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Influence of alkali treatment on internal microstructure and tensile properties of abaca fibers

Ming Cai[a,b], Hitoshi Takagi[c,*], Antonio N. Nakagaito[c], Masahiro Katoh[c], Tomoyuki Ueki[c], Geoffrey I.N. Waterhouse[d], Yan Li[a]

[a] School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai 200092, China
[b] Graduate School of Advanced Technology and Science, The University of Tokushima, 2-1 Minamijosanjima-cho, Tokushima 770-8506, Japan
[c] Institute of Technology and Science, The University of Tokushima, 2-1 Minamijosanjima-cho, Tokushima 770-8506, Japan
[d] School of Chemical Sciences, The University of Auckland, Auckland 1142, New Zealand

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ABSTRACT

The objective of this study is to investigate the effect of alkali treatment on the internal microstructure and tensile properties of abaca fibers. The abaca fibers were immersed in aqueous solutions of NaOH (5, 10, or 15 wt%) for 30 min, rinsed and dried. The fibers were subsequently characterized by scanning electron microscopy, X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FT-IR), and tensile strength tests. The lumen is a hollow region in each elementary fiber of the abaca fiber bundles. It was found that the lumen of the abaca fibers completely collapsed after 10 and 15 wt% NaOH treatment, due to swelling of the fibers. The fibers also became twisted after these alkali treatments. It was found that cellulose I in abaca fibers was partially transformed to cellulose II after 15 wt% NaOH treatment, as evidenced by XRD measurements. FT-IR analysis indicated that the alkali treatment led to a gradual removal of binding materials; such as hemicelluloses and lignin, from the abaca fibers, resulting in the separation of abaca fiber bundles into individual elementary fibers. The tensile strength of alkali-treated abaca fibers did not vary with alkali concentration. The Young's modulus of the abaca fibers treated with 5 wt% NaOH solution increased by 41%, whereas those treated with 10 and 15 wt% NaOH solution decreased by 24 and 29%, respectively. A non-linear behavior was observed in the stress–strain curves of the abaca fibers after 10 and 15 wt% alkali treatment, which could be attributable to the twisting of the fibers.

1. Introduction

Due to economic incentives and increasing environmental awareness, natural fiber reinforced thermoplastic or thermoset composites have attracted many researchers' attention (Liu et al., 2012a; Saenghirunwattana et al., 2014; Takagi and Asano, 2008; Zhang et al., 2013). The advantages of using natural fibers in industrial applications relate to their light weight, low cost, nontoxicity, biodegradability, and high specific stiffness. These characteristics make natural fiber–reinforced composites suitable for application in automotive and aircraft industries. The European Union legislation implemented in 2006 has expedited the application of natural fiber–reinforced plastics in automobiles. Car manufacturers must make vehicles in such a way that more than 85% of the vehicle's total weight can be recycled (Holbery and Houston, 2006). Regarding potential industrial application, fiber strength is one of the most important characteristics. Natural fibers include sisal (Li et al., 2008), flax (Zhang et al., 2013), ramie (Yu et al., 2014), bamboo (Takagi and Ichihara, 2004), and abaca (Liu et al., 2013) exhibit good strength and are thus suitable for fabrication of fiber–reinforced composites.

Abaca (i.e., Manila hemp) is a species of banana and grows as a commercial crop in the Philippines. Abaca fiber has a high tensile strength (600–900 MPa) and Young's modulus (30–50 GPa) (Müssig et al., 2010; Shibata et al., 2003). Higher values compared to other strong fibers, such as sisal fiber which possess a tensile strength of 511–635 MPa and Young's modulus between 9.4 and 22.0 GPa (Bledzki and Gassan, 1999). Abaca fiber reinforced composites have been used for under-floor protection of passengers Daimler AG vehicles (Knothe et al., 2000). Importantly, abaca fibers satisfy the stringent quality requirements of road transportation, especially resistance to influences such as dampness, exposure to

* Corresponding author. Tel.: +81 88 656 7359; fax: +81 88 656 9082.
E-mail address: takagi@tokushima-u.ac.jp (H. Takagi).

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the elements, and stone strike (Bledzki et al., 2007). Understanding the unique physical and chemical properties of abaca fibers, and the structure–function relationship of the fibers, is critical to their effective utilization in industrial applications.

A weakness of the natural fibers is their high water absorption characteristics and weak interfacial bonding with the matrix material of composites. This is the reason why natural fibers have not completely replaced conventional fiber materials in high-load applications. Natural fiber–reinforced composites have been used in the automotive industry, but their application is generally limited to parts such as door panels, seat backs, and other interior panels (Holbery and Houston, 2006). Due to the large industrial potential of natural fibers, their surface modification is becoming an important field of research. The majority of research in the area of fiber improvement focuses on the fiber–matrix interfacial adhesion and decreasing water absorption (Bledzki et al., 2010; Fu et al., 2008; Liu et al., 2009).

Alkali treatment (i.e., mercerization) is one of the most popular and lowest cost methods used for surface modification of natural fibers. It has been reported that the surface area of the alkali-treated fibers is increased compared to untreated fibers, which in turn leads to better interfacial contact of the fiber with its surrounding composite matrix (Boopathi et al., 2012; Gassan and Bledzki, 1999; Kobayashi et al., 2011; Mwaikambo and Ansell, 2002; Sangappa et al., 2014).

The lumen of natural fibers contributes to the high sound absorption performance (Yang and Li, 2012) and also plays a greater role than crystal structure and chemical compounds, on the transverse thermal conductivity of unidirectional composites (Liu et al., 2012b). The lumen is a hollow structure in the center of the abaca fibers that strongly influences the properties of natural fibers. The effect of the alkali treatment on the lumen of abaca fibers, and in turn the mechanical strength of such alkali-treated fibers, has received little attention in the literature, motivating the current study.

This study aimed to explore the relationship between the internal microstructure and tensile properties of abaca fibers by alkali treatment. XRD and FT-IR were used to follow alkali-induced structural and chemical changes in the fibers, respectively. The obtained structural and chemical information, combined with mechanical tests on the same untreated and treated fibers, serve to guide the development of the surface modification processes of natural fibers for advanced composite applications.

2. Materials and experimental methods

2.1. Materials

Abaca fibers were supplied from the Philippines. The abaca fibers were treated with three different aqueous NaOH solutions (5, 10, and 15 wt%) for 30 min under a vacuum condition around 13 kPa (98 Torr). Then, the fibers were taken out from the solution and washed several times using fresh tap water until the pH was around 7, to remove NaOH from the abaca fibers. Finally the abaca fibers were dried in a vacuum desiccator oven at 80 °C for 2 h.

2.2. Morphological examination of abaca fibers

The fracture surface and lateral surface of untreated and alkali-treated (5, 10, and 15 wt% NaOH solution) abaca fibers were examined by a scanning electron microscope JEOL-JSM-6390 (JEOL Ltd., Japan). The fracture surface of the sample was examined after each tensile test. Then, the sample was coated with Pt–Pd to prevent specimen charging under electron beam. Specimens were imaged at an accelerating voltage of 1.5 kV.

2.3. XRD measurements

The diffraction spectra were obtained at room temperature (20–22 °C) from radiation generated by a Rigaku MultiFlex X-ray Diffractometer (Rigaku Corporation, Japan). The measurements were carried out at 40 kV and 20 mA with a detector placed on a goniometer scanning the range from 5° to 40°, at a scan speed of 2°/min. Table 1 shows 2θ values calculated using the following equations (Spence and Zuo, 1992):

$$2\theta = 2\sin^{-1}\left(\frac{n\lambda}{2d_{hkl}}\right) \quad (1)$$

$$\frac{1}{d_{hkl}^2} = \frac{1}{a^2}\frac{h^2}{\sin^2\beta} + \frac{1}{b^2}k^2 + \frac{1}{c^2}\frac{l^2}{\sin^2\beta} - \frac{2hlcos\beta}{ac\sin^2\beta} \quad (2)$$

where θ is the angle of diffraction, n is an integer, λ is the wavelength of the X-ray ($\lambda = 1.5406$Å), and d_{hkl} is the crystallite dimension in the direction perpendicular to the crystallographic plane *hkl*. The cellulose structure is monoclinic, namely $a \neq b \neq c$ and $\alpha = \gamma = 90\,^{\circ}\mathrm{C} \neq \beta$.

2.4. FT-IR measurements

FT-IR was performed at room temperature (20–22 °C) using a Bio-Rad VARIAN FTS 3000MXT spectrometer (Varian, Inc., USA). The infrared spectra of untreated and 5, 10, and 15 wt% alkali-treated abaca fibers were measured using finely powdered samples. The powdered sample was mixed with KBr at a weight ratio of KBr: sample = 100:1. This mixture was molded into a pellet by using a hand-operated press machine.

2.5. Mechanical characterization of abaca fibers

To carry out tensile tests, the fibers were split into parcels, of which three were treated with 5, 10, and 15 wt% NaOH solution and one was an untreated control sample. Each treated or untreated abaca fiber was stuck on a paper frame, as shown in Fig. 1. Ten fiber samples were tested for each alkali treatment condition.

Table 1
Different cellulose types by crystallographic structure.

Cellulose type	Lattice parameters (Å)			2θ (deg.)		
	a	*b*	*c*	$10\bar{1}$	002	040
Na–cellulose I (EI; Oudiani et al., 2011)	8.8	10.3	25.3			
Na–cellulose IV (EI; Oudiani et al., 2011)	9.6	10.3	8.7			
Cellulose I (Borysiak and Doczekalska, 2005)	8.3	10.3	7.9	16.0	22.6	34.5
Cellulose II (Borysiak and Doczekalska, 2005)	8.1	10.3	9.1	20.2	22.2	34.5

(2θ is the angle of diffraction and was calculated from the lattice parameters. β is the inter-axial angle between *a* and *c*. Cellulose I, $\beta = 84$. Cellulose II, $\beta = 64$. The geometry of both celluloses is monoclinic (Borysiak and Doczekalska, 2005).)