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Research paper

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

Nor Kartini. Jaafar[1]*, Ab Malik Marwan Ali[1, 2], Muhamad Zu Azhan Yahya[3]* , Rosnah Zakaria[1,2], Siti Zafirah Zainal Abidin[1]

[1]*Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.*
[2]*Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.*
[3]*Faculty of Defence Science and Technology, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia.*
Corresponding author E-mail: norka603@salam.uitm.edu.my

Abstract

Composite grafted polymer electrolyte based on chitosan grafted poly(methyl methacrylate) (Ch-g-PMMA) have been prepared and investigated. The lithium triflouromethanesulfate 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, T_g. 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, biocompatible 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 particularly 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 ***methylmethacrylate*** (MMA) is presented. The grafted polymer Ch-g-PMMA, lithium triflouromethanesulfate (LiCF$_3$SO$_3$ or LiTf), ethylene carbonate (EC) and silicon dioxide (SiO$_2$) 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 LiCF$_3$SO$_3$, EC and SiO$_2$ were purchased from Sigma-Aldrich INC, USA. Acetone and acetic acid were purchased from Mallinclerod 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 ^{60}Co–γ-ray field. The facility of ^{60}Co–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 ^{o}C until a constant weight was obtained. Different concentrations (2-10 wt.%) of SiO_2 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.

2.3. Characterization

The glass transition temperature (T_g) and the decomposition temperature (T_d) of the grafted polymer and grafted polymer electrolyte complex film was measured by using NETZSH, 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, WEIS510, 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 for ionic transport. The addition of plasticizer, ethylene carbonate (EC) to grafted polymer electrolytes also can reduce the glass transition temperature, T_g [13,14]. The reduction in T_g 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} Scm^{-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 ionic 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 assembly of the excess silica, which reduces the polymer–filler interface and hence reduces the conducting pathways. As the silica content is increased to 6 wt. %, conducting pathways are again created but for the conduction of ions giving maximum value of conductivity of 4.21 x 10^{-4} Scm^{-1}. The structural modification is induced via Lewis acid-base reactions between the ceramic surface states and the Ch-g-PMMA segments, as proposed by Wieczorek et al. [15]. The Lewis acid character of the added ceramics would compete with the Lewis acid character of the lithium cations for the formation of complexes with the Ch-g-PMMA chains. Thus, the ceramics would act as cross-linking centers for the Ch-g-PMMA segments, thus lowering the grafted polymer chain reorganization tendency and promoting an overall structure stiffness. Such a structure modification would provide Li+ conducting pathways at the ceramics' surface, thus accounting for the improvement in ionic transport. The specific actions of the polar surface group of the filler, may also act as Lewis-acid base interaction centers with the electrolyte ionic species, thus lowering ionic coupling, the expected effect being the promotion of salt dissociation via a sort of ion –ceramic complex formation. The conductivity does not continue to rise indefinitely, with increasing concentration of SiO_2 particles. It falls once an optimum concentration of SiO_2 is crossed. At high concentrations, SiO_2 tends to impede ionic movement by acting as mere insulators.

The conductivity-temperature studies for the Ch-g-PMMA-salt-plasticizer complexes is depicted in Fig.3. The linear variation of log σ versus 10^3 / T plots suggests an Arrhenius-type conductivity mechanism which is a thermally activated mechanism. Linear relation is observed in all characterized grafted polymer electrolytes, meaning that there is no phase transition in the polymer matrix. Since the conductivity-temperature data follows Arrhenius behavior, therefore the nature of cation transport is quite similar to that in ionic crystals, where ions jump into neighbouring vacant sites [16,17]. Lithium ion migrates through the conduct pathway which is formed by the lattice structure of grafted polymer chains, while EC plasticizer is dispersed in it to help the migration of ions. As temperature increases, the polymer can expand easily and produce free volume. Thus, ion solvated molecules or polymer segments can move into the free volume. The resulting conductivity is presented by overall mobility of ion and polymer which is determined by free volume around the polymer chains. The increase in free volume leads to the increase in ionic mobility and practicallycompensated the retarding effect of the ion clouds.

The value of E_A for plastisizer system is listed in Table 1 while Fig. 4 shows the variation of E_A with the amount of EC in the grafted polymer electrolyte complexes. It can be seen that the sample with addition of 30 wt.% of EC has the highest ionic conductivity and the lowest E_A compared with other samples. The low activation energy for the lithium ion transport was due to the completely amorphous nature of the polymer electrolyte that facilitates the fast ion motion in the polymer network. The above results also show the plasticized system with EC has higher ionic conductivity and lower activation energy compared to the unplasticized system.

Table 1: Activation energy E_A value for plastisizer system.

Designation	E_A (eV)
90[50Ch-g-PMMA-50 $LiCF_3SO_3$]-10EC	0.160
80[50Ch-g-PMMA-50 $LiCF_3SO_3$]-20EC	0.145
70[50Ch-g-PMMA-50 $LiCF_3SO_3$]-30EC	0.090
60[50Ch-g-PMMA-50 $LiCF_3SO_3$]-40EC	0.125
50[50Ch-g-PMMA-50 $LiCF_3SO_3$]-50EC	0.170

The conductivity-temperature studies for the Ch-g-PMMA-salt-plasticizer-filler complexes is shown in Fig. 5. From the figure, it is clearly observed that the composite grafted polymer electrolytes show Arrhenius behaviour. The explanation of temperature dependence of composite grafted polymer electrolytes is similar as gel grafted polymer electrolytes which is attributed to the free volume of grafted polymer matrix. This result is in agreement with that reported by Miyamoto and Shibayama [18] who explained 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_A of composited system is listed in Table 2 while Fig.6 depicts the variation of E_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_A compared with other samples. Ramesh and Wen [10] claimed that the low E_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_A value for composite system.

Designation	E_A (eV)
98[70 [50Ch-g-PMMA-50 $LiCF_3SO_3$]-30EC]-2SiO_2	0.24
96[70 [50Ch-g-PMMA-50 $LiCF_3SO_3$]-30EC]-4 SiO_2	0.22
94[70 [50Ch-g-PMMA-50 $LiCF_3SO_3$]-30EC]-6 SiO_2	0.05
92[70 [50Ch-g-PMMA-50 $LiCF_3SO_3$]-30EC]-8 SiO_2	0.10
90[70 [50Ch-g-PMMA-50 $LiCF_3SO_3$]-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 have 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 votalization 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_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_g is found to be ~100 °C. This plasticized sample presents a lower value of T_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_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 1.42×10^{-4} S cm^{-1} at 50 wt.% of LiTf concentration. Addition of EC and SiO_2 have 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} Scm^{-1}. While, ionic conductivity is increased to 4.21 x 10^{-4} Scm^{-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_g value of plasticized grafted polymer electrolyte is 100 °C which is lower when compared to the plasticizer-free sample due to lubricating effects.

References

[1] Buchi, F.N., Gupta, B., Haas, O. and Scherer,G.G. (1995). Performance of Differently Cross-Linked, Partially Fluorinated Proton Exchange Membranes in Polymer Electrolyte Fuel Cells,J. Electrochem. Soc. 142, 3044
[2] Scherer,G.G.,Momose, T. and Tomiie. K. (1988). Membrane-water electrolysis cells with a fluorinated cation exchange membranes J Electrochem. Soc. 135, 3071.
[3] Muzzarelli, R. A. A.; Muzzarelli, C. Adv. Polym. Sci. 2005, 186, 151,
[4] Yahya, M . Z . A., Ali, A . M .M., Mohammat, M.F., Ibrahim, S.C., Darus, Z.M., Hanafiah, M.A.K.M., Mustafa, M. and Harun, M.K. (2006). Ionic conduction model in salted chitosan membranesplasicized with fatty acid , Journal of Applied Sciences 6(6) 1287-
[5] 1291.
[6] Yahya, M.Z.A and Arof A.K. (2003). Effect of oleic acid plasticizer on chitosan–lithium acetate solid polymer electrolytes, Eur. Polym. J.,39,897.
[7] Yahya, M.Z.A. and Arof, A.K. (2004). Conductivity and X-rayphotoelectron studies on lithium acetate doped chitosan films, Carbohydrate Polymers 55, 95-100.
[8] E. Bucio, R. Aliev, G. Burillo, Radiation Physics and Chemistry 52 (1998) 193
[9] A.U. Ahmed, W.H. Rapson, Journal of Polymer Science Part A 9 (1971) 2129.
[10] Appetecchi, G. B, Croce, F. and Scrosati, B. (1995). Kinetics and stability of the lithiumelectrode in poly(methylmethacrylate)-based gel electrolytes, Electrochim. Acta 40, 991.
[11] Ramesh, S. and Wen L. C. (2010) . Investigation on the effects of addition of SiO2 nanoparticles on ionic conductivity, FTIR, and thermal properties of nanocomposite PMMA–LiCF3SO3–SiO2, Ionics 16, 255-262.
[12] Tan Winie, Hanif, N.S.M. , Chan, C.H., Arof, A.K. (2014). Effect of the surface treatment of the TiO2 fillers on the properties of hexanoyl chitosan/polystyrene blend - based composite polymer electrolytes. Ionic 20:347-352.
[13] Kumar,,R., Sharmaa,S., Pathakb,D., Dhiman,N., Arorac,N. (2017). Ionic conductivity, FTIR and thermal s tudies of nano - composite plasticized proton conducting polymer electrolytes , Solid State Ionics 305, 57–62.
[14] Morales, E. and Acosta J .L. (1997). Thermal and electrical characterization of plasticized polymer electrolytes based on polyethers and polyphosphazene blends, Solid State Ionics 96 , 99-106.
[15] MacFarlane,D.R., Sumn,J., Meakin,P., F asoulopoulos, P., Hey,J., Forsyth, M. (1995). Stucture-property relationships in plasticized solid polymer electrolytes. Electrochimica Acta 40 , 2131-2136.

[16] Wieczorek, W., Stevens, J.R. Florjanczyk, Z. (1996) . Composit polyether based solid electrolytes. The Lewis a base approach, Solid State Ionics 85,76.

[17] Soquet, J.L.,.Levy, M. and Duclot, M. (1994). A single microscopicapproach for ionic transport in glassy and polymer electrolytes, Solid State Ionics 70-71, 337-345

[18] Ramesh, S. and Arof, A.K. (2001) . Structural, thermal and electro chemical cell characteristics of poly (vinyl chloride)-based polymer electrolytes, Journal of Power Sources 99 , 41-47.

[19] Miyamoto, T., Shibayama, K. (1973). Free-volume model for ionic conductivity in polymers, J Appl Phys 44,5372.

[20] Ratner, M. and Shriver, D..F (1988). Ion transport in solvent-free polymers, Chem Rev (Washington, DC) 88:109

[21] Mano, V. Felisberti, M.I., Matencio, T., De Paoli, M.A. (1996) . Thermal, mechanical and electrochemical behaviour of poly (vinyl chloride)/polypyrrole blends (PVC/PPy), Polymer 37, 5165-5170.

[22] Ahmad S., Bohidar H . B., Ahmad S, Agnihotry S . A. (2006). Role of fumed silica on ion conduction and rheology in nanocomposite polymeric electrolytes, Polymer 47,3583–3590.

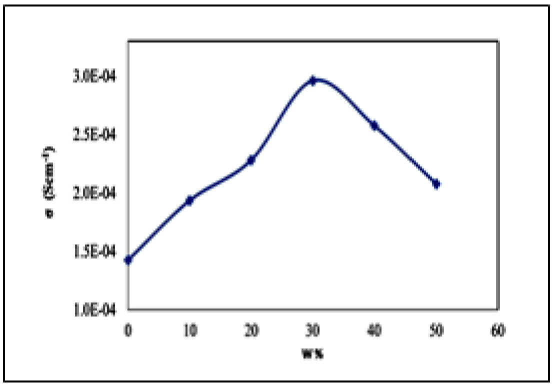

Fig. 1: Conductivity Values of Different Concentrations of EC in Ch-g-PMMA-salt Films (30°C)

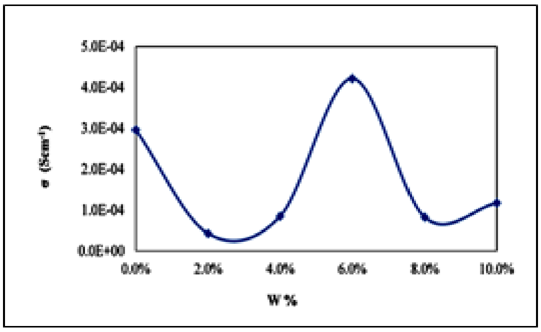

Fig. 2: Conductivity Values of Different Concentrations of SiO_2 in Ch-g-PMMA-salt-Plasticizer Films (30 °C).

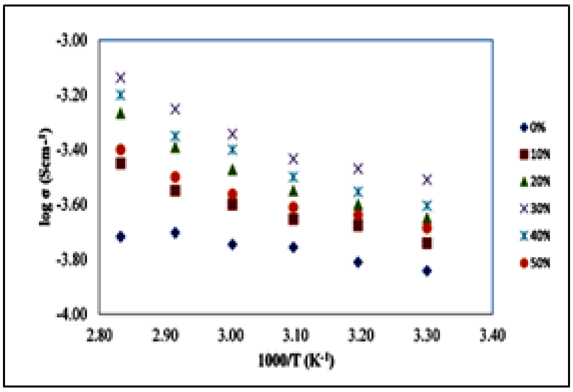

Fig. 3: Arrhenius plots of Ch-g-PMMA-salt film with different plasticizer (EC) concentrations

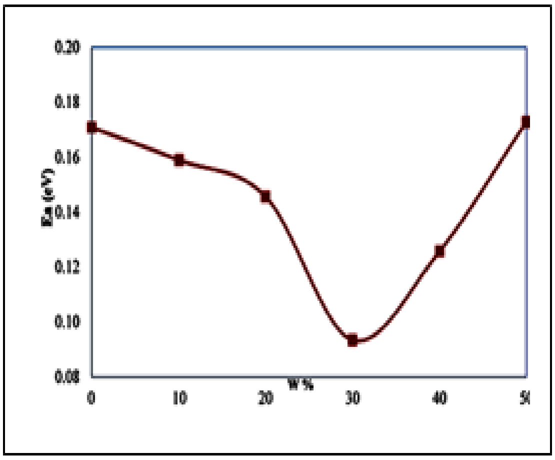

Fig. 4: Activation energy variation with different plasticizer (EC) concentrations

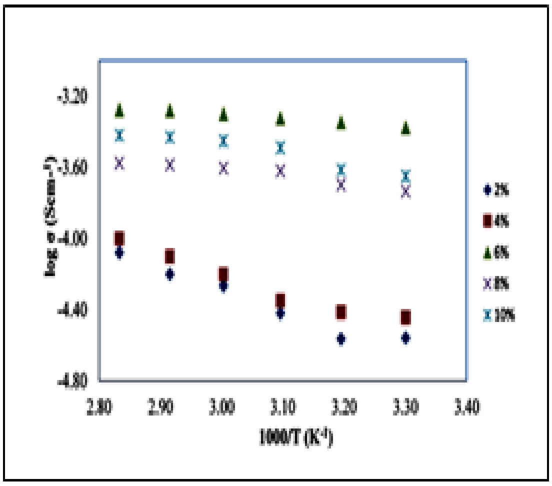

Fig. 5: Arrhenius plots of Ch-g-PMMA-salt plasticizer-composite film with different SiO_2 concentrations

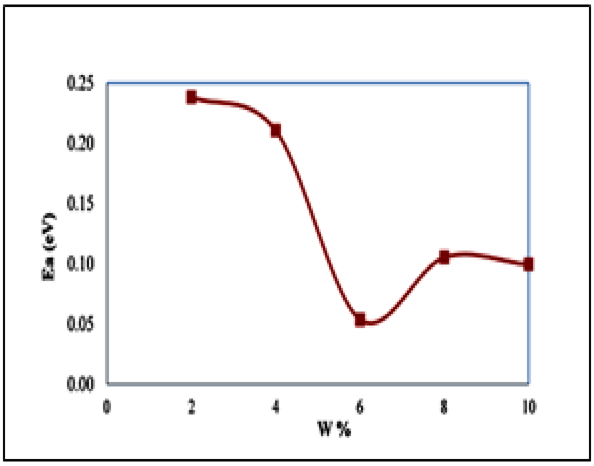

Fig.6: Activation energy variation with different SiO_2 concentrations

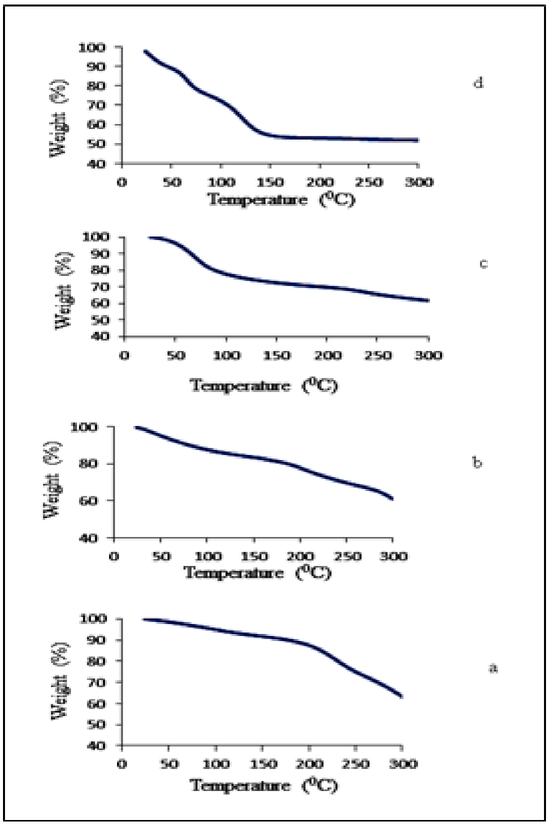

Fig. 7: TGA thermograms of (a) Ch-g-PMMA (b) Ch-g-PMMA+50% LiTF (c) Ch-g-PMMA+50% LiTf + 30% EC (d) Ch-g-PMMA+50% LiTf + 30% EC +6 % SiO_2

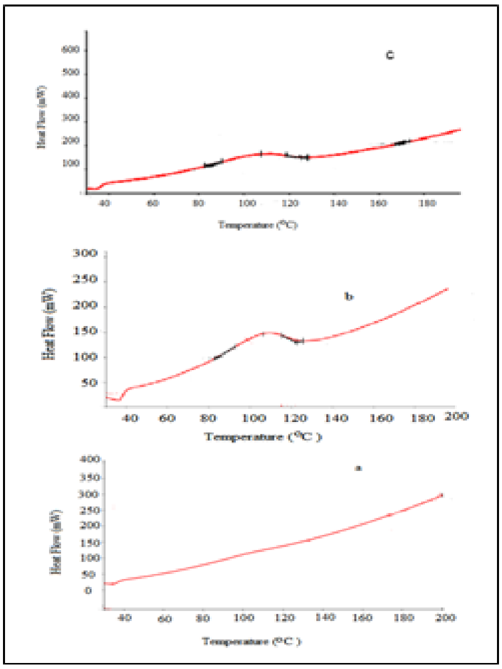

Fig 8: DSC thermograms of (a) ch-g-PMMA+50% LiTf (b) ch-g-PMMA+50% LiTf+ 30% EC (c) ch-g-PMMA+50% LiTf+ 30% EC +6 % SiO_2