Applied Tropical Agriculture
Volume 21, No.1, 153-158, 2016.
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Effect of chemical modification on physicochemical properties of coir, empty fruit bunch and palm kernel fibres

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ABSTRACT

The coir (CCF, called coir fibres), empty fruit bunch (EFB) and palm kernel fibres (PKF) were chemically modified using mercerization, alkaline bleaching and acetylation reaction. The influence of these treatments on the physicochemical properties of the fibres was investigated. The chemical modification of these fibres resulted in improvement in ash content, bulk density, and iodine absorption number of the fibres. The moisture content of CCF fibres was reduced by 37.68%, 58.80% and 67.39% when mercerized, alkaline bleached and acetylated respectively. EFB fibres' moisture content was reduced by 38.54%, 61.46% and 68.82% when mercerized, alkaline bleached and acetylated respectively. Mercerized PKF fibres had moisture content 42.16% less than unmodified fibres. Alkaline bleached and acetylated PKF fibres had moisture content 67.03% and 72.93% respectively less than unmodified fibres. The effect of treatments on pH values of acetylated fibres was observed to be inversely related to that of bulk density. Morphology study showed that the chemically modified fibres had smoother surfaces and wider pore sizes compared to unmodified fibres.

Key words: Acetylation; Density; Fibres; Mercerization; Physicochemical

INTRODUCTION

Coconut and Palm trees are grown purposely for their nut and oil contents. A mature fruit contains single seed surrounded by a soft pulp called fibre (George *et al.* 2001). Among several types of fibres that can be obtained from coconut and palm trees are the soft pulp covering the coconut kernel; called coir fibres (CCF), while empty fruit bunch (EFB) and palm kernel fibres (PKF) cover oil palm fruit and palm kernel respectively (Rozman *et al.* 2003). These natural fibres belong to the class of fruit fibres and their major chemical compositions are pectin, hemicelluloses, lignin and cellulose (Bledzki *et al.* 2008). They are post harvest agro-waste materials. Presently, they are very useful in chemical (polymer) industry as environmentally friendly fillers (Khalil *et al.* 2001). The monolithic conventional thermoplastic/thermosetting polymer lacks some of the desired properties for modern day technology and the only way to harmonize the present technology with the future engineering materials required is reinforcing the conventional polymer with natural fibres, such as CCF, EFB, PKF etc (Ishidi *et al.* 2011). Addition of any of these natural fibres (especially when chemically modified) into the polymer matrices enhances mechanical property among other properties of the composites (Khalil *et al.* 2001) and serves as a means of transforming waste to wealth (Ishidi *et al.* 2011). The major problem encountered when lignocellulosic (natural fibres) materials are to be used to reinforce thermoplastic/thermosetting polymer is incompatibility between hydrophilic natural fibres and hydrophobic thermoplastic/thermosetting polymer (Maya and Rajesh, 2008). A good interfacial adhesion between natural fibres and polymer matrix can be achieved through chemical modification of the natural fibres according to Sreekala and Thomas, (2003). These treatments reduce hydrophilic nature of the natural fibres; stabilize the cell wall against moisture, improve dimensional stability, environmental degradation and compatibility with hydrophobic polymer (Bledzki *et al.* 2008). Bledzki and Gassan (1999) investigated the role of chemical treatment on properties of jute and pine fibres and reported that chemical treatments reduce the hydrophilic nature of the natural fibres; stabilize the cell wall against moisture, improve dimensional stability, environmental degradation and compatibility with hydrophobic polymer. In this research work, mercerization, alkaline bleaching and acetylation reaction were carried out and the effect of these chemical treatments on the physicochemical properties of CCF, EFB and PKF fibres were determined.

MATERIALS AND METHODS

Materials

The coir fibres were obtained from Cassava Avenue, FUTA road, Akure. The empty fruit bunch and palm kernel fibres were obtained from FUTA research farm, Akure, Ondo state, Nigeria. Reagents used were of AnalaR grade.

Experimental Techniques

Physical Treatment of the Fibre Samples

Coir (CCF), empty fruit bunch (EFB) and palm kernel fibres (PKF) were soaked with hot detergent solution (2%) at temperature 80ºC on thermo started hot plate to eliminate oil, wax and other impurities. The fibres were then dried in the oven at 105ºC for 2 hours, cooled in desiccators, ground and sieved to uniform sizes (Suradi *et al.* 2009).

Chemical Composition of Coconut Coir, Empty Fruit Bunch and Palm Kernel Fibres

Percentage pectin, hemicellulose, lignin and cellulose in CCF, EFB and PKF were determined using standard methods (ASTM, 2001).

Chemical Treatment of the Fibre Samples

The physically treated CCF, EFB and PKF fibers were divided into four parts each. The first portion was treated with NaOH (5%) solution, called mercerization process (Ray *et al.* 2001). The second portion was treated with H_2O_2 (2%) in NaOH (25%) solution, called alkaline bleaching process (Sun *et al.* 2004; Habibi *et al.* 2008) and the third portion treated with combination of acetic acid (10%) and acetic anhydride (10%) with a drop of conc. H_2SO_4 as catalyst, called acetylation process (Bledzki *et al.* 2008). All the treatments were carried out at room temperature (except acetylation that was carried out at 60ºC) for 2 h in liquor ratio 1:200. At the end of the treatment time, each of the treated fibres was washed with distilled water, until they were free of chemicals used for their various treatments. The samples were then oven dried at 105ºC for 2 h. The last portion of each of the fibres were not treated and they served as control samples.

Physicochemical Properties of the Fibres

Ash Content

Each of unmodified, mercerized, alkaline bleached and acetylated CCF, EFB and PKF fibres (about 0.5 g) was put in a crucible of known mass and heated in a muffle furnace at 500ºC for 1 h. The heated samples were cooled in desiccators and weighed. The ash content of each of sample was calculated using equation 1 (Pattabhi *et al.* 2008). Ash content $= \frac{W_2 - W_3}{W_2 - W_1} X100\%$......(1)

Where; W_1 = Weight of crucible; W_2 = Initial weight of crucible with sample; W_3 = Final weight of crucible with sample

Determination of pH

Each of unmodified, mercerized, alkaline bleached and acetylated CCF, EFB and PKF fibres (0.1g each) was boiled in beaker (250 mL) containing boiling distilled water (100 mL) for 5 min. The solution was diluted to 200 mL with distilled water and cooled at room temperature as described by Adebayo and Elelu, (2011). The pH of each was measured using Fotic 20 Labtech digital pH meter

Iodine Number

The iodine number of each of unmodified, mercerized, alkaline bleached and acetylated CCF, EFB and PKF fibres was determined by adding fibre sample (about 0.1 g) to 10 ml of HCl (5%), boiled for 5 min and cooled. Exactly 20 mL of iodine solution (0.1 N) was added to each of the sample solutions and stirred for at least 30 min using a magnetic stirrer. At the end of the reaction time, each of the sample solutions was titrated with $Na_2S_2O_3$ (0.2 N) and two drops of starch indicator was added just before the end point. The procedure was repeated for the blank and the iodine absorption number of each of the sample was calculated using equation 2 (Adebayo and Elelu, 2011).

$$\text{Iodine number} = \frac{12.69(B-A)N}{W}\text{..........(2)}$$

where B= Blank titre value in $Na_2S_2O_3$; A= Sample titre value in $Na_2S_2O_3$ Normality; W= Mass of the sample

Bulk Density

The bulk density of each of unmodified, mercerized, alkaline bleached and acetylated CCF, EFB and PKF fibres was determined by weighing an empty measuring cylinder, cylinder containing fibre sample and cylinder filled with water. The weight of each was determined from the difference in weight of the filled and empty measuring cylinder. The bulk density was determined by dividing the weight of each by the volume of measuring cylinder using equation 3.

$$\text{Bulk density} = \frac{W_2 - W_3}{V}\text{.......(3)}$$

where, W = Mass of empty measuring cylinder; W_2 = Mass of cylinder filled with water; W_3 = Mass of cylinder filled with sample; V = Volume of measuring cylinder

Moisture Content

Each of unmodified, mercerized, alkaline bleached and acetylated CCF, EFB and PKF fibres (about 0.100 g) was put in a crucible of a predetermined weight and placed in an oven for 3 h at temperature of 105ºC. The samples were removed and cooled in a desiccator, the cooled sample was weighed and returned to the oven for 15 min at 105ºC, sample removed, cooled in desiccator and reweighed. This was repeated at 105ºC for 15 min until a constant weight was obtained. The loss in weight was noted as moisture content. The percentage moisture content was calculated as using equation 4 (Alinnor and Madu, 2007).

$$\text{Moisture content} = \frac{W_1 - W_2}{W_1} x\ 100\% \ldots\ldots (4)$$

where W_1 = Weight of wet fibre sample and W_2 = Weight of dry fibre sample.

Surface Morphology of the Fibres

The scanning electron micrographs of the samples were taken using XL 20 Philips SEM. The surface morphology of the fibres was studied with the microscope operated at 10.0 kV. The samples were coated with a 10 nm thick layer of gold.

RESULTS AND DISCUSSION

Chemical Composition of Coconut Coir, Empty Fruit Bunch and Palm Kernel Fibres

Table 1 shows the percentage composition of unmodified empty fruit bunch (UEFB) and unmodified palm kernel fibres (UPKF) in order cellulose > lignin > hemicellulose > pectin. Unmodified coir fibres (UCCF) displayed order lignin > cellulose > hemicellulose > pectin. These observations agreed with the findings made by Rakesh *et al.* (2011), in chemical modifications of natural fibre for composite material.

Physicochemical properties of the Fibres

The Physicochemical properties of each of unmodified, mercerized, alkaline bleached and acetylated CCF, EFB and PKF fibres are summarized in Table 2. The percentage moisture content of the fibre samples were found to be in order CCF < EFB < PKF. This observation shows that CCF has the least inherent water retention property, followed by EFB and PKF has the highest. Acetylated fibres have the lowest moisture content, suggesting acetylation to have highest hydrophilic nature of fibre conversion to hydrophobic nature, followed by alkaline bleaching, while mercerization gave the least conversion. The observations agreed with Suradi *et al.* (2009), in influence of pre-treatment on the properties of lignocellulose based biocomposite. The ash content gives the total inorganic constituent present in the fibres. UCCF, UEFB and UPKF fibres have ash contents of 3.2%, 1.97% and 2.58% respectively. The chemical modifications led to increase in ash content of the fibres in the following order alkali bleached > mercerized > acetylated fibre (Table 2). The highest ash content in the alkali bleached fibres might be as a result of absorption of high content of sodium from 25% NaOH treatment, followed by that of mercerized fibres that equally absorbed sodium from 5% NaOH treatment. The sodium absorbed by these fibres is inorganic matter that might actually lead to increase in ash content. Acetylation is a treatment that led to dissolution of pectin and degradation of lignin contents in the fibres and the reduction in these compositions of the fibres decreased the fibre volatile matter and this led to increase in ash content as it was reported by Adebayo and Elulu (2011). The bulk density of the fibres is in order acetylated fibres > unmodified fibres > mercerized fibres > alkaline bleached fibres. This shows that acetylation reaction led to increase in bulk density of the fibres, while other modification reactions led to decrease in bulk density (acetylation reaction led to increase in weight of the treated fibres, while mercerization and alkaline bleaching led to reduction in weight of the treated fibres).

Table 1: Chemical composition of UCCF, UEFB and UPKF

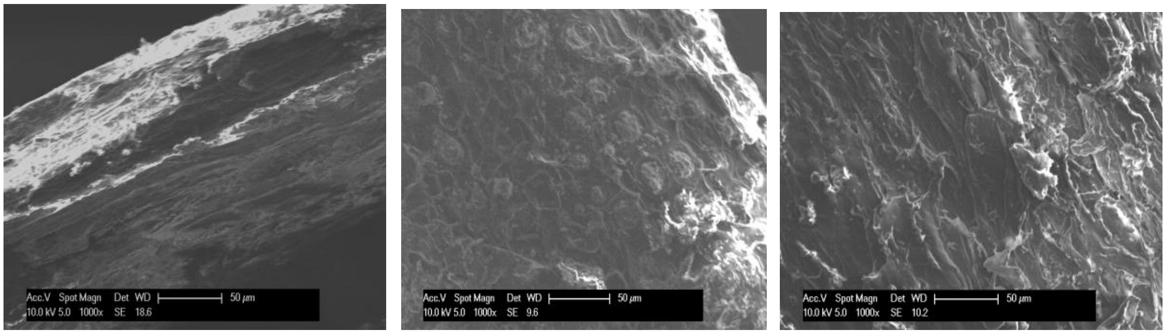
Composition	UCCF	UEFB	UPKF
Pectin (g)	$1.93^{d}\pm0.05$	$2.00^{d}\pm0.06$	$2.44^{d}\pm0.41$
Hemicellulose (g)	$9.01^{c}\pm0.07$	$13.71^{c}\pm0.12$	$14.05^{c}\pm0.39$
Lignin (g)	$47.69^{a}\pm0.63$	$21.64^{a}\pm0.33$	$30.00^{b}\pm0.74$
Cellulose (g)	$40.77^{b}\pm0.63$	$61.63^{d}\pm0.17$	$51.82^{a}\pm1.49$
Total	99.40	98.98	98.31

Means ± std of triplicate determinations. Means follow the same superscript are not significantly different (P≤0.05) by Duncan's multiple range test. where: UCCF = Unmodified coir fibre; UEFB = Unmodified empty fruit bunch fibre; UPKF = Unmodified palm kernel fibre

Table 2: Physicochemical properties of modified and unmodified CCF, EFB and PKF fibres

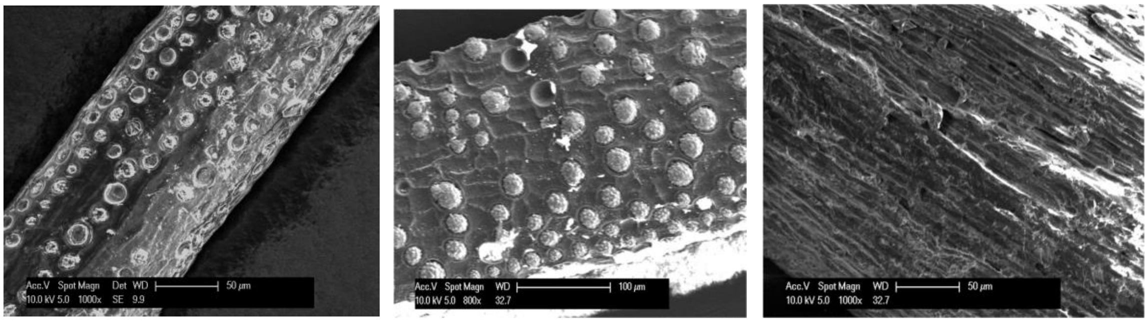
Fibre	MC (%)	AC (%)	BD (g/cm^3)	pH	IN
UCCF	$9.66^{c}\pm0.24$	$3.27^{g}\pm0.06$	$0.723^{ef}\pm0.04$	6.9^{g}	$31.40^{i}\pm0.16$
MCCF	$6.02^{e}\pm0.08$	$4.61^{d}\pm0.02$	$0.782^{d}\pm0.02$	9.4^{d}	$56.88^{d}\pm0.47$
BCCF	$3.98^{gh}\pm0.03$	$6.54^{a}\pm0.03$	$0.885^{c}\pm0.02$	11.9^{a}	$64.81^{b}\pm0.70$
ACCF	$3.15^{i}\pm0.08$	$3.95^{f}\pm0.06$	$1.000^{a}\pm0.02$	5.6^{j}	$35.11^{h}\pm0.10$
UEFB	$12.09^{b}\pm0.24$	$1.97^{j}\pm0.03$	$0.677^{f}\pm0.03$	6.3^{i}	$37.77^{g}\pm0.16$
MEFB	$7.43^{d}\pm0.08$	$4.51^{e}\pm0.04$	$0.763^{de}\pm0.00$	8.2^{f}	$57.54^{d}\pm0.45$
BEFB	$4.66^{f}\pm0.03$	$6.00^{b}\pm0.00$	$0.858^{c}\pm0.02$	11.4^{c}	$70.39^{a}\pm0.41$
AEFB	$3.77^{h}\pm0.08$	$3.25^{g}\pm0.02$	$0.967^{ab}\pm0.04$	5.1^{l}	$41.13^{f}\pm0.43$
UPKF	$15.44^{a}\pm0.24$	$2.58^{i}\pm0.03$	$0.580^{g}\pm0.03$	6.5^{h}	$26.32^{k}\pm0.30$
MPKF	$8.93^{d}\pm0.08$	$3.92^{f}\pm0.00$	$0.705^{f}\pm0.06$	9.1^{e}	$50.10^{e}\pm0.40$
BPKF	$5.90^{e}\pm0.03$	$5.23^{c}\pm0.00$	$0.853^{c}\pm0.01$	11.8^{b}	$62.82^{c}\pm0.37$
APKF	$4.18^{g}\pm0.08$	$2.65^{h}\pm0.00$	$0.945^{b}\pm0.02$	5.4^{k}	$28.65^{j}\pm0.11$

Means ± std of triplicate determinations. Means follow the same superscript are not significantly different (P≤0.05) by Duncan's multiple range test. Where: MC = Moisture content; AC = Ash content; BD = Bulk density; pH = Acidity/alkalinity; IN = Iodine number; UCCF = Unmodified coir fibre, MCCF = Mercerized coir fibre, BCCF = Alkaline bleached coir fibre, and ACCF = Acetylated coir fibre



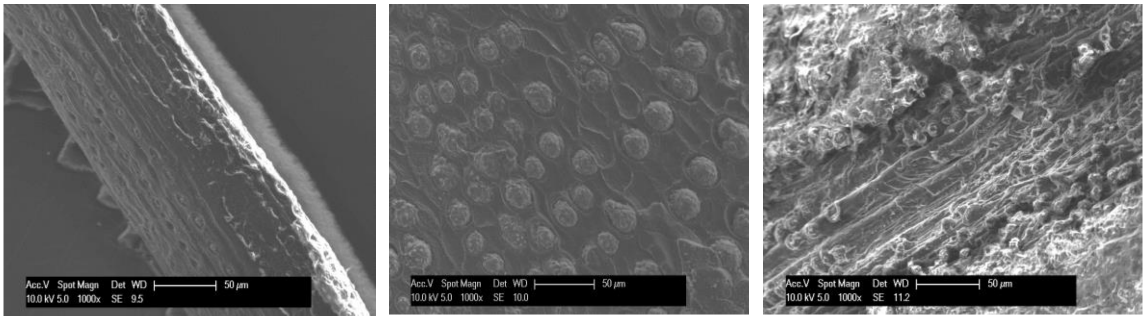
UEFB UPKF UCCF

Plate 1: Scanning Electron Microscope images of the unmodified empty fruit bunch (UEFB), palm kernel (UPKF) and coir fibres (UCCF)



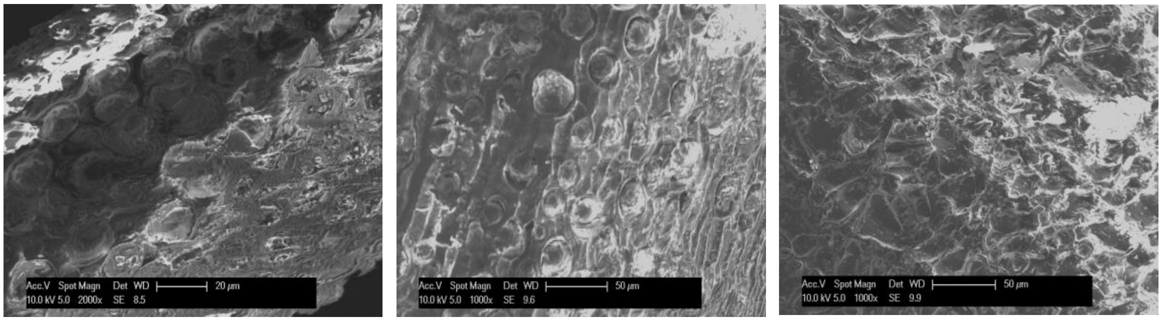
MEFB MPKF MCCF

Plate 2: Scanning Electron Microscope images of the mercerized empty fruit bunch (MEFB), palm kernel (MPKF) and coir fibres (MCCF)



BEFB BPKF BCCF

Plate 3: Scanning Electron Microscope images of the alkaline bleached empty fruit bunch (BEFB), palm kernel (BPKF) and coir fibres (BCCF)



MEFB MPKF MCCF

Plate 4: Scanning Electron Microscope images of the acetylated empty fruit bunch (AEFB), palm kernel (APKF) and coir fibres (ACCF)

The pH of CCF, EFB and PKF fibres is the measurement of degree of acidity or alkalinity of the fibres. The factors that dictate the pH values of the fibres are nature, preparation, inorganic matter, kind of treatment and chemically active oxygen groups on the surface of the fibres. The pH values of the unmodified fibres are 6.9, 6.3 and 6.5 for CCF, PKF and EFB respectively. These results are similar to the result reported for physic nut plant (Adebayo and Elulu, 2011). Chemically modified fibres have higher pH values in order alkaline bleached> mercerized fibres, but acetylated fibres have lower pH than untreated fibres. The increase in pH of the alkaline bleached and mercerized fibres might be due to absorption of sodium from treatment solution and reduction in pH of the acetylated fibres might be due to acetic acid as bye product from the modification reaction (Rakesh *et al*. 2011). The iodine absorption number is an indicator of porosity in fibre materials (Adebayo and Elulu, 2011), that reflects better development of micro-porous structures in modified fibres in relation to unmodified ones as the iodine number of alkaline bleached fibres > mercerized fibres > acetylated fibres > unmodified fibres (Table 1). This increase in porosity and pore sizes of the modified fibres might have given good adsorptive capacity to the natural fibres and these attributes might make them fit for adsorption of heavy metals, dyes, pigments and other organic pollutants from waste-water according to Adebayo and Elelu, (2011).

Morphological Study

The micrographs of the fibres are shown in Plates 1-4. The unmodified fibres have rough surfaces and small pore sizes as shown in Plate 1. The surface roughness and small pore sizes of the unmodified fibres were due to the presence of impurities (Suradi *et al*. 2009). The chemical treatments of the fibres might improve physical and mechanical interlocking of the natural fibres to the matrices leading to better interfacial bonding between fibres and matrices, as a result of increase in pore sizes according to Myrtha *et al.* (2008). The mercerized fibres have most of their impurities and residual hemicellulose removed; appeared cleaner with wider pore sizes and clearly seen silica nodules (Plate 2) as a result of alkaline reaction with cementing materials of the fibres and splitting the fibers into finer filaments (Bhat *et al.* 2011). The alkaline bleached CCF, EFB and PKF fibres have not only their lignin component degraded but also most of their hemicellulose removed with formation of widest pore sizes on the surfaces of the fibres (Plate 3). These observations are in agreement with the findings made by Suradi *et al.* (2009). After the treatment with acetic anhydride, the surfaces of the fibres appear smoother with a little increase in surface pore sizes (Plate 4) as a result of conversion of hydroxyl group on the fibres surface to hydrophobic acetyl group. This observation is in line with the one made by Khalil *et al.* (2001) in the effect of acetylation on interfacial shear strength between plant fibres and various matrices.

CONCLUSION

The data obtained from chemical treatments of fibres indicated that polymer reinforcement fillers and adsorbents with favourable physicochemical properties could be produced through mercerization, alkaline bleaching and acetylation of coir, empty fruit bunch and palm kernel fibres.

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