



## The Effect of Fiber Treatment on the Water Absorption of *Piliostigma* Reinforced Epoxy

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### ABSTRACT

In this paper, the water absorption behaviour of 14 days hardened composites based on *Piliostigma* fiber and a thermosetting matrix (Epoxy) was studied. The water absorption tests were carried out in order to study the durability of the composites. The comparative study of water absorption behaviour of composites reinforced with fiber and chemically modified in three reagents (NaOH, KMnO<sub>4</sub>, BPO) respectively confirmed that surface treatment of the fibres influences the sorption process. The most significant decrease in hydrophilicity of *Piliostigma* was found in the case of *Piliostigma* fiber that was modified by BPO. This decrease relates to change in the chemical composition of the *Piliostigma* fiber, especially due to a decrease in the average degree of cellulose polymerization as well as the hemicellulose content. The chemical composition effect on the surface modification was analysed by means of Fourier Transform Infrared Spectroscopy (FTIR). The experimental spectroscopic information was compared with theoretical analysis of molecular vibrations. The result obtained from this comparison confirmed that the chemical modification of the composites was successfully carried out.

**Keywords:** Chemical treatment, Composite, Hydrophilicity, Natural fiber, Thermosetting, Water absorption

### INTRODUCTION

Bio-based materials are in the foreground of current research in the field of composite materials. Over the past years, increasing attention has been devoted to research on composites reinforced with natural fibers. The major aim was to study incorporation of plant fibers as an environmentally friendly, reinforcing agent into composites. Currently, certain automotive and construction industries have been interested in composites reinforced with natural plant fibers as alternative materials for glass-fiber reinforced composites in structural applications Saiki (2008). Composite materials based on polymer matrix reinforcement by natural fibers are usually referred to, in the literature, as “biocomposites”. Polymer composites containing different fillers and/or reinforcements are frequently used for automotive application. In recent years, many of such composites were developed for their application into interior and exterior parts of cars in order to ensure the overall lower weight of the vehicle and an increase in sustainability of the automotive manufacturing process. (Holbery and Houston, 2006; Bledzki *et al.*, 2006). In view of the current trends in growing environmental and economic forces, architects, engineers, developers and owners are seeking efficient, innovative building solutions that preserve non-renewable resources. In the building industry, one of the current ways of

achievement of sustainable development is to use easily renewable raw material resources and to develop “green concrete”. New composites based on natural cellulosic fibers with inorganic matrix (lime) represent a group of lightweight materials providing a healthy living in buildings (Le Troëdec *et al.*, 2011; Preikss *et al.*, 2013). However, two major factors that currently limit the large-scale production of natural fiber composites are poor adhesion between the fiber and a chosen matrix and the hydrophilic nature of many of the fibers, this results in weak adhesion of the matrix acting as a binder with the fiber surface and does not lead to desired mechanical properties in the composite (Srinivasa *et al.*, 2011). The hydrophilic nature of many fibers is a major problem for their use as reinforcement materials in polymers. Hydrophilic behaviour of plant fibers depends on their composition and specific structure. Water absorption in fibers and biocomposites has been found to significantly influence their dimensional and structural properties. The understanding of the hygroscopic behaviour of plant fibers as well as composites reinforced with cellulosic fibers is a key issue for use in different weathering conditions (Célino *et al.*, 2014) and in order to improve their long-term performance characteristics (Saikia and Bora, 2003). Therefore, it is important to study in detail the water absorption behaviour of fiber reinforced composites in order to estimate, not only

the consequences that the water absorbed may have, but also the durability of natural fiber composites aged under water storage conditions. As a measure taken to reduce high moisture/water absorption ability of organic filler in composites, chemical treatments (Bledzki *et al.*, 2012; Le Troedec *et al.*, 2009; Kabir *et al.*, 2012) or physical treatments of the fibers surface could be applied (Renouard *et al.*, 2014 : Sgriccia and Hawley, 2007; Thomsen *et al.*, 2006). Generally, chemical treatment of natural fibers reduced the overall water uptake of fibers (Patel *et al.*, 2012) and can positively or negatively affect strength parameters of composite in dependence on plant and matrix kind, treatment conditions of fibrous filler, cellulose content, etc.

## MATERIALS AND METHOD

### Fiber Extraction

Fresh samples of *P.thonningii* bark were collected locally from Madobi local government area of Kano state, Nigeria and were cut to sizes between two nodes. The upper skin was removed by scrapping without damaging the fiber surface. These were then cut into sizes of 200mm in length. The fibers were washed with distilled water to remove unwanted organic materials present on the surface. These fibers were then spread over a water proof sheet and stored in an enclosed shed to reduce their moisture content. After two weeks, the long fibers were cut to lengths of 120mm with widths of 3mm, using pairs of scissors. Due to the low moisture content of the fibers, fungus was not found to grow on their surface during storage. The fibers after cutting were again washed with water to remove any fine particles or organic materials that might have adhered to their surface during storage and cutting. The fibers were then dried under shade, for 3 days (Velmurugan *et al.*, 2012).

### Matrix

Epoxy is a thermosetting polymer that cures (polymerizes and cross links) when mixed with a hardener, under ambient or elevated temperature conditions. The epoxy resin used in this study was a Bisphenol-A-Diglycidyl-Ether (BADGE) grade LM-556, having a density of 1.5 g/cm<sup>3</sup>. The hardener used was Triethylene tetramine (TETA) grade HY-951. The matrix material was prepared with a mixture of the epoxy binder and the hardener HY-951 at a ratio of 2:1.(Niharika and Acharya, 2013). The epoxy and the hardener were supplied by Ciba Geigy Ltd.

### Composite Preparation

A mold was used for casting the composite sheets. The usual hand lay-up technique was used for preparation of the samples. A calculated amount of epoxy resin and hardener

(ratio of 2:1 by volume) was thoroughly mixed with gentle stirring to minimize air entrapment. For quick and easy removal of composite sheets, a mold release agent was applied at the inner surface of the mold. After keeping the mold on a glass sheet, a thin layer of mixture was poured. The required amount of fiber was then distributed on the mixture. The remaining mixture was then poured into the mold. Care was taken to avoid formation of air bubbles. The mold was allowed to cure at room temperature, for 2 hours. After a 2 hours period, the samples were taken out from the mold and kept for further experimentation.

### Chemical Modification of *Piliostigma Thonningii* Fiber

The chemical modification of dried *Piliostigma* fiber was made by three different solutions: sodium hydroxide, Benzoyl peroxide and Potassium permanganate. The specification of the chemical treatment conditions was described by Tijjani (2015).

## SAMPLE CHARACTERISATION

### Fourier-Transform Infrared (FTIR) Spectroscopy

The FTIR technique was utilised in order to help identify the functionality of compounds in the composite materials and to investigate sample compositions. Also, to help monitor any interactions/reactions between functional groups in the different components in the polymer blends and the composites (Pavia *et al.*, 1979). The FTIR analysis was performed using an Agilent infrared spectrometer. The unmodified and modified fibers were analysed using an attenuated total reflectance (ATR) mode of operation, over a 650-4000 cm<sup>-1</sup> wave number range, at a resolution of 4 cm<sup>-1</sup>.

### Water Absorption Test

The water absorption test used in this study followed an ASTM standard test method D570 (ASTM 1998). The test specimen was in the form of a bar 150 mm long, 25 mm wide and 3.2 mm thick. Before the measurement, the sample was dried in an air oven at 50°C for 24 hours. This was then cooled in desiccators, immediately weighed to the nearest 0.1 g, which was taken as the dry initial weight of the sample,  $W_1$ . The sample was then placed in a container of distilled water maintained at a temperature of 50°C for 24 hours. After 24 hours, the Specimen was removed from water. Excess water was wiped off from the surface of the sample with a dry cloth, and the sample was immediately weighed to the nearest 0.1g, which is designated as  $W_2$ . For each biocomposite sample, three specimens were measured, and the percent water absorption was obtained from the relation:

$$\% \text{ weight gain/loss} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (\text{Egwaikhide et al., 2007})$$

Where:  $W_1$  = initial weight of the sample  
 $W_2$  = final weight of the sample

## RESULTS AND DISCUSSION

### Fourier Transform Infrared Analysis of the Samples

The effect of chemical modification on the various fiber surfaces was observed using FT-IR Spectroscopy. The comparison of the representative FT-IR spectra of the untreated *Piliostigma fiber* and the modified *Piliostigma fiber* (Figs. 1a - 1d) show a reduction in O-H stretching intensity. Also, shifting of the peaks from  $3293\text{cm}^{-1}$ ,  $3283\text{cm}^{-1}$ ,  $3248\text{cm}^{-1}$ , and  $3235\text{cm}^{-1}$  could be observed for the untreated sample, the alkali treated sample, the potassium permanganate treated sample and the benzoyl peroxide treated sample respectively, at the wave numbers mention above. This is likely due to the breaking of hydrogen bond between the O-H groups of cellulose and hemicellulose molecules (Saha *et al.*, 2010). Peaks at  $2920\text{cm}^{-1}$ ,  $2857\text{cm}^{-1}$ ,  $2865\text{cm}^{-1}$ , and  $2855\text{cm}^{-1}$  predominantly arise from C-H stretching (Jonoobi *et al.*, 2010). The absorption peak at  $1721\text{cm}^{-1}$  is associated to carbonyl C=O stretching of acetyl groups of hemicellulose (Haque *et al.*, 2009). The absorbance peak at  $1441\text{cm}^{-1}$  (Saha *et*

*al.*, 2010) were assigned to  $-\text{CH}_3$  asymmetric deformation of lignin. However these peaks are detected in the alkaline treated *Piliostigma fiber* very weakly this weakening indicates the removals of lignin. After the mercerisation process, the bands at  $1718\text{cm}^{-1}$  and  $1245\text{cm}^{-1}$  attributed to the stretching vibrations of C=O and C-O groups respectively disappeared these kinds of groups are present in lignin and hemicellulose structures (Fávaro *et al.*, 2010). After permanganate oxidation, as shown in Fig.1(c), a decrease in intensity is observed for the aromatic band of cellulose and lignin unit and an increase in band intensity at  $1721\text{cm}^{-1}$  confirming the formation of quinines on the fiber surface. This confirmation is also supported by visual inspection of colour change on the fiber during oxidation. Increase in peak intensity at  $1022\text{cm}^{-1}$  suggested that NaOH treatments increase hydroxyl group concentration on the fiber, which would promote more active sites for fiber/matrix interface (Mwaikwambo and Ansell, 2012).

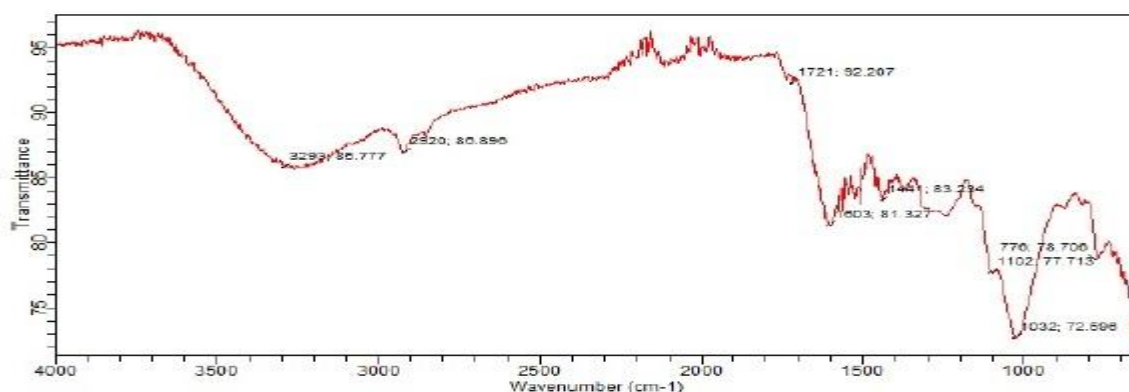


Fig. 1 (a): FT-IR Spectra of Untreated *Piliostigma thonningii* Fiber

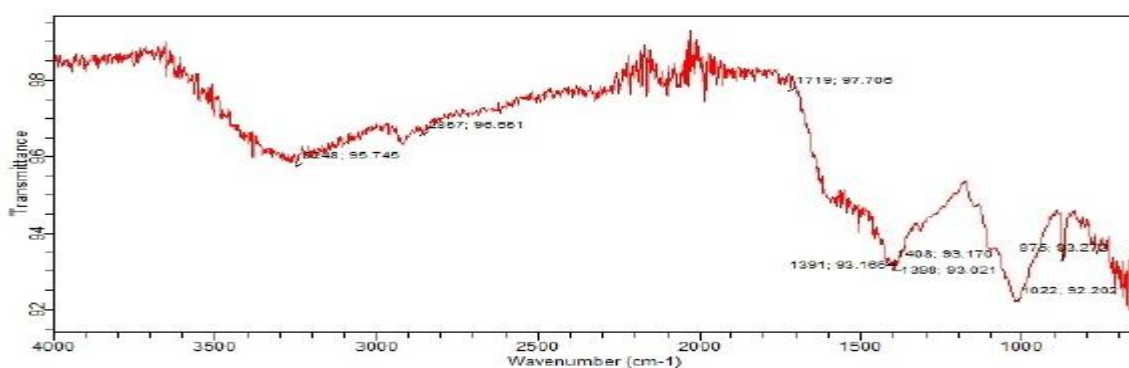
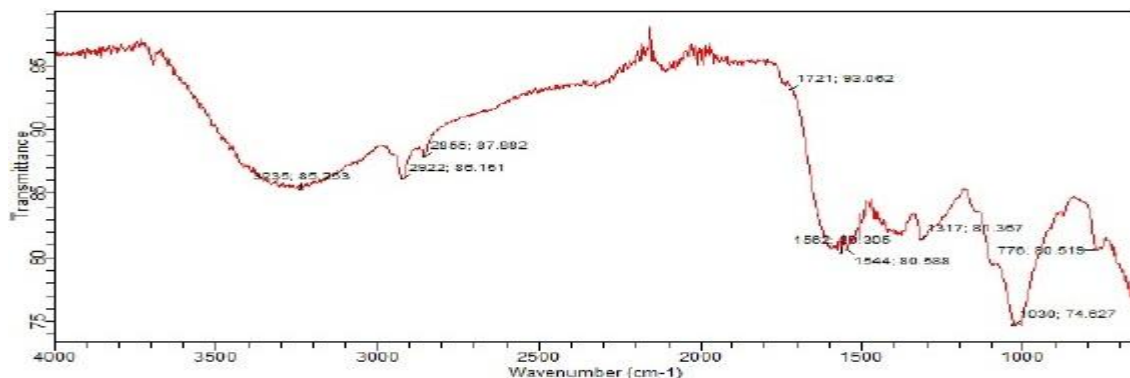
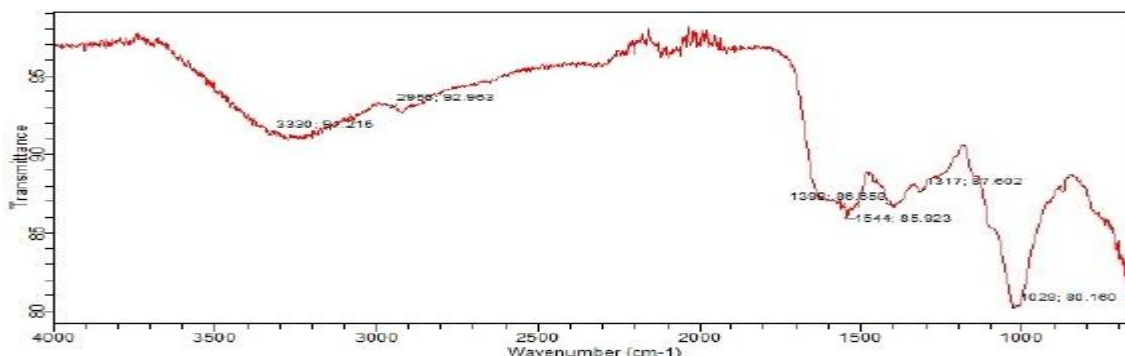


Fig. 1 (b): FT-IR Spectra of Sodium Hydroxide Treated *Piliostigma thonningii* Fiber



**Fig. 1 (c): FT-IR Spectra of Potassium Permanganate Treated *Piliostigma thonningii* Fiber**

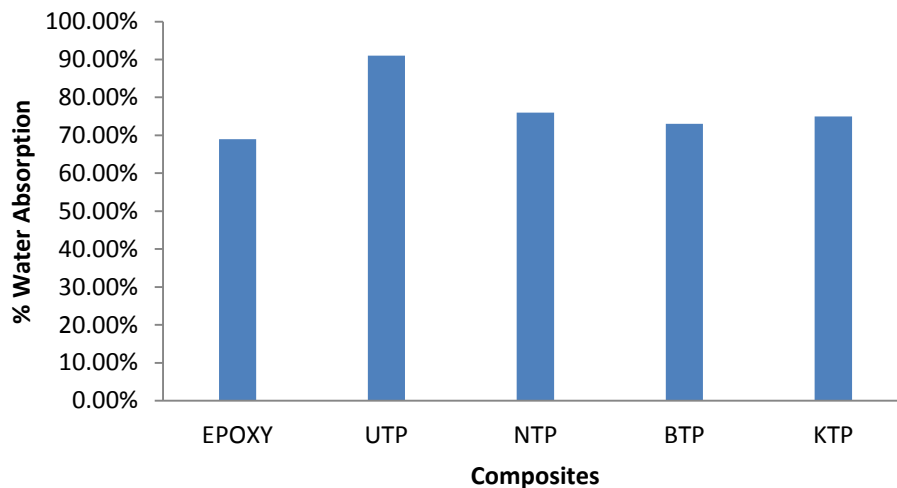


**Fig. 1 (d): FT-IR Spectra of Benzoyl peroxide treated *Piliostigma thonningii* fiber**

From the FT-IR results above it can be seen that surface impurities such as lignin, hemicellulose, and waxes had been effectively removed by modification with chemical reagents, as a result increasing the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites (Valadez-Gonzales *et al.*, 1999). It should also be noted that alkaline treatment or mercerization is one of the most used chemical treatment on natural fibers and the most important modification done by alkaline treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness resulting in better mechanical interlocking.

**Water Absorption**

The water absorption property of a composite material could depend on its water percentage content in the fiber, on fiber orientation, on temperature, on area of the exposed surface, on permeability of fibers, on void content, and on hydrophilicity of the individual components, etc (Dhakal *et al.*, 2007). Also the effect of water absorption is an important consideration where the material has been designed for applications in contact with water. Fig. 2 gives the result of percent water absorption of the composites, conducted at room temperature



**Fig. 2: Percent Water Absorption of the Composites**

Where: UTP- Untreated *Piliostigma thonningii* fiber reinforced composite

NTP- Sodium hydroxide treated *Piliostigma thonningii* fiber reinforced composite

BTP- Benzoyl peroxide treated *Piliostigma thonningii* fiber reinforced composite

KTP- Potassium permanganate treated *Piliostigma thonningii* fiber reinforced composite

EPOXY- Pure epoxy and hardener composite

From the results above, it can be seen that a reduction in water absorption occurred when the surface treated fiber composite is compared with the corresponding untreated material. This can be attributed to the good interfacial interaction between the fiber and the matrix. This could also be because the chemical treatments have led to more hydrophobic materials, consequently reducing water absorption. This can also be attributed to better fiber matrix with the fiber material (Sreekumar *et al.*, 2009). It was observed that there were fewer cracks in the treated composites in comparison to the untreated composites. The EPOXY, UTP, NTP, BTP, KTP, showed water absorption of 0.69%, 0.91%, 0.76%, 0.73% and 0.75% respectively. It can be said therefore that the chemical modifications carried out has reduced the polar groups in the fiber materials replacing some of the hydroxyl groups on the surface of the fibers (Ghali *et al.*, 2011). It should also be noted that the matrix had little effect on the amount of water absorbed as pure epoxy composites demonstrated around the same water content between 0.5% to 1.0% on exposure (Tajvidi and Ebrahimi, 2003).

It can be clearly seen from Fig. 2 that compatibility between the fibers and the matrix brings about resistance to water absorption, largely due to the hydrophobic characteristic of BADGE. BTP composites appear to present better resistance to water absorption. This is because their percent water absorption values are the lowest when compared with the other composites. Consequently, the composites with minimum water absorption could be the most suitable for the many

applications that the composite can be subjected to, including their use in interior parts of aircraft, car door panels etc.

## CONCLUSIONS

The overall study shows that surface treatment of the fiber materials influences their water absorption behaviour. The maximum value of water absorbability of the composites decreases in following order: UTP > EPOXY > NTP > KTP > BTP. The most significant decrease in hydrophilicity of *P. thonningii* was found in the case of composites that were treated with the peroxide reagent. This relates to a change in the chemical composition of the fiber, especially leading to a decrease in the amount of lignin and hemicellulose content.

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