

## Microstructural defects in coir fibre under thermal and chemical treatments

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**Abstract** : Microstructural defects in coir fibres and their variations with thermal treatment in the temperature range 0° to 200° and alkali treatment in concentration range 5% to 30% have been studied by using X-ray line broadening technique. Presuming the presence of paracrystallinity, the two structural parameters, namely, the paracrystalline domain size and distortion have been calculated for differently treated fibres. It is observed that the paracrystalline disorder of coir fibre around 120°C is minimum and microcrystalline size and paracrystalline distortions are anisotropic in nature. Compared to other directions, the [101] direction in coir is more susceptible to thermal and alkali treatments. The effect of the thermal treatment is more pronounced than that of the alkali treatment.

**Keywords** : Microstructural defects, coir fibre, thermal and chemical treatments

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### 1. Introduction

Coir is a multicellular biopolymer in which crystalline cellulose is arranged helically in a matrix consisting of noncrystalline ligno-cellulosic complex [1]. Fibrous polymers like coir consist of long chains of thread like molecules which assume random configuration due to various factors [2]. These molecular chains when arranged approximately parallel to one another give rise to crystalline phase whereas excessive folding and twisting of the chains produce amorphous domains. These considerations led to the two phase model [3] of fibrous polymers which envisages a crystalline phase with domain boundaries embedded in matrix of amorphous materials.

In between these extreme phases an intermediate one, called paracrystalline phase, exists and constitutes an essential part of the molecular arrangement of fibrous polymers. In paracrystalline phase, the lattice structure is quasi periodic in which the atoms are neither

regularly arranged as in crystalline phase, nor randomly distributed as in amorphous state, but occupies an intermediate state. The unit cells are dissimilar, and consequently, the cell parameters become statistical quantities both in magnitude and direction and hence the distortions are of second kind [2,3]. Mitra and Mukherjee [2,3], in course of their studies on cellulosic fibres showed that paracrystallinity dominates a considerable region in these polymers due to the complex arrangement of the molecular chains. They further concluded that their polymeric properties could be described in a better way by considering paracrystallinity. Paracrystalline substances are usually characterized by two structural parameters, domain size and paracrystalline distortion, designated as  $\bar{M}$  and  $D$  respectively. Following these authors, Sao *et al* [4] also characterized ramie fibres in terms of these structural parameters and observed that these defects increased with alkali and thermal treatment. In case of coir, which is still more complex in composition due to the presence of considerable amount of non-cellulosic matter, these defects, and their variations with thermal and alkali treatment, are expected to be more pronounced. In view of these facts, the present work was undertaken to investigate the changes in microstructure in terms of paracrystallinity in alkali and heat treated coir fibres.

## 2. Experimental

Bristle ratted fibres were obtained by courtesy of Central Coir Research Institute, Alleppey, Kerala, India. Fine uniform fibres were separated out and impurities from the surface were removed by gently rubbing the surface followed by prolonged washing with distilled water and drying. The fibres were treated with 5%, 10%, 15%, 20% and 30% by weight of NaOH solution respectively for two hours each. Some fibres were thoroughly washed with distilled water to remove alkali completely to get mercerized samples. To get soda-cellulose samples, the excess of alkali was removed by gently pressing the surface of the fibres. For thermal treatment, the fibres were treated at temperatures 0°C, 27°C, 65°C, 120°C, 200°C and 300°C respectively each for two hours under vacuum of  $10^{-2}$  torr. The treated fibres were made powder of 200 mesh size by prolong grinding and sieving.

X-ray diffractograms of the samples were recorded in a Philips X-ray diffractometer (PW1710) in the angular range  $5^\circ (2\Theta)$  to  $90^\circ (2\Theta)$ . The reflection peaks 002, 101 and  $10\bar{1}$  were separated from the partially overlapped composite profile by using the method developed by Mitra and Bhattacharjee [5]. Owing to the absence of higher order reflections, refined variance-range single line technique of Mitra and Mukherjee [2,3] has been used to calculate the values of microcrystalline size ( $\bar{M}$ ) and distortion parameter ( $g_p$ ), presuming the presence of paracrystallinity in the sample.

## 3. Theoretical considerations

Single line technique based on variance of X-ray diffraction line profile is used in the present investigation. It is shown by Mitra and Mukherjee [3] that the variance  $W(s)$  of a fine profile can be written as

$$W(s) = K_{os} \sigma(s) - W_{os}, \quad (1)$$

where  $W(s) = W_{2\theta} (\cos \theta / \lambda)^2$  (2)

and  $\sigma(s) = (\cos \theta / \lambda) \delta(2\theta)$  (3)

$s = (2 \sin \theta / \lambda),$

and  $\delta(2\theta)$  is the angular range over which one evaluates  $W_{2\theta}$  on  $2\theta$  scale. The parameters  $K_{os}$  and  $W_{os}$  are given by

$K_{os} = (1/2\pi^2)(D + 1/\bar{M})$  (4)

and  $W_{os} = (1/4\pi^2)(D^2 + 2D/\bar{M}),$  (5)

where  $D = (2\pi^2 r^2 g_p^2) / d.$

Here  $d$  is the interplaner spacing of the corresponding reflecting planes. Thus we find from eq (1) that  $W(s)$  versus  $\sigma(s)$  will be a straight line, from the slope and intercept of which  $M$  and  $D$  can be determined.

4. Results and discussion

Figures 1 and 2 and Table 1 summarize the results of the present investigation. Figure 1 distinctly shows that the crystallite size parameter  $\bar{M}$  is larger and the corresponding

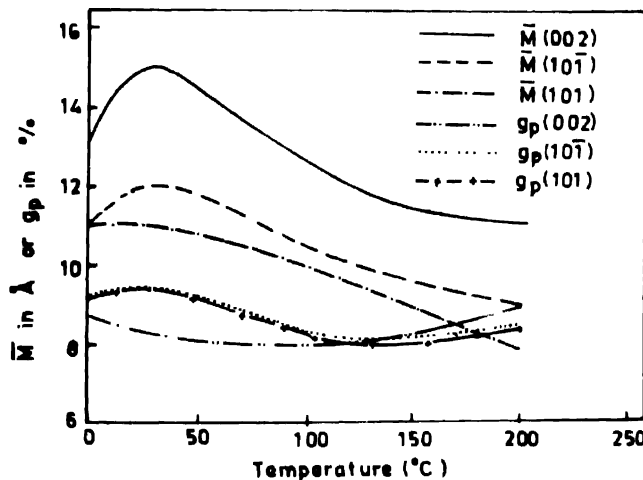


Figure 1. Variation of paracrystalline domain size ( $M$ ) and paracrystalline distortion ( $g_p$ ) of coir fibre with the temperature of thermal treatment

distortion parameter  $g_p$  is less along  $[002]$  direction as compared to  $[101]$  and  $[10\bar{1}]$  directions. Similar results were obtained by Mitra and Mukherjee [2,3] for jute and ramie fibres. These observation also indicate that in native cellulose  $I$  lattice,  $(002)$  planes coincide

with the plane of the chain ring and are more stable while (101) and (10 $\bar{1}$ ) planes are more vulnerable to structural distortions. Distortions along these directions may also be enhanced

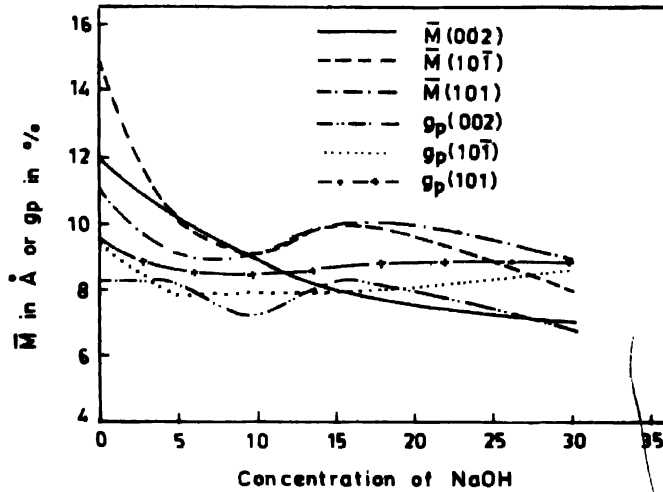


Figure 2. Variation of paracrystalline domain size ( $M$ ) and paracrystalline distortion ( $g_p$ ) of coir fibre with the concentration of NaOH solution for alkali treatment.

by diffusion of lower molecular weight molecules in the interchain space of the coir fibre. The temperature variation of  $\bar{M}$  corresponding to all the planes are more or less similar. In all cases, after an initial rise upto around 30°C which is most pronounced for (002) plane, all curves decrease consistently. The  $g_p$  values corresponding to (101) and (10 $\bar{1}$ ) planes, with a

Table 1. A comparison of paracrystalline domain size ( $M$ ) and paracrystalline distortion ( $g_p$ ) of mercerized and soda-cellulose treated coir fibres at 15% NaOH concentration with those of the raw fibres

Sample	Direction	$\bar{M}$ (in Å)	$g_p$ (in %)
Raw	[002]	15 ± 0.2	8.4 ± 0.2
	[101]	12 ± 0.2	9.4 ± 0.2
	[10 $\bar{1}$ ]	11 ± 0.2	9.4 ± 0.2
Mercerized (15 %)	[002]	8 ± 0.2	8.2 ± 0.2
	[101]	10 ± 0.2	7.9 ± 0.2
	[10 $\bar{1}$ ]	10 ± 0.2	8.7 ± 0.2
Soda-cellulose treated (15 %)	[002]	10 ± 0.2	8.5 ± 0.2
	[101]	9 ± 0.2	8.5 ± 0.2
	[10 $\bar{1}$ ]	10 ± 0.2	9.1 ± 0.2

slight initial rise, decrease steadily up to around 125°C, beyond which tend to rise marginally. However, the distortion  $g_p$  corresponding to [002] decreases initially upto around

30°C when  $M$  along [002] direction is found to reach a maximum value; thereafter it decreases slowly upto 130°C, beyond which, like other cases, tends to rise slowly. This behaviour further supports the anisotropic nature of the thermal variation of  $\bar{M}$  and  $g_p$ . The vulnerability to thermal degradation accompanying decrease of  $M$  and increase of  $g_p$  become more prominent beyond 125°C.

Figure 2 illustrates the variational pattern of the microstructural parameters  $M$  and  $g_p$  with concentration of NaOH. It is observed that both  $\bar{M}$  and  $g_p$  corresponding to all reflections in general, decrease by varying extent, upto a concentration of about 10%. However, above this concentration,  $\bar{M}$  continues to decrease steadily, while  $g_p$ , after undergoing irregular variation between 10% to 20%, finally decreases steadily along [002] direction.  $M$  values corresponding to (101) and (10 $\bar{1}$ ) pplanes also found to increase steadily in the concentration range 10% to 15%, beyond which show a tendency to decrease. However,  $g_p$  values corresponding to these planes show only a marginal increase with increase in concentration of NaOH.

The results clearly show that the variation of  $\bar{M}$  and  $g_p$  with alkali treatments are also anisotropic. However, unlike thermal treatment, alkali treatment appears to affect (002) planes more than the other planes. The decrease in  $\bar{M}$  at low concentration may probably be due to depolymerization [6]. This indicates that at low concentration of alkali, most likely, the amorphous and highly distorted small paracrystalline domains are affected. It appears that these highly distorted paracrystalline domains lie on the fringe of crystallite so that at higher concentration, the alkali slowly penetrates the fringe boundary and affects the crystallites causing further distortion.

In soda cellulose coir sample, the changes in the size parameter appear to be much less and almost independent of the direction. However, the magnitude as well as the pattern of variation of distortion parameter remains more or less the same as in the case of mercerized samples.

Thus it may be concluded that, in general, the paracrystalline disorder in thermally treated coir fibre is minimum around 125°C. Size and distortion parameters vary anisotropically and the effects of thermal treatment are more than that of the alkali treatment. The soda cellulose samples are more distorted than the mercerized ones.

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