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Effect of nano TiO₂ and Al₂O₃ filler on the mechanical and thermal properties of PVC-PEG polymer blend nano composites

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Abstract: Polymer membranes find wide spread applications in lithium batteries, fuel cells and solar cells. Poly vinyl chloride (PVC) and poly ethylene glycol (PEG) blend polymer films were prepared through solvent casting method with tetrahydrofuran (THF) as common solvent. PVC-PEG polymer-TiO₂ membranes and PVC-PEG polymer-Al₂O₃ membranes of different weight percentage of nano TiO₂/Al₂O₃ particles have been prepared and their effects on the mechanical and thermal properties are studied. The tensile strength of PEG polymer-TiO₂ membranes and PVC-PEG polymer-Al₂O₃ membranes are higher than that of the PEG polymer-membranes without filler.

Key words: PVC, PEG, Polymer membrane, Tensile strength, Thermal stability.

Introduction

Gel polymer electrolytes (GPEs) are potential candidates to be used as electrolyte membranes in high energy density rechargeable lithium batteries, fuel cells, solar cells, and electrochromic windows. GPEs can be formed using many different polymer systems¹. Lithium ion battery has been studied widely and deeply in the energy sources rapid growth time, especially the electrode material. As we all know, superior performance of lithium ion battery is determined by active electrode material and excellent electrolytes. The gel polymer electrolytes have been reported with sufficient mechanical strength, high ionic conductivity at room temperature, stable and well compatibility with lithium electrodes².

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-spinning³. 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. Our group has recently reported a new strategy to fabricate mechanically flexible GPEs with satisfactory electrochemical performance⁴.

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 films⁵. 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 properties⁶. It has been reported that the addition of ceramic nanoparticles such as TiO₂, LiAlO₂ or SiO₂ 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 devices⁷.

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%⁸. Poly(vinyl chloride) (PVC) was aminated by treating the resin with a concentrated aqueous solution of ethylenediamine. The aminated PVC was then reacted with hexamethylene diisocyanate to incorporate the isocyanate group onto the polymer backbone. The isocyanated PVC was further reacted with poly(ethylene glycol) (PEG) of molecular weight 600 Da. The thermal stability of the modified polymer was found to be lowered by the incorporation of PEG. Static platelet adhesion studies using platelet-rich plasma showed significantly reduced platelet adhesion on the surface of the modified polymer compared to control PVC⁹. Poly vinyl chloride (PVC) is the most widely used polymer after polyethylene and polypropylene. Moreover, it is inexpensive, chemically stable, biocompatible, and sterilizable¹⁰. The chemistry and biological applications of polyethylene glycol (or "PEG") have been the subject of intense study both in academics and in industry¹¹. Titanium oxide nanoparticles are one of the most interesting materials at the present time. Under ongoing development, they attract increasing attention not only for their unique properties, but also for their potential applications in industries such as pigments, cosmetics, catalysts, photocatalysts etc.¹². Al₂O₃ is one of the most widely used engineering ceramic materials due to its high elastic modulus, high wear resistance and chemical corrosion resistance, high-temperature stability and the retention of strength at high temperatures¹³.

Experimental

In the present work PVC-PEG polymer-TiO₂ membranes (T) and PVC-PEG polymer-Al₂O₃ membranes (A), of different weight percentage of nano TiO₂/Al₂O₃ particles have been prepared and their effect on the mechanical and thermal 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 and nano filler TiO₂/Al₂O₃ of 50 nm size 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° 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. Figure 1 shows the photograph of the PVC-PEG polymer membrane. The specimen are cut as per ASTM: D638 standard to carry out the tensile test (Figure 2). The tensile test was conducted as per ASTM: D638 standard in a universal testing machine (UTM).



Figure 1. PVC-PEG polymer membrane (T1/A1)



Figure.2.PVC-PEG polymer membrane specimen for tensile tests

Results and discussion

Scanning electron microscopy analysis

The scanning electron microscopy (SEM) photographs of PVC-PEG polymer membrane without filler (T1/A1), PVC-PEG polymer-5 wt% of TiO₂ membrane (T3) and PVC-PEG polymer-5 wt% Al₂O₃ membrane (A3) of the same magnification are presented in figures 2, 3 and 4 respectively.. The membrane without filler exhibits a porous structure and the pore size has increased in PVC-PEG polymer-5 wt% of TiO₂ membrane. But the porosity has remarkably reduced and the developments of micro-pores are seen for PVC-PEG polymer-5 wt% Al₂O₃ membrane.

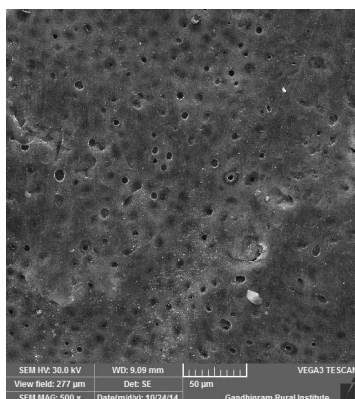


Figure.2. SEM photograph of PVC-PEG polymer membrane without filler (T1/A1)

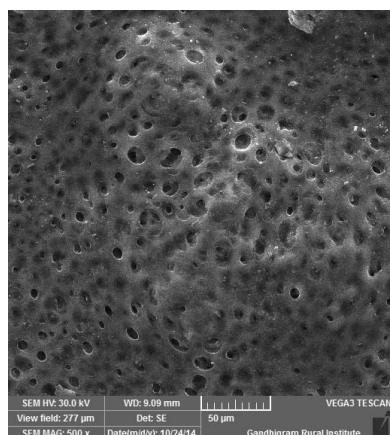


Figure.3. SEM photograph of PVC-PEG polymer-5 wt% of TiO_2 membrane (T3)

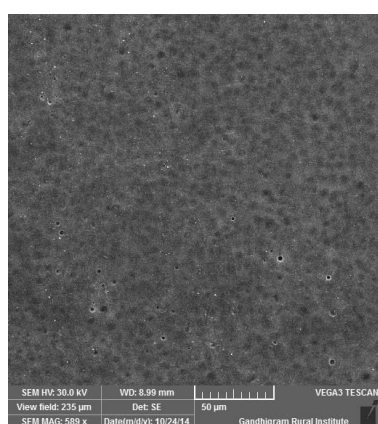


Figure.4.SEM photograph of PVC-PEG polymer-5 wt% Al_2O_3 membrane (A3)

Mechanical Properties

Table 1 shows the composition and tensile strength of PVC-PEG polymer-membrane without filler (T1/A1), PVC-PEG polymer- TiO_2 membranes (T) and PVC-PEG polymer- Al_2O_3 membranes (A), of different weight percentage of nano $\text{TiO}_2/\text{Al}_2\text{O}_3$ 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 make the membrane more rigid and stiff, whereas more PEG reduces the mechanical strength of the membrane.

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

Specimen code	PVC (wt%)	PEG (wt%)	Filler (Nano $\text{TiO}_2/\text{Al}_2\text{O}_3$) (wt%)	Tensile Strength, MPa
T1/A1	50	50	0	0.9448
T2	48.75	48.75	2.5 % TiO_2	1.1811
T3	47.5	47.5	5.0 % TiO_2	1.2598
T4	46.25	46.25	7.5 % TiO_2	1.1814
A2	48.75	48.75	2.5 % Al_2O_3	1.9685
A3	47.5	47.5	5.0 % Al_2O_3	1.8504
A4	46.25	46.25	7.5 % Al_2O_3	1.7717

The tensile strength of PEG polymer- TiO_2 membranes and PVC-PEG polymer- Al_2O_3 membranes are higher than that of the PEG polymer-membranes without filler. For both the TiO_2 and Al_2O_3 nano filler added specimen, the tensile strength increases initially reaching a maximum value at 5 wt% and then the tensile strength decreases. At lower weight percentage, the nano $\text{TiO}_2/\text{Al}_2\text{O}_3$ filler particles are uniformly well distributed in the membrane, whereas at higher weight percentage the agglomeration of nano filler $\text{TiO}_2/\text{Al}_2\text{O}_3$

particles, results in an increase in the particle-particle interaction than the particle-polymer matrix interaction. The PVC-PEG polymer- Al_2O_3 membranes (A) have higher strength than that of PVC-PEG polymer- TiO_2 membranes (T). The porosity has remarkably reduced for PVC-PEG polymer- Al_2O_3 membranes resulting in higher tensile strength than that of the PVC-PEG polymer- TiO_2 membranes.

Thermo gravimetric analysis

The thermal stability of a polymeric material depends on the inherent characteristics of the constituents as well as on the molecular interactions between different macromolecules¹⁴. The thermal stability of the polymer membranes is an important parameter for guaranteeing acceptable performance during high temperature operation, which is related to safety concerns. The thermal stability of the PVC-PEG polymer- TiO_2 membranes (T) and PVC-PEG polymer- Al_2O_3 membranes (A), with particles of different weight percentage of nano $\text{TiO}_2/\text{Al}_2\text{O}_3$ were studied through thermo gravimetric analysis (TGA). Figure 5 shows the thermal stability of PVC-PEG polymer- Al_2O_3 membranes (A3). Up to 150°C around 10 % weight loss is observed, mainly due to the presence of moisture, which has been acquired during loading of the specimen or the evaporation of residual solvent. The membranes have about 80 % weight loss in the temperature range $200\text{--}300^\circ\text{C}$. All the PVC-PEG polymer- TiO_2 membranes (T) and PVC-PEG polymer- Al_2O_3 membranes (A) almost have the same trend.

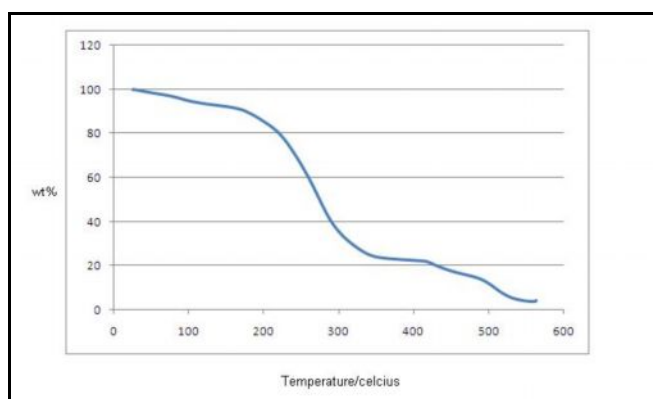


Figure.5.TGA curve of PVC-PEG polymer- Al_2O_3 membranes (A3)

Conclusion

PEG polymer- TiO_2 membranes and PVC-PEG polymer- Al_2O_3 membranes of different weight percentage of nano $\text{TiO}_2/\text{Al}_2\text{O}_3$ particles have been prepared and their effects on the mechanical and thermal properties are studied. The tensile strength of PEG polymer- TiO_2 membranes and PVC-PEG polymer- Al_2O_3 membranes are higher than that of the PEG polymer-membranes without filler. The PVC-PEG polymer- Al_2O_3 membranes have higher strength than that of PVC-PEG polymer- TiO_2 membranes. The PVC-PEG polymer- Al_2O_3 membrane with 2.5 wt% Al_2O_3 exhibits higher tensile strength over other compositions.

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