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Gamma radiation induced conductivity control and characterization of structural and thermal properties of hydroxyl propyl methyl cellulose (HPMC) polymer complexed with sodium iodide (NaI)

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ABSTRACT

The present study was undertaken to characterize the ionic conduction behavior, structural and thermal properties of Solid polymer electrolyte films based on Hydroxypropyl methylcellulose (HPMC) complexed with Sodium Iodide (NaI) upon gamma irradiation with different doses of 20, 60 and 100KGy. The dissolution of the salt into the polymer host and the structural properties of pure and NaI complexed HPMC polymer electrolyte films before and after irradiation with different doses were confirmed by X – Ray diffraction (XRD) studies. The XRD results revealed that the amorphous domains of HPMC polymer matrix was increased with increase in the NaI salt concentration and with the increasing dose and the percentage of crystallanity is found to be high in pristine unirradiated HPMC films. The thermal properties of pure, unirradiated and irradiated complexed electrolyte films were studied using Differential Scanning Calorimetry (DSC). It is observed that the total enthalpy of fusion (ΔH_f) is maximum for unirradiated pristine HPMC films. The variation of film morphology was examined by Scanning electron microscopy (SEM). Fourier transform infrared spectral (FTIR) studies for pure, unirradiated and irradiated complexed HPMC films revealed the vibrational changes that occurred due to the effect of dopant salt in the polymer. Direct current (dc) conductivity was measured in the temperature range of 313–383K. The magnitude of conductivity was found to increase with the increase in the concentration of the salt, temperature and for higher doses of radiation. The composition HPMC: NaI (5:4) is found to exhibit the least crystallanity and the highest conductivity.

Keywords: Gamma Irradiation, polymer electrolytes, XRD, DSC, SEM, FT-IR, dc conductivity

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INTRODUCTION

The study of effects of high energy ionizing radiation on conducting polymers is receiving increased attention for the development of radiation resistant materials. Conducting polymers have emerged as material of interest in research and industrial application. They are likely to replace metals and alloys in many applications, because of their light weight, ease of fabrication and stability. Polymers that exhibit high electrical conductivity and stable even in the doped form have been successfully synthesized. Efforts are being made to improve the physical and chemical properties of the existing polymers and to develop new materials which respond to external stimuli, by changing their shape, size and properties. Preparation of high ionic conductivity polymers are materials of recent interest, because of their applications as electrolytes in solid state batteries [1-4]. Radiation effects on polymers having electrical conductivity are being widely studied. Several high technology industries require conducting polymers that exhibit a specific response upon exposure to radiation [5-7]. Electronic industry requires materials that undergo radiation induced scission or cross-linking for resist applications, while aerospace and medical applications require highly radiation stable materials. For Space applications and practical situations like sterilization of food packed in a polymer foil or sheet, damage to the polymers by nuclear irradiation needs to be experimentally studied and understood [8-9]. The design and development of appropriate chemistry for these applications require complete understanding of the effects of radiation on the polymeric materials. The structural, optical, and electrical properties of materials undergo changes upon exposure to nuclear radiations. Radiation causes the structural modifications leading to the change in their density and other properties.

In case of ionizing radiation like gamma radiation, the initial absorption is typically a spatially random process and leads to free radical or ionic species production and can involve side group or main chain scission or cross linking. Even small amounts of radiation can induce significant changes in the physical or mechanical properties of a polymer, with the extent of these changes being dependent upon the chemical structure of a particular polymer the total radiation dose absorbed and the rate at which it is deposited. In some cases, even a few crosslinks or scission sites per molecule can dramatically affect the strength or solubility of a polymer. Polymer coatings on substrates such as metals, plastics and optical fibers etc, make them more resistant to temperature, humidity, and exposure to nuclear environment [6]. The electrical conductivity of polymers makes them suitable materials as cathodes in rechargeable batteries. Several of these types of batteries have been fabricated. Polymer batteries have long life and are rechargeable. Lithium batteries are especially important since they show a high discharging voltage [10-11]. The polyanilines, polythiophene and polypyrrole are very useful materials for fabricating electro optical display devices [12]. The systematic development of electro – Optical polymer device structures for optical multichip modules [13] and Polythiophene as an optical memory element [14], the electrochromic devices [15] such as display and thermal “smart windows” have been reported. Polymers with high conductivity have unique properties which make them appealing alternatives for specific materials, currently employed for the fabrication of biosensors [16]. Microlithography [17-18] is an essential part in the fabrication of microelectronic devices like IC, VLSI (very large scale integration) ULSI (ultra large scale integration).Lithography process are of many types like electron beam, ion beam, X-ray, and photo lithography. Lithography process is used to open windows in device fabrications. While almost all of today's commercial devices are made by photolithographic techniques that utilize 365-436nm UV radiation. In radiation chemistry, polymers are classified as scission polymers and cross-linking polymers, most biopolymers are classified as scission polymers. Recent developments in this filed have proved that a variety of biopolymer could be cross linked by irradiation of high energy radiation, and HPMC polymer tends to exhibit such radiation cross-linking. HPMC is a water soluble biopolymer which is successfully used in controlled release drug preparations in pharmaceutical field [19-20] because it works as a pH-independent gelling agent. Swelling as well as erosion of it occurs simultaneously and contributes to overall drug release. It is a widely accepted pharmaceutical excipient, because HPMC is available in a wide range of molecular weights and the effective control of gel viscosity is easily possible [21-26]. The gamma irradiation on the HPMC complexed NaI may increase the segmental mobility resulting in the decreasing crystallanity. Thus, the study of radiation effects on polymeric materials that exhibit conductivity has become a very important and fascinating field which has got great technological importance in the field of material science. In view of its importance the present work is being initiated. The scope of the work is to synthesize conductive polymer films that exhibit high electrical conductivity and to study their properties like structural, thermal and electrical conduction behavior before and after irradiation. The study of the modification in the properties of the conductive polymers after controlled irradiation and development of radiation resistant polymers is the main scope of the work.

MATERIALS AND METHODS

2.1 Materials and Preparation of Polymer Electrolyte Films

Pure HPMC and various compositions of complexed films of HPMC with NaI salt were prepared by solution cast method using double distilled water as solvent. Hydroxypropyl methylcellulose was purchased from (HPMC E15LV), Loba Chemicals India, and Sodium Iodide (NaI) were purchased from S. D. fine chemicals India. To prepare the polymer electrolyte films, HPMC polymer was blended with inorganic salt of Sodium Iodide (NaI). 5g of HPMC in 100ml double distilled water was dissolved and desired amounts from (1% - 4%) of Sodium Iodide was added and stirred continuously for 8hours.The completely soluble homogeneous solution was filtered through Whatmann No 41 filter paper and degassed. Then the clear solution of HPMC:NaI was poured on to a clean and leveled glass plates (30cm X 40cm) to evaporate at room temperature for 5 days and peeled off from the glass plate. The final films were vacuum dried thoroughly and stored in desiccators to avoid the absorption of moisture. NaI is hygroscopic in nature and the higher concentration of NaI has got the tendency to absorb more moisturizer. However HPMC:NaI (5:5) polymer films were also prepared and was found that with increasing concentration of NaI, the film is shifting towards an amorphous structure and the films obtained are not stable and are not with uniform thickness. Hence the optimal doping with NaI is carried out only upto 4% and polymer electrolyte films HPMC:NaI (5:1, 5:2, 5:3, 5:4) were prepared.

2.2 Instrumentation

The XRD studies of the films were made with an X-ray source with CuKα radiation of wavelength 1.5406$\AA$. The surface morphology of these polymer films were observed using JEOL 840, resolution at 20Kv, 10nm scanning electron microscope (SEM). The samples were gold coated using the sputter coater at 10 mA current under 10^{-2} torr vacuum for 3 minutes before imaging. Fourier transform infrared (FTIR) spectra of these films were recorded using Thermo – Nicolet 6700. The measurements were taken over a wave number range of 400 – 4000cm^{-1}. The Differential Scanning Calorimetry (DSC) measurements have been taken in the temperature range of 30 – 200^{0}C with the help of Differential Scanning Calorimeter Model: METTLER-TOLEDO DSC1 thermal analysis system at a heating rate of 10^{0}C per minute. The temperature dependent dc conductivity of the reported polymer electrolyte samples were measured in the temperature range of (313K – 383 K) using Keithley Electrometer (Model 617). The disk sample (13mm in diameter) was sandwiched between the finely polished stainless steel electrodes. Silver paste is deposited on both sides of well-polished sample pallets for good electrical contact. The bulk resistance is determined from the intersection of the high frequency semicircle with the real axis in the complex impedance plots. The electrical conductivity is calculated using the formula

$$\sigma = \left(\frac{1}{R}\right)\left(\frac{t}{A}\right) \tag{1}$$

Where ‘t’ is the thickness of the sample in mm, ‘R’ is the resistance in MΩ and ‘A’ is the area of the sample in mm^2

2.3 Gamma Irradiation

Films of pure HPMC and various compositions of complexed films of HPMC with NaI has been gamma irradiated in air by ^{60}Co source at a dosage rate of 2.5 kGy / hour for 20, 60, and 100 kGy dosages as the mechanical properties and wear resistance of the polymer saturate at above 100 kGy irradiation [27] Muratoglu [28], the proposed study was carried out upto 100 kGy dosage level, which was performed at M/s Microtrol sterilization private limited, Bangalore, India.

RESULTS AND DISCUSSION

Table 1. Position of most intense peak 2θ (^{0}), d – Value ($\AA$) and the percentage of crystallanity for unirradiated pure HPMC and NaI complexed HPMC films.

Sample	2θ (^{0})	d – Value ($\AA$)	X_C (%)
Pure HPMC	21.26	4.175	65.29
HPMC:NaI (5:1)	21.42	4.14	44.7
HPMC:NaI (5:2)	22.30	3.98	32.8
HPMC:NaI (5:3)	22.44	3.95	34.9
HPMC:NaI (5:4)	21.98	3.77	30.99

Table 2. Percentage of crystallanity (X_C) for gamma irradiated with 20KGy, 60KGy, & 100KGy for pure HPMC and NaI complexed HPMC films

Dose rate	**20KGy**	**60KGy**	**100KGy**
Sample	X_C (%)	X_C (%)	X_C (%)
Pure HPMC	67.6	61.5	55.4
HPMC:NaI (5:1)	40.7	39.5	42.1
HPMC:NaI (5:2)	43.0	33.4	21.3
HPMC:NaI (5:3)	38.2	28.1	29.5
HPMC:NaI (5:4)	23.5	11.47	11.20

3.1 XRD Studies

X-ray diffraction is most useful for the determination of the nature of the sample, phase identification, quantitative identification of the mixture of phases, particle size analysis etc. The ionic conductivity in a polymer electrolyte is determined by the amorphous nature of the polymer, hence it is necessary to determine the crystalline and amorphous nature of the polymer electrolyte films. XRD patterns of unirradiated and 20KGy, 60KGy, 100KGy gamma irradiated pure and HPMC complexed films are shown in Figs 1, 1a, 1b, and 1c. For unirradiated samples, pure HPMC shows a broad peak at $2\theta = 21.26^0$ (d spacing = 4.175 $\AA$) indicating its semi-crystalline nature of the polymer. This diffraction peak is shifted to 21.42^0 (d spacing = 4.14 $\AA$) in 5:1 system and almost at 22.5^o in other complexes. There is a nucleation of crystalline order which gives an additional Bragg-like reflection almost at $2\theta = 27.83^0$ (d spacing = 3.20 $\AA$) for pure HPMC and is shifted to around 29^0 in all other complexed systems with broad peaks. The mentioned peaks are less intense and are almost found to be disappearing in the polymer electrolyte systems indicating that the addition of NaI salt causes a decrease in the degree of crystallanity and a simultaneous increase in the amorphisity of the HPMC complex. Absence of peaks corresponding to the NaI salt in these complexes indicates that the inorganic salt is thoroughly mixed with the host polymer matrices. No sharp peaks were observed for the higher concentration of NaI salt in the polymer suggesting the dominant presence of amorphous phase [29] therefore it may be confirmed that the complexation has been taken place in the amorphous phase. The irradiated sample of pure HPMC and complexed HPMC shows decrease in the intensity and the broad peaks implying that crystallinity decreases. Normally, for pure HPMC, an increase in crystallinity is observed at lower irradiation dose (20KGy), whereas crystallinity decreases at higher doses [30]**.** However, in HPMC:NaI polymer electrolyte systems the presence of NaI prevent polymer chain reorganization resulting in decreased crystallinity compared to pure HPMC [31]. As the radiation dose increases, the peaks gets broadened up and almost found to be disappearing to a 100KGy irradiation indicating that degree of crystallinity is decreased. Here the dominating amorphous phase results in greater ionic diffusivity with high conductivity. From Table **1.** and Table **2** It is clear that percentage of crystallanity decreases with addition of NaI salt and values are in good agreement with the interpreted results from XRD patterns. The percentage of the degree of crystallinity (X_c) was determined from the ratios of the area under the crystalline peak and the respective halos using the method [32-33]

$$X_c = \frac{A_c}{A_c + A_a} X\ 100 \tag{2}$$

Where A_c and A_a are the area of crystalline and amorphous (halo) regions respectively.

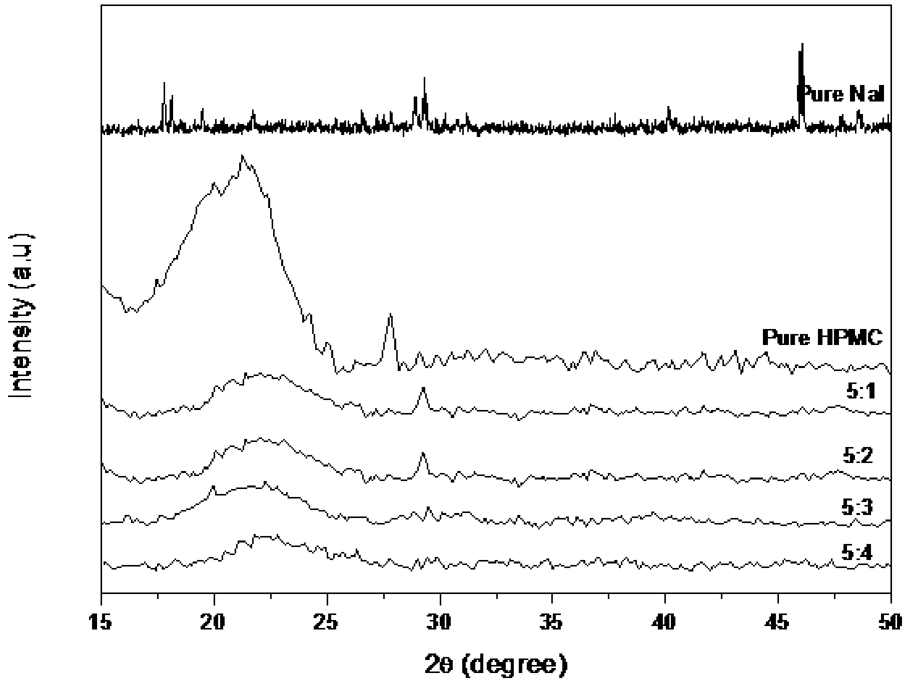


Fig. 1. XRD pattern of unirradiated a pure NaI salt, b pure HPMC, c (HPMC:NaI) (5:1), d HPMC:NaI (5:2), e HPMC:NaI (5:3), and f HPMC:NaI (5:4) polymer electrolyte films

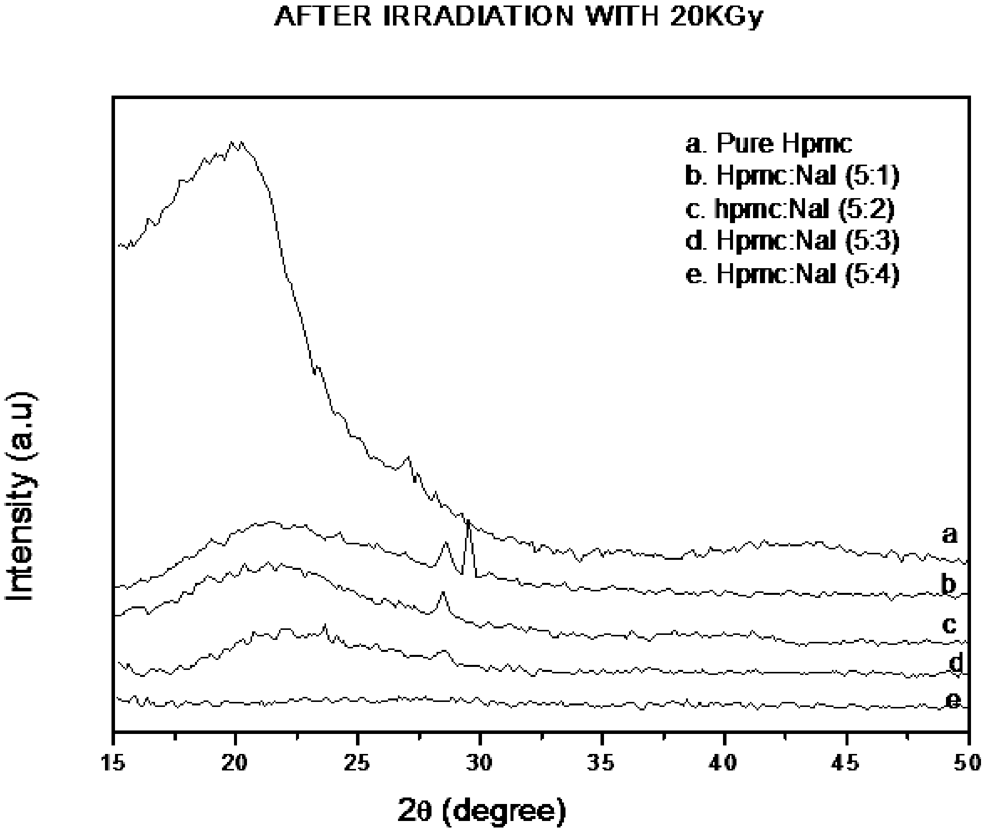


Fig. 1a XRD pattern of irradiated a pure NaI salt, b pure HPMC, c (HPMC:NaI) (5:1), d HPMC:NaI (5:2), e HPMC:NaI (5:3), and f HPMC:NaI (5:4) polymer electrolyte films

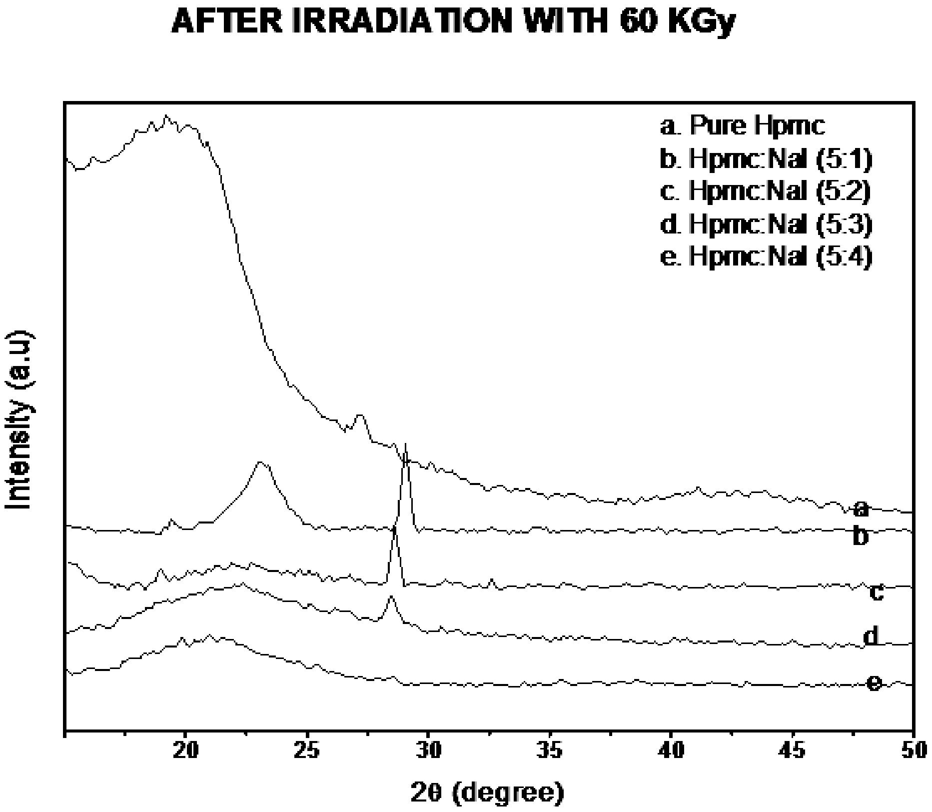


Fig. 1b XRD pattern of irradiated a pure NaI salt, b pure HPMC, c (HPMC:NaI) (5:1), d HPMC:NaI (5:2), e HPMC:NaI (5:3), and f HPMC:NaI (5:4) polymer electrolyte films

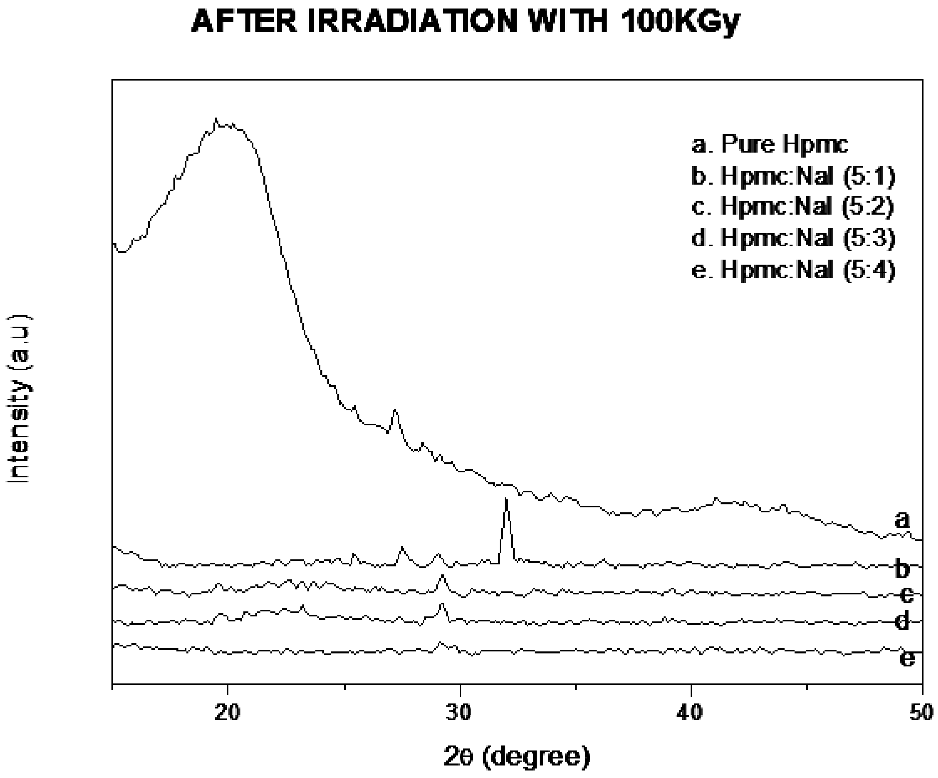
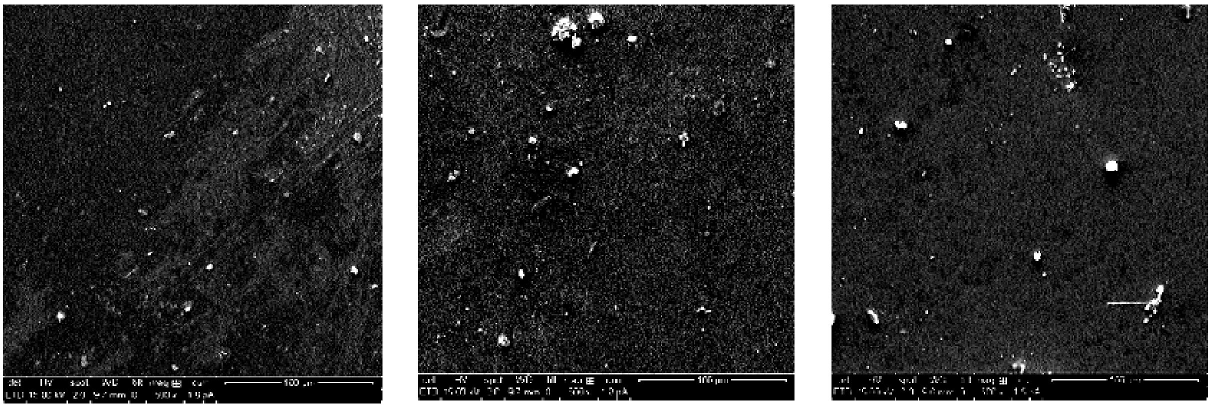


Fig. 1c XRD pattern of irradiated a pure NaI salt, b pure HPMC, c (HPMC:NaI) (5:1), d HPMC:NaI (5:2), e HPMC:NaI (5:3), and f HPMC:NaI (5:4) polymer electrolyte films

3.2. Scanning Electron Microscope

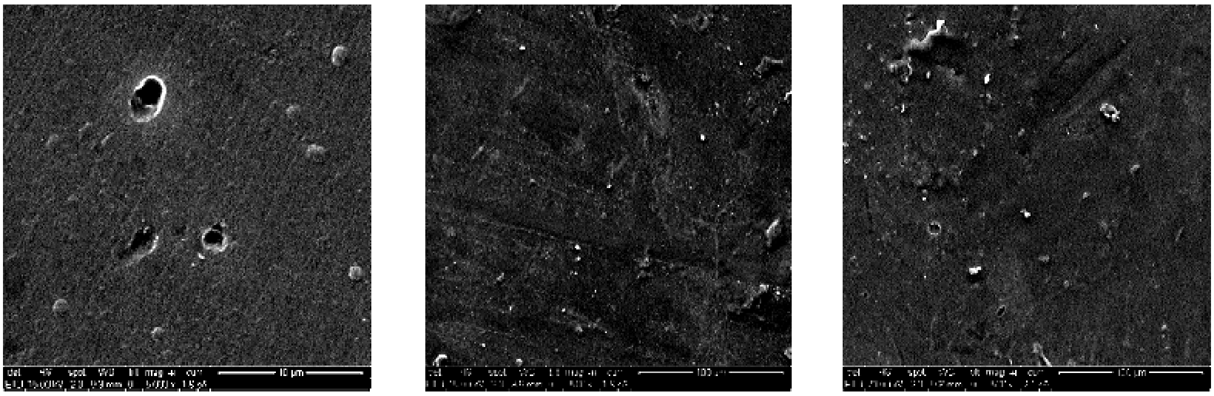
Scanning electron microscopy (SEM) is often used to study the compatibility between the various components of the polymer electrolytes through the detection of phase separation and interfaces [34-35]. The compatibility of the polymer matrix and the inorganic dopants has great influence on the properties like mechanical, thermal, and ionic conductivity of the polymer electrolyte systems. The scanning electron microscopy of the pure HPMC and HPMC:NaI (5:1) and (5:4) polymer electrolytes before and after irradiation shown in Figs 2,2a,2b,2c is uniform type but different degrees of roughness. SEM of unirradiated pure HPMC films exhibits no features attributable to any crystalline morphology, so the semi crystallanity of HPMC is likely to be submicroscopic in nature. The increase in the degree of roughness with the increase in concentration of NaI salt indicates the segregation of the dopant in that host polymer matrix therefore morphological studies clearly indicate the phase segregation phenomenon in these complexed polymer electrolyte systems. It is observed that irradiated pure HPMC shows porous structure with well dispersed pores for low doses at 20KGy. On the other hand, at higher doses (60,100KGy) the porous structure is disrupted possibly due to recrystallization of the polymer. The two phase microstructure in the SEM image reflects the phase separation at higher doses. After irradiation with high doses, significant changes in surface morphology were observed in other HPMC complexed films. Considerable damage in the polymeric structure was observed after irradiation, which is also responsible for decrease in crystallinity of the material as indicated by XRD analysis.



a b c

Fig. 2 SEM Photographs of unirradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

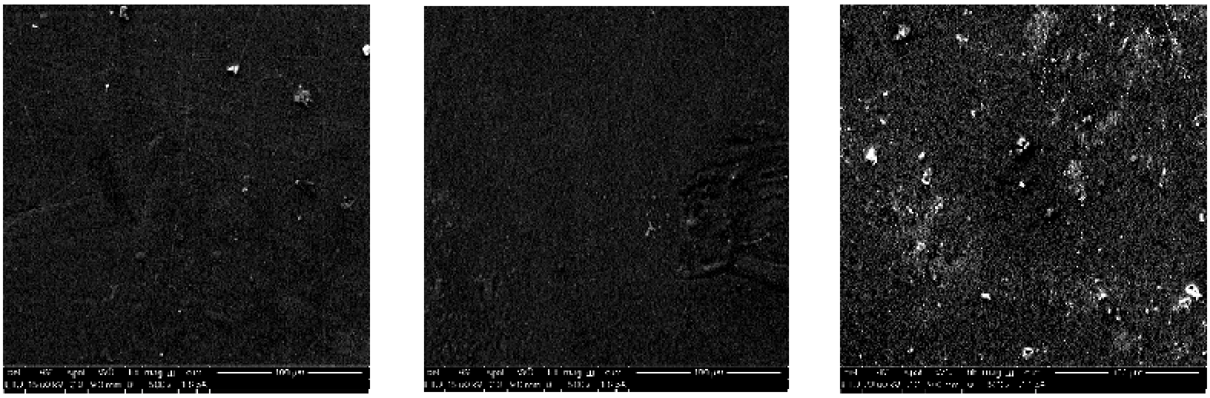
AFTER IRRADIATION WITH 20KGy



a b c

Fig. 2a SEM Photographs of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

AFTER IRRADIATION WITH 60KGy



a **b** **c**

Fig. 2b SEM Photographs of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

AFTER IRRADIATION WITH 100KGy

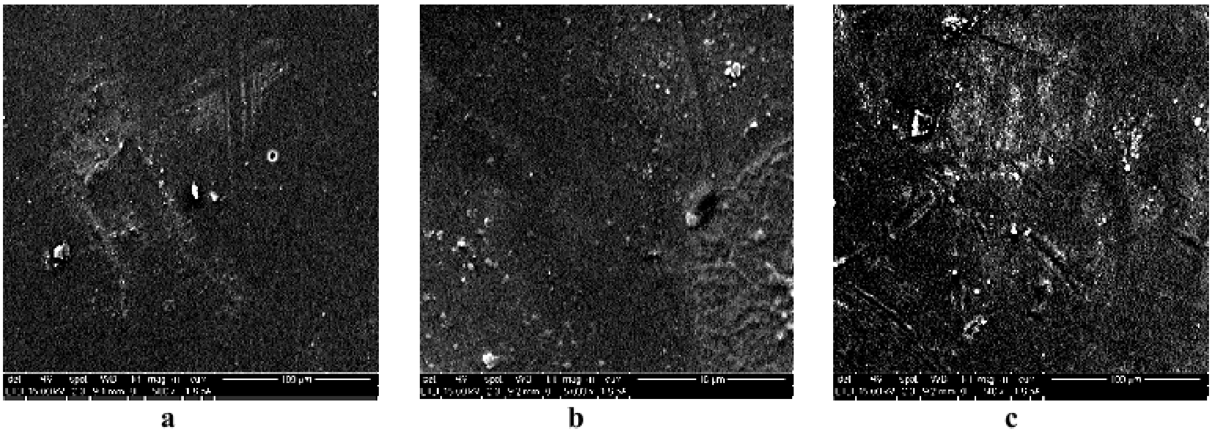


Fig. 2c SEM Photographs of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

3.3 FTIR Spectral studies

The FTIR spectra of pure HPMC and NaI complexed HPMC of different compositions (5:1, 5:4) before and after irradiation (20KGy, 100KGy) are shown in Figs 3, 3a and 3b. The following changes in the spectral features have been observed after comparing the spectrum of complexed HPMC with that of pure HPMC and NaI before and after irradiation. The absorption band in the region 3498- 3996cm^{-1} is due to the intermolecular hydrogen - bonded O-H stretching frequency of HPMC which is shifted to 3496-3585, and 3762cm^{-1} in the 5:1 and 5:4 NaI salt complexed HPMC films before irradiation and 3465-3542cm^{-1}, 3400-3500cm^{-1} for pure HPMC where are as for 5:1 and 5:4 NaI salt complexed it shifted to 3461-3733 cm^{-1}, 3653-3802 cm^{-1} after irradiation. In addition to this, the stretching of methyl and hydroxypropyl showed an absorption band at 2900 cm^{-1}in pure HPMC and is shifted to 2961 and 3110cm^{-1} respectively in 5:1, 5:4 complexed films before irradiation and 3620cm^{-1},3649cm^{-1} and 3673cm^{-1} in pure as well as in HPMC:NaI complexes after irradiation. The C-H,OCH, and CCH assymmetric bending vibration of methyl group in CH_3O in pure HPMC exhibited absorption at 1500 cm^{-1} shifted to1459 - 1471cm^{-1} in the complexed films respectively. Notably the deformation is found to be six membered cyclic group and asymmetric bending vibration of methyl group in CH_3O is gives rise to a peak at 1650 and 1459 cm^{-1} in pure HPMC, and is shifted to 1669 and 1471 cm^{-1} in the complexed films due to complexation of salt.1639cm^{-1}, 1630cm^{-1} and 1626cm^{-1} in pure and complex irradiated films. The ethereal C-O-C group stretching vibration occurring at 1091 cm^{-1} in pure HPMC is shifted to1026 – 1076 and 1306 – 1087cm^{-1} in 5:1 and 5:4 salt complexed polymer electrolyte films respectively.1081cm^{-1} for irradiated pure HPMC shifted to 1052-1029cm^{-1} in 5:1, and 1041-1017cm^{-1} in 5:4 irradiated complexes. The peak at 850cm^{-1} is associated with the CH_2 rocking mode of HPMC shifted to 851-895cm^{-1} in unirradiated HPMC:NaI complexes and 855-886 cm^{-1}, 898-854cm^{-1} in irradiated samples respectively. All these changes in the FTIR spectra are clear indications for the complexation of HPMC with NaI salt.

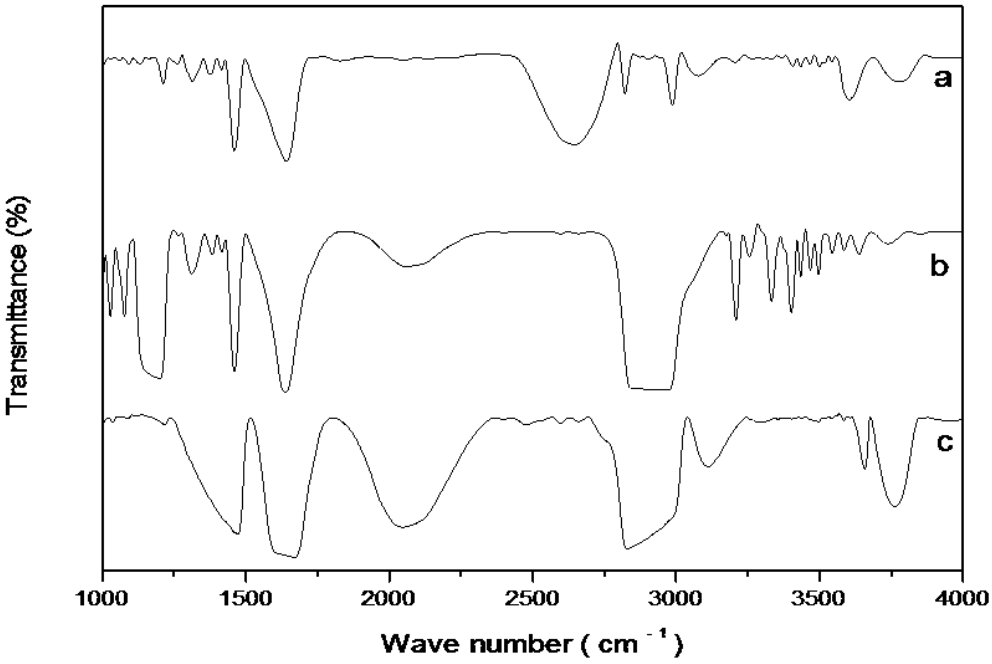


Fig. 3 FTIR spectra of unirradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

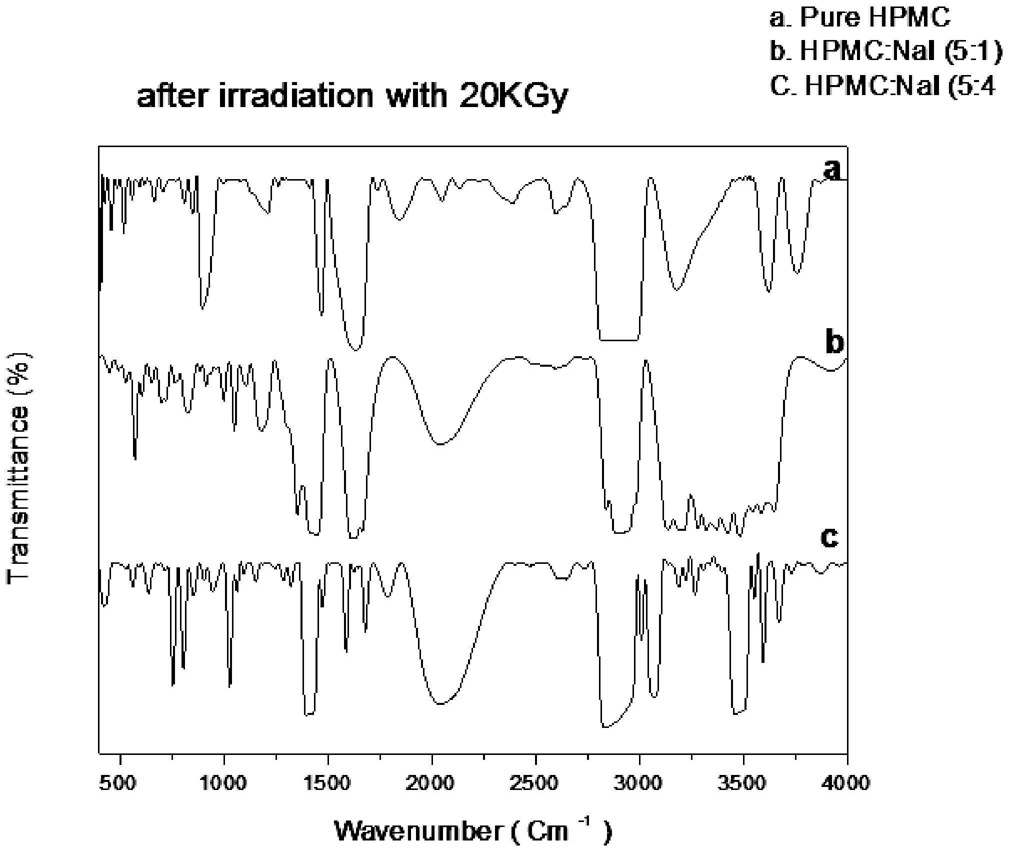


Fig. 3a FTIR spectra of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

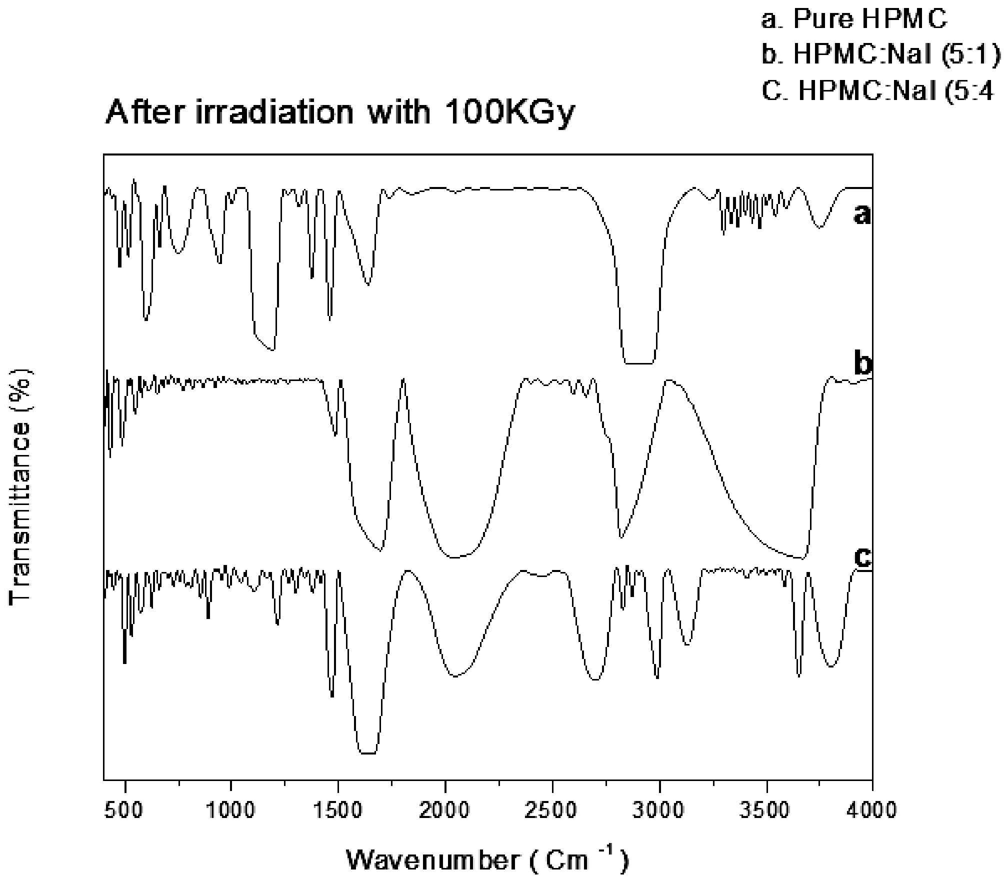


Fig. 3b FTIR spectra of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

3.4 Differential Scanning Calorimetry (DSC) Studies

The DSC thermograms for pure HPMC and HPMC:NaI (5:1), (5:4)before and after irradiation are shown in figs 4, 4a, 4b, 4c, before irradiation for Pure HPMC shows the endothermic transition starts from 50^0C to 91^0C with a broad peak value at 72.16 ^{0}C [25]. This shifts to 81.33 ^{0}C and 83.33 ^{0}C in the HPMC:NaI (5:1, 5:4) systems indicating the presence of NaI in the polymer matrix increases the melting temperature. Both pure and HPMC:NaI systems shows only one endothermic broad peak. This peak shifts towards to higher temperature as the NaI salt concentration increases. The enthalpy was calculated from the heat flow integral. Table 3 shows the enthalpy of fusion (ΔH_f) which is given by the area under the melting endotherm decreases for all HPMC:NaI complexes because the crystllanity reduces in all HPMC:NaI polymer films. From Table 1 and Table 2. it is clear that the percentage of crystallnity reduces in all HPMC:NaI complexses when compared with the pure HPMC polymer films. For irradiated pure HPMC samples it was observed that as the dose rate increases the melting temperature (T_m) as well as the enthalpy of fusion (ΔH_f). However from table 4, for irradiated HPMC complexed with NaI systems, it was observed that as the dose rate increases the melting temperature and enthalpy of fusion increases for HPMC:NaI (5:1) and decreases as the NaI salt concentration increases.

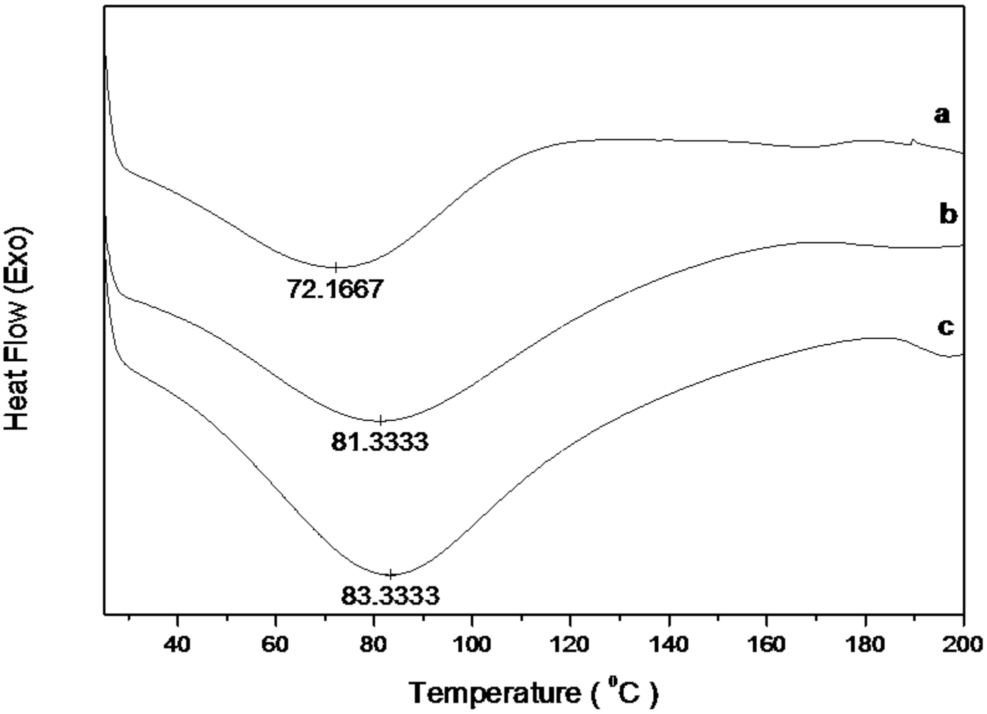


Fig. 4 DSC curves of unirradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

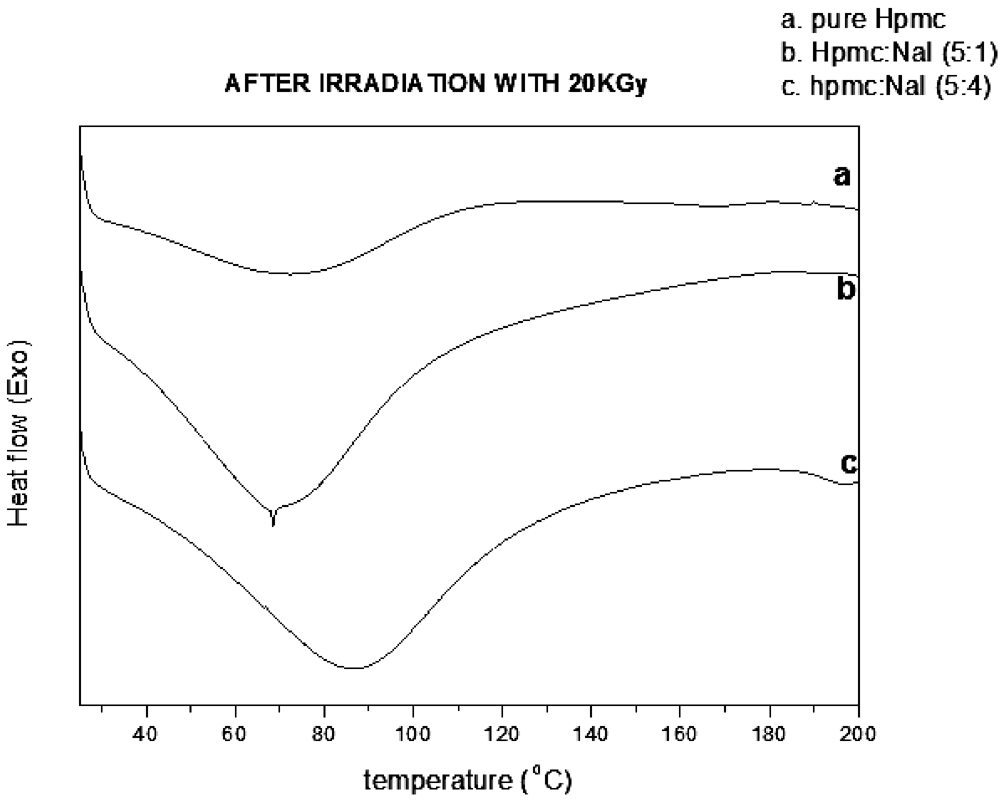


Fig. 4a DSC curves of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

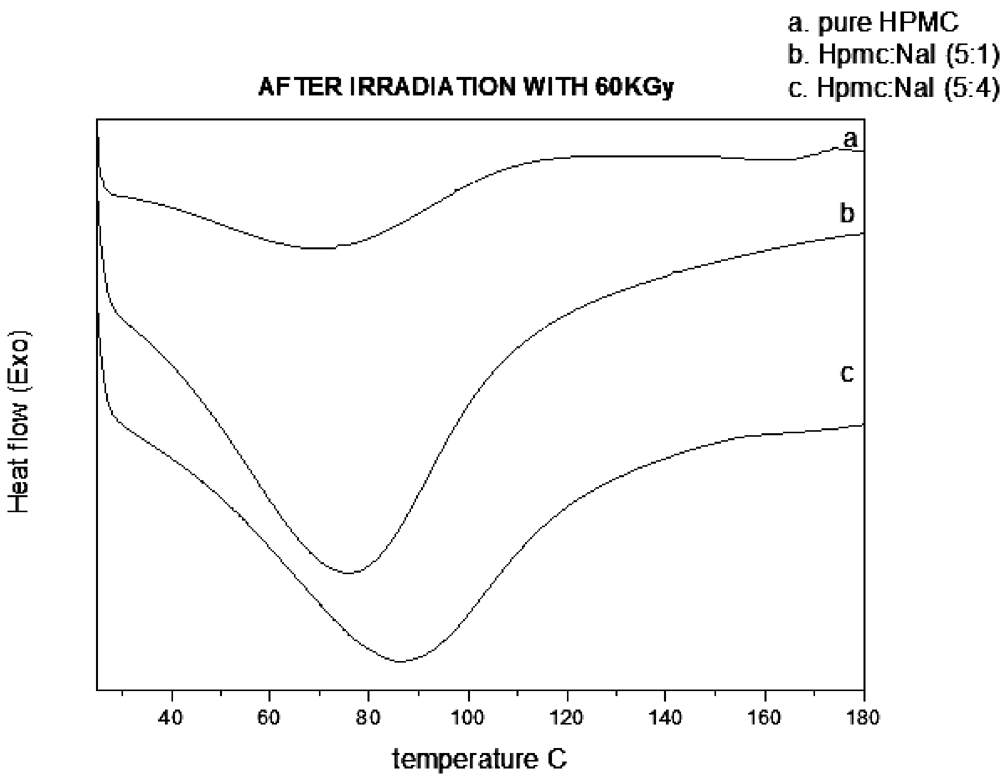


Fig. 4b DSC curves of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC : NaI (5:4)

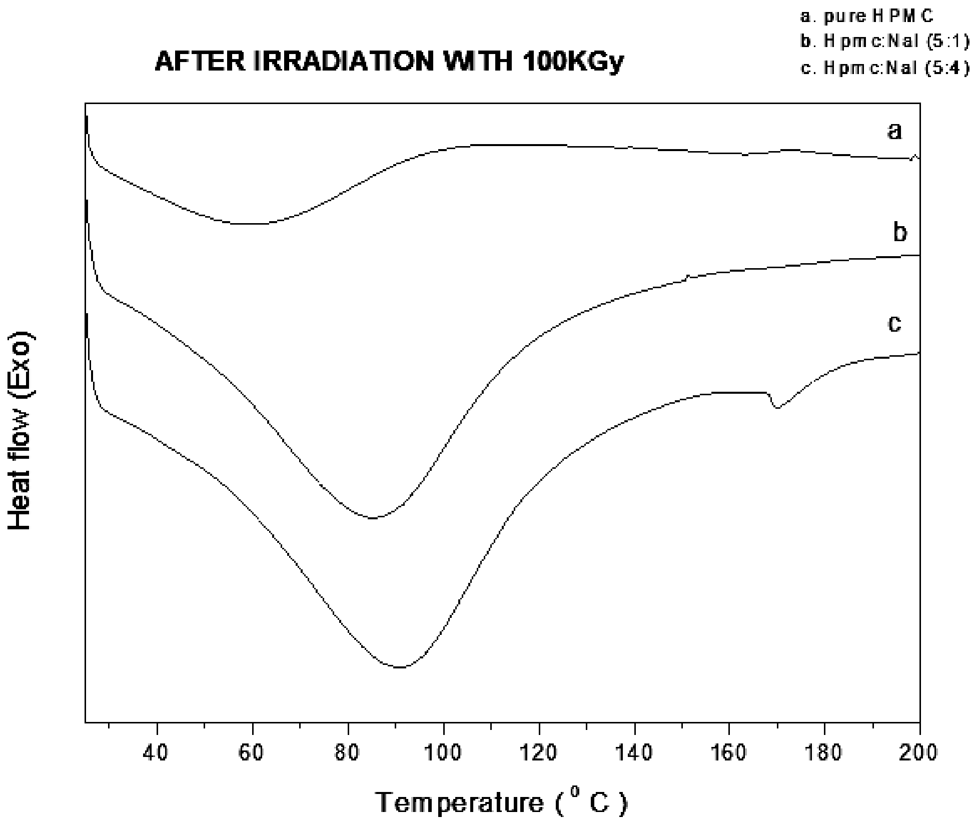


Fig. 4c DSC curves of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:4)

Table 3. Heat of fusion (ΔH), Peak temperature for unirradiated pure HPMC and NaI complexed HPMC films.

Sample	**Peak temp (^{0}C)**	**Enthalpy of fusion (ΔH_f) J/g**
Pure HPMC	72.11	146.32
HPMC:NaI (5:1)	81.27	105.28
HPMC:NaI (5:4)	83.24	53.62

Table 4. Heat of fusion (ΔH), Peak temperature for gamma irradiated with 20KGy, 60KGy, & 100KGy for pure HPMC and NaI complexed HPMC films

Dose rate	**20KGy**		**60KGy**		**100KGy**	
Samples	**Peak temp ^{0}C**	**(ΔH_f) J/g**	**Peak temp ^{0}C**	**(ΔH_f) J/g**	**Peak temp ^{0}C**	**(ΔH_f) J/g**
Pure HPMC	72.11	34.21	69.62	23.62	59.45	31.21
HPMC:NaI (5:1)	68.38	20.25	75.86	47.92	84.86	83.31
HPMC:NaI (5:4)	86.54	74.77	86.36	68.80	90.18	36.57

3.5 Electrical Conductivity Studies

The variation of temperature dependent conductivity of unirradiated and irradiated pure HPMC and HPMC:NaI polymer electrolytes as a function of inverse temperature for different compositions of NaI in the temperature range of 313 – 383 K are as shown in the figs 5,5a,5b,5c. The temperature dependence of electrical conductivity (σ) follows Arehenius equation

$$\sigma = \sigma_0 \; exp^{\left(-E_a/_{KT}\right)} \tag{3}$$

Where σ_0 is the pre-exponential factor, E_a is activation energy, K is the Boltzmann constant and T is absolute temperature. From plots for unirradiated (Fig 5.) films it is clear that the conductivity is found to increase with increase in temperature for pure HPMC as well as in all the compositions of HPMC:NaI polymer electrolyte films. Similar behavior was observed in number of other polymer electrolyte systems [36-40]. As expected the increase in temperature leads to increase in ionic conductivity because as the temperature increases the polymer chains flex at increased rate to produce more free volume resulting in enhanced polymer segmental mobility. The increase in conductivity with increase in temperature may be attributed to the transitions from crystalline to semi-crystalline phase and then to amorphous phase and is interpreted as hopping mechanism between local coordinate sites, local structural relaxation, and segmental motion of polymer [41]. This decrease in the degree of crystallanity and increase in the amorphisity was confirmed with XRD studies. As the amorphous region increases progressively, however the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This in turn favor the hopping interchain and intrachain ion movements hence the conductivity of the polymers become high. For low dose irradiation of pure and HPMC:NaI systems, the decreasing trend in the magnitude of ionic conductivity (Table 5 5a,5b) is observed as compared to that for the unirradiated samples. This could be attributed to the fact that during irradiation the energy deposited in the polymer causes chain scission or produce radicals which subsequently decay or cross-link with neighboring radicals resulting in formation of closely spaced radicals which in turn results in chain folding and cross-linking of polymers, causing the formation of new crystalline regions [42] leading to a decrease in ionic conductivity, however as the radiation dose increases the ionic conductivity also increases which can be interpreted as at higher dose level the bonds in the polymer chains are broken and chain scission process dominates, which leads to faster ion transport through the polymer matrix assisted by the increased segmental motion of the polymer backbone [43-45]which results in increase in ionic conductivity.

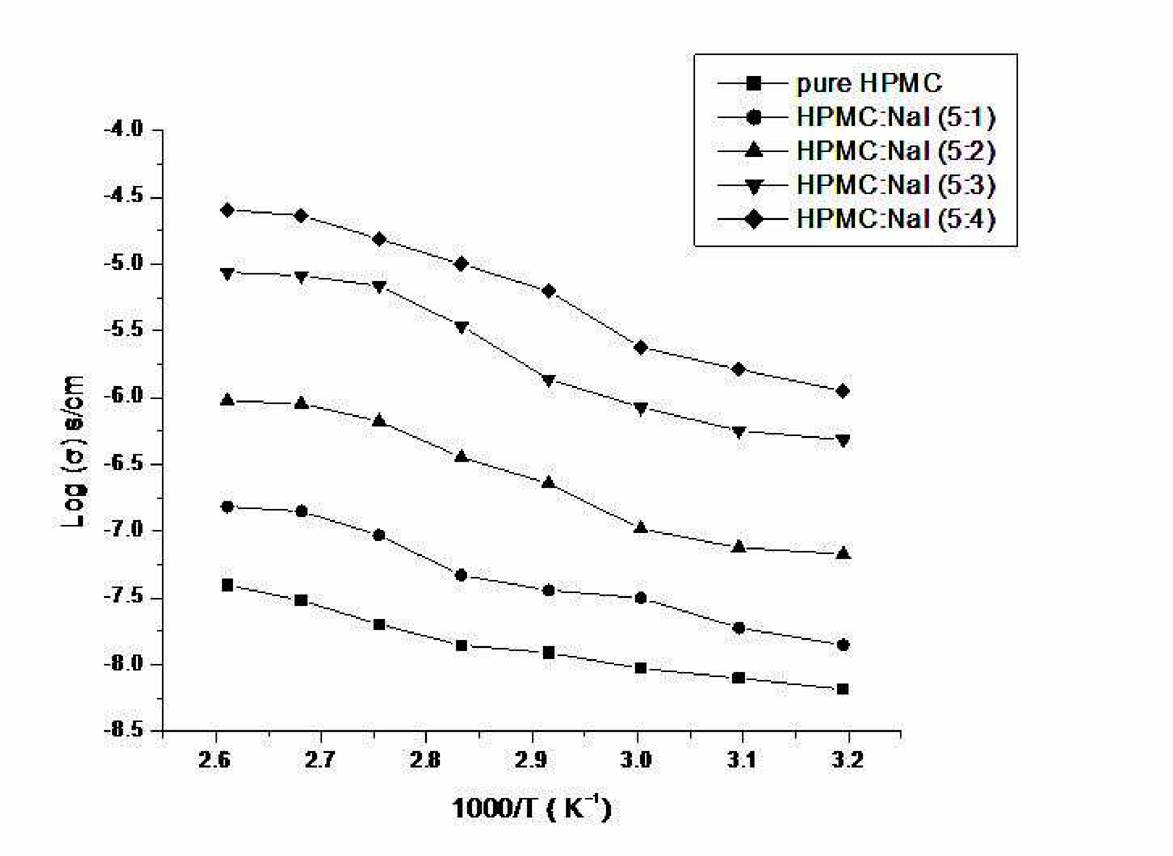


Fig. 5 Temperature dependen conductivity of unirradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:2), d HPMC:NaI (5:3), and e HPMC:NaI (5:4) polymer electrolyte films

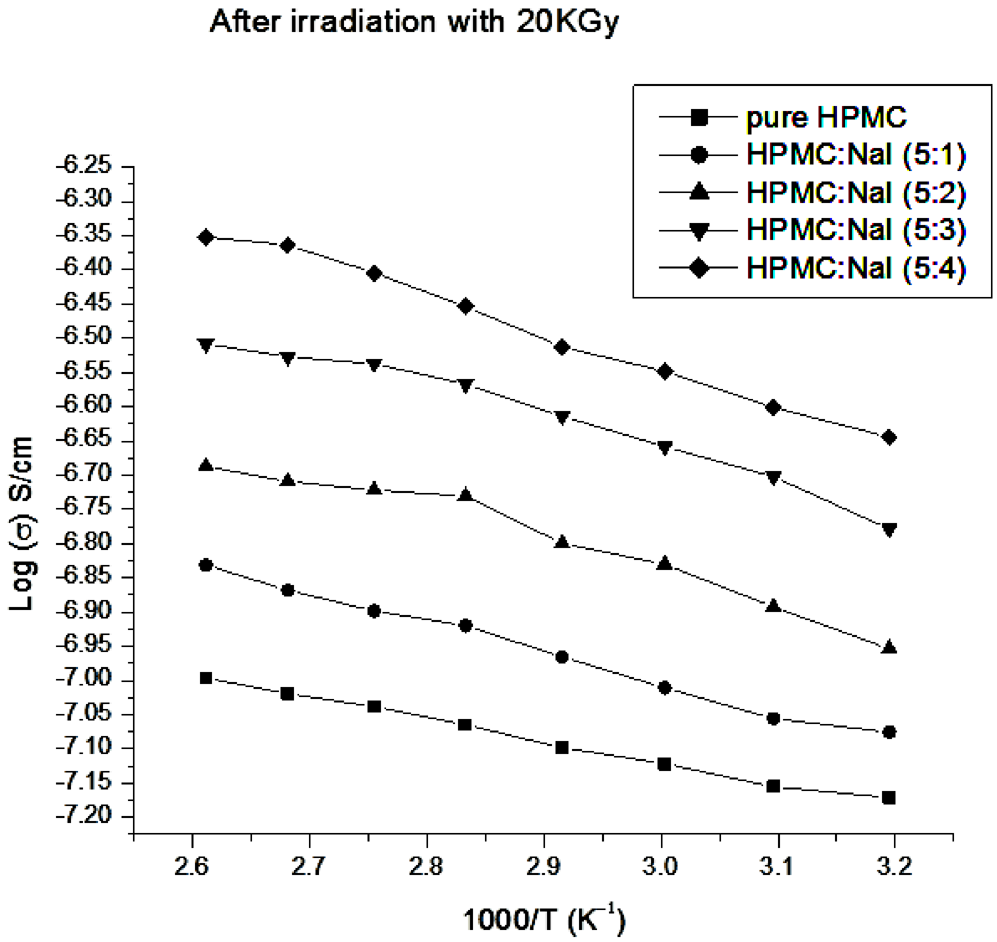


Fig. 5a **Temperature dependent conductivity of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:2), d HPMC:NaI (5:3), and e HPMC:NaI (5:4) polymer electrolyte films**

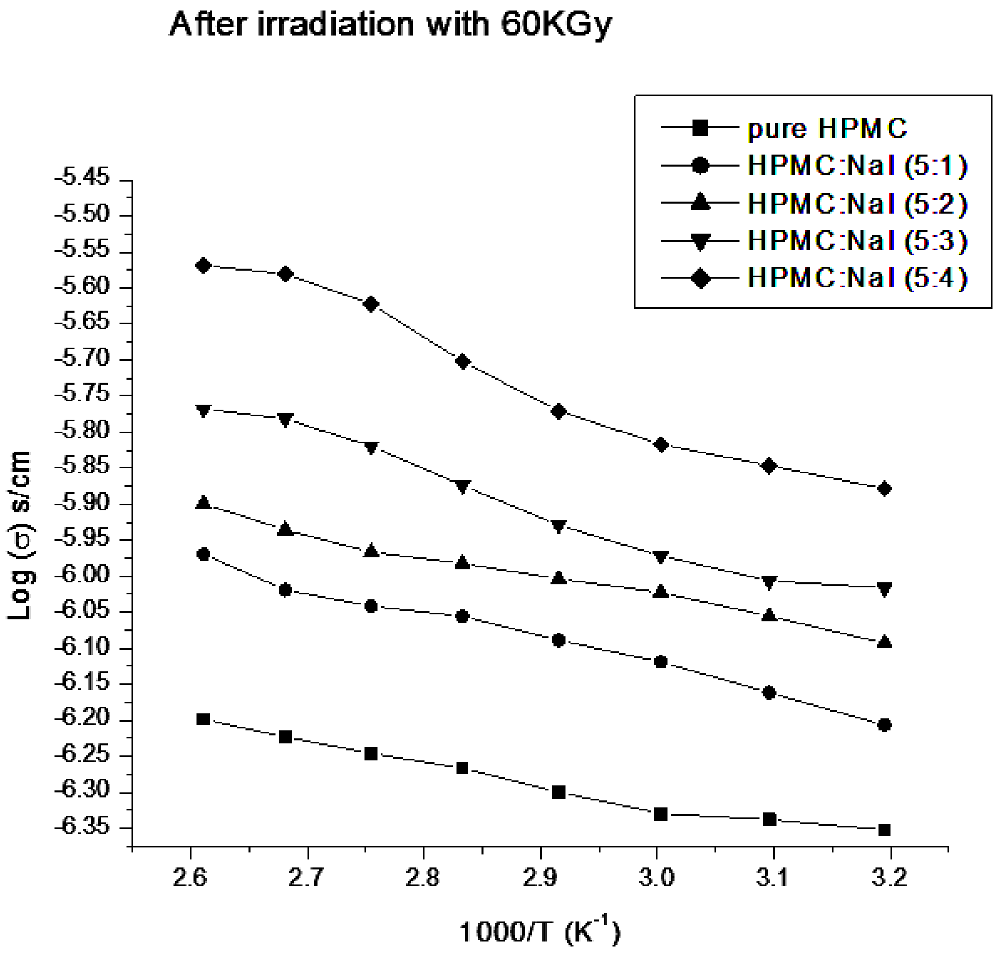


Fig. 5b Temperature dependent conductivity of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:2), d HPMC:NaI (5:3), and e HPMC:NaI (5:4) polymer electrolyte films

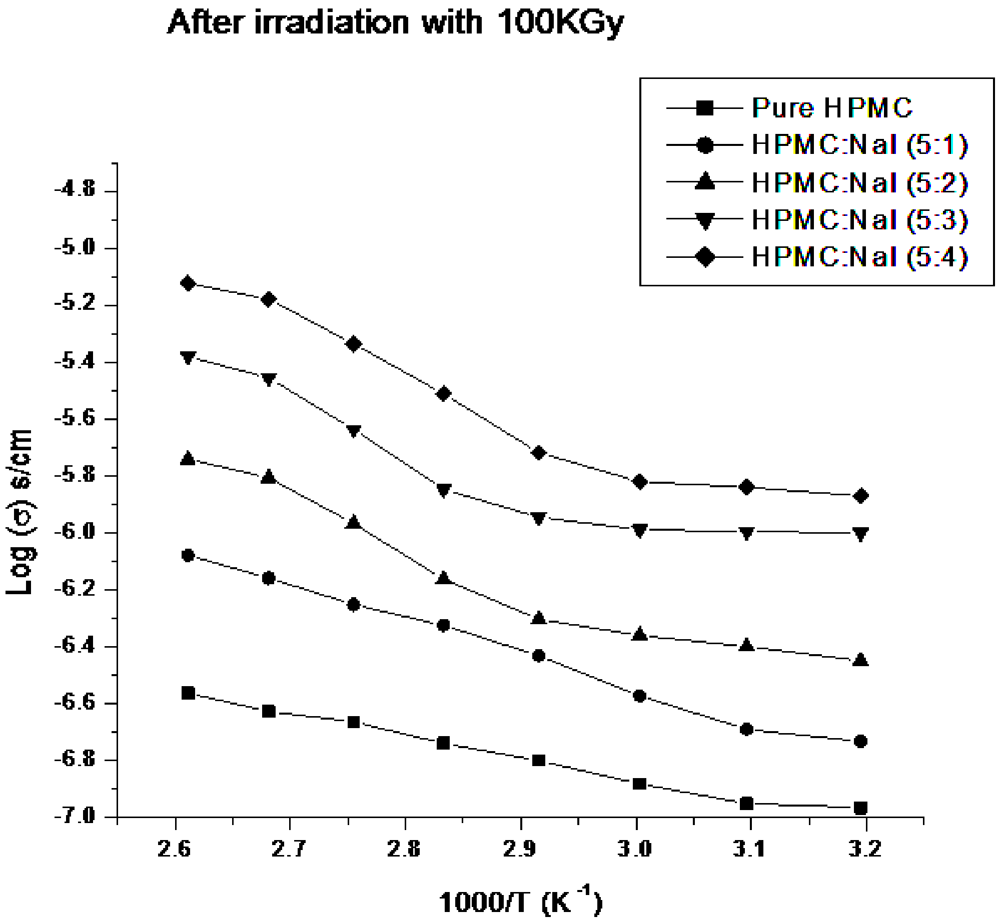


Fig. 5c Temperature dependent conductivity of irradiated a pure HPMC, b (HPMC:NaI) (5:1), c HPMC:NaI (5:2), d HPMC:NaI (5:3), and e HPMC:NaI (5:4) polymer electrolyte films

Table 5. Temperature dependent conductivity values at different temperatures for unirradiated pure HPMC, and (HPMC:NaI) polymer electrolyte films.

Conductivity (σ) (Scm^{-1})				
Sample	**313K**	**333 K**	**353 K**	**383K**
Pure HPMC	6.530 x 10^{-9}	9.372 x 10^{-9}	1.395 x 10^{-8}	3.947 x 10^{-8}
HPMC:NaI (5:1)	1.402 x 10^{-8}	3.159 x 10^{-8}	4.687 x 10^{-8}	1.528 x 10^{-7}
HPMC:NaI (5:2)	6.733 x 10^{-8}	1.044 x 10^{-7}	3.586 x 10^{-7}	9.477 x 10^{-7}
HPMC:NaI (5:3)	4.840 x 10^{-7}	8.479 x 10^{-7}	3.452x 10^{-6}	8.675 x 10^{-6}
HPMC:NaI (5:4)	1.126 x 10^{-6}	2.389 x 10^{-6}	1.002 x 10^{-5}	2.556 x 10^{-5}

Table 5a Conductivity values at different temperatures for 20KGy irradiated pure HPMC, and (HPMC:NaI) polymer electrolyte films

Sample	Conductivity (σ) (S Cm^{-1})			
	313K	333 K	353 K	383k
Pure HPMC	6.739 x 10^{-8}	7.562 x 10^{-8}	8.614x 10^{-8}	1.008 x 10^{-7}
HPMC : NaI (5:1)	8.400 x 10^{-8}	9.764 x 10^{-8}	1.203x 10^{-7}	1.474 x 10^{-7}
HPMC : NaI (5:2)	1.112 x 10^{-7}	1.478 x 10^{-7}	1.859 x 10^{-7}	2.053 x 10^{-7}
HPMC : NaI (5:3)	1.665 x 10^{-7}	2.195 x10^{-7}	2.711 x 10^{-7}	3.105 x 10^{-7}
HPMC : NaI (5:4)	2.267 x 10^{-7}	2.828 x 10^{-7}	3.518 x 10^{-7}	4.443 x 10^{-7}

Table 5b. Conductivity values at different temperatures for 100KGy irradiated pure HPMC, and (HPMC:NaI) polymer electrolyte films

Sample	Conductivity (σ) (S Cm^{-1})			
	313K	333 K	353 K	383k
Pure HPMC	1.083 x 10^{-7}	1.314 x 10^{-7}	1.822 x 10^{-7}	2.734 x 10^{-7}
HPMC : NaI (5:1)	1.850 x 10^{-7}	2.677 x 10^{-7}	4.730 x 10^{-7}	8.334 x 10^{-7}
HPMC : NaI (5:2)	3.558 x 10^{-7}	4.355 x 10^{-7}	6.870 x 10^{-7}	1.811 x 10^{-6}
HPMC : NaI (5:3)	1.000 x 10^{-6}	1.026 x 10^{-6}	1.421x 10^{-6}	4.162 x 10^{-6}
HPMC : NaI (5:4)	0.135 x 10^{-5}	0.151 x 10^{-5}	0.308 x 10^{-5}	0.752 x 10^{-5}

CONCLUSION

The complexation of the salt with the host polymer before and after irradiation is confirmed by XRD and FTIR studies. XRD study shows the percentage of crystallanity decreases with the increasing of NaI salt and radiation doses. Normally, for pure HPMC, an increase in crystallinity is observed at lower irradiation dose (20KGy), whereas crystallinity decreases at higher doses**.** However, in HPMC:NaI polymer electrolyte systems the presence of NaI prevent polymer chain reorganization resulting in decreased crystallinity compared to pure HPMC. SEM analysis of pure and complexed polymer electrolytes before and after irradiation shows a uniform type but with different degrees of roughness and exhibits no features attributable to any crystalline morphology. The DSC results revealed that the presence of NaI in the polymer matrix increases the melting temperature in unirradiated films, however it is observed that the heat of fusion (ΔH_f) is high for pristine HPMC films. The increase in conductivity with the increasing temperature, NaI salt concentration and the radiation dose level is attributed to the decrease in the degree of crystallanity and the simultaneous increase in amorphousity. Also the hopping mechanism of ion movement as ions primarily transport in amorphous phase. Therefore this material established a new polymer electrolyte system. The HPMC:NaI (5:4) system before and after irradition increases the amorphous phase and enhances the conductivity. Thus the polymer electrolyte systems HPMC:NaI with an enhanced amorphous phase and conductivity requires further investigation for electrochemical cells device application.

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