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EFFECT OF HNO_3 TREATED TIO_2 ON STRUCTURAL AND ELECTRICAL PROPERTIES OF HEXANOYL CHITOSAN/POLYSTYRENE-$LICF_3SO_3$-TIO_2 COMPOSITE POLYMER ELECTROLYTES

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ABSTRACT

In searching for solutions to reduce battery weight for military applications, films of composite polymer electrolytes comprised of hexanoyl chitosan/polystyrene containing lithium trifluoromethanesulfonate ($LiCF_3SO_3$) and titanium oxide were prepared using solution casting technique. Two types of TiO_2 filler were used, which are untreated TiO_2 and HNO_3-treated TiO_2. The effect of untreated and HNO_3-treated TiO_2 on the structural and electrical behavior of the prepared electrolyte systems has been investigated by using X-ray diffraction and impedance spectroscopy, respectively. The ac conductivity was calculated using $\sigma(\omega) = \sigma_{dc} + A\omega^s$ formula in the temperature range from 283 K to 353 K. The conduction mechanism of the H-chitosan/PS-$LiCF_3SO_3$-TiO_2 and H-chitosan/PS-$LiCF_3SO_3$-HNO_3-treated TiO_2 can be interpreted based on the correlated barrier hoping model at 4 and 6 wt.% of TiO_2 respectively.

Keywords: hexanoyl chitosan; polystyrene; composite polymer electrolytes.

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1. INTRODUCTION

While able to benefit from technology, the army is facing a number of challenges in their operations today and in the future. One of the major challenges is in the power sources arena. Today's soldier carries a wide array of electronic devices such as computers, communications equipment, weapon system and all requiring portable power. The army is aware of the situation and has identified problem areas of battery weight, space and power source carried by the soldier [1]. One area identified to further study is the electrolyte for battery system using polymer electrolyte. Polymer electrolyte offers reduction in size, weight and thermal management properties in line with the requirement of future military systems. With better process efficiency, the batteries can be designed to be lighter in weight hence reducing the operational physical load of soldiers which may contributes to longer endurance and reduce fatigue during operations.

Polymer electrolytes are of immense interest due to their applicability in energy conversion and storage devices. They present significant advantages over liquid electrolytes such as safer design, simpler stacking and hermetic sealing processes, superior in density, flame-resistance and shape suitability in the requirements of the application [2-3]. In order to achieve high performance, a battery electrolyte must possess high ionic conductivity, be stable at both the high potential of the battery cathode and the low potential of the battery anode. Various approaches to enhance the ionic conductivity of polymer electrolytes have been suggested in the literature such as by addition of plasticizer, filler and blending polymer [4-5]. The recent technique developed for solid polymer electrolyte is the dispersion of nano-size inorganic ceramic filler particles such as Al_2O_3, SiO_2, TiO_2, SnO_2, ZnO and ZrO into the polymer electrolytes system called composite polymer electrolytes (CPE). It has been shown that the addition of fillers to semicrystalline PEO-alkali metal salt complexes leads to the decrease in the crystallinity of the electrolyte and enhancement in ionic conductivity [6]. Also, the uses of fillers improve mechanical stability of the polymer electrolytes. Changes in the ionic conductivity of CPEs result from the Lewis acid-base interactions between the fillers and the polymer electrolytes components.

From ac conductivity, further information on ionic conduction model can be determined to get more insight on ion conduction mechanism. Various models reported such as small polaron tunneling model (SPT) overlapping large polaron tunneling model (OLPT), correlated barrier hopping model (CBH) and quantum mechanical tunneling model (QMT) have been reported to discuss the ac conduction mechanism in amorphous materials such as semiconductors and glasses [7]. However, there are limited researches available regarding the use of such models to explain the ionic conduction mechanism in polymeric materials.

In order to obtain a balance for the compatibility of filler and polymer electrolytes, several investigations have been carried out such as synthesis of new polymer matrix, preparation of polymer single-ion conductor and doping with filler. Thus, in this research we prepared blended based polymer of hexanoyl chitosan and polystyrene doped with $LiCF_3SO_3$. Two types of TiO_2 filler were used, which are untreated TiO_2 and HNO_3-treated TiO_2. The effect of untreated and HNO_3-treated TiO_2 will be investigated on their ionic conductivity, crystalline fraction, dielectric constant and ionic conduction model.

2. RESULTS AND DISCUSSION

A structural study of solid polymer electrolyte was investigated by XRD. XRD analysis was performed to determine the degree of crystallinity and to observe the glassy nature of the H-chitosan/PS polymer electrolyte.

The degree of crystallinity in the prepared samples were estimated from the ratio of integrated intensity of the peak at $2\theta \approx 6.86°$to the total integrated of the spectrum, using the Equation (1)

$$X_C = \frac{I_C}{I_T} \tag{1}$$

where X_C is the degree of crystallinity, I_C is the $2\theta \approx 6.86°$peak intensity and I_T is the total integrated intensity.

Fig. 1 shows the variation in the degree of crystallinity as a function of untreated and treated TiO_2 concentration. The crystallinity degree was estimated from the peak at $2\theta \approx 6.86°$ using the same method as discussed previously [9]. It can be observed that for both the untreated and treated TiO_2-added electrolyte system, the degree of crystallinity decreases with addition of TiO_2 up to 6 wt.% which is from 19.62% to 13.52 and 14.43% respectively. The reduction of crystallinity will produce more amorphous phase in the system. The amorphous phase makes the electrolyte more flexible, resulting in increase of the segmental motion of the polymer [10]. At 8%, the crystallinity of H-chitosan/PS increases drastically to 22.34%. This indicates that 6 wt.% of TiO_2 is the optimum amount and beyond this weight percentage, the presence of TiO_2 leads to recrystallization of H-chitosan/PS. This observation will be supported with ionic conductivity as discussed below.

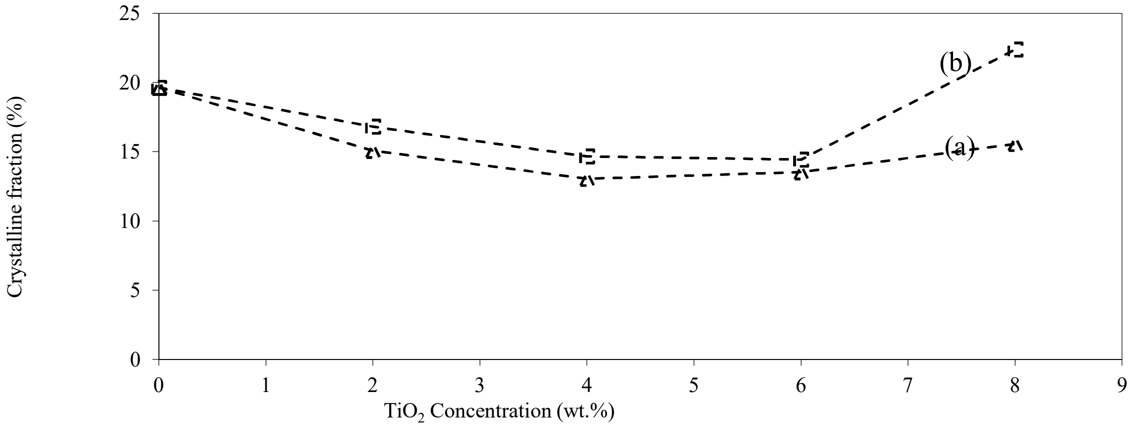


Fig.1. The variation in crystalline fraction for composite electrolyte system as a function of (a) untreated TiO_2 and (b) HNO_3-treated TiO_2 concentration

The variation of room temperature conductivity as a function of untreated and treated TiO_2 concentration is depicted in Fig. 2. The ionic conductivity of H-chitosan/PS electrolytes without TiO_2 filler was 7.21×10^{-5} S cm^{-1}. With addition of 2 wt.% TiO_2, the ionic conductivity of both the untreated and treated TiO_2 systems decreases to around 7.00×10^{-6} and 5.86×10^{-6} S cm^{-1}. Small amount of filler was not able to overcome the rate of ion association of $LiCF_3SO_3$. The conductivity increases with further increase in filler content, reaches a maximum and thereafter decreases with increasing filler content beyond the optimum concentration. The maximum conductivity achieved was 2.27×10^{-4} S cm^{-1} at 4 wt.% for untreated TiO_2 and 1.47×10^{-4} S cm^{-1} at 6 wt.% for HNO_3-treated TiO_2. We found that untreated TiO_2 able to improve the conductivity up to twice while treated TiO_2 only half compared to without filler. The conductivity enhancement is due to presence of oxygen sites as conduction pathways from TiO_2, hence help to increase in the number of mobile Li^+ cation. However, HNO_3-treated TiO_2 systems produce lower ionic conductivity compared to untreated TiO_2 systems because treated TiO_2 have more acidic sites that help to increase the degree of ion association. Treated TiO_2 decreased the conductivity by decreasing the anionic contribution due to the HNO_3-treated TiO_2 grain surface consists of solely OH group and it shown that anion of salt has larger affinity towards filler surface acid site than cation as reported in our previous work [11]. At 10 wt.% TiO_2, the ionic conductivity decreases significantly even below the unfilled electrolytes. This behavior is due to the recrystallization of polymer host as observed in XRD analysis. The conductivity variations observed also could be attributed to the variation in the number of free ions in the samples. This is reflected in the dielectric constant, εr versus frequency curves as illustrated in Fig. 4.

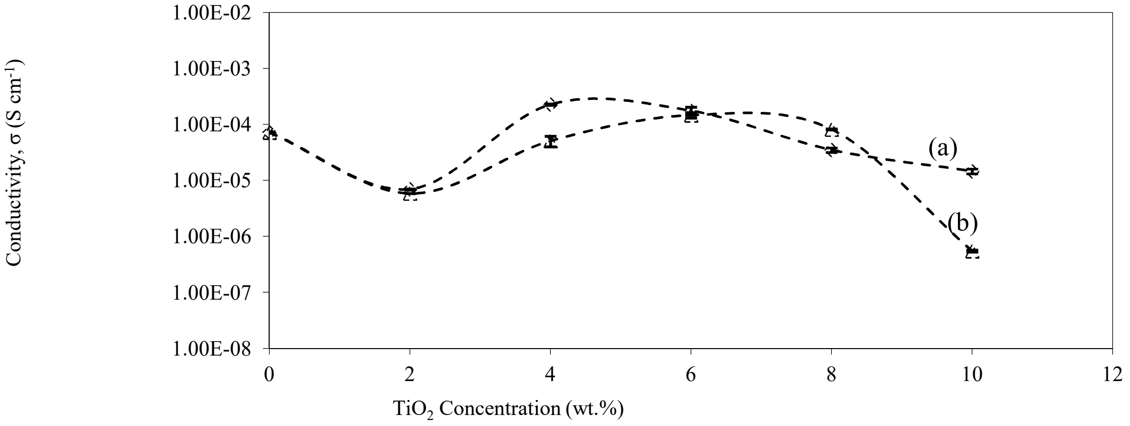


Fig.2. Ionic conductivity of H-chitosan/PS-$LiCF_3SO_3$ polymer electrolytes as a function of TiO_2 concentration at room temperature (a) untreated TiO_2 and (b) HNO_3-treated TiO_2

Fig. 3 represents the plot of ionic conductivity (log σ) versus the inverse absolute temperature for untreated and HNO_3-treated TiO_2 electrolyte system respectively. The measurement was carried out from 283 K to 383 K. Within the temperature range investigated, the variations of log σ with 1/T are linear with $R^2 = 0.953$ and 0.985 for untreated TiO_2 and HNO_3-treated TiO_2. This indicates that the conductivities of the studied electrolyte systems are thermally activated which indicating that this system obeyed the Arrhenius rule [12]. Therefore, as temperature was increased, the number of free lithium ions was also increased. Hence, it increases the conductivity of the electrolytes [13]. The graph shows that conductivity 4 wt.% untreated TiO_2 is higher than 6 wt.% HNO_3-treated TiO_2. Activation energy, E_a for ionic conduction were obtained from the slope of the plots in Fig. 3 and E_a for 4 wt.% untreated TiO_2 and 6 wt.% HNO_3-treated TiO_2 was 0.048 and 0.096 eV. E_a is the energy required for an ion to begin migration from one donor site to another. This ion migration results in conduction. It can be observed that high conducting sample exhibits low value of E_a. This indicates that ions in high conducting sample require lower energy to begin migration.

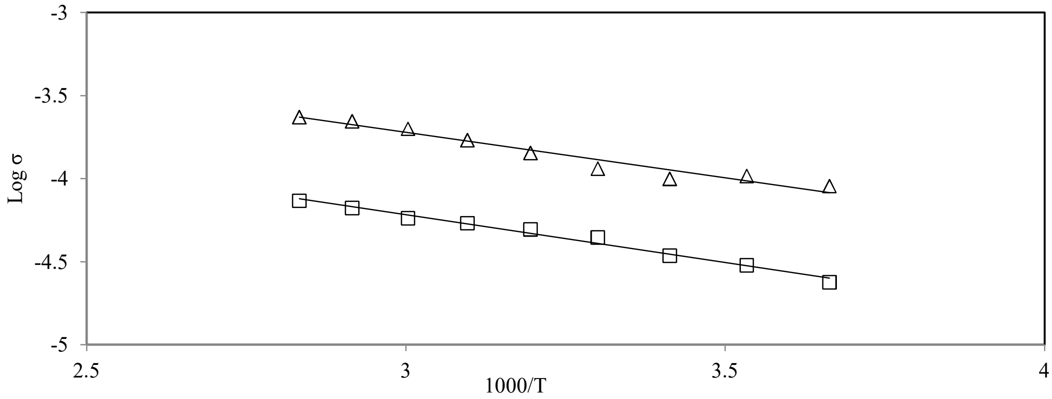


Fig.3. Temperature dependence of conductivity for H-chitosan/PS-$LiCF_3SO_3$ with a) 4 wt.% untreated TiO_2 and b) 6 wt.% HNO_3-treated TiO_2

The dielectric constant represents the stored charge in a material. Since charge is carried by ions, therefore it can be deduced that the increase in dielectric constant reflects the increase in the number of ions [14]. Fig. 4 shown frequency dependence of dielectric constant, ε_r for H-chitosan/PS-$LiCF_3SO_3$ with untreated TiO_2 and HNO_3-treated TiO_2. The untreated TiO_2 system has higher dielectric constant value than HNO_3-treated TiO_2 system. This suggests that the untreated TiO_2 system has higher number of free ions compared with HNO_3-treated TiO_2 system and leading to higher conductivity. The calculated number of mole of H^+ for untreated and HNO_3-treated TiO_2 are 6.11×10^{-5} and 7.40×10^{-4} mol/g respectively. The acidic H^+ site acts as anion trapper [15]. The treated TiO_2 possesses more H^+ anion trapper on its surfaces compared to untreated TiO_2. The reduce number of free anions in the system contribute to the decrease in the total conductivity. This explains why the conductivity achieved for the HNO_3-treated TiO_2-added system is lower than the untreated TiO_2-added system.

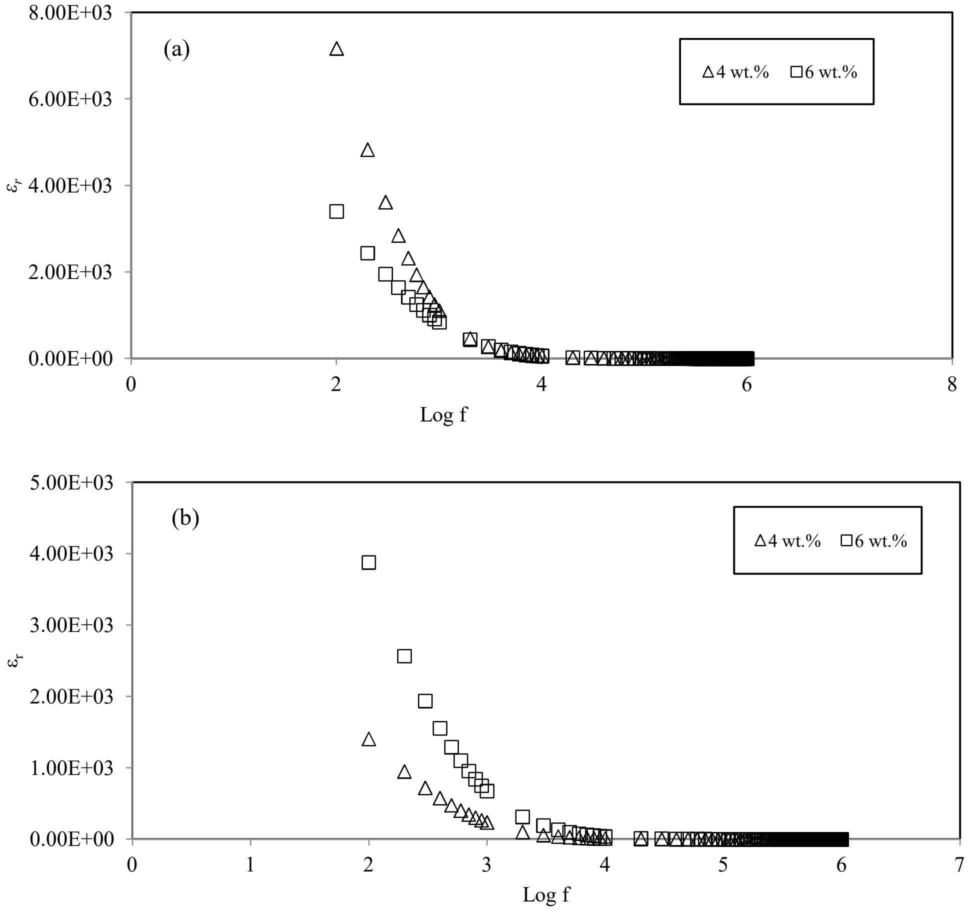


Fig.4. Frequency dependence of dielectric constant, ε_r for H-chitosan/PS-$LiCF_3SO_3$ with a) untreated TiO_2 and b) HNO_3-treated TiO_2

The ac conductivity can be obtained from the dielectric constant, ε_r and loss tangent, $\tan\delta$ according to the Equation (2)

$$\sigma_{ac} = \varepsilon_0\varepsilon_r\omega * \tan\delta \qquad (2)$$

where $\varepsilon_0 = 8.85 \times 10^{-14}$ F cm^{-1}. In general, the phenomena of the conductivity-frequency dispersion are analyzed using the Jonscher's universal power law as stated in Equation (3)

$$\sigma(\omega) = \sigma_{dc} + A\omega^s \qquad (3)$$

where the dc conductivity, σ_{dc} is the frequency-independent component, A is a parameter dependent on temperature and s is the power law exponent with values in the range $0 < s < 1.0$. $\sigma(\omega)$ is generally believed to reflect the mechanism of charge transport among charge carriers. The Jonscher universality is not limited to analyze the AC conductivity in glass but has been extended to study the ac conductivity of polymer electrolytes [16]. In order to understand the conduction mechanism, different models have been proposed to explain the

AC conductivity [17]. These models are quantum mechanical tunneling (QMT), the correlated barrier hopping (CBH) and overlapping large polaron tunneling (OLPT) [18-19]. In the QMT model, the *s* is independent of temperature. In the CBH model, *s* decreases with increasing temperature. While, for the OLPT model, *s* decreases to a minimum value and increases again as temperature increases. Fig. 5 and 6 depict the plot of log [σ(ω)-σdc] versus log ω at various temperatures for untreated TiO_2 and HNO_3-treated TiO_2. Values of exponent *s* can be evaluated from the slope of each plots.

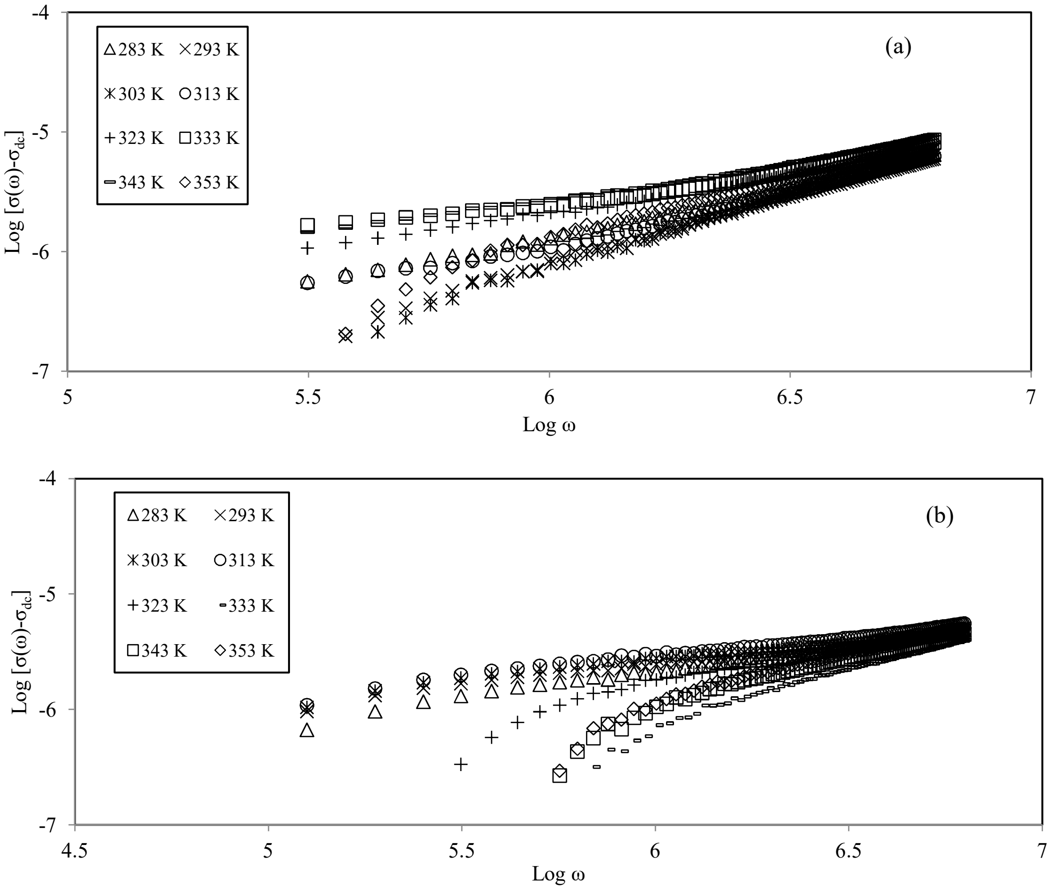
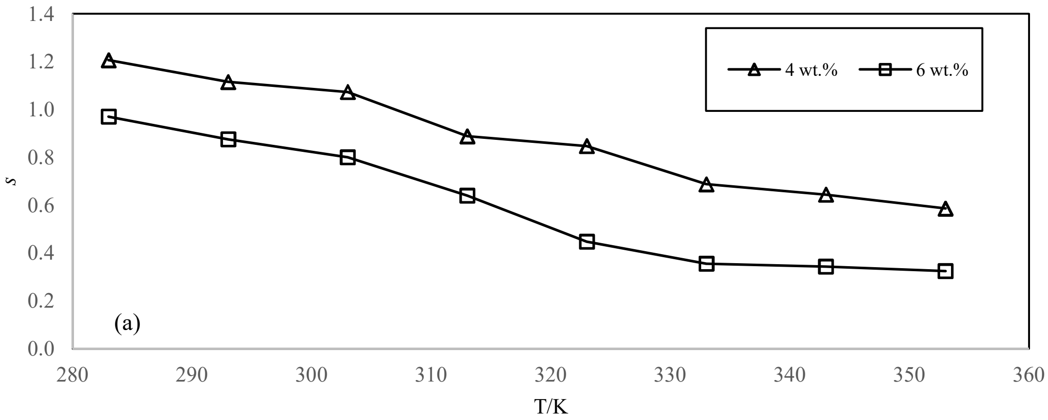


Fig.5. Plot of log [σ(ω) - σ_{dc}] versus log ω for a) 4 wt.% and b) 6 wt.% HNO_3-treated TiO_2 at different temperatures

Fig. 6 shows the variation of exponent *s* with temperature for both treated and untreated sample containing 4 and 6 wt.% TiO_2. It can be observed that the power law exponent s for 4 wt.% and 6 wt.% untreated TiO_2 and HNO_3-treated TiO_2 decreases continuously with increasing temperature. Thus, the conduction mechanism for both electrolytes the systems can be interpreted as the correlated barrier hopping (CBH) model which means that the ions hop over a barrier between two complexation sites. According to [20], conduction mechanism for electrolytes chitosan doped silver triflate ($AgCF_3SO_3$) also follows the CBH model below 358 K.



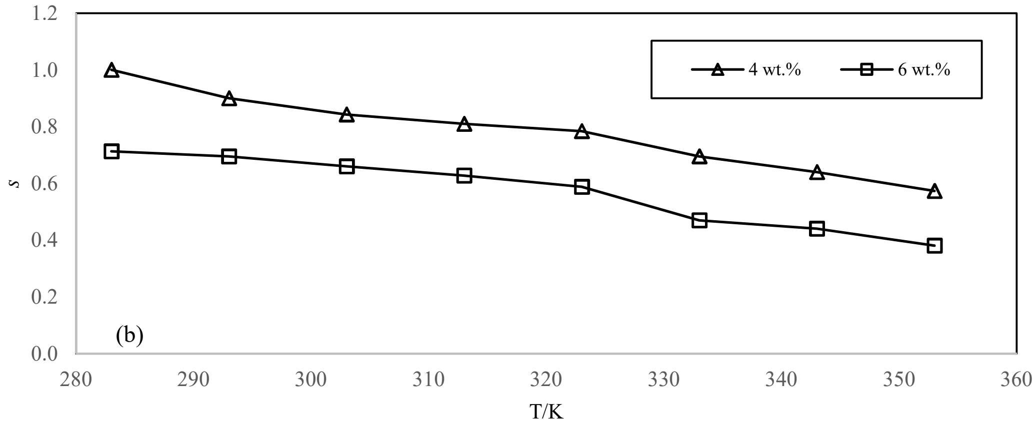


Fig.6. Variation of exponent s with temperature for a) untreated TiO_2 and b) HNO_3-treated TiO_2

3. EXPERIMENTAL

H-chitosan prepared by acyl modification technique and used tetrahydrofuran (THF) as the media. Details of H-chitosan preparation were described in this paper [8]. $LiCF_3SO_3$ from Acros Organics were dried at 100°C for 24 hours prior to use. TiO_2 powder with particle size of 30-40 nm obtained from Nanostructured and Amorphous Material Inc. were used as the inorganic filler. TiO_2 was acid-treated by stirring in diluted HNO_3 solution (0.83 v/v %) for 8 hours at 80°C, rinsed with de-ionized water until the filtrates were neutralized and then dried for 12 hours at 100°C.

Films of H-chitosan/PS blend were prepared by solution casting technique. The two polymers were first dissolved separately in an appropriate amount of THF. Then, the required amounts of $LiCF_3SO_3$ and TiO_2 were added. The resulting mixture was then stirred at room temperature until complete dissolution and homogenous. The solution obtained were cast in glass petri dishes and allowed to completely evaporate slowly at room temperature to form films. The films were kept in a desiccator for continuous drying.

In order to investigate the structure of polymer electrolyte films, XRD scans was taken using X-Pert PRO XRD which employs Cu-Kα X-radiation of wavelength $\lambda = 1.5418$ Å between a 2θ angle of 5° to 80°. The impedance measurement of the films was carried out using HIOKI 3532-50 LCR Hi Tester in the frequency range of 100 Hz to 1 MHz and in the range of temperature from 283 to 333 K. The prepared electrolyte film was sandwiched between two stainless steel electrodes with diameter 2.5 cm under spring pressure. The ionic conductivity, σ of the sample was calculated using Equation (1).

$$\sigma = \frac{t}{R_b A} \tag{4}$$

where t is the sample thickness, A is the effective contact area and R_b is the bulk resistance which can be obtained from the complex impedance plot.

4. CONCLUSION

The effect of treated and untreated TiO_2 on the structural and electrical properties of CPE H-chitosan/PS-$LiCF_3SO_3$. XRD results revealed the crystallinity of the H-chitosan/PS decreased as both types of TiO_2 added in the CPE up to maximum amount, which are 4 % for treated TiO_2 and 6 wt.% of treated TiO_2. Beyond this composition of TiO_2, the crystallinity of H-chitosan/PS increased significantly. The variation in conductivity followed the trend of crystallinity fraction, which optimum ionic conductivity can be observed at 4 wt. % for treated TiO_2 and 6 wt.% of treated TiO_2 systems. The difference in conductivity with varying TiO_2 content also be understood on the basis of free ion concentration as reflected in the variation in dielectric constant. The ac conductivity for H-chitosan/PS-$LiCF_3SO_3$-TiO_2 and H-chitosan/PS-$LiCF_3SO_3$-HNO_3-treated TiO_2 electrolyte systems follows the Jonscher's universal power law. From this law, we concluded that the conduction mechanism for these CPE systems can be interpreted based on the CBH model.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] Roller D P, Slane S. Wearable lithium-ion polymer batteries for military application. In IEEE Battery Conference on Applications and Advances, 1998, pp. 71-74

[2] Liang B, Tang S, Jiang Q, Chen C, X. Shengliang S, Yan X. Preparation and characterization of PEO-PMMA polymer composite electrolytes doped with nano-Al_2O_3. Electrochimica Acta, 2015, 169:334-341

[3] Masoud E M. Nano lithium aluminate filler incorporating gel lithium triflate polymer composite: Preparation, characterization and application as an electrolyte in lithium ion batteries. Polymer Testing, 2016, 56:65-73

[4] Pradeepa P, Edwinraj S, Prabhu M R. Effects of ceramic filler in poly (vinyl chloride)/poly (ethyl methacrylate) based polymer blend electrolytes. Chinese Chemical Letters, 2015, 26(9):1191-1196

[5] TianKhoon L, Hassan N H, R. Hassan, Rahman M Y A, Vedarajan R, Matsumi N, Ahmad A. One-pot synthesis nano-hybrid ZrO_2-TiO_2 fillers in 49% poly (methyl methacrylate) grafted natural rubber (MG49) based nano-composite polymer electrolyte for lithium ion battery application. Solid State Ionics, 2015, 276:72-79

[6] Wieczorek W, Such K, Plocharski J, Wyciślik H. Modifications of crystalline structure of PEO polymer electrolytes with ceramic additives. Solid State Ionics, 1989, 36(3-4):255-279

[7] Ahlawat N, Aghamkar P, Agarwal A, Ahlawat N. Study of conduction mechanism in Fe_2O_3 doped $Na_2O.Bi_2O_3.B_2O_3$ semiconducting glasses. Physica B, 2016, 482:58-64

[8] Zong Z, Kimura Y, Takahashi M, Yamane H. Characterization of chemical and solid state structure of acylated chitosan. Polymer, 2000, 41(3):899-906

[9] Rolsi N H A, Chan C H, Subban R H Y, Winie T. Studies on the structural and electrical properties of hexanoyl chitosan/polystyrene-based polymer electrolytes, Physic Procedia, 2012, 25:215-220

[10] Masoud E M, Hassan M E, Wahdaan S E, Elsayed S R, Elsayed S A. Gel P (VdF/HFP)/PVAc/ lithium hexafluorophosphate composite electrolyte containing nano ZnO filler for lithium ion batteries application: Effect of nano filler concentration on structure, thermal stability and transport properties. Polymer Testing, 2016, 56:277-286

[11] Winie T, Rosli N H A, Ahmad M R, Subban R H Y, Chan C H. TiO_2 dispersed hexanoyl chitosan-polystyrene-$LiCF_3SO_3$ composite electrolyte characterized for electrical and tensile properties. Polymer Research Journal, 2013, 7:386-396

[12] Muthuvinayagam M, Gopinathan C. Characterization of proton conducting polymer blend electrolytes based on PVdF-PVA. Polymer, 2015, 68:122-130

[13] Aminah S A M, Ahmad A, Talib I A, Rahman M Y A. Morphology, chemical interaction, and conductivity of a PEO-ENR50 based on solid polymer electrolyte. Ionics, 2009, 16(2):161-170

[14] Sengwa R J, Dhatarwal P, Choudhary S. Effects of plasticizer and nanofiller on the dielectric dispersion and relaxation behaviour of polymer blend based solid polymer electrolytes. Current Applied Physics, 2015, 15(2):135-143

[15] Egashira M, Utsunomiya Y, Yoshimoto N, Morita M. Effects on the surface treatment of the Al2O3 filler on the lithium electrode/solid polymer electrolyte interface properties. Electrochimica Acta, 2006, 52(3):1082-1086

[16] Chatterjee B, Kulshrestha N, Gupta P N. Nano composite solid polymer electrolytes based on biodegradable polymers starch and poly vinyl alcohol. Measurement, 2016, 82:490-499

[17] Raghu S, Archana K, Sharanappa C, Ganesh S, Devendrappa H. Electron beam and gamma ray irradiated polymer electrolyte films: Dielectric properties. Journal of Radiation Research and Applied Sciences, 2016, 9(2):117-124

[18] Chandel N, Mehta N, Kumar A. Investigation of a.c. conductivity measurements in a-Se80Te20 and a-Se80Te10M10 (M=Cd, in, Sb) alloys using correlated barrier hopping model. Current Applied Physics, 2012, 12(2):405-412

[19] Shukur M F, Majid N A, Ithnin R, Kadir M F Z. Effect of plasticization on the conductivity and dielectric properties of starch-chitosan blend biopolymer electrolytes infused

with NH4Br. Physica Scripta, 2013(T157):1-6

[20] Aziz S B, Hazrin Z, Z Abidin. Electrical and morphology analysis of chitosan: AgTf solid electrolyte. Materials Chemistry and Physics, 2014, 144(3):280-286

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