

Effect of Ceramic Particles on the Properties of PVC-PEG Polymer Composites

T.Sornakumar , D.Ravindran , K.Janarthan , P. Sankar

Abstract— Polymer membranes find wide spread applications in lithium batteries, fuel cells and solar cells. Lead titanate (PbTiO_3) particles were synthesized by solid state milling process. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies of the PbTiO_3 particles were conducted. Polyvinyl chloride (PVC), poly ethylene glycol (PEG) and PbTiO_3 particles blend polymer were prepared through solvent casting method with tetrahydrofuran (THF) as common solvent. PVC-PEG- PbTiO_3 polymer membranes of different weight percentage of PbTiO_3 particles have been prepared and their effects on the tensile strength were studied.

Key words: PVC, PEG, Lead titanate, Polymer membrane, Tensile strength

I. INTRODUCTION

Lithium ion batteries are now triggering great attention since they are considered the most suitable power source for electric and hybrid vehicles. However, the safety issues associated with the presence of organic, flammable solvents as the electrolyte are still preventing a large diffusion of the technology in these emerging markets. Solid polymer electrolytes, such as polyethylene oxide (PEO), are considered the best choice to overcome the safety hazards, however problems associated with their low conductivity at lower temperature still need to be addressed. A very promising alternative was represented by the gelified systems, such as those based on poly(vinylidene) fluoride (PVdF), consisting of a polymer membrane acting as matrix for the organic liquid part, generally organic carbonates. This solution was considered as a compromise between safety and performances in terms of ionic conductivity and rate capability when employed in lithium cells. Different approaches have been taken in the past to prepare PVdF gel-type conducting membranes, such as those based on casting procedures or on electro-spinning (Lombardo et al, 2014) [1]. Rapid growth of versatile-shaped electronic devices has impelled the development of flexible lithium-ion batteries as a suitable power source. The design of portable and bendable electronic equipment, such as rollup displays and wearable devices, requires the development of flexible batteries. Making a bendable lithium-ion battery requires the development of soft electrodeactive materials, such as metal oxide nanoparticles or

nanocoatings for cathodes and lithium foil or nanocarbon materials for anodes. As for the separator, polymer electrolyte with electrolyte leakage-proof, reliability, less flammability and high energy density plays an essential role in the development of flexible batteries.

Due to the unique soft matter characteristics, gel polymer electrolytes (GPEs) have been extensively investigated in the past decades. The GPEs, however, suffer from a trade off issue between mechanical properties and ionic conductivity (Ma et al, 2014) [2]. Polymer films with directional preference for ion transport are desirable for electrochemical, purification, sensor and stimuli-response, and organic transistor applications as the anisotropy can increase mass transport efficiency, permeability, sensitivity and response times, and reduce gate leakage in the nonpreferred direction. Since then, applying external mechanical, electrical or magnetic fields, solvent casting methods, electrospraying block-co-polymers (BCPs), liquid crystals polymer templating, and tailoring crystalline polymer morphology have been demonstrated to increase ion flux anisotropy in polymer electrolyte films (Smith et al, 2014) [3]. Polymer electrolytes based on polyacrylonitrile (PAN, poly(ethylene oxide) (PEO), poly esters and poly(vinylidene fluoride) (PVDF) have been widely studied. Recently, the poly(vinylidene fluoride) (PVDF) has been identified as a potential host for lithium polymer batteries because of its appealing properties (Xiao et al, 2014) [4]. The addition of ceramic nanoparticles such as TiO_2 , LiAlO_2 or SiO_2 to PEO-LiX or PEO-like polymers induces consistent improvement in the transport properties as well as the mechanical strength. Nanoparticles are believed to kinetically inhibit crystallization from the amorphous state. However, the ceramic dispersed PEO-LiX composite electrolytes exhibit still an insufficient ionic conductivity at room temperature with implications for the general requirement of practical electrochemical devices (Ahn et al, 2003) [5].

Homogeneous-reinforced (HR) polyvinyl chloride (PVC) hollow fiber membranes consisting of coating layer and matrix layer were fabricated via coating process. The maximum pure water flux and protein permeation flux of HR PVC membranes were obtained as the PVC concentration reached to 10 wt.% and PEG molecular weight was 2000. The increase of PVC concentration and PEG molecular weight brought about the increase of protein rejection rate and the decrease of membrane porosity. The tensile strength of HR membranes decreased slightly compared with matrix membrane and was nearly 19 MPa, but the elongation at break was opposite which was nearly 102% (Liu et al, 2013) [6]. Poly vinyl chloride

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(PVC) is the most widely used polymer after polyethylene and polypropylene. Moreover, it is inexpensive, chemically stable, biocompatible, and sterilizable (Wilkes et al, 2005) [7]. The chemistry and biological applications of polyethylene glycol (PEG) have been the subject of intense study both in academics and in industry (Samuel Zalipsky and Milton Harris, 1997) [8].

Polyethyleneglycols or polyethyleneoxides (PEOs) with a molecular structure indicated as HO- (CH₂-O-CH₂)_n-OH, are liquids or low melting wax like solids. Polyethyleneoxides have some specific interactions with CO₂. The PEG segments can dissolve large amount of acidic gases. The gas permeation flux through PEG segments is also high, because of its chain flexibility. However, it is difficult to obtain a thin film of PEG alone because of its weak mechanical and thermal strength. For that reason, a large number of PEG (PEO) based copolymers and polymer blend membranes have been prepared, where PEO segments provide high selectivity and high permeation rates. This is in addition to that the other component provides us with the film-forming ability with chemical and thermal stability. Polyvinylchloride (PVC) with molecular structure of (CH₂-CHCl)_n is a thermoplastic polymer with glass transition temperature of 87^oC. It is a glassy polymer with high chain compactness and low polymeric chain segmental motion. Therefore, its gas permeability is low.

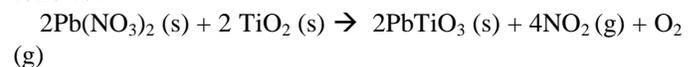
PVC is a chemically and mechanically stable polymer that can be easily processed. By blending the PEG to PVC the high gas selectivity properties of PEG and high mechanical and chemical stability of PVC are combined and the membrane with high performance ability can be prepared (Sadeghi et al, 2008) [9]. PEG is used in most of the applications of aqueous phase partitioning. PEG is biocompatible and biodegradable polymer and has adhesive and flocculent properties. Blend of PEG or PES with other polymers has been studied in order to modify the physical properties and extend its practical applications. Till now, less work has been done on blending PEG or PES with other polymers such as PVC. It is well known that miscibility and crystallization behaviors play crucial roles in physical properties of polymer blends. The most common and particularly important miscible polymer owes hydrogen bonding and electrostatic interactions between the different groups on the polymeric structure of the components. The weak hydrogen bond is postulated between halogen-containing polymers, such as PVC, and the oxygen containing polymers. This type of interaction is responsible for the miscibility of various polymers (Taha A. Hanafy, 2013) [10].

ABO₃-type perovskite crystals are important for numerous technological applications in electrooptics, waveguides, laser frequency doubling, high capacity computer memory cells, etc (Piskunov et al, 2004) [11]. Ferroelectric materials are a class of materials that possess high dielectric constants, relatively low dielectric loss, high electrical resistivity, moderate dielectric breakdown strength, and strong electromechanical and electrooptical behaviors. They exhibit spontaneous

polarization and the ability to switch polarization direction. Ferroelectrics with perovskite structure (ABO₃), such as barium titanate (BaTiO₃) and lead titanate (PbTiO₃), are the most studied ferroelectric oxides because of their versatile properties for use in thin film capacitors, electronic transducers, actuators, high-k dielectrics, pyroelectric sensors, and nonlinear optics. The particles with nanoscopic dimensions have received considerable research attention due to the unconventional chemical and physical properties (e.g., electronic, optical) at the nanoscale, for example, the size dependent optoelectronic properties of semiconducting quantum dots and the size dependent magnetic properties of multiferroic nanocrystals. Moreover, nanoparticles can serve as ideal building blocks for bottom-up nanofabrication for developing low-cost, miniaturized electronic devices whose functionalities are enabled by the properties of the individual nanoparticles and their arrangement (Wang et al, 2010) [12].

II. EXPERIMENTAL

The lead oxide free lead titanate (PbTiO₃) were first synthesized by solid state milling process. The synthesis of lead titanate (PbTiO₃) nano particles is obtained as a result of repeated homogeneous mixing of titanium oxide (TiO₂) and lead dinitrate (Pb(NO₃)₂). After mixing, the fine powder is then heated in a reaction temperature of 100^oC in a muffle furnace using an alumina crucible. This process is repeated again and again to remove lead oxide. Finally, PbTiO₃ particles are calcined at 600 ^oC temperature. The chemical reaction for lead titanate (PbTiO₃) in equimolar ratio are as follows :



Solvent casting method is preferred for synthesizing the polymer membranes. In the present work PVC-PEG-PbTiO₃ polymer membranes of different weight percentage of PbTiO₃ particles have been prepared and their effects on the mechanical properties are studied. Poly vinyl chloride (PVC) with average molecular weight 60,000 was procured from Sigma-Aldrich. Poly ethylene glycol (PEG) (molecular weight - 600) was procured from CDH, India. The solvent tetrahydrofuran (THF) was procured from Merck. The appropriate weight percentage of polymer PVC and PEG was first dissolved in the solvent and after complete dissolution, the filler PbTiO₃ were added slowly. The viscous solution was then stirred slowly at constant rate for a period of 14-16 h to get a homogeneous solution and cast on an ultrasonically cleaned glass plate. The residual solvent was allowed to evaporate slowly at room temperature and further dried in temperature controlled oven at 50^o C for 12 h to remove traces of THF if any present in the membrane. The mechanically stable, free standing thin membranes thus obtained were kept in vacuum desiccators for further drying. The thickness of the specimen is 1 mm. The specimens were cut as per ASTM: D638 standard to carry out the tensile test. The tensile test was conducted as per ASTM: D638 standard in a universal testing machine (UTM).

III. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern of PbTiO_3 particles calcined at 600°C is shown in figure 1. The X-ray diffraction (XRD) pattern of PbTiO_3 particles shows the crystallinity of PbTiO_3 particles. The scanning electron micrographs (SEM) of PbTiO_3 particles calcined at 600°C at different magnifications are shown in figure 2 and figure 3. The scanning electron microscopy (SEM) of PbTiO_3 particles shows the size and shape distribution of the PbTiO_3 powders.

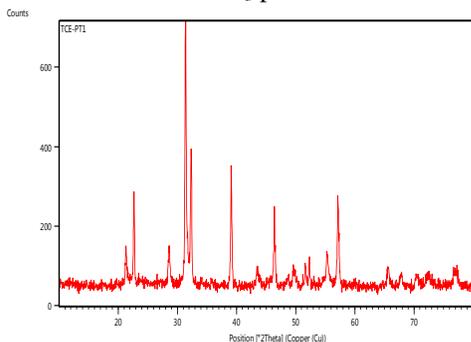


Figure.1.XRD pattern for lead titanate powder

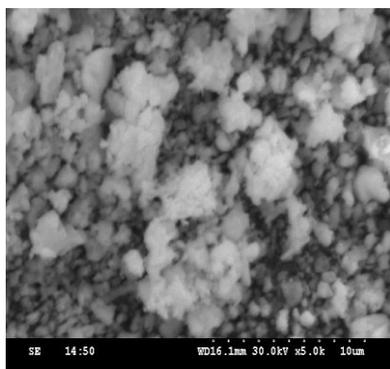


Figure.2.SEM of PbTiO_3 powders

Figure 3 shows the tensile testing of PVC-PEG- PbTiO_3 polymer membrane. Table 1 shows the composition and tensile strength of PVC-PEG- PbTiO_3 polymer membranes of different weight percentage of PbTiO_3 particles. In the preparation of the membrane the weight percentage of polymers PVC and PEG were taken in equal ratio as the mechanical property of the membrane strongly depends on both the polymers. Generally the increase in PVC content makes the membrane more rigid and stiff, whereas more PEG reduces the mechanical strength of the membrane.



Figure.3.Tensile testing of PVC-PEG- PbTiO_3 polymer membrane

Table.1.Composition and tensile Strength of the PVC-PEG- PbTiO_3 polymer membranes

Sl .No.	PVC(wt %)	PEG(wt %)	PbTiO_3 (wt %)	Tensile Strength, MPa
1.	50	50	0	1.18
2.	47.5	47.5	5	1.73
3.	45	45	10	1.96
4.	40	40	20	0.95

The tensile strength of PVC-PEG- PbTiO_3 polymer membranes are higher than that of the PVC-PEG polymer membranes without filler for the 5 % and 10 % wt PbTiO_3 . For PbTiO_3 filler added specimen, the tensile strength increases initially reaching a maximum value at 10 wt% and then the tensile strength decreases. At lower weight percentage, the PbTiO_3 filler particles are uniformly well distributed in the membrane, whereas at higher weight percentage of 20 % the agglomeration of filler PbTiO_3 particles results in an increase in the particle-particle interaction than the particle-polymer matrix interaction.

IV. CONCLUSION

PVC-PEG- PbTiO_3 polymer membranes of different weight percentage of PbTiO_3 particles have been prepared and their effects on the mechanical properties are studied. The tensile strength of PVC-PEG- PbTiO_3 polymer membranes are higher than that of the PVC-PEG polymer membranes without filler for the 5 % and 10 % wt PbTiO_3 . The PVC-PEG- PbTiO_3 membrane with 10 wt% PbTiO_3 exhibits higher tensile strength over other compositions.

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