IR and X-Ray Diffraction Studies of Raw and Chemically Treated Pineapple Leaf Fiber (PALF)

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SYNOPSIS

IR and X-ray diffraction studies have been carried out on raw and chemically treated pineapple leaf fiber (PALF). The degree of crystallinity, as found by X-ray diffraction and the crystallinity index as found by infrared methods, decreases on treatment with NaOH and $NaClO_2$ solutions. The decrease of crystallinity with lower concentration of NaOH is attributed to the conversion of intermediate or semicrystalline regions to amorphous ones and with higher concentration to structural changes and with $NaClO_2$ solution to the disorientation caused due to removal of cementing material lignin.

INTRODUCTION

The pineapple leaf fiber (PALF) is multicellular in nature and obtained from the leaf of pineapple plant.[1] The fibers are mainly composed of cellulosic and noncellulosic materials like hemicellulose, lignin, etc., which act as cementing materials. The chemical composition of the PALF is given in Table I.

The noncellulosic constituents play an important role in the physical properties of the fiber. On removing the noncellulosic constituents of PALF by chemical treatment, degree of crystallinity and crystallinity index change. The degree of crystallinity, i.e., the amount of crystalline cellulose present in a cellulosic fiber cannot be exactly defined, as neither the crystalline portions are perfect crystals nor the noncrystalline portion completely disordered. Apart from truly crystalline and truly amorphous, there are some regions of intermediate order the molecular configuration of which is liable to change by the chemical treatment. The present paper on the changes of degree of crystallinity of PALF on chemical ($NaClO_2$ and NaOH) treatment was undertaken as no such work has been reported.

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EXPERIMENTAL

Materials

(1) Raw pineapple leaf fiber (PALF)
(2) Delignified ($NaClO_2$ tr.) PALF
  (a) Residual lignin content 2.84%
  (b) Residual lignin content 2.09%
  (c) Residual lignin content 1.80%
(3) Alkali (NaOH) treated PALF
  (a) Treated with 5% NaOH solution
  (b) Treated with 10% NaOH solution
  (c) Treated with 18% NaOH solution

PALF samples (representative of the whole lot) are taken from the middle portion of the reeds and treated with alkali (NaOH, w/v) solution of different concentration (i.e., 5, 10, and 18%) for 1 h at room temperature (30°C) with occasional shaking.[2] After treatment, the samples were washed with distilled water, dilute hydrochloric acid, and finally distilled water and air-dried. Treatment with NaOH solution of different concentrations removed mainly hemicellulose with other constituents.

Delignification was carried out by the chlorite method[3] which does not affect other constituents of the fiber. The fiber specimens were treated with 0.5 and 0.7% sodium chlorite solution with different temperatures between 45 to 80°C (liquor ratio 1 :

Table I Chemical Compositions of PALF (Defatted)[a]

Constituents	Percentage
α-Cellulose	68.50
Hemicellulose	18.80
Lignin	6.04
Pectin	1.10
Fat and wax	3.20
Ash	0.90
Others (protein, organic acid, etc.)	1.46

[a] The calculations are based on oven dry basis.

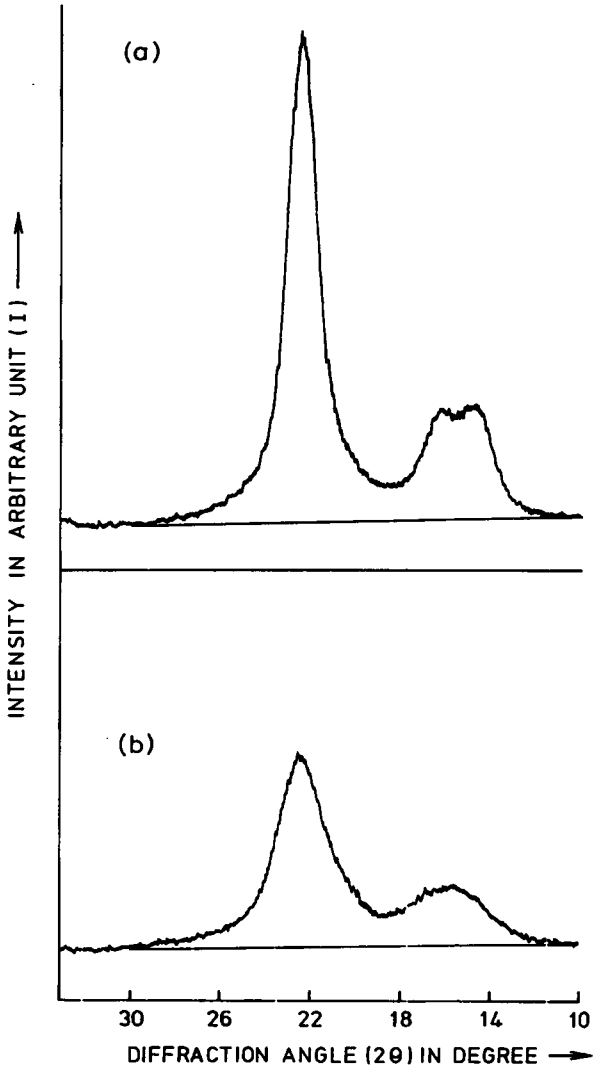

Figure 1 X-ray diffractograms: (a) Ramie (2% gum content); (b) raw PALF.

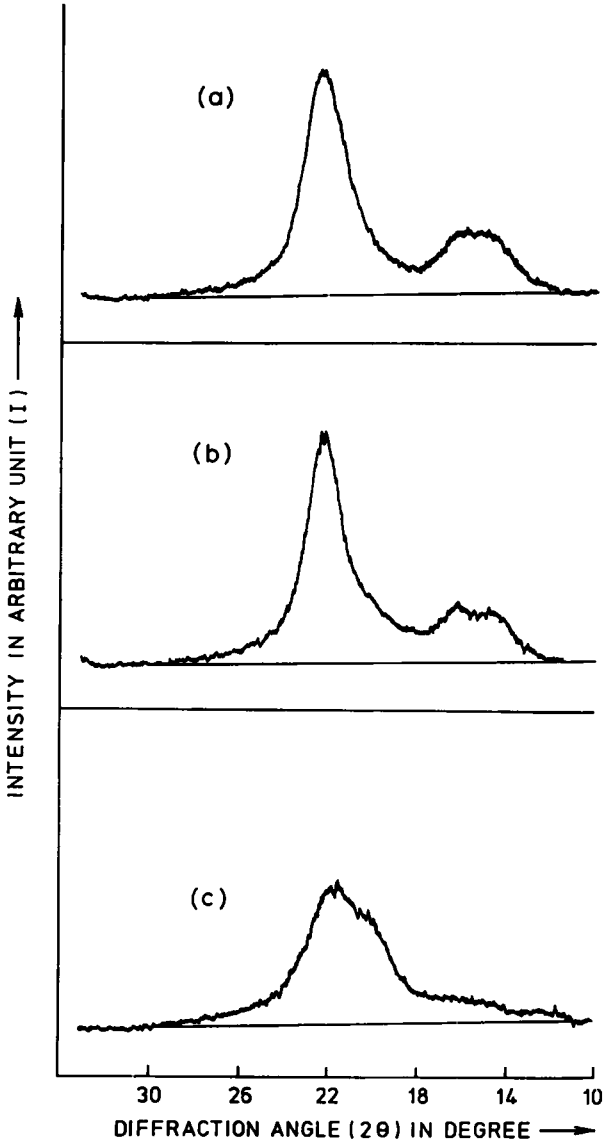

Figure 2 X-ray diffractograms of PALF: (a) 5% NaOH treated; (b) 10% NaOH treated; (c) 18% NaOH treated.

25) at pH 4 (buffered with acetic acid and sodium acetate) for 2 h. The chemical constituents of the fibers are determined by standard methods.[3-6] The hemicellulose and lignin contents of the PALF samples after chemical treatments are shown in Table II.

Methods

For the determination of degree of crystallinity, 200 mg of small pieces of PALF were taken in a glass plate and X-ray diffractograms were recorded by Philips X-ray diffractometer with Ni-filtered CuK_{α}

Table II Percentage of Hemicellulose and Lignin Content in the Raw and Chemically Treated PALF

Specimen	Chemical Treatment	Temperature of Treatment (°C)	Hemicell (%)	Lignin (%)
Raw	—	30	18.80	6.04
5%	NaOH	30	11.16	5.44
10%	NaOH	30	7.28	5.06
18%	NaOH	30	7.10	4.98
0.5%	$NaClO_2$	45	15.60	2.84
0.5%	$NaClO_2$	80	14.80	2.09
0.7%	$NaClO_2$	80	13.20	1.80

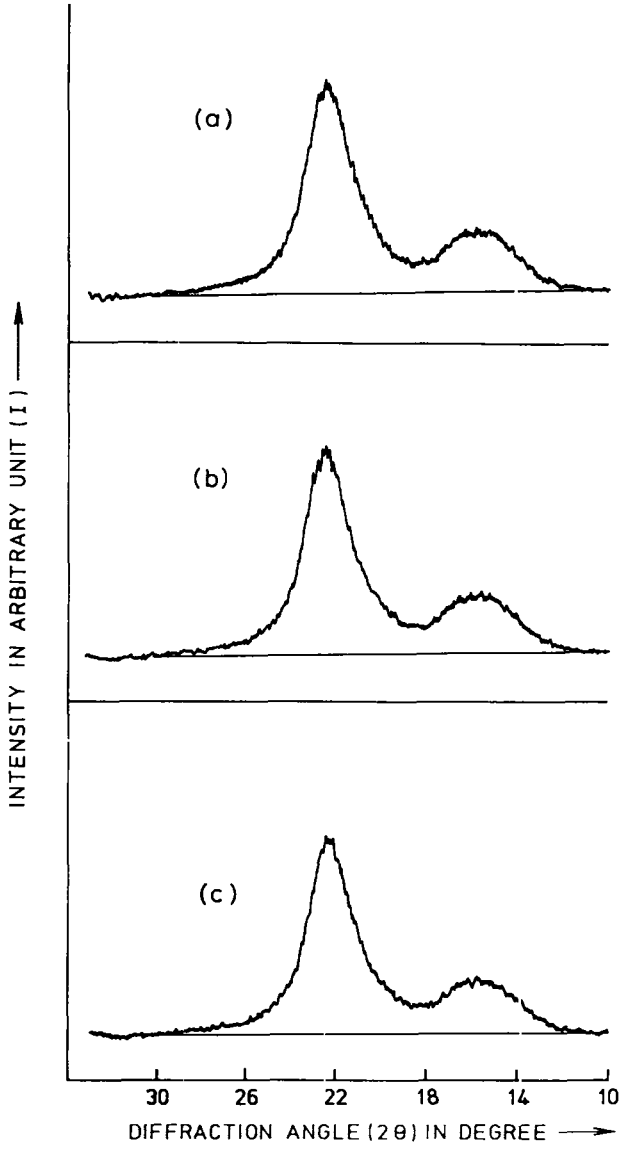

Figure 3 X-ray diffractograms of PALF: (a) 0.5% $NaClO_2$ treated at 45°C; (b) 0.5% $NaClO_2$ treated at 80°C; (c) 0.7% $NaClO_2$ treated at 80°C.

radiation at 40 kV and 30 mA. The value 70% for the degree of crystallinity for ramie has been taken as standard. The value for the degree of crystallinity has been found by comparing the crystalline area in the intensity curve of ramie with that of PALF (Figs. 1–3) following the methods adopted by Hermans and Weidinger[7] and later by Gupta[8,9] in the case of NaOH-treated jute fibers.

The above samples were cut into small pieces by scissors. KBr pellets were made by mixing about 2 mg of the sample with 200 mg of KBr at a pressure of 8^+ tons. The IR spectra were recorded with the help of a Shimadzu double beam IR spectrophotometer (Model IR-440). A KBr pellet without sample was used in the reference beam. Infrared crystallinity index is defined as the ratio of the absorbance of the maximum about 900 cm^{-1}. To compare the X-ray result of crystallinity with that of infrared, the crystallinity index from IR spectra was also found following O'Connor et al.[10] The values obtained by infrared method show a similar trend with those obtained from X-ray diffraction measurements. Some of the results of IR for raw and chemically treated PALF are shown in Figures 4–6.

RESULTS AND DISCUSSION

Degree of crystallinity and crystallinity index values of raw and chemically treated PALF are given in Table III. From the results it is observed that, due to the treatment of NaOH solution there is decrease of crystallinity and from X-ray and IR results (Figs. 1–6), it is observed that the trend is consistent. In natural cellulose fibers, the regions of intermediate order in the structure play an important role in the determination of the degree of crystallinity.[11–13] With the treatment of NaOH solution, the intermediate regions gradually become amorphous and, therefore,

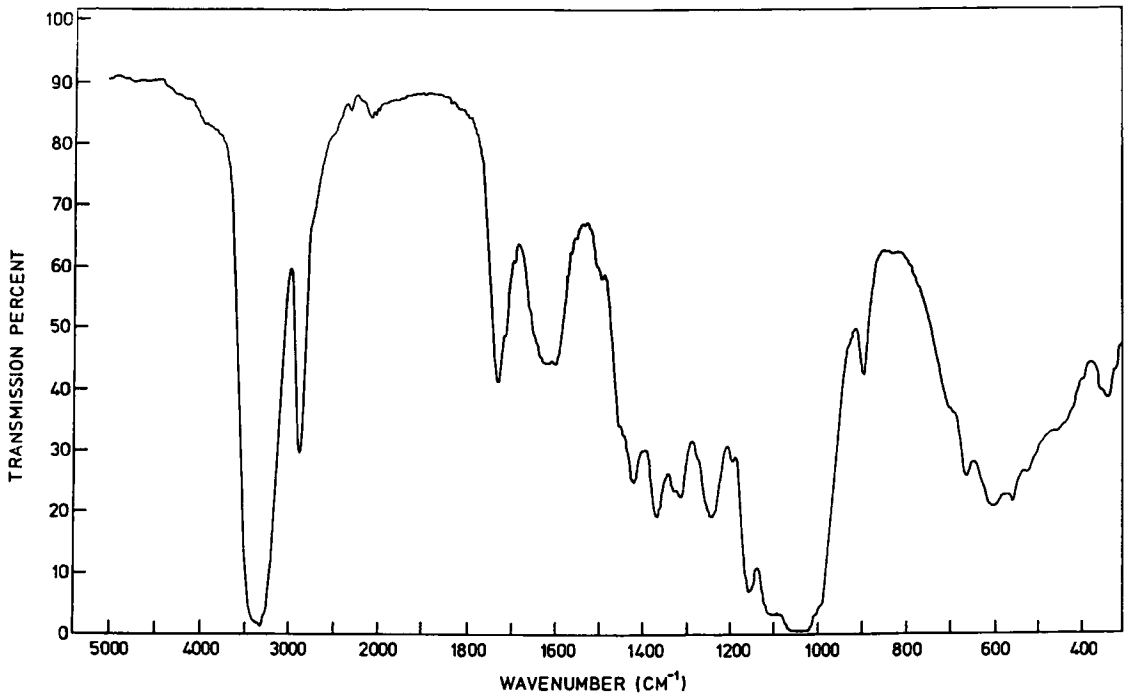

Figure 4 IR spectra of raw PALF.

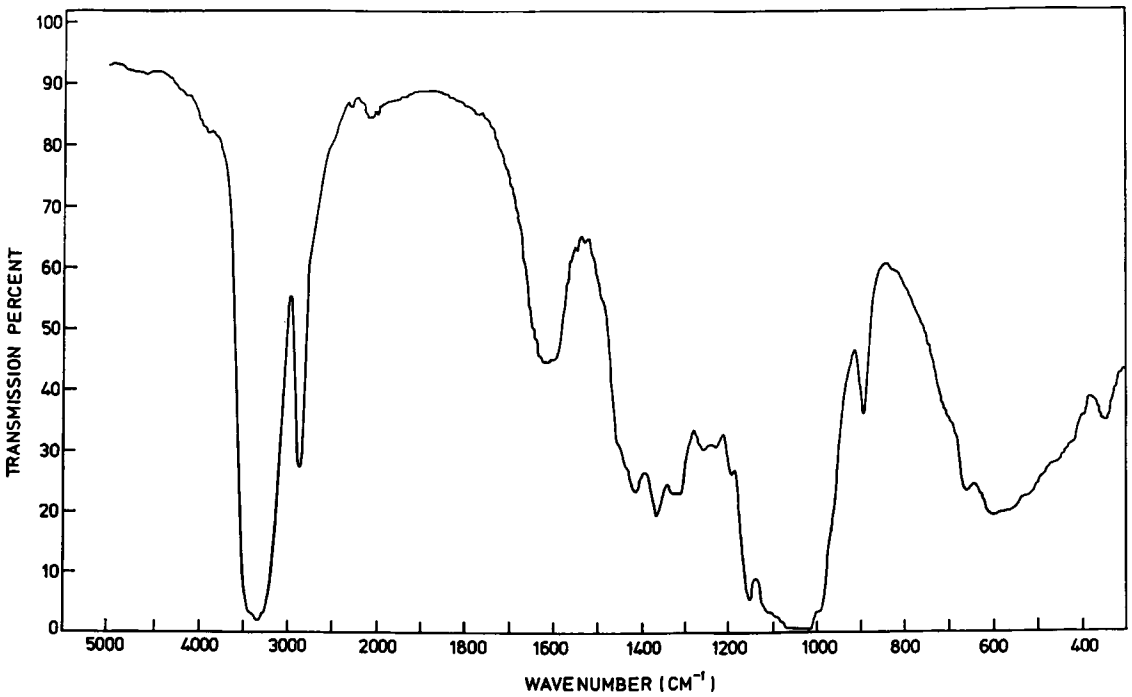

Figure 5 IR spectra of 18% NaOH treated PALF.

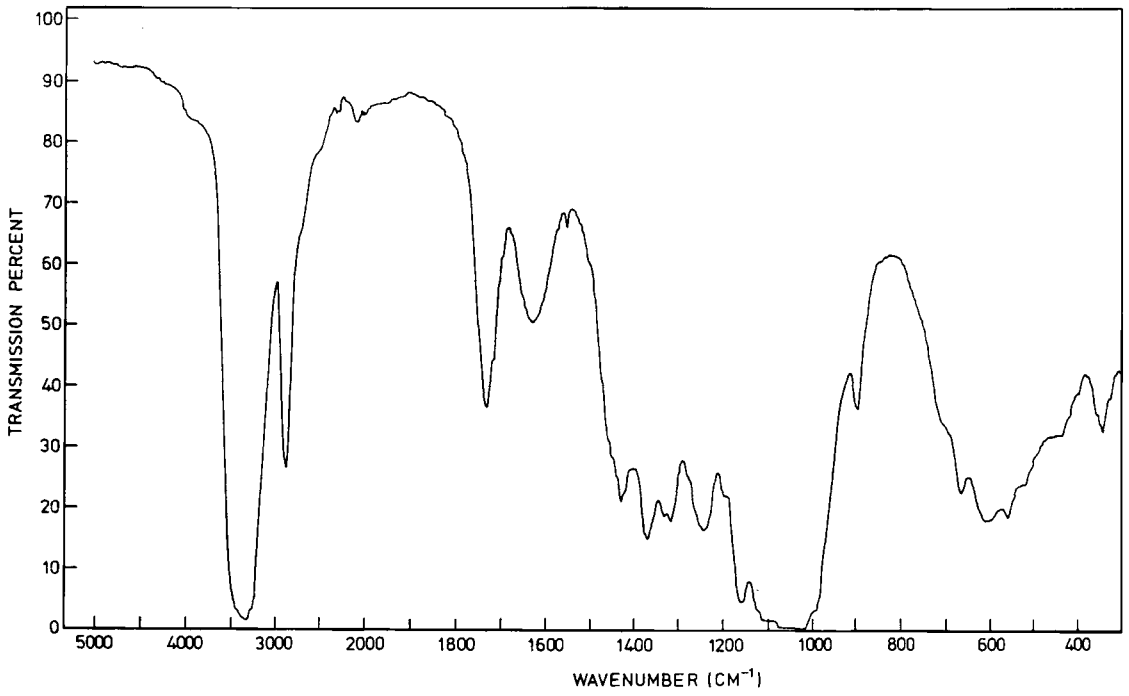

Figure 6 IR 0.7% $NaClO_2$ treated at 80°C PALF.

these regions which were contributing to crystalline reflections add to the continuous background scattering. In case of cotton fibers it was shown by Chidambareswaran et al.[13] that with lower concentration of NaOH the conversion of cellulose I fraction into amorphous regions predominates over the transformation to cellulose II fraction, and, on the other hand, for higher concentration this order was reversed. It is reported by Revol and Goring[14] that in most lignified plant cells lignin and hemicellulose are deposited between the microfibrils to give an interrupted lamellar structure and without removal of these noncellulosic incrustants the cellulose I to cellulose II transformation will be restricted. With

Table III Degree of Crystallinity (DC) and Crystallinity Index (CI) of Raw and Chemically Treated PALF

Specimen	Chemical Treatment	Temperature of Treatment (°C)	DC as Found from the Intensity Curves after Comparing with Ramie	Lignin and Hemicellulose Content (%)	Cellulose Content (%)	DC Corresponding to Cellulose Content 98% as in Raw Ramie	CI (Infrared)
Degummed ramie (gum content 2%)	—	30	70	—	98.00	70	—
PALF sample							
Raw	—	30	44	24.84	68.50	63	0.669
5%	NaOH	30	42	16.60	76.74	54	0.615
10%	NaOH	30	39	12.34	81.00	47	0.580
18%	NaOH	30	30	12.08	81.26	36	0.399
0.5%	$NaClO_2$	45	43	18.44	74.90	56	0.537
0.5%	$NaClO_2$	80	42	16.89	76.45	54	0.495
0.7%	$NaClO_2$	80	40	15.00	78.34	50	0.474

the treatment of $NaClO_2$ solution the lignin is removed and in this case also the degree of crystallinity goes on decreasing. This may be due to the removal of lignin which acts as a cementing material and on delignification an increase in disorder in the structure takes place.[15]

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