

Studies on Morphological Parameters, Radius of Gyration, Correlation Length and Invariant of HPMC Polymer Doped with Ferrous (II) Oxide Using SAXS Method

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ABSTRACT

It shed light on morphological parameters which influence radius of gyration, correlation length and invariant of Hydroxy Propyl Methyl Cellulose (HPMC) polymer doped with ferrous (II) oxide (FeO) using small angle X-ray scattering (SAXS) method. SAXS patterns have been recorded for different composition and gives an information about the structure of the polymer on a scale of about 800Å, in which the variation of scattered intensity with angles from 0° to 2.5° has been measured for different composition of FeO with host polymer of HPMC. Employing para-crystalline model and exponential distribution function of phase lengths (amorphous and crystalline), we find a good agreement between the measured and predicted scattering except for a very small range of angles on the low angle side of the peak intensity. The method enabled quantitative parameters describing morphology of the two phases, amorphous and crystalline, consistent with the SAXS intensity distribution. A stepping procedure has been employed to compute the final parameters which gave the best fit between the calculated and experimental data. This was done by minimizing the statistical goodness-of-fit parameter chi-square. It is observed that there are significant changes in distribution of phase lengths due to different percentage weight of FeO in HPMC contents. Additionally,

SAXS data has been used to estimate (i) radius of gyration (R_g), (ii) correlation length (L_{cor}) and (iii) invariant (Q) parameters. A functional representation of the long period and also radius of gyration at different dopant concentrations is adopted by viewing them as realizations of a continuous-time stochastic process observed with measurement error. This allows one to estimate the mean functional relationship between long period and the dopant concentration.

Keywords: Morphological parameters, HPMC, Ferrous oxide, SAXS method, Phase lengths, Radius of gyration

INTRODUCTION

Conducting polymers are a class of materials that conduct without being heated. The era of conducting polymers began with the invention of ionic conduction in Polyethylene based electrolyte in 1973 by Wright [1]. In recent years, there is an increased interest in the research activity in conducting polymers to bring out new materials which are suitable for electronics, opto-electronics, and electrical devices [2,3]. The use of polymers as conducting materials solves many problems such as cost, processability, leakage, power loss and fabrication, weight of the device, good mechanical properties, etc. [4]. Barring a few conducting polymers, majority of the polymers are non-conductors or having remarkably low conductivity. Blending two or three polymers to get a binary or ternary system or doping an inorganic salts or use of plasticizer, in the polymers and their blend matrix do change the conducting aspect of a polymer. This procedure inhibits more number of charge carriers and also provides a more flexible backbone for polymer network. Characterization of Hydroxy Propyl Methyl Cellulose (HPMC) and HPMC polymer blends has been carried out by Somashekarappa et al using WAXS technique [5]. HPMC is chosen in our study as a host polymer in the preparation of HPMC/FeO films, since not many reports of investigations are available using SAXS technique.

The results of the investigation do correlate AC conductivity, stability and microstructure details of these doped films do suggest that there are indeed interesting results with regard to conducting polymers in keeping view of other social obligations like polymer doped with inorganic salts are degradable and environmental friendly.

EXPERIMENTAL

Sample Preparation

HPMC was purchased from Loba chem, Mumbai and FeO samples were synthesized by solution combustion method. Pure and doped films were prepared by using solvent cast method [6,7]. HPMC (5%wt) was dissolved in 100 ml of distilled water with continuous stirring. After complete dissolution the solution was filtered using filter paper to remove un-dissolved particles. FeO of different (%wt) 0.01 g - 0.05 g was dissolved in distilled water, added to 100 ml of 5% HPMC solution and stirred continuously using magnetic stirrer for 20 minutes to ensure uniform mixing of the solutions in the polymer matrix. Solution was allowed for a while and then poured onto the clean glass plate and allowed to dry for a week. After drying, the films were peeled out of the glass plate and stored in desiccators to avoid moisture.

SAXS Recording

Small angle X-ray scattering (SAXS) recordings of the prepared samples were carried out along drawn axis using X-ray diffractometer with Ni filtered Cuka radiation of wavelength 1.5406Å, with a graphite monochromator. Samples were scanned in the 2θ range 0° - 2.5° with a step of 0.005° . Specifications used for the recording are 30 kV and 15 mA. SAXS pattern of pure and doped HPMC films contain both amorphous and crystalline region in the form of band and these SAXS profiles are given in Figure 1(a-f).

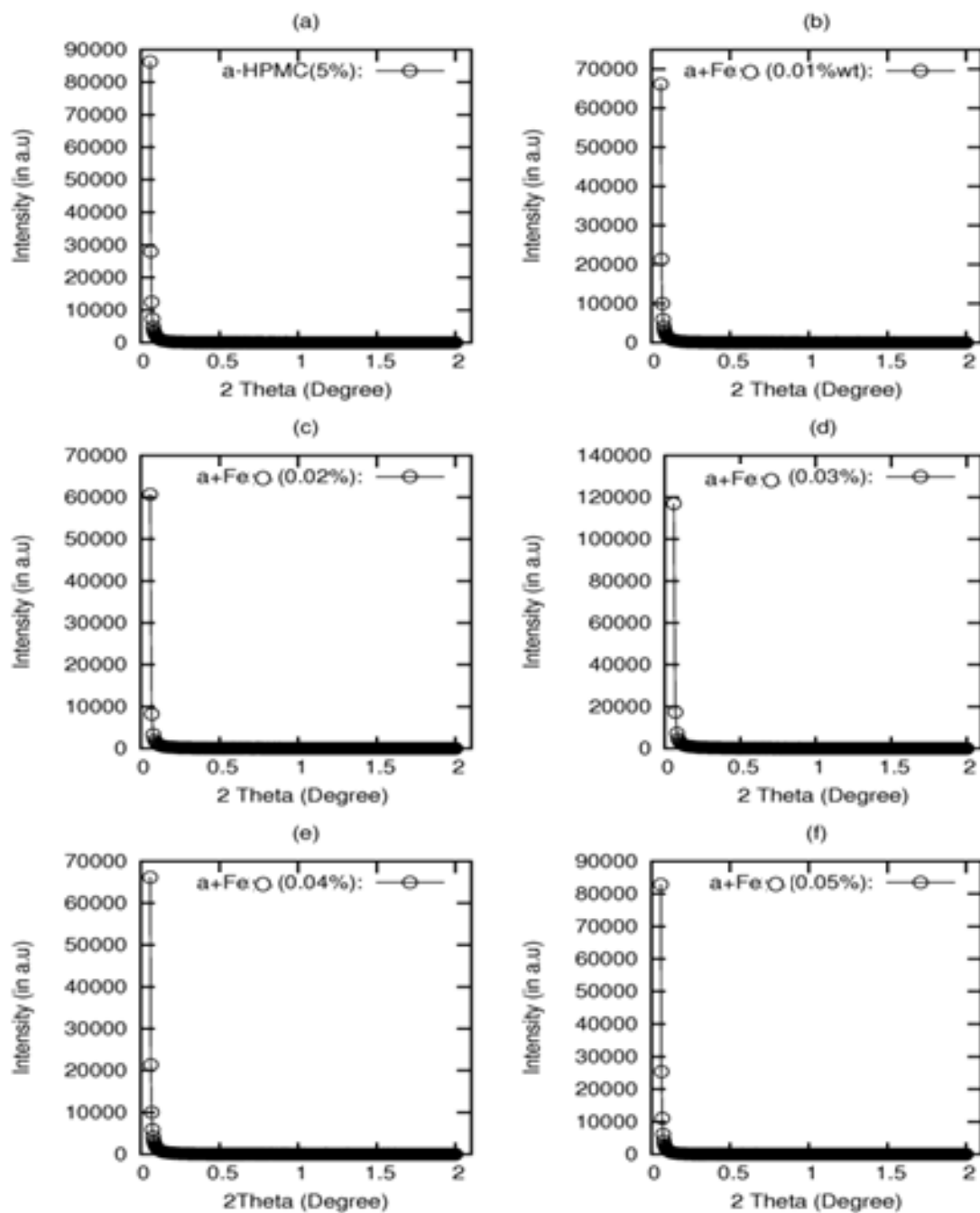


Figure 1: The SAXS profiles of Pure and FeO doped HPMC polymer (a) Pure HPMC (5%wt), (b) HPMC + FeO (0.01%wt), (c) HPMC + FeO (0.02%wt), (d) HPMC + FeO (0.03%wt), (e) HPMC + FeO (0.04%wt), (f) HPMC +FeO (0.05%wt). Data Analysis.

SAXS Data Analysis and Computation

Quasi-periodic alternation of electron density in cotton fibers has been investigated by SAXS studies [8,9]. It is now well established that the structure contains stacks in which crystalline lamellae are separated by less dense amorphous regions. Hosemann and Bachi [10] have obtained the following relations.

$$I_B(S) = \frac{\Delta\rho^2 N}{(2\pi S)^2} \left\{ \frac{|1 - H_Y|^2(1 - |J_Z|^2) + |1 - J_Z|^2(1 - |H_Y|^2)}{|1 - H_Y J_Z|^2} \right\}$$

(1a)

$$I_C(S) = \frac{\Delta\rho^2}{2(\pi S)^2} \Re \left\{ \frac{J_Z(1 - H_Y)^2(1 - (H_Y J_Z)^N)}{(1 - H_Y J_Z)^2} \right\} \quad (1b)$$

$$I_S = I_B(S) + I_C(S) \quad (1c)$$

I(S) is the intensity of scattering by one paracrystal entity as a function of S ($= \frac{2\sin\theta}{\lambda}$) where 2θ is the scattering angle and λ is the wavelength of the radiation. (H_Y, J_Z) are the Fourier transforms of the normalized distributions of the lengths of the units of the two phases. N is the number of repeating units in the paracrystal, and Δρ is the difference between the electron densities of the phases.

In this approach, Equation (1) has been developed into a form which is easier to compute the two phase lengths in polymer composites [18,19] in terms of exponential distribution function.

It has been shown by Hall et al. [10,11] that Equation (1) can be reduced to

$$\frac{2I(\pi s)^2}{\Delta\rho^2} = \frac{C}{F} + \frac{D+E}{F^2} \quad (2a)$$

$$\text{Where } F = 1 + A^2 B^2 - 2AB \cos X \quad (2b)$$

$$C = N\{1 - A^2 B^2 - A(1 - B^2)\cos\phi - B(1 - A^2)\cos\chi\} \quad (2c)$$

$$D = \frac{B(1 - A^2)(1 - A^2 B^2)\sin X \sin\phi + \{(1 + A^2 B^2)\cos X - 2AB\}}{G}$$

$$E = \frac{\{(1 + A^2)\cos\phi - 2A\}}{G} \quad (2d)$$

$$G = 1 - A^N B^N \cos NX \quad (2e)$$

$$E = A^N B^{N+1} \sin NX \{ (1 - A^2 B^2) \{ (1 + A^2) \cos\phi - 2A \} \sin X (1 - A^2) \{ (1 + A^2 B^2) \cos X - 2AB \} \sin\phi \} \quad (2f)$$

Equation 2(a-d)) has been obtained by taking

$$H_Y = A \exp(-i\chi) \quad (3a)$$

$$J_Z = B \exp(-i\phi) \quad (3b)$$

$$\text{and } X = \chi + \phi \quad (3c)$$

Where X is the distribution width. We have used the exponential distribution function for the phase lengths [12,13,18,19]. The normalized function is given by

$$h(x) = \alpha \exp(-\alpha(X - \varepsilon)) \quad (4)$$

Where $\alpha = \frac{1}{2\gamma\langle Y \rangle}$; $\varepsilon = \langle Y \rangle (1 - 2\gamma)$. γ is a parameter controlling both the skew and the dispersion of distribution provided 0 < γ < 0.5, lengths less than ε are not possible, as this would cause h(x) to be negative. By taking the Fourier transform of this function, we get

$$A = \frac{1}{(1 + 4\gamma^2\langle Y \rangle^2 S^2)^{\frac{1}{2}}} \quad (5)$$

$$\chi = S\varepsilon_Y + \cos^{-1} \left\{ \frac{1}{(1 + 4\gamma^2\langle Y \rangle^2 S^2)^{\frac{1}{2}}} \right\} \quad (6)$$

Similarly

$$B = \frac{1}{(1 + 4\gamma^2\langle Z \rangle^2 S^2)^{\frac{1}{2}}} \quad (7)$$

$$\phi = S\varepsilon_Z + \cos^{-1} \left\{ \frac{1}{(1 + 4\gamma^2\langle Z \rangle^2 S^2)^{\frac{1}{2}}} \right\} \quad (8)$$

Thus with the exponential distribution function for each phase, we have A, B, χ and φ which can be used in Equation (2) and the intensity can be calculated as a function of S using the parameters describing the distribution. Here suffixes y and z refer to the two phases present in the polymer composites.

Radius of gyration (R_g) is defined as the root mean square of the distances of all the electrons (particles) from the electronic center of gravity of the representative molecule [14] and can be estimated using Guinier's plot of $\log_{10} I(s)$ versus S^2 . From the slope, one can compute the radius of gyration using the relation.

$$R_g = \frac{1}{2\pi} \sqrt{3 \times 2.303 \times \text{slope}} \quad (9)$$

This procedure was repeated for different composition of FeO with host polymer of HPMC. Invariant (Q) is defined as the second moment of the SAXS curve. The invariant can be computed using expression.

$$Q = \int_0^\infty I(q) q^2 dq \quad (10)$$

The Q values obtained for different composition of FeO with host polymer of HPMC. Correlation length (L_{cor}) is the mean width of the correlation function which is computed by taking the Fourier transform of the given SAXS curve. For the scattering along the meridional direction is given by

$$I(s) = \frac{KL_{cor}^2}{(1+4\pi^2L_{cor}^2s^2)} \quad (11)$$

The correlation length is determined from the slope and intercept (K) of a plot of $I(s)^{-1}$ versus s^2 for obtained values for different composition of FeO with host polymer of HPMC.

Estimates of Mean Function and Correlation Surface

The mean function is estimated by first pooling together all available measurements $[\theta_{ij}, t_{ij}]$ for $i=1, \dots, n$ and $j=1; \dots; n_i$. Noting that this implies a borrowing of information from within and across samples or preparations, we can use (t_{ij}) . The covariance surface is estimated by taking pair wise products of θ_{ij} and $\mu(t_{ij})$. Once the estimate of the covariance has been obtained, estimates of the eigenfunctions $[\varphi_k, t_{ij}]$, functional principal scores (A_k) and eigenvalues (λ_k) are computed leading to the required prediction of θ_{ij} . The procedures to estimate the eigenfunctions, eigen values, functional principal component scores (FPC) are technically involved and can be referred to [15,16] Equation which gives the predicted behavior of θ_{ij} , as a function of t for i 'th sample is

$$\hat{\theta}_i(t) = \mu(t) + \sum_{k=1}^K \hat{A}_{ik} \varphi_k(t) \quad (12)$$

Where the infinite sum has been truncated to an appropriate

finite constant K.

RESULTS AND DISCUSSION

The best fit between the experimental and simulated profile was obtained with an exponential distribution function for all the samples is as shown in Figure 2(a-f). A fit to the experimental data is observed for a range of scattering angles (2θ) between 0.006° and 0.16° . The normalized exponential probability distribution functions of phase lengths (crystalline and amorphous) for this model shown in Figure 3, are obtained from the model parameters given in Table 1 and employing equation (4) for the two phases Y and Z. The results displayed in Figures 3(a) and 3(b) demonstrate corresponding changes in the distribution of phase lengths along the drawn axis of different composition of FeO with host polymer of HPMC. From Table 1, it is evident that the phase length (amorphous ($\langle Y \rangle$)) perpendicular to the drawn axis, there is decrease of increasing trend and for the crystalline length ($\langle Z \rangle$), there is increase of decreasing trend due to change in volume fraction of the crystalline lamellae and also the change in electron density contrast between the crystalline and amorphous regions [17] for different composition of FeO with host polymer of HPMC. A simple explanation for such a behavior is due to breaking of inter- and intra- weak hydrogen bonds, which results in polymer network which favors more ordered pockets in a polymer matrix. Further physical studies are required to correlate these micro-structural changes in different composition of FeO with host polymer of HPMC. Several parameters pertaining to the amorphous phase and the long period of the fiber were derived from the modeling of the SAXS data.

Table1. Values of morphological parameters for different composition of FeO with host polymer of HPMC using SAXS data.

| Sample | Periodicity in Å | Phase ratio | $\langle Y \rangle$ | $\langle Z \rangle$ | $\langle Y \rangle$ | $\langle Z \rangle$ | $\langle \chi^2 \rangle$ |
|--------------------|------------------|-------------|---------------------|---------------------|---------------------|---------------------|--------------------------|
| HPMC (5%wt) | 1541.0 | 0.462 | 0.069 | 0.105 | 716.18 | 835.54 | 3.019 |
| HPMC+ FeO(0.01%wt) | 1591.0 | 0.460 | 0.075 | 0.115 | 731.86 | 859.14 | 2.593 |
| HPMC+ FeO(0.02%wt) | 1331.3 | 0.443 | 0.024 | 0.044 | 590.33 | 741.00 | 10 |
| HPMC+ FeO(0.03%wt) | 1595.0 | 0.430 | 0.0365 | 0.235 | 686.28 | 909.72 | 0.401 |
| HPMC+ FeO(0.04%wt) | 1507.0 | 0.450 | 0.079 | 0.099 | 678.15 | 828.65 | 7.678 |
| HPMC+ FeO(0.05%wt) | 1500.0 | 0.460 | 0.055 | 0.090 | 690.00 | 810.00 | 6.325 |

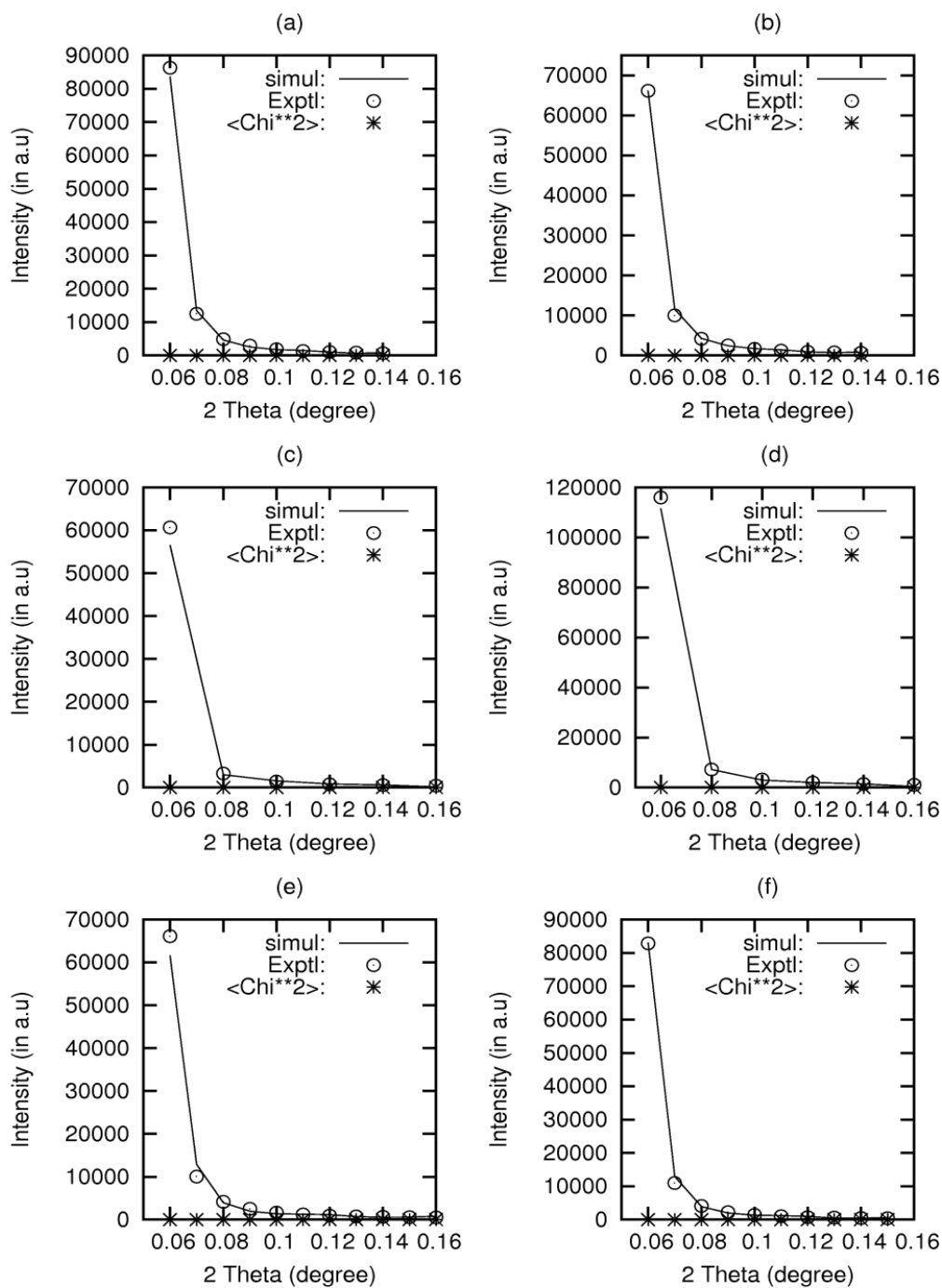


Figure 2: The experimental and simulated SAXS profiles of Pure and FeO doped HPMC polymer (a) Pure HPMC (5%wt), (b) HPMC + FeO (0.01%wt), (c) HPMC + FeO (0.02%wt), (d) HPMC + FeO (0.03%wt), (e) HPMC + FeO (0.04%wt), (f) HPMC +FeO(0.05%wt).

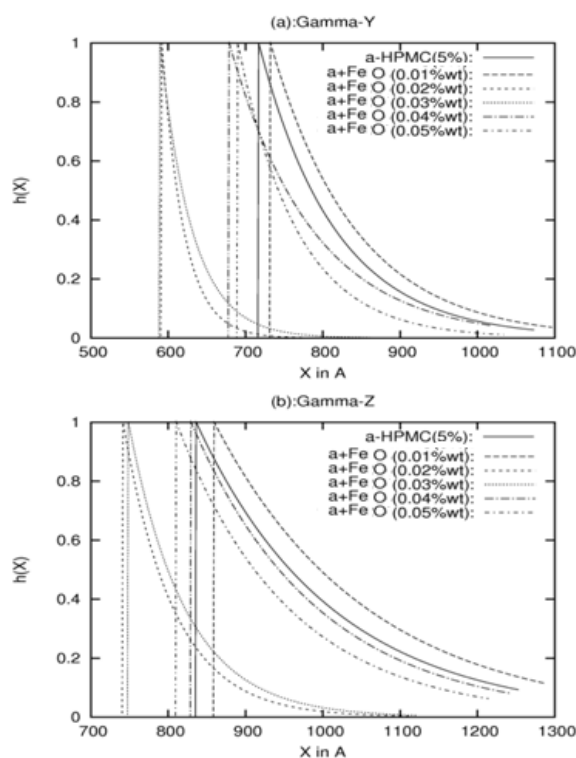


Figure 3: The normalized Exponential distribution functions of the lengths of the phases (crystalline and amorphous) belonging to HPMC with FeO of different composition.

The results suggest that the amorphous phase of the fibers is influenced by the composition of FeO with host polymer of HPMC than the lamellar structure itself. Further the treatment of different composition of FeO with HPMC conditions with increase in percentage of weight of FeO. The composition were adapted to those conditions, they are probably too low to cause further considerable changes in the two phases fibrillar structure. Within the treatment levels used, only the highest changes the long period significantly, but there is slight significant difference in the crystallinity (0.02) according to the treatment conditions. For further study these SAXS

profiles have been used for the analysis in order to compute the radius of gyration (R_g), the invariant (Q) [18-21] and correlation length (L_{cor}) [22].

We observe that the values of radius of gyration varies from 166 to 237 Å for different composition of FeO with host polymer of HPMC are given in Table 2 and the change in radius of gyration value along the drawn axis due to localized breaking of polymer network [23]. Kratky [24] has reported a value of 75 Å for a dried silk sample which is very low compared to our values.

Table 2: Values of radius of gyration (R_g), correlation length (L_{cor}) and invariant (Q) for different composition of FeO with host polymer of HPMC.

| Sample | R_g in Å | L_{cor} in Å | Q in Å ⁻² |
|--------------------|----------------|----------------|--------------------------|
| HPMC (5%wt) | 169.36 ± 4.5% | 58.58 | 6.791 × 10 ⁻⁴ |
| HPMC+ FeO(0.01%wt) | 167.20 ± 4.6% | 44.92 | 6.791 × 10 ⁻⁴ |
| HPMC+ FeO(0.02%wt) | 237.17 ± 5.2% | 41.18 | 6.791 × 10 ⁻⁴ |
| HPMC+ FeO(0.03%wt) | 229.80 ± 4.3% | 79.38 | 6.791 × 10 ⁻⁴ |
| HPMC+ FeO(0.04%wt) | 166.70 ± 4.3% | 44.92 | 6.791 × 10 ⁻⁴ |
| HPMC+ FeO(0.05%wt) | 166.81 ± 0.62% | 56.26 | 6.791 × 10 ⁻⁴ |

The correlation length for different composition of FeO with host polymer of HPMC varies from 41.18 to 79.38Å and it is given in Table 2. Also, the invariant is of the order of 11 in silk fiber as reported by Kratky in his paper. These results of Kratky are obtained with a small angle x-ray recording which occurs in the range 65 to 75Å and they do mention that there are maxima observed at higher resolution of the order 500 to 600Å. Here we have carried out our analysis in the range of 1500Å region and hence we observe higher values for radius of gyration and almost same range of values for the invariant.

On the other hand, correlation length for different composition of FeO with host polymer of HPMC varies from 41.18 to 79.38Å. These values are pretty low compared to the approximate estimation of correlation length of 200 nm by Miller et al [22] in fibers along axial direction. They also mentioned that there are very large uncertainties in the determination of correlation lengths. But direct Atomic Force Microscopy (AFM) measurements show that the crystals are within 100 Å or less in fibers and are in agreement with our results reported here. In fact these are believed to give rise to the power law scattering in the SAXS experiments.

Figure 1(a-f) indicates that with same value in 'Q' the invariant, there is an increase in the values of radius of gyration up to FeO (0.02%wt) and then decreases up to FeO(0.05%wt). This is due to change in volume fraction of the crystalline lamellae and also the change in electron density contrast between the crystalline and amorphous regions [17] for different

composition of FeO with host polymer of HPMC. This is in agreement with the observed increase in lamellar value for nylon6, 6 [25].

Functional Analysis Result

We report, in detail, the results and plots obtained for the long periodicity of crystalline and amorphous areas. Computations were performed using the FPCA package (written in MATLAB: The MathWorks Inc., Natick, MA, USA) available at <http://www.stat.ucdavis.edu/PACE/>.

We observe from Figure 4(a) that long periodicity typically decreases with increase in dopant concentration. The mean function has been estimated by solving the optimization problem given in equation (6) of Reference [16] by combining measurements across samples. Figure 4(b) shows a screen plot, which plots the percentage of variance in the measurement values of crystallite area (as a function of dopant concentration) that can be explained by the varying number of eigenfunctions used in the expansion. The plot suggests that only two principal components or eigenfunctions of the auto covariance operator are needed; this is shown in Figure 4(c), which is a plot of the two estimated eigenfunctions. From this we can infer that, since approximately 93% of the variation is expressed in the first two eigenfunctions, the functional relationship between crystallite area and dopant concentration is mostly linear.

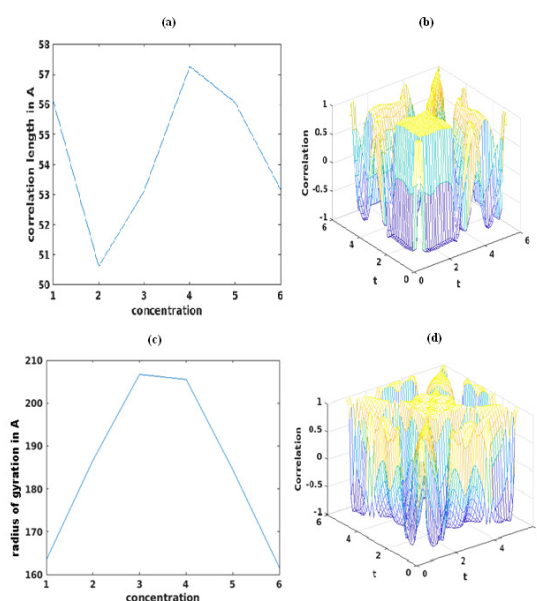


Figure 4: a) Correlation between long periodicity with concentration, (b) mean value determined by stochastic process for long periodicity, (c) Correlation between radius of gyration with concentration and (d) mean value of radius of gyration computed by stochastic process for FeO HPMC composites.

CONCLUSION

The simulated SAXS patterns from a Hosemann's paracrystalline model for different composition of FeO with host polymer of HPMC agree very well with the experimental data. The changes in the morphological parameters are due to the breaking of inter- and intra-weak hydrogen bonds, which results in a polymer network that favors more ordered pockets in a polymer matrix belonging to different composition of FeO with host polymer of HPMC. The changes also observed in amorphous and crystalline lengths within HPMC with different composition of FeO arises not only due to organizational changes of the structures along the length of the meridional direction, but also due to unfolding of the molecular chains [26]. This agreement is well supported for the variation of radius of gyration and correlation length along the drawn axis due to localized breaking of polymer network. Functional analysis does confirm that there is a correlation between the long periodicity and concentration of iron particles in these polymer composites.

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