

Electrical performance of soft polymer ionic membranes with mono and multi polymer systems

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Abstract

We prepared the Polyvinyl alcohol (PVA)/CdCl₂ and PVA/Polyvinylpyrrolidone (PVP)/CdCl₂ composites by solution blending known as the soft polymer ionic membrane (SPIM). The loading of CdCl₂ divalent ions demonstrates an influence over the electronic structure was confirmed by UV analysis. The bright divalent ionic morphology observed by scanning electron microscopy (SEM). The optimization of specific capacitance (C_p) and the dielectric constant disclosed as a function of an external DC bias potential. The trend of polarization was inversely proportional to the DC bias with the PVA system and directly to the PVP system. We disclosed the dielectric constant as a function of ionic loading. The optimized dielectric constant for various applications.

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Keywords: Ionic composite; Electronic structure; Morphology; Dielectric; DC bias

1. Introduction

PVA is a unique water soluble polymer used for casting the films due to easy processing [1]. The varying grades of PVA exhibit interesting electrical properties [2]. The modification of virgin PVA achieved by inducing alkyl halide, lead oxide and piezoceramics to improve electrical properties [3–5]. Ion induced polymer membranes was highly applicable for battery electrolyte, fuel cells [6]. Polymer Polyvinylpyrrolidone (PVP) is well known as Polyvidone or Povidone. It is water-soluble polymer consist of the

monomer N-vinylpyrrolidone. It preferred for various bio and pharmacy applications due to an inhibitor of recrystallisation property. PVP is especially useful as an additive for batteries, ceramics, fiberglass, inks, inkjet paper and in the chemical-mechanical planarization process [7]. The solution blending of PVA with PVP achieved homogeneously due to common solvent as water [8]. The CdCl₂ is having a polycrystalline and divalent in nature. It exhibit impulse electrical properties as a function of the temperature control the activation energy 0.52 eV [9]. The breed bio membrane studies of CdCl₂ in veterinary science able to administer the drug and maintain the morphological abnormalities were reported [10,11]. By using the electrophoereric technique and thermodynamic effect structure of CdCl₂ in the solute form was confirmed

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and co-related to the diffusion coefficient [11]. Recently the experimental and simulated studies on the variation of electrical properties related to the decrease in crystallization of PVA induced CdCl_2 was confirmed to know the role of divalent ions [12]. In our previous report structure, morphology, electrical impedance and conductivity of these composites shown feasibility for electrolyte application [13]. The loading of divalent ions exhibits modification of structure and decrease in conductivity from 10^{-10} to 10^{-8} S/m. We proposed the CdCl_2 dispersion with PVA and PVA/PVP systems. We disclosed the role of an external DC bias potential under wideband of a frequency range at ambient condition. The ionic-interface issue is well understood by microscopic morphology. This investigation is done in view of basic research to obtain dielectric constant under external control of DC bias potential.

2. Importance of Cd compounds

The Cd ions were occurred in the form of compounds with various organic and inorganic elements. Based on the nature of compounds it would preferred for the various applications from thin films, batteries (with Ni compound) to polymer composite domain. Cadmium chloride is used in electroplating, photocopying, calico printing, dyeing, mirrors, analytical chemistry, vacuum tubes, and lubricants and as a chemical intermediate in production of cadmium-containing stabilizers and pigments. Hence in the present work CdCl_2 preferred to obtain the soft polymer ionic memberane by mono and multipolymer system [13].

3. Experimental and materials

Polymer PVA with MW 1,25,000, LR grade make SD fine Chem., Mumbai and PVP with MW 10,000 AR grade, make sigma Aldrich used as received. Distilled water was used as solvent to prepare the polymer syrup. White powder of CdCl_2 MW 228.35 (make-Thomas Baker) dissolved with polymer syrup in distilled water by the loading of CdCl_2 . The samples were dried for 36 h at room temperature 35°C . Soft polymer composites were obtained and used as it is for further characterization.

3.1. Synthesis of polymer/ CdCl_2 composites

The protocol to obtain the polymer/ CdCl_2 composites shown in Fig. 2 a–b). The polymer syrup was

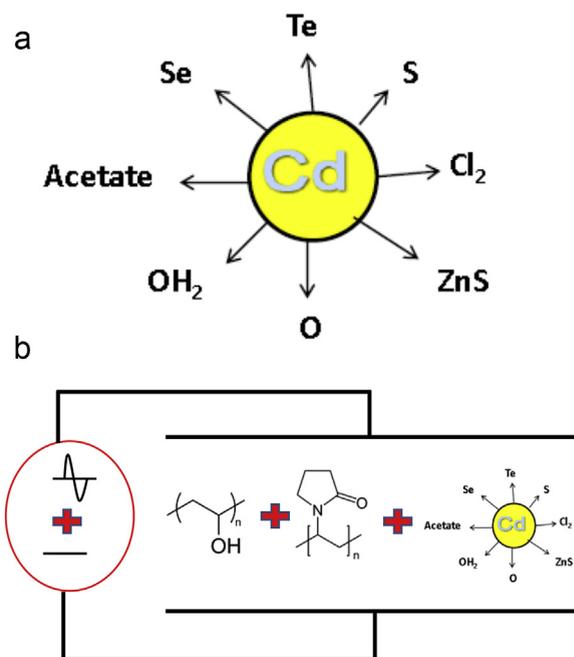


Fig. 1. a)Cd compounds with organic and inorganic elements, b) Basic protocol of SPIM testing under DC bias circuit mono and multi-polymer systems composites (5, 10 wt% CdCl_2).

mixed with CdCl_2 powder (by wt%). The mixture was poured into a petri dish to obtain ion induced polymer membrane. Samples labeled as C_1 – C_3 were PVA/ CdCl_2 . C_4 – C_6 were polymer with equal amount of PVA and PVP/ CdCl_2 . The loading of CdCl_2 is induced by 5, 10, 15 by wt%.

3.2. Basic principle of the SPIM test

The SPIM kept across the electrode fixture assembly with impedance analyzer and an external DC bias voltage supplied (in the range 0–40 V) simultaneously. Combined AC and DC will increase the strength of input signal across the electrode. The exact circuit is shown Fig. 1. It is having unique advantage to control the polarization as bulk property of SPIM externally. In our previous work we have made an attempt to address the electrical properties of polymers, composites, gels as function of DC bias [2,3,5,6,17].

4. Results and discussions

4.1. UV–visible spectroscopy

Optical Properties of PVA/PVP films doped with different concentration of CdCl_2 were investigated using UV–visible in the wavelength range

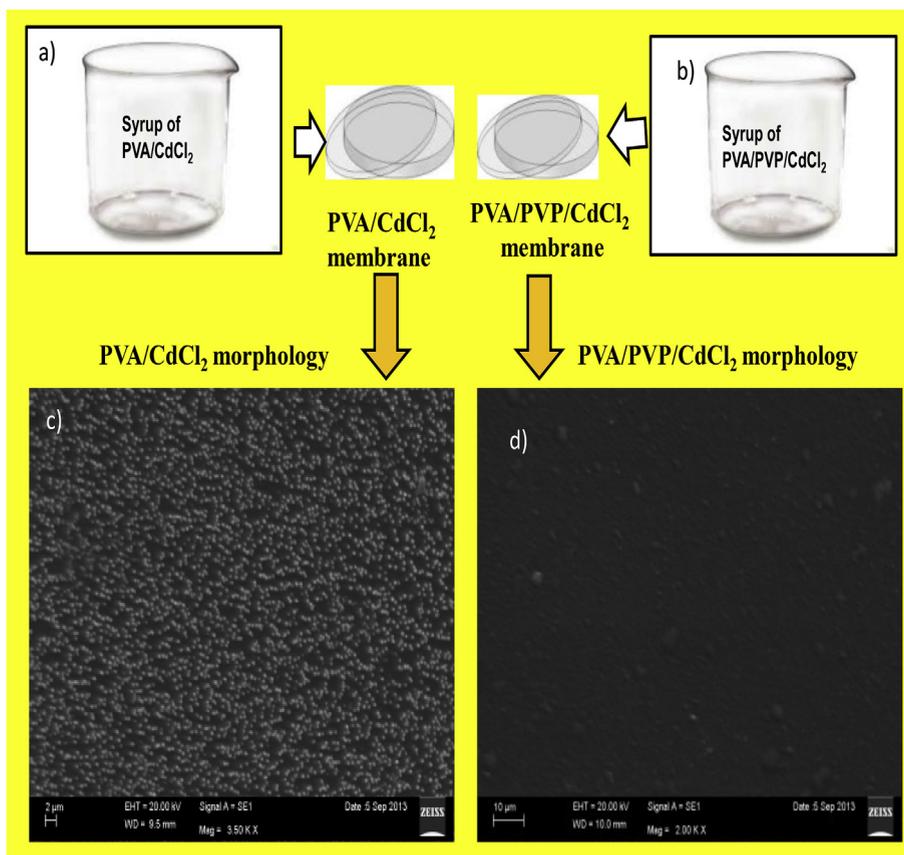


Fig. 2. a–b) Synthesis of CdCl_2 induced polymer composites, c–d) Morphology of with mono and multi-polymer systems.

190–350 nm of PVA/ CdCl_2 and PVA/PVP/ CdCl_2 is shown in Fig. 3. The observed spectra are characterized by the main absorbance edge for sample C_1 and C_2 at around 212 nm which is considered to be due to $n \rightarrow \pi$ transition of PVA [14]. This peak was shifted

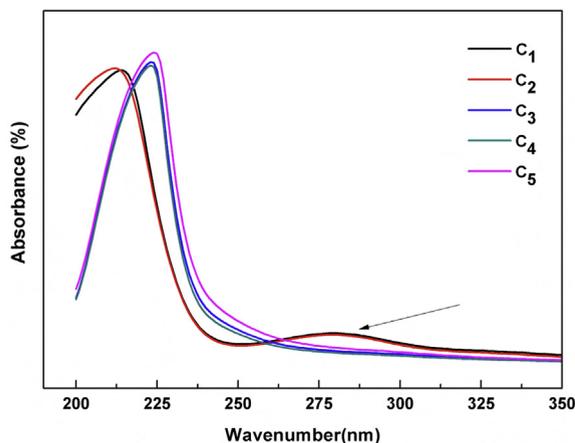


Fig. 3. UV of C_1 – C_3 PVA/ CdCl_2 composites (5, 10, 15% CdCl_2) and C_4 – C_5 PVA/PVP/ CdCl_2 composites (5, 10 wt% CdCl_2).

towards higher wavelength (225 nm) with the addition of PVP and increasing the CdCl_2 content in samples (C_3 – C_5). Also the intensity of this peak was increased with the addition of PVP and CdCl_2 in PVA. Another absorption shoulder was observed in sample C_1 and C_2 at about 270–280 nm which may arise due to unsaturated bonds of PVA, mainly $\text{C}=\text{O}$ bond and attributed to $\pi \rightarrow \pi^*$ transition [14]. The shift in the absorption peak is may be due to the complexation between PVA/PVP blend and CdCl_2 which may reflect the change in the crystalline of polymer matrix due to the addition of CdCl_2 [15].

4.2. Morphology of mono and multipolymer/ CdCl_2 composites

CdCl_2 impact on morphology with PVA and PVA/PVP system was identified by using a Zeiss electron microscope shown in Fig. 2 c–d). The bright domains represent the presence of occupied CdCl_2 ions in PVA system [22]. The morphology of divalent ions composed with polymer system. The additional

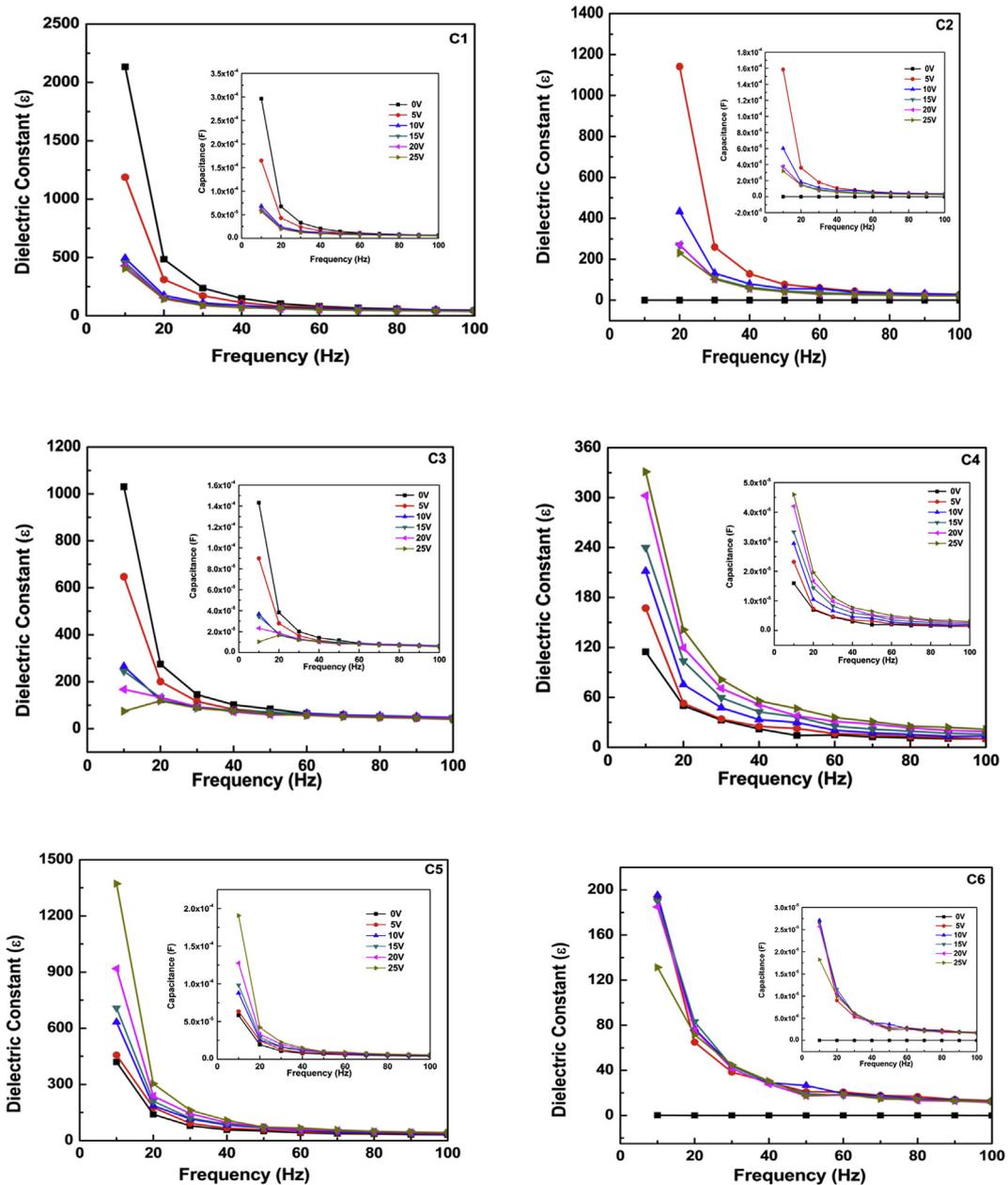


Fig. 4. Dielectric constant as a function of DC bias voltage (inset specific capacitance) of C1–C3 PVA/CdCl₂ and C4–C6 PVA/PVP/CdCl₂ composites (5, 10, 15% CdCl₂).

polymer PVP capped the aggregated network and disappear the bright spots [23]. The morphology shows significant impact on electrical properties [16,20].

4.3. Electrical properties of mono and multipolymer system with CdCl₂ ions

The specific capacitance and dielectric constants were measured by N4L, PSM1735 Impedance

analyzer. The DC bias operated from 0 to 25 V (externally and simultaneously) under wide frequency range from 10 Hz to 100 Hz. The composites with PVA system shown dielectric trend inversely proportional for 5 and 15% of CdCl₂ loading shown in Fig. 3 C1–C3 (inset of specific capacitance). For 10% loading of CdCl₂ demonstrate the influence of DC bias 5 and 10 V offer maximum polarization. It may be due ionic polarization due to CdCl₂ ions. It is supported by

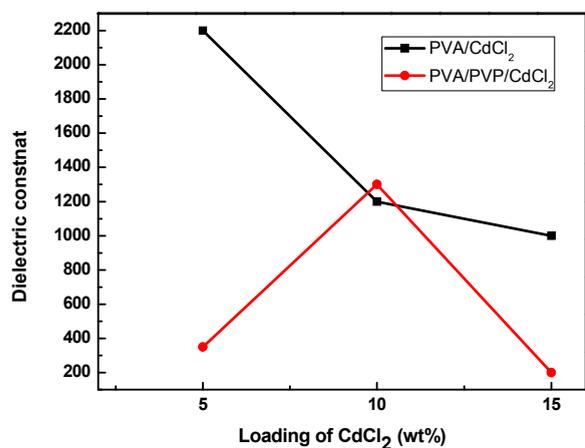


Fig. 5. Dielectric constant versus loading of CdCl₂ with mono and multi polymer systems C1–C3) PVA/CdCl₂ and C4–C6) PVA/PVP/CdCl₂ composites (5, 10, 15% CdCl₂).

the low frequency polarization based on the principle of Maxwell–Wagner dielectrics model. Furthermore, the role of divalent ions reinforced in the crosslinked network of mono and multi polymer systems co-related to the morphology and the polarization impact was disclosed with composition of PVP system. The chemical and physical structure and crystallization phase was reported based on the principle of increase interplaner distance with mono and multi polymer systems [17–20]. Fig. 3 C4–C6 with inset of specific capacitance demonstrates the polarization of PVA/PVP/CdCl₂ (with 5,10,15 wt% CdCl₂ loading). The DC bias applied across these samples is directly proportional to the dielectric constant. The optimization of polarization is achieved under external control of bias potential.

Hence the controlled dielectric process is suitable as one of the best mediums of electrode applications. The results lead to choose the desired moiety of polymer systems to fabricate the electrode system for battery and electronic applications. The ions respond under various external stimuli. The temperature dependent relaxation process of SIMS is in progress to understand the relaxation mechanism (see Figs. 4 and 5).

The soft ionic membranes demonstrates an excellent dielectric constant value 2200 with PVA system (for 5 wt%). However, further increase in loading of CdCl₂ ions decreases the dielectric constant values. It may be due to majority of ions saturates the polarization process. The multipolymer system of PVA/PVP composed with divalent ions demonstrates the maximum dielectric constant = 1300 (for 10 wt%).

Basically PVP is an amorphous polymer and due to the presence of the rigid pyrrolidone group, it form the various complexes with many inorganic salts [24]. It maybe supported to disclose and the electrical polarization.

We have already claimed the composition of modified blend structure with mono and multipolymer system. The increase in interplaner distance as a function of CdCl₂ loading confirmed from our previous report. However, the OH stretching of polymer systems were confirmed by FTIR report. It was due to the intercalation between the polymer system with CdCl₂ composition [20]. Further, scope of this investigation may be useful for the better shape memory polymer applications [21].

5. Conclusions

In the present investigation the electronic structure of SPINM was confirmed by UV analysis as function of CdCl₂ loading. The morphology of PVA/CdCl₂ and PVA + PVP/CdCl₂ systems reveals brighter and dark contrast morphology. The optimization of dielectric constant and specific capacitance as a function of DC bias were measured and useful to external control. The magnitude of the dielectric constant is inversely proportional for PVA system and directly proportional with additional PVP system. The SPIM is further useful to fabricate suitable electrolyte with desirable dielectric constant. It may be developed as shape memory polymer applications too.

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References

- [1] C.A. Finch, Polyvinyl Alcohol, John Wiley & Sons, Bristol, Great Britain, 1971.
- [2] G.M. Joshi, S.M. Pawde, Effect of molecular weight on dielectric properties of polyvinyl alcohol films, *J. Appl. Polym. Sci.* 102 (2) (2006) 1014–1016.
- [3] G.M. Joshi, T. Cuberes, DC bias function of electrical characterization of PVA induced nickelchloride composite film, *Ionics* 19 (6) (2013) 947–950.
- [4] G.M. Joshi, S.K. Pasha, K. Chidambaram, Modified PVA moiety with PbO as humidity sensor, *Compos. Interfaces* 20 (5) (2013) 331–341.

- [5] G.M. Joshi, S.M. Khatake, S. Kaleemulla, N.M. Rao, T. Cuberes, *Curr. Appl. Phys.* 1 (2011) 1322.
- [6] G.M. Joshi, K. Deshmukh, Electrical characterization of polymer composite gel under biasing as polar medium, *Ionics* 20 (4) (2014) 529–534.
- [7] F. Haaf, A. Sanner, F. Straub, Polymers of N-vinyl pyrrolidone: synthesis, characterization and uses, *Polym. J.* 17 (1985) 143–152.
- [8] C.S. Pokhrel, A. Dhakshinamoorthy, K. Jayaraman, J. Pragasam, K.S. Nagaraja, Crystal growth, thermal analyses and electrical conductivity of CdCl₂–PbCl₂ system, *J. Cryst. Growth* 252 (2003) 511–516.
- [9] A.G. Lymberopoulos, V.P. Kotsaki-Kovatsi, A. Taylor, N. Papaioamtou, P. Bikas, Effects of cadmium chloride administration on the macroscopic and microscopic characteristics of ejaculates from chios ram-lambs, *Theriogenology* 54 (2000) 1145–1157.
- [10] E.V. Kerkhove, V. Pennemans, Q. Swenne, Cadmium and transport of ions and substances across cell membranes and epithelia, *Biometals* 23 (2010) 823–855.
- [11] A.C.F. Ribeiro, J.C.S. Gomes, L.M.P. Veríssimo, C. Romero, L.H. Blanco, M.A. Estes, Diffusion of cadmium chloride in aqueous solutions at physiological temperature 310.15 K, *J. Chem. Thermodyn.* 57 (2013) 404–407.
- [12] M.B. N.Prakash, A. Manjunath, R. Somashekar, Studies on AC electrical conductivity of CdCl₂ doped PVA polymer electrolyte, *Adv. Cond. Matter Phys.* 2013 (2013) 1–6.
- [13] G. Hirankumar, S. Selvasekarapandian, N. Kuwata, J. Kawamura, T. Hattori, Thermal, electrical and optical studies on the poly(vinyl alcohol) based polymer electrolytes, *J. Power. Sources* 144 (2005) 262–267.
- [14] E.M. Abdelrazek, I.S. Elashmawi, S. Labeeb, Chitosan filler effects on the experimental characterization, spectroscopic investigation and thermal studies of PVA/PVP blend films, *Phys. B* 405 (2010) 2021–2027.
- [15] E.M. Abdelrazek, I.S. Elashmawi, Characterization and physical properties of CoCl₂ filled polyethyl-methacrylate films, *Polym. Compos.* 29 (2008) 1036–1043.
- [16] N. Chen, L. Hong, Embedding poly (styrene sulfonic acid) into PVDF matrix—a new type of proton electrolyte membrane, *Polymer* 45 (2004) 2403–2411.
- [17] M. Khutia, G.M. Joshi, K. Deshmukh, M. Pandey, *Compos. Interfaces* 22 (3) (2015) 167–178.
- [18] G.M. Joshi, A. Sharma, R. Tibrawala, S. Arora, K. Deshmukh, S. Kalainathan, R.R. Deshmukh, *Poly-PlastTech. Eng.* 53 (6) (2014) 588–595.
- [19] S. Marino, G.M. Joshi, A. Lusuardi, M. Teresa Cuberes, Ultrasonic force microscopy on poly(vinyl alcohol)/SrTiO₃ nanoperoovskites hybrid films, *Ultramicroscopy* 142 (3) (2014) 32–39.
- [20] M. Pandey, G.M. Joshi, K. Deshmukh, J. Ahmad, Impedance spectroscopy and conductivity studies of CdCl₂ doped polymer electrolyte, *Adv. Mater. Lett.* 6 (2) (2015) 165–172.
- [21] C. Liu, H. Qin, P.T. Mather, Review of progress in shape-memory polymers, *J. Mater. Chem.* 17 (2007) 1543–1558.
- [22] S. Bhushan, S. Pillai, Photoconductivity and photoluminescence in chemically deposited (Cd-Zn)S: CdCl₂, Tb films, *Crystal Res. Tech.* 43 (7) (2008) 762–768.
- [23] K.F. Csáki, M. Nagy, F. Csempesz, Influence of the chain composition on the thermodynamic properties of binary and ternary polymer solutions, *Langmuir* 21 (2) (2005 Jan 18) 761–766.
- [24] M. Ravi, S. Bhavani, Y. Pavani, V.V.R. Narasimha Rao, Investigation on electrical and dielectric properties of PVP: KClO₄ polymer electrolyte films, *Ind. J. Pure Appl. Phys.* 51 (2013) 362–366.