WOOD RESEARCH
61 (6): 2016
851-860

INFLUENCE OF THICKNESS AND MOISTURE CONTENT ON THE MECHANICAL PROPERTIES OF MICROFIBRILLATED CELLULOSE (MFC) FILMS

Xuexia Zhang, Yan Yu, Zehui Jiang, Hankun Wang
International Centre For Bamboo and Rattan, Department of Biomaterials
Beijing, P.R. China

Sfa and Beijing Co-Built Key Laboratory for Bamboo and Rattan Science and Technology
Beijing, P.R. China

(Received January 2016)

ABSTRACT

Microfibrillated cellulose (MFC) films with a layered structure and controlled thickness were successfully prepared, from bamboo processing resides as the source material, using ultrasonication followed by simple vacuum filtration. The effects of thickness and moisture content on the mechanical properties of the films were then investigated. It was shown that tensile stress and elongation at break were notably affected by the thickness of the MFC film, where the tensile stress and elongation at break of the film increased from 124 to 179 MPa and 0.9 to 5.5 %, respectively, as film thickness increased from 7.4 to 205.4 μm. However, no notable effect of thickness was observed on the Young's modulus (~10.8 GPa). It was also found that moisture content has a significant impact on the tensile properties of MFC films, in lowering the Young's modulus from 12 to 2 GPa and tensile stress from 180 to 90 MPa, and increasing the elongation at break from 4.2 to 17.5 %, as moisture content increased from 3 to 60 %. This is due to the effect of water in softening MFC films, resulting in a reduction in strength and increase in flexibility.

KEYWORDS: Microfibrillated cellulose (MFC), films, thickness, moisture content.

INTRODUCTION

Microfibrillated cellulose (MFC) has become a material of great interest in the last decade because of its biodegradability, renewability and unique physical and mechanical properties (Siró and Plackett 2010). This material is extracted from the principal axis of cellulose, the most abundant natural organic material in the world, by a variety of mechanical fiber disintegration methods (Boufi and Gandini 2015). Therefore, MFCs are high aspect ratio fibers with 10 – 100 nm in width and up to several micrometers in length, depending on their origin (Besbes et al. 2011).

Although wood remains the main source of MFC, diverse non-wood sources (such as bamboo) are also being used (Lavoine et al. 2012). Bamboo is widely found in tropical and subtropical regions and is commonly used to manufacture flooring and furniture (Gao et al. 2010). China is the largest producer and consumer of bamboo in the world, but due to the special characteristics of bamboo culms and the limited processing and technological capacity of most manufacturers, over 60 % of the processed bamboo becomes residue, such as bamboo branches, nodes, epidermis and wax (Xie et al. 2014). Today, these bamboo processing residues are either burned or used for bio-products by liquefaction (a costly process), while their use as a viable source of MFC has not been given much attention (Xie et al. 2015). It should be noted that processed bamboo residues are rich in cellulose, which justifies the rationale to produce MFC (Wang et al. 2015). In this study, the use of bamboo parenchyma cells is proposed to obtain MFC by screening processed bamboo residues.

MFC can be produced by several methods of mechanical fibrillation, such as high-pressure homogenization, cryocrushing, grinding and ultrasonication (Alila et al. 2013). Among these methods, ultrasonication is particularly attractive because it can be easily carried out without significantly deteriorating fiber properties (Chen et al. 2013; Cozzolino et al. 2014). Ultrasonication can produce very strong mechanical oscillations due to acoustic cavitation, to effectively break interfibrillar hydrogen bonds in cellulose and gradually disintegrating it into fibrils (Lu et al. 2013). Therefore, ultrasonication was chosen as the method to prepare MFC in this study.

Due to its exceptional mechanical properties, flexibility and high aspect ratio, MFC has also been used successfully to produce nanocomposite films to improve their mechanical, barrier, thermal and optical properties (Syverud and Stenius 2009; Jonoobi et al. 2015). Although MFC has been widely investigated for its reinforcement capacity in nanocomposite films (Iwamoto et al. 2007; Nakagaito and Yano 2008; Siqueira et al. 2010), few studies have reported on the mechanical properties of neat MFC films (Kumar et al. 2014), which can be affected by the source of cellulose (Fukuzumi et al. 2009), MFC disintegration procedures (Qing et al. 2013), film preparation techniques (Syverud and Stenius 2009; Sehaqui et al. 2010) and drying conditions (Sim et al. 2015). Moreover, the effects of film thickness have not been considered in most studies. Therefore, this study also investigates the relationship between MFC film thickness and its mechanical properties, as well as the effect of moisture content of neat MFC film on its mechanical properties.

MATERIALS AND METHODS

Preparation of MFC

The processed residues of Moso bamboo (*Phyllostachys pubescens*) for flooring production were used as the source material in this study (Yiyang Taohuajiang Bamboo Ltd, Zhejiang, China). The majority of the residues was composed of large granules, mixed in with fibers. The residues were first ground into bamboo particles and passed through a 200-mesh (75 μm) sieve, and then stored for chemical purification.

The bamboo particles were then washed in hot water at around 90°C for 6 h to remove dust and impurities. During the chemical treatment stage, the bamboo particles were first treated with acidified sodium chlorite at 75°C for 1 h to extract lignin. This step was repeated until the samples turned white in color (Abe and Yano 2010). Then, the delignified samples were treated with 5 wt % potassium hydroxide at 90°C to remove hemicellulose, residual starch and pectin. Finally, the samples were filtered and rinsed with distilled water until pH neutral.

After chemical treatment, 0.5 wt % purified bamboo particles were treated with high-frequency ultrasound waves for 50 min (Fig. 1) with an ultrasonic generator (JY99-IIND, Ningbo Science Biotechnology Co., Ltd., China) at a frequency of 19.5-20.5 kHz under 540 W in an ice-water bath.

Preparation of MFC films

After ultrasonication, MFC gel was obtained. The MFC gel was diluted and homogenized for 15 min using high-shear mixing (Ultra-turrax, IKA, T18), followed by vacuum filtration on the top of a 0.22 μm filter membrane until a wet circular film was formed. Then, the samples were air-dried at room temperature. The amount of sample used varied for different MFC film thickness, of approximately 10, 25, 80, 100 and 200 μm. The thickness of MFC films was measured using SEM micrographs at the cross-section.

To test the effect of moisture content on the mechanical properties of MFC film, three groups of 80 μm thick MFC films with target moisture contents of 3, 10 and 60 %, were prepared by immersing them in pure water until the respective target moisture contents were reached. Afterwards, the water on the surface of the films was wiped off with filter paper, and all samples were kept under the same conditions until further testing.

Shrinkage of MFC films from surface drying

The shrinkage of MFC films from surface drying was determined by surface area shrinkage (Eq.):

$$Shrinkage = \frac{S_b - S_a}{S_a} \times 100 \qquad (\%)$$

where: S_b and S_a - the surface area before and after drying expressed as mm^2.

Mechanical property tests of MFC films

The mechanical properties of MFC films were tested on a high-resolution tensile testing machine with a max load of 50 N (Instron 5848, Norwood, MA, USA). Samples were conditioned at an ambient environment of 25˚C, 12 % RH for 24 h prior to testing. MFC films were then cut into small rectangular specimens with dimensions of 5 (W) × 30 mm (L). At least five samples were tested in each group. A constant strain rate of 1 mm/min was used and the pretension was 10 mN during testing. All mechanical tests were carried out under an environment of 25˚C and 15-35 % RH.

Morphological observations of MFC films

The cross-sections and surfaces of MFC films were observed using a Field Emission Gun Scanning Electron Microscope (FE-SEM, XL30, FEI, USA). All samples were coated using a Leica EM SCD 005 coater for 90 sec at 30 mA. SEM images were taken at an accelerating voltage of 7 kV at various magnifications.

RESULTS AND DISCUSSION

Morphology and surface shrinkage of MFC films at different thicknesses

Fig. 1A shows the microstructure of the untreated bamboo processing residue, mainly composed of parenchyma cells (thick arrow) and a minority of thin bamboo fibers (thin arrow). Fig. 1B and D show SEM images of the samples after chemical purification and 50 min of ultrasonic treatment (Fig. 1C). These images indicate that the bamboo parenchyma cells were successfully disintegrated into MFCs during the ultrasonication process.

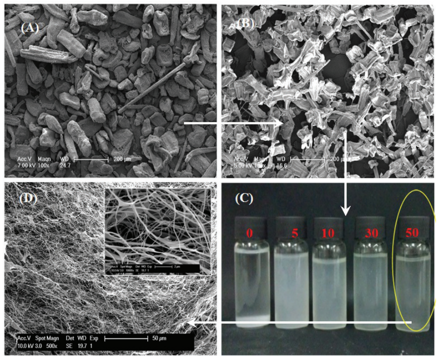

Fig. 1: SEM images of bamboo processing residues composed of bamboo fibers (thin arrow) and parenchymal cells (thick arrow) A), bamboo residues after chemical purification B), samples after different ultrasonic time (marked with the samples in min) C) and SEM images of MFC after 50 min of ultrasonication treatment D).

During the filtration and air-drying process, MFCs move closer together as water evaporates, resulting in strong intermolecular hydrogen bonds and forming solid fibril networks (Peng et al. 2012). The morphologies of the resulting MFC films of different thickness are shown in Fig. 2. The average thickness of the 5 sample groups were: 7.4, 24.7, 80.0, 100.0 and 205.5 µm. The thickness of the film is mainly controlled by adjusting the volume of the MFC gel filtered. As the thickness increased from 7.4 to 205.5 µm, the surface of the dried MFC films became noticeably rougher. This is explained by the agglomeration of MFCs into MFC bundles during filtration, given that fibril clogging occurs during filtration, particularly in thicker films. A higher amount of MFC agglomeration results in a rougher surface on the film (Baez et al. 2014). As shown in Fig. 2, all the cross-sections of the MFC films indicate a sandwich-like layered structure. This layering has been reported previously by several authors (Henriksson et al. 2008; Aulin et al. 2009; Stevanic et al. 2012). Irregularly shaped pores (shown by arrows) are observed to be unevenly spread over the cross-section of MFC films. A porous structure has also been reported as an important indicator of the mechanical properties of MFC films, as films with less pores demonstrate greater strength, due to an increase in hydrogen bonds (González et al. 2014).

The effect of film thickness on surface shrinkage is shown in Fig. 3. As film thickness increased from 7.4 to 205.5 µm, surface shrinkage also increased linearly from 10 to 80 %. The shrinkage of the MFC film is related to the degree of fibril bonding induced by drying, as Sim et al. (2015) reported that MFC films shrink more than 80 % when dried at room temperature. Therefore, it is postulated that hydrogen bonds in the MFC gel increased with longer treatment time.

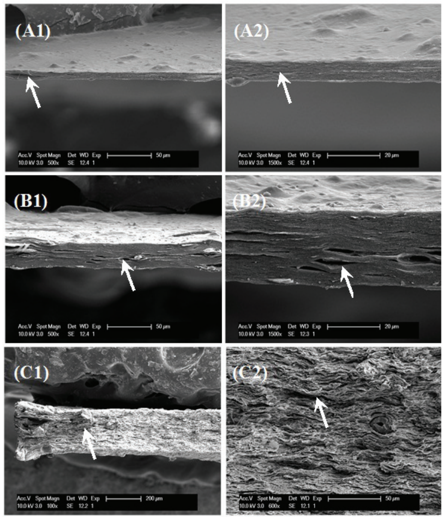

Fig. 2: SEM images of the fracture surface of MFC films at different thickness: 7.4 A1-2), 24.7 B1-2) and 205.5 µm C1-2).

As filtration continued, water transport also became hindered by fibril clogging, and therefore the slower removal of water may have driven the MFCs to come together and agglomerate (Peng et al. 2012).

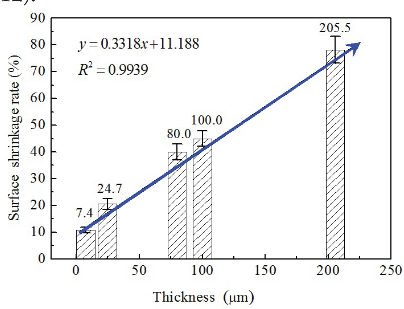

Fig. 3: Surface shrinkage plotted as a function of film thickness, and the numbers nest to each bar represent film thickness in µm.

Mechanical properties of MFC films at different thickness

The typical stress-strain curves of MFC films at different thickness are presented in Fig. 4A. MFC films obtained from the same source material but with different thickness showed different shapes of stress-strain curves. Thinner MFC films (thickness of less than 80 µm) only showed elastic deformation after around 0.7-1.3 % strain. As thickness increased, the plastic deformation region started to appear, i.e., the failure of the 205.5 µm film occurred after approximately 4 % strain. The elongation of the film at break also increased obviously with increasing film thickness (Fig. 4B).

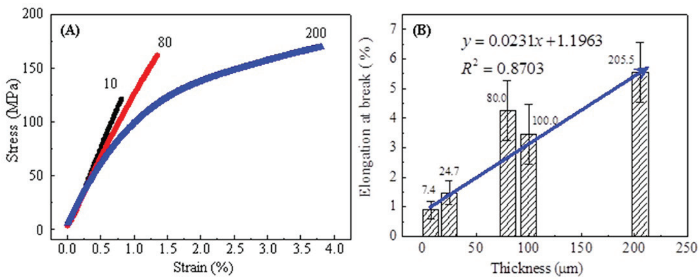

Fig. 4: Typical tensile stress-strain curves and elongation at break of MFC films, where the numbers indicate the film thickness A); Elongation at break plotted as a function of film thickness B).

As the thickness of the MCF film increases, so does the strength of the film (Fig. 5B). However, no significant change was observed on the Young's modulus as thickness increased (Fig. 5A). It is known that the Young' modulus is mainly influenced by factors such as fibril orientation, the bonding degree of fibrils and the Young's modulus of individual fibrils (Kulachenko et al. 2012; González et al. 2014). The Young's modulus was not affected by the film thickness because all MFC film samples were prepared from the same source using the same treatment process, and the films were composed of fibrils that were randomly oriented despite their varied thicknesses. In the present work, the average Young's modulus of MFC films was approximately 10.8 GPa, which falls within the Young's modulus range (5-18 GPa) reported by other authors (Fukuzumi et al. 2009; Qing et al. 2013; Baez et al. 2014). In contrast, tensile stress increased significantly as thickness increased, and thinner films demonstrated less strength due to its brittle failure behavior, whereas the greater strength of thicker films are attributed to a higher elongation at break as shown in Fig. 4B.

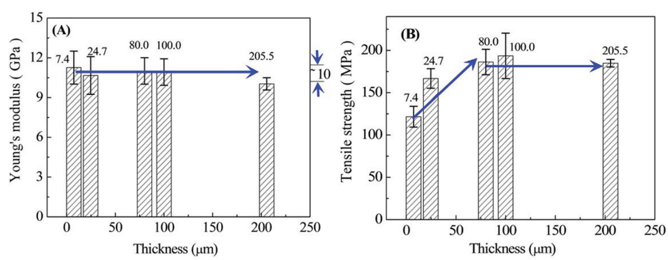

Fig. 5: Tensile properties of MFC films plotted as a function of film thickness.

Mechanical properties of MFC films with different moisture contents

The impact of moisture content on the mechanical properties of MFC films was also studied, as the final properties of MFC films are often affected by their poor resistance to moisture (Aulin et al. 2009). The stress-strain curves of MFC films with varying levels of moisture content (Fig. 6) showed that the presence of moisture impaired the tensile properties of the film. MFC films with a lower moisture content appeared much stiffer and brittler compared to those with higher moisture content. As moisture content increases, the Young's modulus and tensile strength decreased from 12- 2 GPa and 180- 90 MPa at 3 and 60 % MC respectively; on the contrary, a significant increase of elongation at break from 4.2 to 17.5 % was observed with increasing moisture content (Fig. 7). This is due to the fact that MFC films are a hydrogen-bond dominant

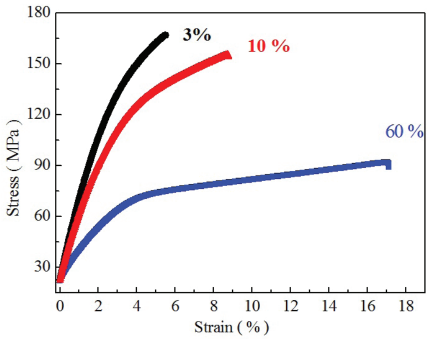

Fig. 6: Typical tensile stress-strain curves of MFC films with moisture content levels of 3, 10 and 60 %.

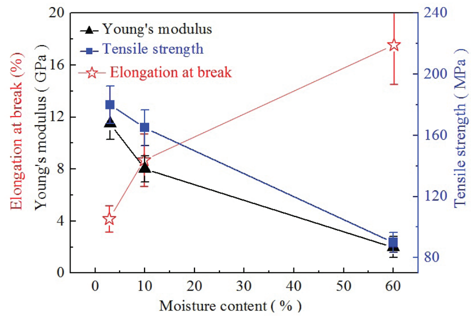

Fig. 7: Tensile properties of MFC films plotted as a function of moisture content A); Elongation at break of MFC films plotted as a function of moisture content B).

solid and its mechanical properties primarily depend on the characteristics of the hydrogen bond network, where water molecules can easily disrupt. Therefore, the increasing presence of moisture results in a weaker and softer film (Zauscher et al. 1996; Peresin et al. 2010).

CONCLUSIONS

In this study, MFC films with varying thickness between 7.4 – 205.5 μm were successfully prepared from MFC gels by vacuum filtration and air drying. The effects of film thickness and moisture content on the mechanical properties of MFC films were then investigated. This study found that, as the thickness of MFC film increased, the tensile stress and elongation at break also increased significantly, while little change was observed for the Young's modulus. It was also found that the tensile properties of MFC films were significantly influenced by its moisture content. As moisture content increased, the Young's modulus and tensile stress decreased significantly but the elongation at break increased. This behavior is most likely attributed to the role of water in weakening the hydrogen bonds between MFCs.

ACKNOWLEDGMENT

The authors gratefully acknowledge financial support from the National Science Foundation of China (31400519) and the State Forestry Administration “948” project (2015-4-48).

REFERENCES

1. Abe, K., Yano, H., 2010: Comparison of the characteristics of cellulose microfibril aggregates isolated from fiber and parenchyma cells of Moso bamboo (*Phyllostachys pubescens*). Cellulose 17(2): 271-277.

2. Alila, S., Besbes, I., Vilar, M.R., Mutjé, P., Boufi, S., 2013: Non-woody plants as raw materials for production of microfibrillated cellulose (MFC): A comparative study. Industrial Crops and Products 41(1): 250-259.
3. Aulin, C., Ahola, S., Josefsson, P., Nishino, T., Hirose, Y., Österberg, M., Wågberg, L., 2009: Nanoscale cellulose films with different crystallinities and mesostructures. Their surface properties and interaction with water. Langmuir 25(13): 7675-7685.
4. Baez, C., Considine, J., Rowlands, R., 2014: Influence of drying restraint on physical and mechanical properties of nanofibrillated cellulose films. Cellulose 21(1): 347-356.
5. Besbes, I., Vilar, M.R., Boufi, S., 2011: Nanofibrillated cellulose from alfa, eucalyptus and pine fibres: Preparation, characteristics and reinforcing potential. Carbohydrate polymers 86(3): 1198-1206.
6. Boufi, S., Gandini, A., 2015: Triticale crop residue: A cheap material for high performance nanofibrillated cellulose. RSC Advances 5(5): 3141-3151.
7. Chen, P., Yu, H., Liu, Y., Chen, W., Wang, X., Ouyang, M., 2013: Concentration effects on the isolation and dynamic rheological behavior of cellulose nanofibers via ultrasonic processing. Cellulose 20(1): 149-157.
8. Cozzolino, C.A., Cerri, G., Brundu, A., Farris, S., 2014: Microfibrillated cellulose (MFC): Pullulan bionanocomposite films. Cellulose 21(6): 4323-4335.
9. Fukuzumi, H., Saito, T., Wata, T., Kumamoto, Y., Isogai, A., 2009: Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation. Biomacromolecules 10(1): 162-165.
10. Gao, L.L., Liu, Y.H., Lei, H., Peng, H., Ruan, R., 2010: Preparation of semirigid polyurethane foam with liquefied bamboo residues. Journal of applied polymer science 116(3): 1694-1699.
11. González, I., Alcalà, M., Chinga-Carrasco, G., Vilaseca, F., Boufi, S., Mutjé, P., 2014: From paper to nanopaper: Evolution of mechanical and physical properties. Cellulose 21(4): 2599-2609.
12. Henriksson, M., Berglund, L.A., Isaksson, P., Lindström, T., Nishino, T., 2008: Cellulose nanopaper structures of high toughness. Biomacromolecules 9(6): 1579-1585.
13. Iwamoto, S., Nakagaito, A.N., Yano, H., 2007: Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites. Appl. Phys. A-Mater. Sci. Process 89(2): 461-466.
14. Jonoobi, M., Oladi, R., Davoudpour, Y., Oksman, K., Dufresne, A., Hamzeh, Y., Davoodi, R., 2015: Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: A review. Cellulose 22: 35-969.
15. Kulachenko, A., Denoyelle, T., Galland, S., Lindström, S.B., 2012: Elastic properties of cellulose nanopaper. Cellulose 19(3): 793-807.
16. Kumar, V., Bollström, R., Yang, A., Chen, Q., Chen, G., Salminen, P., Toivakka, M., 2014: Comparison of nano-and microfibrillated cellulose films. Cellulose 21(5): 3443-3456.
17. Lavoine, N., Desloges, I., Dufresne, A., Bras, J., 2012: Microfibrillated cellulose. Its barrier properties and applications in cellulosic materials: A review. Carbohydrate polymers 90(2): 735-764.
18. Lu, Y., Sun, Q., She, X., Xia, Y., Liu, Y., Li, J., Yang, D., 2013: Fabrication and characterisation of α-chitin nanofibers and highly transparent chitin films by pulsed ultrasonication. Carbohydrate polymers 98(2): 1497-1504.

19. Nakagaito, A.N., Yano, H., 2008: The effect of fiber content on the mechanical and thermal expansion properties of biocomposites based on microfibrillated cellulose. Cellulose 15(4): 555-559.
20. Peng, Y., Gardner, D.J., Han, Y.D., 2012: Drying cellulose nanofibrils: In search of a suitable method. Cellulose 19(1): 91-102.
21. Peresin, M.S., Habibi, Y., Vesterinen, A.H., Rojas, O.J., Pawlak, J.J., Seppälä, J.V., 2010: Effect of moisture on electrospun nanofiber composites of poly (vinyl alcohol) and cellulose nanocrystals. Biomacromolecules 11(9): 2471-2477.
22. Qing, Y., Sabo, R., Zhu, J.Y., Agarwal, U., Cai, Z., Wu, Y., 2013: A comparative study of cellulose nanofibrils disintegrated via multiple processing approaches. Carbohydrate polymers 97(1): 226-234.
23. Sehaqui, H., Liu, A., Zhou, Q., Berglund, L.A., 2010: Fast preparation procedure for large, flat cellulose and cellulose/inorganic nanopaper structures. Biomacromolecules 11(9): 2195-2198.
24. Sim, K., Ryu, J., Youn, H.J., 2015: Structural characteristics of nanofibrillated cellulose mats: Effect of preparation conditions. Fibers and Polymers 16(2): 294-301.
25. Siqueira, G., Bras, J., Dufresne, A., 2010: Cellulosic bionanocomposites: A review of preparation, properties and applications. Polymers 2(4): 728-765.
26. Siró, I., Plackett, D., 2010: Microfibrillated cellulose and new nanocomposite materials: A review. Cellulose 17(3): 459-494.
27. Stevanic, J.S., Bergström, E.M., Gatenholm, P., Berglund, L., Salmén, L.A., 2012: Rabinoxylan/nanofibrillated cellulose composite films. Journal of Materials Science 47(18): 6724-6732.
28. Syverud, K., Stenius, P., 2009: Strength and barrier properties of MFC films. Cellulose 16(1): 75-85.
29. Wang, H., Zhang, X., Jiang, Z., Li, W., Yu, Y., 2015: A comparison study on the preparation of nanocellulose fibrils from fibers and parenchymal cells in bamboo (*Phyllostachys pubescens*). Industrial Crops and Products 71: 80-88.
30. Xie, J., Hse, C. Y., Shupe, T. F., Qi, J., Pan, H., 2014: Liquefaction behaviors of bamboo residues in a glycerol-based solvent using microwave energy. Journal of Applied Polymer Science 131(9): 40207, doi:10.1002/app.40207.
31. Xie, J., Qi, J., Hse, C., Shupe, T.F., 2015: Optimization for microwave-assisted direct liquefaction of bamboo residue in glycerol/methanol mixtures. Journal of Forestry Research 26(1): 261-265.
32. Zauscher, S., Caulfield, D.F., Nissan, A.H., 1996: The influence of water on the elastic modulus of paper. Tappi Journal 79(12): 178-182.

Xuexia Zhang, Yan Yu, Zehui Jiang, Hankun Wang*
International Centre for Bamboo and Rattan
Department of Biomaterials
Beijing
P.R. China
Phone: 86-010-84789909
*Corresponding author: wanghankun@icbr.ac.cn

Sfa and Beijing Co-Built Key Laboratory for Bamboo
and Rattan Science and Technology
Beijing
P.R. China