

## Effects of CdCl<sub>2</sub> concentration and gamma irradiation on the structural, thermal and electrical conductivity properties of HPMC polymer electrolyte films.

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**Abstract:** Solid polymer electrolyte films based on hydroxypropyl methylcellulose (HPMC) with different concentrations of cadmium chloride (CdCl<sub>2</sub>) were prepared by solution cast method. Different techniques has been employed to investigate the effects of structural, thermal and ionic conductivity behavior of these polymer electrolyte films upon gamma irradiation with different doses of 20, 60 and 100 kGy. The dissolution of the salt into the polymer host and the structural properties of pure and CdCl<sub>2</sub> (1% - 4%) (wt. %) complexed HPMC polymer electrolyte films before and after irradiation was confirmed by X – ray diffraction (XRD) studies. XRD results revealed that the amorphous domains of HPMC polymer matrix was increased with increase in the salt concentration and with the gamma dose. The percentage of crystallinity is found to be high in pristine unirradiated HPMC films. The thermal properties of these polymer electrolyte films before and after irradiation were studied using differential scanning calorimetry (DSC). The results revealed that the presence of CdCl<sub>2</sub> in the polymer matrix increases the melting temperature, however it is observed that the total enthalpy of fusion ( $\Delta H_f$ ) is maximum for unirradiated pristine HPMC films. The variation of film morphology was examined by scanning electron microscopy (SEM). Direct current (dc) conductivity was measured in the temperature range of 313–383K. The magnitude of conductivity was found to increase with increasing concentration of the salt, temperature and for higher dose of radiation. The composition HPMC:CdCl<sub>2</sub> (5:4) for unirradiated and irradiated samples, found to exhibit the least crystallinity and the highest conductivity.

**Keywords:** Polymer electrolytes, gamma irradiation, XRD, SEM, DSC, dc conductivity

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### I. Introduction

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. Various research groups have studied the effect of inorganic dopants on the polymer hosts. The formation of a complex between the polymer and the dopant results in considerable increase in electron mobility resulting in enhanced electrical conductivity. Electrical conductivities can be varied to several orders of magnitude by changing dopant concentrations so that electronic property control is feasible over the entire range from insulator to semiconductor and then to metal. Several high technology industries require conducting polymers that exhibit a specific response upon exposure to radiation [1-3]. Electronic industry requires materials that undergo radiation induced scission or cross-linking for resist applications, while aerospace and medical applications require high radiation resistant 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 [4-5]. The design and development of appropriate chemistry for these applications require complete understanding of the effects of radiation on the polymeric materials. The structural, thermal and electrical properties of materials undergo changes upon exposure to nuclear radiations. The irradiation of polymeric materials with ionizing radiation (gamma rays, X rays, accelerated electrons, ion beams) leads to the formation of very reactive intermediates. These intermediates can follow several reaction paths, which result in rearrangements and/or formation of new bonds. The ultimate effects of these reactions can be the formation of oxidized products, grafts, scission of main chains (degradation) or cross-linking. 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. 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 radiation chemistry, polymers are classified as scission polymers and cross-linking polymers. Most biopolymers are classified as scission polymers. Recent developments in this field have proved that a variety of biopolymer could be cross linked by irradiating with high energy radiations [6] and HPMC polymer tends to exhibit such radiation cross-linking. They are cellulose ethers, and it is well known that derivatives of cellulose

can readily change its physiochemical properties and its functions of cellulose. Many forms of degradation are possible due to the composition of the medium, pH, temperature and/or the presence of different ions and oxygen. However, to modify the properties of HPMC in order to broaden its useful properties, crosslinking is one of the most popular methods. Its characteristics could be altered by crosslinking such as swelling degree, transport properties, mechanical properties, chemical stability, thermal stability as well as biodegradation rate [7-9]. The microwave irradiation (H. Somashekarappa et al 2013) and high energy electron beam irradiation (Sangappa et al. 2008) on HPMC polymer results changes in crystallinity as well as microstructure and thermal stability [10-11].

Many research articles are available which incorporates cadmium ion in its polymeric system for its application as polymer electrolyte materials. There also exists some cadmium ion conducting polymer electrolytes based on poly-ethylene-oxide (PEO) (S Kilarkaje et al) [12] and poly vinyl alcohol (PVA) ( M.B Nanda Prakash et al) [13]. In the present study, HPMC polymer electrolytes were prepared by incorporating CdCl<sub>2</sub> as the doping salt. HPMC polymer has been chosen because of its appealing properties. HPMC is well known and of major interest to be used as environmental friendly products. It is proved to be more thermally stable than those derived from cellulose such as carboxymethylcellulose (CMC), hydroxyethylcellulose (HEC), and methylcellulose (MC) [14]. It is a biopolymer, eco-friendly and water soluble [15-16]. It has ability to dissolve high concentrations of a wide variety of metal salts and an excellent film forming capacity. Its charge storage capacity can be influenced by the addition of inorganic salt like CdCl<sub>2</sub> to provide good amorphous and compatible nature. It has semi crystalline nature which occurred in two phases (amorphous and crystalline). Amorphous phase enhances higher ionic conduction in the system meanwhile crystalline phase provides strong mechanical support to the polymer electrolytes. Cadmium chloride is a compound of cadmium and chlorine having rhombohedral symmetry. It is a hygroscopic solid and highly soluble in water. Cadmium is resistant to corrosion and as a result it is used as a protective layer when deposited on other metals. It is also used for photocopying, dyeing and electroplating. It is a fast-ion conducting salt and very malleable in a number of crystalline and amorphous materials. Its incorporation in a polymeric system may be expected to allow the more free charges and these free charges contribute to development of the charge transportation mechanism and inter-intra electronic transition [12, 17]. Gamma irradiation is a very clean, easy and cost effective process, has been regarded as a very useful method used to generate crosslinking or scission in water-soluble polymers. Gamma irradiation effects on pure and HPMC:CdCl<sub>2</sub> polymer electrolyte films may bring about remarkable structural, thermal and morphological changes, which results enhancement in their performance and properties such as crystallinity, conductivity, electrochemical stability, sensitivity, solubility, etc. In view of its importance the present work is being initiated and efforts have been made to synthesize polymer electrolyte films that exhibit electrical conductivity and to study their properties like structural, thermal and ionic conductivity behavior before and after irradiation. The study of the modification in the properties of the conducting polymers after controlled irradiation and development of radiation resistant polymers is the main scope of the work.

## **II. Experimental**

### **2.1 Materials and Preparation of Polymer Electrolyte Films.**

Pure HPMC and various compositions of complexed films of HPMC with CdCl<sub>2</sub> salt were prepared by solution cast method using double distilled water as solvent. Hydroxypropyl methylcellulose (HPMC E15LV) was purchased from Loba Chemicals India, and cadmium chloride (CdCl<sub>2</sub>) was purchased from S. D. fine chemicals India. To prepare the polymer electrolyte films, HPMC polymer was blended with inorganic salt CdCl<sub>2</sub>. 5g of HPMC in 100 ml double distilled water was dissolved and desired amounts of (1% - 4%) (Wt %) CdCl<sub>2</sub> was added and stirred continuously for 6 - 8 h. The completely soluble homogeneous solution was filtered through Whatmann No 41 filter paper and degassed. Then the clear solution of HPMC:CdCl<sub>2</sub> was poured on to a clean and leveled glass plates (30 cm X 40 cm) 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. CdCl<sub>2</sub> is hygroscopic in nature and the higher concentration of CdCl<sub>2</sub> has got the tendency to absorb more moisture. However HPMC: CdCl<sub>2</sub> (5:5) polymer films were also prepared and was found that with increasing concentration of CdCl<sub>2</sub> salt, the obtained films are not stable and are not with uniform thickness. Hence the optimal doping with CdCl<sub>2</sub> is carried out only upto 4% and polymer electrolyte films HPMC: CdCl<sub>2</sub> (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 CuK $\alpha$  radiation of wavelength 1.5406 Å. The surface morphology of these polymer films were observed using JEOL 840, resolution at 20 Kv, 10 nm scanning electron microscope (SEM). The samples were gold coated using the sputter coater at 10 mA current under 10<sup>-2</sup> torr vacuum for 3 minutes before imaging. The Differential Scanning Calorimetry (DSC)

measurements have been taken in the temperature range of 30 – 200 °C with the help of Differential Scanning Calorimeter Model: METTLER-TOLEDO DSC1 thermal analysis system at a heating rate of 10 °C per minute. The temperature dependent dc conductivity of the reported polymer electrolyte samples were measured in the temperature range of (313 – 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

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

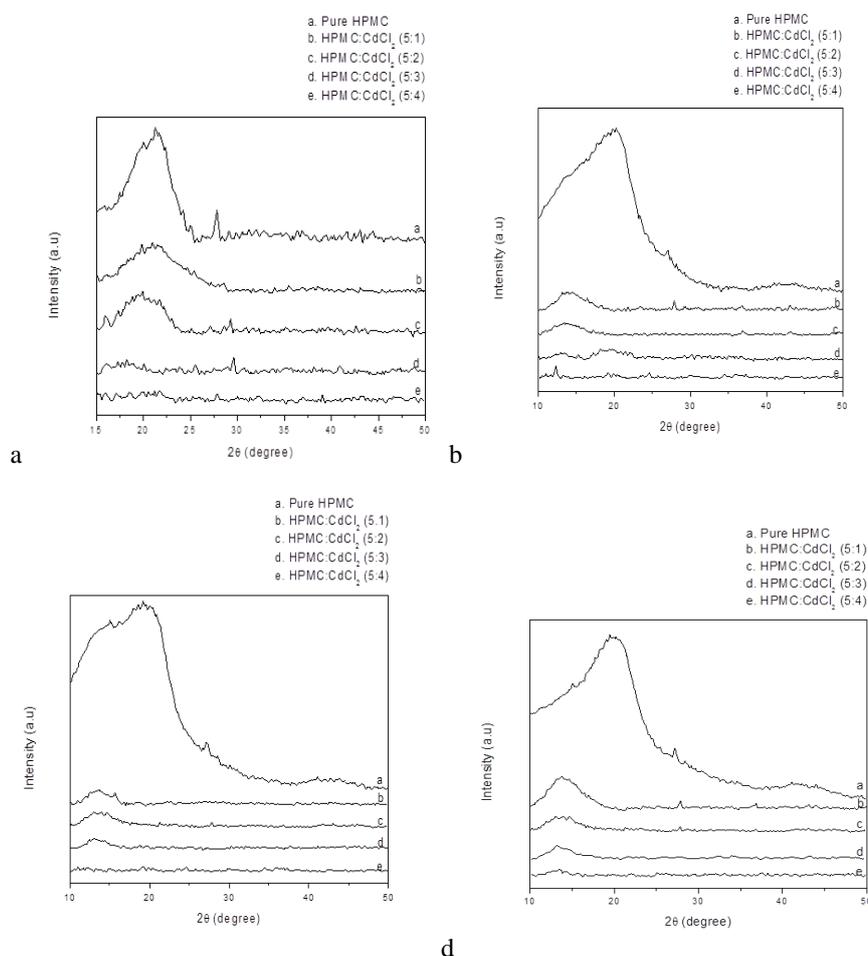
Where ‘t’ is the thickness of the sample in mm, ‘R’ is the resistance in MΩ and ‘A’ is the area of the sample in mm<sup>2</sup>

### 2.3 Gamma irradiation

Films of pure and various compositions of CdCl<sub>2</sub> complexes of HPMC has been gamma irradiated in air by <sup>60</sup>Co source for different doses 20, 60, and 100 kGy. As the mechanical properties and wear resistance of the polymer saturate at above 100 kGy irradiation [18] Muratoglu [19], the proposed study was carried out up to 100 kGy dose, which was performed at M/s Microtrol sterilization private limited, Bangalore, India.

## III. Results And Discussion

### 3.1 XRD studies



**Fig. 1.** XRD pattern of **a** unirradiated and **b** 20 kGy, **c** 60 kGy, **d** 100 kGy irradiated pure and HPMC:CdCl<sub>2</sub> polymer electrolyte films.

**Table 1** Position of the most intense peak  $2\theta$  ( $^{\circ}$ ), d – Value ( $\text{\AA}$ ) and the percentage of crystallinity for unirradiated pure and CdCl<sub>2</sub> complexed HPMC films.

Sample	$2\theta$ ( $^{\circ}$ )	d – Value ( $\text{\AA}$ )	$X_c$ (%)
Pure HPMC	21.26	4.18	65.29
HPMC:CdCl <sub>2</sub> (5:1)	20.96	4.23	52.66
HPMC:CdCl <sub>2</sub> (5:2)	19.93	4.44	45.42
HPMC:CdCl <sub>2</sub> (5:3)	18.05	4.91	33.29
HPMC:CdCl <sub>2</sub> (5:4)	16.95	5.72	18.95

**Table 2** Percentage of crystallinity ( $X_c$ ) for 20, 60 & 100 kGy gamma irradiated pure and CdCl<sub>2</sub> complexes of HPMC polymer electrolyte films.

Dose rate	20 kGy	60 kGy	100 kGy
Sample	$X_c$ (%)	$X_c$ (%)	$X_c$ (%)
Pure HPMC	67.6	45.5	32.4
HPMC:CdCl <sub>2</sub> (5:1)	45.16	41.47	30.16
HPMC:CdCl <sub>2</sub> (5:2)	35.95	33.68	31.05
HPMC:CdCl <sub>2</sub> (5:3)	26.43	21.65	15.36
HPMC:CdCl <sub>2</sub> (5:4)	15.15	10.59	8.85

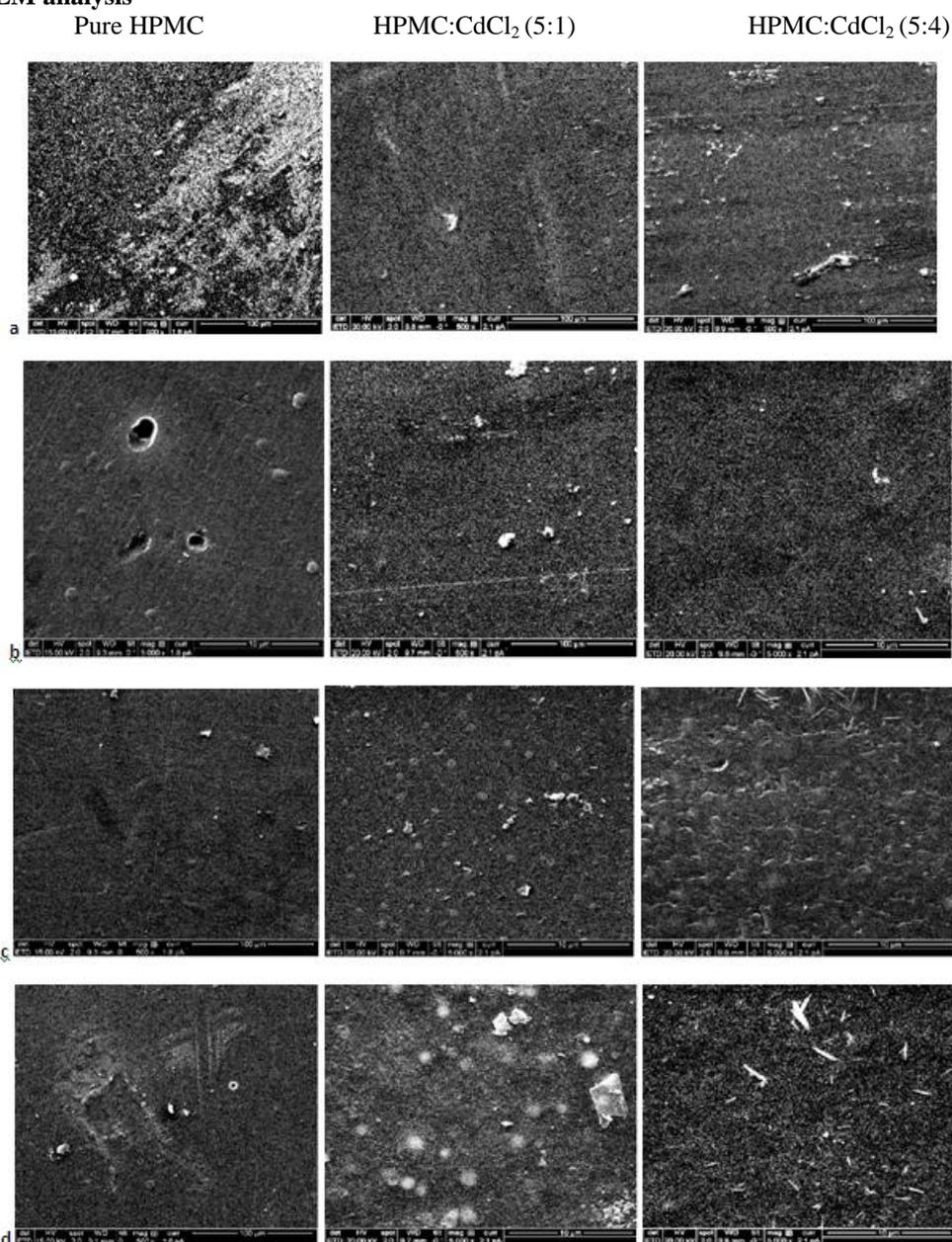
X-ray diffraction is most useful for the determination of the nature of the sample. The ionic conductivity in polymer electrolyte is determined by the amorphous nature of the polymer. Hence it is necessary to determine the crystalline and amorphous nature of the polymer electrolyte films. XRD patterns of unirradiated and 20, 60, 100 kGy gamma irradiated pure and HPMC:CdCl<sub>2</sub> complexed films are shown in Figure 1. For unirradiated samples, pure HPMC shows a broad peak at  $2\theta = 21.26^{\circ}$  (d spacing = 4.175  $\text{\AA}$ ) corresponding to its semi-crystalline nature of the polymer [20]. This diffraction peak is shifted to  $20.96^{\circ}$  (d spacing = 4.234  $\text{\AA}$ ) in HPMC:CdCl<sub>2</sub> complexes of 5:1 system and almost at  $19.93^{\circ}$  (d spacing = 4.44  $\text{\AA}$ ) and  $18.24^{\circ}$  (d spacing = 4.91  $\text{\AA}$ ) in 5:2 and 5:3 systems of polymer electrolytes. Whereas for 5:4 system this diffraction peak almost disappears. There is a nucleation of crystalline order which gives an additional Bragg-like reflection almost at  $2\theta = 27.83^{\circ}$  (d spacing = 3.20  $\text{\AA}$ ) for pure HPMC and is shifted to around  $28^{\circ} - 30^{\circ}$  in all other complexed systems with broad peaks and with decreasing intensity. The mentioned peaks are less intense and are almost found to be disappearing in the polymer electrolyte systems at higher concentrations of CdCl<sub>2</sub> indicating that the addition of the salt causes a decrease in the degree of crystallinity and a simultaneous increase in the amorphosity of the HPMC complexes. Absence of peaks corresponding to the CdCl<sub>2</sub> 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 the salt in the polymer suggesting the dominant presence of amorphous phase [21]. Therefore it may be confirmed that the complexation has been taken place in the amorphous phase. The irradiated sample of pure and HPMC:CdCl<sub>2</sub> shows decrease in the intensity with broad peaks, implying that crystallinity decreases. Normally, for pure HPMC, a slight increase in crystallinity is observed at lower irradiation dose (20 kGy), which may be due to the cross linking of the polymer chain or by the formation of the single or multiple helices, which induces more crystalline region in the polymer samples. However during irradiation at higher doses (60 kGy, 100 kGy) the peaks get broadened and the intensity decreases indicating that the degree of crystallinity is decreased. In HPMC:CdCl<sub>2</sub> polymer electrolyte systems the presence of CdCl<sub>2</sub> prevent polymer chain reorganization resulting in decreased crystallinity compared to pure HPMC. As the radiation dose increases, the peaks corresponding to HPMC:CdCl<sub>2</sub> systems in all the compositions of polymer electrolyte films shifts between  $13^{\circ} - 14^{\circ}$ . Also the peaks gets

broadened up and almost found to be disappearing at 100 kGy irradiation, indicating that degree of crystallinity is decreased. Hence it is worth mentioning that during irradiation, the energy deposited in the polymer causes chain scission or produce radicals which subsequently decay or cross-link with neighboring radicals, i.e. both chain scission and cross-linking occur during irradiation. 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 crystallinity decreases with addition of CdCl<sub>2</sub> salt concentration and the increasing gamma dose. The 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 [10, 22].

$$X_c = \frac{A_c}{A_c + A_a} \times 100 \quad (2)$$

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

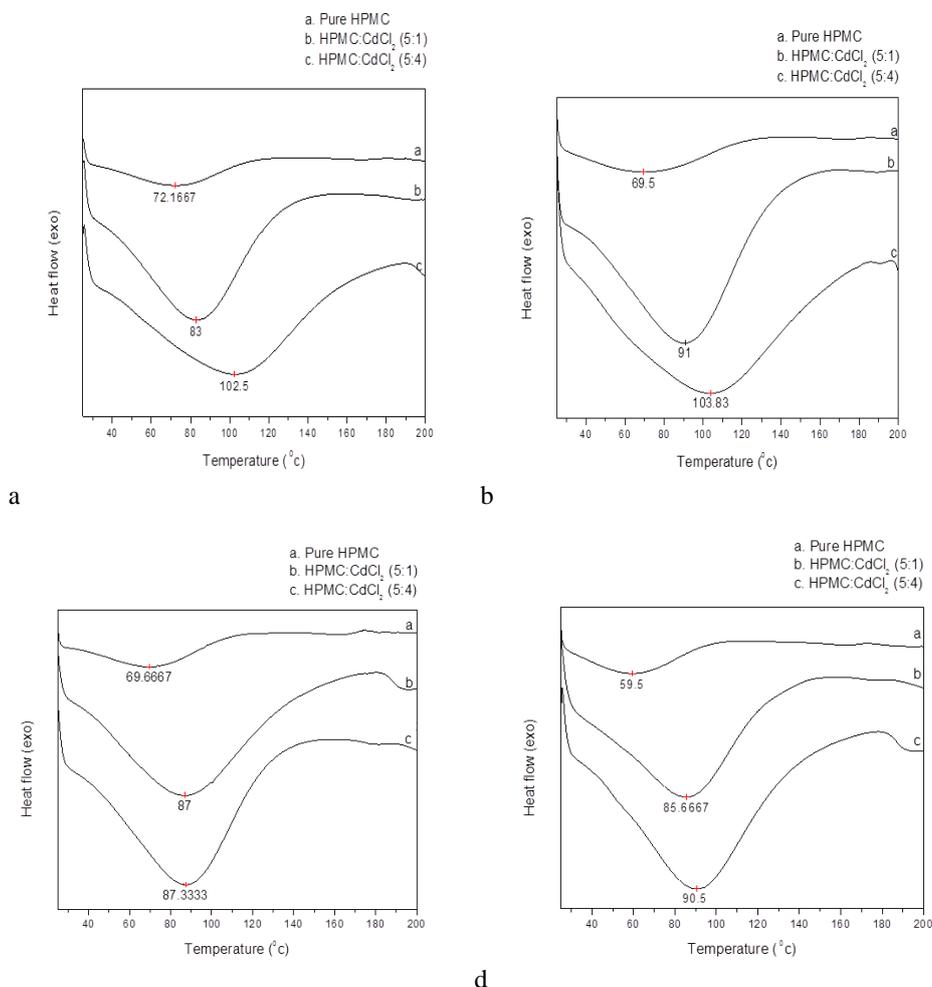
### 3.2 SEM analysis



**Fig. 2** SEM Photographs of **a** unirradiated, **b** 20 kGy, **c** 60 kGy, **d** 100 kGy gamma irradiated pure and , (HPMC:CdCl<sub>2</sub>) (5:1, 5:4) polymer electrolyte films

Scanning electron microscopy is often used to study the compatibility between the various components of the polymer electrolytes through the detection of phase separation and interfaces. 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. SEM of the pure and HPMC:CdCl<sub>2</sub> (5:1) and (5:4) polymer electrolytes before and after irradiation shown in Figure 2 is of uniform type but with different degrees of roughness. Unirradiated pure HPMC films exhibits no features attributable to any crystalline morphology, so the semi crystallinity of HPMC is likely to be submicroscopic in nature. The surface of the unirradiated films is smooth and homogeneous, however when the CdCl<sub>2</sub> salt concentration and the gamma dose increases, an increase in the degree of roughness is observed. Also the dense structure of the film indicates the segregation of the dopant in that host polymer matrix. It is observed that irradiated pure HPMC shows porous structure with well dispersed pores for low doses at 20 kGy. On the other hand, at higher doses (60,100 kGy) the porous structure is disrupted possibly due to recrystallization of the polymer. Whereas HPMC:CdCl<sub>2</sub> (5:1) system shows the formation of porous structure on the surface at higher doses (60, 100 kGy), may be due to the rapid penetration of cadmium ions into the polymer matrix at higher doses. For HPMC:CdCl<sub>2</sub> (5:4) systems, rod-like structures appear due to the irradiation effects. Figures 2b and 2c show the surface full of small cavities and the loosely bound rod-like structures on the surface [12]. Therefore two phase microstructure in the SEM image reflects the phase separation at different concentration (5:1, 5:4) of CdCl<sub>2</sub> salt and at higher doses. Considerable damage in the polymeric structure was observed during irradiation, which is also responsible for decrease in the crystallinity of the material as indicated by XRD analysis.

### 3.3 Differential scanning calorimetry studies



**Fig. 3** DSC curves of **a** unirradiated and **b** 20 kGy, **c** 60 kGy, **d** 100 kGy irradiated pure HPMC and (HPMC:CdCl<sub>2</sub>) (5:1, 5:4) polymer electrolyte films.

**Table 3** Heat of fusion ( $\Delta H_f$ ), Peak temperature for pure and HPMC:CdCl<sub>2</sub> (5:1, 5:4) Polymer electrolyte films.

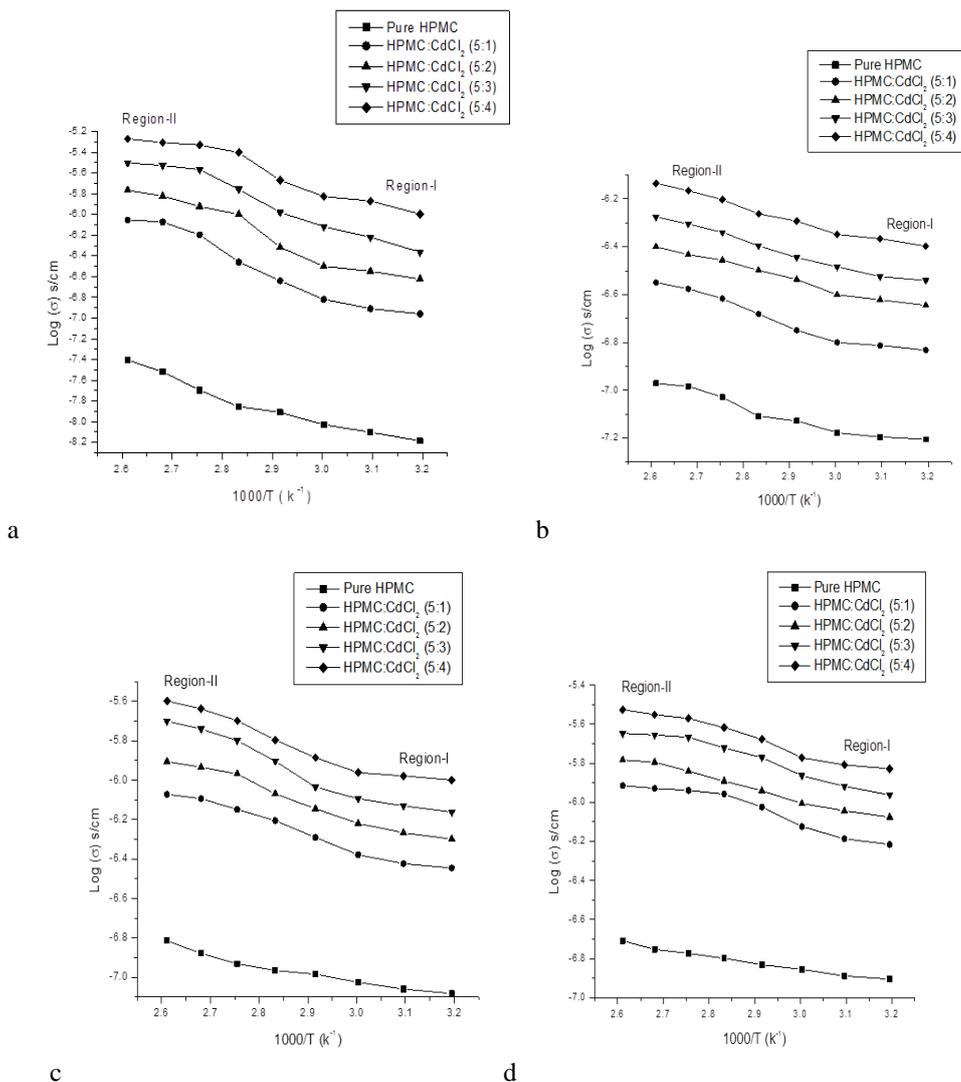
Sample	Onset (°C)	Endset (°C)	Peak temp (°C)	Enthalpy of fusion ( $\Delta H_f$ ) J/g
Pure HPMC	50.12	91.28	72.16	146.32
HPMC: CdCl <sub>2</sub> (5:1)	62.23	114.15	83.00	116.62
HPMC: CdCl <sub>2</sub> (5:4)	79.07	131.52	102.5	41.76

**Table 4.** Heat of fusion  $\Delta H_f$ , peak temperature and 20, 60, 100 kGy gamma irradiated pure and HPMC:CdCl<sub>2</sub> (5:1, 5:4) polymer electrolyte films.

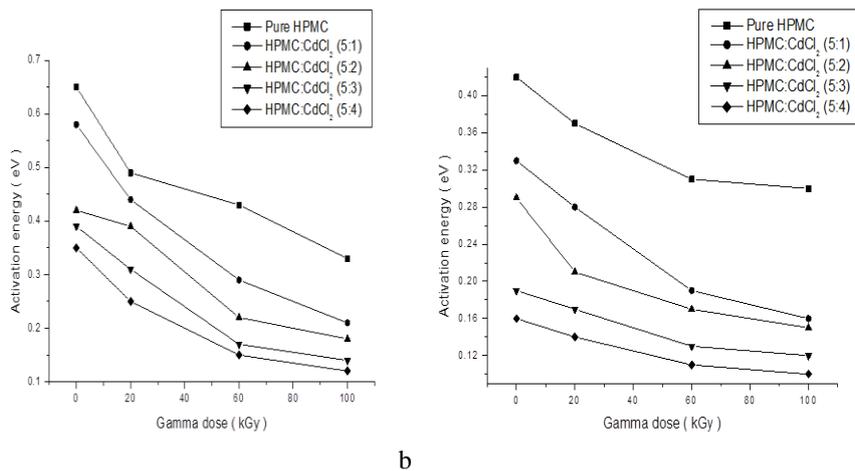
Dose rate	0 kGy		20 kGy		60 kGy		100 kGy	
	Peak temp (°C)	( $\Delta H_f$ ) J/g	Peak temp (°C)	( $\Delta H_f$ ) J/g	Peak temp (°C)	( $\Delta H_f$ ) J/g	Peak temp (°C)	( $\Delta H_f$ ) J/g
Pure HPMC	72.16	146.32	69.5	119.21	69.62	31.21	59.45	23.62
HPMC:CdCl <sub>2</sub> (5:1)	83	52.52	91	59.99	87	42.57	85.66	26.89
HPMC:CdCl <sub>2</sub> (5:4)	102.5	41.76	103.8	35.78	88.5	31.29	90.5	13.43

The DSC thermograms of unirradiated and 20, 60, 100 kGy gamma irradiated pure and HPMC: CdCl<sub>2</sub> (5:1) and (5:4) are shown in Figure 3. It is observed that the unirradiated pure HPMC shows broad endothermic transition starts from 50 °C to 91 °C with a broad peak value at 72.16 °C [10]. This endothermic peak shifts to 83 °C and 103 °C in the HPMC:CdCl<sub>2</sub> (5:1, 5:4) systems indicating that, the presence of CdCl<sub>2</sub> in the polymer matrix increases the melting temperature and are thermally more stable. However, pure HPMC during irradiation (20, 60, 100 kGy), shows a broad endothermic melting peak temperature, which decreases to 69.5 °C, 69.62 °C and 59.45 °C respectively. For irradiated HPMC:CdCl<sub>2</sub> (5:1, 5:4) systems, though the melting peak increases to 91 °C and 103.8 °C at 20 kGy, however during irradiation for 60 and 100 kGy, this melting peak decreases to 87 °C, 88.5 °C and 85.66 °C, 90.50 °C respectively for 5:1, 5:4 of HPMC:CdCl<sub>2</sub> complexes. The enthalpy was calculated from the heat flow integral. Table 3 and Table 4 shows the enthalpy of fusion ( $\Delta H_f$ ), which is given by the area under the melting endotherm, decreases for pristine HPMC as well as for all HPMC: CdCl<sub>2</sub> complexes before and after irradiation. The relative percentage of crystallinity reduces in all HPMC: CdCl<sub>2</sub> polymer films. From Table 1 and Table 2, it is clear that the percentage of crystallinity reduces in all polymer electrolyte complexes when compared with the pristine and irradiated HPMC polymer films. However the crystallinity reduces to a minimum of 19 % for unirradiated HPMC:CdCl<sub>2</sub> complexes of 5:4 ratio compared with the 65 % crystallinity for the polymer host. Whereas, for irradiated (100 kGy) HPMC:CdCl<sub>2</sub> complexes of 5:4 ratio, the crystallinity reduces to a minimum of 9 %, when compared with the 32 % crystallinity of the irradiated (100 kGy) HPMC polymer host.

### 3.4 Electrical conductivity studies



**Fig. 4** Temperature dependent conductivity of **a** unirradiated, **b** 20 kGy, **c** 60 kGy, **d** 100 kGy gamma irradiated polymer electrolyte films



**Fig. 5** Variation of activation energy in a region-I, b region-II for different gamma doses.

**Table 5** Conductivity values and activation energy at different temperatures for unirradiated pure and HPMC:CdCl<sub>2</sub> polymer electrolyte films

Sample	Conductivity ( $\sigma$ ) ( $S\text{cm}^{-1}$ )				Activation energy (eV)	
	313 K	333 K	363 K	383 K	Region I	Region II
Pure HPMC	6.530 E <sup>-9</sup>	9.372 E <sup>-9</sup>	2.012 E <sup>-8</sup>	3.947 E <sup>-8</sup>	0.65	0.42
HPMC:CdCl <sub>2</sub> (5:1)	1.099 E <sup>-7</sup>	1.515 E <sup>-7</sup>	6.371 E <sup>-7</sup>	8.866 E <sup>-7</sup>	0.58	0.33
HPMC: CdCl <sub>2</sub> (5:2)	2.382 E <sup>-7</sup>	3.165 E <sup>-7</sup>	1.197 E <sup>-6</sup>	1.718 E <sup>-6</sup>	0.42	0.29
HPMC: CdCl <sub>2</sub> (5:3)	4.352 E <sup>-7</sup>	7.658 E <sup>-7</sup>	2.711 E <sup>-6</sup>	3.150 E <sup>-6</sup>	0.39	0.19
HPMC: CdCl <sub>2</sub> (5:4)	1.014 E <sup>-6</sup>	1.493 E <sup>-6</sup>	4.689 E <sup>-6</sup>	5.383 E <sup>-6</sup>	0.35	0.16

**Table 6** Conductivity values and activation energy at different temperatures for 20 kGy irradiated pure and HPMC:CdCl<sub>2</sub> polymer electrolyte films.

Sample	Conductivity ( $\sigma$ ) ( $S\text{cm}^{-1}$ )				Activation energy (eV)	
	313 K	333 K	363 K	383 K	Region I	Region II
Pure HPMC	6.224 E <sup>-8</sup>	6.642 E <sup>-8</sup>	9.351 E <sup>-8</sup>	1.068 E <sup>-7</sup>	0.49	0.37
HPMC:CdCl <sub>2</sub> (5:1)	1.471 E <sup>-7</sup>	1.582 E <sup>-7</sup>	2.416 E <sup>-7</sup>	2.819 E <sup>-7</sup>	0.44	0.28
HPMC: CdCl <sub>2</sub> (5:2)	2.263 E <sup>-7</sup>	2.506 E <sup>-7</sup>	3.500 E <sup>-7</sup>	3.980 E <sup>-7</sup>	0.39	0.21
HPMC: CdCl <sub>2</sub> (5:3)	2.877 E <sup>-7</sup>	3.282 E <sup>-7</sup>	4.570 E <sup>-7</sup>	5.297 E <sup>-7</sup>	0.31	0.17
HPMC: CdCl <sub>2</sub> (5:4)	4.010 E <sup>-7</sup>	4.482 E <sup>-7</sup>	6.265 E <sup>-7</sup>	7.335 E <sup>-7</sup>	0.25	0.14

**Table 7** Conductivity values and activation energy at different temperatures for 100 kGy irradiated pure and HPMC:CdCl<sub>2</sub> polymer electrolyte films

Sample	Conductivity ( $\sigma$ ) ( $S\text{cm}^{-1}$ )				Activation energy (eV)	
	313 K	333 K	363 K	383 K	Region I	Region II
Pure HPMC	1.245 E <sup>-7</sup>	1.398 E <sup>-7</sup>	1.688 E <sup>-7</sup>	1.95 E <sup>-7</sup>	0.33	0.3
HPMC:CdCl <sub>2</sub> (5:1)	6.083 E <sup>-7</sup>	7.518 E <sup>-7</sup>	1.149 E <sup>-6</sup>	1.216 E <sup>-6</sup>	0.21	0.16
HPMC: CdCl <sub>2</sub> (5:2)	8.412 E <sup>-7</sup>	9.860 E <sup>-7</sup>	1.443 E <sup>-6</sup>	1.647 E <sup>-6</sup>	0.18	0.15
HPMC: CdCl <sub>2</sub> (5:3)	1.091 E <sup>-6</sup>	1.369 E <sup>-6</sup>	2.154 E <sup>-6</sup>	2.251 E <sup>-6</sup>	0.14	0.12
HPMC: CdCl <sub>2</sub> (5:4)	1.483 E <sup>-6</sup>	1.693 E <sup>-6</sup>	2.688 E <sup>-6</sup>	2.977 E <sup>-6</sup>	0.12	0.10

The radiation-induced dc electrical change could in principle, be used as a measure of gamma ray absorbed dose. This induced dc electrical conductivity ( $\sigma$ ) is carefully studied in the dose range up to 100 kGy and in the temperature range of 313 – 383 K. The variation of  $\log \sigma$  on 1/T for the unirradiated and irradiated pure and doped HPMC films with different concentrations of CdCl<sub>2</sub> ( 1, 2, 3 and 4 wt %) were studied. Figure 4 shows the temperature dependent dc conductivity for the pure and HPMC:CdCl<sub>2</sub> systems before and after gamma irradiation at 20, 60, and 100 kGy. The temperature dependence of electrical conductivity ( $\sigma$ ) follows Arrhenius Eq.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (3)$$

Where  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy,  $K$  is the Boltzmann constant and  $T$  is absolute temperature. From the plots of Fig 4 for unirradiated samples, 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:CdCl<sub>2</sub> polymer electrolyte films. Whereas for the plots of irradiated samples from Figs 4a, 4b and 4c, the dc conductivity increases as the temperature and gamma dose increases. However, the HPMC:CdCl<sub>2</sub> samples

irradiated at 20 kGy shows a slight decrease in electrical conductivity when compared with samples irradiated with 100 kGy at higher temperatures. Hence it is observed that the induced changes in electrical conductivity are dose-dependent and can be attributed to the creation of induced charge carriers in the HPMC polymer matrix at different concentrations of the doping salt. This dependence of the dc conductivity on the gamma dose might be explained as follows. At the beginning, increase in gamma dose would result in an increase in the number of charge carriers created. This increasing number of carriers will continue to take place as gamma dose increases until we approach a situation at which most of the possible charge carriers are already created. After this threshold dose limit, we might expect no more increase in the dc conductivity, and a saturation limit might be achieved. The increase in conductivity at high temperature may be accounted for by the liberation of electrons or ions through the amorphous region of HPMC, and/or, probably, the internal stresses in the doped sample may also play a role in the motion of charge carriers [23].

The increase in conductivity with increasing the salt concentration 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 the polymer. This decrease in the degree of crystallinity and increase in the amorphousity 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 favors the hopping interchain and intrachain ion movements hence the conductivity of the polymer electrolytes become high. The dc conductivity data for unirradiated and 20, 100 kGy irradiated HPMC and HPMC:CdCl<sub>2</sub> complexes are listed in Tables 5, 6, and 7. The data shows that the carrier concentration increases with increase in gamma irradiation. This is because the effect of ionizing gamma irradiation on polymer is to rupture chemical bonds and create energetic free electrons, ions, and radicals, which are able to migrate through the network. Further, the irradiation was carried out in air, and, hence, the formed gaseous ions around the films may produce space charge in the surface of the samples leading to a change in electrical conductivity [24]. Such a variable response to gamma irradiation could be accounted for, by its relatively high Cadmium content. The properties of the amorphous phase obviously play a major role in determining the overall response of the material [25-26]. Figure 4 reveals that the conductivity does not show any abrupt change with the temperature, indicating that the electrolyte exhibits amorphous nature. The activation energy  $E_a$  is a combination of defect formation and defect migration, which can be calculated from the slopes of linear fit of Arrhenius plots of  $\log \sigma$  versus  $1000/T$  using expression

$$E_a = \text{Slope} \times 2K \quad (4)$$

Where  $E_a$  is the activation energy (eV), K is the Boltzmann constant.

The activation energies evaluated for the unirradiated and 20, 100 kGy irradiated samples are listed in Tables 5, 6, 7. It is obvious that from Figure 5, the values of the activation energy vary as a function of the absorbed dose. They decrease with increasing gamma dose and CdCl<sub>2</sub> salt concentration for each particular sample. Therefore, it can be suggested that the value of  $E_a$  is due to the energy that is required to provide a conductive condition for the migration of ions. The activation energies in the two regions (region-I and region II) show a decreasing trend as the dopant concentration increases confirming the increase in amorphous nature of polymer electrolyte. This may be explained in terms of formation of charge transfer complexes. However, the electrical conductivity for different concentrations of CdCl<sub>2</sub> doped HPMC in regions I and II, Cadmium ions are coordinated through ionic bonds with the hydroxyl group belonging to the different chains in HPMC. This, in turn, reduces the intermolecular interaction between chains and expands the space between them. In other words, the addition of cadmium increases the volume required for ionic carriers drift in the polymer. This leads to an increase in the ionic mobility and a reduction in the activation energy. This is in complete accordance with the observed results from the graph also this is in good agreement with the earlier reported results [12] and indicates the low activation energy for CdCl<sub>2</sub> ion transport is due to dominant presence of amorphous nature of polymer electrolyte that facilitates the fast Cd<sup>2+</sup> ion motion in polymer network. In addition, gamma irradiation seems capable to make some sort of variation in the amorphous regions reflecting a change in the structure of HPMC:CdCl<sub>2</sub> system. The amorphous nature also provides a bigger free volume in polymer electrolyte system with the increase in temperature. It is observed that HPMC:CdCl<sub>2</sub> (5:4) system has highest conductivity and low activation energy region when compared with pure and other complexes of HPMC.

#### IV. Conclusion

The complexation of the salt with the host polymer before and after irradiation is confirmed by XRD studies. XRD study shows the percentage of crystallinity decreases with the increasing concentration of CdCl<sub>2</sub> salt and gamma dose. For pure HPMC, a slight increase in crystallinity is observed at low radiation dose (20 kGy), whereas crystallinity decreases at higher doses. This may be due to the cross linking of the polymer chain or by the formation of the single or multiple helices, which induces more crystalline region in the polymer

samples. In HPMC:CdCl<sub>2</sub> polymer electrolyte systems the presence of CdCl<sub>2</sub> prevent polymer chain reorganization resulting in decreased crystallinity compared to pure HPMC. Hence it may be mentioned that during irradiation, the energy deposited in the polymer causes chain scission or produce radicals which subsequently decay or cross-link with neighboring radicals, i.e. both chain scission and cross-linking occur during irradiation. SEM analysis of unirradiated, films shows a uniform type but with different degrees of roughness and exhibits no features attributable to any crystalline morphology. It is observed that during irradiation, pure HPMC shows porous structure with well dispersed pores for low doses at 20 kGy. On the other hand, at 60 kGy, the porous structure is disrupted possibly due to recrystallization of the polymer. Whereas for HPMC:CdCl<sub>2</sub> system shows surface full of small cavities and the loosely bound rod-like structures due to irradiation effects at higher doses (60, 100 kGy). This may be due to the rapid penetration of cadmium ions into the polymer matrix at higher doses. Considerable damage in the polymeric structure was observed during irradiation, which is also responsible for decrease in the crystallinity of the material.

DSC results revealed that the presence of CdCl<sub>2</sub> in the polymer matrix increases the melting temperature in unirradiated films, on the other hand this broad endothermic melting peaks decreases in both pure as well as in complexed polymer films during irradiation. However it was found that the heat of fusion ( $\Delta H_f$ ) is high for pristine HPMC films compared with the CdCl<sub>2</sub> complexed films, before and after irradiation.

The increase in conductivity with the increasing temperature, salt concentration and the radiation dose is attributed to the decrease in the degree of crystallinity and the simultaneous increase in amorphousity. This is because the effect of ionizing gamma irradiation on polymer is to rupture chemical bonds and create energetic free electrons, ions, and radicals, which are able to migrate through the network, leading to a change in electrical conductivity. Also the hopping mechanism of ion movement as ions primarily transport in amorphous phase. The activation energy values obtained from conductivity data for the regions (region-I and region-II) decreases in both unirradiated and irradiated systems as the ionic conductivity increases which confirms the conduction in these polymer electrolytes is predominantly ionic. Therefore this material established a new polymer electrolyte system. The HPMC:CdCl<sub>2</sub> (5:4) system before and after irradiation increases the amorphous phase and enhances the conductivity. Thus the polymer electrolyte systems HPMC: CdCl<sub>2</sub> with an enhanced amorphous phase and conductivity requires further investigation for electrochemical cell device application.

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