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Synthesis and dielectric investigations of bismuth sulfide particles filled PVA: Polypyrrole core-shell nanocomposites

Vidyashree Hebbar, R.F. Bhajantri*

Department of Physics, Karnatak University, Dharwad 580 003, Karnataka, India

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ABSTRACT

High dielectric composites of bismuth sulfide (Bi_2S_3) filled in poly (vinyl alcohol) (PVA)/polypyrrole (PPy) blend were prepared. Fourier Transform Infrared Spectroscopic analysis infers the encapsulation of Bi_2S_3 particles by PVA: PPy matrix. The thermal activation is estimated using Coats and Redfern equation from thermogravimetric analysis results. SEM micrographs revealed that Bi_2S_3 filled PVA:PPy blend composite films possess smooth surface and homogeneous dispersion of particles. The frequency dependence of dielectric constant, loss tangent and electric modulus were analyzed. The characteristic relaxation times for dielectric loss within the composites are calculated. The AC conductivity is maximum for 8 wt% of bismuth sulfide particles. The dielectric parameters and AC conductivity are temperature dependent. The dielectric response parameter *s* follows the correlated barrier hopping model and accordingly effective barrier height (W_m) of the composite for 8 wt% Bi_2S_3 filled PVA: PPy are determined.

1. Introduction

Electrically conducting polymer matrices are of enormous and effective interest for their exploitation in the field of polymer research and molecular engineering, since they own high conductivity as compared to other polymers and are used as a replacement for metals [1]. Polypyrrole (PPy) is one of the capable conducting polymers which have got increased attention because of its practical applications based on the ease of synthesis, low cost, excellent environmental and thermal stability, relatively low density and high conductivity [2]. It has a potential application in the field of electronic devices such as an actuator, supercapacitor etc. [3]. PPy can act as a potential energy storage material, because of its intrinsic electrical conductivity and redox properties [4]. However, PPy is limited with insolubility, poor processability and lack of essential mechanical strength, which hinder its capacity for huge production. The limitations of PPy can be conquered by introducing it into the other mechanically stable polymers while producing the composite or by blending with a suitable polymer matrix. PVA is one of the most preferable semi-crystalline polymers for the fabrication of environmental friendly, biodegradable, and water-soluble polymer composite as it owns excellent adhesion, and renowned chemical and physical properties [5,6].

The inorganic materials covered with conducting polymers are of much interest, as they possess environmental stability and easy processability and also expose the specific properties of the inorganic core [7]. The one-dimensional filler particles gained extensive attention because of their large aspect ratio. Bi_2S_3 is a V–VI group compound, *n*-type crystalline semiconductor. The earlier reported band gap of bulk Bi_2S_3 is 1.3 eV-1.7 eV that lies in the visible solar energy spectrum and in turns it is a promising material for the photovoltaic applications [8,9]. Several studies have been reported on the morphologies of Bi_2S_3 in the form of particles, nanorods, nanotubes, nanowires, nanoflakes and nanoflowers [10]. It has been proposed to be useful as a good solid-state thermoelectric material, due to its significant thermoelectric properties [11].

The electrical properties of polymer nanocomposites are different from those of bulk materials due to an increased number of interfacial atoms and defects. The AC impedance approach is used for characterizing the electrical properties of polymeric materials. The dielectric property of the composites depends on the volume fraction, size, and also shape of conducting fillers, as well as other factors such as preparation method, the interfacial interaction between the fillers and the polymer. Various new technological applications require energy storage capacitors (i.e., batteries) in order to be functional. In other words, the high dielectric permittivity is needed for the extensive application. High dielectric constants have been reported for a variety of materials in recent years, including ceramics, ceramic/polymer and polymer/polymer (or organic/polymer) composites [12]. On the other hand, the polymer nanocomposites with one-dimensional filler provided with a drawback of high dielectric loss. Moreover, polymer-coated inorganic

* Corresponding author.
E-mail address: rfbhajantri@gmail.com (R.F. Bhajantri).

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materials endow a new kind of material with improved electrical, optical, magnetic, and dielectric properties and enhanced stability that has substantial applications in the photovoltaics, thermoelectrics, infrared spectroscopy and also field emission techniques [7].

Numerous works have been reported on PVA: PPy composite, however only a few works have been reported on metal sulfides filled PVA: PPy composites. Harun et al. reported the preparation of PVA: PPy composite polymer films by chemical oxidative polymerization by using $FeCl_3$ as dopant and oxidant. The variation of dielectric properties in the frequency range from 20 Hz to 1 MHz at room temperature with the concentration of $FeCl_3$ was studied [13]. Goutam Chakraborty et al. studied the electrical transport properties of CNT-PVA: PPy system. They reported the semiconducting nature and also DC magnetoconductivity of the composites [3]. M. T. Ramesan synthesized CuS filled PVA: PPy composites using ammonium persulfate as oxidant and reported the AC and DC conductivity study of the samples [14]. J. Liu et al. studied the dielectric properties of Bi_2S_3/poly(vinylidene fluoride) composites and reported the dielectric permittivity for 10% filler doped sample is about 100 at 10^3 Hz [15].

The objective of the present work is to build up a multifunctional composite with convenient conductivities and superior physical properties. With this orientation, pure PVA: PPy blend and different amount of bismuth sulfide particles coated with PVA: PPy blend composites were synthesized by in-situ chemical oxidative polymerization. The acquired polymer nanocomposite films were characterized for structural (FT-IR), thermal (TGA) and morphological (SEM) variations. The dielectric properties and AC conductivity with frequency at room temperature were measured. The composite exhibiting highest conductivity, considered for the further study with temperature and process of conduction is discussed.

2. Experimental

2.1. Materials

Pyrrole monomer (C_4H_5N) with the molecular weight 67.09 g mol^{-1} purchased from Spectrochem Pvt. Ltd. Mumbai, India was stored under refrigeration before use for the synthesis. The other materials such as $FeCl_3$ (M. W.= 169.21 g mol^{-1}), polymer polyvinyl alcohol (PVA) ([(-C_2H_4O-)$_n$], M. W. ~1,25,000 g mol^{-1}) were obtained from M/s. s. d. fine chemical Limited, Mumbai, India. Bismuth nitrate pentahydrate (98% ($Bi(NO_3)_3{\cdot}5H_2O$, M. W. = 485.07 g mol^{-1}, Alfa Aesar, England) and Sodium sulfide ($Na_2S{\cdot}9H_2O$) were used for the preparation of the samples without further purification.

2.2. Synthesis of Bi_2S_3 particles

The weighed amount of $Bi(NO_3)_3{\cdot}5H_2O$ was added to the distilled water to get 0.01 M concentration. The mixture is allowed for continuous stirring up to three hours and the clear white solution was obtained. To this solution, 0.03 M of $Na_2S{\cdot}9H_2O$ was added drop by drop until the solution turned into dark brown. The resultant mixture was left for 12 h to stabilize [13]. The precipitate obtained is washed with absolute ethanol and distilled water several times to remove unreacted contents, and dried at 60 °C to get dark brown colored Bi_2S_3 particles.

2.3. Synthesis of PVA: PPy blend composite

The pre-weighed quantity (1.5 g) of the polymer PVA is dissolved completely in distilled water (30 ml) by heating to a temperature of 40 °C, with continuous stirring. The solution is left to cool to room temperature. 0.5 ml of cooled pyrrole monomer diluted in 15 ml of distilled water is added to the viscous PVA solution and stir for 30 min to get the homogeneous mixture. The above mixture in kept in an ice bath to maintain the temperature 0-5 °C. The polymerization of pyrrole was carried out using Ferric chloride as the oxidizing agent. It is notable that PPy-based composites produced using $FeCl_3$ present a higher level of conductivity than those prepared using other oxidizing agents [16]. 2.187 g of $FeCl_3$ is dissolved in 5 ml of distilled water and is added dropwise to the PVA: pyrrole mixture, along with continuous stirring. The black homogeneous mixture formed designates the polymerization. The composite film is obtained by casting this solution into the Petri dishes kept in hot air oven at a constant temperature of 30 °C, for the evaporation of the water content. Black colored composite films were peeled off after complete drying.

2.4. Synthesis of Bi_2S_3 filled PVA: PPy blend composite

The aforementioned procedure for the polymerization of pyrrole in PVA medium is followed but in presence of different wt% of Bi_2S_3 particles (1%, 3%, 5%, 8%). Here, bismuth sulfide particles are added prior to the addition of monomer. All the films were stored in a vacuum desiccator for further investigation. The thickness of the prepared composite films was measured using Mitutoyo-7327 dial thickness gauge, which is obtained in the range 320–340 μm (± 1 μm).

2.5. Characterizations

The FT-IR spectroscopy analysis of polymer blend nanocomposite films was carried out on ThermoFisher NICOLET FT-IR-6700 by KBr pelleting method in the wave number range of 400–4000 cm^{-1} with the resolution 4 cm^{-1}. The polymer films were mixed with KBr salt in the ratio 1:100 and crushed with an agate mortar and pestle to make the pellets. The TGA thermograms of the prepared samples were obtained on TA instruments model SDT Q600 V20.9 Build 20 from 25 °C to 600 °C at a rate of 10 °C min^{-1} in the platinum crucible under flowing Nitrogen at a rate of 60 ml/min. The weight of the dried composite film utilized in the analysis is about 5 mg. The Scanning Electron Microscopy (SEM) of gold sputtered 1 wt% and 8 wt% Bi_2S_3 filled PVA: PPy polymer film samples was recorded on JEOL Model JSM - 6390LV in SEI mode with the resolution of 10 μm and the acceleration voltage of 15 kV. The morphological images of pure PVA: PPy blend), 3 wt% and 5 wt% Bi_2S_3 filled PVA: PPy films were recorded using CARL ZEISS instrument with an acceleration voltage of 5 kV and the scanning was done with WD about 4.7 mm in FEI mode. The prepared polymer nanocomposite films were cut into a small disk of diameter 1.5 cm and were placed between the stainless-steel electrodes of diameter 1.3 cm to measure the dielectric parameters. The dielectric properties of the composites were studied on HIOKI-IM 3570 high precision Impedance Analyzer in the frequency range 4 Hz to 5 MHz in LCR mode. The variation of dielectric properties with temperature is measured with the help of dry temperature calibrator (Model DPI-1100) set at the temperatures 303 K, 313 K and 323 K (± 1 K) on the same impedance analyzer. The measurement temperature is restricted to this range because of the hardening of the composite films beyond this temperature. Frequency dependent values of series capacitance (C) and loss tangent (tan δ) were taken for the different samples. Prior to the sample measurements, the open circuit and closed circuit calibration were performed for the instrument to eliminate the effect of stray capacitance.

The real part (permittivity) and imaginary part (dielectric loss) of the complex relative dielectric function

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' \quad (1)$$

are calculated with the relation $\varepsilon' = Cd/\varepsilon_o A$ where, C is capacitance value, d is the thickness of the sample, A is the area of the electrode and $\varepsilon_o (= 8.85 \times 10^{-12}$ F $m^{-1})$ is permittivity of free space and ε'' is the dielectric loss ($\varepsilon'' = \varepsilon' \tan \delta$) [17].

The complex electric modulus composed of the real part (M') and imaginary part (M'') is determined by the following equation [18]