Influence of Crystallinity on Ion Conductivity of PEO-based Solid Electrolytes for Lithium Batteries

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Abstract: In this work, poly(vinyl chloride) (PVC)/poly(ethylene oxide) (PEO) polymer electrolytes for secondary batteries were prepared using a solution casting technique. In addition, their crystallinity, ionic conductivity and mechanical properties were investigated. A binary mixture of carbonate solvent was used as a plasticizer, and lithium perchlorate (LiClO$_4$) was used as a salt. The morphology and mechanical properties of the polymer electrolytes were characterized by scanning electron microscopy (SEM) and a universal tensile machine (UTM). The crystallinity of the polymer electrolytes was evaluated by differential scanning calorimetry (DSC). The ionic conductivity of the polymer electrolytes was measured using the frequency response analyzer (FRA) method. As a result, the mechanical properties of the polymer electrolytes did not show any significant changes up to 5 wt%, despite the phase separation of the composite. The ionic conductivity of polymer electrolytes containing 2 wt% PVC showed the highest ionic conductivity, 2.35×10^{-3} (S/cm) at 25 °C. This ion conductivity was dependent on the reduced crystallinity by the addition of PVC moieties.

Keywords: polymer electrolytes, PVC/PEO, ionic conductivity, mechanical properties.

Introduction

Lithium secondary battery using solid polymer electrolyte is an attractive energy source for portable devices. In comparison of solid electrolytes with the liquid electrolytes, the former one offers many advantages, viz. solid-state non-corrosive medium, high automation potential for electrode preparation and cell and assembly techniques, broad operating temperature range, no separator, no filling procedure, intrinsic safety, etc.[1] Moreover solid polymer electrolyte makes the fabrication of safe batteries possible and permits the development of thin batteries with design flexibility.

Conventional poly(ethylene oxide)-based polymer electrolytes are the most commonly studied. The electrolytes exhibit a conductivity which ranges from 10^{-8} to 10^{-5} S cm^{-1} at room temperature.[2] This excludes practical application at ambient temperature.[3,4]

This leads to some problems such as leakage and loss of electrode-electrolyte contact, as encountered in devices based on liquid electrolytes.

In the last decade, the addition of ceramic fillers in the polymeric complexes have raised great interests, and it has been reported that the addition of Al$_2$O$_3$,[3-6] TiO$_2$[7-9] and other fillers such as SiO$_2$ and related oxides[10-12] to PEO-based polymeric electrolytes improved the conductivity to a considerable extent. A gel-type membrane is achieved by immobilizing a liquid solution (for example, propylene carbonate and/or ethylene carbonate solutions of a lithium salt) into a polymeric matrix.[13] These electrolytes, however, lose their mechanical strength because of the addition of plasticizers.[14-18] The films have to be hardened by either chemical or physical curing, which results in high processing costs.

To bypass this limitation, one of the approaches undertaken is the blending method.[19-24] The polymer blend electrolyte is composed of at least two polymers: one that absorbs the electrolyte's active species and one that is tougher and sometimes, substantially inert, which enhances the mechanical integrity of the polymer blend. It is a good strategy for suppressing the crystallinity and enhancing the ionic conductivity.[25] Among them, PVC is a suitable candidate when

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blended with PEO. PVC is a commercially available polymer, which acts as good mechanical stiffener and is highly compatible with many polymers.[26,27]

Recently, our group have studied the effects of the polymer matrix, plasticizer and in organic nano-filler on the electrochemical properties of polymer electrolytes.[28-30] In this work, the effects of PVC/PEO blend based polymer electrolytes on the electrochemical properties and mechanical properties were studied.

Experimental

Materials. Poly(vinyl chloride)(PVC) and poly(ethylene oxide)(PEO) with average molecular weights of 5.5×10^4 (Aldrich) and 2.0×10^5 (Aldrich), respectively, were used without further purification. Lithium perchlorate (LiClO$_4$, purity > 95%) was obtained from Aldrich and dried at 80 °C for 24 h before use. Solid ethylene carbonate (EC, 98%) also was acquired from Aldrich and used without further purification. Tetrahydrofuran (THF) was purchased from Jin Chemical Pharmaceutical Co. Ltd.

Preparation of Polymer Electrolytes. All of the polymer-blend electrolytes (PBEs) were prepared using the solution casting technique. The PBE system entailed the use of PEO and LiClO$_4$ salt in a molar ratio [EO]:[Li] of 16:1, with a different weight ratio of PVC. The preparation of PBE films involved first the dissolution of PVC, PEO and EC in THF at 40 °C for several hours, after which LiClO$_4$ was added to the PVC/PEO/10 wt% EC solution prepared. After a completely homogenous mixture was obtained, it was cast onto a glass plate and allowed to dry at 40 °C overnight. Finally, the resultant films were dried in a vacuum oven at 40 °C to evaporate any residual solvent.

Characterization of Polymer Electrolytes. The thermal behaviors of the PEO-based electrolyte films were characterized by differential scanning calorimetry (DSC 6 series) obtained from Perkin Elmer Co. Ltd. The polymeric electrolytes samples were loaded in sealed aluminum pans, and measurements were taken within the 30 to 300 °C temperature range at a heating rate of 5 °C/min under a nitrogen atmosphere. Approximately 8 mg of each film specimen was used.

Electrochemical measurements were carried out using a frequency response analyzer (FRA) AUTOLAB with a PGSTAT 30 (potentiostat/galvanostat) (EcoChemie, The Netherlands) electrochemical instrument in the 10 kHz - 10 Hz frequency range on SS (stainless steel) / composite electrolyte / SS cells. The conductivity value (σ) was calculated from the bulk resistance (R_b), which was determined by equivalent circuit analysis software.
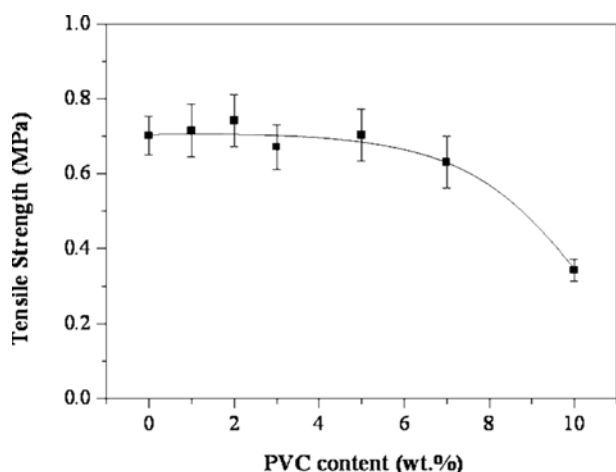
The mechanical strength of the PBEs was carried out by means of an Instron Model 4482 universal-testing machine. The thickness of the test pieces were between 1 and 3 mm. All measurements were conducted using crosshead speed 10 mm/min.

Results and Discussion

Figure 1 shows SEM images of the PBEs containing various PVC contents. In the case of the (a) sample, that is a PEO/EC/LiClO$_4$ film containing no PVC, a rather homogeneous morphology is shown. By increasing the PVC content from 1 to 10 wt%, the film morphology was changed. First of all, at (d) 3 wt% content, the small white spot had been appeared. For higher contents in the case of (e), (f) and (g), the more heterogeneous morphology was shown, indicating PVC could be functioned as a structural defects or aggregated parts in the film, Besides, the white parts was made more prominent by increasing the PVC content. These behaviors could be explained by the phase separation phenomena between PEO and PVC chains. For (a) sample without PVC, the white spots are related with the lithium salt that are crystallized with polymer chains or precipitated
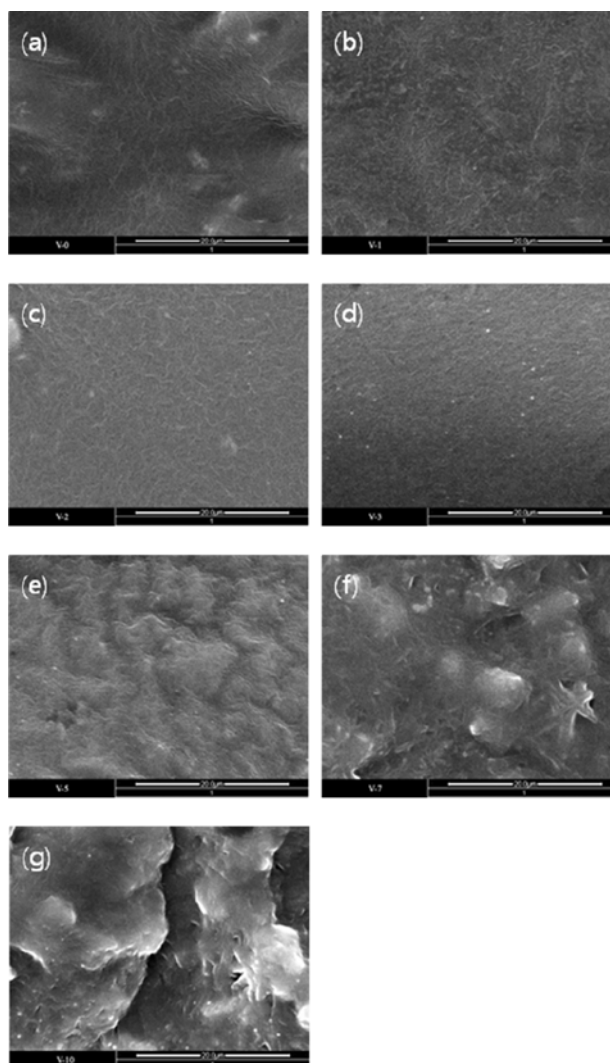
Figure 1. SEM images of PBEs containing (a) 0 wt%, (b) 1 wt%, (c) 2 wt%, (d) 3 wt%, (e) 5 wt%, (f) 7 wt%, (g) 10 wt% of PVC.
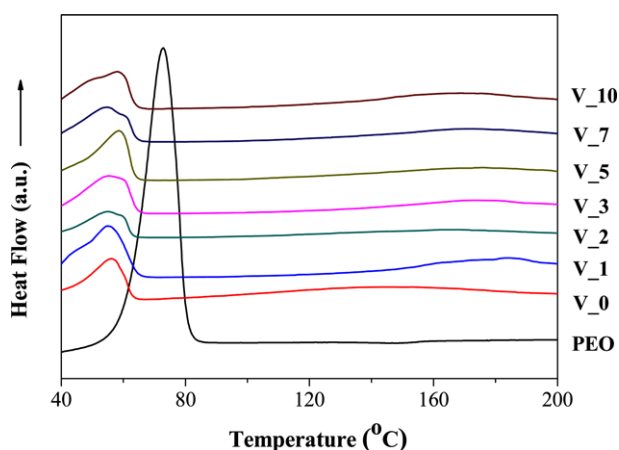
Figure 2. The variation of tensile strength at peak values in PBEs with PVC content.

Table I. DSC Data for PBEs with PVC of Different Weight Contents

Code	wt%[a]	Melting Temperature, T_m (°C)	Heat of Fusion, ΔH_f (J/g)
Pure PEO	0[b]	72.9	133.65
V-0	0	56.3	57.10
V-1	1	55.3	56.52
V-2	2	54.9	53.12
V-3	3	55.5	55.15
V-5	5	58.7	59.23
V-7	7	54.6	59.51
V-10	10	57.8	59.11

[a]PVC Content in wt%. [b]Pure PEO sample.

by local high concentration.

Mechanical studies were carried out to study the effect of PVC addition in polymer electrolytes. The variation of tensile strength at peak values in PBEs with respect to PVC contents are presented in Figure 2. It was found that the tensile strength at peak values was around 0.7 MPa, that is to say, the mechanical properties of the PBEs didn't show significant changes up to 5 wt% even though the phase separation of the polymer electrolytes were observed as confirmed by SEM images.

Figure 3 shows the DSC result of PEO/EC with different contents of PVC. The DSC studies indicated that the PEO crystallinity (χ_c) was deteriorated by the addition of the EC, and further deteriorated by the addition of the PVC. The value χ_c has been defined as the enthalpy ratio of PEO samples to the complete crystalline PEO. It can be calculated with the equation:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^o} \tag{1}$$

where ΔH_f^o (133.65 J/g) is the melting enthalpy of a completely crystalline PEO sample and ΔH_f is the experimental enthalpy.[31]

The melting temperature and the heat of fusion values are listed in Table I. The endothermic curves began to rise at the melting point, and the peaks at the melting temperature (T_m), attributed to the melting of the PEO-rich crystalline phase, weakened and shifted to lower temperatures with an increase of the PVC content to 2 wt%.

Figure 4 displays the crystallinity changes in the electrolytes of varying PVC contents. The PEO/EC (10:1) without PVC shows it as 57.10 J/g, the estimated crystallinity being 42.72%. This indicates that the EC reduced the crystallinity of the PEO by plasticizer effects. By the addition of 2 wt% PVC, the melting temperature could be decreased to 54.9 °C, and the crystallinity, to 39.75%. It could be concluded that the crystallinity of the PEO were decreased mainly due to the structural deterioration effected by EC and Li salt. This crystallinity was further reduced slightly by adding PVC. At PVC amounts over 3 wt%, the melting temperature and

Figure 3. DSC curves of pure PEO and PBEs with PVC content.
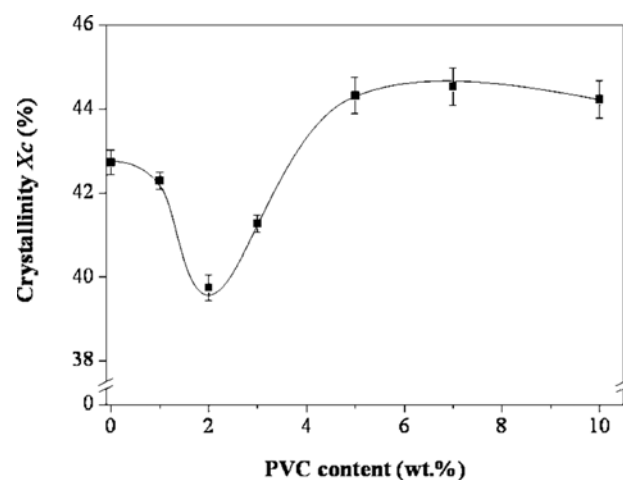
Figure 4. Relative crystallinity (χ_c) of PBEs with PVC content.
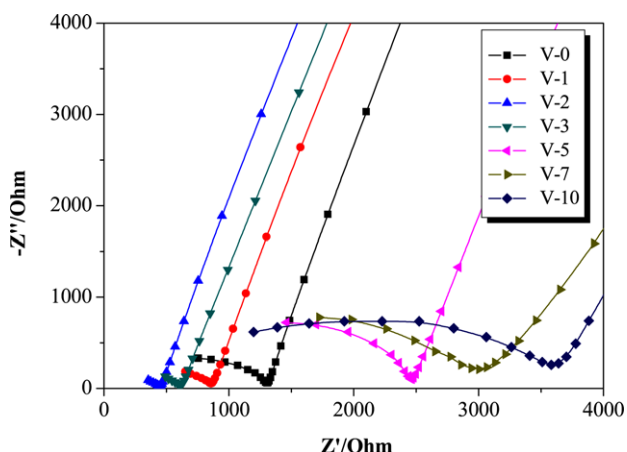
Figure 5. Impedance plots for PBEs with PVC content.

crystallinity were increased.

In order to enhance the ion conductivity, studies on the effects on the ion-conducting behavior of PBEs systems of adding specific amounts of PVC were carried out. The conductivity was measured by sandwiching the electrolytes between stainless steel electrodes. The bulk resistance (R_b) was determined by equivalent circuit analysis software. The conductivity values (σ) were calculated from the equation

$$\sigma = (1/R_b)\,(t/A) \tag{2}$$

where t is the thickness of the electrolyte film, and A is the area of the film.

Figure 5 shows the impedance plots versus PVC contents for the PBEs at 25 ºC. The approximate bulk-resistance value could be obtained with reference to the touch point at the x-axis. By contrast, the PBEs containing 2 wt% PVC showed the smallest-diameter semicircles.

Figure 6 plots the conductivity versus the PVC contents for the PVC x wt%/(PEO)$_{16}$/LiClO$_4$/EC electrolytes at 25 ºC. An increase in the conductivity was observed after adding 2 wt% PVC, attaining the maximum value of 2.35×10^{-3} (S/
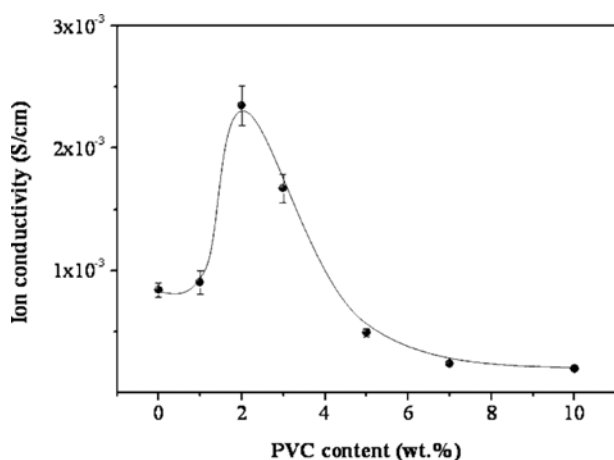
Figure 6. Room temperature ion conductivity versus PVC content.

cm). Subsequently, the ionic conductivity decreased with the addition of PVC contents over 3 wt%, due mainly to the increased aggregation of PVC additives. Furthermore, these behaviors could be explained by the increase of intermolecular interaction between the PEO and PVC chains, resulting in a decrease of PBE crystallinity due to the specifically lower PVC crystallinity. The above DSC results imply also that ionic conductivity is strongly dependent on the degree of crystallinity.

In this work, blend-based PEO-PVC polymer electrolytes were prepared and their mechanical properties, crystallinity, and ionic conductivity were studied. Consequently, the mechanical properties of the PBEs didn't show prominent changes up to 5 wt% even though the phase separation of the composites. The crystallinity of the PEO was decreased mainly due to the structural deterioration effected by EC and Li salt. This crystallinity was further reduced slightly by adding PVC. The highest value ionic conductivity of the polymer-blend electrolytes, 2.35×10^{-3} (S/cm), was observed at 2 wt% PVC.

Therefore, it was concluded that the using of an amorphous element as polymer electrolytes led to an increase in ionic conductivity of solid electrolytes in a useful polymer secondary batteries.

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