APPLICATION OF SILANE COUPLING AGENTS TO ABACA FIBERS FOR HYDROPHOBIC MODIFICATION

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In this study, two organotrialkoxysilane coupling agents: 3-(trimethoxysilyl) propyl methacrylate (TMPS) and octyl triethoxy silane (OTES), were employed for hydrophobic modification of abaca fibers. This approach was deemed to address the inherent hydrophilicity of abaca fibers, which limits their ability to serve as filler for polymer composites. Hydrophobized abaca fibers can discourage high moisture absorption, which usually causes poor fiber dispersion and fiber–matrix interfacial adhesion in fiber reinforced polymer composites. Fourier-transform infrared (FTIR) spectroscopic measurements and significantly higher contact angles exhibited by the fibers modified with these silane agents, compared to those of untreated abaca, verified the successful hydrophobic modification of the fiber materials.

Keywords: abaca fibers, composite, chemical modification

INTRODUCTION

The utilization of natural fibers as reinforcement for various resins, in lieu of synthetic fiber materials, for polymer-based composite preparation has received a lot of attention due to their low cost, natural abundance, renewability, eco-friendliness, remarkable specific strength and low density.[1-7] Also, processing these materials, unlike conventional fibers, does not result in any harmful gases and is not abrasive to the processing equipment. Furthermore, in considering natural fibers for composites, a balance between sustainability and product performance can be achieved. Commercially, natural fiber composites are used in the manufacture of different parts of automotives, boats, sporting equipment and in many other commodities.

One particular natural fiber of interest is that of abaca (*Musa textilis*), which is endemic to the Philippines.[8-10] Abaca fiber morphologically resembles that of a banana plant, with 12-30 stalks stemming from a central root system, giving a shrubby appearance and a false trunk. Each of the stalks can grow up to 4-8 m and these are mechanically stripped, tuxied or decorticated to produce the abaca fiber.[11] The fiber is made up of around 66% cellulose, 25% hemicelluloses, 14% lignin and 0.7 water.[12] Its remarkable mechanical properties are related to three microstructural features: a high Runkel ratio, meaning a high cell wall volume to lumen width (empty cavity within the fiber) proportion;[13] high cellulose content, compared to that of hemicelluloses and lignin;[11] and a microfibril angle with orientation close to the fiber bundle.[14] A particular case in point highlighting the commercial value of this fiber as a composite additive material is when A. G. Daimler successfully developed and patented a polypropylene composite reinforced by abaca fibers to be used as under-floor components and covering of spare tire wheels of a Mercedes-Benz A-Class passenger car, meeting rigorous quality requirements for road transportation.[15-17]

What limits the maximum utilization of natural fibers, such as abaca, as promising alternatives to traditional resin reinforcement materials is their inherent hydrophilic nature. The high hydrophilicity of natural fibers can lead to high moisture absorption and, when they are used as fillers in composite materials, results in poor fiber dispersion and fiber–matrix interfacial

adhesion.[18-23] To address these issues, fiber surface modification is considered.

This study focuses on the surface modification of abaca fibers using two kinds of organotrialkoxysilane coupling agents: 3-(trimethoxysilyl) propyl methacrylate (TMPS), and octyl triethoxy silane (OTES) (Fig. 1). To verify the successful modification of the abaca fibers, Fourier transform infrared (FTIR) spectroscopic measurements of the modified abaca fibers (using different silane agents) and unmodified abaca (as control) were conducted. FTIR spectroscopy is a good characterization tool to use in determining the functional groups present in a sample.[24-26] The wetting behavior of the modified and unmodified fibers was characterized through contact angle (CA) analysis.

EXPERIMENTAL
Materials
Abaca fibers were obtained from the Department of Science and Technology of the Philippine Textile Research Institute (PTRI-DOST). Two types of organotrialkoxysilane coupling agents were used as received: 3-(trimethoxysilyl) propyl methacrylate (TMPS) and octyl triethoxy silane (OTES).

Preparation of organosilane solutions as a dip bath
To prepare the organotrialkoxysilane dipping solution, the solvent consisted of ethanol:water in a 4:1 mole ratio. An appropriate amount of silane coupling agent was then added to prepare a 1:10 mole ratio (silane:solvent). The mixture was then stirred at a constant rate for 2 hours and the pH was adjusted to 4.00 using acetic acid. This is a modified method reported by Mendes *et al.*[27]

Immersion of fibers in organosilane solutions
Abaca fiber samples (0.50 g) were dipped in the organotrialkoxysilane solution for 3 hours, then taken out of the solution and allowed to stand on a surface at room temperature. Then, they were washed with an ethanol/water mixture to remove excess silane and, finally, were oven dried prior to characterization.

Characterization of silane-modified and unmodified abaca fibers
The organo-modified fibers were analyzed using Fourier-transform infrared (FTIR) spectroscopy to verify the success of the modification of the fiber materials. Also, contact angle (CA) analysis was performed to characterize their surface properties in comparison with those of unmodified abaca fiber.

Fourier-transform infrared (FTIR) spectroscopy
This technique was utilized to monitor the modification of the abaca fiber after the reaction with various silane coupling agents. The FTIR spectra of the samples were obtained on a Thermo Scientific Class 1 Nicolet 6700 FTIR spectrometer, in the range of 400-4000 cm^{-1}, with 16 scans performed. Each of the tested samples was ground, added to KBr and then pelletized prior to FTIR analysis.

Contact angle (CA) analysis
Abaca fibers were compressed into a pellet ring-like structure. Each sample was placed on the holder platform of the contact angle setup. Using a micropipette, 5 μL of distilled water was applied onto five random locations on the fiber surface. The static water contact angle of each sample was determined from the capture photo of the droplet, using a Theta Lite Optical Tensiometer TL-100, controlled with OneAttension software, capable of determining the contact angle of a water droplet calculated from the live image with advanced machine vision capability.

RESULTS AND DISCUSSION
Surface modification of abaca fibers using silane coupling agents
Silane coupling agents are often utilized in the preparation of composite materials as modifying agents for the filler component through the introduction of functional groups or long, non-polar carbon structures. They have a general structure: $(RO)_3$-Si-R′-X, where X is an organofunctional group, R′ is a carbon linkage, and RO is a hydrolyzable group, like an alkoxy group.[28-29] Figure 1 shows the structure of the organotrialkoxysilane coupling agents used in the abaca fiber modification.

After silane modification of the abaca fibers, the samples were subjected to FTIR spectroscopic analyses. Figure 2 shows the stacked FTIR spectra of the modified abaca fibers, as well as that of the unmodified abaca fiber (control). There exists a peak at 3450 cm^{-1} corresponding to hydroxyl stretching in the spectra of all abaca samples, which is linked to the -OH groups in the cellulose component of the abaca fibers. For the modified abaca fibers, unique peaks are observed at 1080 cm^{-1} (Si-O-Si) and at 1260-1200 cm^{-1} (Si-O-C), which are characteristic of the silicon bond vibrations, as reported elsewhere.[30-32] These peaks are absent in the spectrum of the unmodified abaca. The difference between the FTIR spectra of the organotrialkoxysilane-modified abaca fibers and that of unmodified abaca has given strong evidence that the surface modification procedure used in this work was successful in

altering the structure of the abaca fibers. The presence of such peaks supports the successful silylation, and therefore, the chemical modification of the abaca fibers.

In the works of Abdelmouleh and co-researchers (2003)[33] and Rutter and Hutton-Prager (2018),[34] different silane coupling agents were utilized to surface modify cellulosic materials. The silane treatment of the fibers, followed by a heat treatment, resulted in the adsorption of the silanes onto the cellulose surfaces; the chemical bonding of the coupling agents onto the cellulose was confirmed by FTIR spectroscopy.
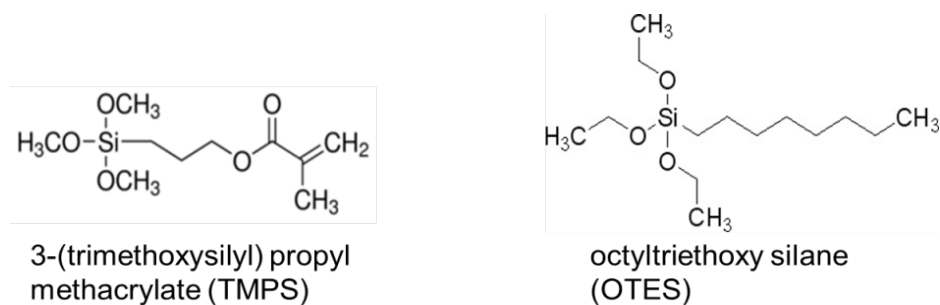

Figure 1: Chemical structure of the organotrialkoxysilane coupling agents used in the study to chemically modify abaca fibers

Some of the -OH groups of the cellulose substrates were shown to react and formed Si-O-Si and Si-O-C peaks, ensuring successful grafting. The silane modified fibers were shown to exhibit higher contact angles than the unmodified cellulose sample, indicating that the hydrophilicity of the cellulose fibers can be significantly decreased through silylation.

Surface hydrophobicity of modified abaca fibers

One of the common ways and a fast, practical tool to characterize surface wettability is contact angle measurement. Wettability or the wetting phenomenon refers to the study of how a liquid dropped on a substrate spreads out. The contact angle reflects the hydrophobic or hydrophilic behavior of a material – in most cases, it is deemed to be connected to different surface properties, such as surface porosity, roughness, heterogeneity, etc.[35-37] The value of the static contact angle made by a liquid droplet deposited on a fiber surface is shown in Figure 3. Since the static contact angle of the water droplet is greater than 90°, this suggests that the affinity between water and the fiber is low; hence the fiber surface is hydrophobic.
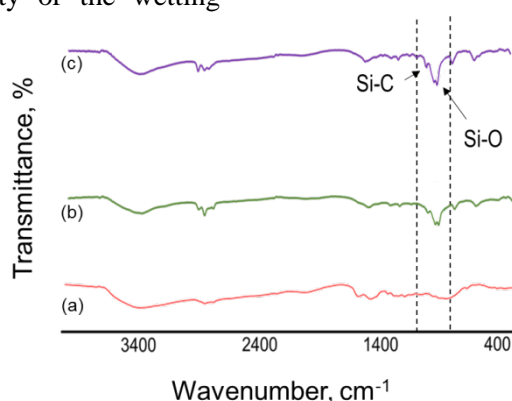

Figure 2: Fourier transform infrared (FTIR) spectra of untreated abaca (a); modified abaca treated with 3-(trimethoxysilyl)propyl methacrylate silane (TMPS) (b); and modified abaca treated with octyltriethoxy silane (OTES) (c)
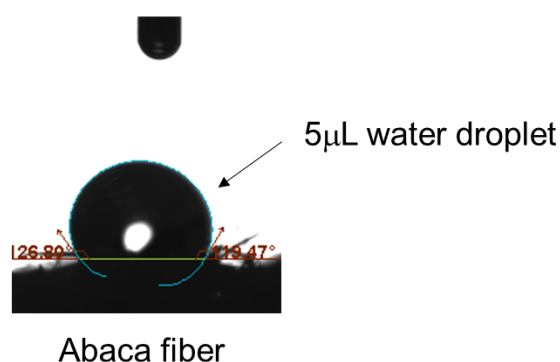
Figure 3: Image of a water droplet applied on the abaca fiber sample for contact angle measurement
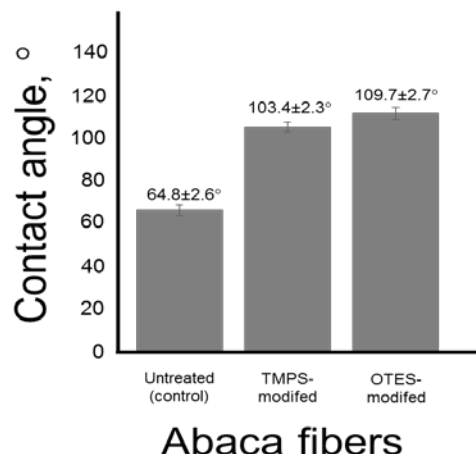

Figure 4: Contact angle of untreated abaca, modified abaca treated with 3-(trimethoxysilyl)propyl methacrylate silane (TMPS); and modified abaca treated with octyltriethoxy silane (OTES)

Both modification treatments utilizing organotrialkoxysilane agents resulted in modified abaca fibers exhibiting higher water contact angles, compared to unmodified abaca fibers. OTES silane agent modified abaca to exhibit an average contact angle of 109.7±2.7°, while the fiber treated with TMPS showed an average of 103.4±2.3°. Meanwhile, the water contact angle of the untreated abaca was 64.8±2.6°. OTES-modified abaca gave higher contact angle values than TMPS-modified fibers, due to its longer alkyl chain.[38] The higher contact angle values exhibited by the silane-modified abaca fibers compared to those of untreated abaca fibers, as well as the successful chemical modification of these fibers, as confirmed by the FTIR spectroscopic measurements, demonstrated that the hydrophobic modification of abaca fibers by the organotrialkoxysilane coupling agents has been achieved.

In the work of Schramm and Amann (2019),[39] various trialkoxysilane modifying agents were used in combination with some polymers to surface modify cotton fabrics. After successful silylation was confirmed, the physico-mechanical properties of the silane-modified cotton materials were assessed. Along with increased hydrophobicity, other characteristics, including dry crease recovery (the ability of cotton to recover from wrinkling) and stiffness, were improved in the modified cotton materials. This modification method can, therefore, bring numerous advantages, making the fibers suitable for diverse applications. Also, the modification treatments utilizing organotrialkoxysilane agents

have been demonstrated efficient in addressing the issue of inherent hydrophilicity in abaca fibers, which prevents their use as filler for polymer composite preparation. Hydrophobized abaca fibers can prevent high moisture absorption, which usually causes poor fiber dispersion and insufficient fiber–matrix interfacial adhesion in natural fiber reinforced polymer composites.

CONCLUSION

This short communication reports on the successful modification of abaca fibers using two organotrialkoxysilane coupling agents: 3-(trimethoxysilyl) propyl methacrylate (TMPS) and octyl triethoxysilane (OTES). The treatment resulted in hydrophobized abaca fibers, as confirmed by the higher water contact angles recorded for the fibers modified by OTES (109.7±2.7°) and TMPS (103.4±2.3°), respectively, compared to that of untreated abaca (64.8±2.6°). In addition, FTIR spectroscopic measurements confirmed the successful chemical bonding of the organotrialkoxysilane agents onto the cellulose structure of the abaca fibers.

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