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ARECA FIBER-REINFORCED POLYESTER BIO-COMPOSITES PULL-OUT ANALYSIS

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ABSTRACT
Although areca fibers have been used by several authors, the Nigerian variety has not yet been thoroughly characterized. In this research the surface of areca fibers was modified by treatment with NaOH or $NaOCl_2$solutions. Lignin content and density of fibers are reduced with the chemical treatment and the $NaOCl_2$treatment causes a significant reduction in moisture absorption. Tensile tests of NaOH (0.25, 0.5, 1, 2, 5, and 10% w/w) and $NaOCl_2$ (1, 2, and 3% w/w) treated fibers were carried out and a reinforcement effect of the areca treated with 2% solutions was observed. TGA measurements showed that with the NaOH treatment the fiber becomes more thermally resistant. SEM micrographs and crystallinity index of areca indicated how different treatments alter the fiber surface. Pull-out tests in polyester resin were performed, evidencing that all treatments were effective in improving interfacial adhesion. The best results were obtained with the 2% $NaOCl_2$treatment. The main advantages of pull-out tests is that without considering composite processing variables, good performance areca/polyester composites may be selected before their laborious and material-consuming preparation begins.

KEYWORDS*:* Areca Fiber: Bio-Composites; Pull-Out; Analysis

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1. INTRODUCTION

Composites were a need in the evolution of engineering materials because by a combination of materials it is possible to overcome, for instance, brittleness and poor process ability of stiff and hard polymers. The simplest combination is of only two materials where one acts as the reinforcement and the other as the matrix. In principle, any isotropic material can be reinforced; the reinforcing material is usually stiffer, stronger or tougher than the matrix and there has to be a good adhesion between the components (Mark, Eisenberg, Graessley, Mandelkern, Samulski, Koening and Wignall. 1993).

Natural vegetable fibers, characterized by a rapid renewability, are environmentally friendly materials at all stages of their life cycle; that is to say, during extraction, production, processing, and disposal. Composites containing vegetable fibers such as sisal present soundproofing properties, the ability to absorb vibrations, and good impact properties due to their better elasticity, especially when modified with crushed fibers (Kozlowski and Mieleniak, 2000). Areca reinforced polyester composites may be considered ecological materials because when burnt they produce less CO_2, CO, and toxic gases than their unreinforced counterpart; also, one has to consider the benefits of all oxygen emissions from the areca plantation.

The application of vegetable fibers to bio-composites is, however, limited by poor resistance to high temperatures (Marcovich, Reboredo and Aranguren, 2001), weak bonding to synthetic polymers, and variability of fiber properties with plant age, part of the plant (Li, Wing, Mai and Ye, 2000), extraction method, etc. For instance, for Li et al (2000), the cellulose and lignin contents of sisal varied from about 50 to 61% and 3 to 4%, respectively, depending on the plant age. Chemical treatments such as acetylation, mercerization, and other superficial fiber modifications carried out with the use of coupling agents (Chand and Rohatgi, 1986) may affect unfavorably the sisal tensile strength. The effects of surface modification such as de-waxing, alkali treatment, cyanoethylation, vinyl grafting, etc. on the properties of bio-composites have been recently studied in order to overcome some of the inconvenience associated with the use of lignocellulosic fibers (Gonzales, Cervantes, Olayo and Franco, 1999).

Other important effects of natural fiber modification are reduction of its moisture absorption (Singh, Verma and Gupta, 1998) and improvement of fiber/matrix adhesion, although loss of fiber strength may occur simultaneously. Nevertheless, these drawbacks may be overcome by judicious choice of processing parameters, proper fiber characterization, and type of areca modification.

The fracture toughness of a composite is governed by the extent of energy absorption processes through various toughness mechanisms which are associated with interface fractures depending primarily on the nature of bonding at the fiber–matrix interface. The fracture behavior of bio-composites may be modified by fiber coating, which alters the mechanism of bond, stress states, and other thermo-mechanical properties at the fiber–matrix interface region (Pochiraju, Tandon and Pagano, 2001; Madu and Okoronkwo, 2018).

The role of the fiber–matrix interface in determining composite properties has been the focus of several investigations (Rong, Zhang, Liu, Yang and Zeng, 2001). A few experimental techniques have been developed to characterize the interface properties, including fiber pull-out tests, fiber fragmentation tests, and fiber push-out (or indentation) tests (Kim, Lu and Mai, 1994).

The development of interfacial de-bonding and the associated stress fields in a single-fiber push-out specimen are very complex because interfacial zones evolve continuously during loading and the stress fields are affected by the adhesive and frictional properties of the interface. It is possible to analyze experimental data obtained from a fiber push-out test using numerical methods such as the axisymmetric damage model and finite element methods. These techniques are capable of modeling zones of adhesion, friction, and open-cracks at the fiber–matrix interface. Direct methods for estimating interfacial shear strength are based on single-fiber composites. The most direct, popular, and reliable method, the fiber pull-out test, involves pulling a partially embedded single fiber out of a block of matrix material. From the resulting tensile stress versus strain plot, the shear strength of the interface and the energies of de-bonding and pull-out may be obtained (Matthews and Rawlings, 1996).

Some authors consider the enhanced toughness the main advantage of natural fibers in composites. Comparing natural fibers such as areca, pineapple, banana, and coir, it has been demonstrated that areca fiber composites have maximum toughness. Strong fibers with high failure strain impart high work to fracture on the composite since toughness of a fiber composite is very dependent on the fiber stress–strain behavior. Again, superficial fiber modification that enhances fiber–matrix adhesion may reduce fiber strength and perhaps, its impact strength (Pavithran, Mukherjee, Bramakumar and Damodaran, 1987).

In this work areca fibers were treated with NaOH and$NaOCl_2$. A thorough fiber characterization was carried out and areca/polyester interface was investigated through pull-out tests in order to find the best areca chemical treatment conditions.

2. EXPERIMENTAL

Areca fibers from the Southeast region of Nigerian, received in the form of yarns, were cut to an adequate length for testing, thoroughly washed with distilled water and dried in air at room temperature for 24 h. Chemical treatment was carried out by stirring the fibers for an hour in 0.25, 0.5, 1.0, 2.0, 5.0, or 10.0% w/w NaOH or 1.0, 2.0, or 3.0% w/w $NaOCl_2$ aqueous solution at room temperature. Treated areca fibers were washed with water until a neutral pH was reached and finally dried at 60 °C for four hours.

A Phillips scanning electron microscope, model SEM505, was used to study fiber surface topographies. Before examination, the fiber samples were sputter coated with a thin layer of gold in a vacuum chamber.

Thermo-gravimetric measurements were carried out in a 50-Shimadzu, at a heating rate of 10 °C/min from 25 °C to 500 °C in a N_2 atmosphere. The degree of crystallinity of the different treated areca fibers was calculated from X-ray diffractograms recorded on a Rigaku/Philips X-ray diffractometer with Ni-filtered Co Kα radiation at 40 KV and 20 mA. An area method was utilized to evaluate the percentage crystallinity (Icr) of the sample (Marcovich et al, 2001).

$$I_{Cr}\,(\%) = \frac{Crystalline\ \ Area}{Total\ \ Area}\,100 \qquad (2.1)$$

where, I_{002} is the area from the (002) plane (peak at 2θ = 22 °) associated with the crystalline region of cellulose and 18 °.

Areca fiber lignin, cellulose, and hemicellulose contents were determined by APTCP M-11/77 and the ash content by TAPPI T13m-54 standards. For characterization of the stress transfer at the polyester– areca interface, a single fiber was embedded in the matrix and the specimen was stretched along the fiber axis until fiber breakage in pull-out tests. (1.0 x 1.0 cm) polyester blocks were prepared with an areca fiber inserted at a 3 mm depth. Pull-out adhesion was defined as:

$$\frac{failure\ \ load}{interfacial\ \ area} = \frac{failure\ \ load\ (pull-out\ \ load)}{\pi.d.l} \qquad (2.2)$$

Table 1. Untreated areca chemical composition

Substance	Content(%w/w)
α-Cellullose	72.0
Hemicellulose	9.1
Lignin	6.5
Extracives	5.1
Ashes*	2.0

Ca, K, Mg, sulfates, phosphates, silicates, carbonates etc.

where D was the diameter and *l* the immersion length.

After the chemical treatment, individual fiber filaments were randomly chosen from the yarn and used to measure tensile strength. At least 17 fibers were tested for each $NaOCl_2$ treatment and in the range of 28–56 fibers were tested for the NaOH treatment; a hundred untreated fibers were also tested. Tensile tests were carried out following ASTM 2256 in a universal testing machine (Emic DL 10.000).

3. RESULTS AND DISCUSSION

Although areca fibers have been characterized by different authors throughout the world, the Nigerian variety still lacks a full investigation. As is widely known, many factors such as climatic conditions, age, type of soil, extractive method, etc. may severely affect the structure of fibers, chemical composition and their physical properties (Gupta and Varma, 1998) and, therefore, it can be very misleading to use literature values when, for instance, predicting the mechanical properties of areca fiber composites.

Table 1 presents chemical composition of untreated areca fibers and Table 2, the influence of different treatments on fiber density. The density is necessary in order to estimate the theoretical density of composites that use those fibers and, in consequence, the fraction of voids.
The chemical treatments decrease fiber density due to the extraction of soluble products in NaOH or $NaOCl_2$, and also affect fiber texture and its dispersion, in the resin when manufacturing composites.

Table 2. Areca fiber density

Treatment	Density (g/cm^3)
None	1,15
2.0%NaoH	1,08
10.0%NaoH	1,05
1.0% $NaOCl_2$	1,07
2.0% $NaOCl_2$	1,07
3.0%$NaOCl_2$	1,07

Table 3. Moisture content of chemically treated areca fibers

Treatment	Moisture content
None	10.6
0.25% NaOH	10.4
0.5% NaOH	10.4
1.0% NaOH	10.2
2.0% NaOH	10.1
5.0% NaOH	10.0
10.0% NaOH	9.8
1.0% $NaOCl_2$	5.4
2.0% $NaOCl_2$	5.5
3.0% $NaOCl_2$	5.6

The untreated areca is rougher, darker and more difficult to homogeneously distribute in the mold in compression molding as a consequence of its higher lignin content (7.6%) when compared to the 2% NaOH (6.5%) and 2% $NaOCl_2$(6.9%) treated fibers. The treatment with 10% NaOH, however, results in a rougher material than the untreated sisal.

Table 3 presents the moisture content of areca fibers after each treatment. One of the drawbacks of vegetable fiber composites is their water uptake during use, which causes a decrease in their mechanical performance. Whilst untreated or NaOH treated areca fibers showed a similar moisture content — around 11% — this value for the acrylamide treated fibers was significantly smaller. Table 4 presents the mean fiber tensile strength after each treatment. Although a high standard deviation was obtained for all treatments (Amico, Mochnacz and Sydenstricker, 2002), the 2% NaOH treatment seems to be the best alkali treatment considering only this effect. The acrylamide treatment also showed a maximum at 2%, but still inferior to the one obtained for the NaOH.

Table 4.Fiber tensile strength (MPa)

Treatment	Mean	Standard deviation
None	214.2	114.9
0.25% NaOH	240.0	123.4
0.5% NaOH	262.8	106.1
1.0% NaOH	256.2	152.5
2.0% NaOH	265.4	148.3
5.0% NaOH	218.0	103.1
10.0% NaOH	186.9	107.8
1.0% $NaOCl_2$	221.2	115.3
2.0% $NaOCl_2$	237.8	116.6
3.0% $NaOCl_2$	146.4	69.4

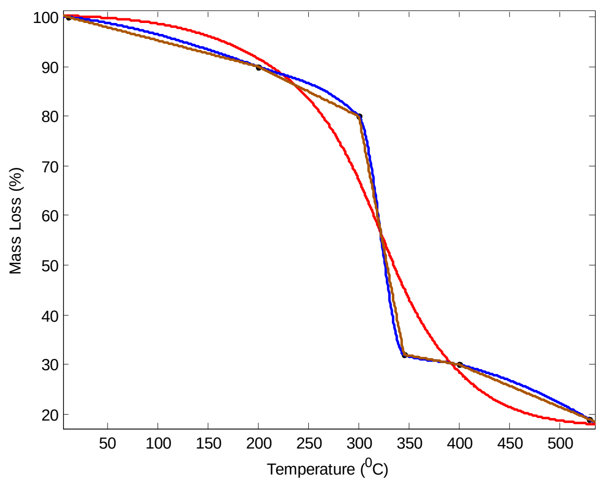

Fig. 1. TGA curves of sisal samples.

Fig. 1 shows TGA curves for untreated and NaOH-treated fibers. It can be seen that treated fibers are more thermally resistant since their onset and peak values are shifted to higher temperatures compared to the untreated fiber. However, in spite of this behavior, the 10% NaOH treated areca is less mechanically resistant. Figs. 2 and 3 show SEM micrographs of areca fibers.

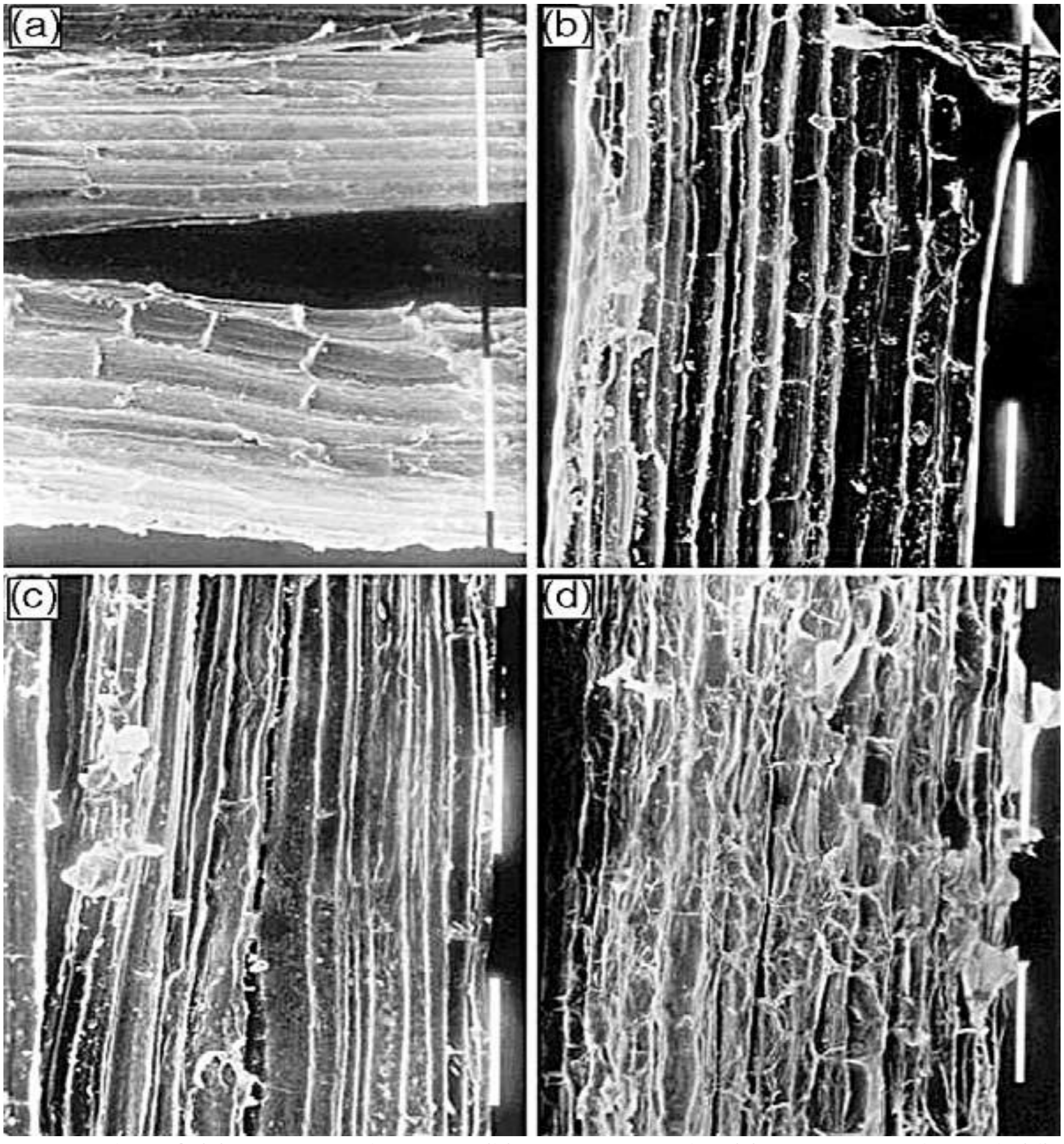

Fig. 2. SEM Micrographs of (a) untreated areca, (b) 1.0% $NaOCl_2$, (c) 2.0%$NaOCl_2$ and (d) 3.0% $NaOCl_2$-treated sisal (magnification: 200x).

In the sequence presented in Fig. 2, it can be inferred that comparing with the untreated areca (Fig. 2(a)), the treatment with $NaOCl_2$ 1, 2, and 3%, (Fig. 2(b, c, and d), respectively) gradually attacks the fiber exposing its inner layers, and in the case of the 3% treatment, significantly altering its surface. It can be seen in Fig. 3 that when the areca is treated with 1% (Fig. 3(a)) and 2% NaOH (Fig. 3(b)), the integrity of the fiber is preserved while in the more severe alkali treatments (5 and 10% NaOH, Fig. 3(c, and d), respectively), the areca looks seriously physically affected.

The treatment with 0.25 and 0.5% NaOH does not cause any apparent effect on the fiber or to the process ability of the composites. However, the more severe treatments turn the areca lighter in color. At the same time, while the 1 and 2% NaOH treatments make the areca smoother, the 5 and 10% alkali treatments make the areca rougher. The treatment with $NaOCl_2$makes the areca processability easier during the composite preparation step, this is also true for the fiber treated with 1 and 2% NaOH. As suggested by the SEM micrographs, the chemical treatment tends to remove substances from the surface of the areca fiber and, hence, may produce an improvement in the wettability property.

The increase of crystallinity index of NaOH-treated areca samples (Table 5) suggests that the alkali treatment extracts amorphous portions (lignin and hemicellulose) of the fibers (Fengel and Wegener, 1989). As the concentration of NaOH or Acrylamide is increased, the diffractogram pattern approximates to one of a pure cellulose sample. This method, which evaluates the nitrogen content of samples, indicated 0.25%, 0.29%, and 0.22% nitrogen content for untreated fibers, 2% NaOH- and 2% $NaOCl_2$-treated fibers, respectively. These concentrations were chosen because they were found to develop the best interface adhesion for each treatment, as is shown by the pull-out and tensile strength results (Tables 6 and 4, respectively). Table 6 shows pull-out results for areca fibers after the different chemical treatments. All treatments improve the interfacial adhesion between areca and polyester. Here, again, the 2% NaOH and 2% $NaOCl_2$ treatments appear to be the best choices. Since these treatments were also the ones to show the highest fiber tensile strength, promising results can be expected for composites produced with these treated fibers because not only is the reinforcement potential higher, but also it becomes easier to properly manufacture them. This kind of evaluation utilizes small amounts of materials and minimizes misleading conclusions deriving from variations in the manufacturing process.

Table.5. Crystallinity index of areca samples

Treatment	I_{cr} (%)
None	70.1
2.0% NaOH	74.1
10.0% NaOH	74.4
1.0% $NaOCl_2$	73.5
2.0% $NaOCl_2$	75.0
3.0% $NaOCl_2$	75.7

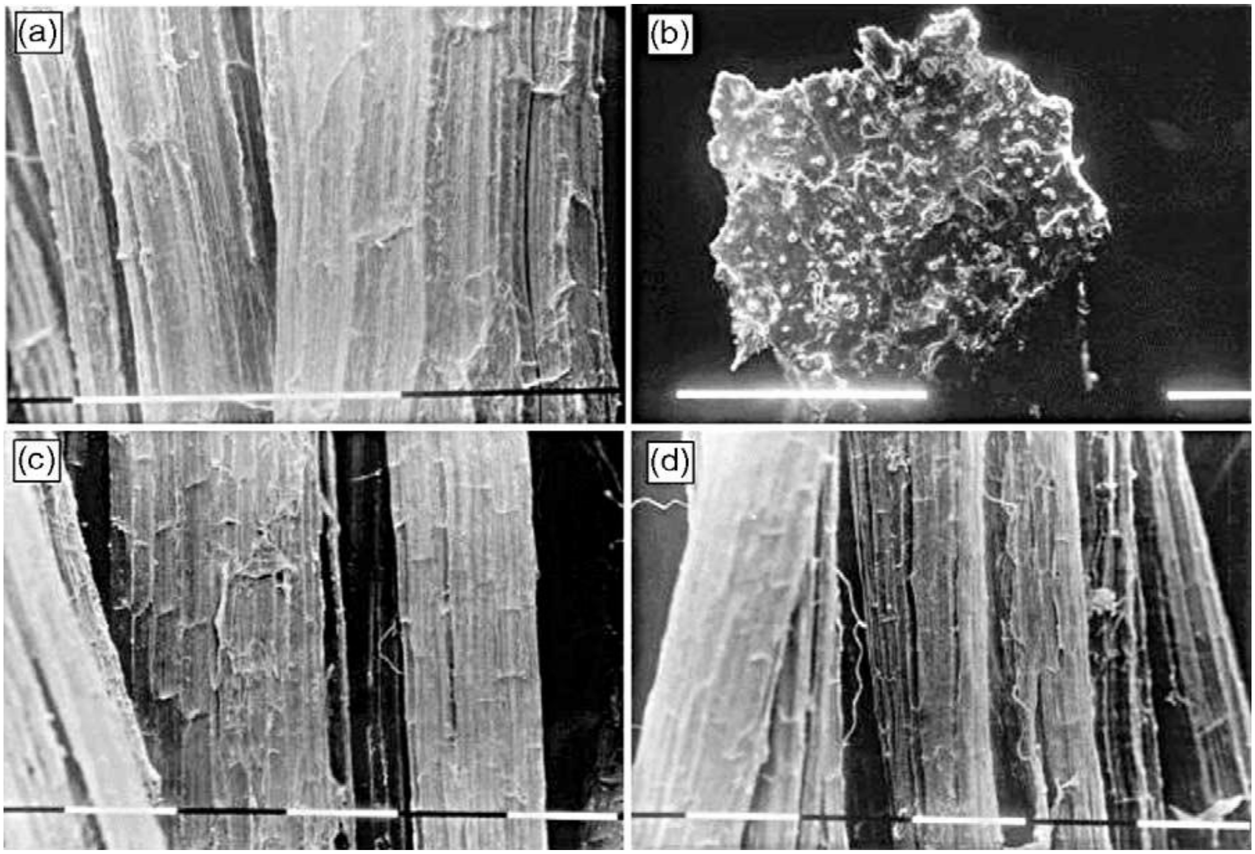

Fig. 3. SEM Micrographs of NaOH-treated areca at different concentrations (a) 0.5% (400 x), (b) 2.0% (400 x), (c) 5.0% (200 x) and (d) 10.0% (200 x).

Table 6: Areca/polyester shear strength measured by pull-out tests

Treatment	Shear strength (MPa)	Standard deviation
None	1.5	0.4
0.25% NaOH	3.4	1.0
0.5% NaOH	4.1	1.0
1.0% NaOH	4.8	0.8
2.0% NaOH	5.8	0.9
5.0% NaOH	5.6	1.3
10.0% NaOH	5.2	1.2
1.0% $NaOCl_2$	4.8	1.4
2.0% $NaOCl_2$	5.7	1.3
3.0% $NaOCl_2$	4.7	1.5

4. CONCLUSION

Compared to untreated and NaOH-treated areca fibers, the best performance areca/polyester composites are likely to be produced when areca fibers are treated with2.0% $NaOCl_2$ aqueous solution. Not only does the reinforcement present higher tensile strength and lower moisture absorption, but also, best results in pull-out tests with polyester matrix.

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