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# Influence of delignification and alkali treatment on the fine structure of coir fibres (*Cocos Nucifera*)

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The present communication reports the effect of a softening treatment carried out with 18% NaOH on the fine structure and structure–property relations in coir fibres. The effect of successive removal of lignin and hemicelluloses on the fine structure has also been studied. Unlike other cellulosic fibres, alkali treatment failed to produce any increase in fibre elongation in coir. However, the spiral structure was found to be considerably modified by swelling. X-ray and infrared spectral measurements revealed that a part of the noncellulosic components does occupy the intracellular space and plays a significant role on fine structural changes produced during the alkali treatment.

## 1. Introduction

For a better utilization of natural cellulosic fibres abundant in our country, information on the structure, properties and their interrelationships is essential. Among the natural fibres, coir occupies a prominent position due to its qualities such as resilience, extensibility and rot-resistance which enhance its commercial and industrial usefulness.

Several studies [1–5] have been carried out in the past to understand the structure, mechanical properties and effect of chemical treatments on coir fibres. Attempts have been made to improve the softness of these fibres by treating them in caustic soda solutions so that their spinnability is enhanced [6].

Structurally coir presents an interesting picture in which cellulose spirals make an angle of about 45° to the fibre axis. Although it is reported [1–5] that swelling in caustic soda does not lead to any change in the spiral angle, a part of the noncellulosic inclusions is removed by the alkali. It would be interesting to see how the treatment affects the fine structure and the structure–property relations. The present communication is intended to discuss this aspect in greater detail.

## 2. Materials and methods

Coconut husks belonging to the variety West Coast Tall were supplied by the Central Plantation Crop Research Institute, Kasaragod, Kerala. Fibres were extracted from the dried husk without any prior retting but after soaking in water for a few hours. From the extracted lot, a small specimen of about 25 g, consisting of fibres of average length (0.10 ± 0.03 m) and diameter (200 ± 25 μm), was prepared and used throughout the study.

### 2.1. Delignification

Fibres were delignified by a standard procedure [7]. Complete delignification required repeated treatments. Delignified fibres were boiled in 1% NaOH for 30 min to obtain 100% pure cellulose in the form of single cells. However, for obtaining the X-ray orientation diagram of the lignin-free material, a partially delignified sample that retained the fibre form was used.

### 2.2. Swelling and stretching

Parallelized bundles of coir fibres mounted on special jaws were swollen slack in water or sodium hydroxide before stretching them back to their original length. After NaOH swelling, the reagent was removed by washing the bundle in water. The swollen and stretched fibres were finally dried in air under taut condition. Fibres were also swollen slack in 18% NaOH for 0.5 and 16 h at room temperature. In addition fully delignified fibres were also treated with the same alkali concentration for 0.5 h at room temperature. After the pre-determined interval (0.5 h/16 h) of treatment in the alkali, samples were washed free of alkali and dried in air.

### 2.3. Tenacity and elongation

The tenacity and breaking elongation of single fibres of untreated as well as slack swollen coir fibres were

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measured by using an Instron Tensile Tester with a gauge length of 5 cm employing the standard procedure [8].

## 2.4. X-ray crystallinity and crystallite orientation

The powder diffractograms were obtained by using a Philips X-ray generator, fitted with a diffractometer and recording accessories, employing Ni filtered $CuK_\alpha$ radiation. Coir fibres cut in a Wiley mill and filtered though a 40 mesh screen were used for this purpose. Total crystallinity and amounts of cellulose I and cellulose II wherever required were computed by Segal *et al.'s* method [9] as modified by Chidambareswaran *et al.* [10]. The breadth, $\beta_{1/2}$ at half maximum intensity of the (0 0 2) reflection was computed by using the normal procedure [8].

For measurement of crystallite orientation, the azimuthal intensity distribution curve of the (0 0 2) arc was obtained by using a well parallelized bundle of coir fibres in a texture goniometer arrangement. The following measures of orientation were computed from this distribution curve.

### 2.4.1. *Spiral angle* ($\theta$)

This is measured as the angular displacement of the intensity maxima of the azimuthal distribution with respect to the equator.

### 2.4.2. *X-ray angle* ($\phi$)

This is the half width in degrees of the azimuthal intensity distribution curve. This is a measure of the distribution of the *b* axes of the crystallites with respect to the spiral direction.

### 2.4.3. *Mean orientation angle* ($\alpha$)

Using the intensity distribution over the entire azimuth from 0 to 90 °, the Hermans' orientation factor $f_x$ [11] is computed. In the case of cellulose I,

$$f_x = 1 - 3/2 \sin^2 \alpha$$

and for mercerized fibres [12] constituting a major lattice of cellulose II,

$$f_x = 1 - 7/2 \sin^2 \alpha$$

These equations are used to calculate the mean orientation angle $\alpha$ which takes into account both the spirality of crystalline fibrils and the distribution of *b* axes around the spiral direction.

## 2.5. Infrared spectra

The IR spectra of finely cut coir fibres were recorded using a Perkin Elmer model 457 infrared grating spectrophotometer in a KBr matrix. The ratio of absorbances of the peak at 342 and 2900 $cm^{-1}$ (Index III) has been used as a measure of the crystallinity [13] for the raw and delignified fibres. The infrared index based on the ratio of absorbances of the peaks at 893 and 2900 $cm^{-1}$ is used to indicate conformational changes occurring during the treatments.

## 3. Results and discussion

Fig. 1 shows the radial X-ray diffractograms of: (a) untreated coir fibres, (b) delignified fibres and (c) mercerized fibres. It can be seen that the untreated coir fibres have a poor diagram. The low resolution of the (1 0 1) and (1 0 $\bar{1}$) peaks is indicative of poor crystalline perfection and of the presence of large amounts of noncellulosic matter. Removal of noncellulosic inclusions during delignification improves the quality of the diagram. The resolution of the (1 0 1) and (1 0 $\bar{1}$) doublet improves and the (0 0 2) peak becomes sharp (Fig. 1b). On treatment with 18% NaOH, some of cellulose I gets converted to cellulose II. The resolution of the cellulose I region improves and the diffractogram shows signs of better crystalline order than the control. These changes contrast with those in cotton fibres in which mercerization leads to crystalline disorder [4].

The effect of delignification and the removal of noncellulosic substances can be better seen from IR spectra given in Fig. 2. This figure shows the spectrum of (a) raw coir fibre, (b) delignified coir, (c) delignified coir treated with 1% NaOH, (d) raw fibre treated with 18% NaOH. The absorption bands observed in the infrared spectrum of coir and their likely origin are given in Table I. Coir is found to contain about 45–50% pure cellulose. As a result the spectrum of raw fibre (Fig. 2a) itself resembles that of cellulose in several regions. However, relatively strong additional peaks are present in 1800–1450 $cm^{-1}$ and 1300–1200 $cm^{-1}$ ranges. In addition, low intensity peaks are observed at 870 and 780 $cm^{-1}$. The most abundant noncellulosic matter in coir is lignin (30–35%), followed by hemicellulose and pectin (15–20%). As a result even after delignification strong bands are observed at 1735 and 1250 $cm^{-1}$ attributable to the hemicellulose part (such as pentosans,

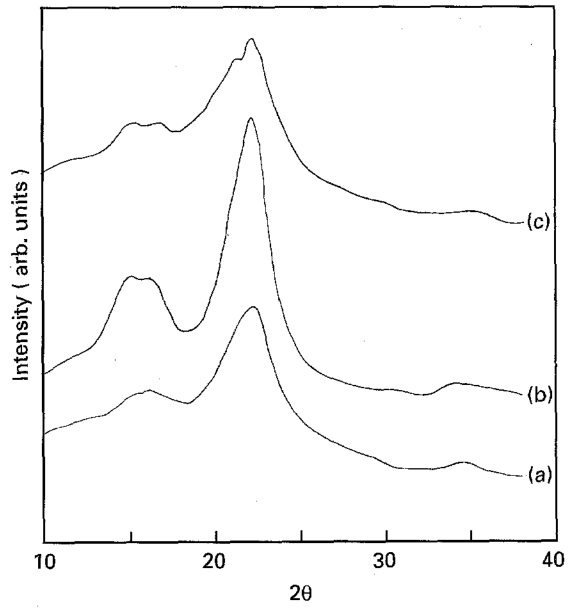

*Figure 1* X-ray powder diffractograms of coir: (a) untreated; (b) delignified; (c) NaOH treated.

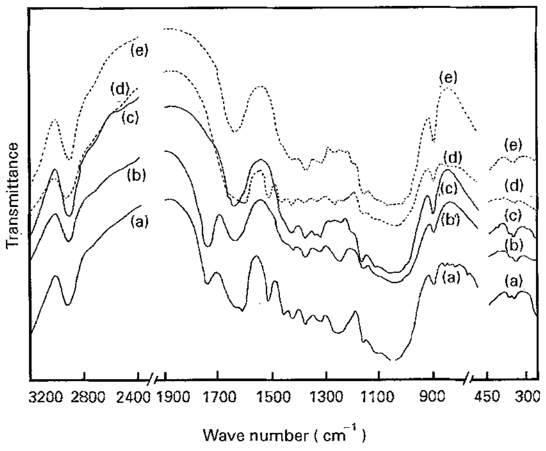

*Figure 2* Infrared spectra of coir: (a) raw; (b) delignified; (c) delignified treated with 1% NaOH; (d) raw treated with 18% NaOH; (e) delignified treated with 18% NaOH.

TABLE II Effect of delignification and NaOH treatments on weight loss and IR index

| Sample | Treatment | Weight loss | Infrared Index |
|---|---|---|---|
| Raw coir | Nil | – | 0.20 |
| Raw coir | NaOH, 18%; 30 min, 30° C | 12.0 | 0.28 |
| Raw coir | NaOH, 18%; 16 h, 30° C | 14.5 | 0.39 |
| Delignified coir | Nil | 32.7[a] | 0.22 |
| Delignified coir | NaOH, 1%; 30 min, boil | 22.9 | 0.36 |
| Delignified coir | NaOH, 18%; 30 min, 30° C | 26.5 | 0.47 |

[a] Weight loss obtained during delignification.

uronic acid, etc.). Treatment of the delignified material in 1% alkali results in 100% cellulose and the spectrum (Fig. 2c) is identical with that of cellulose albeit with relative intensity changes owing to the poorer crystalline order of the cellulose in coir. A treatment with 18% NaOH of the raw fibre also produces substantial changes in the spectrum. The peak due to carbonyl absorption of the hemicellulose (1735 cm$^{-1}$) part disappears. Changes are noticeable also in the 1300–1200 cm$^{-1}$ region. The broad peak in this region separates into two, with one becoming sharper than the other. A spectral study of the alkali soluble components (which also includes some lignin) showed that the sharper peak is due to alkali-insoluble lignin.

Table II gives the absorbance ratio for the 893 cm$^{-1}$ band with respect to the peak at 2900 cm$^{-1}$. The table also gives weight loss values during successive treatments. The intensity changes in the 983 cm$^{-1}$ band can be influenced by conformational changes occurring during decrystallization/conversion of cellulose I to cellulose II [15]. In the case of raw coir fibres where cellulose occurs only as the cellulose I lattice, the ratio is found to be 0.2. Delignification did not produce any significant change in the ratio. However treating with boiling 1% NaOH increased the ratio considerably indicating the occurrence of some conformational changes during boiling in 1% alkali despite no change in the lattice structure. Treatment of raw fibre in 18% NaOH increased the ratio further, obviously due to a change in the lattice structure. However, the maximum effect was observed in delignified fibre treated with 18% NaOH. This observation makes it rather clear that the intracrystalline regions in coir fibre are only marginally affected by 18%

TABLE I Wave numbers of infrared bands, their origins and approximate intensity in the spectra of coir fibres (before and after treatments)

| Approximate wave no./wave no. range (cm$^{-1}$) | Intensity | Probable origin |
|---|---|---|
| 2920–2880 | M | $CH_2$, CH stretching |
| 1740–1725[b] | M | C–O stretching |
| 1660[a] | M | aromatic ring vibration |
| 1640–1630 | M–S | peak due to adsorbed water |
| 1605–1600[b] | M | aromatic ring vibration |
| 1505–1500[b] | W–M | phenyl ring vibration |
| 1465[a] | M–S | OH in plane bending |
| 1425 | M | $CH_2$ deformation |
| 1372[a] | W–M | CH bending, $CH_3$ deformation |
| 1333 | sh | OH in plane bending |
| 1320 | M | $CH_2$ wagging |
| 1260–1220[b] | M | aliphatic and aromatic C–O groups absorption |
| 1160 | M | antisym, C–O–C stretching |
| 1125 | M | – |
| 1110 | M | antisym. in phase ring stretching |
| 1060–980 | S | skeletal vibrations involving CO groups |
| 895 | W | antisym. out of phase ring stretching |
| 835[b]} | VW | CH out of plane in phenyl ring |
| 780} | | |
| 350–340 | W–M | out of plane vibrations involving the rings |

[a] Bands of enhanced intensity appear in these regions when compared with spectra of purified coir (i.e. spectra c and e in Fig. 2).
[b] These bands are exclusively due to lignin and hemicellulose and are totally absent in the spectra of purified coir.
Key: VW = very weak; W = weak; sh = shoulder; M = medium; S = strong.

TABLE III Mechanical and structural properties of raw and treated coir fibres

| Sample | Tensile data | | X-ray data | | | | | | | IR index III |
|---|---|---|---|---|---|---|---|---|---|---|
| | Tenacity (mN/d.tex) | Elongation (%) | Crystallinity | | | | | Orientation | | |
| | | | CI (%) | CII (%) | Total (%) | AM (%) | $\beta^{\circ}_{1/2}$ | θ° | φ° | |
| Untreated | 12.4 | 27.4 | 28 | 0 | 28 | 72 | 3.2 | 42 | 43 | 0.26 |
| Delignified | – | – | 49 | 0 | 49 | 51 | 2.4 | 45 | 47 | 0.39 |
| NaOH treated[a] | | | | | | | | | | |
| (a) 1/2 h | 13.5 | 26.2 | 27 | 11 | 38 | 62 | 2.2 | 24 | 54 | – |
| (b) 16 h | – | – | 8 | 19 | 27 | 73 | 2.8 | – | – | – |

[a]Slackswelling only; mN/d, tex = millinewton/decitex.
Key: CI = cellulose I; CII = cellulose II; AM = amorphous.

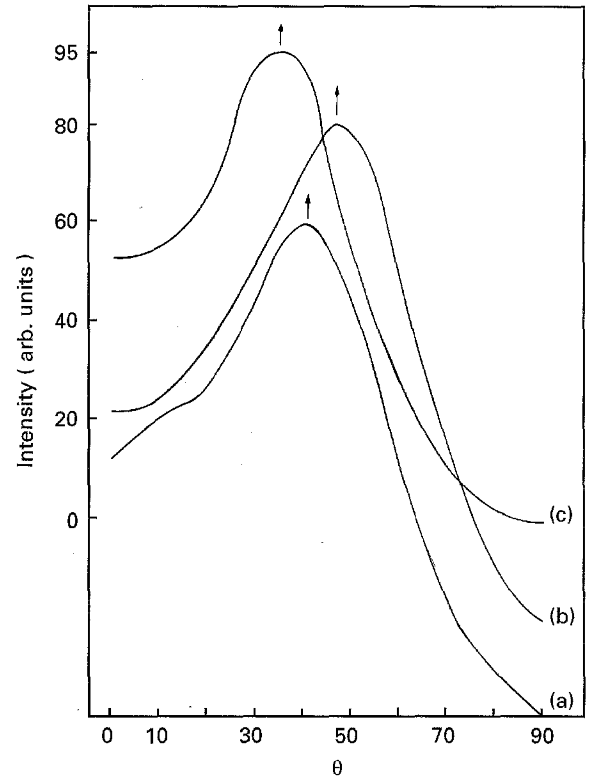

*Figure 3* Azimuthal intensity distribution curves of coil (a) untreated; (b) delignified; (c) swollen and stretched in water.

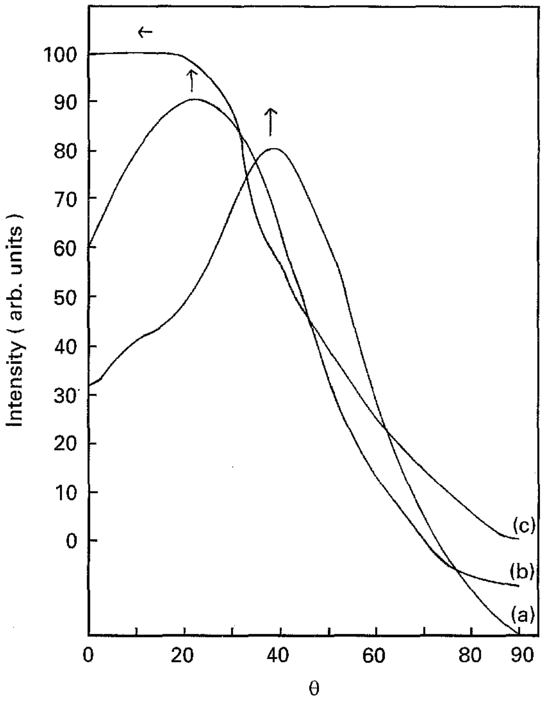

*Figure 4* Azimuthal intensity distribution curves of coir (a) untreated (b) swollen slack in NaOH; (c) swollen slack in NaOH and stretched.

alkali. During this treatment only the low ordered regions (intercrystalline regions along with smaller crystallites) alone are converted to cellulose II. If lignin is present in the intracrystalline regions it can hinder the penetration and swelling by alkali and thereby affect the conversion of cellulose I to II. However a prolonged treatment for 16 h of raw fibre in 18% NaOH increases the conversion (Table III), thereby indicating the influence of lignin in preventing faster access to the crystalline regions. When the material is fully delignified no such resistance of accessibility to crystalline regions by alkali is offered, resulting in a higher value for the absorbance ratio even at shorter intervals as is evident from Table II.

The azimuthal intensity distribution curves for coir fibres before and after delignification are presented in Fig. 3a and b. Also included in the figure is the distribution obtained on fibres after stretching in water (Fig. 3c). The spiral angle position is marked in the figure by an arrow. In the untreated fibre, the spiral angle θ is about 40 °. This rises to 45 ° on delignification. Stretching in water straightens the spiral to some extent resulting in reduced θ values of about 34 ° and the distribution also becomes narrower.

Swelling in NaOH introduces considerable changes in the azimuthal distribution curve as can be seen from Fig. 4b. The spiral angle decreases after NaOH swelling contrary to earlier reports [1, 5] of its insensitiveness to swelling treatments. The *b* axes distribution is also considerably broadened indicating that a fair amount of randomness has been introduced in the orientation of cellulose. The broadening of the *b* axes distribution can be due to the removal of some of the intracellular matter by the alkali treatment which might have had an orienting influence on the cellulose. Stretching the swollen fibres does not improve the

TABLE IV Orientation measures of swollen and stretched coir

| Sample details | Spiral angle ($\theta°$) | X-ray angle ($\phi°$) | Mean orientation angle ($\alpha°$) | Hermans' orientation factor, $f_x$ |
|---|---|---|---|---|
| Untreated | 40 | 48 | 36 | 0.12 |
| NaOH swollen and stretched | 10 | 45 | 27 | 0.37 |
| Swollen in water and stretched | 34 | 35 | 31 | 0.23 |

*b* axes distribution significantly as seen from Fig. 4c. On the other hand, the spiral angle decreases considerably and the maximum distribution shifts to a very low angle, as can be noted from the arrow mark. It is not possible, however, to fix the spiral angle value unambiguously in this case as the peak is broadened to a great extent.

The tenacity and breaking elongation values of fibres before and after NaOH treatment are given in Table III. Also included in the table are the crystallinity and orientation measures of the above fibres in addition to those of the fibres after delignification. After NaOH treatment, the tenacity marginally improves whereas there is a very little decrease in the breaking elongation. This decrease was found to be insignificant. Although spiral straightening should have led to considerably decreased elongation, the retention of this property after NaOH treatment seems to be due to a combination of factors. Firstly, there is no significant shrinkage after NaOH treatment. Secondly, about 12% noncellulosic matter is dissolved away in NaOH in the 30 min treatment. Prolonging the treatment to 16 h did not significantly increase the weight loss. The removal of the intercellular and intracellular noncellulosic substances should confer greater flexibility on the load bearing elements, thus allowing for greater slippage and readjustment that could enhance fibre elongation. Thirdly, the more random distribution of crystallites after NaOH treatment, as seen from the orientation diagram in Fig. 4 as well as from weight loss data in Table II, should also be expected to favour the slippage mechanism. These factors seem to have conspired to offset the decrease in elongation that would have been caused by the straightening of the fibrillar spiral.

From the data in Table III it can be noted that crystallinity increases during delignification primarily due to the removal of intracellular inclusions. The decreased $\beta_{1/2}$ value is also indicative of a higher crystallite organization and better order in delignified fibres. Treatment in NaOH for one hour induces conversion of cellulose I to cellulose II with the treated fibres showing a higher total crystallinity. Prolonging the treatment in NaOH for 16 h seems to promote further lattice conversion to cellulose II but the total crystallinity is restored to the low value of the untreated fibre. Even so, the $\beta_{1/2}$ values are less than that of the control indicative of higher crystalline perfection after NaOH treatment.

As already noted, the spiral angle $\theta$ decreases after NaOH treatment. Interestingly this decrease is accompanied by the broadening of the *b* axes distribution suggesting that the intracellular inclusions originally present had an orienting influence on the fibrils. Due to the partial removal of the intracellular inclusions (NaOH treatment removes mostly hemicelluloses and some lignin) the crystallities suffer disorientation leading to a broader distribution resulting in higher $\phi$ values.

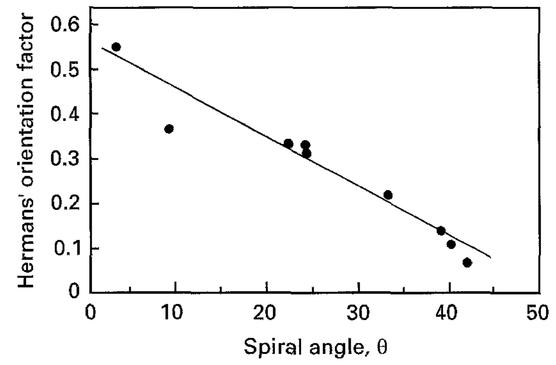

*Figure 5* Plot of Hermans' orientation factor $f_x$ against spiral angle $\theta$ for coir swollen and stretched to different levels.

The various orientation measures calculated for the swollen and stretched coir fibres are presented in Table IV. It can be noted that stretching the swollen fibres decreases the spiral angle considerably although the *b* axes distribution is not much different. As a result, the mean orientation angle proportionately decreases leading to an increase in the Hermans' orientation factor.

It would not be out of place to discuss here the factors that influence the Hermans' orientation factor $f_x$ for coir fibres. It was noticed that the orientation factor $f_x$ is greatly influenced by the extent of spirality but only marginally affected by the *b* axes distribution. This fact could be made more clear by looking at Fig. 5 in which the $f_x$ value is plotted against spiral angle. This relationship clearly brings out the dominating influence of spiral angle on $f_x$. The Hermans' orientation factor $f_x$ for coir fibres having a spiral angle of 45 ° is about 0.08. However Varma *et al.* [5] have quoted an $f_x$ value of 0.90 and have noted that it does not change during alkali treatment. Our results show that the $f_x$ value for the control is of the order of 0.1 and a slack treatment in NaOH raises the value to about 0.32. With stretch, the value reaches a limit of 0.55. A very high value of 0.91 seems untenable for a fibre which has a spiral angle of around 45 ° and a broad *b* axes distribution of about 40 °. The intensity of X-ray diffraction from crystallites oriented closer to the fibre axis has a higher weightage in the calculation of $f_x$ and because of this one finds increased $f_x$ values as spirals are straightened during chemical treatment.

## 4. Conclusions

1. Delignification and removal of noncellulosic inclusions lead to improvement in quality of the X-ray spectrum of coir fibres.

2. The distribution of orientation of crystallites in coir fibres indicates that the intracellular inclusions present in untreated fibres has an orienting influence on the fibrils. On treatment with NaOH, the spiral angle decreases and a fair amount of randomness is introduced in the orientation of the crystallites due to the removal of noncellulosic matter.

3. Infrared spectra of successively purified coir fibres indicate that lignin is present even in the intracrystalline regions of the raw technical fibres.

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