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Effect of alkali treatment on interfacial bonding in abaca fiber-reinforced composites

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ABSTRACT

Abaca fibers demonstrate enormous potential as reinforcing agents in composite materials. In this study, abaca fibers were immersed in 5, 10 or 15 wt.% NaOH solutions for 2 h, and the effects of the alkali treatments on the mechanical characteristics and interfacial adhesion of the fibers in a model abaca fiber/epoxy composite system systematically evaluated. After 5 wt.% NaOH treatment, abaca fibers showed increased crystallinity, tensile strength and Young's modulus compared to untreated fibers, and also improved interfacial shear strength with an epoxy. Stronger alkali treatments negatively impacted fiber stiffness and suitability for composite applications. Results suggest that mild alkali treatments (e.g. 5 wt.% NaOH for 2 h) are highly beneficial for the manufacture of abaca fiber-reinforced polymer composites.

1. Introduction

The use of natural plant fibers as reinforcing agents in composite materials has attracted widespread scientific and industrial interest over the past decade [1–4]. This interest originates from the natural abundance and low cost of such fibers, as well as the inherent physical properties of natural fibers such as their light weight and high specific modulus [5]. Amongst the various plant fibers under consideration for use in polymer composites, abaca (i.e. Manila hemp) produced in Philippines possesses the most desirable mechanical properties. Abaca fibers contain 56–64 wt.% cellulose, 25–29 wt.% hemicelluloses, 11–14 wt.% lignin and a small proportion of fats, pectin, ash and waxes [6,7].

Abaca fiber-reinforced composites have been used in automotive applications, including under-floor protection in passengers vehicles (e.g. Daimler AG series) [8]. Abaca fiber was the first plant fiber to meet the stringent quality requirements of road transportation, which can be attributed to its resistance to influences such as dampness, exposure to the elements and stone strike [9]. Obtaining large quantities of high quality abaca fiber with consistent characteristics is essential for the industrial composite applications (e.g. variations in fiber quality from batch-to-batch or year-to-year are highly undesirable as this could yield composites with low or unpredictable strength). The most important factor in obtaining good plant fiber reinforcement in a composite is the interfacial adhesion between the matrix polymer and the fiber [10]. However, a common shortcoming of many plant fiber-reinforced composites is weak interfacial adhesion with the matrix, which generally can be traced to the hydrophilic nature of plant fibers. Therefore, in order to develop composites with improved mechanical properties, it is necessary to impart a degree of hydrophobicity to the fibers by suitable chemical treatments [11–13].

Alkali treatment (a form of mercerization) is one of the most useful methods for the surface modification of cellulosic fibers. A considerable body of work has been reported on improving the mechanical properties of natural fibers and their composites by alkali treatment [14–17]. Manalo et al. [18] found that a 6 wt.% NaOH treatment increased the bending, tensile, compressive and stiffness of bamboo fiber reinforced polyester composites by 7, 10, 81 and 25%, respectively. Gomes et al. [19] reported that a 10 wt.% concentrated alkali treatment of curaua fibers improved the mechanical properties of curaua/PLA composites. The 10 wt.% alkali treatment increased the toughness and strength of curaua fibers compared to untreated curaua fibers. Saha et al. [20] reported that dipping jute fibers in a 0.5 wt.% alkali solution increased in the tensile strength of the fibers by up to 65%. Hossain [21] reported that a 5 wt.% alkali solution afforded the best mechanical properties for single sugarcane fiber bundles. Cai

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et al. [22] determined that abaca fiber strength varied with alkali treatment, with a 5 wt.% NaOH concentration being near optimal. Results were rationalized in terms of the effect of the alkali treatment on fiber microstructure. From the studies described above, it is not obvious as to what is the best alkali treatment for improving the mechanical properties of cellulose-based natural fibers for composite applications.

The macro-mechanical performance of fiber-reinforced composites increase is generally rationalized in terms of the interfacial shear strength (IFSS) of the fiber with its surrounding polymer matrix. The methods used to establish IFSS are not standardized, thus it is often difficult to compare the work of different groups. Methods commonly used to measure the IFSS between the fiber and the matrix in include microbond, pull-out test, three-fiber test and push-out test [23–25]. Single fiber pull-out tests offer a number of distinct advantages over the aforementioned tests for IFSS determination, not least of which are simplicity and ease of reproducibility. However, standardized methods have yet to be developed for single fiber pull-out tests, currently limiting the potential of the method for comparing IFSS determined by different groups for different natural fiber containing composites.

In the present work, we describe a novel single fiber pull-out test for examining IFSS in natural fiber-polymer composites. Alkali treated abaca fibers embedded in an epoxy resin were used as test samples. By varying the alkali concentration, the interfacial adhesion of the fibers with the epoxy resin could be varied allowing the full potential of the single fiber pull-out test to be gauged. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform-infrared spectroscopy (FT-IR) were used to analyze structural and chemical changes in the fibers after alkali treatments, and SEM was used to examine the fiber-epoxy interface. Results guide the development of new and improved processes for the manufacture and testing of abaca fiber-reinforced composites.

2. Materials and experimental methods

2.1. Materials

Abaca fibers were obtained from the Philippines, and typically cut to a length of 20 mm. The abaca fibers (70–80 mg) were subsequently immersed in an aqueous NaOH solution (100 mL, concentration: 5, 10 or 15 wt.%) for 2 h under vacuum (around 13 kPa) to ensure good penetration of the alkali solutions into the fiber bundles. The fibers were then removed from the alkali solution and washed several times using fresh tap water until the pH of the rinsing liquid was approximately 7 to ensure complete removal of the NaOH from the abaca fibers. Finally the abaca fibers were dried in a vacuum oven at 80 °C for 2 h.

2.2. XRD

Wide-angle X-ray diffraction patterns were obtained on a Rigaku MultiFlex X-ray Diffractometer (Rigaku Corporation, Japan). The measurements were carried with the Cu X-ray tube operating at 40 kV and 20 mA, with a detector placed on a goniometer scanning the range from 5° to 40° at scan speed of 2°/min.

2.3. FT-IR

Fourier transform infrared spectra of untreated and alkali-treated fibers were performed by dispersing powdered fiber samples in KBr pellets (mass ratio; abaca fiber:KBr = 1:100), using a Bio-Rad FTS 3000 MX spectrometer (Varian, Inc., USA).

2.4. SEM

Morphologies of the untreated and alkali-treated fibers were examined using a scanning electron microscope JEOL-JSM-6390 (JEOL Ltd., Japan). For the SEM study, the fiber samples were lightly coated with Pt-Pd to minimize specimen charging under the electron beam. Specimens were imaged at an accelerating voltage of 1.5 kV.

2.5. Fiber tensile tests

The mechanical properties of the fibers, including tensile strength, Young's modulus and strain at break, were determined using an Instron (model 5567, Instron Corporation, USA). For each test sample, as abaca fiber bundle was glued on a paper frame with 10 mm gauge length. The cross sectional area of the abaca fiber bundles is elliptical and so the average cross-sectional area (A) was calculated from two fiber perpendicular diameters (d_1 and d_2) using the equation: $A = \pi d_1 d_2/4$. The diameters were measured by using a digital microscope VHX-600 (Keyence Corporation, Japan). The tensile tests were performed using a load cell of 500 N at a cross head speed of 1.0 mm/min. Before each tensile test, the supporting paper frame was cut in the middle.

2.6. Single fiber pull-out tests

The single fiber pull-out test is an experimental method commonly used to measure the interfacial shear strength (IFSS) between a single fiber and a bulk of matrix material that surrounds the fiber [26]. Here, a novel single fiber pull-out tests is described. A single fiber was threaded through the eye of a sewing needle. The needle, together with the fiber, was punctured through the wall of a silicon rubber box. The needle was then removed, leaving one end of the fiber inside the silicon rubber box, with the embedded length ranging from 500 μm to 1000 μm and determined using an optical microscope. The fiber critical length is 1000 μm, above which the interfacial shear stress (IFSS) between the fiber and the epoxy no longer increases linearly with the embedded area of the fibers. The procedure was repeated on all four sides of the silicon rubber box. Epoxy was mixed with curing agent and accelerator and then poured into the box and cured at room temperature for 24 h. Afterwards, the epoxy block was carefully removed from the silicon rubber box and post-cured at 60 °C for 2 h. Each block produced 4 test pieces after cutting. The single fiber pull-out test system is shown in Fig. 1(a), the test sample in Fig. 1(b) along with a schematic of the pull-out test (Fig. 1(c)). The pull-out tests were performed using a load cell of 500 N at a cross head speed of 1.0 mm/min, and carried out on a universal mechanical testing machine, ETM-D with automatic extensometer (Shenzhen Wance Testing Machine Co., Ltd. P. R. of China).

The IFSS between the fiber and matrix material is calculated as follows [27,28]:

Interfacial shear stress (τ),

$$\tau = \frac{Failure\ load}{Interfacial\ area} = \frac{F_{max}}{\pi \times d \times L} \quad (1)$$

where F_{max} is the maximum force recorded by the load cell, d is the diameter of the fiber, and L is the embedded fiber length in the matrix.

3. Results and discussion

3.1. Surface morphologies of alkali-treated abaca fibers

Cross-sectional SEM micrographs of untreated and alkali-treated abaca fiber bundles are shown in Fig. 2. In the cross section