

Study of polyvinylalcohol/polyionic organic semiconductor as thermistor

Anandraj J, Girish M. Joshi*, Mayank Pandey

Polymer Nanocomposite Laboratory, Center for Crystal Growth, VIT University, Vellore 632014, Tamil Nadu, India

*Corresponding author, Tel: (+91) 416-2202727; Fax: (+91) 416-2243092; E-mail: girish.joshi@vit.ac.in

Received: 16 March 2016, Revised: 16 September 2016 and Accepted: 21 December 2016

DOI: 10.5185/amp.2017/405
www.vbripress.com/amp

Abstract

We have demonstrated the successful preparation of polyvinyl alcohol (PVA) composed CuBi_2S_3 polyionic (PI) composites. Polymer composites were sensitive to the external stimuli, the modified PVA moiety exhibits excellent electrical property as a function of temperature. The volume resistance measured by impedance analyzer (40 to 150°C) under broadband frequency (50Hz -1MHz). The negative temperature coefficient (NTC) was observed in the temperature range of 40 to 150°C. It offers the nonlinear resistivity, $\rho = 10^5$ ($\Omega\text{-m}$) across pure PVA moiety. The influence of polycationic-ions crucial to obtain the gradual decrease of resistivity (ρ) up to 10^4 ($\Omega\text{-m}$). The thermistor characteristics were disclosed as function of polyionic loading (wt %). Copyright © 2017 VBRI Press

Keywords: Electrical properties, composite, polyionic, thermistor.

Introduction

Polyvinyl alcohol (PVA) is a solid pigment [1], ceramic products [2], plastic [3], cement [4], fibers [5], non-woven fabrics [6], catalyst pellets and cork compositions which has widely used in different areas of research including biological and medical field [7]. It is one of the most important polymeric material and has an excellent film forming, glossy in nature and better for recasting. PVA is semi crystalline polymer that is available in a range of grades that vary by the degree of hydrolysis [8]. The basic electrical and mechanical properties of PVA are based on the degree of polymerization.

The electrical resistivity of polymers (such as polyvinyl alcohol, polyvinylchloride, polystyrene and polyethylene) is in the order of 10^{15} Ω cm [9]. The electrical properties of these polymeric materials can be increased by incorporation of filler into polymer matrix because the dispersed filler will enhance various physical properties of the polymers [10]. The electrical conductivity of PVA can be optimized by loading the filler. The composite not only combine the important properties of dopant and polymers but also exhibits many new properties that compare to virgin single-phase materials [11]. The cationic, anionic and multi-ionic fillers with PVA were demonstrated better electrical performance with silver, zinc, tungsten oxide, KNO_3 , MgCl_2 , NiCl_2 , and PbTiO_3 . From this literature, we motivated to select the polyionic entity as the Copper Bismuth Sulphide (CuBi_2S_3).

It is a ternary compound belongs to semiconducting material, new emerging semiconductor and is believed to be a potential candidate for photovoltaic application.

Initially polyionic possess suitable optical properties for solar cells ($E_g = 1.4\text{eV}$ and a high optical absorption coefficient $\alpha > 10^4\text{cm}^{-1}$). Besides it consists of comparatively earth abundant, cheap as well as non-toxic elements. It was widely used in many applications such as hydrogen storage, high energy batteries and catalytic fields. Based on these promising characteristics numerous methods have been reported to deposit polyionic thin films such as reactive sputter, co-evaporation, sulphurization of the electroplated metallic stacks and solid state reaction [12-15]. Various methods were used for the production and characterization of copper bismuth sulphide nanocrystals in the present era [16-17].

In the present research work we have selected the PVA with copper bismuth sulphide (CuBiS) metal precursor to study and disclosed the resistivity as a function of temperature with varying concentration of polyionic composite. It was feasible for the thermistor applications.

Experimental

Materials

PVA graduals-LR grade supplied by SDFL, Mumbai, India, (molecular weight 85.000). CuBiS was prepared as mentioned in the reference [16].

Casting of PVA/ CuBiS composite films

Mixture of PVA with polyionic were prepared by solution casting method at different weight ratio of polyionic (0, 10, 20, 30 wt %). First PVA powder was dissolved in distilled water by gently stirred at 410 rpm at 60°C to get

complete dissolution. The required quantity of polyionic was mixed separately with distilled water and added to the polymeric solution with continuous stirring at 350 rpm at 30 °C for 12 hr. The solution so obtained was poured in the petri dish at 35 °C for 48 hr to get composite film. The composite film was peeled from the petri dish and kept for further characterization.

Results and discussion

Morphology of pure and modified ionic composites

Poly vinyl alcohol (PVA) and polyionic composite was investigated by using scanning electron microscope (SEM). It provides the ionic network of fillers, phase separation, polymer network, aggregation, thermal impact possessing of composites. The surface morphology of the samples annealed at different weight ratio is shown in fig1. The SEM image shows the polygon shape granules is obtained without doping in **Fig. 1(a)**.

The SEM image obtained for 10wt% of polyionic doping levels is shown in **Fig 1(b)**. The bright spots present on the surface because of the presence of polyionic entity. This results in significant change in surface morphology of PVA/polyionic composites. We demonstrated some bright aggregations uniformly occupied polyions cross-linked with PVA. In **Fig 1(c)** shows the SEM image formed at 20 wt% loading of polyionic shows the very clear presence of micro-cracks and voids composed with PVA system is observed. It may be due to increase in the doping level. In **Fig. 1(d)** shows the SEM image formed at 30 wt% addition of polyions exhibit bubble spots is obtained throughout the substrate. It is clear that the particles have highly mono dispersive in nature. It was observed that the microstructure of PVA and polyionic film changed due to introduction of different amounts of polyionic into PVA. The SEM analysis reveals that PVA and polyionic formed composites.

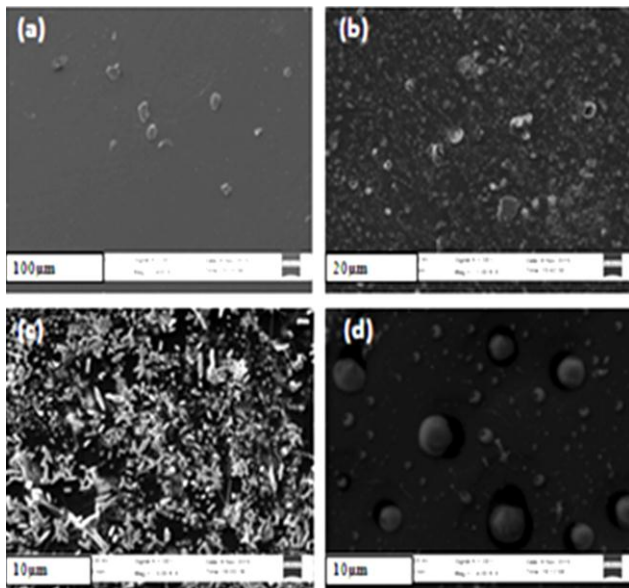


Fig.1. SEM micrographs of (a) PVA/PI: 100:0, (b) PVA/PI: 90:10, (c) PVA/PI: 80:20, (d) PVA/PI: 70:30 composites,

Testing of pure and modified composite as thermistor

The relationship between the electrical resistivity (ρ) and temperature ($^{\circ}\text{C}$) plots with different weight ratio of polyionic concentration is shown in fig (2). The electric resistance of PVA and polyionic was measured in the temperature range from 29 to 150 $^{\circ}\text{C}$. It can be seen that the resistivity – temperature characteristics are changed with weight percentage. From the graph, we understood that resistance of the thermistor decreases almost linearly (i.e. quasi linear behavior) with increase in temperature [18]. The resistivity obtained in this work can be primarily attributed to the grain size of the samples. Large grain size implies small number of insulating grain boundaries and hence lower energy barrier to electron conduction resulting in lower resistance [19]. At small weight percentage, it exhibits low temperature resistivity and increasing the weight percentage the room temperature gradually increase. This change in resistance and temperature characteristics of thermistor from exponential to quasi linear is mainly due to the contribution of polyionic composite. It is clear that polyionic reinforced polymer composite demonstrates a negative temperature coefficient thermistor behavior effects over a wide temperature range from 90 to 150 $^{\circ}\text{C}$ and gradually become strong. The resistivity varied gradually with increasing the temperature.

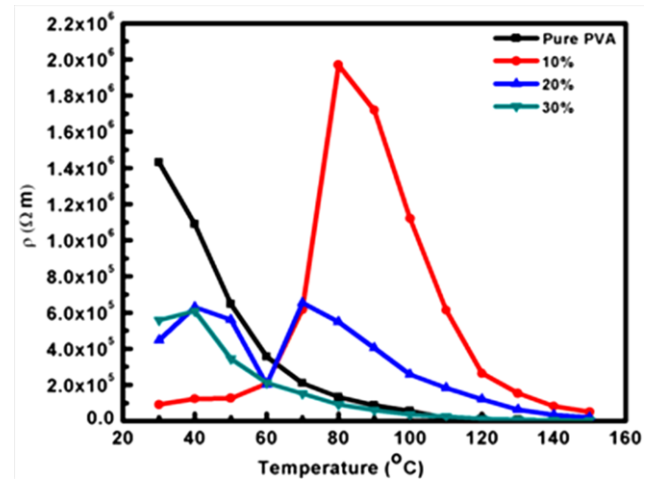


Fig. 2. Temperature dependent resistivity of pure PVA, PVA/PI: 90:10, PVA/PI: 80:20, PVA/PI: 70:30

Conclusion

In the present investigation, we prepared the PVA/polyionic composite films by solution casting method. SEM morphology represents the presence of polyionic entity and exhibits the bubble spot and micro cracks shapes present on the surface. We propose that adding the lower amount of polyionic loading with polymer demonstrated the stable NTC thermistor property and loading of 10% polyions with PVA system exhibit better (NTC) thermistor property. The electrical characterization of composite films was performed by impedance analyzer to confirm the change in resistivity as function of temperature.

Acknowledgements

The authors would like to thank Naval Research Board, Defense Research and Development Organization (NRB-DRDO), New Delhi Project No. 259/Mat/ 11–12, for providing electrical characterization and VIT University for providing SEM under DST-FIST project.

References

1. Cholakis, C.H.; Zingg, W.; Sefton, M.V.; *J. Biomed. Mater. Res.*, **1989**, *417*, 23.
DOI: [10.1002/jbm.820230404](https://doi.org/10.1002/jbm.820230404)
2. Garrel, D.R.; Gaudreau, P.; Zhang, L.M.; Reeves, I.; Brazeau, P.; *J. Surg. Res.*, **1991**, *51*, 297.
DOI: [10.1016/0022-4804\(91\)90111-x](https://doi.org/10.1016/0022-4804(91)90111-x)
3. Horiike, S.; Matsuzawa, S.; *J. Appl. Polym. Sci.*, **1995**, *58*, 1335.
DOI: [10.1002/app.1995.070580815](https://doi.org/10.1002/app.1995.070580815)
4. Paradossi, G.; Covalieri, F.; Chiessi, E.; Spagnoli, C.; Cowman, M.K.; *J. Mater. Sci - Mater. Med.*, **2003**, *14*, 687.
DOI: [10.1023/A:1024907615244](https://doi.org/10.1023/A:1024907615244)
5. Zhai, M.; Yoshii, F.; Kume, T.; *Carbohydr. Polym.*, **2003**, *52*, 311.
DOI: [10.1016/S0144-8617\(02\)00292-8](https://doi.org/10.1016/S0144-8617(02)00292-8)
6. Ramaraj, B.; *J. Appl. Polym. Sci.*, **2007**, *103*, 909.
DOI: [10.1002/app.25237](https://doi.org/10.1002/app.25237)
7. Vadivelu M.A.; Ramesh Kumar C.; Joshi G.M.; Ahmad, *Comp. Interf.*, **2016**, *26*(9), 847.
DOI: [10.1080/09276440.2016.1176853](https://doi.org/10.1080/09276440.2016.1176853)
8. Demerlis, C.C.; Schonekar, D.R.; *J. Food Chem. Toxicol.*, **2003**, *41*, 319.
DOI: [10.1096/S0278-6915\(02\)00258-2](https://doi.org/10.1096/S0278-6915(02)00258-2)
9. El-Khodary, A.; Oraby, A.H.; Abdelnaby, M.M.; *J. Magn. Magn. Mater.*, **2008**, *320*(11), 1739.
DOI: [10.1016/j.jmmm.2008.01.030](https://doi.org/10.1016/j.jmmm.2008.01.030)
10. Raja, V.; Sarma, A.K.; Narasimha Rao, V.V.R.; *J. Mater. Sci. Lett.*, **2003**, *57*, 4678.
DOI: [10.1016/S0167-577X\(03\)00384-7](https://doi.org/10.1016/S0167-577X(03)00384-7)
11. Podgrabinski, T.; Svorcik, V.; Mackova, A.; Hnatowicz, V.; Sajdl, P.; *J. Mater. Sci. – Mater. Electron.*, **2006**, *17*, 871.
DOI: [10.1007/s10854-006-0040-1](https://doi.org/10.1007/s10854-006-0040-1)
12. Mesa, F.; Gordillo, G.; *J. Phys. Conf. Ser.*, **2009**, *167*, 1
DOI: [10.1088/1742-6596/167/1/012019](https://doi.org/10.1088/1742-6596/167/1/012019)
13. Gerein, N.J.; Haber, J.A.; *Chem. Mater.*, **2006**, *18*, 6297.
DOI: [10.1021/cm061453r](https://doi.org/10.1021/cm061453r)
14. Colombara, D.; Peter, L.M.; Huthings, K.; Rogers, K.D.; Schafer, S.; Dufton, J.T.R.; Islam, M.S.; *Thin Solid Films*, **2012**, *16*, 5165.
DOI: [10.1016/j.tsf.2012.04.003](https://doi.org/10.1016/j.tsf.2012.04.003)
15. Yan, Chang.; Gu, Ening.; Liu, Fangyang.; Lai, Yanqing.; Li, Jie.; Liu, Yexiang, *Nanoscale*, **2013**, *5*, 1789.
DOI: [10.1039/c3nr33268c](https://doi.org/10.1039/c3nr33268c)
16. Anandraj, J.; Joshi, G.M.; *J. Mater. Sci. – Mater. Electron.*, **2016**, *16*, 5148.
DOI: [10.1007/s10854-016-5148-3](https://doi.org/10.1007/s10854-016-5148-3)
17. Jain, V. K, Abhishek, V; *Physics of Semiconductor Devices*; Springer : Newyork, **2014**.
DOI: [10.1007/978-3-319-03002-9](https://doi.org/10.1007/978-3-319-03002-9)
18. Joshi, G.M.; Teresa C.; *Ionics.*, **2013**, *19* (9) 947.
DOI: [10.1007/s11581-013-0908-z](https://doi.org/10.1007/s11581-013-0908-z)
19. Hean, L.; Lingb, Z.Y.; Wua, M.Y.; *Ceram. Int.*, **2015**, *41*, 10142.
DOI: [10.1016/j.ceramint.2015.04.113](https://doi.org/10.1016/j.ceramint.2015.04.113)