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Effect of Potassium Permanganate Treatment on the Macromolecular, Morphological, Thermal and crystallographic structures of Plantain (*Musa paradisiaca*) Fiber

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Abstract

Natural fiber extracted from Plantain (*Musa paradisiaca*) fibers were treated with potassium permanganate ($KMnO_4$)—acetone solution solution at various concentrations for different soaking time. In order to identify the effect of this chemical modification on the macromolecular, morphological, crystallographic structures and thermal properties of the fibers, X-Ray Diffraction (XRD), Fourier Transform Infra-red (FTIR), Thermogravimetric analysis (TGA) and Scanning Electron Microscope (SEM) was used. Wide angle X-Ray Diffraction analysis shows significant change in the macromolecular and the crystallographic parameters of the fiber, Fourier Transform Infra-red (FTIR) spectral confirm the partial removal of wax, hemicellulose, and lignin content. Thermogravimetric analysis (TGA) shows that thermal stability of the fibres increases after treatment, while Scanning Electron Microscope (SEM) micrographs indicate enhance surface roughness of treated fibres. Treated Fibres with 0.05% $KMnO_4$-acetone solution for 3min (05K3) was found to have the highest degree of crystalinity, bulk density, good thermal stability, crystallite size and enhance surface roughness

Keywords: *Natural fiber, Plantain fiber, Potassium permanganate, Thermal properties ……*

1. Introduction

Natural fiber (NF) are not only biodegradable and renewable but possess some unique advantages over conventional fiber such as light weight, low cost, high modulus, high specific strength and safe manufacturing processes [1-3]. Poor wettability, high moisture content, and incompatibility with some polymeric matrix are some of its major disadvantage [4]. Over the years researchers have suggested the use of chemicals treatment of natural fiber as a way of overcoming these challenges [2-4].The use of potassium permanganate (KMn04) as chemical modification for some natural fiber has been proven to be very effective [5], as results has shown that high thermal stability [6], increase tensile strength [7], increase stiffness [7-9], changes in macromolecular and crystallographic structure were all observed after treatment [10]. To access the suitability of natural fiber in different potential application, an understanding of its structural parameters is of extreme important; hence it is essential to understand the structural changes caused by the use of chemicals in fiber modification [10]. The objective of this research therefore, is to investigate the effect of KMnO4 treatment on plantain (*Musa paradisiaca*) fiber with a special emphasis on the macromolecular, morphology, thermal and crystallographic parameters of the fiber.

2. Experimental

2.1. Fiber material

Plantain (*Musa paradisiaca*) pseudo stem were collected from a local farm in south west Nigeria state of Ondo after the harvest season and the fiber were extracted using water ratting methods as reported by Paridah *et al* [11].

2.2. Treatment of Fiber

The extracted fibers were treated as describe by Annapurna *et.al*. [10]. KMnO4-acetone solution having concentration of 0.01%, 0.05%, and 0.10% $KMnO_4$, was used to treat the fiber for a period of 1, 2 and 3 minutes each, after which the solution was decanted and the fibers washed with acetone to remove excess solution present in the fibers. Finally, the fibers were dried at 60^{o}C in the oven for 12 hrs. Untreated fiber was denoted as UT and treated fibers are designated as 01K1, 01K2, 01K3, 05K1, 05K2, 05K3, 1K1, 1K2 and 1K3 respectively. Here K symbolizes to KMnO4 treatment. The prefixes of K denote the concentration of $KMnO_4$ acetone solution i.e. 01, 05, 1 for 0.01%, 0.05% and 0.10% concentrations respectively. However, the suffixes of K denotes the soaking time for the fibers in the solution in minutes

2.3. *Characterization*

In order to study the effect of treatment on the crystallographic structures of plantain (*Musa Paradisiaca*) fibres, X-ray diffraction (XRD) was carried out using a Siemens D-5000 powder diffractometer with monochromatic CuK_a radiation (k = 1.5418 Å), using an acceleration voltage of 40 kV and 40 mA. The diffraction angle was scanned from 5 ^{o} to 50^o 2θ, at a step size of 0.05^o, and a rate of 5.00 ^{o}/min. The degree of Crystallinity was measured using Bruker/Siemens diffraction software package (Topas Rietveld Refinement software) While crystallite size was determine using the Debye Scherrer equation.

$$\sigma = \frac{k\lambda}{\beta cos\theta}$$

Where,

σ = is the particle size (Å), K = Constant (usually k = 0.89); λ = Wavelength of the incident X-ray beam ($\lambda_{CuK\alpha}$ = 1.5418 Å), β = Full width at half maximum of the X-ray diffraction peaks (rad) and θ = Bragg angle of X-ray diffraction peak. The density measurements of the fibres were done as per ASTM D3800-99. Chemical compositions of the raw and treated fibres were investigated by the Tianjin GangDong FTIR 650-spectrometer spectrum in the mid-

IR range i.e. from 400 cm^{-1} to 4000 cm^{-1}. Thermal analysis (TGA) of the fiber was determined using NETZSCH thermo gravimetric balance, (model TG – 209), the analysis was carried out from 40-500^{o}C at a heating rate of 10^{o}C min^{-1}. Fiber morphology was examined by SEM (Zeiss GeminiSEM)

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

XRD patterns of the untreated and KMnO4- treated fibers are shown in figure 1. And crystallographic structural parameters are shown in Table 1, while The highest degree of crystalinity for the 05K3 is shown by maximum increase in the intensity of the crystalline peak at 22.5^{o} followed by 05K2 and is least for 1K3. Concentration of KMnO4 at 05K2 and 05K3 may have oxidize surface of the plantain fiber effectively and successfully etch out lignin binding thousands of micro-fibrils together inside the fiber, this will result in the removal of the non-crystalline materials and rearrangement of cellulose micro-fibril, thus the increment in the degree of crystalinity. The increase of crystallite size observed in 05K2 and 05K3, may also be due to reduction in crystal defect and distortion after treatment which lead to increase in fiber bulk density. Whereas, higher concentration and prolong soaking period resulted in removal of lignin along with cellulosic material which resulted in decrease in crystallites size, bulk density and degree of crystalinity as show in table 1.

Table 1: Various crystallographic and physical parameters of for Untreated and $KMnO_4$ Treated Fibers

Fiber	Degree of crystalinity (%)	Crystallite Size (Å)	Density(g/cc)
UT	53.07	23.39	1.33
01K1	57.60	24.46	1.37
05K1	56.52	24.92	1.35
1K1	52.71	22.31	1.31
01K2	57.87	25.22	1.40
05K2	58.50	25.44	1.47
1K2	51.57	23.03	1.29
01K3	55.99	26.57	1.36
05K3	61.26	26.19	1.54
1K3	50.78	20.21	1.25

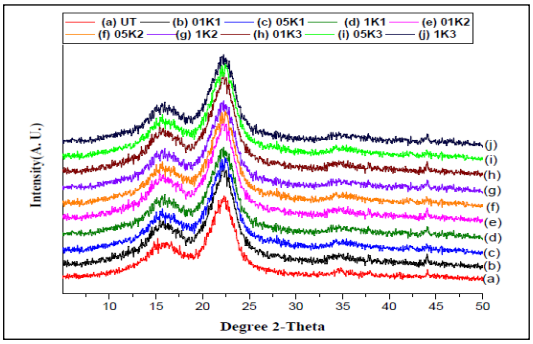


Figure 1: XRD pattern of plantain fibers before and after $KMnO_4$ Treatment

3.2. Infra-red (FTIR) analysis

FTIR Spectra of untreated and $KMnO_4$-treated plantain fibers are exhibited in figure 2. Broad absorbance peak at 3200-3400 cm^{-1} correspond to O-H stretching of hydrogen bond network, which shows decrease with increasing

soaking period of plantain fiber in $KMnO_4$-acetone solution. Prominent decrease at this range can be observed at 05K3, suggesting that the $KMnO_4$-effectively oxidized the O-H groups of cellulose and hemicellulose. However at higher concentration (1K3), it was observed that the intensity tends to increase which is due to the incorporation of more polar group as a result of cellulose degradation. Peaks 2850cm^{-1} correspond to C-H stretching vibration of methyl group which also seem to be affected by the $KMnO_4$ treatment. The peaks at 1730cm^{-1} corresponds to C=O stretching vibration of pectin and waxes, the least intensity was observed at 05K3, which confirm substantial removal of wax from fiber after treatment. The peaks at 1520 cm^{-1} correspond C=C aromatic symmetrical stretching of lignin shows remarkably decrease at 05K3 thus showing that there was effective etching out of lignin from fiber surface at this concentration and time, however at higher concentration degradation of the fiber set in due to excessive oxidation and results in increase intensity afterward

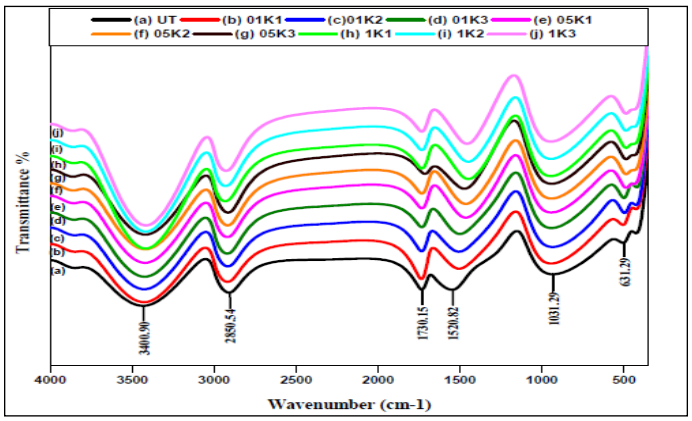


Figure 2: IR Spectral for Untreated and $KMnO_4$ Treated Plantain Fibers

3.3. Fiber morphology (SEM) analysis

The longitudinal surface morphology of $KMnO_4$ treated plantain fibers are shown in the Fig. 3(a-d). The fiber surfaces of untreated plantain fiber are shown to be cover with waxes and other impurities, with $KMnO_4$ treatment the fiber roughness increases. 05K3 fiber showed uniform surface roughness of the fiber. This might be due to the effective oxidation of the fiber surface when it is soaked in 0.05% of concentration of KMnO4 – acetone solution for 3 min which lead to the better roughness of the fiber due to the removal of lignin, waxy material along with the impurities from the fiber. Higher concentration and prolong soaking time (1K3), shows surface degradation, the degradation may become severe with increase in period of treatment at this concentration.

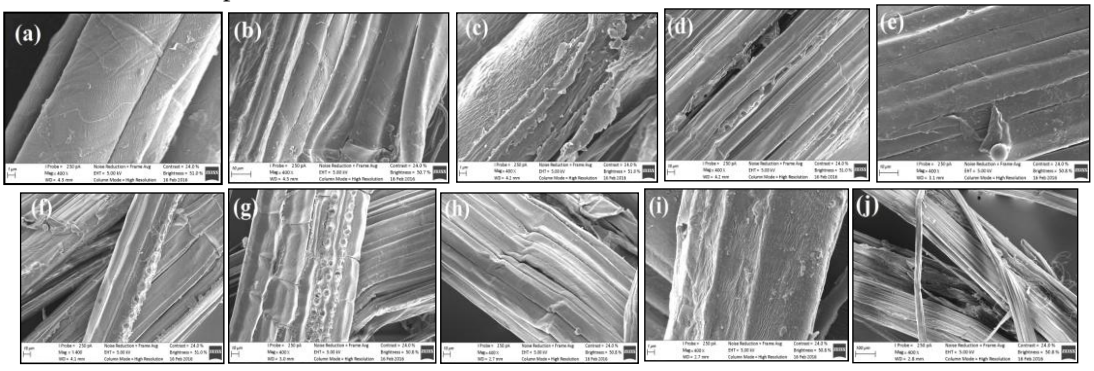
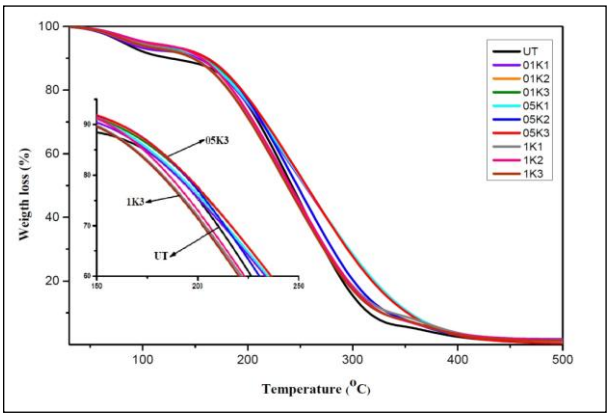


Figure 3: Longitudinal morphology of (a) UT (b) 01K1 (c) 01K2 (d) 01K3 (e) 05K1 (f) 05K2 (g) 05K3 (h) 1K1 (i) 1K2 (j) 1K3

3.4. Thermogravimetric analysis (TGA) analysis

Thermogravimetric analysis (TGA) thermographs of $KMnO_4$, Treated Fibers fiber samples are shown in figure 4. Three major decomposition stages was observed, the first stage (40-150^oC) was due to primary change by moisture evaporation, second stage decomposition (150-250^oC) is due to hemicellulose and cellulosic degradation, while the final stage (250-500^oC)was as a result of lignin decomposition. Lower concentration of $KMnO_4$, Treated Fibers (0.01-0.05%), showed higher thermal stability when compare to the untreated fiber, this indicate that $KMnO_4$ treatments effectively oxidizes the fiber and breaks the hydrogen bond between the O-H groups of cellulose and hemicelluloses, whereas at higher concentration and treating period (1K3), there was excessive oxidation which lead to degradation of cellulose and decrease in thermal stability of fiber.



4. Conclusion

The macromolecular study of untreated and $KMnO_4$ treated, plantain (*Musa paradisiaca*) fibers suggests that the degree of crystalinity, crystallite size and bulk density were all affected by the chemical modification as maximum reduction of OH group and lignin content are observed. SEM micrograph confirms changes on fiber as the surface became rougher after treatment; improve thermal stability after treatment at lower treatment concentration was also obtained. Finally it is concluded that optimum treatment of plantain (*Musa Paradisiaca*) fibers surface is when immersed in 0.05% of KMnO4-acteone solution for 3 min

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