Effects of EC Plastisizer and SiO2 Nano-Filler on Electrical and Thermal Properties of Chitosan-G-PMMA based Solid Polymer Electrolytes

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Abstract

Composite grafted polymer electrolyte based on chitosan grafted poly(methyl methacrylate) (Ch-g-PMMA) have been prepared and investigated. The lithium trifluoromethanesulfonate salt (LiCF3SO3 or LiTf), ethylene carbonate (EC) and SiO2 are applied as a salt, plasticizer and ceramic filler, to the polymer host system. Impedance spectroscopy was performed at room temperature. The highest conductivity of 1.63 x 10^-4 Scm-1 was obtained for the grafted polymer with 50 wt. % of LiCF3SO3 and enhanced to 2.23 x 10^-4 Scm-1 with the addition of 30 wt. % EC. The conductivity is further enhanced to 4.21 x 10^-4 Scm^-1 with the addition of 6 wt. % SiO2. Both additives caused a reduction of the Ch-g-PMMA crystalline phase content and increased segmental flexibility leading to conductivity enhancement.

Keywords: Chitosan-g-PMMA, Grafting, Gamma radiation, Ionic conductivity, Plastisizer, Composited, Glass temperature

1. Introduction

The ionic conductivity in polymer electrolytes takes place in the amorphous phase, where the ion conduction is mediated by local motion of the polymer chain segments above the glass transition temperature, Tg. The enhancements of conductivity have been achieved either by reducing the crystallinity of polymers or by lowering the glass-transition temperature. Therefore, various approaches such as blending, copolymerization, plasticization and composite fabrication technique have been introduced to enhance the ionic conductivity of the polymer electrolyte. [1,2]

In recent years [3], chitosan (an N-deacetylated derivative of chitin) has been extensively studied due to its biodegradable, bio-compatible and non-toxic nature. Although several studies [4-6] have proven that chitosan could be used as a polymer matrix for ionic conduction, however a major drawback of these chitosan polymer electrolyte membrane for practical application is that they are semi crystalline in nature with low ionic conductivity. Studies [7,8] revealed that the crystallinity of the polymer may be decreased by grafting the polymer with a less crystalline or amorphous monomer via radiation-induced graft polymerization technique. This is due to the fact that the incorporation of side chain grafts, which particularity have an amorphous nature, exerts a dilution effect on the grafted film by increasing the amorphous content at the expense of crystallinity. The increase of amorphous content thus increases the conductivity of the polymer film.

The most striking advancements in the ionic conductivity of polymer electrolytes have been attained through the incorporation of substantial amounts of plasticizers. In addition to reduce the crystalline content and increasing the polymer segmental mobility, plasticizers can result in greater ion dissociation which allows greater number of charge carriers for ionic transport. However, the use of plasticizer tends to decrease the mechanical strength of polymer electrolytes, particularly at high degree of plasticization. One of the most promising ways to improve morphological and electrochemical properties of polymer electrolyte is addition of ceramic filler [9-12]. In this work, the modification of chitosan by radiation induced copolymerization with methacrylate (MMA) is presented. The grafted polymer Ch-g-PMMA, lithium trifluoromethanesulfonate (LiCF3SO3 or LiTf), ethylene carbonate (EC) and silicon dioxide (SiO2) were then used in the preparation of solid grafted polymer electrolytes (SGPE), gelled grafted polymer electrolyte (GGPE) and composited grafted polymer electrolyte (CGPE). The addition of salt, plasticizer and dispersoid fillers were thought to enhance the grafted polymer ionic conductivity.

2. Experimental

2.1. Materials

Materials comprised of chitosan, MMA and LiCF3SO3. EC and SiO2 were purchased from Sigma-Aldrich INC, USA. Acetone and acetic acid were purchased from Mallinckrodt Baker INC, USA. All reagents were used without further purification. Doubly distilled water was used throughout the experiments.
2.1. Preparation of composited Ch-g-PMMa based electrolytes

The grafted polymer electrolytes were prepared using two-steps procedure. The first step involved the preparation of grafted polymer by graft copolymerization of MMA onto chitosan using simultaneous irradiation technique. 0.5 g chitosan was dissolved in 50 ml 1% acetic acid solution and then 0.5 g of MMA solution was added accordingly. After complete dissolution, the solutions were irradiated in a 0°C–γ-ray field. The facility of 0°C–γ-ray source was supplied by One Stop Gamma Sterilizing Center, Malaysian Nuclear Agency (NUCLEAR MALAYSIA).

Upon irradiation, the grafted sample solutions were cast into petri dishes and left to form a grafted chitosan film. The homopolymer formed in the reaction was removed via Soxhlet extraction using acetone for 8 h. The grafted copolymer was then dried in a vacuum oven at 40 °C until a constant weight was obtained. Different concentrations (2–10 wt.%) of SiO2 was then separately doped into optimized Ch-g-PMMa–LiTf–EC electrolyte which provides the highest conducting gelled sample. Each sample was prepared using solution cast technique.

2.2. Characterization

The glass transition temperature (Tg) and the decomposition temperature (Td) of the grafted polymer and grafted polymer electrolyte complex film was measured by using NETZSCH, DSC 200F3 located at the polymer lab, Faculty of Applied Sciences, UiTM Shah Alam. The conductivity of the grafted polymer electrolytes was measured using a Won A Tech, WEISS10, Multichannel electrochemical impedance spectroscopy (EIS) System that has been interfaced to a computer. The conductivity–temperature study was conducted in the temperature range of 303–373 K.

3. Results and discussion

3.1. Conductivity

In addition to reducing the crystalline content and increasing the polymer segmental mobility, plasticizers can result in greater ion dissociation which allows greater number of charge carriers forionic transport. The addition of plasticizer, ethylene carbonate (EC) to grafted polymer electrolytes also can reduce the glass transition temperature, Tg [13,14]. The reduction in Tg softens the polymer backbone and increases segmental motion resulting in an enhancement in conductivity. The maximum conductivity is achieved by addition of 30 wt.% plasticizer (EC) which is 2.23 x 10⁻⁴ S cm⁻¹. The variation of conductivity as a function of weight percent (wt.%) of plasticizer in a Ch-g-PMMa-50% LiTf system at room temperature is shown in Fig. 1. It can be observed that the room conductivity of the plasticized Ch-g-PMMa-50% LiTf system increases to the maximum value of 2.23 x 10⁻⁴ S cm⁻¹ when 30 wt.% EC was added. The addition of EC plasticizer to grafted polymer electrolyte can establish attractive forces between EC molecules and grafted polymer chain segments. These attractive forces reduce the cohesive forces between the grafted polymer chains and increase the segmental mobility which resulted in facilitating greater ion dissociation which allows greater numbers of charge carriers for ionic transport, thus enhancing the ion conductivity. However, the decrease in conductivity upon the addition of higher than 30 wt. % EC could be ascribed to the occurrence of ion association which decreases the number of free mobile ions available in the system.

The variation of conductivity as a function of weight percent (wt.%) of filler in a Ch-g-PMMa-50% LiTf -30 % EC system at room temperature is shown in Fig.2. When silica is first added to the grafted polymer complex, the conductivity decreases due to blocking of existing conducting pathways and the possible assem-
that ionic conductivity increased with increasing temperature as a result of the free volume model, where, as the temperature increases, the polymer electrolyte can expand easily and produces free volume. Therefore, ions, solvated molecules, or the polymer segments can move into the free volume, causing it to increase [19]. Thus, this enhances the ion and polymer segmental mobility that will, in turn, enhance the ionic conductivity.

The value of $E_\text{a}$ of composited system is listed in Table 2 while Fig.6 depicts the variation of $E_\text{a}$ with the amount of SiO$_2$ in the grafted polymer electrolyte complexes. It can be seen that 6.0 wt.% SiO$_2$ added sample has the highest ionic conductivity and the lowest $E_\text{a}$ compared with other samples. Ramesh and Wen [10] claimed that the low $E_\text{a}$ is due to the amorphous nature of the polymer electrolytes that facilitate the fast Li ions motion in the polymer network. The above result also shows that the composite system has higher ionic conductivity and lower activation energy compared to the polymer electrolyte without filler.

Table 2: Activation energy $E_\text{a}$ value for composite system.

| Designation | $E_\text{a}$ (eV) |
|-------------|------------------|
| 98\% [50Ch-g-PMMA-50 LiCF$_3$SO$_3$-30EC]-2SiO$_2$ | 0.24 |
| 96\% [50Ch-g-PMMA-50 LiCF$_3$SO$_3$-30EC]-4 SiO$_2$ | 0.22 |
| 94\% [50Ch-g-PMMA-50 LiCF$_3$SO$_3$]-6 SiO$_2$ | 0.05 |
| 92\% [50Ch-g-PMMA-50 LiCF$_3$SO$_3$-30EC]-8 SiO$_2$ | 0.10 |
| 90\% [50Ch-g-PMMA-50 LiCF$_3$SO$_3$-30EC]-10 SiO$_2$ | 0.09 |

### 3.2 Thermal properties

Thermal stability of grafted polymer complexes after addition of LiTf salt, EC plasticizer and SiO$_2$ filler could be evaluated by determining the weight loss of the samples after heating over the temperature range of 20°-400°C. The TGA thermograms of pure Ch-g-PMMA, Ch-g-PMMA+LiTf, Ch-g-PMMA+LiTf + EC and Ch-g-PMMA+LiTf + EC + SiO$_2$ are presented in Fig. 7 (a), 7 (b), 7 (c) and 7 (d) respectively. All samples actually start to lose mass at temperatures below 100°C. This initial loss resulted from residual solvent evaporation and the transition of polymer samples. Volatilization of monomers and oligomer absorbed in the matrix can also be responsible for this initial loss [20]. The thermal stability of the polymer electrolyte decreases with the addition of plasticizer. This is because, in the region between 200°C and 300°C, weight loss of ~33% for plasticized sample is observed compared with only ~25% for pure Ch-g-PMMA. However, the sample of composited electrolyte becomes severely degraded until temperature of 150°C with weight loss of ~55%. These observations suggest that the composited sample has been relatively stable in the temperature range of 150-400°C. The weight loss is stable after addition of SiO$_2$ due to the binding between the grafted polymer chains that become tighter. Thus, the ability of volatilization becomes lesser [21].

The DSC thermogram of a pristine Ch-g-PMMA-LiTf sample heated at controlled rate is presented in Fig. 8. (a). It can be observed that the $T_\text{g}$ for pure Ch-g-PMMA-LiTf is ~118°C. While, the DSC thermogram of Ch-g-PMMA-EC sample is depicted in Fig.8 (b). The value of $T_\text{g}$ is found to be ~100°C. This plasticized sample presents a lower value of $T_\text{g}$ compared to the plasticizer-free sample due to lubricating effects [13]. The plasticizer behaves like a solvent when mixed with polymer and results in lowering of the dipole-dipole interactions due to the presence of the plasticizer molecules between the polymer chains [20]. The decrease in $T_\text{g}$ help to soften the polymer backbone and increase its segmental motion. Such segmental motion produces voids, which enables the easy flow of ions through the material when there is an applied electric field. However, it can be observed that the crystallization temperature increases to 105°C with addition of SiO$_2$, but the temperature is still below the pure Ch-g-PMMA crystallization temperature. The increase in crystallization temperature in this sample shows that the polymer electrolyte is stable and difficult to change phase from amorphous to crystalline state when heated. Thus, this would correlate to the improvement in mechanical properties.

### 4. Conclusion

The electrical properties of grafted polymer Ch-g-PMMA based polymer electrolytes have been presented. The highest conductivity for the salted system at room temperature was obtained to be 1.42 x 10$^{-4}$ S cm$^{-1}$ at 50 wt.% of LiTf concentration. Addition of EC and SiO$_2$ has enhanced the ionic conductivity performance of the highest conducting sample in salted system of the polymer electrolyte. The plasticized sample at room temperature with 30 wt.% EC concentration was found to have maximum value at 2.96 x 10$^{-4}$ S cm$^{-1}$. While, ionic conductivity is increased to 4.21 x 10$^{-4}$ S cm$^{-1}$ when the highest conducting sample in plasticized system was added with 6 wt.% of SiO$_2$. The thermal stability of the grafted polymer electrolyte has decreased with the addition of plasticizer but the grafted polymer electrolyte was relatively stable after the temperature of 150°C with addition of SiO$_2$. The $T_\text{g}$ value of plasticized grafted polymer electrolyte is 100°C which is lower when compared to the plasticizer-free sample due to lubricating effects.

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Fig. 1: Conductivity Values of Different Concentrations of EC in Ch-g-PMMA-salt Films (30°C)

Fig. 2: Conductivity Values of Different Concentrations of SiO₂ in Ch-g-PMMA-salt-Plasticizer Films (30 °C).

Fig. 3: Arrhenius plots of Ch-g-PMMA-salt film with different plasticizer (EC) concentrations

Fig. 4: Activation energy variation with different plasticizer (EC) concentrations

Fig. 5: Arrhenius plots of Ch-g-PMMA-salt plasticizer-composite film with different SiO₂ concentrations

Fig. 6: Activation energy variation with different SiO₂ concentrations
Fig. 7: TGA thermograms of (a) Ch-g-PDMA (b) Ch-g-PDMA-50% LTI (c) Ch-g-PDMA-50% LTI + 10% EC (d) Ch-g-PDMA-50% LTI + 20% EC + 5% SiO₂.

Fig. 8: DSC thermograms of (a) Ch-g-PDMA-50% LTI + 20% EC + 5% SiO₂ (b) Ch-g-PDMA-50% LTI + 10% EC (c) Ch-g-PDMA-50% LTI + 10% EC + 5% SiO₂.