Supported by tetfund

THE EFFECT OF CHEMICAL MODIFICATIONS ON HYDROPHILIC NATURE AND SURFACE MORPHOLOGY OF *Eleas guinensis* NATURAL FIBERS

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Received: February 28, 2020 **Accepted:** April 12, 2020

Abstract: The hydrophilic nature and surface morphology of three different chemically modified and unmodified natural fiber materials, namely coir fiber (*Eleas coniferus*), palm kernel fiber and empty fruit bunch fiber (*Eleas guinensis*) were studied. The fibers were cleansed with 2% hot detergent liquor ratio 1:100, rinsed thoroughly with distilled water and oven-dried to constant weight, before chemically modified using sodium hydroxide (NaOH), alkaline hydrogen peroxide (H_2O_2) and acidified acetic anhydride $(CH_3CO)_2O$. The first two treatments led to fiber weight reduction, while the acidified acetic anhydride treatment gave the fiber weight increment. All the treated fibers were found to be of less hydrophilic nature than their untreated ones, which was confirmed by gravimetric analysis and Fourier Transform Infrared Spectra (FT-IR), respectively. Scanning Electron Microscope (SEM) gave the fibers morphology that showed smoother surfaces in modified fibers than unmodified fibers.

Keywords: Agro-waste, hydrophilic, hydrophobic, morphology, natural fiber

Introduction

Natural fibers have attracted the attention of the research community mainly because they are cheap and abundant – mostly agro-waste, readily available and turning out to be an alternative solution to the ever depleting petroleum sources. The production of 100% natural fiber based materials as substitute for petroleum-based products is not an economical solution. A more viable solution would be to combine petroleum and bio-based resources to develop a cost-effective product with diverse applications. The application of natural fiber-reinforced composites for example has been extended to almost all fields. Natural fibers can impart excellent characteristics such as low weight, high strength and stiffness, and higher thermal stability to reinforced composite matrices (Belgacem and Gandini, 2005).

Natural fibers are water-loving (hydrophilic) in nature as they are derived from lignocellulose, which contain strongly polarized hydroxyl groups. These fibers, therefore, are inherently incompatible with hydrophobic thermoplastics, such as polyolefins. The major limitations of using these fibersas reinforcements in such matrices come from their strong affinity for water. The limitations include poor interfacial adhesion between polar-hydrophilic fiber and nonpolar hydrophobic matrix, and difficulties in mixing due to poor wetting of the fiber with the matrix. This in turn would lead to composites with weak interface. This notable disadvantage of natural fibers – polarity-induced-hydrophilicity – makes it incompatible with hydrophobic matrix and results in poor interfacial bonding between the fibers and the matrix. This in turn leads to impaired/poor mechanical properties of the composites. Interestingly, these defects can be remedied by chemical modifications of fibers so as to make it less hydrophilic, with smoother surfaces (more crystalline) suitable for compositing. This paper reviews the effects of chemical modifications – mercerization (NaOH treatment), acetylation (CH_3COOH treatment) and bleaching (H_2O_2 treatment) on the hydrophilicity, degree of swelling as well as surface morphologies of natural fibers.

Materials and Methodology

Materials

The materials used in this research work were empty fruit bunch (EFB) fibers, palm kernel fibers (PKF) and coconut coir fibers (CCF) obtained from the Federal University of Technology, Akure's teaching and research farm as shown in Plate 1. These plant materials were identified at Crop, Soil and Pest Management Department, the Federal University of Technology, Akure, Nigeria. The reagents were obtained from Chemistry Department, the Federal University of Technology, Akure, Nigeria. All the reagents used were of analytical grade.

Plate 1A: Coir fiber from coconut

Plate 1B: Palm fronds for empty fruit bunch (EFB) fiber and palm kernel (PKF) fiber

Plate 1C: Hard kernels after palm oil processing

Plates 1: Showing pictures of the sources of natural fibers

Methods

Physical preparation of natural fibers

The natural fibers were physically treated using Jabar *et al.* (2016) method; fibers were pretreated with 2% detergent solution in liquor ratio 1:200 at 80ºC for 1 h, washed with distilled water and finally oven dry at 105ºC to a constant weight.

Chemical modification of the natural fibers

The physically treated EFB, CCF and PKF were divided into four equal parts. Three of them were chemically modified using sodium hydroxide (NaOH), acidified acetic anhydride $(CH_3CO)_2O$ and alkaline hydrogen peroxide(H_2O_2).

Mecerization

0.5 g portions of each fiber material were accurately weighed and subjected to chemical modifications using 100 mL of 5% sodium hydroxide $(NaOH)$ with continuous stirring for a period of 2 h at room temperature. The fibers were then thoroughly washed with distilled water to get them free from the chemical used for their surface modification and oven dried at 105^0C for 1 h.

Alkaline bleaching

0.5 g portions of each fiber material were treated with 2% H_2O_2 in 25 % $NaOH$ solution – alkaline hydrogen peroxide, with continuous stirring for a period of 2 h at room temperature. The fibers were then thoroughly washed with distilled water to free their surfaces from the alkaline hydrogen peroxide used for their surface modification and oven dried at 105ºC for 1 h.

Acetylation

0.5 g portions of each fiber material were treated with 20% acetic acid (CH_3COOH)/acetic anhydride $(CH_3CO)_2O$ solutions, with 1 h stirring in 10% acetic acid catalysed with a drop of conc. H_2SO_4 before finally treated with 10% acetic anhydride for another 1h.

The treatments were done at room temperature except for acetytilation (60^oC). At the end of the chemical treatments, the fibers were thoroughly washed with distilled water to get them free from the chemicals used for their surface modification and oven dried at 105ºC for 1 h.

Schemes of chemical treatments

i) Mercerization

$$Fiber-OH + NaOH \xrightarrow{2h/30^oC} Fiber-O^-Na^+ + H_2O \rightarrow FiberO^-H^+$$

Fiber-I + Alkali → Alkali-fiber + Fiber-II

Mercerization of natural fibers from cellulose I to II (Maya and Rajesh, 2008)

ii) Alkaline Bleaching

$$Step\ I: H_2O_2 \rightarrow 2HO^*$$

$$Step\ II: Fibre-H + HO^* \xrightarrow{NaOH/2h/30^oC} Fibre + H_2O$$

Fiber + Hydrogen peroxide → Bleached fiber + Water

Alkaline bleaching of natural fiber (Rakesh *et al.*, 2008)

iii) Acetylation

$$Fibre-OH + (CH_3CO)_2O \xrightarrow[60^oC/Conc\ H_2SO_4]{CH_3COOH} Fiber-O-COCH_3 + CH_3COOH$$

Fiber + Acetic anhydride → Acetylated fiber + Acetic acid

Esterification of natural fiber (Bledzki *et al.*, 2008; Khalil *et al.*, 2001)

The remaining one not treated was used as standard. Fourier transform infra-red (FT-IR) spectroscopic and scanning electron microscopic (SEM) analyses were used to confirm chemical surface modifications of CCF, EFB and PKF Fibers.

Hydrophilicity of fibers

The hydrophilic nature and degree of swelling of the fibers were determined gravimetrically according to ASTM D570-99.

Results and Discussion

Confirmation of chemical modification of CCF, EFB and PKF

The FT-IR spectra and SEM morphologies of CCF, EFB and PKF are similar to one another. The major difference in the spectra of the fibers is the absence of peak 1726.46 cm^{-1} in mercerized (Fig. 1B) and alkaline bleached (Fig. 1C) fibers. This peak appears clearly in unmodified fibers (Fig. 1A) and more intense in acetylated fibers (Fig. 1D). The absence of this peak confirms degradation of hemicellulose and lignin in mercerized and alkaline bleached fibers according to Jabar *et al.* (2016) in chemical modification of coir, empty fruit bunch and palm kernel fibers for polymer reinforcement. The more intense of the acetyl functional group at 1726.46 cm^{-1} in acetylated fibers is as a result of replacement of –OH in unmodified fibers with acetyl functional group in acetylated fibers according to Khalil *et al.* (2001), in the effect of acetylation on interfacial shear strength between plant fibers and various matrices.

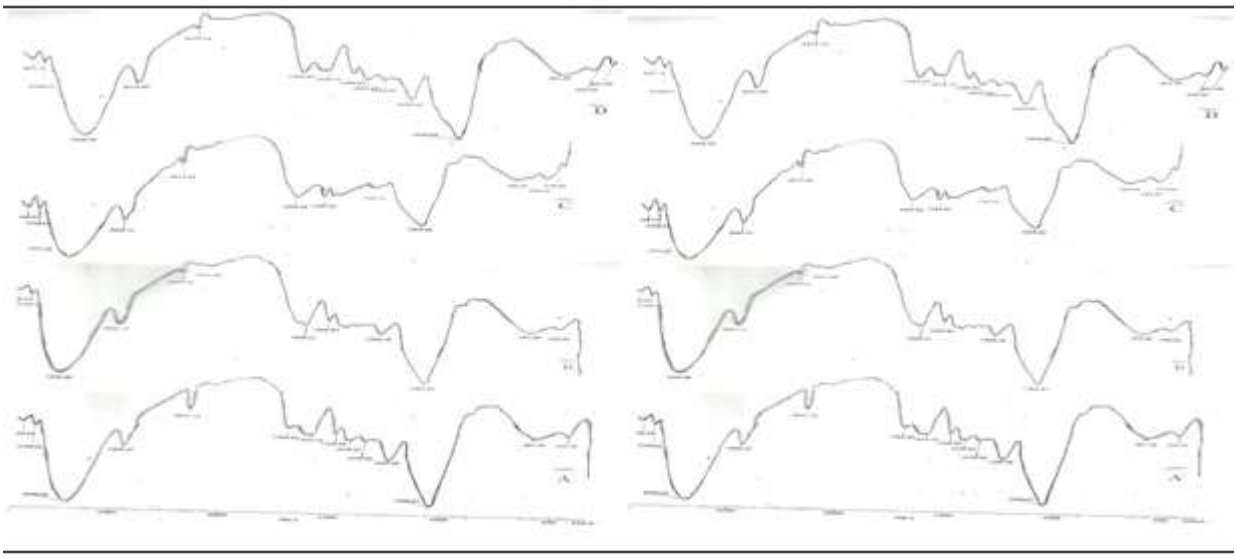

Fig. 1: IR spectra of unmodified (A), mercerized (B), alkaline bleached (C) and acetylated (D) coir fibers

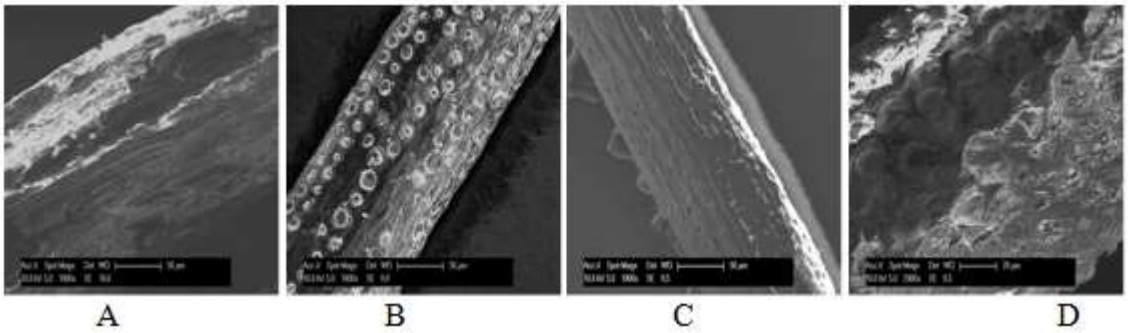

Plate 2: A, B, C and D are SEM images of UCCF, MCCF, BCCF and ACCF fibers, respectively

Unmodified fibers have rough surfaces as shown in Plate 2. The surface roughness of the untreated fibers was due to the presence of residual silica nodules, hemicellulose, lignin and other impurities, according to the findings of Mwaikambo and Ansell (2002).

The mercerized fibers have most of their impurities and residual hemicellulose removed. They appear cleaner with wider pore sizes and clearly seen silica nodules. This is as a result of alkaline reaction with cementing materials of the fibers and splitting the fibers into finer filaments according to Bhat *et al.* (2011).

In the case of alkaline bleached fibers, the fibers 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 fibers (Plate 2C). These observations agreed with the observation of Suradi *et al.* (2009).

After treatment with acetic anhydride, the surfaces of the CCF, EFB and PKF fibers appear smoother with a little increase in surface pore sizes (Plate 2D). This is as a result of conversion of hydroxyl group on the fibers surface to hydrophobic acetyl group (Khalil *et al.*, 2001).

Hydrophilic nature of fibers

The affinity for water of both the unmodified and modified fibers is presented in Fig. 2. Mercerization treatment reduces moisture content of CCF by 42.16%, EFB by 36.06% and PKF by 37.68%. Alkaline bleaching treatment reduces moisture content of CCF by 61.79%, EFB by 63.11% and PKFby 59.30%. Acetylation treatment reduces moisture CCF by 72.93% EFB by 68.81% and PKF by 67.39%. This observations show that modification enhances compatibility of the hydrophilic fibers with hydrophobic matrix according to Khalil *et al.* (2001).

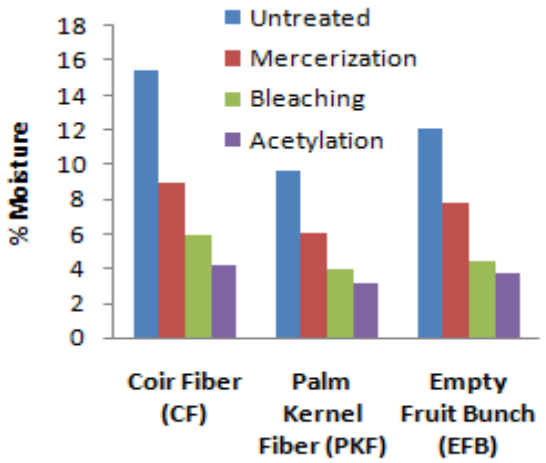

Fig. 2: Effect of chemical treatment on moisture content of fibers

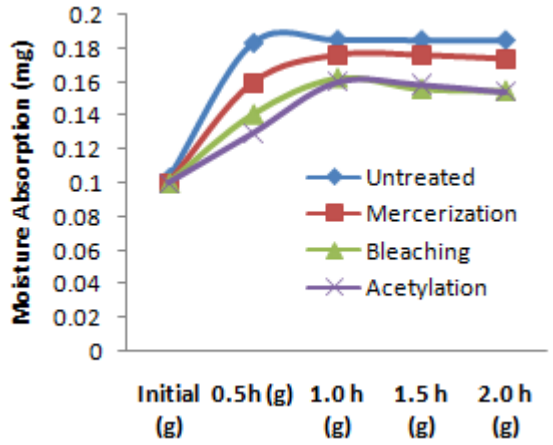

Fig. 3: Effect of chemical modification on degree of swelling of CCF in water

Degree of swelling of fibers in water

Affinity for water was measured by soaking both unmodified and chemically modified fibers in water for 2 h and measuring their degree of swelling at every 0.5 h interval. However, the optimum degree of swelling was observed at 1 h. Degree of swelling reduces by 27.46% in acetylated, 25.03% in alkaline bleached and 7.41% in mercerized CCF (Fig. 3). Other fibers followed this same trend observed in CCF.

Conclusion

Chemical modifications of coconut coir fibers (CCF), empty fruit bunch fibers (EFB) and palm kernel fibers (PKF) decreased the fibers' hydrophilicity. The surface morphologies of the fibers were equally enhanced when chemically modified; the effect is most pronounced on ACCF. Therefore, chemical modification will make CCF, EFB and PKF more compactable with hydrophobic matrix during compounding.

Conflict of Interest

Authors have declared that there is no conflict of interest reported in this work.

References

Bhat I, Abdul Khalil HPS, Ismail H & Alshammari T 2011. Morphological, spectroscopic and thermal properties of alkali-treated and chemical modified oil palm empty fruit bunch and oil palm frond fibers: A comparative study. *Bioresources Technology*, 6(4): 4673-4685.

Bledzki AK, Mamun AA, Lucka-Gabor M & Gutowski VS 2008. The effect of acetylation on properties of flax fiber and its polypropylene composites. *Express Polymer Letter*, 2(6): 413-422.

Jabar LL, Adetuyi AO, Owolabi BJ & Ayoade GW 2017. Chemical modification of coir, empty fruit bunch and palm kernel fibers for polymer reinforcement. *FUTA J. Engr. and Engr. Techn.*, 11(1): 29-36.

Khalil HPSA, Ismail B, Rozman HD & Ahmad MN 2001. The effect of acetylation on interfacial shear strength between plant fibers and various matrices. *European Polymer Journal*, 37: 1037-1045.

Maya JJ & Rajesh DA 2008. Recent developments in chemical modification and characterization of natural fiber-reinforced composites. *Polymer Composite*, 187-207.

Belgacem MM & Gandini A 2005. The surface modification cellulose fibres for use as reinforcing elements in composite materials. *Composite Interfaces*, 12: 41.

Mwaikambo LY & Ansell, M P 2002. Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization. *J. Appl. Poly. Sci.*, 84(12): 2222-2234.

Rakesh K, Sangeeta O & Aparna S 2011. Chemical modification of natural fiber for composite material. *Der. Chemical Snica*, 2(4): 219-228.