An Efficient Dispersive Agent — KCl for Ultrasonic Preparation of Microfibrillated Cellulose (MFC)

Xuexia Zhang, Yan Yu, Wanju Li, Dan Ren, and Hankun Wang *

The suitability of saturated salt solutions as a dispersive agent for preparing microfibrillated cellulose (MFC) from bamboo processing residue through ultrasonication was evaluated. The effect of pure water and KCl solution on the rheological behavior and morphologies of prepared MFC were compared. The results show that the viscosity of MFC suspension dispersed in KCl solution decreases by several orders of magnitude compared to the water counterpart. SEM images demonstrate that MFCs with comparable quality can be prepared using either pure water or KCl solution as a dispersive agent. A high concentration of bamboo processing residue (~2 wt.%) dispersed in salt solutions was found to possess comparable viscosity with a low concentration of MFC suspension (~0.5 wt.%) dispersed in water. This indicates that the application of salt solutions as dispersive agents in ultrasonication has great potential to improve the productivity of MFC prepared from plant materials.

Key words: Microfibrillated cellulose; Ultrasonic treatment; Salt solution; Viscosity

*Contact information: Department of Biomaterials, International Center for Bamboo and Rattan, State Forestry Administration of China No.8 Futong Dong Dajie, Wangjing Area, Chaoyang District, Beijing 100102 China; *Corresponding author: wanghankun@icbr.ac.cn*

INTRODUCTION

Microfibrillated cellulose (MFC) is the aggregate of elementary cellulose fibrils extracted from the cell walls of plant materials, showing promising potential in many industrial fields (Eichhorn *et al.* 2010; Deepa *et al.* 2011; Jonoobi *et al.* 2012; Missoum *et al.* 2013). Ultrasonication is a simple and efficient method to extract MFC from plant or non-plant materials (Zhao *et al.* 2007; Wang and Cheng 2009; Tischer *et al.* 2010; Chen *et al.* 2011a,b,c). During an ultrasonic process, cellulose molecular chains absorb ultrasonic energy through a process called cavitation, which can produce a violent shock to break the relatively weak hydrogen bonding between cellulose fibrils and release them from plant cell walls (Suslick 1990). Nevertheless, cavitation can occur only in a limited range around an ultrasonic probe. To ensure that all the plant materials have a chance to get into the working distance of the ultrasonic probe, the initial concentration of plant materials in a dispersive medium should be very low to ensure acceptable mobility during the whole ultrasonication process. Iotti *et al.* (2011) found that higher concentrations of MFC resulted in increased viscosities; this was attributed to the more numerous fibrils facilitating the creation of a network and structure, by the creation of bonds between fibrils. Chen *et al.* (2013) found that a concentration higher than 1.2 wt.% would adversely influence the isolation of cellulose fibrils from cell walls by ultrasonication. Therefore, a low initial concentration of plant materials (< 1.0 wt.%) is normally required

for ultrasonication in pure water (Chen *et al.* 2011a,b,c; Lu *et al.* 2013; Xiao *et al.* 2015). This low concentration is obviously unattractive in terms of industrial production.

One of the approaches to overcome this limitation is to improve the mobility of MFC suspensions during the ultrasonic treatment process. The mobility of a MFC suspension is strongly related to the structure of MFC, which is influenced by factors such as temperature, pH, and ionic concentration (Agoda-Tandjawa *et al.* 2010). Therefore, the present study aims to explore the feasibility of using saturated salt solution as a dispersive agent to prepare MFC from bamboo processing residues by ultrasonic treatment. Bamboo processing residues normally contain a high ratio of parenchymal cells (nearly 80% by weight), which can be easily fibrillated by ultrasonic treatment (Wang *et al.* 2015). The morphologies and flow properties of the resulted MFC dispersed in pure water and KCl solution were analyzed and compared. It is thought that the substitution of pure water with salt solution as the dispersive agent could significantly increase the efficiency of MFC preparation because a higher concentration of bamboo starting material can be adopted.

EXPERIMENTAL

Raw Materials

Moso bamboo (*Phyllostachys pubescens*) processing residues were kindly provided by a bamboo flooring plant in Yiyang City, Hunan Province, China. These residues were air-dried and further ground, followed by passing through a 200-mesh (75 μm) sieve. The sieved powders were oven-dried and stored at room temperature. A photograph of bamboo processing residue and its corresponding SEM image are shown in Fig. 1, which confirmed that the sieved bamboo particles were mainly composed of parenchymal cells.

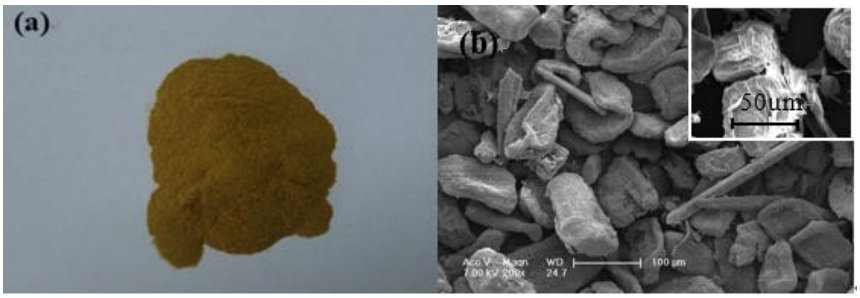

Fig. 1. (a) Bamboo processing residue and (b) corresponding SEM image

Potassium chloride (KCl) (Sinopharm Chemical, China) and other chemicals were all of laboratory grade and used without further purification.

Chemical Purification

To facilitate the fibrillation of parenchymal cells, bamboo residues should be purified first through a mild chemical pretreatment. Briefly, the sieved bamboo particles were washed in hot water at approximately 90 °C to remove possible dusts and organic impurities. They were then dewaxed in a Soxhlet apparatus with a 2:1 (v/v) mixture of phenethyl/alcohol for 6 h. Afterwards, lignin in the samples was removed using an

acidified sodium chlorite solution at 75 °C for 1 h. This process was repeated four times, until the solution became clear and transparent. The samples were then treated with 2 wt.% potassium hydroxide at 90 °C to remove hemicelluloses, residual starch, and pectin. Finally, the purified samples were washed thoroughly with pure water and kept in a water-swollen state to avoid the regeneration of strong hydrogen bonding between cellulose molecules during the drying process (Hult *et al.* 2001).

Ultrasonic Treatment

After chemical purification, the cellulose-rich materials were dispersed in pure water with a weight concentration of 0.5 wt.%. The same starting materials were also dispersed in saturated KCl solution with a weight concentration of either 0.5 wt.% or 2.0 wt.%. All samples were treated with an ultrasonic generator (JY99-IIND, Ningbo Science Biotechnology Co. Ltd., China) at 19.5 to 20.5 kHz under 540 W in an ice-water bath.

Viscosity Measurements of MFC Suspensions

MFC suspensions were removed at set time intervals for viscosity measurements during the ultrasonic treatment. Shear viscosity was measured using a rotary rheometer (Brookfield, LVDV-IIIU, USA) to evaluate the effect of different dispersive agents on the fluidity of MFC suspension. The testing temperature was 20 °C, and the torque (dynamic viscosity coefficient) was set at approximately 50% for all samples. A duplicate of each measurement was performed.

Scanning Electron Microscope (SEM)

MFC suspensions in salt solution were washed with pure water to remove excess ions and dispersed in water again. All samples were first put into a cylindrical mold, frozen in a liquid N_2 bath for 30 min, and then freeze-dried (Labconco, USA) for 48 h. The dried samples were mounted onto a SEM sample stage with carbon conductive tape and coated with a thin layer of platinum by an ion sputter coater (Leica EM SCD005, Germany). The morphologies of the MFC obtained were observed with a field-emission scanning electron microscope (FE-SEM, XL30, FEI, USA). Measurement of the cellulose fibril widths was conducted using an image analysis software (Image-Pro Plus 6.0).

RESULTS AND DISCUSSION

Viscosity Differences of MFC Suspensions

Figure 2a shows the viscosity differences of MFC suspensions dispersed in pure water and KCl solution as a function of ultrasonic treatment time. In the initial period of ultrasonication, both the suspensions showed low viscosity and tended to precipitate because of gravity. The shear viscosity then increased with ultrasonic treatment time, but at strikingly different values and rate. For the former, the shear viscosity started to rise sharply from 20 min and increased by several orders of magnitude at 30 min. The gel-like behavior at that point was due to an inherently entangled network structure formed by long fibrils and fibril aggregates (Pääkkö *et al.* 2007). In the case of the KCl dispersive agent, the shear viscosity of MFC suspension remained rather low, at only 135 cP even after 70 min of ultrasonication. Because the high viscosity of MFC suspension is primarily caused by the strongly entangled and disordered gel networks formed by

inherently connected cellulose fibrils, the reduction in the viscosity of the MFC suspension with KCl solution as a dispersive agent could be attributed to the weakening or even full breakage of this network by breaking the balance between repulsive and attractive forces between the fibrils with the salt addition (Saarikoski *et al.* 2012).

As shown in Fig. 2b, the flow abilities of MFC water dispersion and KCl solution dispersion varied markedly after 40 min of ultrasonication. The MFC suspension with KCl as the dispersive agent (b2) still showed a good flow ability, whereas the MFC water dispersion (b1) lost its flow ability and completely turned into a viscous mass. This phenomenon can be explained by the principle of electrostatic repulsion. When MFCs are dispersed in pure water, the slightly negative charge on their surface allows the fibrils to electrostatically repel each other, resulting in high stability and viscosity of the system (Karppinen *et al.* 2012). When KCl is added, the electrostatic repulsive forces between the isolated cellulose fibrils are screened by the presence of the ionic K^+, thus altering the fibril-fibril interactions; consequently, the stable cellulose fibrils network is broken and individual fibril elements start to move. The phenomenon described here is analogous to the shear thinning behavior of MFC suspensions, where MFC suspensions show a decrease in viscosity with increasing shear rate (Herrick *et al.* 1983; Taipale *et al.* 2010).

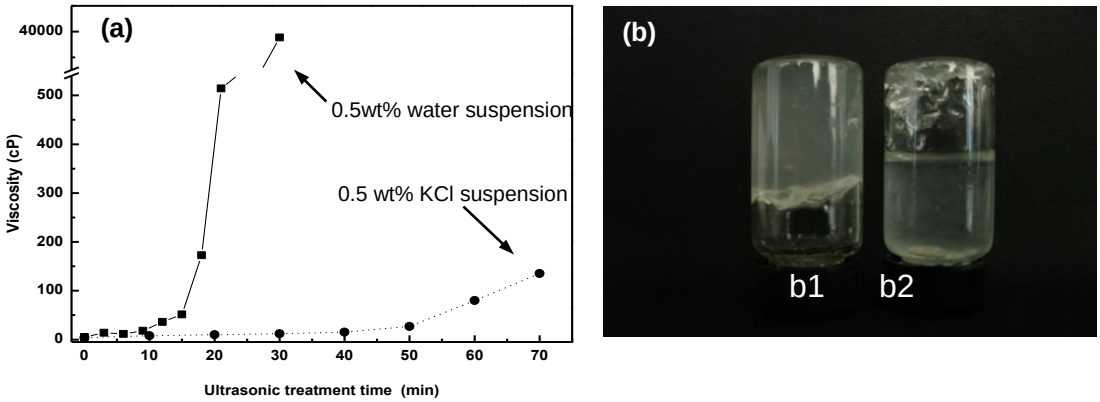

Fig. 2. Comparison of viscosity of 0.5 wt.% MFC suspensions in water and KCl solutions as a function of ultrasonic treatment time: (a) flow ability of 0.5 wt.% MFC suspension dispersed in (b1) pure water and (b2) KCl solution

Morphological Differences of MFC Preparations

Figure 3 compares the morphological differences of MFC prepared in water and KCl solution after ultrasonication for 50 min. This time period is considered optimal, based on earlier work (Wang 2013). A higher magnification (Fig. 3b and d) reveals a highly entangled network, which typically consists of cellulose fibrils with a wide size distribution from 10 to 100 nm, both for pure water and KCl solution. It can therefore be concluded that the salt solution did not negatively affect the release of the cellulose microfibrils from parenchymal cells. The morphologies of MFC from the lower portion of the KCl solution are presented in Fig. 3e; larger fibril aggregates and even some unfibrillated fiber fragments can be observed. This is a common feature of all mechanical methods, which normally produce MFC consisting of some microfibril aggregates or even a certain amount of unfibrillated fibers with a wide size distribution (Zimmermann *et al.* 2004; Cheng *et al.* 2009). These larger fibril aggregates could be further disintegrated through ultrasonication.

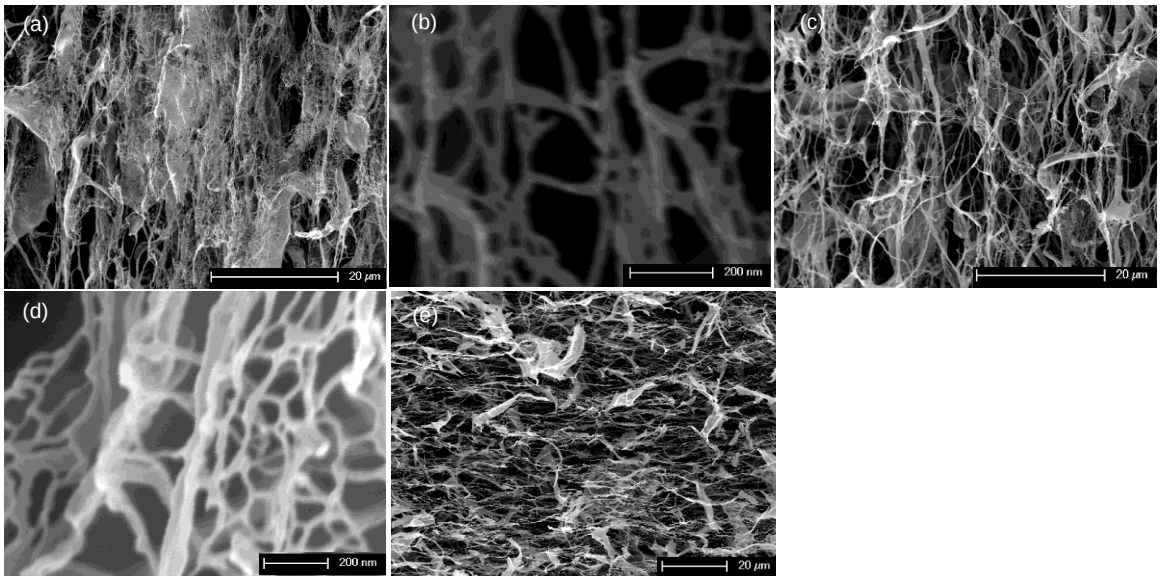

Fig. 3. SEM images of 0.5 wt.% MFC dispersed in (a, c) pure water and (b, d, and e) KCl solution

The Effect of Initial Concentration on the Dynamic Viscosity of MFC Suspensions

MFC dispersed in KCl solution exhibited a dramatically lower viscosity and good flow ability, thus providing the possibility of using higher initial concentrations of parenchymal cells for ultrasonication. The viscosity of MFC suspensions *versus* ultrasonic treatment time dispersed in KCl solutions with a concentration of 2.0 wt.% and in pure water with a concentration of 0.5 wt.% is compared in Fig. 4.

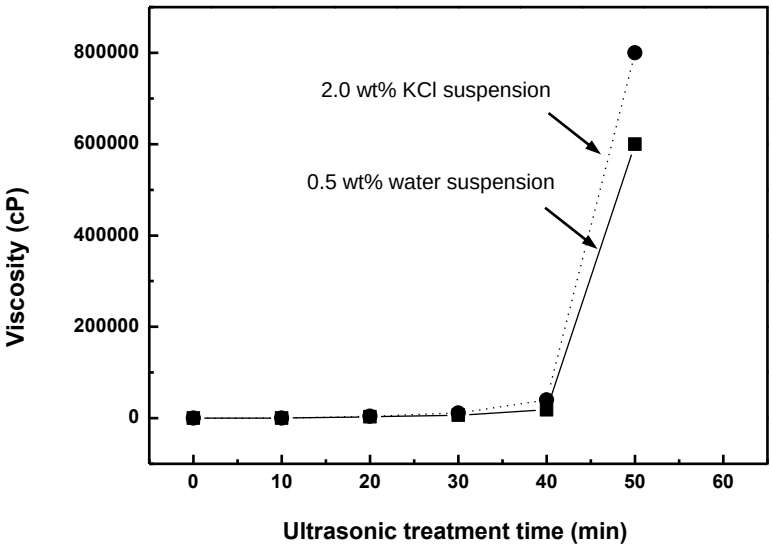

Fig. 4. Comparison of viscosity of MFC suspensions in KCl solution with a concentration of 2.0% and pure water with a concentration of 0.5 wt.% as a function of ultrasonic treatment time.

Fifty minutes of ultrasonication increased the viscosity of 2 wt.% MFC dispersed in KCl solution to approximately 800,000 cP, which is only a little higher than the viscosity value of around 600,000 cP of 0.5 wt.% MFC in pure water. Obviously, a higher initial concentration of starting materials means a higher productivity for MFC preparation. In the present case, it can be roughly estimated that the preparation efficiency of MFC with KCl solution as an ultrasonic medium was increased by four times compared with that using pure water as the dispersive medium.

CONCLUSIONS

1. The viscosity of MFC suspensions can be greatly reduced with a KCl solution as a dispersive agent. This improvement in fluidity will increase the working efficiency of ultrasonication, as plant materials have more chances to encounter the ultrasonic probe.
2. Morphological observation reveals a comparable quality of MFC whether they are dispersed in pure water or KCl solution. A high initial concentration of parenchymal cells (~2 wt.%) with KCl solution as the dispersive agent produced MFC suspensions with shear viscosity comparable with the low concentration suspension (~0.5 wt.%) dispersed in pure water. This indicates the application of salt solutions as dispersive agents in ultrasonication has the potential to improve the productivity of MFC prepared from plant materials.

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