Contact Angles of Single Bamboo Fibers Measured in Different Environments and Compared with Other Plant Fibers and Bamboo Strips

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The objective of this paper was to investigate the contact angles of single bamboo fibers at different temperatures and relative humidities in comparison to terylene fibers. Comparative tests were done for three other natural fibers (ramie, jute, and kendir) under the same conditions. Contact angles were also measured for bamboo strips. The results showed that with increasing temperature and constant relative humidity, the contact angles of bamboo fibers decreased, whereas those of terylene fibers increased. The contact angle of the bamboo fiber increased significantly, while that of the terylene fibers rose a little with increasing relative humidity at constant temperature. The contact angles of the single bamboo fibers were higher than those of ramie fibers, but lower than jute and kendir fibers after the same chemical treatment because of different diameters, surfaces, and chemical components. In comparison with bamboo strips, the contact angles of single bamboo fibers were much higher and changed with a different trend. Meanwhile the contact angles of cross-section, radical section, and tangential section of bamboo also changed differently.

Keywords: Single bamboo fibers; Bamboo strips; Contact angle; Temperature; Relative humidity

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INTRODUCTION

Increasing concerns for the environment have sparked renewed interest in the development of biodegradable, mechanical bio-composite in which natural fibers serve as a reinforcement to enhance strength and stiffness (Mohanty *et al*. 2000; Pietak *et al*. 2007). Due to low density, high mechanical performance, and problem-free disposal, natural fibers derived from plants offer a promising alternative to other technological reinforcing fibers presently available (Mohanty *et al*. 2000; Aranberri-Askargorta *et al*. 2003). As a kind of natural fiber, bamboo fibers are becoming a primary feed-stock for weaving, paper making, and the fiber-based composite industry (Chen *et al*. 2011).

The wetting of bamboo fibers' surface by liquid is relevant to a range of industrial processes mentioned above, because it provides information on the interaction between the solid–liquid, solid–vapor, and liquid–vapor interfaces (McHale *et al*. 1997). One of the most common methods for measuring wettability is contact-angle measurement. The degree to which liquids wet a fiber determines how easily the liquid can penetrate fiber assemblages (Aranberri-Askargorta *et al*. 2003). However, it is difficult to measure the contact angle of liquid on individual bamboo fibers because the fiber length is too small to be handled easily, and the wetting force of a single fiber in solution is difficult to measure accurately (Deng and Abazeri 1997). Foote (1939), Jones and Porter (1976), and Grindstaff (1969) have attempted the optical measurements of contact angles of liquids against fibers. However, it was difficult to accurately measure the contact angle of liquid on the very small wood fibers using an optical technique that results in poor reproducibility. Decades later, Hodgson and Berg (1988) and Krueger and Hodgson (1994, 1995) measured fiber–liquid contact angles employing the Wilhelmy principle, in which the downward force upon a single fiber is suspended vertically through the liquid surface. Deng and Abazeri (1997) measured a group of separated fibers instead of measuring the contact angle of a single fiber.

One of the most frequently used methods of contact-angle assessment is the sessile drop technique (Amaral *et al*. 2002; Qian *et al.* 2010), which is also used in optical measurements. With the technique developing, Chen *et al.* (2011) determined contact angles of single bamboo fibers using the optical method with a Krüss DSA 100 device (Hamburg, Germany). That conquered the many problems mentioned previously, such as poor reproducibility with the optical method (Foote 1939; Jones and Porter 1976; Porter 1969), difficulty making the single natural fiber immersed in liquid with a method in line with the Wilhelmy principle (Hodgson and Berg 1988; Krueger 1994, 1995), *etc.* Chen *et al.* (2011) investigated contact angles of single bamboo fibers treated chemically or untreated, and found that contact angles of single bamboo fibers treated by ultrasound during separation were lower than those of untreated bamboo fibers.

For better utilization of bamboo fibers in so many areas, knowing how to measure the contact angle of single bamboo fibers is not enough. It is also essential to know about the interrelationships between the contact angle of a single bamboo fiber and the measurement environment conditions to provide more precise information about wettability, and the difference of contact angle in comparison to other natural single fibers and bamboo strips. Detailed knowledge about those aspects is still lacking. An attempt has therefore been made to investigate the change occurring in the contact angle of a single bamboo fiber at different temperatures and humidities, and single terylene (PET) fibers were measured as reference samples to find out how environmental conditions affected the contact angle of different fiber types (natural plant fibers and chemical synthetic fibers) with the method used by Chen *et al.* (2011). In addition, the contact angles of bamboo fibers and other natural fibers with the same chemical treatment were investigated and the difference between the contact angle of single bamboo fibers and bamboo strips was also calculated.

EXPERIMENTAL

Fiber Preparation

Materials were taken from 2-year-old Cizhu bamboo (*Neosinocalamus affinis*) grown in Qionglai, Chendu, Sichuan Province, China. The lower part of the bamboo trunk was cut into strips (20 mm longitudinally and 2 × 2 mm in cross-section). Then the bamboo strips, as well as the ramie (*Boehmeria nivea*), jute (*Corchorus capsularis*), and kendir (*Apocynum venetum*) provided by Hunan Zhuzhou Xuesong Co., were immersed in a chemical solution (one part 30% hydrogen peroxide (H_2O_2) and one part 100% glacial acetic acid (HAc) and kept at 60 ^{o}C for 22 h to separate the fibers (Wang *et al*. 2011; Chen *et al*. 2011). All the obtained fibers were washed to neutrality and air-dried to a constant weight before being put in a humidity chamber under specified conditions of relative humidity. The terylene fibers were provided by Ningbo Shuaibang Chemical Fiber Co. The terylene fibers were washed in distilled water and acetone in turn to remove any dust and grease.

Contact Angles of Single Fibers

Contact-angle testing of distilled water on single fibers was conducted with a Krüss DSA 100 device equipped with environmental chambers assisted by a temperature chamber and a humidity chamber. The given temperature and humidity limits were 160 °C to −30 °C and 0% to 100%. Single fibers were obtained using fine-tipped tweezers and mounted on a slatted platform with double-sided tape. Then the platform was put in the environmental chambers and moved into position using CCD cameras in the x, y, and z directions. First of all, the humidity in the environment chamber was kept at 30%, but the temperature was changed from 20 °C to 70 °C. And then the temperature in the environment chamber was kept at 20 °C while the humidity was changed from 10% to 80%. The temperature and the humidity in the environment chamber were maintained for 5 min after being adjusted to target value. The CCD cameras recorded the process of a water droplet dropping on a single fiber until disappearing gradually. The baseline for a sessile drop static contact-angle measurement was made at the liquid–solid interphase. Contact angles were calculated using the ellipse method in the DSA 3 software (Fig. 1), an accurate measurement applied by various researchers (Amaral *et al*. 2002; Wu and Yuris 2006). Six samples were tested for each fiber type.

Contact angles of four kinds of natural fibers (bamboo, ramie, jute, and kendir) were also conducted with the Krüss DSA 100, and the temperature and humidity were kept at 20 °C and 30%, respectively. Five samples were tested for each fiber type.

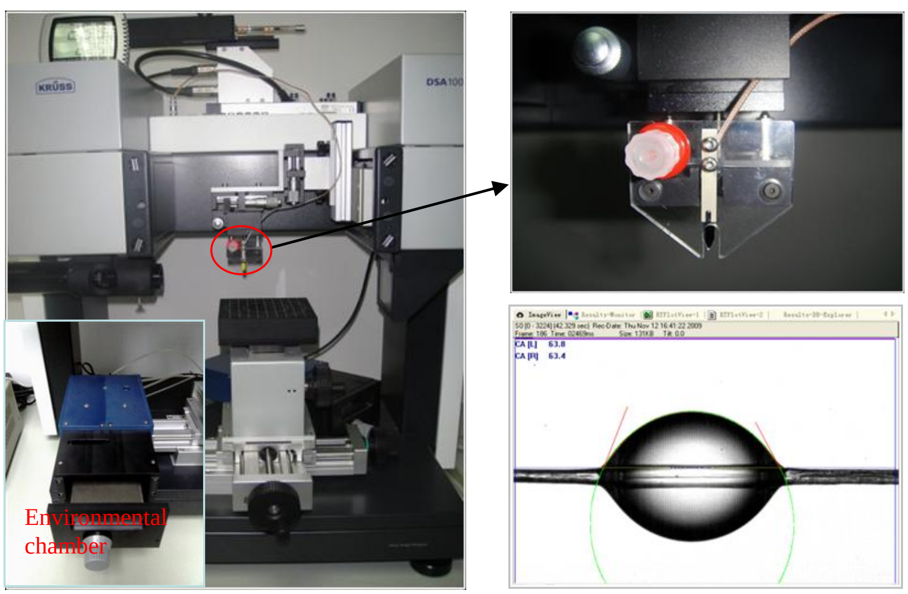

Fig. 1. Contact angle measured by a Krüss 100 and calculated by DSA 3 software

Photographs of the four natural fiber types were taken with a field emission scanning electron microscope (ESEM) (FEI Co., XL30 ESEM FEG, Hillsboro, OR) with 10 replications. Chemical components were analyzed by the FT-IR spectra instrument (Thermo Nicolet, Nexus 670, US) with three replications. Transmission spectra with a spectral resolution of 4 cm^{-1} were acquired from single air-dried fibers. A total of 64 scans were co-added per sample spectrum.

Contact Angles of Bamboo Strips

Bamboo was cut into small strips (10 mm longitudinally and 3 × 5 mm in cross-section) with smooth cross-section, radical section, and tangential section. Contact angles of bamboo strips were measured with an OCA 20 (Data Physics Instruments, Germany). Contact angles were calculated using the ellipse method. And the room temperature and relative humidity were 25 °C and 13%, respectively. Three samples were tested for each section of bamboo.

RESULTS AND DISCUSSION

Contact Angles of Single Fibers Measured at Different Temperatures

When the humidity in the environmental chamber was kept at 30%, the contact angle of a single bamboo fiber decreased with the increasing temperature, but that of a single terylene fiber increased (Fig. 2).

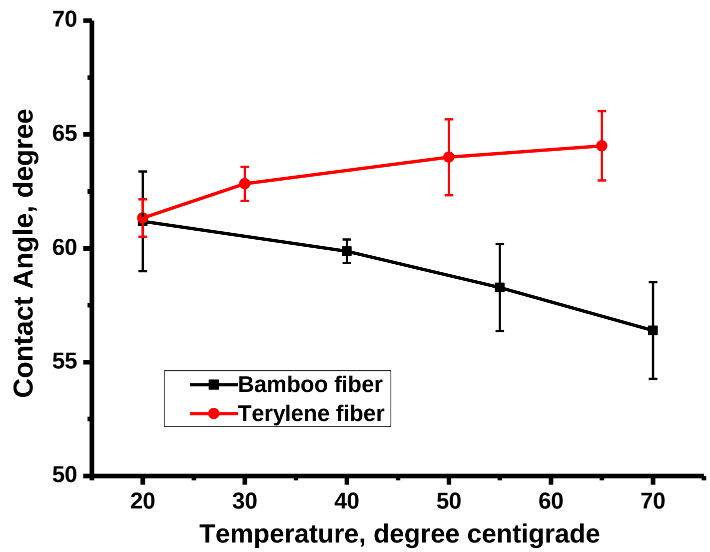

Fig. 2. Contact angles of single fibers measured at different temperatures

The single bamboo fiber is a relatively complicated and unstable natural plant fiber and is mainly made up of cellulose, hemicellulose, and lignin which are easily affected by environmental conditions, especially the hemicellulose (Mohanty *et al*. 2000). The changing temperatures lead to a change in the amount of water present in the fiber at equilibrium. Subsequently, upon contact with a water droplet, the water already contained within the fiber affects the contact angles of single fibers, as can be observed macro-scopically (Prasad *et al*. 2004; Pietak *et al*. 2007). With the increasing temperature, the single fiber lost water, and the ability for absorbing water increased, leading to a lower contact angle. Moreover, the trend of the change in contact angle was more distinct when the temperature is higher and higher, which also can be observed in Fig. 2. However, a single terylene fiber, consisting of polyethylene terephthalate, is an example of a synthetic fiber, the surface of which is not expected to change significantly in response to changes in relative humidity. The terylene fibers are made by melt-spinning, and the heat resistance is good. The contact angle of a single terylene fiber may be affected mainly by the surface tension of water. As is known, there are three-phase equilibriums in the sessile drop experiment. The interfacial tensions of the solid–vapor, liquid–vapor, and solid–liquid interfaces, and the contact angle, are related through Young's Equation (Adamson 1990),

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{1}$$

where θ is the contact angle. γ_{sv} and γ_{sl} represent, respectively, the interfacial tension of the solid and the liquid in equilibrium with liquid vapor. γ_{sl} is the interfacial tension between the solid and the liquid. When the temperature is increased, the surface tension of the water is decreased, but not significantly (Mei *et al.* 2008). Thus, γ_{sl} and γ_{sv} decreased a little. From the equation it can be deduced that the contact angle of the single terylene fiber increases a little, because it is mainly determined by the change of surface tension of the water. However, for a single bamboo fiber, the change caused by the fiber itself is much more significant than that caused by the surface tension of the water so that the latter can be ignored.

Contact Angles of Single Fibers Measured at Different Humidities

As shown in Fig. 3, the contact angles of both a single bamboo fiber and a single terylene fiber increased with increasing humidity. The fact that a greater change was observed in the case of bamboo may be attributed to the hydrophilic groups on its surface (Bismarck *et al.* 2002). The bamboo fiber attracts moisture through hydrogen bonding because the cell wall polymers contain hydroxyl and other oxygen-containing groups (Rowell and Banks 1985).

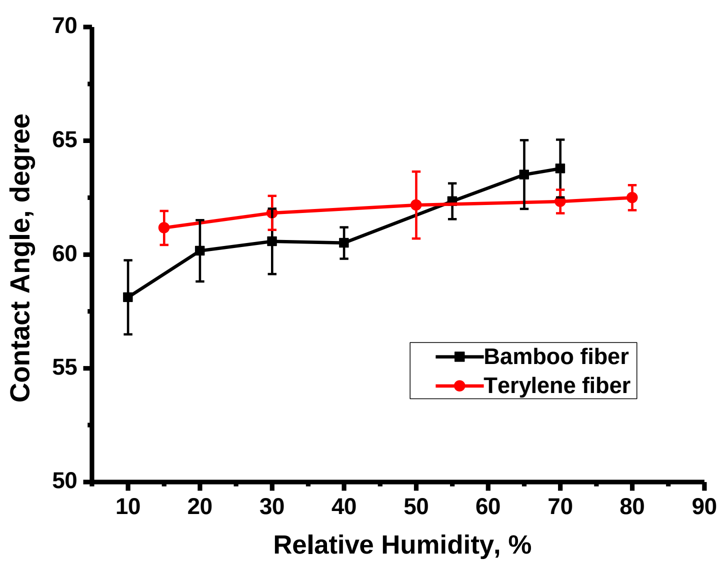

Fig. 3. Contact angles of fibers measured at different humidities

The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, noncrystalline cellulose, lignin, and surface of crystalline cellulose also play major roles (Mohanty *et al*. 2000). However, the single terylene fiber, lacking a hydrophilic group, has lower affinity for water. This explains why the contact angle of a single terylene fiber barely changed with increasing humidity.

Contact Angles of Several Kinds of Single Natural Fibers

Table 1 and Fig. 5 show that the diameter of a bamboo fiber was as thick as jute, but much thinner than that of ramie or kendir. For instance, the diameter of jute fiber was only half that of ramie fiber. And also there were nodes on the surface of ramie fiber, in contrast to the other fibers. Figure 3 indicates that kendir fibers had significantly lower penetration/evaporation times than jute or bamboo fibers. However, due to significant differences in fiber diameter among natural fiber types, a correction factor, the product diameter·time, was applied, as shown in Fig. 6. Ramie was then found to have a significantly higher diameter·time than other natural fibers. Meanwhile the contact angles of ramie fibers were smallest, while the contact angles of bamboo fibers were larger than ramie fibers but smaller than those of both jute and kendir fibers (shown in Fig. 4). The diameter·time, surface condition, and chemical composition may all be reasons for the contact-angle differences among the fibers.

Table 1. Diameter of Single Fibers

Diameter*	Bamboo	Ramie	Jute	Kendir
Mean / μm	15.95	32.69	16.03	21.31
Std	2.88	7.76	3.40	1.90
CV	0.18	0.24	0.21	0.09

*Eight samples for each type

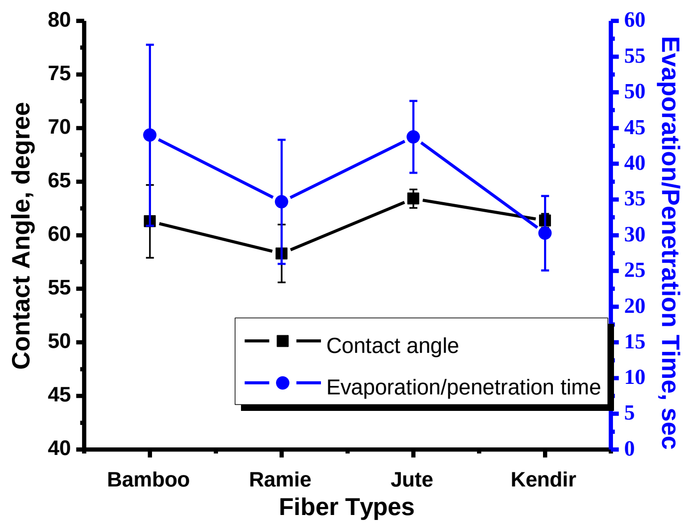

Fig. 4. Contact angles and evaporation/penetration time of single fibers

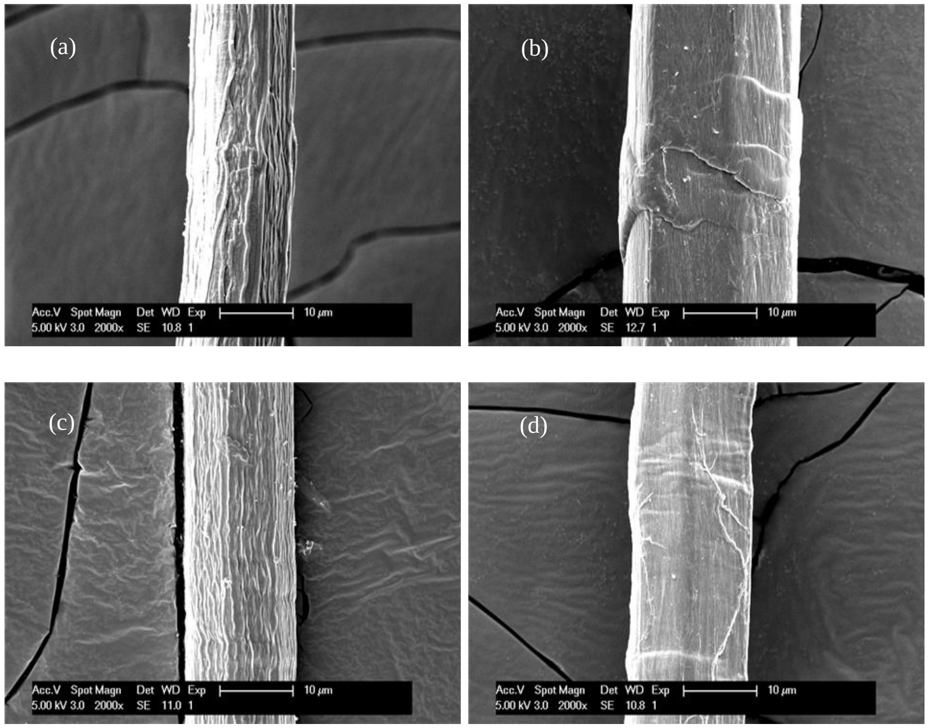

Fig. 5. ESEM images of (a) bamboo fiber, (b) ramie fiber, (c) jute fiber, (d) kendir fiber

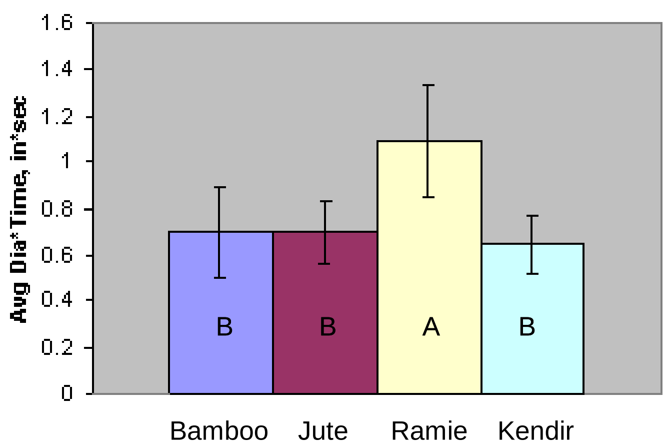

Fig. 6. Significant analysis with diameter-time interactive analyzed by SAS

The components of four natural fiber types were analyzed by FT-IR spectra (Fig. 7). The band observed in the OH valency vibration range between 3700 and 3000 cm^{-1} was the most intense in the four fiber types spectra, with a relatively sharp band maximum at 3430 cm^{-1} (Fig. 7A). The band shape and maximum position were the same for the four fiber types, whereas the intensity was a little different. A peak at 3200 cm^{-1} may be associated with strongly bound water, and a peak at approximately 3600 cm^{-1} with more loosely bound water, as discovered by Olsson and Salmen (2004) in a study of water sorption on cellulose and hemicellulose in paper. As all three plant polymers and water absorb in the OH and CH valency ranges, it is difficult to determine how the components affect the contact angle without analyzing the fingerprint region.

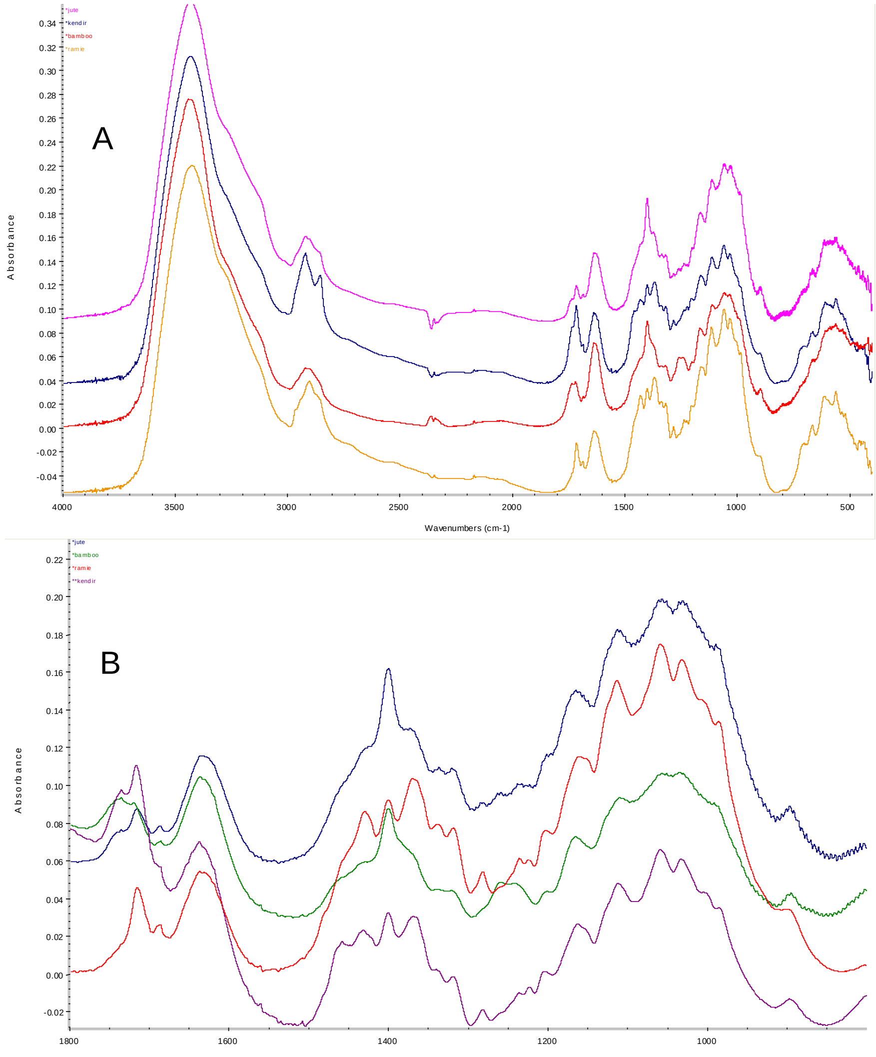

Fig. 7. FT-IR spectra of jute, kendir, bamboo, and ramie fibers: (A) full-range spectra; and (B) spectra in the fingerprint region from 1800 to 800 cm^{-1}

The most intense bands in the fingerprint region at 1060 cm^{-1} and 1035 cm^{-1} (Fig. 7B), were attributed to CO stretching vibrations (Fengel and Ludwig 1991). They were of slightly higher intensity in ramie and kendir than in jute and bamboo, as were the other carbohydrate bands at 1105 cm^{-1} (ring asymmetric vibration) and 1160 cm^{-1} (C-O-C asymmetric vibration) (Burgert *et al*. 2005; Wang *et al*. 2009). These results indicate that cellulose and hemicellulose are more prominent in ramie and kendir. In comparison with bamboo and jute, the presence of the peaks at 1429 cm^{-1} (aromatic skeletal vibration) and 1367 cm^{-1} in ramie and kendir show that lignin was present.

Figures 5 and 7 indicate that both surface conditions and components of ramie and kendir were similar, as they were for bamboo and jute. Therefore, the difference between the contact angles of ramie and kendir may be related to the diameter·time factor. Possibly that is why the contact angle of ramie was lower than for kendir. The surfaces of kendir and ramie are smoother than those of bamboo and jute (Fig. 5), and this means the contact angles of kendir and ramie should be smaller (Silva and Al-Qureshi 1999; Pietak *et al*. 2007). However, the hydroxyl-rich cellulose and especially hemicellulose were more prominent in ramie and kendir (Fig. 7) than in bamboo and jute, thus attracting moisture through hydrogen bonding (Mohanty *et al*. 2000), and finally compensating for the loss of contact angle due to the smooth surface.

Contact Angles of Single Bamboo Fibers and Bamboo Strips

The contact angle of bamboo strips changed differently compared with that of bamboo fibers, no matter which section was looked at (Fig. 8). Contact angles of bamboo fibers changed only several degrees from the time of dropping a water droplet on the surface to its time of disappearance, and there was a short equilibrium phase. By contrast, the contact angle of bamboo strips decreased much more during that process, and there was no equilibrium phase (Fig. 8). The measurement of the equilibrium contact angle of a small droplet of fluid partially wetting a flat solid surface provides information on the solid–liquid interfacial energy. However, if the spreading power $S = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv})$ of the surface is positive, then the liquid spreads completely, and no equilibrium contact angle exists (McHale *et al.* 1997). That is why bamboo strips exhibited no equilibrium contact angle. At the cell level, the component may affect the contact angle more than the structure does. However, at the macroscopic level, the structure may be mainly responsible for contact angles.

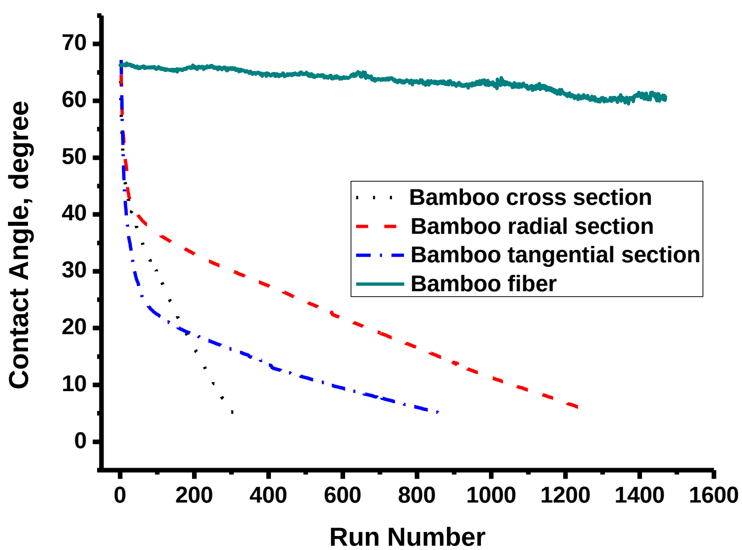

Fig. 8. Contact angles of bamboo measured at different sections

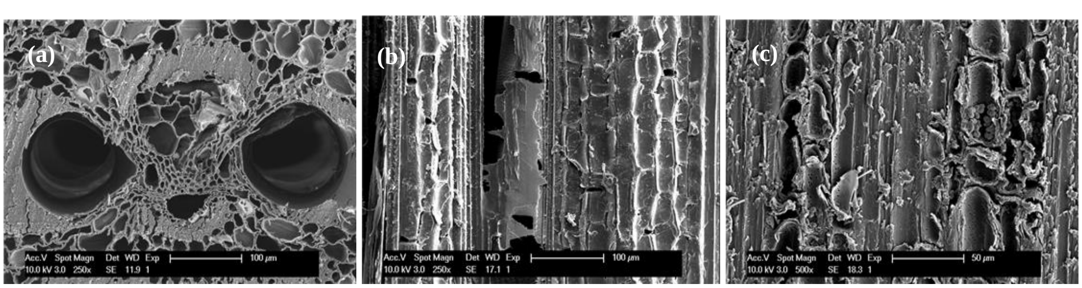

Fig. 9. ESE Microscope images of bamboo (a) cross-section, (b) radial section, and (c) tangential section

The contact angles of three different sections of bamboo also changed differently. The contact angles of the bamboo cross-section decreased much faster than those of radial and tangential sections, as shown in Fig. 9. There were more and bigger pores on the bamboo cross-section than on the bamboo radial and tangential sections, which was conducive for the permeation of water. Also the components and extracts of the different sections can account for the differences in changes in contact angles. To a certain extent, the change trend of the bamboo radial section was similar to that of the bamboo tangential section. Figure 8 shows that the pores were similar for the bamboo radial and tangential sections.

CONCLUSIONS

1. The contact angle of natural plant fibers, such as single bamboo fibers, changed significantly when environmental temperature and humidity were changed, especially when the humidity was varied. The contact angle of chemical synthetic fibers, single terylene fiber for example, changed little with changed temperature and almost remained the same when the humidity changed. Therefore, it is necessary to confirm the environmental temperature and humidity before measuring the contact angle of natural plant fibers. However, measuring the contact angle of chemical synthetic fibers only involves consideration of the environmental temperature.
2. The contact angle of single bamboo fibers was higher than ramie fibers, but lower than that of jute and kendir fibers; contact angles of four natural fibers with the same treatment were still different, even though the treatment itself may decrease the difference.
3. The contact angles of bamboo strips were much lower than that of a single bamboo fiber, which was in accordance with differences in the structure, chemical components, and extractives. At a cell level, the components were the main influencing factors, as well as the structure and the diameter, but at the macro level the structure was the main factor.

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REFERENCES CITED

Adamson, A. W. (1990). *Physical Chemistry of Surfaces*, 5th Ed., Wiley, New York.

Amaral, M., Lopes, M. A., Santos, J. D., and Lilva, R. F. (2002). "Wettability and surface charge of Si3N4-bioglass composites in contact with simulated physiological liquids," *Biomaterials* 23, 4123-4129.

Aranberri-Askargorta, I., Lampke, T., and Bismarck, A. (2003). "Wetting behavior of flax fibers as reinforcement for polypropylene," *J. Colloid Interface Sci.* 263(2), 580-589.

Bismarck, A., Aranberri-Askargorta, I., and Springer, J. (2002). "Surface characterization of flax, hemp and cellulose fiber; Surface properties and the water uptake behavior," *Polym. Composites* 23(5), 872-894.

Burgert, I., Gierlinger, N., and Zimmermann, T. (2005). "Properties of chemically and mechanically isolated fibers of spruce (*Picea abies* [L.] Karst.). Part 1: Structural and chemical characterisation," *Holzforschung* 59, 240-246.

Chen, H., Wang, G., and Chen, H. T. (2011). "Properties of single bamboo fibers isolated by different chemical methods," *Wood Fiber Sci.* 43(2), 1-10.

Deng, Y., and Abazeri, M. (1997). "Contact angle measurement of wood fibers in surfactant and polymer solutions," *Wood Fiber Sci.*, IPST Technical Paper Series 675, pp. 7-8.

Fengel, D., and Ludwig, M. (1991). "Moglichkeiten und Grenzen der FRIR-Spektroskopie bei ber Charakterisierung von Cellulose. Teil 1. Vergleich von verschiedenen Cellulosefasern und Bakterien-cellulose," *Das Papier* 45, 45-51.

Foote, J. (1939). "A method for the measurement of the contact angle formed between a liquid surface and a fiber, and the application of this and swelling data to pore diameter measurements," *Paper Trade J.* 10, 40-48.

Grindstaff, T. (1969). "A simple apparatus and technique for contact-angle measurements on small-denier single fibers," *Textile Res. J.* 39, 958-962.

Hodgson, K., and Berg, J. (1988). "Dynamic wettability properties of single wood pulp fibers and their relationship to absorbency," *Wood Fiber Sci.* 20(1), 3-17.

Jones, W., and Porter, M. (1967). "A method for measuring contact angles on fibers," *J. Colloid Interface Sci.* 24, 1-3.

Krueger, J., and Hodgson, K. (1994). "Single-fiber wettability of high sized pulp fibers," *Tappi J.* 77(7), 83-87.

Krueger, J., and Hodgson, K. (1995). "The relationship between single fiber contact angle and sizing performance," *Tappi J.* 78(2), 154-161.

McHale, G., Kab, N. A., Newton, M. I., Rowan S. M. (1997). "Wetting of a high-energy fiber surface," *J. Colloid Interface Sci.* 186, 453-461.

Mei, C. X., Wang, G. P., and Liu, Y. (2008). "The relationship between surface tension coefficient of liquid and temperature and consistency," *J. Xianyang Normal University* 23(6), 21-22.

Mohanty, K., Misra, M., and Hinrichsen, G. (2000). "Biofibres, biodegradable polymers and biocomposites: An overview," *Macromol. Mater. Eng.* 276/277, 1-24.

Olsson, A. M., and Salmen, L. (2004). "The association of water to cellulose and hemicellulose in paper examined by FTIR spectroscopy," *Carbohyd. Res.* 339, 813-818.

Pietak, A., Korte, S., Tan, E., Downard, A., and Staiger, M. P. (2007). "Atomic force microscopy characterization of the surface wettability of natural fibres," *App. Sur. Sci.* 253, 3627-3635.

Prasad, B., Sain, M., and Roy, D. (2004). "Structure property correlation of thermally treated hemp fiber," *Macromol. Mater. Eng.* 289(6), 581-592.

Qian, H., Bismarck, A., Greenhalgh, E. S., and Shaffer, M. S. P. (2010). "Carbon nanotube grafted silica fibres: Characterising the interface at the single fibre level," *Composites Sci. Tech.* 70, 393-399.

Rowell, R. M., and Banks, W. B. (1985). "Water repellency and dimensional stability of wood," Gen. Tech. Rep. FPL-GTR-50, U.S. Department of Agriculture Forest Service, Forest Products Laboratory, Madison, WI, 24 pp.

Silva, H. L. G., and Al-Qureshi, H. A. (1999). "Mechanics of wetting systems of natural fibers with polymeric resin," *J. Mater. Process Tech.* 92(93), 124-128.

Wang, X. Q., Fei, B. H., and Ren, H. Q. (2009). "FTIR spectroscopic studies of the photo-discoloration of Chinese fir," *Spectrosc. Spect. Anal.* 29(5), 1272-1275.

Wang, G., Shi, Q. S., Wang, J. W. Yu, Y., Cao, S.P., and Cheng, H. T. (2011). "Tensile properties of four types of individual cellulosic fibers," *Wood Fiber Sci.* 43(4), 353-364.

Wu, X. F., and Yuris, A. D. (2006). "Droplet on a fiber: Geometrical shape and contact angle," *Acta Mech.* 185, 215-225.

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