

Radial distribution function of natural fibres and synthetic water soluble polymers using X-ray diffraction

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Radial distribution functions for few natural polymers like silk, cotton, and synthetic water soluble polymers like polyvinyl alcohol, hydroxy propyl methylcellulose and carboxy methyl cellulose have been studied using their X-ray diffraction data. It is observed that the radial distribution function for the polymers of the same family gives same correlation function, showing that the pair correlation or the radial molecular arrangement between the nearest neighbors in these polymers are same, irrespective of their nature and existence. The detailed report of radial distribution functions of polymers is briefly explained in this study and the comparison between the samples belonging to the same family is carried out on the basis of inter-molecular interactions. The microstructural parameters like crystallite size and lattice strain are also computed for all the samples using W-H plot method. The crystallite sizes obtained for these polymers are compared and then interpreted with the obtained pair correlation functions. It is observed that the natural fibres show higher correlation function than synthetic polymers studied in comparison, this is due to ordered arrangement of molecules which are found only in some pockets of a general amorphous regions of natural polymers. The standard method of computation of pair correlation value using X-ray data is also given here.

Keywords: Cotton, Microstructural parameters, Natural polymers, Pair correlation, Silk, X-Ray diffraction

1 Introduction

Characterization of polymers using X-Ray diffraction technique is extensively used and many such related works have been reported since past two decades¹⁻³. One such prominent characterization is deriving the structure of few cotton and silk fibres, and also reporting the microstructural parameters⁴. Recently the synthetic water soluble polymers have attracted our interest for developing a good conducting polymer. We have prepared many water soluble polymer composites till date⁵⁻⁷ and reported structure and physical properties of polymers and polymer blends. With an interest of investigating the nature of interaction between nearest neighbors between polymer chains, a standard in-house algorithm has been developed to obtain pair correlation function as a function of distance from a reference point where X-rays interact with the polymer sample. Hence, an attempt has been made in this study to observe the changes in the radial distribution of molecules in these polymers. We have selected few wild silk samples and cotton fibres based on their availability. The water soluble films of poly vinyl alcohol (PVA), carboxy

methyl cellulose (CMC) and hydroxy propyl methyl cellulose (HPMC) were prepared separately by solution casting method and then used for their characterization.

The silk fibres, like Muga, Tassar and Eri, a type of wild silk fibre with a primary structure that is considerably different from that of mulberry silk fibroin were chosen for the study. Jayadhar and Sahana were the cotton fibres used which belong to family Malvaceae and genus *Gossypium*^{8,9}.

The pair correlation function, commonly known as radial distribution function, gives the density of the particles arranged from the centre or from the point of reference as a function of radial distance. Usually the pair correlation function $g(r)$ is used as the measure of structural arrangement of molecules in a condensed matter. With this concept we have also made an attempt in revealing the molecular arrangement in polymers. The X-ray diffraction data obtained for these polymers were used to calculate the radial distribution function by using an in-house program developed by us.

2 Materials and Methods

Natural polymer fibres such as silk and cotton were taken in their raw form and water soluble polymers like carboxy methyl cellulose (CMC), hydroxyl propyl methyl cellulose (HPMC) and polyvinyl alcohol (PVA)

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were drawn into thin films by solution casting method. The casted polymer films were taken in the sample holder of Rigaku-Denki miniflex II desktop X-Ray diffractometer with the settings of 30kV and 15mA, scanning rate of 5° per minute and for the range of 5°-40° with step size of 0.02°. The X-ray scans were recorded under this condition and the obtained results were taken for the further characterizations. If the crystallite size and strain broadening exist simultaneously then crystallite size and strain can be calculated by Williamson-Hall plot. For relative comparison of the parameters, W-H plot is reasonably reliable one¹⁰. The W-H plot considers both limited size of the crystals and the presence of crystallographic distortions which leads to Lorentzian intensity distributions. The slope of the W-H plot represents the average strain in the crystal, whereas intercept with the y-axis gives the average crystallite size. The Williamson-Hall relation is given by,

$$\beta \frac{\cos \theta}{\lambda} = \frac{1}{D} + 4\varepsilon \frac{\sin \theta}{\lambda} \quad \dots (1)$$

where β is the full width at half maximum (FWHM) of the peak measured in radians; D , the average crystallite size; and ε , the average lattice strain. We have computed the microstructural parameters using X-ray diffraction data with and without instrumental broadening corrections. For instrumental broadening corrections, we have used silicon as standard sample by employing Stoke's method¹¹. The crystallite size calculated is shown in Table 1 and the XRD profiles obtained are shown in Fig. 1.

2.1 Pair Correlation or Radial Distribution Function.

Radial distribution of materials can be obtained by Fourier transformation of the total structure factor that is measured in the X-Ray scattering equipments. The standard algorithm used to derive the pair correlation function is given below:

$$g(r) = 1 + \frac{1}{2\Pi^2 r \rho_0} \int_0^\infty Q [S(Q) - 1] \sin(Qr) dQ \quad \dots (2)$$

where ρ is the average number density of the sample; and Q , the scattering vector, as defined below:

$$Q = |k_f - k_i| = \frac{4\pi \sin \theta}{\lambda}; \quad \dots (3)$$

$S(Q)$, the structure factor; and $S(Q) \propto I(Q)$. In fact analysis of liquid and amorphous structures is often based on $g(r)$ ¹². An in-house program has been written to get the pair correlation function from the given X-ray powder patterns. Further the amplitude of the wave scattered by the sample [$\psi_s(\vec{Q})$] is given by summing the amplitude of scattering from each atom in the configuration^{13,14}, as shown below:

$$\psi_s(\vec{Q}) = \sum_{i=1}^N f_i \exp(-i\vec{Q} \cdot \vec{r}_i) \quad \dots (4)$$

where \vec{Q} is the scattering vector; \vec{r}_i , the position of atom i ; and f_i , the x-ray scattering form factor for the i^{th} atom. It is to be noted that for absolute information about the scatterer, we need the intensity data for

Table 1—Microstructural parameters calculated for natural fibres and water soluble polymers using W-H plot

Silk	Before broadening corrections		After broadening corrections	
	Average crystallite size, Å	Average crystallite strain, %	Average crystallite size, Å	Average crystallite strain, %
Natural fibres				
ERI	42.9 ± 4	(0.21 ± 0.02)	37.2 ± 3	(0.21 ± 0.02)
MUGA	120.4 ± 8	(2.9 ± 0.2)	107.7 ± 8	(4.62 ± 0.4)
TASSAR	35.9 ± 3	(0.66 ± 0.06)	32.2 ± 3	(0.7 ± 0.02)
JAYADHAR	47.2 ± 4	(0.45 ± 0.04)	39.2 ± 3	(1.14 ± 0.1)
SAHANA	39.6 ± 4	(1.12 ± 0.1)	31.2 ± 3	(2.96 ± 0.3)
Water soluble polymers				
CMC	24.9 ± 0.2	(0.8 ± 0.08)	24.2 ± 0.2	(1.5 ± 0.1)
HPMC	14.9 ± 0.1	(1.7 ± 0.1)	26.5 ± 0.2	(3 ± 0.3)
PVA	44.5 ± 0.4	(1.78 ± 0.2)	39.9 ± 0.4	(2.9 ± 0.3)

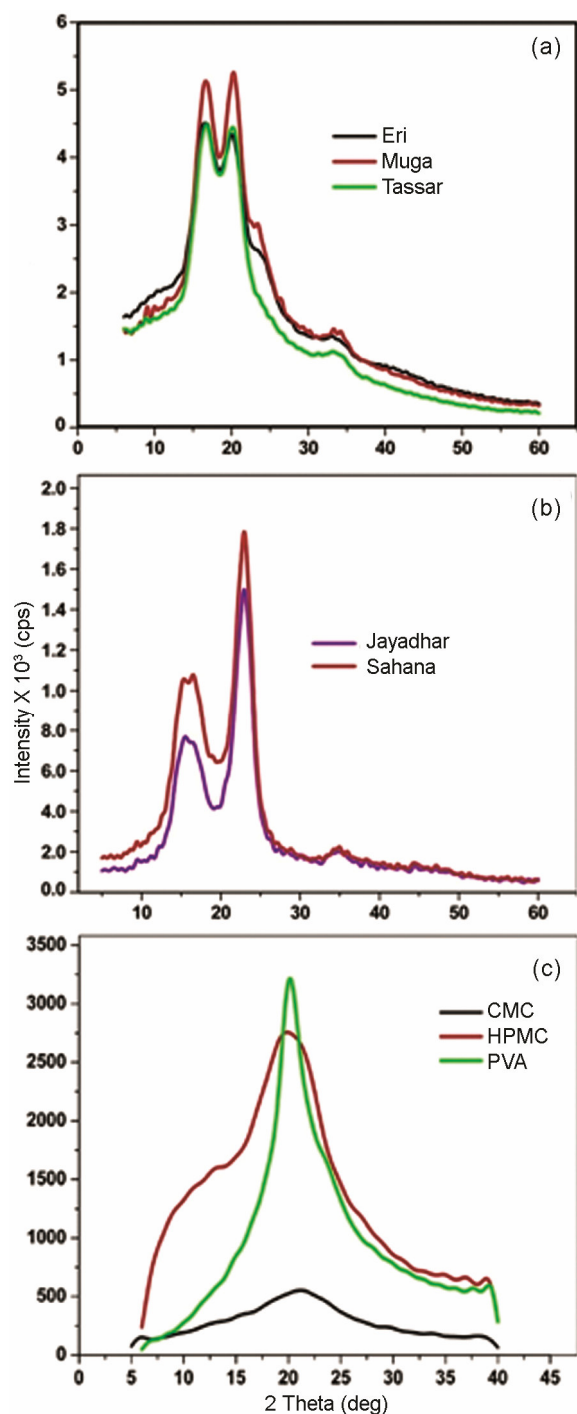


Fig. 1—Consolidated XRD plots of (a) silk, (b) cotton and (c) water soluble polymers

Q ranging from 0 to infinity. However, for a relative comparison between polymer derivatives, window function like information is good enough. Hence, we have carried out the pair correlation studies of polymer derivatives. Normalized pair correlation

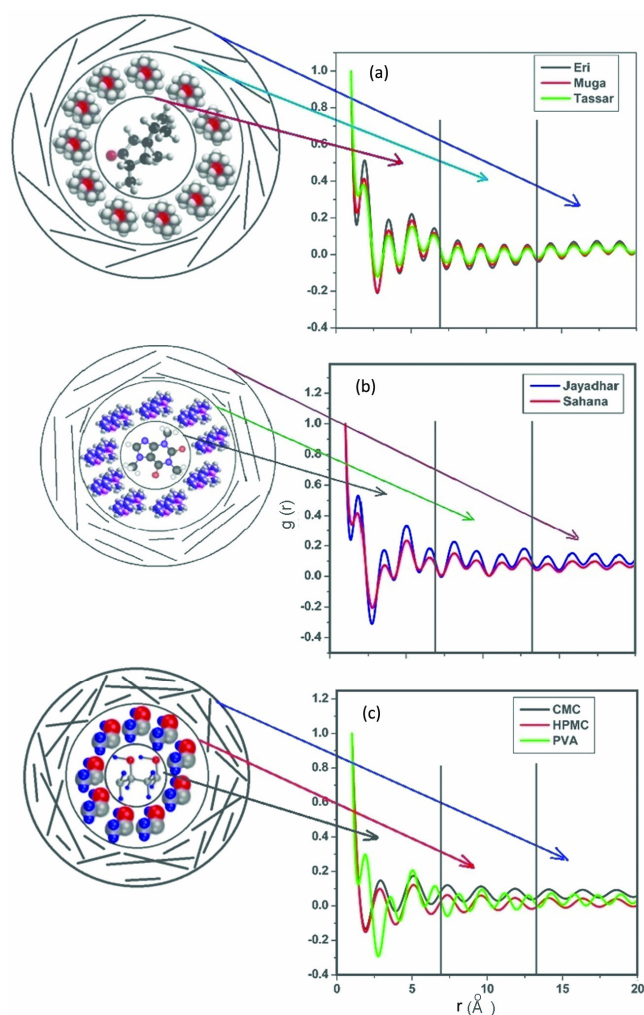


Fig. 2—Pair Correlation function obtained for (a) silk fibres, (b) cotton fibres and (c) water soluble polymers.

function obtained for these polymers are shown in Fig. 2. The average crystallite size derived by employing W-H plot method and the pair correlation are reported briefly.

3 Results and Discussion

Normalized pair correlation function obtained for natural silks shows that the correlation between chains in Eri is higher in the region of 2 \AA and drops off at larger distances from a reference point. Normally for perfect crystalline materials the correlation exists even beyond 10 \AA regions. This clearly indicates the reason for observing low crystalline like order in silks. A similar trend is observed in the case of cotton fibres wherein the correlation in Jayadhar is higher as compared to that in Sahana cotton fibres. The higher correlation indicates that the extent of ordering is

more in Jayadhar compared to that in Sahana cotton fibres. This is exactly what is observed in the computed microcrystalline parameters in Jayadhar being higher as compared to that in Sahana cotton fibres. We observe a significant behavior of correlation in the case of PVA wherein it is noted that the interaction exists even at distances of around 2\AA , whereas for CMC and HPMC, the interaction occurs for distance lying near 3\AA . This interaction drops off for distances beyond 7\AA for all polymers. This is the reason for observing higher crystallite size values in the case of PVA when compared to CMC and HPMC and also the reason for referring PVA as highly crystalline. This is supported by the crystallite sizes obtained for these polymers which are calculated by W-H plot method. The crystallite sizes obtained is shown in the Table 1.

4 Conclusion

The pair correlation function obtained for these samples shows that the correlation function obtained is same for the species of same family which is an outstanding result, as the radial arrangement of crystallites in these samples of same family do exhibit the same distribution but the changes occur only in the intensity of the distribution which is due to the variation in the crystallite size. Further, the nearest neighbor interaction is more in PVA, Eri silk and Jayadhar cotton compared to other respective polymers, which show more crystalline behavior. In fact, for all polymers studied here, the interaction drops

off for distances greater than 7\AA , showing that crystalline like order exists only in certain regions surrounded by amorphous like polymer network.

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