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Structure and Electrical Properties of Polymer Electrolyte Based on Plasticized Chitosan Grafted Polymethyl Methacrylate (Ch-g-PMMA)-Magnesium Triflate for Electrochemical Double Layer Capacitor

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Abstract

Polymer electrolytes have received much attention as materials used in batteries, supercapacitors, sensors and solar cells. Most of the polymer electrolytes reported are based on synthetic polymer, therefore it is difficult to recycle as it has poor degradability and ends up being a waste. In recent years, biopolymers gained much interest in replacing environmentally unfriendly polymers. Various studies have been done to accomplish polymer electrolytes with high conductivity and long-term safety. This study's objective is to prepare plasticized Ch-g-PMMA-based polymer electrolyte by introducing the magnesium triflate salt and glycerol plasticizer. The grafted polymer of Ch-g-PMMA was prepared using gamma (γ) radiation. The grafted polymer of Ch-g-PMMA with 0.4 g of $Mg(Tf)_2$ and different concentrations of glycerol has been prepared by using the solution casting technique. To achieve this study, the prepared plasticized Ch-g-PMMA-$Mg(Tf)_2$ polymer electrolytes are characterized by XRD, FTIR, EIS and LSV techniques. XRD was carried out to determine the change in crystallinity and the amorphous structure of the plasticized Ch-g-PMMA-$Mg(Tf)_2$ polymer. FTIR reveals the occurrence of complexation between Ch-g-PMMA polymer, $Mg(Tf)_2$ salt and glycerol plasticizer. The grafted Ch-g-PMMA-$Mg(Tf)_2$ was added with different concentrations of glycerol from 0 to 50 wt%. The Ch-g-PMMA-$Mg(Tf)_2$ polymer electrolyte with 50 wt% of glycerol shows the highest ionic conductivity of 1.50×10^{-4} $S\cdot cm^{-1}$ compared with other samples. The increase in mobility of ions and the number of charge carriers has enhanced ionic conductivity. Based on the LSV analysis, the highest conducting Ch-g-PMMA-$Mg(Tf)_2$ polymer with 50 wt% of glycerol was found electrochemically stable up to 3.2 V. The goal of this study is to determine the structure and electrical properties as well as the window stability of plasticized Ch-g-PMMA-$Mg(Tf)_2$. The best outcome was produced by adding the 50 wt% of glycerol into the Ch-g-PMMA-$Mg(Tf)_2$ which increased further by 1 order of magnitude.

Keywords: Chitosan, Ch-g-PMMA, Magnesium triflate, Glycerol, Plasticizer, Amorphous, Ionic conductivity

Introduction

A polymer electrolyte is widely applied in many electrochemical devices such as batteries, fuel cells, supercapacitors and electrochromic devices. A polymer electrolyte is a membrane with transport properties that are similar to that of common liquid ionic solutions [1]. Natural polymer electrolyte has been sought to substitute synthetic polymer electrolyte in the commercialized industry due to their advantages. Natural polymer is cheaper, eco-friendly and biodegradable. For example, chitosan, starch, cellulose and polyethylene glycol. Compared to the other biodegradable polymer electrolyte, chitosan has some advantages to offer such as being non-toxic, high nitrogen content, good molecular biocompatibility and reproducible [2].

Chitosan received the most attention among biopolymers due to its biodegradable, non-toxic and biocompatible polymer. Chitosan is made up of 1,4 linked-2-deoxy-2-aminoglucose, which is obtained by N-deacetylation of chitin [3]. Its application is extended to the pharmaceutical, cosmetics and food industries. Chitosan is composed of a lone pair of the nitrogen atom and oxygen atom in its structure which could facilitate ion complexation with the salt. Many studies have been done on copolymerization between chitosan and other polymers to overcome some of the limitations of chitosan, such as its poor mechanical strength, low thermal resistance and low selectivity as an adsorbent [4]. PMMA also has a few advantages of being hydrophilic and chemically stable, abundant in raw materials and easy to synthesize [5]. The graft copolymer that comes from grafting PMMA onto chitosan has potential applications in various industries including biomaterial, agriculture and pharmaceuticals [6]. Chitosan-g-PMMA is a grafted polymer electrolyte based on grafting between chitosan and poly(methyl methacrylate) (PMMA). The gamma radiation induced graft polymerization technique was used to prepare a grafted copolymer (chitosan-g-poly(methyl methacrylate)) (PMMA) [7]. The magnesium triflate, $Mg(Tf)_2$ was selected as a salt due to its big size of anions (Tf^-) as it can effectively dissociate and produce ions. Glycerol is considered to be an excellent plasticizer for bio-polymer-based films among other plasticizers due to its good mechanical properties [8]. It was discovered that the electrolyte containing the highest amount of glycerol had the highest ionic conductivity [9].

Abdullah *et al.* [10] have also reported a conductivity value of 2.06×10^{-3} S·cm^{-1} for Chitosan-PEO-NH_4NO_3-EC. The grafted polymer of Ch-g-PMMA/30 % LiTf with 30 wt% EC as plasticizer has an ionic conductivity value of 2.23×10^{-4} S·cm^{-1} has been reported by Jaafar *et al.* [11]. Aziz *et al.* [9] have obtained and it has reported a conductivity value of 8.57×10^{-4} S·cm^{-1} for CS/40 wt% NH_4SCN with 40 wt% of glycerol. Jaffar *et al.* [7] have reported ionic conductivity of 4.05×10^{-5} S·cm^{-1} for Chitosan-g-PMMA with 60 wt% LiTf salt. Ionic conductivity of 3.57×10^{-5} S·cm^{-1} has been reported by Wang *et al.* [2] for 90 wt% CA/10 wt% $Mg(Tf)_2$ with 10 wt% of EMITf. The plasticized CS:MC doped with 40 wt% of NH_4L has a conductivity value of 6.65×10^{-4} S·cm^{-1} has been reported by Aziz *et al.* [12]. Azahar *et al.* [13] have studied and obtained CS-TF-10 % $LiBF_4$ with maximum ionic conductivity 2.699 ± 0.28 mS·cm^{-1}. Higher values of ionic conductivity of 1.255×10^{-4} S·cm^{-1} for chitosan (CS) with 70 % of $MgCl_2$ have been reported by Helen *et al.* [14]. Aziz *et al.* [15] also reported a conductivity value of 1.20×10^{-3} S·cm^{-1} for CS-$LiClO_4$. Maximum conductivity of 3.5×10^{-3} S·cm^{-1} for composition PVA: CS: 40 % NH_4SCN incorporated with 42 wt% of glycerol was reported by Aziz *et al.* [16]. However, the development of a magnesium ion-conducting membrane based on Ch-g-PMMA with $Mg(Tf)_2$ and glycerol has not been reported so far. Therefore, an attempt has been made in this study to develop 1 g of grafted Ch-g-PMMA-$Mg(Tf)_2$ with different concentrations of glycerol from 0 to 50 wt% has been prepared by a solution casting technique and are characterized by XRD, FTIR, EIS and LSV techniques.

Materials and methods

Grafted polymer electrolytes were prepared by graft co-polymerization of MMA onto chitosan through simultaneous irradiation technique of gamma (γ) radiation. Chitosan was added to 1 % acetic acid and adding MMA solution accordingly. The solution was stirred until it is completely dissolved. The obtained solution was irradiated in a ^{60}Co–γ-ray field. The ^{60}Co–γ-ray source was carried out using the One Stop Gamma Sterilizing Center, SINAGAMA, Malaysian Nuclear Agency (NUCLEAR MALAYSIA). The grafted sample solution was cast into a petri dish and left at room temperature to form a grafted chitosan-PMMA film. Then, the homopolymer formed was removed using acetone via Soxhlet extraction for 8 h. The grafted copolymer was dried in a vacuum at 40 °C until a constant weight was determined. Sample grafted polymer salt-plasticized electrolyte was prepared by adding 0.6 g of Ch-g-PMMA into a 1 % acetic acid solution. The 0.4 g of 40 wt% of $Mg(Tf)_2$ salt was added into the solution and stirred overnight until it is completely dissolved. Ch-g-PMMA-$Mg(Tf)_2$ solution were doped separately with different concentrations percentage of glycerol (0, 10, 20, 30, 40 and 50 wt%) as shown in **Table 1**. All samples were cast into different petri dishes and left at room temperature to form a Ch-g-PMMA-$Mg(Tf)_2$-glycerol film. The film was kept in a silica gel desiccator for further drying to eliminate any moisture.

Table 1 Composition of glycerol plasticizer.

Designated	Glycerol (g)	Glycerol (wt%)
S1	0	0
S2	0.11	10
S3	0.25	20
S4	0.43	30
S5	0.67	40
S6	1.00	50

XRD was used to analyze the change of crystallinity and the amorphous structure of the plasticized Ch-g-PMMA-Mg(Tf)$_2$ polymer electrolyte. XRD was performed using X'Pert PRO, PAN Anlytical, DY2536 located at the Faculty of Applied Sciences, UiTM Shah Alam in a wide 2θ range ($5 \leq 2\theta \leq 85$). XRD analysis for Ch-g-PMMA-Mg(Tf)$_2$-glycerol film has been undertaken at room temperature. FTIR was used to study the complexation between Ch-g-PMMA polymer, Mg(Tf)$_2$ salt and glycerol plasticizer. The spectra of the samples were carried out at a wavenumber of 700 to 2,000 cm^{-1} in a transmittance mode at 303 K (room temperature). The impedance spectrum was carried out using HIOKI Impedance Tester which is placed at the IMADE laboratory, Institute of Science (IOS) to study the ionic conductivity of the grafted polymer together with salt and plasticizer. The frequency of impedance spectroscopy measurement is between 100 Hz to 1 MHz with stainless steel as an electrode. The electrolyte film will be sandwiched between 2 stainless steel (SS) electrodes. Linear sweep voltammetry (LSV) analysis will be measured at a sweep rate of 5 mV·s^{-1} from a potential range of 0 - 2.5 V.

Results and discussion

X-Ray Diffraction (XRD) is an effective tool used in studying crystallinity and the amorphous structure of the polymer electrolyte. **Figures 1(a) - 1(b)** show the XRD patterns of Ch-g-PMMA-Mg(Tf)$_2$ and Ch-g-PMMA-Mg(Tf)$_2$ doped with glycerol at 50 wt%, respectively. In the XRD pattern of a sample, the sharp line shows that it is more crystalline in nature. Therefore, if there is a broad peak in the XRD pattern, it shows that the sample is more amorphous in nature. In **Figure 1(a)**, the peak at $2\theta = 18.88$ ° is observed. Hence, in **Figure 1(b)**, the peak is shifted at $2\theta = 20.48$ °. By adding the glycerol of 50 wt% of glycerol to Ch-g-PMMA-Mg(Tf)$_2$, the broadness of the peak increases, whereas its intensity reduces. Chitosan shows peaks at $2\theta = 20.48$, 38.4 and 44.7 ° which imply the crystalline structure of the chitosan's membrane. The existence of chitosan amorphous structure was shown via the presence of the peaks at the range ($35 \leq 2\theta \leq 55$ °) [17]. The amino and hydroxyl groups were developed due to the intermolecular and intramolecular hydrogen bonding throughout an absorbed water molecule, creating a crystalline structure for the chitosan. The plasticizer helps to weaken the intermolecular and intramolecular of the chitosan which can be observed in **Figure 1(b)** whereas the peaks are reduced [18]. The peak at $2\theta = 65$ and 78.18 ° are most likely chitin peaks from the incomplete deacetylation process of the chitin to the chitosan [19]. There is also a peak of Mg(Tf)$_2$ that is shown at $2\theta = 30.66$ ° in **Figure 1(a)** which is similar to the studies by Farhana *et al.* [20]. Based on this observation, the Mg(Tf)$_2$ was not completely diluted in the solution. These peaks may be present as magnesium ion is divalent and have a strong attraction force [21]. Therefore, the peak disappeared in **Figure 1(b)** which shows that the Mg(Tf)$_2$ was fully diluted in the solution of plasticized polymer electrolyte. As the plasticizer concentration increases, the intensity of the peak decreases. Reduced broadness suggests a less amorphous character [22]. Additionally, it lessens crystallinity to some extent. This demonstrates how an increase in the amorphous phase and the number of ions results in an increase in ionic conductivity. Hence, peaks broadening from the XRD analysis showed the amorphous structure of the polymer electrolytes whereas the ionic conductivity improved when the amorphous structure increased.

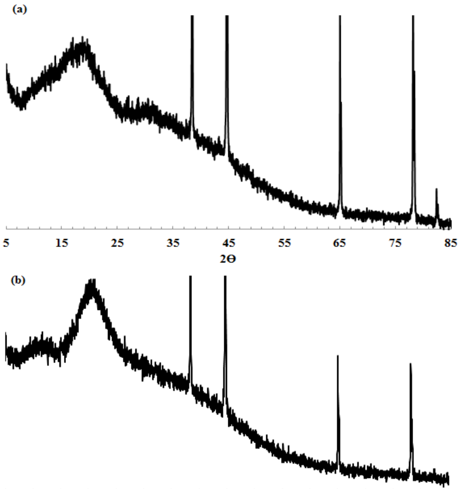

Figure 1 (a) XRD pattern of Ch-g-PMMA-Mg(Tf)$_2$ with 0 and (b) 50 wt% of glycerol.

An efficient tool to study the complexation between Ch-g-PMMA polymer, Mg(Tf)$_2$ salt and glycerol plasticizer. FTIR analysis was used to study the changes in the intensity of the bands, the shifting of bands and the appearance of new bands [23]. **Figure 2** shows the FTIR spectrum of Ch-g-PMMA-Mg(Tf)$_2$ with different concentrations of glycerol (0 and 50 wt%). The FTIR spectra of the samples at wavenumber ranged from 700 to 2,000 cm^{-1}. The vibration peak observed at 1,634 cm^{-1} is due to the carbonyl C=O-NHR band of pure chitosan [11]. The peak at 1,438 cm^{-1} was probably an absorption peak of pure PMMA which is corresponding with the O-CH$_3$ symmetric bending mode [24]. The band of Mg(Tf)$_2$ was observed at 1,029 and 1,247 cm^{-1}. This is due to the existence of the triflate anion CF$_3$SO$_3$ which is assigned to symmetric SO$_3$ and asymmetric SO$_3$, respectively. This peak shows the bonding of grafted polymer electrolyte and salt. The C=O band in plasticized Ch-g-PMMA-Mg(Tf)$_2$ with 50 wt% of glycerol (1,729 cm^{-1}) seems to have broadened that implying the plasticizer just interacts physically with the grafted polymer and salt. There is also no electrochemical reaction between the grafted polymer with glycerol or between the plasticizer and the salt [11]. Thus, there was a bonding between Ch-g-PMMA-Mg(Tf)$_2$ and glycerol.

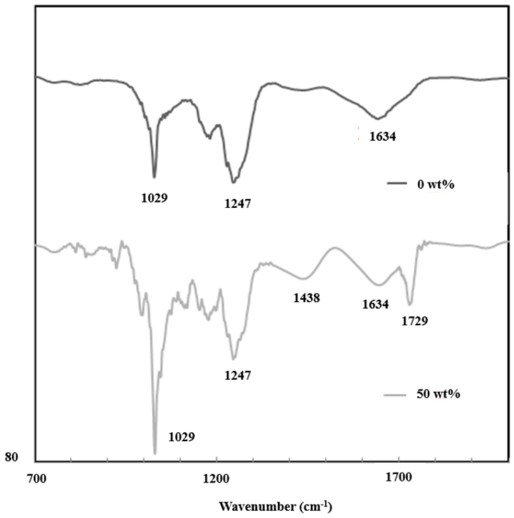

Figure 2 FTIR spectrum of Ch-g-PMMA-Mg(Tf)$_2$ with 0 and 50 wt% of glycerol.

The electrical properties of the grafted polymer with salt and plasticizer have been analyzed by Electrical Impedance Spectroscopy (EIS) at room temperature (303 K). **Figure 3** represents the Ch-g-PMMA-Mg(Tf)$_2$ with several concentrations of glycerol at room temperature. The ionic conductivity (σ) was calculated using the equation below:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where, t is the thickness of the film, R$_b$ is the bulk resistance and A is the film electrolyte contact area with an electrode.

The bulk resistance (R$_b$) can be determined from the impedance plot. The bulk resistance of the membrane was obtained using the plot's intercept of the semicircle on the real axis. The concentration of ions will be increased when the bulk resistance (R$_b$) decreases. The calculated ionic conductivity value for Ch-g-PMMA-Mg(Tf)$_2$ with different concentrations of glycerol is shown in **Table 2**. Ionic conductivity of Ch-g-PMMA-Mg(Tf)$_2$ with 0 wt% is 1.49×10^{-5} S·cm^{-1}. The peak dropped at the weight percent of glycerol at 20 to 30 wt% which is may due to the decrease in the mobility of ions or the number of charge carriers. The mobility of ions decreases as the concentrations of glycerol increase because of the steric crowding of ions that collides with each other and create barriers in their travels [25]. **Figure 3** shows a sudden peak after adding a small amount of plasticizers. This peak indicates the increase in number of the charge carrier. This sudden increase may be due to the interaction between charge carriers and interchains [26]. By adding the glycerol of up to 50 wt% to Ch-g-PMMA-Mg(Tf)$_2$, ionic conductivity gets increases. The conductivity value is increased by 1 order of magnitude due to the plasticization effect (glycerol). This is due to the increased number of amorphous states and mobility of ions. The enhancement of the amorphous state will reduce the crystallinity which enhances the fast movement of ions which is shown in the XRD result. The plasticizing solvent, glycerol contributes to the increase in ionic mobility and the increase of the charge carriers in the films which leads to the improvement of ionic conductivity [27]. Hence, the highest ionic conductivity has been observed for the Ch-g-PMMA-Mg(Tf)$_2$-50 wt% with the value 1.50×10^{-4} S·cm^{-1}.

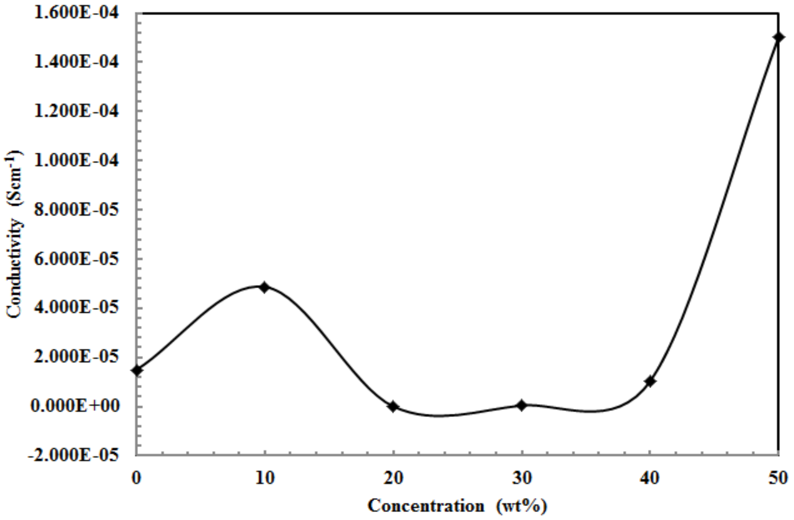

Figure 3 Conductivity with different weight percent of plasticizer (0, 20, 30, 40 and 50 wt%).

Table 2 Ionic conductivity of Ch-g-PMMA-Mg(Tf)$_2$ with different weight percent of glycerol at room temperature.

Glycerol (wt%)	σ (S·cm^{-1})
0	1.49×10^{-5}
10	4.85×10^{-5}
20	2.30×10^{-8}
30	4.48×10^{-7}
40	1.04×10^{-5}
50	1.50×10^{-4}

One of the important characteristics of selecting a good electrolyte for application in electrochemical devices is a great potential stability window [28]. The electrochemical stability of the highest ionic conductivity of glycerol which is Ch-g-PMMA-Mg(Tf)$_2$-50 wt% has been studied by LSV analysis. **Figure 4** shows the graph of current versus voltage whereas the breakdown voltage for the electrolyte can be measured. The sudden increase in the current indicated the breakdown process of the plasticized polymer electrolyte. Based on **Figure 4**, the electrochemical stability of Ch-g-PMMA-Mg(Tf)$_2$-50 wt% of glycerol is found to be around 3.2 V. No current flow within 0.5 and 2.5 V, indicating that no electrochemical reaction is taking place below this potential window. The increase in the current above 3.2 V is associated with the decomposition of the polymer electrolyte, indicating the electrochemical reaction occurring within the polymer electrolyte. As the potential increases more than 3.2 V, rapid changes of current from 0.005 to 0.02 A can be observed. The electrolyte in this study is capable to withstand the operating voltage in the battery system. Thus, the film can be used as an electrolyte in a rechargeable magnesium battery due to rechargeable batteries generally function between 3.0 and 4.5 V [29].

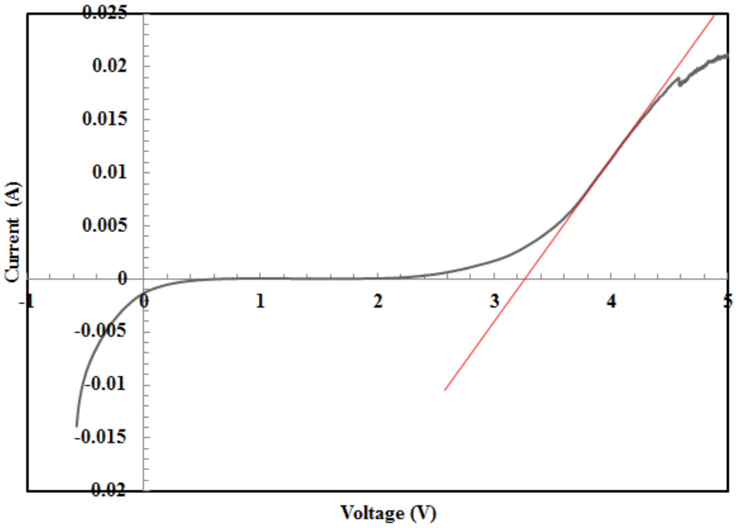

Figure 4 Linear sweep voltammetry of Ch-g-PMMA-$Mg(Tf)_2$ with 50 wt% of glycerol.

Conclusions

Ch-g-PMMA with magnesium triflate, $Mg(Tf)_2$ and different concentrations of glycerol have been developed. The Ch-g-PMMA-$Mg(Tf)_2$-glycerol has been characterized by different techniques such as XRD, FTIR, EIS and LSV. The structure properties of plasticized Ch-g-PMMA based polymer electrolytes were analyzed by XRD (**Figure 1**) and FTIR (**Figure 2**). The electrical properties were determined by the ionic conductivity results obtained by EIS. The ionic conductivity of grafted Ch-g-PMMA-$(MgTf)_2$ was increased by adding different concentrations of glycerol up to 50 wt% which is tabulated in **Table 2**. The peak suddenly dropped at 20 - 30 wt% and slightly increased after adding 40 wt% of glycerol. The peak drastically increased which shows that Ch-g-PMMA-$Mg(Tf)_2$ with 50 wt% of glycerol has got more amorphous state and it gets the highest ionic conductivity value which is 1.50×10^{-4} $S\cdot cm^{-1}$. The conductivity is increased further by one order of magnitude due to the addition of glycerol as a plasticizer. The electrochemical stability of Ch-g-PMMA-$Mg(Tf)_2$ with 50 wt% of glycerol has been found at 3.2 V by LSV analysis. Based on this study, the electrolyte is capable to withstand the operating voltage in the battery system. The satisfactory findings were obtained which will be useful in the future when fabricating the Electrical double-layer capacitors (EDLC). It is hoped that the current findings will serve as the polymer electrolytes used in electrochemical devices that are safer and can be used long-term. More research is required in order to more accurately assess the possible effectiveness of polymer electrolytes in EDLC. Future research will have to be done into the fabrication of magnesium ion batteries as their applications are in mainly small devices such as cellular phones and portable computers.

Acknowledgements

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