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Microstructural parameters in microwave (MW) irradiated hemp fiber using wide angle x-ray scattering study (WAXS)

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ABSTRACT

An experimental study was undertaken to investigate the effect of microwave (MW) heating on natural hemp fibers (NHF). The changes in microstructural parameters in these natural polymer fibers have been studied using wide angle X-ray scattering (WAXS) method. The crystal imperfection parameters such as crystallite 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.

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KEYWORDS

Microstructural parameters;
WAXS;
Hemp fiber.

INTRODUCTION

Natural hemp fiber (NHF) is a semicrystalline polymer (*Cannabis Sativa L.*). The NHF is one of the most important fibers, which has lignocellulosic used as a raw material for the manufacture of cost effective environmentally friendly composite materials. It is also one of the most important materials used in several industries, in particular textile industry^[1]. This natural polymer consists of Cellulose (70.2-74.4%), Hemicellulose (17.9-22.4%) and lignin (3.7-5.7%)^[2]. Cellulose the most abundant biopolymer on earth, is poly (β -1, 4, D anhydroglucopyranose), which through a regular network of inter and intramolecular hydrogen bonds is or-

ganized into perfect stereoregular configuration.

Natural cellulose fibers widely used are cotton fibers and bast fibers such as flax, hemp and kenaf. Natural cellulose fibers are replacing synthetic fibers in many applications due to their biodegradability, improved acoustics of products, higher processing and operational safety, higher strength and stiffness, lower weight and lower production cost^[3]. NHF have low density than the glass fibers with almost similar stiffness. This stiffness arises due to high crystallinity in the NHF^[4]. Lighter polymer materials can potentially be made with hemp fibers as an additional reinforcement^[5]. Natural cellulose based fibers are increasingly gaining attention as their application are diverse, a few of them used as

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building materials, and also as structural parts for motor vehicles.

Enormous work has been carried out and reported on the effect of various solvents on hemp fibers. NHF is used as a renewable source of hygienic and environmental friendly fibers^[6-8]. Recently thermal studies have been carried out on lignocellulosic fibers and fabrics^[9-11]. With appropriate composition of NHF in polymer materials, and by varying relevant quality parameters one can prepare blends appropriate to applications^[12]. For this purpose it is essential to have knowledge of micro crystalline parameters in NHF. The changes in crystal imperfection parameters like crystallite size $\langle N \rangle$, lattice strain (g in %) and enthalpy (α^*) and surface weighted crystallite size (D_s) in NHF have not been studied so far. Hence we have carried out X-ray line profile analysis (LPA) on NHF samples exposed to microwave (MW) irradiation for different time duration. These changes are correlated with other physical measurements, in this paper.

EXPERIMENTAL

Sample preparation

The raw material used in this study was NHF samples (*Cannabis Sativa L.*) taken from Gulbarga region of Karnataka state (India). The samples were made into small bundles and subjected to microwave (MW) irradiation for a given period of time, with the power of 800 Watt and frequency 2450 MHz.

X-Ray diffraction measurements

The XRD diffractograms of the NHF polymer samples were recorded using a Bruker D8 Advance X-ray diffractometer with Ni filtered, CuK α radiation of wavelength $\lambda = 1.5406 \text{ \AA}$, with a graphite monochromator. The scattered beam was focused on a detector. The specifications used for the recordings were 40kV, 30mA. The samples were scanned in the 2θ range 10-50° with a scanning speed and step size of 1°/min and 0.01° respectively.

Theory

Micro structural parameters such as crystal size ($\langle N \rangle$) and lattice strain (g in %) are usually determined by employing Fourier method of Warren and

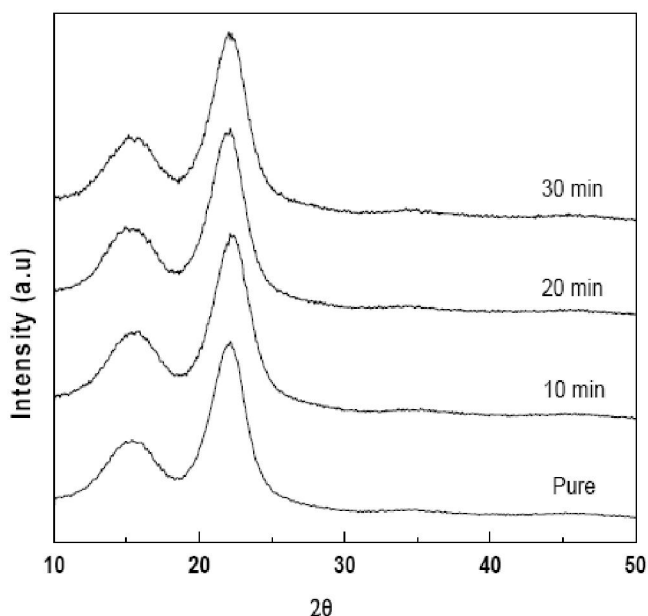


Figure 1 : X-ray diffractograms of hemp fibers

Averbach^[13,14], and Warren^[15]. 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;

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

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;

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

For a paracrystalline material, $A_d(n)$ can be obtained, with Gaussian strain distribution^[16],

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

Here, ' m ' is the order of the reflection and $g = (\Delta d/d)$ is the lattice strain. Normally one also defines mean square strain $\langle \epsilon^2 \rangle$, which is given by g^2/n . This mean square strain is dependent on n , whereas not g ^[17,18]. 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^[13,14] 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, which we feel, may be inadequate to describe polymer diffraction patterns^[17-19]. 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^[20]. 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 parameters^[21].

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 have^[22],

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

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

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

Here, 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;

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

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

Substituting for $P(i)$ in equation (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^[17]. 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 ($\langle N \rangle d_{\text{hkl}}$).

All the distribution functions were put to test in order to find out the most suitable crystal size distribution function for the profile analysis of the X-ray diffraction.

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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^[23]. With these values in the equations give numbers earlier give the corresponding values for the width of distribution. These are only rough estimates, so the refinement procedure must be sufficiently robust to start with such values. Here we compute;

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

where, BG represents the error in the background estimation, npt is number of data points in a profile, I_{cal} is intensity calculated using equations (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^[24]. We have used pure and Microwave (MW) irradiated NHF samples. The computed crystal imperfection parameters along with reported physical parameters are given in the TABLE 1 for different distribution functions for each of the samples.

TABLE 1 : Microstructural parameters of microwave (MW) irradiated polymer samples computed by various distribution functions.

Sample	Exponential					Reinhold					Lognormal				
	$\langle N \rangle$	g in %	α^*	D_s	delta	$\langle N \rangle$	g in %	α^*	D_s	delta	$\langle N \rangle$	g in %	α^*	D_s	delta
Pure	7.58±0.24	0.5±0.02	0.014	30.36	0.032	7.55±0.26	0.5±0.02	0.014	30.24	0.035	8.04±0.41	0.5±0.03	0.014	32.20	0.050
10 min	7.35±0.26	0.5±0.02	0.014	29.08	0.035	7.30±0.29	0.5±0.02	0.014	28.89	0.040	7.91±0.53	0.5±0.03	0.014	31.29	0.060
20 min	7.63±0.33	0.4±0.02	0.011	30.68	0.043	7.60±0.24	0.3±0.01	0.008	30.56	0.031	8.19±0.52	0.4±0.02	0.011	32.93	0.060
30 min	7.62±0.67	0.5±0.03	0.012	30.26	0.049	7.56±0.23	0.5±0.02	0.014	30.02	0.037	8.17±0.43	0.5±0.03	0.014	32.44	0.050

RESULTS AND DISCUSSION

Figures 2(a-d), 3(a-d) and 4(a-d) show the comparison between simulated and experimental profiles for Microwave (MW) irradiated and pure NHF polymer samples for clear 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 heated at different time duration. 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), surface weighted crystallite size (D_s) are given in TABLE 1. It is evident from TABLE 1 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 TABLE 1 as delta.

From the TABLE 1, it is clear that the crystallite size $\langle N \rangle$ is 7.58, and surface weighted crystallite size

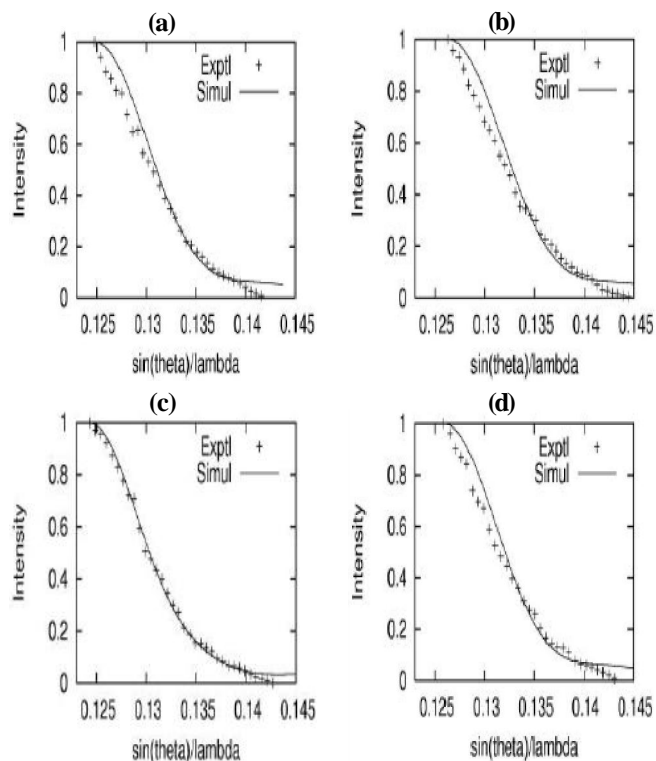


Figure 2 : (a-d) Experimental and simulated intensity profiles of x-ray reflection of hemp polymer fibers obtained with exponential column length distribution function.

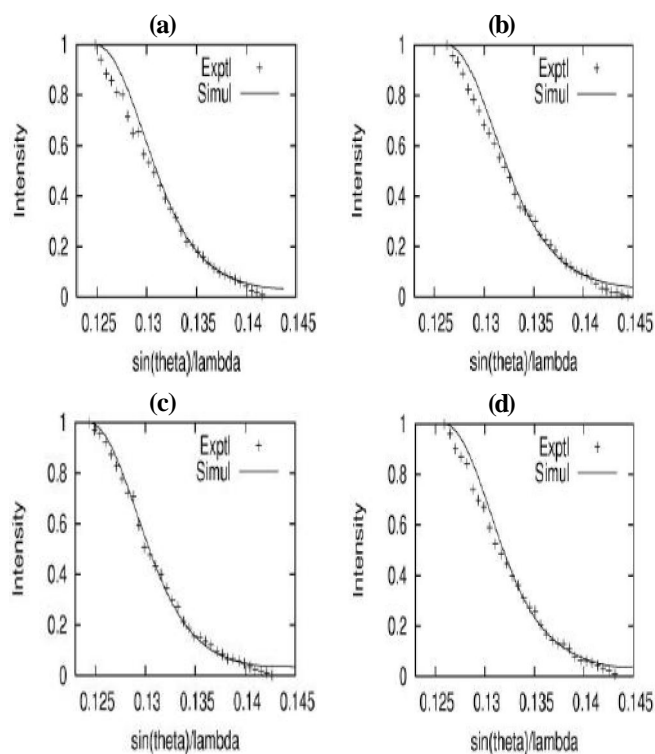


Figure 3 : (a-d) Experimental and simulated intensity profiles of x-ray reflection of hemp polymer fibers obtained with reinhold column length distribution function.

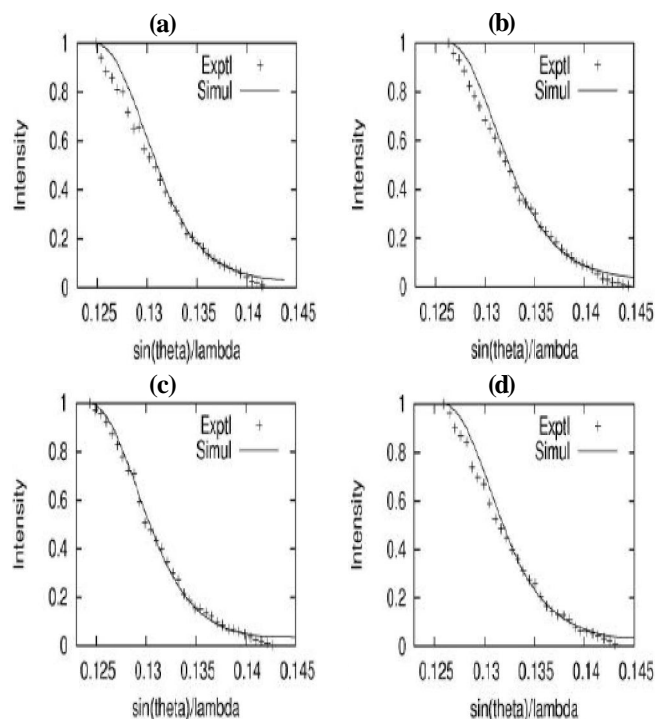


Figure 4 : (a-d) Experimental and simulated intensity profiles of x-ray reflection of hemp polymer fibers obtained with lognormal column length distribution function.

(D_s) is 30.36 Å for pure sample. For 10 min micro-

wave irradiated sample crystallite size is 7.35 and D_s is 29.08 Å, in the case of 20 min heated sample crystallite size 7.63 and D_s is 30.68 Å and 30 min heated sample has 7.62 and D_s is 30.26 Å. From all the cases it was found that the crystallite size and surface weighted crystallite size (D_s) is almost same, there is no much change occurs during the treatment.

The variation of the lattice strain (g in %) lies between 0.4 and 0.5% in case of exponential distribution for NHF polymer samples. From the obtained microcrystalline parameters ($\langle N \rangle$, g in %), one can estimate the minimum enthalpy (α^*), which defines the equilibrium state of microparacrystals in all the polymer fibers, using the relation postulated by Hosemann^[25]

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

The estimated minimum enthalpy is given in TABLE 1. It is observed here that the value of α^* lies between 0.011 and 0.014 for these fibers. The value of enthalpy decreases with increasing exposure time, which corresponds to the state with lower ordered polymer network. We have observed that the lattice strain and its variation are very small and are almost insignificant.

CONCLUSION

From the wide angle X-ray scattering (WAXS) study of microwave (MW) irradiated NHF polymer samples; we have observed that even though there is not much change in the position of the X-ray reflections, a small change in the values of micro structural parameters occurs. The small change in microstructural parameters in polymer is due to microwave irradiation. We have shown that among the three asymmetric crystallite size distributions, Exponential gives a better fit in polymer fibers. 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 phenomenon's like 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 general measure crystallite size, only upto a certain limit. The changes in polymer network with different exposure time are quantified here in terms of microstructural

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parameters. Our study indicates that microwave irradiated polymer samples have a slightly 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 microwave irradiation of NHF polymer samples, the duration upto 30 min is not sufficient to break the hydrogen bonds. This indicates that these fibers are resistant to microwave irradiation.

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