



# Effects of potassium iodide (KI) on crystallinity, thermal stability, and electrical properties of polymer blend electrolytes (PVC/PEO:KI)



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## ABSTRACT

Potassium ion conducting solid polymer blend electrolytes based on PVC/PEO:KI of various compositions were prepared by solution-casting technique. The structural changes along with K<sup>+</sup> ion–polymer blend electrolyte interactions and the thermal stability of the samples were studied by X-ray diffraction, Fourier transform infrared spectroscopy, differential scanning calorimetry, scanning electron microscopy, and thermo-gravimetric analysis. Electrical properties were measured as a function of composition and temperature using complex impedance spectroscopy. The electrical conductivity exhibited Arrhenius type of behavior, with the activation energy decreasing with increasing KI concentration. The conductivity of the polymer blend (PVC/PEO) sample was obtained at ambient temperature (303 K) as  $3.09 \times 10^{-6} \text{ S cm}^{-1}$ , and for the PVC/PEO:KI (42.5:42.5:15) electrolyte as  $3.66 \times 10^{-4} \text{ S cm}^{-1}$ , the conductivities were greatly enhanced at 363 K to  $8.23 \times 10^{-4}$  and  $1.30 \times 10^{-2} \text{ S cm}^{-1}$ , respectively. The ionic transference number of the PVC/PEO:KI (42.5:42.5:15) electrolyte was determined to be 0.98. The increase in amorphous phase and free K<sup>+</sup> ion concentration was responsible for the conductivity improvement in the electrolyte system.

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## 1. Introduction

Polymer electrolytes have the prospective to play an important role in large-scale electrochemical energy storage devices such as batteries. In the past two decades, they have been tailored as electron or ion conductors. When combined with appropriate salts, their ionic conductivity extends to the level of an electrolyte. Polymer electrolytes possess several advantages over traditional liquid electrolytes, e.g. safety and multifunctionality. Single-ion conductors are a unique class of polymer electrolytes that have no classical counterpart.

Among various solid-state electrolytes, gel polymer electrolytes (GPEs), which are generally composed of polymer matrix and liquid electrolyte, are widely used in lithium-ion batteries owing to their excellent ionic conductivity, low rates of safety failure, and mechanical flexibility [1–3]. In general, conventional GPEs are prepared using a pre-designed frame via solution casting of liquid state mixtures (i.e., liquid electrolytes and polymers dissolved in organic solvents or liquid electrolytes/polymerizable monomers), followed by solvent evaporation or chemical cross-linking for solidification. Conducting polymers contain  $\pi$ -electron backbone responsible for their unusual electronic properties such as high electrical conductivity, low energy optical transitions, low ionization potential, and high electron affinity. This extended ( $\pi$ -conjugated) system of the conducting polymers has

single and double bonds alternating along the polymer chain. The higher values of the electrical conductivity obtained in such organic polymers have led to the name ‘synthetic metals’. Since the discovery of high electrical conductivity from blending polyethylene oxide (PEO) with potassium salts by Fenton et al. [4], polymer electrolytes have attracted a lot of interest, because of their potential use in thin film batteries [4]. Polymer electrolytes consist of polar polymers and ionizable salts. The progress of polymeric systems with high ionic conductivity is one of the main objectives in polymer research. This is due to their potential applications in solid state batteries [5–8]. Polymer batteries possess advantages such as high ionic conductivity, high energy density, solvent-free condition, leak proof, wide electrochemical stability windows, easy processability, and light weight.

One of the most studied polymers is polyethylene oxide (PEO), also known as polyethylene glycol (PEG). Polyethylene oxide (PEO) is considered to be one of the most capable conducting polymers due to its high pseudo-capacitance, good environmental stability, safety, low cost, facile synthesis, and good conductive ability at doping state, which is beneficial to the increase of electron and ion exchange rate [9–11]. Polyethylene oxide (PEO) can act as a host for sodium and potassium salts, thus producing a solid electrical conductor polymer/salt complex. The resistance of PEO to protein adsorption is generally attributed to a steric repulsion effect, by which the polymer prevents the protein from reaching the substrate surface [12,13]. Indeed, in aqueous environments, PEO molecules are highly mobile and strongly hydrated, attaining extremely large exclusion volumes [14,15]. PEO is the most

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appropriate base material due to its ability to play a host to various metal–salt systems for a wide range of concentrations. It also acts as a good binder for other phases and has excellent chemical stability. The chemical structure of PEO consists of sequential oxy-ethylene group  $-\text{CH}_2-\text{CH}_2-\text{O}-$  that has a series of polar group  $-\text{O}-$ , which can associate with metal cations. Hence, PEO can solvate a wide variety of salts even at very high salt concentrations, e.g.  $\text{LiX}$  ( $X = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{ClO}_4, \text{SCN}, \text{CF}_3\text{SO}_3, \text{BF}_4, \text{AsF}_6$ , etc. [16,17]). However, PEO has  $\text{C}-\text{C}, \text{C}-\text{O}, \text{C}-\text{H}$  bonds only, and the reactivity is exceedingly low owing to the good chemical and electrochemical stability [18].

PVC is the only general purpose plastic that allows free, wide and seamless adjustment of the required physical properties of products such as flexibility, elasticity, and impact resistance, by adding plasticizers, additives, and modifiers. Polyvinyl chloride (PVC) has an amorphous nature with polar chlorine atoms in the molecular structure; therefore, it mixes well with various other substances. The required physical properties of end products (e.g., anti-fouling, prevention of microbial growth, anti-mist, fire retarding) can be freely designed through formulation with plasticizers and various additives, modifiers and coloring agents. Polyvinyl chloride (PVC) has a high mechanical strength and wear-resistance [19]. Compared with polyimides and celluloses, PVC is relatively cheap and ideal for the formation of PVC/PEO blends. It has been demonstrated that the addition of PVC into PEO improves the mechanical property of PEO membranes [20], and suppresses the crystallization of PEO [21,22]. These approaches include synthesizing new polymers [23], cross linking two polymers [24], blending of two polymers [25], adding plasticizers to polymer electrolytes [26], adding inorganic inert fillers [27] to make composite polymer electrolytes (CPEs).

Potassium salt was selected as a dopant to prepare the present polymer blend complex electrolyte system. Potassium iodide is a component in the electrolyte of dyes sensitized solar cells (DSSC) along with iodine. The activity of a salt in an electrolyte has a direct impact on the performance of electrochemical cells, because it can affect both the potential between phases and transport through the electrolyte. The usage of potassium complexed electrolyte films has been found to exhibit several advantages over lithium counterparts. The mobility of smaller ions ( $\text{Li}^+$  and/or  $\text{Mg}^{+2}$ ) is lower than that of cations with larger sizes ( $\text{K}^+$  and/or  $\text{Zn}^{+2}$ ) in the polymer electrolytes [28], because smaller cations are embedded or captured by the polymeric network. Furthermore, the interaction between  $\text{Li}^+$  ions and the polar groups of polymer is stronger than  $\text{K}^+$  ions, thus  $\text{Li}^+$  ion transfer requires higher activation energy in the polymer electrolytes [29,30]. For the present work, we have adopted one of the above techniques, namely blending, because of the ease of preparation and easy control of physical properties within the compositional regime. The inherent merits of using blend-based polymer electrolytes have been exemplified by several research groups [31,32], detailed studies of the blend-based polymer electrolytes can furnish valuable information on the relative importance of various factors, which affect the electrical, thermal and mechanical properties of the polymer blend electrolytes.

Although solid polymer electrolytes have great potential in solid state batteries, there are only limited studies on potassium ion complexed PVC/PEO electrolyte systems. In the present work,  $\text{K}^+$  ion conducting solid polymer blend electrolytes based on PVC/PEO:KI of different compositions were prepared by solution-casting technique, and the structure, thermal stability, and ionic conductivity of the solid polymer blend electrolytes were systematically studied.

## 2. Experimental

### 2.1. Materials

PVC and PEO were obtained from Aldrich (USA) and used without further purification to prepare solid polymer blend electrolytes. PVC, PEO, and KI were dried by heating at 50 and 60 °C under vacuum for 5 and 10 h, respectively. PVC is a polymer with good insulation properties.

Because of its higher polar nature, the electrical insulating property is inferior to non-polar polymers such as polyethylene and polypropylene. Electric dipoles are formed in the mers due to polarity of the  $\text{C} = \text{Cl}$  bond. It creates a physical, or secondary, bond between adjacent chains owing to permanent dipoles. The structure of PEO is  $(-\text{CH}_2-\text{CH}_2-\text{O}-)$ . The helix conformation of PEO that is the basis of structural unit in the crystalline phase has two turns in a fiber identity period of 19.3 Å. This polymer, in its pure form, is chemically and electrochemically stable, since it contains only strong unstrained  $\text{C}-\text{O}, \text{C}-\text{C},$  and  $\text{C}-\text{H}$  bonds [33]. Potassium iodide (KI) salt (Sd. Fine-Chem. Limited, China) was used as dopant. Aqueous solutions of potassium iodide are usually neutral or slightly alkaline; a pH of 7 to 9 is typical. Tetrahydrofuran (THF) (Merck) was used as common solvent. Circular disks of aluminum electrodes (area = 1.132 cm<sup>2</sup>) were used as blocking electrodes in the electrochemical measurements.

### 2.2. Preparation of polymer electrolyte films

Appropriate amounts of PVC, PEO, and KI were dissolved in THF and the solutions, and were magnetically stirred for 12–15 h at room temperature to obtain a homogeneous solution. Pristine blend films of PVC/PEO (50:50) and various compositions of KI doped PVC/PEO were obtained in various weight percentage ratios (47.5:47.5:5, 45:45:10, 42.5:42.5:15). The stirred solutions were cast onto polypropylene dishes and allowed to evaporate slowly at room temperature, followed by vacuum drying. The final composite product was vacuum dried at 45 °C thoroughly under a vacuum of 10 mbar to remove any residual solvent. The reaped films were stored in highly evacuated desiccators to avoid any moisture absorption. Film thickness was measured by the capacitance method, and later verified by the gravimetric method. The values were found to approximately 100 μm with an accuracy of about ± 5 μm.

### 2.3. Characterization techniques

The X-ray diffraction (XRD) patterns of prepared samples were obtained on an X-ray diffractometer (type PANalytical, Netherlands) using monochromatized  $\text{Cu K}\alpha$  (0.15418 nm) at a scan rate (2θ) of 0.05°s<sup>-1</sup>. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. The Fourier transform infrared spectroscopy (FTIR) of pristine PVC/PEO and KI salt complexed PVC/PEO films was recorded using EO-SXB IR spectrometer at a resolution of 4 cm<sup>-1</sup>. The spectra were obtained in the wave number range of 400–3800 cm<sup>-1</sup>. Differential scanning calorimetry (DSC) measurements were carried out using NETZSCH DSC 204 in the range of 47–77 °C, and all the measurements were taken at a heating rate of 5 °C min<sup>-1</sup> under nitrogen atmosphere. The morphology of the samples was characterized by JOEL JSM 840A scanning electron microscope (SEM). The conductivity of these solid polymer blend films was investigated with the cell consisting of two blocking stainless steel electrodes. Impedance measurements were carried out in the temperature range of 303–363 K using 3532-50 LCR Hi-Tester over a frequency range of 100–1 MHz. The instrument was interfaced to a computer for data collection. The optical absorption profiles of these samples were recorded at room temperature in the wavelength range of 200–600 nm using UV-VIS-NIR (Model UV-3100) spectrophotometer.

## 3. Results and discussion

### 3.1. Structural properties

X-ray diffraction studies were carried out to investigate the semi-crystalline nature of PVC/PEO blend and possible changes in semi-crystalline behavior due to the addition of KI. XRD patterns of pristine, complexed PVC/PEO blend membranes (Fig. 1) exhibit significant peaks at around 19.63°, 23.31°, and 24.06° and low intense peaks at around

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