DOI: 10.1002/masy.200950302

Ion- Beam Modification of Peo Based Polymer Electrolytes

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Summary: In this paper, we report the ion beam interaction with a well explored ion conducting polymer electrolyte, *viz.*, polyethylene oxide complexed with sodium iodide (PEO:NaI). Li^{3+} ions at 50 MeV were bombarded on the film at different flux. The conductivity modulation of the films has been reported due to interaction at different fluence. The increase in the total conductivity is explained in terms of the change in the number of charge carriers and the dielectric constant of the polymer electrolyte films.

Keywords: crosslinking; dielectric properties; inorganic polymers; irradiation

Introduction

Ion beam – polymer interaction is of scientific interest for last two decades. The possible effects of high energy ion's interaction with the polymer materials have been studied in many contexts.[1,2] In general, an energetic ion impinging on a polymer material can initiate a series of reactions that transforms the basic chemical structure of the polymer, thereby fundamentally altering its properties. Change in physical and chemical properties are observed due to energy transfer by the ion to the polymer matrix. Formation of tracks and related devices has mainly been reported so far.[3] But the modification studies of the structure of the polymer electrolyte with ion beam are rare in literature.[4–7] It is expected that the chain length of a polymer should change due to ion beam exposure. This in turn will increase the amorphicity of the polymer and hence the conductivity will also change. It is reported that low dose of ions cut the long chains and create regions of local increased amorphicity, but a higher dose exposure may cause the release of hydrogen and hence, carbonization of polymer films may also occur.[4,8] Here we report the ion beam interaction with a polymer electrolyte with varying dose of the ions. A well studied ion conducting polymer electrolyte,[9] polyethylene oxide complexed with sodium iodide (PEO:NaI), was exposed to the high energy nuclear beam. Thin, self supporting films of the polymer-salt complex were exposed to Li^{3+} ion beams at 50 MeV from the Pelletron accelerator which penetrated through the films. The fluence of the ion beam was gradually increased up to the limit where the back bone of the polymer film does not collapse and hydrogen is released from the chain. It has been shown that the total conductivity gets drastically modified after exposure of the beam. To make a comparison, we are also reporting the irradiation effect of another system PEO:NaI+ Si. We have calculated the variation in the number

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of charge carriers on exposure, and a correlation with the conductivity and the dielectric constant has also been drawn.

Experimental Part

Poly(ethylene oxide), (PEO, $\langle M_w \rangle \sim 5 \times 10^6$ g/mol, Aldrich) and sodium iodide (NaI, CDH) were used as procured. Self-supporting films of the polymer-salt complex were obtained by solution casting method.[10] The desired amount of the polymer and the salt were dissolved in anhydrous methanol (MeOH, Qualigens). The cation to monomer ration was fixed at $[Na^+]:[EO] \approx 0.065$. The solution was stirred for more than 8 hours for complete complexation and to obtain a viscous mixture. The viscous mixture was then cast in polypropylene Petridishes in N_2 atmosphere. The solvent was allowed to evaporate slowly and a self supporting film was prepared. Films of ~10 to 100 μm thickness (solvent free) were thus obtained. Before any experiment, the films were vacuum dried to avoid any traces of the solvent. For the preparation of (PEO:NaI) + Si films, weighed amount of silicon in the form of powder was added to the methanolic solution of the polymer and the salt. The detailed studies (structural and electrochemical) of this composite system will be published elsewhere.[11]

The films were then exposed to Li^{3+} ions at 50 MeV (at Inter-University Accelerator Centre, IUAC) using the Pelletron, a tandem Van de graaf type accelerator. Prior to exposure the charge state of the ion and its energy was calculated using the standard SRIM program and matched with the film thickness. The dose of the ions were varied from 10^9 to 10^{13} by changing the beam current/and time of exposure. The exposed samples were then characterized for their possible changes in structural, thermal and electrical properties and compared with the pristine samples. The conductivity values of the films, before and after irradiation, were calculated from the bulk resistance values obtained from the a.c. complex impedance spectroscopic data in the range 10^4 to 10^2 Hz using a HIOKI LCR Hi Tester (model 3522). The films were sandwiched between two stainless steel discs and hold in a spring loaded sample holder. The conductivity (σ) was calculated from the impedance data, using the relation $\sigma = d/R\,A$, where d and A are the thickness and area of prepared polymer film, and R is bulk resistance obtained from the first intercept on the x-axis of the impedance data in the complex plane. The dielectric constant of the films was evaluated using the impedance data at 10 kHz frequency.

Results and Discussions

Conductivity Behavior

Figure 1 shows the variation in conductivity of the PEO:NaI films without Si and also with three different Si contents at room temperature. The conductivity of all the compositions increases drastically after ion beam exposure. The conductivity further increases to its maximum value after passing through a dip and then finally decreases to its minimum value (for compositions with 0, 30 and 50 wt% of Si). Interestingly, then, it shows further increases with increase in ion dose. The following lines discuss the possible explanations (assuming five regions A-E of the curve) for this behavior.

(a) Region A: The initial increase in conductivity from its pristine value is attributed to the local amorphization due to low dose of the beam. The formation of local amorphous regions leads to the availability of more path way for the ions to migrate. It may be noted that in these systems, ions move only through the amorphous regions and not through the crystalline parts.[12] Thus the formation of local amorphous regions assists the ions to migrate *vis-à-vis* the conductivity. It may be noted that the crystalline parts of the polymer–salt complex are formed by the local ordering of the chain around the cations. One cation may get entrapped by four or more nearby equal energetic ether

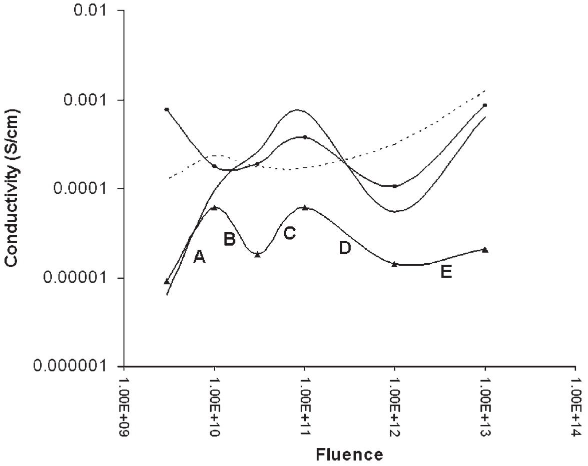

Figure 1.
Variation in conductivity with the increasing Li^{3+} ion dose. Full line is for PEO:NaI; –●–●– for 30 wt% of Si; – △ – △ – for 50 wt% and ----- for 80 wt% of Si. The regions A-E are explained in text.

oxygen sites.[13] The amorphization will therefore mean the release of free cations and hence enhanced conductivity. The conductivity plot for different compositions of the pristine samples is shown in Figure 2 for comparison. Further, it is known that increase in the content of Si or its oxides in the polymer films modifies the crystalline nature of the polymer electrolyte films[11,14] and thus the ion beam effect is not so pronounced. Though the pattern is almost similar but the beam damage is clearer for no Si or less Si films only. As could be seen for the film containing 80 wt% of Si, the increase is not so pronounced.

(b) Region B: The first decrease in the conductivity isotherm is attributed to the charge association or the formation of the higher charge multiplates. The charge carriers which were made free due to amorphization may form higher charge multiplates and hence decrease the

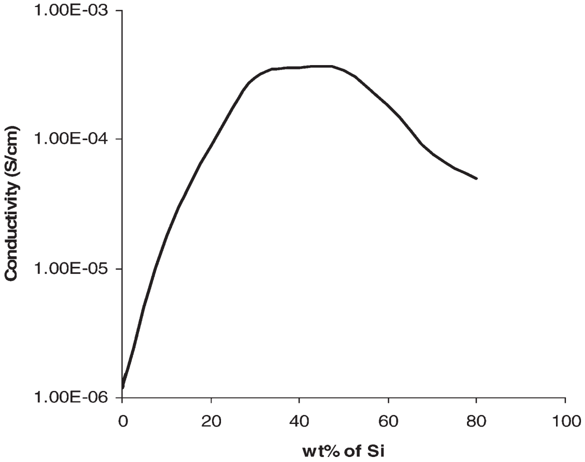

Figure 2.
The conductivity isotherm of the (PEO + NaI):Si polymer composite electrolyte (without any ion beam exposure).

conductivity.[15,16] This statement is supported by our calculations of the number of charge carriers as discussed in the next paragraph.

(c) Region C: The further increase of the conductivity is attributed to the chain scissoring effect due to the ions. Similar observations have been reported by many workers due to electron beam, γ- and ion beam exposure of the polymer electrolyte films.[4,17] It has been shown by IR studies and crystallinity measurements that at lower dose the amorphicity increases and the bond breaking results which can hike the conductivity values to maximum.[18]

(d) Region D: On further increase of the dose, the crosslinking process dominates and hence the crystallinity starts increasing. As a result the conductivity drops down.

(e) Region E: Finally the slow increase in conductivity is due to the electronic conduction in the matrix. This is confirmed by the ion transport measurements of the samples – results not shown here. The electronic transport number is found to increase after high dose.

Dielectric Constant and the Number of Charge Carriers

Figure 3 shows the variation in the dielectric constant for all the four series at different ion doses. The initial increase, as discussed above, is due to the possible scissoring of the chains by the ions. The small segments find more freedom and hence the segmental motion is higher. Similar observation has been verified by IR spectra.[18] The sharp increase at 10^{11} fluence (ions cm^{-2}) is due to the enhanced scission and re-arrangements of the chains. The dielectric constant then decreases and attains almost constant value for the PEO:NaI films. The chain segments start partially ordering (re-crystallization) and hence the decrease in the dielectric constant values causes a drop in the conductivity.[19,20] This is indicative of further damage and stable configuration of the matrix. It may be noted that this behavior is more pronounced in the films with no or only a small content (30 wt %) of Si. Si, when added to the matrix, gives better mechanical strength to the film and enhanced total crystallinity. For films with high Si content, the variation in dielectric constant is similar but actually suppressed due to the Si framework.

Since the conductivity σ of the polymer electrolyte is given as the product of the charge carrier density n, charge of the carrier q and its mobility μ, *i.e.* ($nq\mu$). Therefore any increase in either of the parameters n or μ will result in an increase in σ. Also, it is very difficult to have any measurement of the mobility of the charge carriers in the solid polymer films. In order

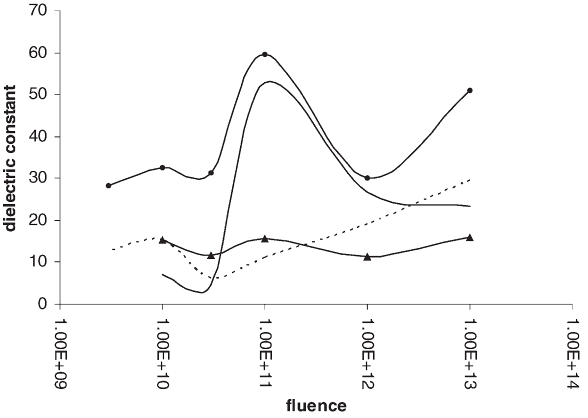

Figure 3.

Plot showing the variation in the dielectric constant of the polymer films with dose of ions. Full line is for PEO:NaI; –●–●– for 30 wt% of Si; – △ – △ – for 50 wt% and ----- for 80 wt% of Si.

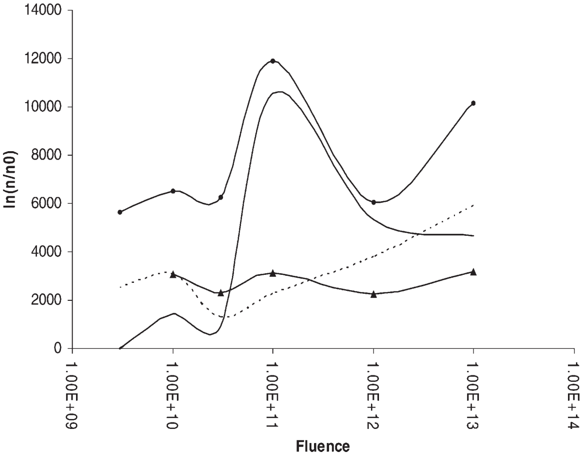

Figure 4.
Change in the relative number of charge carriers with the ion dose for polymer films with different Si content. The dashed line is for 80 wt%, –●–●– for 30 wt% of Si; – △ – △ – for 50 wt% and the full line is for 0 wt% of Si in PEO:NaI films.

to estimate the contribution of the number of free charge carriers in the total conductivity we have used the dielectric constant data of the films. The electrolyte dissociation theory of Barker[21] was employed and using the following relation the relative change in the carrier concentration was calculated.

$$n = n_0 \exp\left\{\frac{-\Delta U}{2\varepsilon kT}\right\}$$

Here, ΔU stands for the dissociation energy of the salt, k is the Boltzmann constant and ε is the dielectric constant of the system at temperature T. We have calculated the relative number of charge carriers (n/n_0). Figure 4 shows the variation in $\ln(n/n_0)$ with fluence. The effect of changing dielectric constant at different ion fluence is directly reflected on the number of free charge carriers. The maximum free charge carriers can be seen at 10^{11} fluence. This affirms our above statement on the possible local amorphization, re-alignment and finally stable damaged crystal network of the polymer and polymer composite matrix. Also, this behavior can be directly correlated with the conductivity behavior discussed above. The initial increase can be attributed to the breaking of the crystalline regions of the PEO and thereby allowing more charge carriers to participate in the conduction. It may be noted that the less ordered regions of the polymer (and the polymer-salt complex) are responsible for the charge conduction and has been established by the free volume measurement of similar systems.[22] Thus the local damage will result to the availability of more carriers and therefore increase in the conductivity. Similarly, the second rise in the conductivity and the (n/n_0) can be attributed to the splitting of the chains of the long PEO. The presence of inert Si in the polymer matrix gives the mechanical strength to the system and the conductivity increases.

Conclusion

The total conductivity of the polymer electrolyte films were found to increase with increasing fluence. The variation in conductivity is explained in terms of the changes in the number of charge carriers due to possible cutting of the chains. The Jump in dielectric constants at fluence 10^{11} is attributed to the possible crystallization of the matrix where as the dip is due to the increased number of local amorphous sites. More studies are still under process in our laboratory to explore this behavior.

Acknowledgements: Authors are thankful to Prof. G.K. Mehta (Former Director NSC), Prof. Suresh Chandra (Emeritus Professor, BHU) for guidance. Help in terms of facilities and encouragement from the Director and Management of the Institutions (HCST, GCET and MIET) are also gratefully acknowledged.

[1] E. Balanzat, S. Bouffard, A. Le Moel, N. Betz, *Nucl. Instr. and Meth.* **1994**, *B91*, 140.
[2] S. Bauffard, B. Gervais, C. Leray, *Nucl. Instr. and Meth.* **1995**, *B 105*, 1.
[3] A. Biswas, D. K. Avasthi, Benoy. K. Singh, S. Lotha, J. P. Singh, D. Fink, B. K. Yadav, B. Bhattacharya, S. K. Bose, *Nucl. Instr. and Meth* **1999**, *B151*, 84; V. Kulshrestha, K. Awasthi, Y. K. Vijay, *International J. of Hydrogen energy* **2007**, *32*(14), 3105.
[4] D. Saikia, A. Kumar, F. Singh, D. K. Awasthi, N. C. Mishra, *J. Appl. Phys.* **2005**, *98*, 043514.
[5] Darraud, B. Bennamane, C. Gagnadre, J. L. Decossas, J. C. Vareille, J. Stejny, *Appl. Opt.* **1994**, *33*(16), 3338.
[6] Bennamane, J. L. Decossas, C. Gagnadre, J. C. Vareille, *Nucl. Instr. and Meth* **1991**, *B62*, 103.
[7] E. S. Dana, E. M. Ford, "*Minerology*", Asia Publising House, Bombay **1962**, 1.
[8] J. P. Durand, A. L. Moel, *Nucl. Instr. and Meth.* **1995**, *B105*, 71.
[9] J. R. MacCallum, C. A. Vincent, *Polymer electrolyte reviews 1 & 2*, Elsevier, New York **1989**.
[10] S. A. Hashmi, A. Kumar, K. K. Maurya, S. Chandra, *J. Phys. D: Appl. Phys.* **1990**, *23*, 1307.
[11] A. Saxena, D. Singh, B. Bhattacharya, (*Under Preparation*).
[12] N. Binesh, S. V. Bhat, *Solid State Ionics* **1999**, *122*, 291.
[13] Y. Ito, K. Kanehori, K. Miyauchi, T. Kudo, *Solid State Ionics* **1987**, *23*, 69.
[14] T. Stergiopoulos, I. M. Arabbtzis, G. Katsaros, P. Falaras, *Nano Lett.* **2002**, *2*, 1259.
[15] E. H. Lee, *Nucl. Instr. and Meth.* **1999**, *B 151*, 29.
[16] S. Bauffard, B. Gervais, C. Leray, *Nucl. Instr. and Meth.* **1995**, *B 105*, 1.
[17] P. Ferloni, A. Magistris, G. Chiodelli, A. Faucitano, A. Buttafava, *Radiat. Phys. Chem.* **1991**, *37*, 615. Th. J. Singh, Ganeshsanjeev, K. Siddappa, S. V. Bhat, *J. Polym Sci.: B: Polymer Physics* **2004**, *42*, 1299.
[18] Rajesh. Kumar, Udayan De, Rajendra. Prasad, *Nucl. Instr. and Meth.* **2006**, *B248*, 279.
[19] A. Kumar, D. Saikia, F. Singh, D. K. Avasthi, *Solid State Ionics* **2006**, *177*, 2575.
[20] F. Hosoi, Y. Aoki, M. Hagiwara, H. Omichi, M. M. Sellah, *Radiat. Eff. Defects. Solids* **1993**, *126*, 351.
[21] R. E. Barker, Jr, C. R. Thomas, *J. Appl. Phys.* **, *35*, 3203.**
[22] B. Halder, R. M. Singru, K. K. Maurya, S. Chandra, *Phys. Rev.* **1996**, *B54*, 7143.