molecular weight of PVA was 78,000 g/mol. Aqueous dispersion of PPy, was obtained from Eeonyx Corporation Ltd. USA. CeO<sub>2</sub> nanopowders were purchased from Sigma-Aldrich, India. Deionized water was used as a solvent in all the experiments and was purified through a Millipore Milli-Q academic system with a resistivity of 18 MΩ cm<sup>-1</sup>.

### 2.2 Sample preparation

The polymer nanocomposites were prepared by dissolving appropriate wt% of PVA in distilled water. Certain amount of aqueous PPy solution was added and continuously stirred for 2 hrs. The CeO<sub>2</sub> powder was sonicated separately in water for 60 minutes. Then this sonicated solution was mixed in to the well dispersed polymer blend solution. The solution was stirred (350rpm) at room temperature (30°C) for 4hrs until the homogeneous dispersion was obtained. The resulting dispersion was casted on to a glass petridish and dried in the oven at 60°C for 8hrs. The nanocomposite films were very flexible and transparent. The synthesis protocol is shown in the Fig. 1.

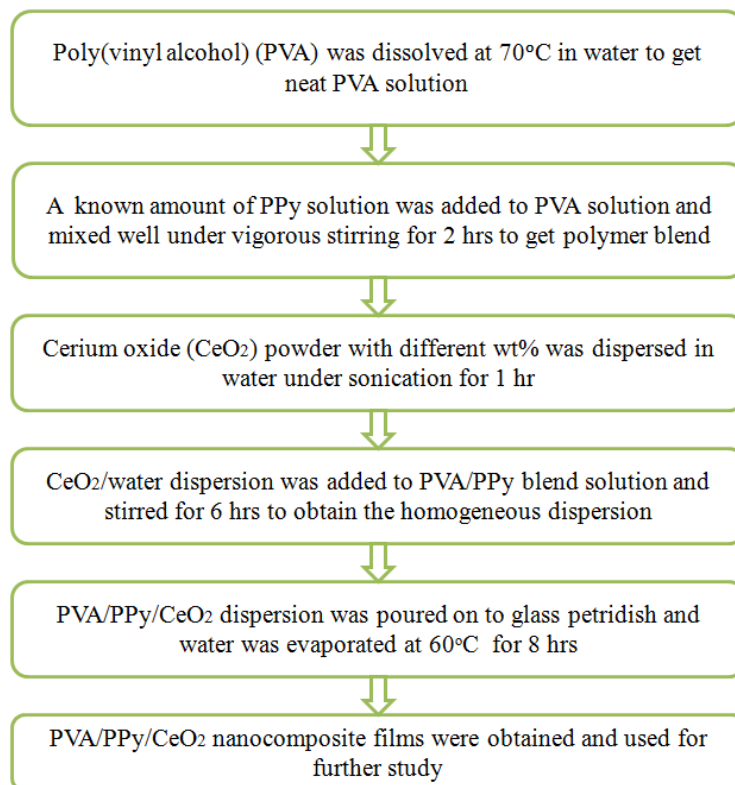


Fig. 1 Protocol for the synthesis of PVA/PPy/CeO<sub>2</sub> nanocomposite films

### 3. Instrumentation

FTIR spectroscopy of PVA/PPy/CeO<sub>2</sub> nanocomposite film was carried out with Fourier Transform Infrared Spectrophotometer (Shimadzu, IRAffinity-1, and Japan) in the wavenumber range 500–4000 cm<sup>-1</sup> in the transmittance mode. X-ray diffraction of PVA/PPy/CeO<sub>2</sub> nanocomposite film was recorded using Cu K $\alpha$  radiation of wavelength  $\lambda=1.54060$  Å with a graphite monochromator produced by a Bruker AXS D8 focus advanced X-ray diffraction meter (Rigaku, Japan, Tokyo) with ‘Ni-filtered’. The scans were taken in the  $2\theta$  range from 10 – 80° with a scanning speed and step size of 1°/mm and 0.01°, respectively. Morphological analyses of PVA/PPy/CeO<sub>2</sub> composite films were carried out by using a Hitachi Quanta 200 FE Scanning Electron Microscope (SEM). The samples were coated with gold in vacuum. The acceleration voltage applied was 10 kV.

The tensile strength of PVA/PPy/CeO<sub>2</sub> nanocomposite film was studied using bench top tester (H50K-S UTM, Tinius Olsen, Horsham, USA) The testing instrument is having PC controlled frames, with the capacity of 50kN. The size of the polymer film used for mechanical studies was 10x20x0.05mm. The dielectric properties of PVA/PPy/CeO<sub>2</sub> nanocomposite films (thickness 50  $\mu$ m) were measured in the frequency range 50 Hz to 20 MHz and temperature in the range of 40–150 °C using an impedance analyzer (E4990A, Agilent, UK) which operates in the frequency range 20 Hz to 30 MHz.

## 4. Result and discussion

### 4.1 FTIR Studies

The FTIR spectra were recorded to find the functional groups present in the polymer nanocomposite films, and also to study the interaction between nanoparticle ( $\text{CeO}_2$ ) and PPy/PVA blend. The peak assignments of PVA/PPy/ $\text{CeO}_2$  nanocomposite were shown in the Table 1. FTIR spectra of pure  $\text{CeO}_2$ , neat PVA and polymer blend with different wt% of  $\text{CeO}_2$  is shown in the Fig. 2. In all FTIR spectrums of PVA/PPy/ $\text{CeO}_2$  nanocomposites a wide band is observed near  $3000\text{--}3500\text{ cm}^{-1}$  which represents O-H stretching vibration in polymers. The peak near  $2930\text{ cm}^{-1}$  is due to C-H stretching. The peak at  $1731\text{ cm}^{-1}$  corresponds to C=O stretching vibration. The band observed at  $1438\text{ cm}^{-1}$  corresponds to C-H bending of PVA. This confirms the presence of PVA in the composite films [12, 13]. In the FTIR spectra of pure  $\text{CeO}_2$  the peak observed near  $2330\text{ cm}^{-1}$  is due to the C-H stretching and peak near  $1746\text{ cm}^{-1}$  is due to the deformation vibration of water molecule. The peak observed near  $1529\text{ cm}^{-1}$  is due to the asymmetric stretching of C=O bond. The peak at  $1331\text{ cm}^{-1}$  is due to Ce-O stretching [14]. This confirms the presence of functional groups of both polymers and nanoparticles in the nanocomposite. All the peaks observed were shifting with the loading % of PPy and  $\text{CeO}_2$ . From this we can confirm that significant interaction has taken place between the polymers and nanoparticles.

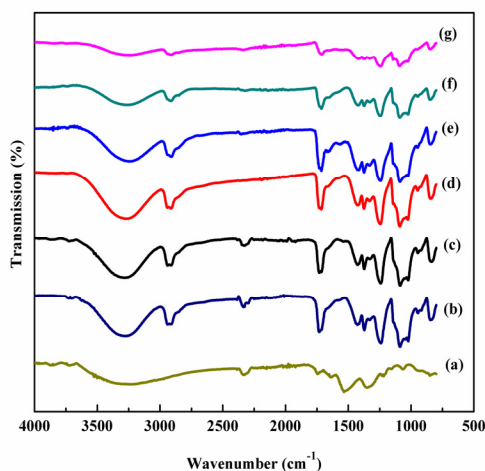


Fig. 2 FTIR spectra of (a) pure  $\text{CeO}_2$  (b) neat PVA (c) PVA/PPy at 50:50 (d) PPy/PVA/ $\text{CeO}_2$  at 25:70:05 (e) 20:70:10 (f) 15:70:15 (g) 10:70:20

**Table 1** FT-IR peak assignment of PVA,  $\text{CeO}_2$ , PVA/PPy/ $\text{CeO}_2$

Wave number ( $\text{cm}^{-1}$ )	Peak assignment PVA	Wave number ( $\text{cm}^{-1}$ )	Peak assignment $\text{CeO}_2$	Wave number ( $\text{cm}^{-1}$ )	Peak assignment PVA/PPy/ $\text{CeO}_2$
3000-3500	O-H stretching	2330	C-H stretching	3000-3500	O-H stretching
2930	C-H stretching	1746	Deformation vibration of $\text{H}_2\text{O}$	2930	C-H stretching
2330	$\text{CH}_2$ stretching	1529	C=O asymmetric stretching	1731	C=O stretching
1731	C=O stretching	1331	Ce-O stretching	1438	C-H bending
1438	C-H bending			1347 & 1533	Ce-O stretching
1347 & 1533	Ce-O stretching			841	N-H wagging
841	N-H wagging				

#### 4.2 XRD Studies

X-ray diffraction (XRD) is used to study the structural properties of the material. In this work the XRD studies were performed to find the influence of  $\text{CeO}_2$  on PVA/PPy blend. The XRD pattern of pure  $\text{CeO}_2$  and nanocomposites as shown in Fig. 3. All the X-ray profiles of nanocomposites exhibit a main peak at  $2\theta = 19.8^\circ$  corresponding to (101) crystal plane for PVA, this peak indicates the semi crystalline nature of PVA [15]. Sharp peaks observed in XRD pattern of polymer nanocomposites and pure  $\text{CeO}_2$  nanoparticles have plane oriented to (111), (200), (220), (311), (222), (400), (311), (420) with corresponding  $2\theta$  values 28, 33, 47, 56, 59, 70, 76, 79. The XRD result shows significant change in the structure of nanocomposite which could be due to the homogeneous dispersion of  $\text{CeO}_2$  in the polymer matrix. All nanocomposites show XRD peaks which are attributed to the presence of  $\text{CeO}_2$  nanoparticles.

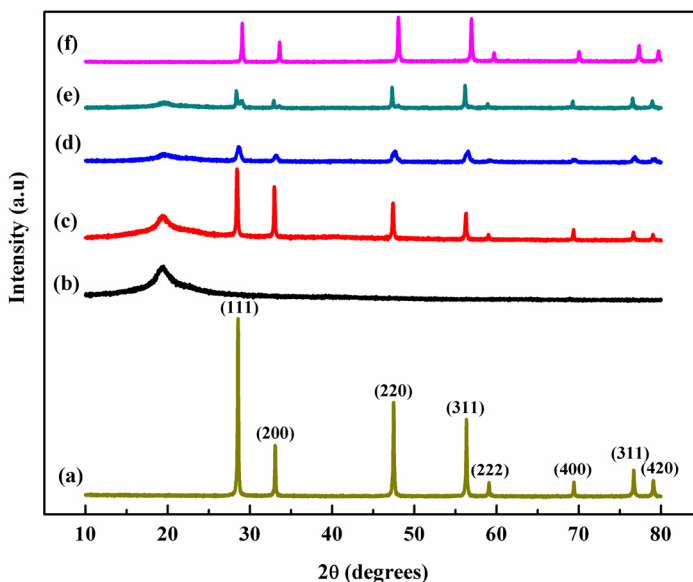


Fig. 3: XRD patterns of composite films having different wt% of filler (a) pure  $\text{CeO}_2$  (b) PVA/PPy at 50:50 (c) PPy/PVA/ $\text{CeO}_2$  at 25:70:05 (d) 20:70:10 (e) 15:70:15 (f) 10:70:20

#### 4.3 SEM analysis

The surface morphology of the pure  $\text{CeO}_2$  and the nanocomposite films was examined by scanning electron microscopy (SEM). The SEM morphology of pure  $\text{CeO}_2$  shows homogeneous structure of particles which is shown in Fig. 4 (a). From the nanocomposite image it was seen that the smoothened surface with low degree of agglomeration shown in Fig. 4(b). When the nanocomposite is loaded with 5%, 10%, 15%, 20% of  $\text{CeO}_2$  nanoparticles 4(c-f) shows different degree of agglomeration, with in the agglomerated areas and it shows clear contours visible between the  $\text{CeO}_2$  particles. The highest concentration of  $\text{CeO}_2$  nanoparticles in the PVA/PPy blend matrix resulted in the agglomeration [16]. From the SEM images it was very clear that the  $\text{CeO}_2$  nanoparticle has been uniformly dispersed in to the polymer matrix with low degree of agglomerations.

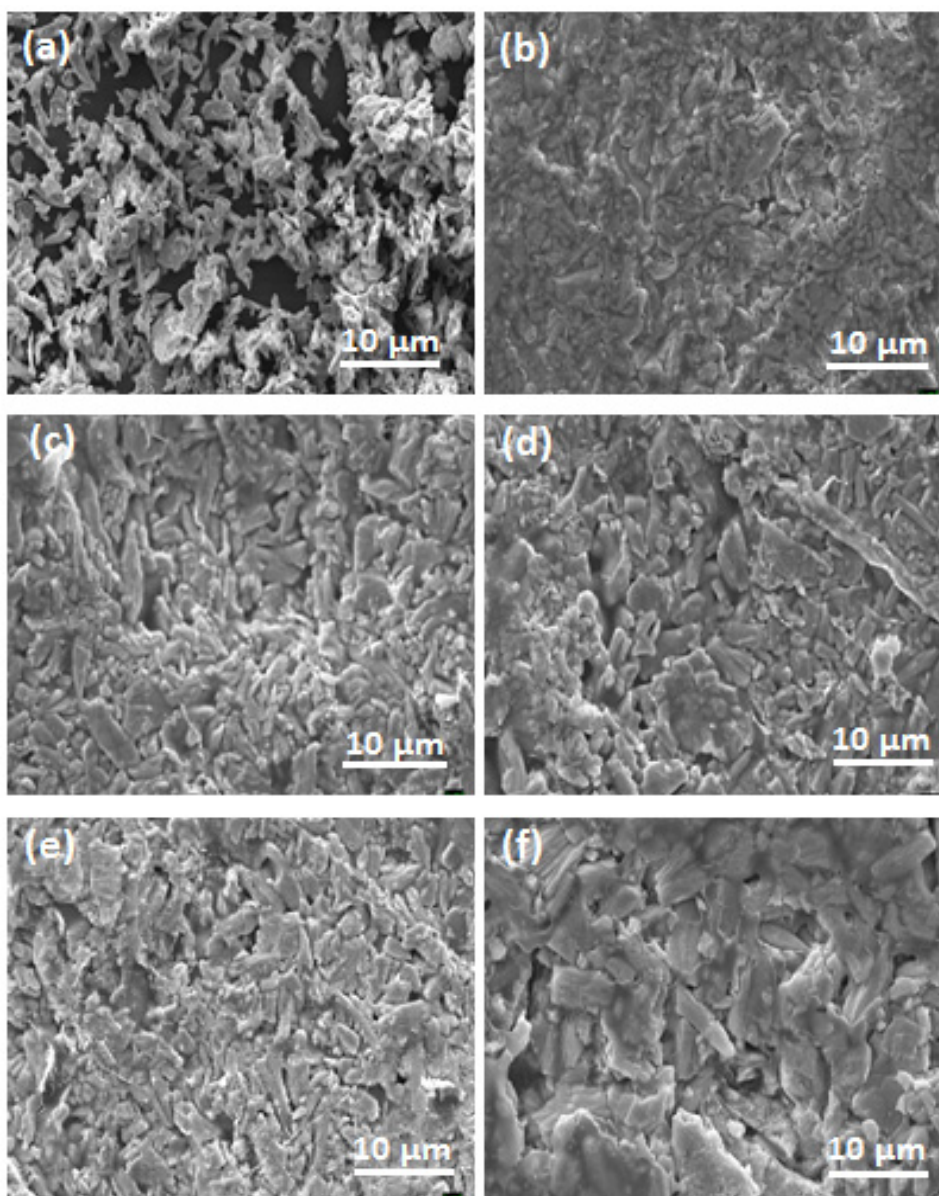


Fig. 4 shows the SEM images of (a) pure CeO<sub>2</sub> (b) PVA/PPy at 50:50 (c) PPy/PVA/CeO<sub>2</sub> at 25:70:05 (d) 20:70:10 (e) 15:70:15 (f) 10:70:20

#### 4.4 Mechanical studies

The force vs. extension graph of polymer nanocomposite films at various wt% of CeO<sub>2</sub> is shown in Fig. 5(a-e). The deformation of films is depending on the applied force [17]. In the present study tensile force was applied on films from which extension of the films were measured. The tensile plots have shown two different regions as elastic and plastic region. While applying force to the polymer films starts elongation according to the force applied. The region which is shown linear extension with the applied force known as elastic region. After

certain force applied to the polymer films, it tends to break in to two. This is known plastic region was represented by the sudden fall in the plots. This indicates that after removing the applied force to the films it does not get back to its original position. From the figures maximum tensile strength was observed for nanocomposites Fig. 5a. By introducing the  $\text{CeO}_2$  in to the nanocomposite which reduces the tensile strength of the nanocomposite films. This is shown in the Fig. 5(b-e). From this we can say that elongation was reduced by increasing the filler content. This indicated that loss in the ductility of the nanocomposites at higher nanoparticle contents.

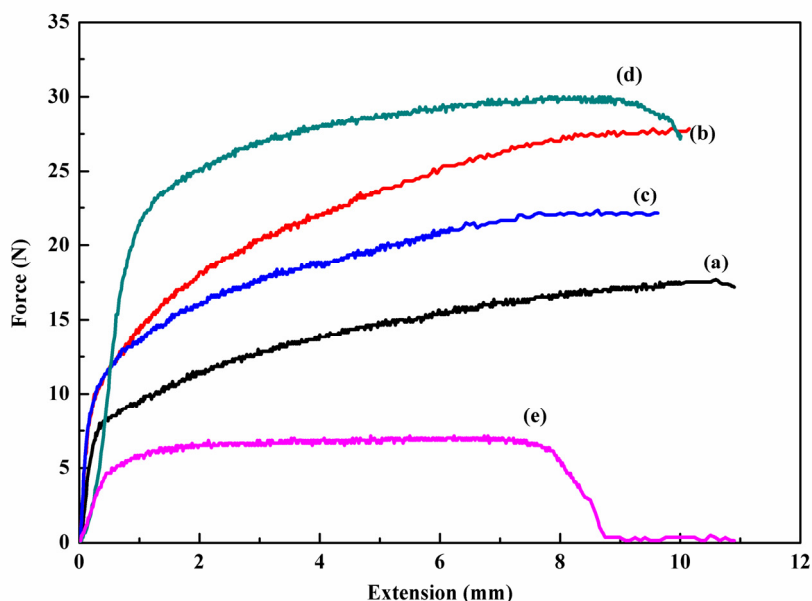


Fig. 5: Tensile strength of nanocomposites (a) PVA/PPy at 50:50 (b) PPy/PVA/ $\text{CeO}_2$  at 25:70:05 (c) 20:70:10 (d) 15:70:15 (e) 10:70:20

#### 4.5 Dielectric studies

Fig. 6(a-e) shows the plots of dielectric constant of PVA/PPy/ $\text{CeO}_2$  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 PVA/PPy blend shows maximum value of 110 at 50 Hz and at  $150^\circ\text{C}$ . By increasing the frequency gradually, the dielectric constant value decreases at 10 KHz for all the temperatures. For 5wt% of  $\text{CeO}_2$  loading in the nanocomposite, the similar changes were observed. When the wt% of  $\text{CeO}_2$  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 do not get enough time to re-orient themselves in the direction of applied electric field. [18, 19].

Fig. 7(a-e) shows the plots of dielectric loss ( $\tan \delta$ ) of PVA/PPy/ $\text{CeO}_2$  nanocomposites in the frequency range of 50 Hz to 20 MHz and the temperature in the range  $40$ – $150^\circ\text{C}$ . For nanocomposites the tangent loss value shows 3 at  $70^\circ\text{C}$ . The dielectric loss decreases from 3.9 at 50 Hz and at  $80^\circ\text{C}$  for 5% of  $\text{CeO}_2$  loading to 2.4 at 50 Hz and at  $150^\circ\text{C}$  for 20% of  $\text{CeO}_2$  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.



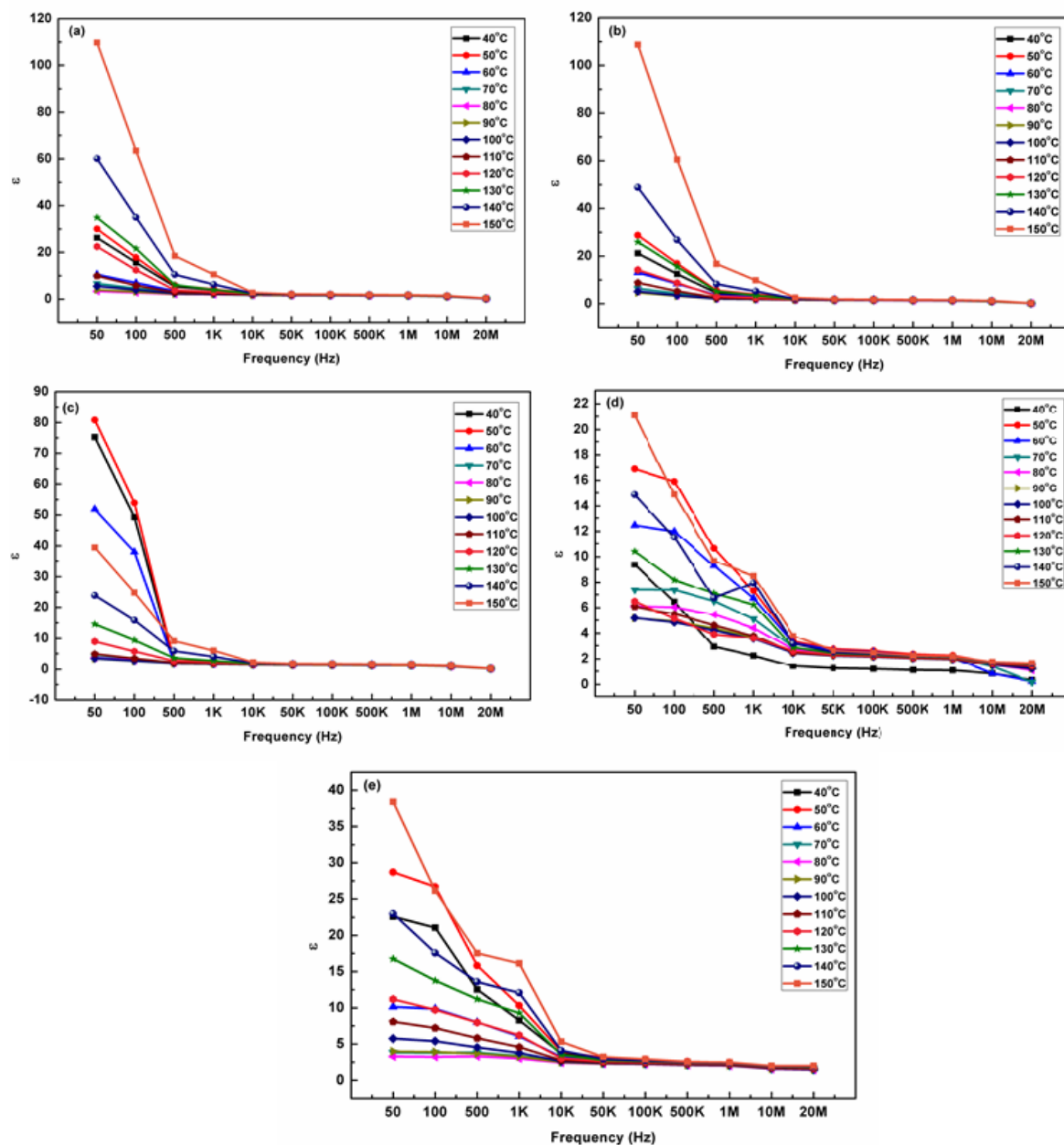


Fig. 6: Dielectric constant of (a) PVA/PPy blend (50/50) wt % (b) PPy/PVA/CeO<sub>2</sub> at 25/70/05 (c) 20/70/10 (d) 15/70/15 (e) 10/70/20



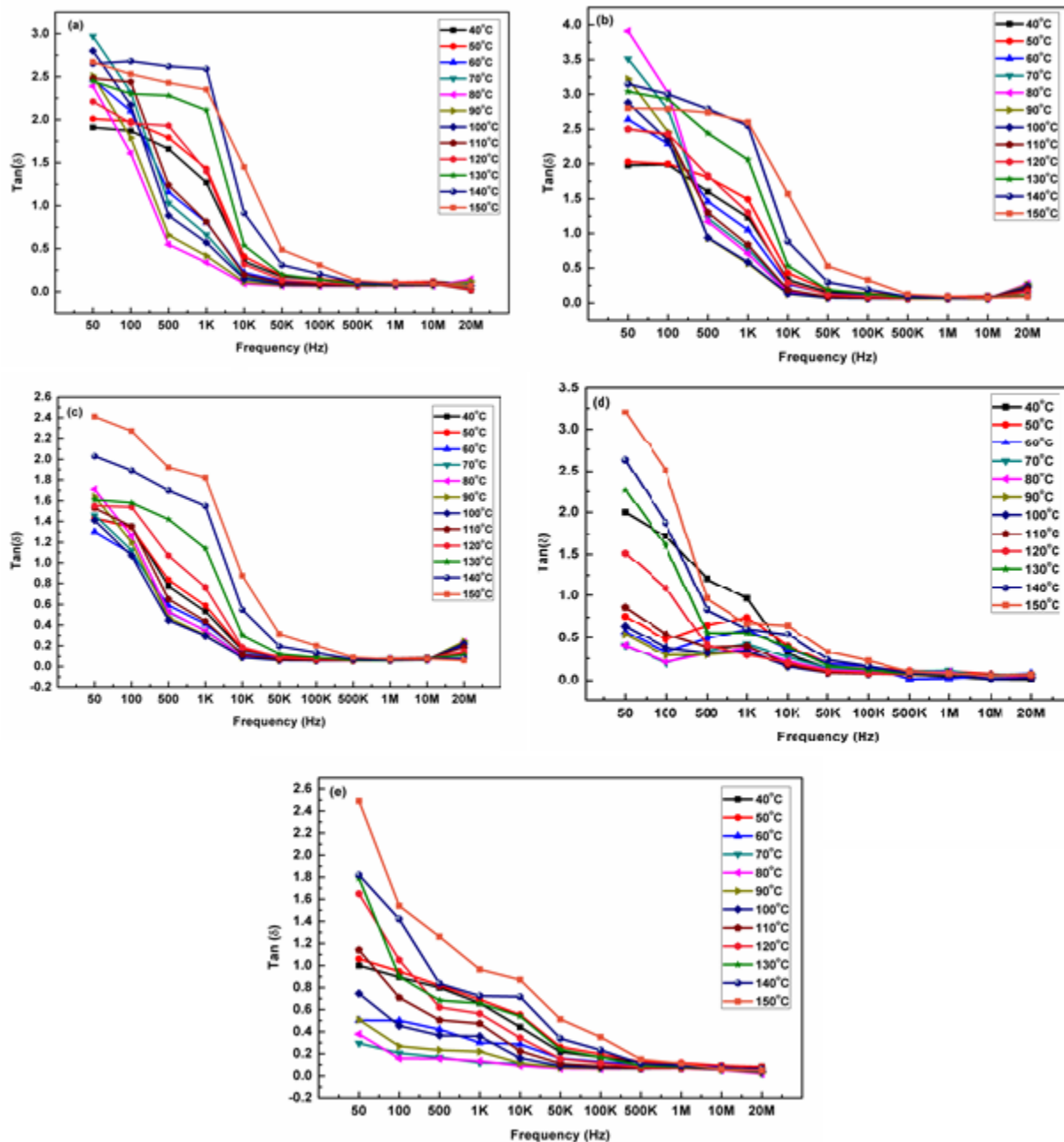


Fig. 7 dielectric loss ( $\tan \delta$ ) of (a) PVA/PPy polymer blend (50/50) wt % (b) PPy/PVA/CeO<sub>2</sub> at 25/70/05 (c) 20/70/10 (d) 15/70/15 (e) 10/70/20

#### 4. Conclusions

PVA/PPy/CeO<sub>2</sub> nanocomposites were successfully prepared by solution casting method. FTIR and XRD spectra revealed the successful incorporation of CeO<sub>2</sub> in to the PVA/PPy matrix. From the SEM results we confirm the homogeneous dispersion of the CeO<sub>2</sub> with the polymer matrix. The mechanical study of PVA/PPy/CeO<sub>2</sub> nanocomposite films demonstrates decreases the tensile strength of the polymer films. 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.

## Acknowledgement

One of the authors, M. K. Mohanapriya would like to acknowledge the management of VIT University for providing XRD and SEM facilities through DST-FIST scheme.

## References

- [1] M. Shibayama, M.Sato, Y.Kimura, H. Fujiwara, S. Nomura, *Polymer*. 29 (1988) 336.
- [2] H.M. Zidan, *J Appl. Polym. Sci.* 88 (2003) 104.
- [3] B. Lobo, M.R.Ranganath, T.S.G. Ravi Chandran, G. Venugopal Rao, V. Ravindrachary, S. Gopal, *Phys Rev B*, 1999.
- [4] D. Kincal, A.Kumar, A.D.Child, J.R.Reynolds, *Synth. Met*, 92 (1998) 53.
- [5] J. C.Vidal, E.Garcia, J.R.Castillo. *Anal. Chim. Acta*. 385 (1999) 213.
- [6] R. Al.Gaashani, S.Radima, N.Tabet, A. R. Daud, *Mater. Sci. Engg.* 177 (2012) 462.
- [7] A.A.Ansari, P.R.Solanki, B.D.Malhotra, *Appl Phys Lett*, 2008 .
- [8] E. Kumar, P.Selvarajan *Exp. Sci.* 11-14 (2010) *Polym. Sci.* 38 (2013) 1037.
- [9] A A.Ansari, P R.Solanki, B. D.Malhotra. *J Biotech*, 142 (2009) 179.
- [10] A.A.Ansari, A.Kaushik, P.R.Solanki, et al. *Electrochem Commun*, 10 (2008) 1246.
- [11] S.M.Pawde, K.Deshmukh, *J Appl. Polym. Sci.* 109 (2008) 1328-1337.
- [12] S.M.Pawde, K.Deshmukh, *J Appl. Polym. Sci.* 109 (2008) 3431-3437.
- [13] D.B.Dupare, M.D.Shirsat, A.S. Aswar, *Chem. Tech.* 18 (2011) 446-450.
- [14] A.Sharma, Pallavi, Sanjay Kumar, *Nano Sci. & Nano Tech.* 2 (2012) 82-85.
- [15] K.Deshmukh, J.Ahmad and M.B. Hagg, *Ionics*. 20 (2014) 957-967.
- [16] J.Ahmad, K.Deshmukh, M. Habib M. B. Hagg, *Arab J Sci. Eng.* 39 (2014) 6805-6814.
- [17] J.Ahmad, K.Deshmukh and M.B. Hagg, *Int. J Polym. Anal. Charact.* 18 (2013) 287-296.
- [18] A.Livi, V.Levita and P.A.Rolla, *J Appl. Poly. Sci.* 50 (1993) 1583-1590.
- [19] K. Deshmukh, M. B. Ahamed, S. K.K. Pasha, R.R. Deshmukh, P.R. Bhagat, *RSC Advances*, 5 (2015) 61933-61945.