

Microstructural Parameters in Electron-Irradiated Hydroxypropyl Methylcellulose Films Using X-Ray Line Profile Analysis

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ABSTRACT: The changes in microstructural parameters in hydroxypropyl methylcellulose (HPMC) polymer films irradiated with 8 MeV electron beam have been studied using wide-angle X-ray scattering (WAXS) method. The crystal imperfection parameters such as crystal size $\langle N \rangle$, lattice strain (g in %), and enthalpy (α^*) have been determined by line profile analysis (LPA) using Fourier method of Warren. Exponential, Lognormal, and Reinhold functions for the column length distributions have been used for the

determination of these parameters. The goodness of the fit and the consistency of these results suggest that the exponential distribution gives much better results, even though lognormal distribution has been widely used to estimate the similar stacking faults in metal oxide compounds. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3983–3990, 2008

Key words: irradiation; WAXS; crystal imperfection parameters; crystal size

INTRODUCTION

Hydroxypropyl methylcellulose (HPMC) is a widely used cellulosic film-forming agent for conventional tablet film coatings.¹ HPMC polymer coatings are known to be hard, but brittle, which can lead to poor coating performance. Usually, pharmaceutical tablets are coated for various reasons such as taste, odor masking, and esthetic enhancement, modification of drug release and for stability improvement. To attain the desired properties from tablet coatings, polymer-based film coatings have become the preferred one. To prevent chipping and breaking of the tablet coating during production and handling, coating films must be durable. Damage to the tablets coating not only impacts the tablet esthetics, but can also compromise product performance. To see the changes in HPMC films, we irradiated the polymer films with different doses.

When polymers are exposed to ionizing radiation, they undergo modification and degradation. On the microscopic level, the polymer degradation is characterized by macromolecular chain splitting, creation of low mass fragments, production of free radicals, oxidation, and crosslinking. These affect the macro-

scopic properties such as mechanical strength, color, electrical conductivity, and so on.^{2,3} Several workers have investigated the effect of electron irradiation on polymers with a view to improve the performance of polymers and to induce a phase transition in certain materials.^{4,5}

However, the changes in crystal imperfect parameters such as crystallite size ($\langle N \rangle$) and lattice strain (g in %) in man-made polymer like HPMC have not been studied so far. Hence, in this work, we have carried out X-ray analysis on EB-irradiated polymer films to determine the microstructural parameters from the intensity profile of a fairly clear X-ray reflection. Fortunately, coherent X-ray scattering inside a material is a nondestructive tool adequate for determining the relative order of the constituent atoms or molecules in crystalline, semicrystalline, or amorphous materials. For this purpose, we have used Warren's Fourier method. This Warren and Averbach^{6–8} theory using the Fourier coefficients of the intensity profile, Somashekar et al.⁹ and Hall and Somashekar¹⁰ have considered various aspects of multiple and single-order methods, and a suitable method has been proposed. Somashekar et al. have extended the single-profile method to man-made polymers.^{11–14} Information obtained from crystallite size and lattice strain analysis can be related to a particular treatment of the materials. Here, we have irradiated polymer film samples with electron beam

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of various doses. Line profile analysis (LPA) of Bragg reflections from such irradiated samples is therefore useful for research, development, quality control, and also for understanding the physical, mechanical, and chemical properties, which is strongly related to the microstructural constituent of the material. Here, we have used three asymmetric functions to find out the one, which gives a better fit with the experimental profile, and to arrive at consistent microstructural parameters such as crystal size, lattice strain, and BG values in films.

EXPERIMENTAL

Sample preparation

The HPMC used in this work were obtained in powder form from Ms. S.D. Fine Chemicals Ltd, Mumbai, and it has approximate molecular weight 200,000 Da. The HPMC films were prepared by the casting method as follows.¹⁵ HPMC powder was dissolved in distilled water and then heated gently with a water bath for complete dissolution. The solution was left to reach a suitable viscosity, after which they were cast into glass dishes and left to dry in a dry atmosphere at room temperature. Samples were transferred to a desiccator to avoid moisture. The thickness of the obtained films was 0.06 mm. The samples were subjected to various integral doses, which were accumulated in steps, in which the irradiation doses were conducted at 0, 25, 50, 75, and 100 kGy.

Electron-beam irradiation of samples

Irradiation of polymer films were done at Microtron Center, Mangalore University, using the electron beam (by lanthanum hexa fluorite source). The monochromatic beam is made to fall on samples kept at particular distance and the following beam features:

1. Beam energy, 8 MeV;
2. Beam current, 20 mA;
3. Pulse repetition rate, 50 Hz;
4. Pulse width, 2.2 μ s;
5. Distance source to sample, 30 cm;
6. Time of exposure, 25 min;
7. Dose range, 0–100 kGy;
8. Atmosphere, air;
9. Temperature, 27°C.

The dose delivered to different samples is measured by keeping alanine dosimeter with sample during irradiation.

X-ray diffraction measurements

XRD diffractograms of the polymer samples were recorded using a Bruker D8 Advance X-ray diffrac-

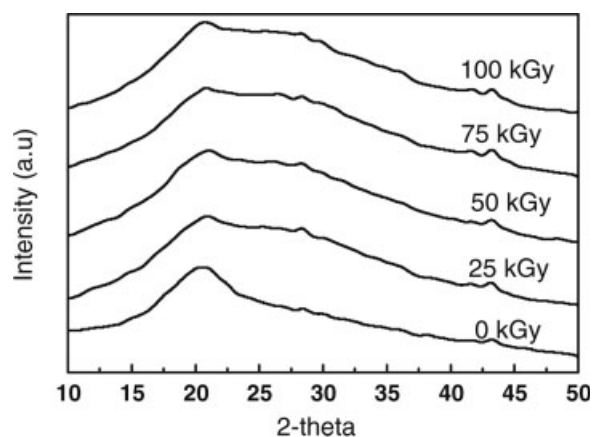


Figure 1 XRD scans of pure and 8 MeV electron irradiated polymer samples.

tometer with Ni-filtered Cu $K\alpha$ radiation of wavelength $\lambda = 1.5406$ Å, with a graphite monochromator. The scattered beam was focused on a detector. The specifications used for the recordings were 40 kV, 30 mA. The samples were scanned in the 2θ range 10° – 50° with a scanning speed and step size of $1^\circ/\text{min}$ and 0.01° , respectively and scans are given in Figure 1.

Theory

Microstructural parameters such as crystal size ($\langle N \rangle$) and lattice strain (g in %) are usually determined by using Fourier method of Warren and Averbach^{6,7} and Warren.⁸ The intensity of a profile in the direction joining the origin to the center of the reflection can be expanded in terms of Fourier cosine series;

$$I(s) = \sum_{n=-\infty}^{\infty} A(n) \cos\{2\pi nd(s - s_0)\} \quad (1)$$

where the coefficients of the harmonics $A(n)$ are functions of the size of the crystallite and the disorder of the lattice. Here, s is $\sin(\theta)/(\lambda)$, s_0 being the value of s at the peak of a profile, n is the harmonic order of coefficient, and d is the lattice spacing. The Fourier coefficients can be expressed as

$$A(n) = A_s(n)A_d(n) \quad (2)$$

For a paracrystalline material, $A_d(n)$ can be obtained with Gaussian strain distribution,¹⁰

$$A_d(n) = \exp\left(-2\pi^2 m^2 n g^2\right) \quad (3)$$

where m is the order of the reflection and $g = (\Delta d/d)$ is the lattice strain. Normally, one also defines mean square strain $\langle \varepsilon^2 \rangle$, which is given by g^2/n . This mean square strain is dependent on n , whereas

not g .^{16,17} For a probability distribution of column lengths $P(i)$, we have

$$A_s(n) = 1 - \frac{nd}{D} - \frac{d}{D} \left[\int_0^n iP(n)di - n \int_0^n P(i)di \right] \quad (4)$$

where $D = \langle N \rangle d_{hkl}$ is the crystallite size and i is the number of unit cells in a column. In the presence of two orders of reflections from the same set of Bragg planes, Warren and Averbach^{6,7} have shown a method of obtaining the crystal size ($\langle N \rangle$) and lattice strain (g in %). But, in polymer, it is very rare to find multiple reflections. So, to determine the finer details of microstructure, we approximate the size profile by simple analytical function for $P(i)$ by considering only the asymmetric functions. Another advantage of this method is that the distribution function differs along different directions. Whereas, a single-size distribution function that is used for the whole pattern fitting may be inadequate to describe polymer diffraction patterns.¹⁶⁻¹⁸ Here, it is emphasized that the Fourier method of profile analysis (single-order method used here) is quite reliable one as per the recent survey and results of Round Robin test conducted by IUCr.¹⁹ In fact, for refinement, we have also considered the effect of background by introducing a parameter [see, for details, regarding the effect of background on the microcrystalline parameters⁹].

The exponential distribution

It is assumed that there are no columns containing fewer than p unit cells and those with more decay exponentially. Thus, we have²⁰

$$P(i) = \begin{cases} 0 & \text{if } p < i \\ \alpha \exp\{-\alpha(i-p)\} & \text{if } p \geq i \end{cases} \quad (5)$$

where $\alpha = 1/(N-p)$. Substituting this in eq. (4), we get

$$A_s(n) = \begin{cases} A(0)(1 - n/\langle N \rangle) & \text{if } n \leq p \\ A(0)\{\exp[-\alpha(n-p)]\}/(\alpha N) & \text{if } n \geq p \end{cases} \quad (6)$$

where α is the width of the distribution function, i is the number of unit cells in a column, n is the harmonic number, p is the smallest number of unit cells in a column and $\langle N \rangle$, the number of unit cells counted in a direction perpendicular to the (hkl) Bragg plane.

The Lognormal distribution

The Lognormal distribution function is given by

$$P(i) = \frac{1}{(2\pi)^{1/2}} \frac{1}{\sigma i} \exp\left\{-\frac{[\log(i/m)]^2}{2\sigma^2}\right\} \quad (7)$$

where σ is the variance and m is the median of the distribution function.

Substituting for $P(i)$ in eq. (4) and simplifying (5), we get

$$A_s(n) = \frac{m^3 \exp[(9/4)(2^{1/2}\sigma)^2]}{3} \operatorname{erfc}\left[\frac{\log(|n|/m)}{2^{1/2}\sigma} - \frac{3}{2}2^{1/2}\sigma\right] - \frac{m^2 \exp(2^{1/2}\sigma)^2}{2} |n| \operatorname{erfc}\left[\frac{\log(|n|/m)}{2^{1/2}\sigma} - 2^{1/2}\sigma\right] + \frac{|n|^3}{6} \operatorname{erfc}\left[\frac{\log(|n|/m)}{2^{1/2}\sigma}\right] \quad (8)$$

The above equation is the one used by Ribarik et al.¹⁶ The maximal value $A_s(0)$ is given by

$$A_s(0) = \frac{2m^3 \exp[(9/4)(2^{1/2}\sigma)^2]}{3} \quad (9)$$

The area-weighted number of unit cells in a column is given by

$$\langle N \rangle_{\text{surf}} = \frac{2m \exp[(5/4)(2^{1/2}\sigma)^2]}{3} \quad (10)$$

and the volume-weighted number of unit cell in a column is given by

$$\langle N \rangle_{\text{vol}} = \frac{3m \exp[(7/4)(2^{1/2}\sigma)^2]}{4} \quad (11)$$

The Reinhold distribution

With the exponential distribution function, $P(i)$ rises discontinuously at p , from zero to its maximum value. In contrast, the Reinhold function allows a continuous change by putting,

$$P(i) = \begin{cases} 0 & \text{if } i \leq p \\ \beta^2(i-p) \exp\{-\beta(i-p)\} & \text{if } i > p \end{cases} \quad (12)$$

where $\beta = \frac{2}{N-p}$ substituting these in eq. (4), we obtain

$$A_s(n) = \begin{cases} A(0)(1 - n/\langle N \rangle) & \text{if } n \leq p \\ [A(0)(n-p+2/\beta)/N]\{\exp[-\beta(n-p)]\} & \text{if } n \geq p \end{cases} \quad (13)$$

where β is the width of the distribution, which has been varied to fit the experimental results. p is the smallest number of unit cells in a column, $\langle N \rangle$ is the number of unit cells counted in a direction perpendicular to the (hkl) Bragg plane, d is the spacing of the (hkl) planes, λ is the wavelength of X-rays used, I is the number of unit cells in a column, n is the harmonic number, and D_s is the surface weighted crystal size ($\langle N \rangle d_{hkl}$).

TABLE I
Microstructural Parameters of Electron-Irradiated Polymer Samples Computed by Various Distribution Functions

Sample (kGy)	Exponential					Reinhold					Lognormal				
	$\langle N \rangle$	g (%)	α^*	D_s	δ	$\langle N \rangle$	g (%)	α^*	D_s	δ	$\langle N \rangle$	g (%)	α^*	D_s	δ
0	4.10 ± 0.09	0.5 ± 0.01	0.010	17.66	0.024	4.07 ± 0.11	0.5 ± 0.01	0.010	17.53	0.026	4.38 ± 0.18	0.5 ± 0.02	0.022	18.87	0.040
25	7.16 ± 0.34	0.4 ± 0.02	0.011	30.41	0.048	7.13 ± 0.38	0.3 ± 0.02	0.010	30.28	0.053	7.75 ± 0.54	0.3 ± 0.02	0.023	32.91	0.070
50	6.48 ± 0.34	0.5 ± 0.03	0.013	27.26	0.053	6.30 ± 0.36	0.5 ± 0.03	0.013	26.50	0.058	7.66 ± 0.68	0.1 ± 0.01	0.008	32.22	0.090
75	7.63 ± 0.67	0.2 ± 0.02	0.006	32.56	0.088	7.65 ± 0.70	0.3 ± 0.03	0.010	32.64	0.092	8.25 ± 0.74	0.5 ± 0.05	0.041	35.20	0.090
100	6.63 ± 0.31	0.5 ± 0.02	0.013	28.43	0.047	6.55 ± 0.33	0.5 ± 0.03	0.013	28.08	0.050	7.89 ± 0.63	0.5 ± 0.04	0.039	33.82	0.080

All the distribution functions were put to test to find out the most suitable crystal size distribution function for the profile analysis of the X-ray diffraction. The procedure adopted for the computation of the parameters is as follows. Initial values of g and N were obtained using the method of Nandi et al.²¹ With these values in the equations give numbers earlier give the corresponding values for the width of distribution. These are only rough estimates, so that the refinement procedure must be sufficiently robust to start with such values. Here, we compute

$$\Delta^2 = [I_{\text{cal}} - (I_{\text{exp}} + \text{BG})]^2 / \text{npt} \quad (14)$$

where BG represents the error in the background estimation, npt is number of data points in a profile, I_{cal} is intensity calculated using eqs. (1)–(13), and I_{exp} is the experimental intensity. The values of Δ were divided by half the maximum value of intensity, so that it is expressed relative to the mean value of intensities and then minimized.

X-ray profile analysis

For the analysis, we have used X-ray diffraction data in the above equations to simulate the intensity profile by varying the necessary parameters till one gets a good fit with the experimental profile. For this purpose, a multidimensional algorithm SIMPLEX is used for minimization.²² We have used pure and 8 MeV electron beam-irradiated HPMC polymer samples. The computed crystal imperfection parameters along with reported physical parameters are given in Table I for different distribution functions for each of the samples.

RESULTS AND DISCUSSION

Figures 2(a–e), 3(a–e), and 4(a–e) show the comparison between simulated and experimental profiles for 8 MeV electron-irradiated and pure polymer films for Bragg's reflection. The simulated profile was obtained with the above equations using appropriate model parameters. This procedure was followed for all the other samples treated at different radiation doses for polymer samples. The computed microcrystalline parameters such as crystallite size (number of unit cells) $\langle N \rangle$, lattice strain g in %, the width of the crystallite size distribution (α), and the standard deviation are given in Table I. It is evident from Table I that all the asymmetric distributions used give more or less similar results. By and large, exponential distribution function gives a better fit than Reinhold/Lognormal distributions. Here, we emphasize that the standard deviation in all the cases for the microstructural parameters are given in

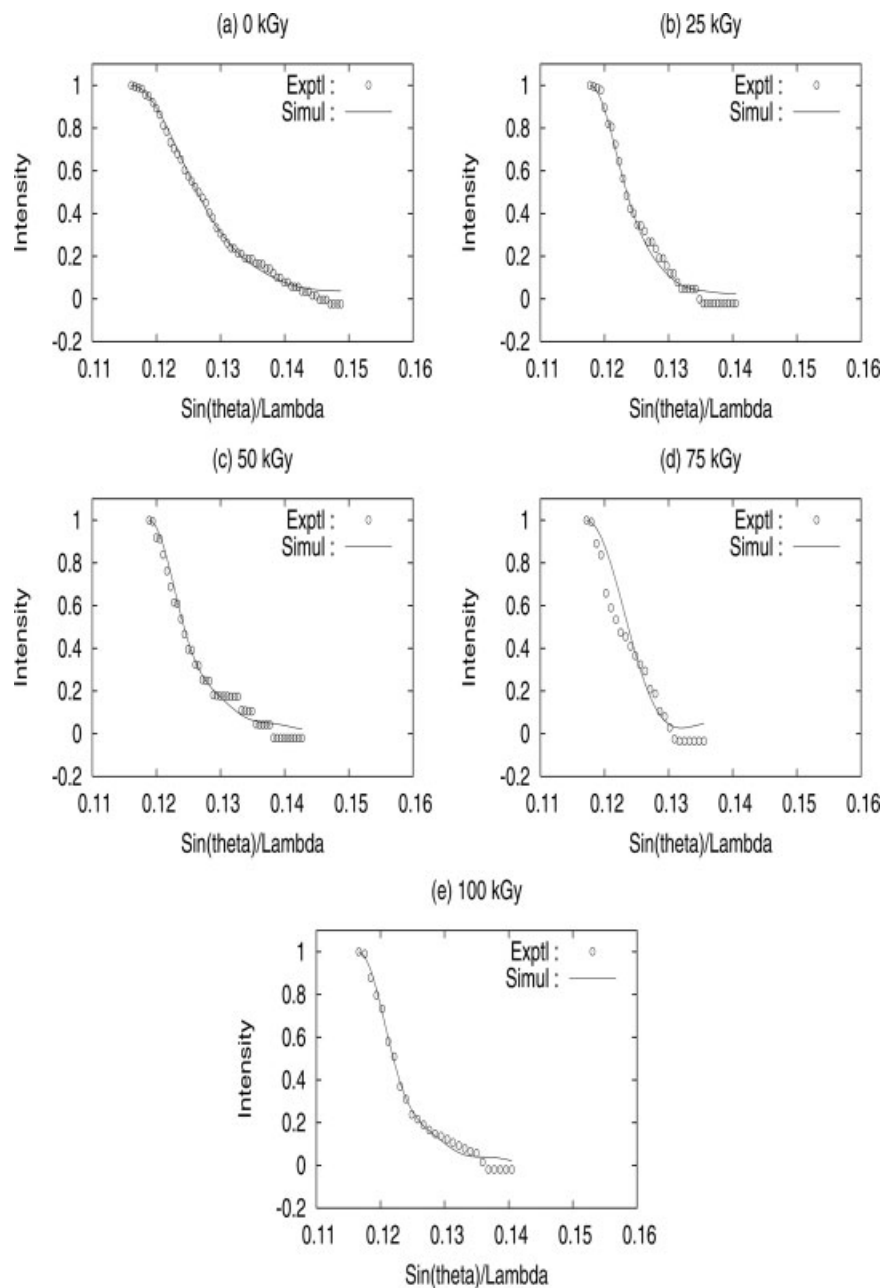


Figure 2 (a–e) Experimental and simulated intensity profiles of X-ray reflection of polymer films obtained with exponential column length distribution function.

Table I as delta. Because exponential distribution function gives a better fit than others, we used the corresponding results given in Table I to infer some important conclusions. From Table I, three important features are to be noted. They are

- i. the value of the surface weighted crystal size D_s is more for electron irradiated polymer films compared to pure polymer film;
- ii. the value of the crystal size is more for electron irradiated polymer films;
- iii. the value of crystallinity is more for unirradiated polymer.

Irradiation of polymers mainly causes two important changes. (1) Degradation of the polymer, whereby main-chain scission takes place, leading to low molecular weight polymer. (2) Cross-linking of small polymer units leading to the formation of a rigid three-dimensional network, whereby a high molecular weight polymer is produced. Both these effects cause changes in physical properties. Degra-

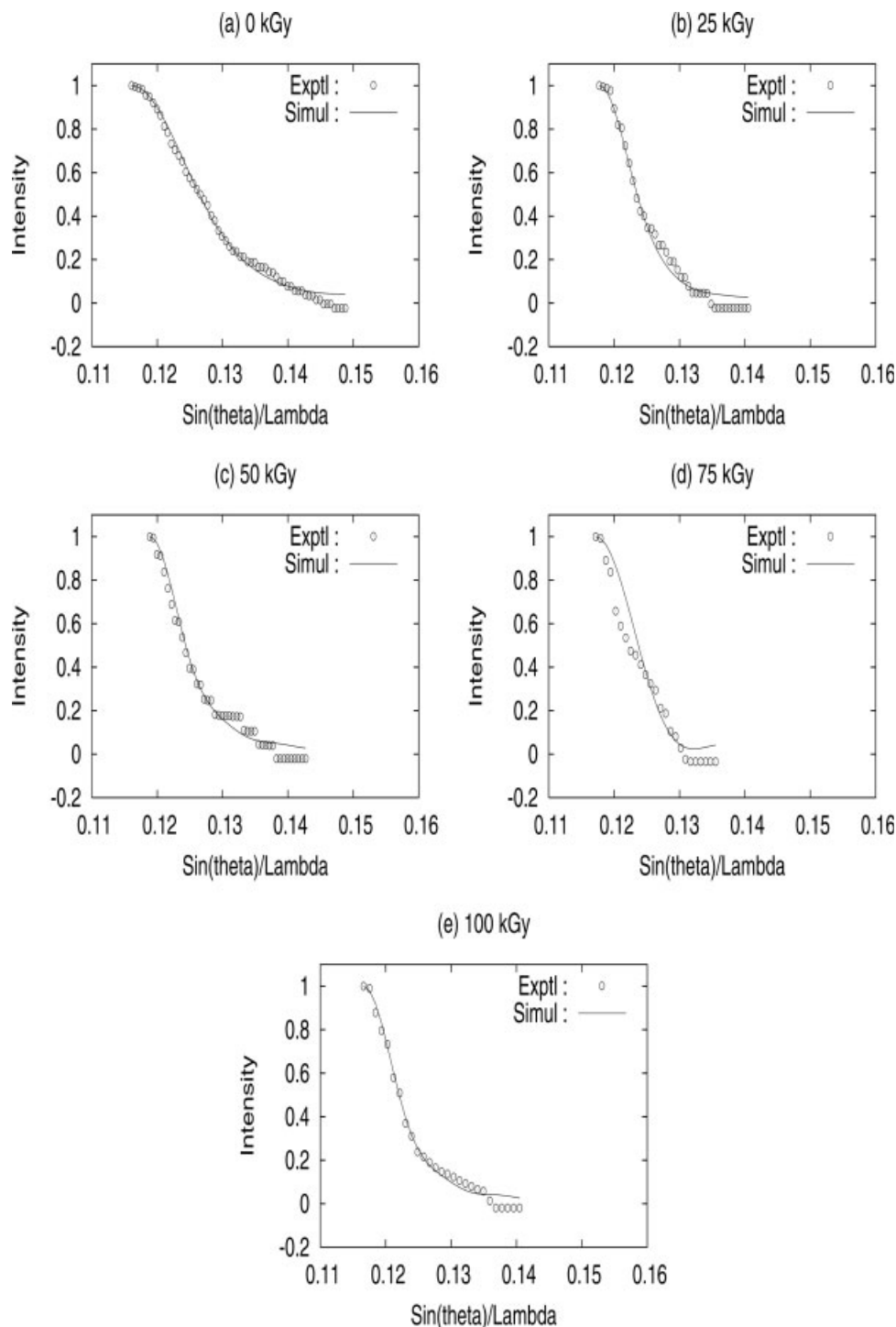


Figure 3 (a–e) Experimental and simulated intensity profiles of X-ray reflection of polymer films obtained with Reinhold column length distribution function.

dation of polymer leads to loss in mechanical strength, whereas cross-linking improves the physical properties. From Table I, it is evident that the crystallite size increases as irradiation dose increases. Normally, the strength of films, irrespective of whether they are natural or not, increases with increase in crystal size values.²³ This aspect suggest that the 75 kGy integral dose irradiated polymer

films is the better one. In this polymer, our results clearly state that changes observed is due to crosslinking.

Crosslinking is the intermolecular bond formation of polymer chain, the degree of crosslinking is proportional to the radiation dose.²⁴ It has been said in the field of radiation chemistry that the crosslinking proceeds in the amorphous area and does not pro-

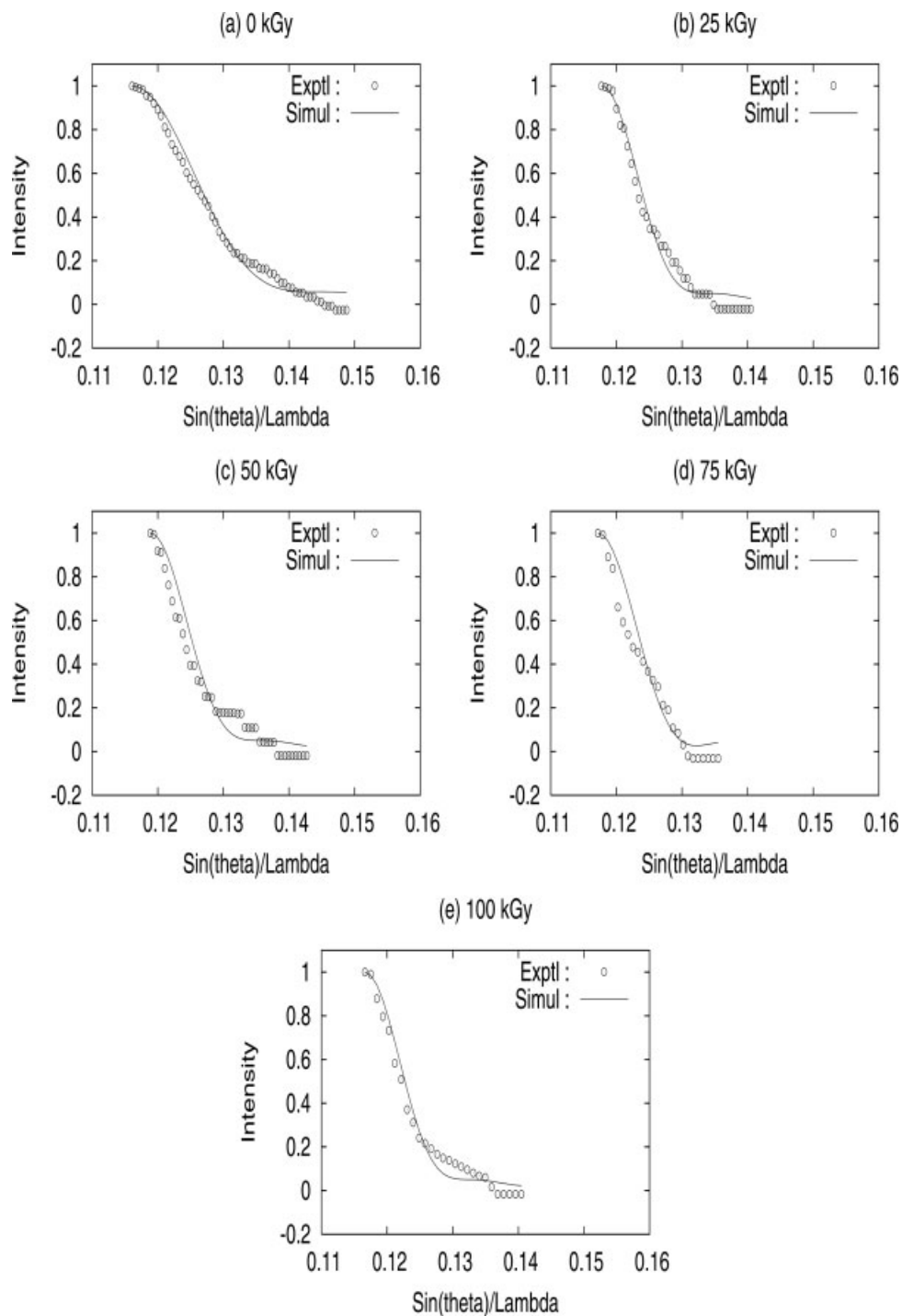


Figure 4 (a–e) Experimental and simulated intensity profiles of X-ray reflection of polymer films obtained with Lognormal column length distribution function.

ceed in crystalline area. From Table II, it is clear that crystallinity of the polymer decreases as irradiation dose increases. Because the molecular motion of the polymer chain is regulated in the crystalline area, the radicals generated in crystalline area cannot encounter with other radicals to crosslink by recombination reaction. On the other hand, in the amorphous area, the radicals can encounter each other to

make crosslinking reactions by micro-Brownian molecular motion of polymer chain. Based on this idea, it is expected that the crystallinity of polymer decreases.

The variation of lattice strain (g) lies between 0.2 and 0.5% in the case of exponential distribution for polymer films. From the obtained microcrystalline parameters ($\langle N \rangle$, g in %), one can estimate the min-

TABLE II
Position of the Most Intense Peak (2 θ), Crystallinity for the Unirradiated and EB-Irradiated HPMC Films

Dose (kGy)	2 θ (°)	<i>d</i> spacing (Å)	Crystallinity (%)
0	20.60	4.3073	42.14
25	20.93	4.2411	26.59
50	21.07	4.2134	24.56
75	20.84	4.2583	20.67
100	20.74	4.2793	19.20

imum enthalpy (α^*), which defines the equilibrium state of microparacrystals in all the polymer films, using the relation postulated by Hosemann²⁵

$$\alpha^* = (\langle N \rangle^{1/2} g) \quad (15)$$

The estimated minimum enthalpy is given in Table I. It is noted here that the value of α^* lies between 0.006 and 0.013 for these films. The value of enthalpy decreases with increasing dose rate, which corresponds to the state with lower ordered polymer network. We have observed that the lattice strain and its variation for various values of the radiation doses (kGy) in polymer films are very small and are almost insignificant. It is evident from Table I that the crystallite size increases with increase in radiation dose rate and reaches a maximum. With further increase in radiation dose rate, the crystal size decreases.

CONCLUSIONS

From the wide-angle X-ray scattering (WAXS) study of electron-irradiated HPMC polymer films, we have observed that even though there is not much change in the position of the X-ray reflections, a significant change in the values of microstructural parameters occurs. The significant change in microstructural parameters in polymer is due to irradiation. This causes the crosslinking of small polymer units leading to the formation of a rigid three-dimensional network. And it is also observed that the crystallinity of the polymer decreases as irradiation dose increases. We have shown that among the three asymmetric crystallite size distributions, exponential gives a better fit in polymer films. The only justification for the good fit that we observed with exponential distribution in these polymers can be interpreted on the basis of extensive usage of this function in condensed matter to explain various phenomenons such as dielectric relaxation, luminescence decay law, and other physical properties. Single-order method that we have used here is capable of estimating both the size and the distortion parameters and could in gen-

eral measure crystallite size, only unto a certain limit. The changes in polymer network with different dose rates are quantified here in terms of microstructural parameters. Our study indicates that electron-irradiated polymer samples have higher values of crystallite size than pure sample. Surprisingly, we observed that the intrinsic strains are very small. It is evident from this study that irradiation of polymer films changes the polymer network and hence the physical properties, leading to a better quality polymer films, depending on the nature of application.

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