

Effect of Alkaline Treatment on the Macromolecular, Thermal, and Crystallographic Structures of Plantain (*Musa paradisiaca*) Fibers

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Natural fibres were extracted from Plantain (*Musa paradisiaca*) pseudostem and modified using sodium hydroxide solution under different conditions in terms of concentration and treatment time. In order to identify the effect of this chemical modification on the macromolecular, thermal, morphological, and crystallographic structures of the fibres, X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), and Thermogravimetric Analysis (TGA) were carried out on both treated and untreated fibres. XRD analysis showed significant changes in the macromolecular and crystallographic parameters of the fibre. FTIR spectra confirmed the partial removal of wax, hemicellulose, and lignin. Thermogravimetric Analysis results indicated enhanced stability of the fibres after treatment, while SEM morphology showed that surface roughness was achieved for all modified fibres. The fibres that were treated at 3% concentration for 4 h (3N4) were found to have enhanced density, surface roughness, and a higher degree of crystallinity. However, degradation was observed at higher concentrations and prolonged treatment.

Keywords: Plantain fibre; Chemical modification; Macromolecular; X-ray diffraction

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INTRODUCTION

Health hazards and environmental concerns associated with the conventional synthetic fibres such as aramid, glass, carbon, *etc.* have motivated manufacturers and scientists of fundamental research to develop alternative materials that are nontoxic, biodegradable, high strength, high modulus, low density, and low cost. In this regard, the abundantly available natural plant fibre has been proved to be a boon in the present energy crisis situation (John and Thomas 2008; Yousif *et al.* 2012; Rokbi *et al.* 2001; Bachtiar *et al.* 2008). Some of the major disadvantages of natural fibre include poor wettability, incompatibility with some polymeric matrices, and high moisture absorption by the fibres (Bachtiar *et al.* 2008). Researchers have over the years suggested the use of chemical treatments for surface modification as a way of overcoming these challenges and improving the properties of natural fibres (Yousif *et al.* 2012; Rokbi *et al.* 2001; Bachtiar *et al.* 2008). Effect of chemical treatments on surface morphology, thermal behaviour, and structure of natural fibres has been reported by various authors (Yousif *et al.* 2012; Rokbi *et al.* 2001; Bachtiar *et al.* 2008; Cao *et al.* 2006; Kaith and Kalia 2008; Calado *et al.* 2000; Kaushik *et al.* 2012).

Pre-treatments of natural fibre can remove surface impurities (Li *et al.* 2008), and chemically modify the surface, reduce moisture absorption processes, and increase surface roughness (Kaith and Kalia 2008; Calado *et al.* 2000; Kaushik *et al.* 2012; Mishra *et al.* 2009). There is also a reduction in the number of free hydroxyl groups of the cellulose, which results in polarity reduction of the cellulose molecules and enhances compatibility with polymer matrices (Calado *et al.* 2000; Kaushik *et al.* 2012). One of the simplest and effective surface modification techniques widely used in natural fibre is the alkaline treatment (Yousif *et al.* 2012; Rokbi *et al.* 2001; Bachtiar *et al.* 2008; Cao *et al.* 2006). Alkaline treatment improves the fibre-matrix adhesion due to the removal of both natural and artificial impurities, improved the fibre wetting by fibrillation, which increases the effective surface area available for contact with wet polymer matrix (Kaushik *et al.* 2012; Mishra *et al.* 2009).

Researchers such as Chimekwene *et al.* (2010), Okafor *et al.* (2012), Alvarez-López *et al.* (2014), and Candena Ch. *et al.* (2017) have all studied plantain fibres as a source of natural fibre and their various applications. However, there is no report on the effect of alkaline treatment on the macromolecular properties of plantain (*Musa paradisiaca*) fibre. This work therefore, is aimed at evaluating the effect of chemical modification on plantain (*Musa paradisiaca*) fibre surface by applying alkaline solution at different concentrations and treatment times. These actions are intended primarily on the fibre bundles, to isolating the technical fibres and removing non-structural matter from them. A subsequent objective was to evaluate the effects of these modifications on the macromolecular, morphology, thermal, and crystallographic parameters of the fibre.

EXPERIMENTAL

Materials and Methods

Plantain (*Musa paradisiaca*) pseudo stem were collected from a local farm in south west Nigeria state of Ondo after the harvest season and the fibre was extracted from 3-year-old stem using water retting methods as reported by Paridah *et al.* (2011). Extracted fibre was pale brown and each fibre length varies from 1 meter to 1.5 meters with a density of 1.33 (g/cc).



Fig 1. Photograph of (a) plantain (*Musa paradisiaca*) species (b) extracted plantain fibre

Treatment of Fibre

The extracted fibres were immersed in alkaline solutions of 1%, 3%, and 5% concentration of sodium hydroxide. The soaking period of fibres was varied as 1, 2, and 4 h. Then the fibres were taken out from the solution and rinsed with distilled water several times to remove residual alkalinity. Neutrality of the fibres was checked by pH paper. The fibres were dried at room temperature for 1 day. The fibres were then put in the air circulating oven until the fibre reached constant weight. Generally, in this work, it took 6 to 8 h to achieve constant weight of the fibre. The fibres were designated as 1N₁, 1N₂, 1N₄, 3N₁, 3N₂, 3N₄, 5N₁, 5N₂, and 5N₄. The prefixes of 'N' denote the concentration of the alkaline solution, whereas the suffixes of 'N' represent the immersion time of the fibre in the solution in hours. The untreated fibres were designated as "UT"

Characterization of Fibre

In order to identify the effect of treatment on the crystallographic structures of plantain (*Musa paradisiaca*) fibres, wide angle x-ray diffraction was carried out using a Siemens D-5000 powder diffractometer with monochromatic CuK α radiation ($k = 1.5418$ Å), using an acceleration voltage of 40 kV and 40 mA. The diffraction angle was scanned from 5° to 50° 2θ , at a step size of 0.05°, and a rate of 5.00 o/min. The degree of crystallinity was measured using Bruker/Siemens diffraction software package (Topaz Rietveld Refinement software). Crystallite size was determined using the Debye Sherrer's formula. Density measurements of the fibres were done as per American Standard of Test and Measurement (ASTM) D3800-99. Chemical compositions of the untreated and treated fibres were investigated by the Tianjin GangDong FTIR 650-spectrometer spectrum in the mid IR range from 400 cm⁻¹ to 4000 cm⁻¹. Thermogravimetry analysis of the fibre was determined using NETZSCH thermal gravimetric balance, (model TG – 209). Fibre morphology was examined by Scanning Electron Microscope Zeiss GeminiSEM) at 15.0 kV.

RESULTS AND DISCUSSION

XRD patterns of untreated and alkaline treated fibre are shown in Fig. 2. The broad peaks at 15.3° and 22.6° in the fibre are characteristic of cellulose I (Patra and Bisoyi 2011; Klemm *et al.* 2005) and correspond to the (101) and (002) planes respectively in the lignocellulose fibres (Ouajai and Shanks 2005). It was observed that with an increase in alkaline concentration in which the fibres were soaked from 1% to 3%, the degree of crystallinity, bulk density, and crystallite size of the fibres was increased, as shown in Table 1. This may be due to the removal of the amorphous part, natural wax, and impurities of the fibres, which increases the percentage of the crystalline part (Patra and Bisoyi 2011). However, at a concentration of 5%, a decrease in the degree of crystallinity, bulk density, and crystallite size was observed, which was attributed to the removal of cellulosic materials along with lignin part at higher concentration and soaking period in the solution (Patra *et al.* 2013; Suardana *et al.* 2011).

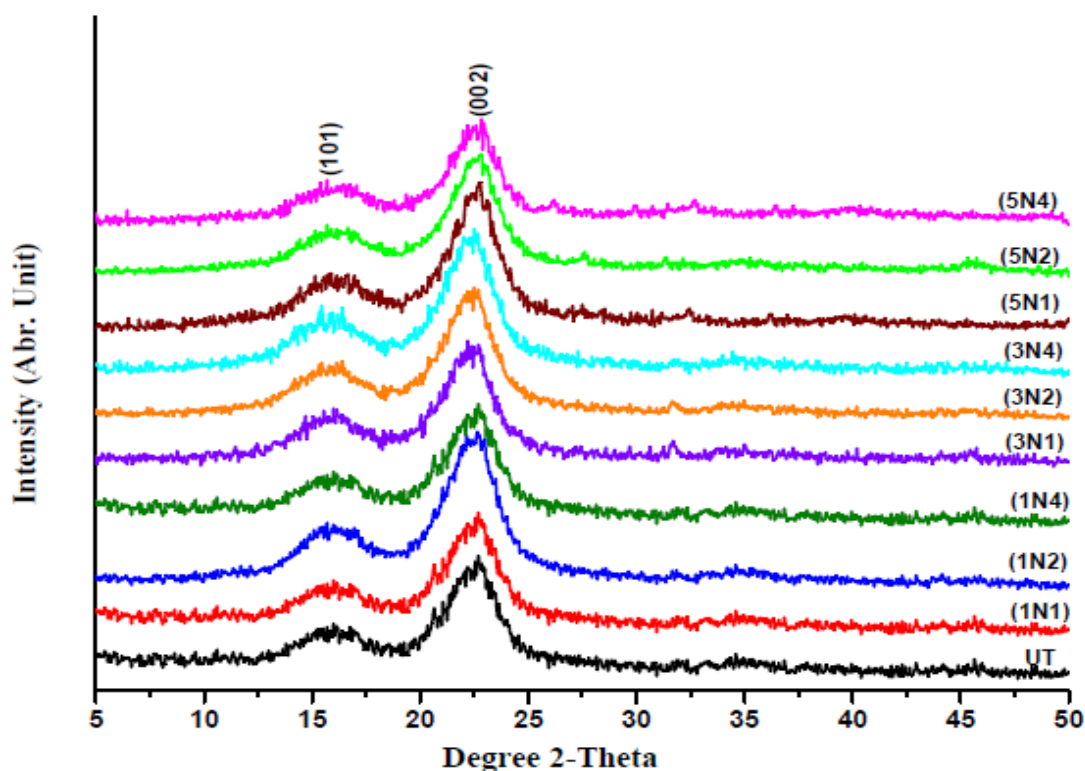


Fig. 2. XRD spectral for untreated and alkaline treated fibres

Table 1. Various Crystallographic and Physical Parameters of Plantain Fibres

Fibre	Degree of crystallinity (%)	Crystallite size (Å)	Density (g/cc)
UT	53.07	23.39	1.33
1N1	53.25	24.30	1.36
1N2	55.19	25.04	1.38
1N4	58.02	25.89	1.44
3N1	55.80	25.15	1.39
3N2	57.36	25.77	1.43
3N4	60.87	27.49	1.53
5N1	54.02	24.39	1.37
5N2	48.23	23.34	1.28
5N4	42.29	22.29	1.21

Figure 3 exhibits the FTIR spectra of untreated and alkaline treated plantain fibres. The band at 1030 cm^{-1} is assigned to aromatic C-H plane deformation for primary alcohol in lignin, which was significantly reduced after alkaline treatment compared to the untreated fibres. The band at $1505\text{--}1525\text{ cm}^{-1}$ corresponds to the aromatic ring of lignin (Patra and Bisoyi 2011); it shows a decreased absorbed intensity ratio after alkaline treatment which confirms the reduction of lignin content. The peak at 1730 cm^{-1} , which corresponds to hemicellulose, was observed to decrease after NaOH treatment; this confirmed the removal of hemicellulose part from the fibre, which may be due to the removal of acetyl group present in the hemicellulose (Patra and Bisoyi 2011). The band at $3300\text{--}3500\text{ cm}^{-1}$ is the characteristic of the axial vibration of hydroxyls from cellulose.

The broadness of this band increased with NaOH treatment due to change of the inter- and intra-molecular hydrogen bonding in polysaccharides (Esmeraldo *et al.* 2010; Barreto *et al.* 2011).

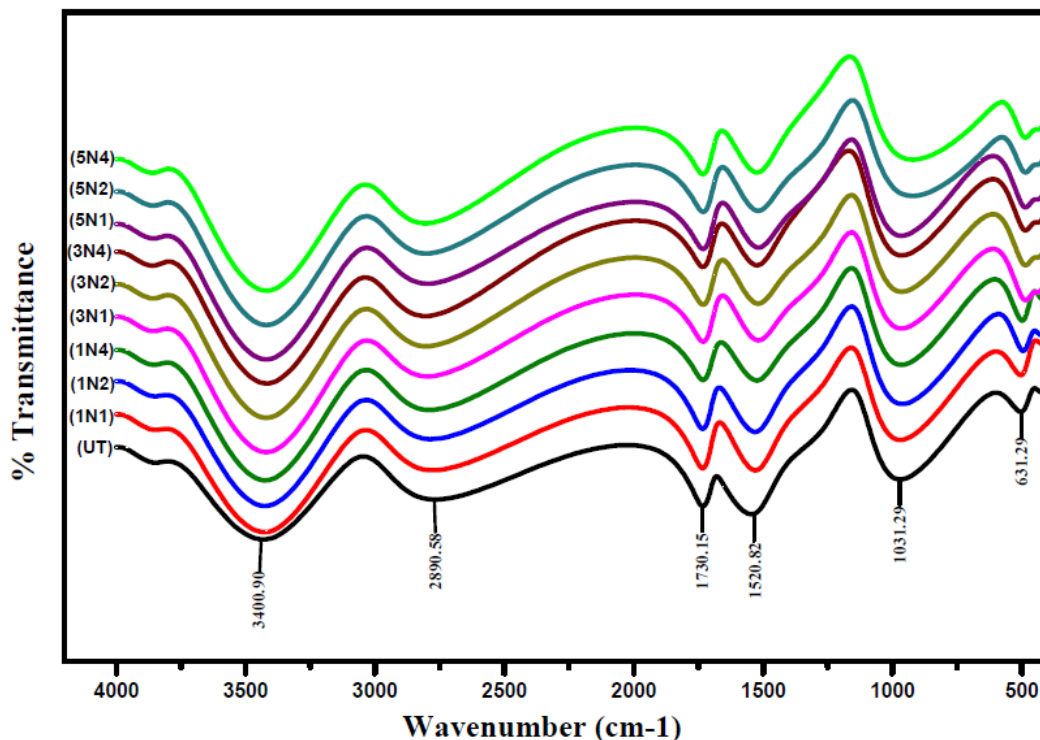


Fig. 3. IR spectral for untreated and alkaline treated fibres

TGA thermographs of alkalinized fibre samples are shown in Fig. 4(a-c). First stage decomposition (80 to 200 °C) was due to primary changes, *i.e.* loss of moisture, as well as the breakdown of hemicellulose and glycoside linkages (Kaushik *et al.* 2012). The alkaline treated fibres in Fig. 4(a & b), showed higher decomposition temperatures compared to the untreated fibres. However, a decrease in thermal stability was observed for 5% alkaline treated fibre in Fig. 4c, an indication that after chemical treatments surface of fibres become more amorphous, which may be due to the degradation of the crystalline part (Kim and Eom 2001).

For the second fibre decomposition stage (250 to 350 °C), the alkalinized fibres had less weight loss than the untreated fibres. These results indicate that portions of hemicellulose and lignin constituents were removed from the fibre after treatment. The final decomposition temperature decreases after alkaline treatments. The decrease in final stage decomposition (350 to 600°C), temperature indicates that after treatments, there was much loss in cellulosic and lignin due to degradation, as observed by other researchers (Kaushik *et al.* 2012).

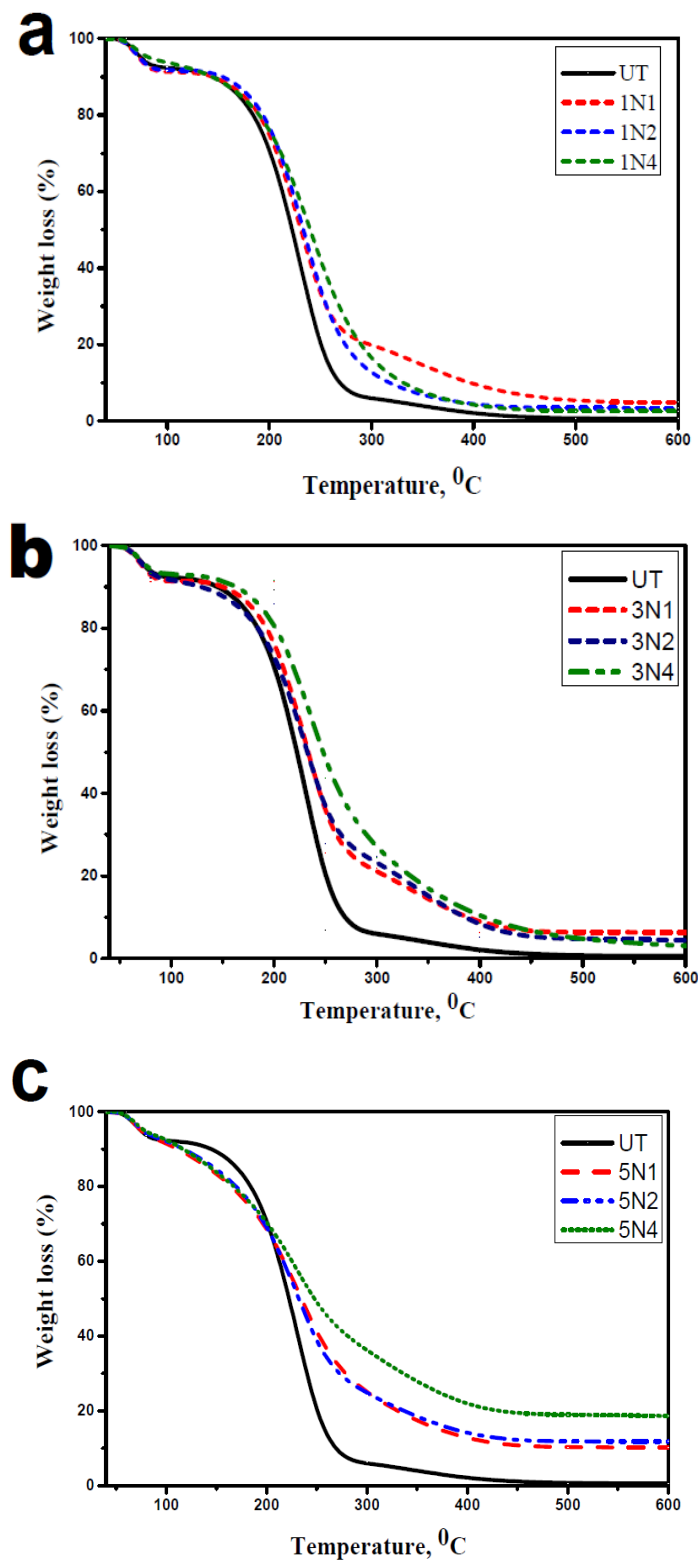
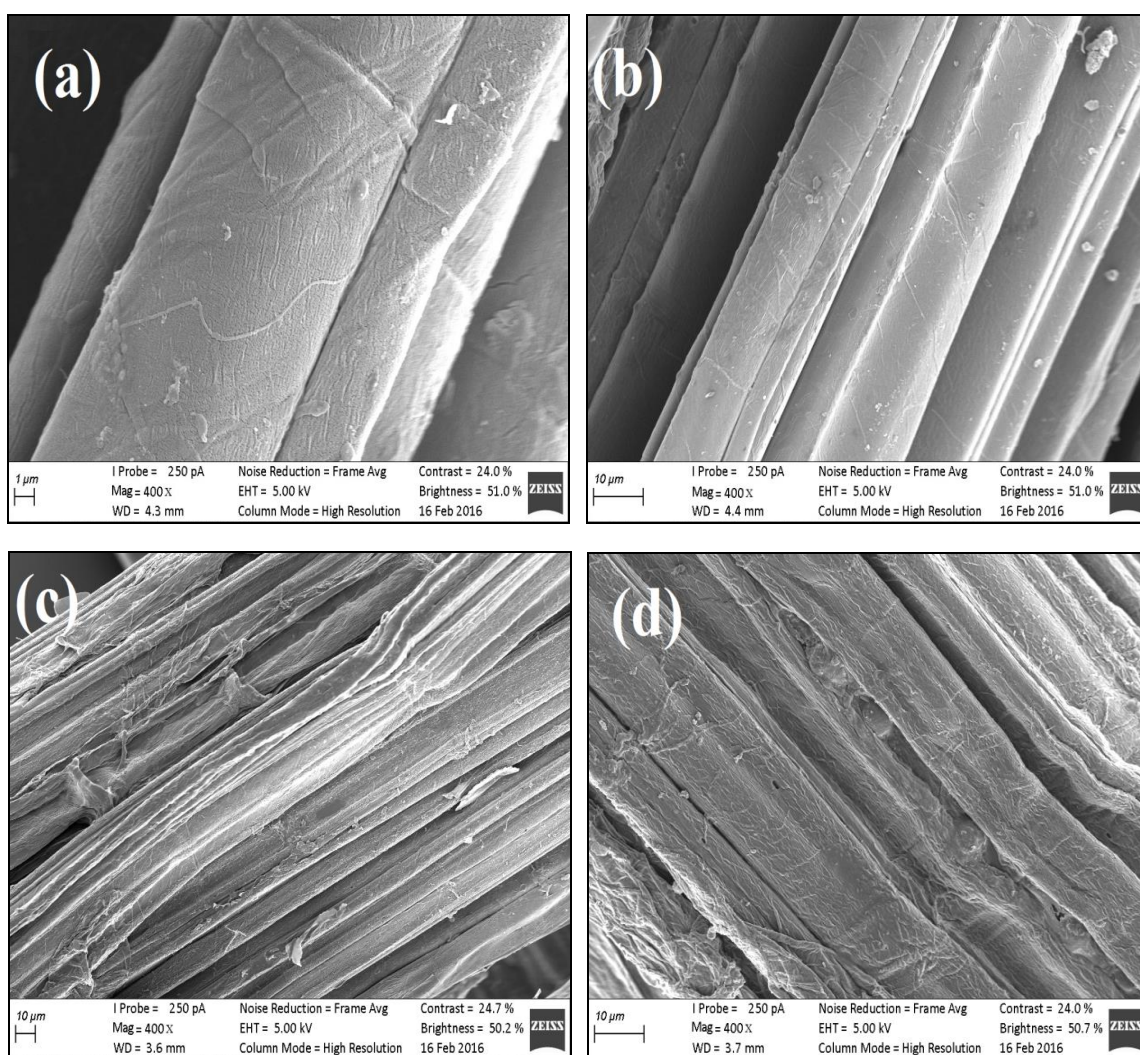


Fig. 4. (a-c) Thermogravimetric curve for untreated and (a) 1% Alkaline Treated Fibres, (b) 3% Alkaline Treated Fibres, (c) 5% Alkaline Treated Fibres

SEM micrographs of alkaline treated fibre are shown in Fig. 5(a-j). It was observed in the untreated fibre (Fig. 5a), that the fibre surface was smooth, presumably covered with waxes and other impurities. The surface roughness of the fibre was increased with increase in the concentration of the alkaline solution from 1% to 5%. This may be due to the removal of hemicellulose, lignin, and surface impurities from the fibre, hence providing a rough surface to the fibre. Maximum surface roughness was observed for 3N4 treated fibre (Fig. 5g), which may be due to the substantial removal of impurities and partial removal of hemicellulose from the fibre. Thus, the fibrous region became more pronounced. On the other hand, higher concentration and longer duration of the soaking period led to the degradation of the fibre, which may be due to degradation of the cellulosic part and over de-lignification of the fibre.



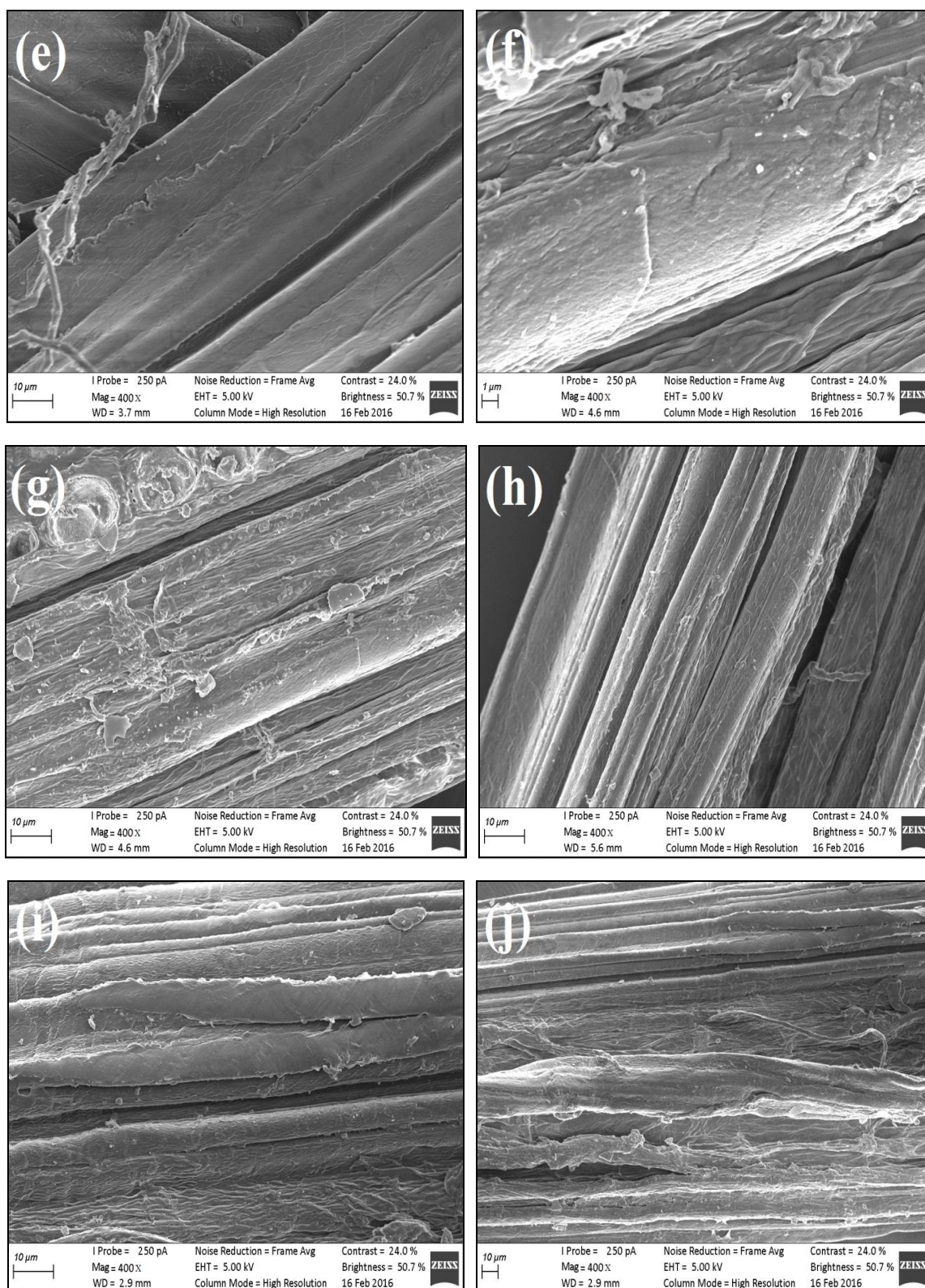


Fig. 4 (a-j). Longitudinal morphology of (a) UT, (b) 1N1, (c) 1N2, (d) 1N4, (e) 3N1, (f) 3N2, (g) 3N4, (h) 5N1, (i) 5N2, (j) 5N4

CONCLUSIONS

The suitability of alkaline treatment for the modification of plantain (*Musa paradisiaca*) fibre was investigated. Macromolecular parameters of the fibre along with crystallographic structures and morphology of the fibre were all affected by the chemical modification. Improved thermal stability, as well as increases in the degree of crystallinity, crystallite size, and bulk density were observed after treatment at optimised condition (3N4). SEM micrographs confirmed changes on fibre surface, as they became rougher after treatment. Reduction of the hemicellulose and lignin groups in the fibre was confirmed by FTIR spectra after alkaline treatment. However, excessive soaking period at high concentration caused the degradation of the fibres.

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