THE INFLUENCE OF ULTRASONIC TREATMENT ON THE BLEACHING OF CMP REVEALED BY SURFACE AND CHEMICAL STRUCTURAL ANALYSES

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Effects of ultrasonic pretreatment on the bleaching of chemimechanical pulp (CMP) fiber of triploid Chinese white Poplar were investigated. Before single-stage hydrogen peroxide bleaching, CMP was sonicated at 1.5% pulp consistency and 50°C for 20min with 90% amplitude and 20s pulse; these conditions showed the most favorable effect of a 3.5% ISO increase of brightness, reaching a final value of 80.2% ISO. The benefit may be because the ultrasound can accelerate heterogeneous reactions, which arise from the impingement of microjets and shockwaves on the solid surface, which are then capable of inducing striking changes in surface morphology, composition, and reactivity. To prove the theory, the surface structure and surface morphology were investigated by SEM and AFM, and the crystalline structure and characteristics of the cellulose in terms of XRD and FT-IR were also evaluated.

Keywords: CMP; Ultrasonic treatment; SEM; AFM; XRD; FTIR

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INTRODUCTION

Due to the shortage of fiber and a growing global demand for some paper grades, such as super-calendered and light-weight coated papers, mechanical pulps may become suitable substitutes for expensive bleached chemical pulps (Li et al. 1996). However, besides the high electrical energy consumption and relatively poor strength properties, figuring out how to produce higher brightness at a reasonable cost and how to reduce color reversion has been the greatest challenge to promote the markets for mechanical pulps (Hoglund 1997).

Lignin-preserving bleaching processes have been commonly used to bleach chemimechanical pulp (CMP), by use of sodium dithionite in reductive bleaching, while hydrogen peroxide is used for oxidative bleaching. Hydrogen peroxide is favored over sodium dithionite due to its higher efficiency in improving the pulp brightness. When a single hydrogen peroxide stage is practiced, an increase of 10 to 15 brightness points is commonly obtained (Li et al. 1996; Zeinaly et al. 2009). However, the bleaching efficiency is still lower than desired. It is reported that only 40% of the added hydrogen peroxide is consumed in the reaction with lignin and less in the decolorizing reaction with chromophoric groups (Dou 1984). Therefore, this has led to increasing interest in improving the efficiency of hydrogen peroxide bleaching (Shen 2008; Li 2008).

Recently Treimanis (2009) suggested that the materials of pulp fibers' surface, which contain comparatively high amounts of lignin, hemicelluloses, and their products

of conversion, requires higher specific consumption of bleaching chemicals. The term "ultrasound" is used to denote sound waves having a frequency of between 20 kHz and 10 MHz, which is above the limits of human audibility (16 Hz to 16 kHz). It is well known that ultrasound can be used to clean the surfaces of objects, and many processes occurring in liquid can be accelerated by means of ultrasound (Suslick 1989; Shi 2006). Powerful ultrasound, having frequencies between 20 kHz and 100 kHz, has been widely used in waste water treatment, the food industry, chemical applications, and manufacturing industries (Mason and Lorimer 1988; Yu 2005). Nowadays, a renaissance in sonochemistry is taking place everywhere, and the study of the application of ultrasound in the pulp and paper making industry is also a rapidly growing research area (Iwasaki 1962; Huang 1995; Tang 2001; Gonze 2003; Mistik 2005; Greenwood 2006; Csóka 2008; Xiao 2008; Zhao 2009; Parker 2009; Shaw 2009). The favorable effects of ultrasound in this industry fall into three areas: pulp refinery, waste paper deinking, and flotation, and surface modification of fibers. The studies suggest that the primary mechanism for sonochemical effects arises from acoustic cavitation (the formation, growth, and collapse of bubbles). During cavitation, bubble collapse produces intense local heating (temperatures of >>5000±K), high pressures of about 50MPa, and very short lifetimes. For this reason, ultrasonic cavitation in liquid-solid systems tends to produce (a) surface damage at liquid-solid interfaces by shock waves and microjets, (b) the generation of high-velocity interparticle collisions in slurries, and (c) the fragmentation of friable solids to increase surface area (Suslick 1999). The goal of the present work is to study the chemical and physical consequences induced by high-intensity ultrasound on CMP pulp fiber.

EXPERIMENTAL

Materials

Triploid Chinese white poplar, the raw material, was received from Shan Dong province, and the seedling was provided by the laboratory of genetics and breeding of Beijing Forestry University. The chemical composition (% dry weight, w/w) was as follows: α-cellulose 41.71%, pentosan 13.05%, holocellulose 75.8%, acid-insoluble lignin 18.77%, and benzene-alcohol extractives 4.02%. All chemicals used in the chemical composition analysis were of analytical or reagent grade.

The CMP was consigned to China National Pulp and Paper Research Institute to be produced, according to the following process: chips→ screening→ steeping with water for two hour→ extrusion and grinding (once)→ streaming under atmospheric pressure (15 min)→ chemistry pretreatment (NaOH 3%(w/v), Na_2SO_3 4%(w/v), liquid ratio 1:4, 100^{o}C, 25min)→refining with Φ300 KRK refiner (Japan) (four-stage, with a refining gap of 1.0mm, 0.5mm, 0.15mm, and 0.06mm, respectively)→ screening→ condensing.

The brightness of the original pulp was 50.7% ISO, and the Canadian Standard Freeness (CSF) was 294 mL.

Ultrasonic Pretreatment

The ultrasonic pretreatment was carried out in a Sonics Vibra Cell (VC *750), which was fitted with a 1 cm diameter titanium horn. All sonication runs were at 20 kHz, under the power of 750W. Other conditions were as follows: the pulp consistency was 1.5%, the temperature was 50°C, the amplitude was 90%, and the pulse, the work time per minute of the reactor, was 20s. Precise digital control of time (up to 40 min) was changed by selecting the specific button.

To obtain the expected pulp consistency (1.5%), 10g (absolute dry) CMP was suspended in the beaker (1000 mL) with 667ml distilled water. After disintegration, the suspension was sonicated at the given conditions for 5-40 min. During sonication, no additional stirring was needed. And the temperature was controlled using a super-recycling water bath.

Bleaching Process

After the ultrasonic pretreatment, some samples of CMP were first chelated with 0.3% EDTA (w/v) at 10% pulp consistency and 70 °C for 30 min. And after being washed, they were bleached with alkaline peroxide by placing 10g (absolute dry) of the substrate, 5% H_2O_2 (w/v), 3%NaOH (w/v) in 90 mL of distilled water. The suspension was stirred gently at 80°C for two hours. For comparison, the control without ultrasound pretreatment was also chelated, washed and bleached with 5% H_2O_2 (w/v), 3%NaOH (w/v) at 10% pulp consistency and 80°C for two hours.

Observation with Scanning Electron Microscopy (SEM)

The fracture surfaces of original triploid Chinese white poplar CMP and ultrasonic pretreated samples were observed by scanning electron microscopy (SEM). Before observation, the samples were vacuum dried. After being put on the microscope stage, the specimens were gold coated with gold-palladium in a Hitachi E-1010 sputter coater (Tokyo, Japan). Then the observation was carried out under a Hitachi S-3400N SEM (Tokyo, Japan).

Atomic Force Microscopy (AFM) Measurement

Variations in surface topography and surface roughness of ultrasonic pretreated samples were evaluated with the use of an atomic force microscope (AFM). AFM measurements were performed with a Shimadzu SPM-9600 microscope (Kyoto, Japan). A 5 μm scan area was used as a total area for the measurements, while the tapping mode was chosen for phase image and three-dimensional image. Since lignin and extractives are rather hydrophobic in nature, they show up as dark areas in the phase imaging, while carbohyrates, i.e. cellulose and hemicellulose, are hydrophilic, and they show up as bright features in the phase imaging. The phase lag is very sensitive to variations in material properties (Bastidas 2005). From the phase image, an evaluated surface will show dark or bright color to indicate the changes of the surface lignin content. And the three-dimensional image could reflect the whole topography of the material surface.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier Transform Infrared (FT-IR) spectra of the untreated and ultrasonic pretreated pulp were determined with a Nicolet 510 device (Thermo Nicolet Corporation, Madison, WI), using a KBr disc containing 1% finely ground samples. The spectra were recorded in the absorption mode in the range 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} and an accumulation of 32 scans.

X-ray Diffraction (XRD) Studies

The crystalline structure of both the ultrasonic pretreated and bleached samples was obtained using wide-angle X-ray diffraction (XRD) on a Shimadzu XRD-6000 diffractometer (Kyoto, Japan). The samples were put on an aluminum holder (25 mm in diameter) and observed under the continuous scanning mode. Cu was used as target, at a voltage of 40 kV and a current of 30 mA, to generate radiation (χ=1.54Å). The X-ray diffractograms were recorded from 5° to 50° 2θ by a goniometer at a scanning speed of 2 °/min. The crystallinity was calculated by the total diffracted area and the area under the crystalline peaks, which were determined by integration after correcting the data for absorption. The ratio of the crystallinity of samples to the standard formless material was taken as the relative crystallinity, represented as follows,

$$C_r = F_c / (F_a + F_c) \times 100\% \quad (1)$$

where C_r is the relative crystallinity, F_a and F_c are the area of crystal and noncrystalline regions, respectively (Sun 2008). All the calculations were carried out by means of the software in the XRD- 6000. Each sample was measured at least twice to obtain the minor error.

RESULTS AND DISCUSSION

It is known that CMP fibers' surface layers contain relatively high amounts of lignin and other heteroaromatic compounds. Recently, it has been stated that these materials require higher specific consumption of bleaching chemicals (Treimanis 2009). Since ultrasound can be used to clean the surfaces of objects and can impart a refining action and emulsification effect, it is quite possible that by ultrasonic pretreatment, the main part of fibers can be exposed, allowing for in-depth bleaching to take place more efficiently. Commonly, brightness is the most important index to define bleaching efficiency. The brightness of the control without ultrasound pretreatment was 76.8%ISO.

Remarkable improvements in bleaching performance were observed, although the ultrasonic pretreatment periods were different. When ultrasonic pretreatment was at 1.5% pulp consistency and 50°C for 20min with 90% amplitude and 20s pulse, the brightness was especially high and reached 80.2% ISO, which adds an increase of 3.5% ISO to the brightness of the control without ultrasound pretreatment. Besides the sonication period, all other conditions also have been optimized (Xing et al. 2010).

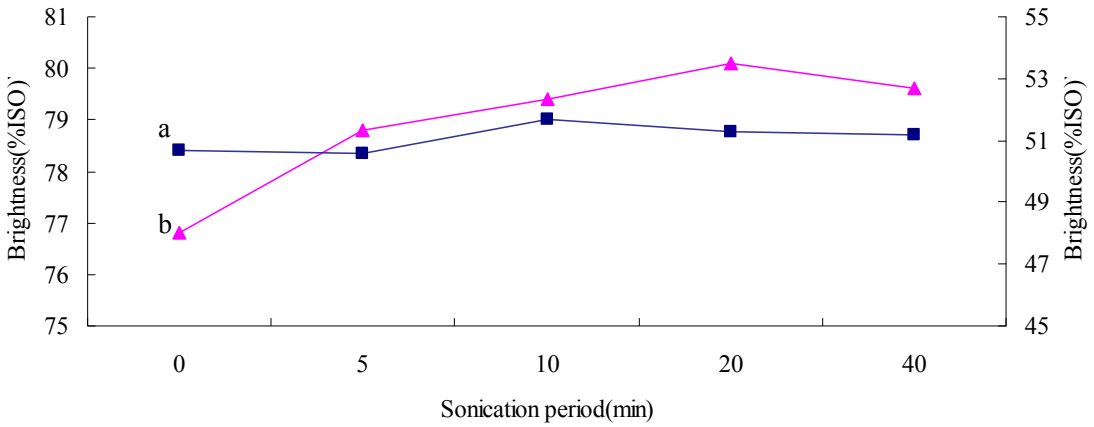


Fig. 1. Effect of ultrasonic pretreatment time on brightness.
(a=brightness of sonicated pulp; b=brightness of sonicated H_2O_2 bleached pulp).

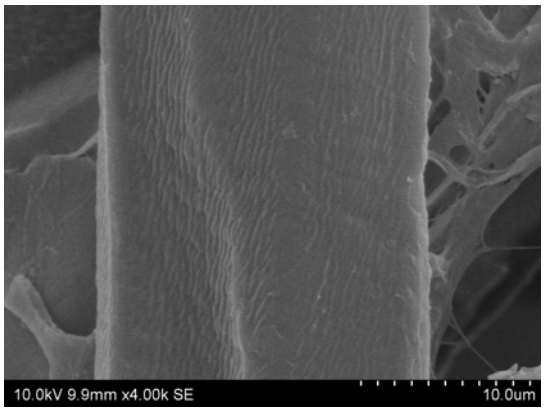
The observed highly favorable effect may be because the ultrasound plays a part similar to that of a phase transfer catalyst (PTC) and promotes the reaction between the pulp (solid-state) and bleaching liquor (liquid-state) (Xing et al. 2010). Also, it is reported (Suslick 1999) that ultrasound can accelerate heterogeneous reactions. The characteristic consequences of ultrasound are because of acoustic cavitation, which refers to the formation, growth, and subsequent collapse of cavities or "cavitation bubbles". When this occurs near to extended liquid-solid interfaces, the cavitation is very different; because of the proximity of a solid surface, bubble collapse becomes nonspherical, driving high-speed jets of liquid into the surface and creating shockwave damage to the surface. In addition, shockwaves created by cavity collapse in the liquid may also induce surface damage and the fragmentation of brittle materials. The impingement of microjets and shockwaves on the surface creates localized erosion, which is responsible for ultrasonic cleaning and many of the sonochemical effects on heterogeneous reactions.

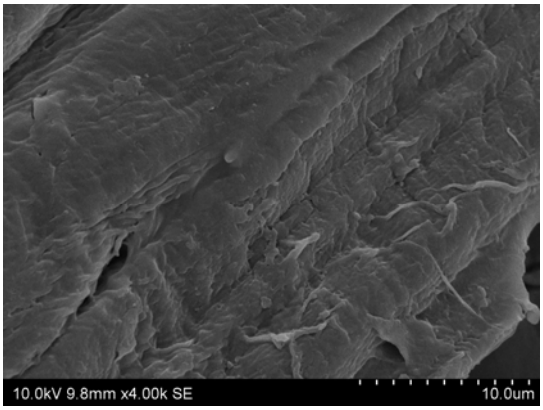
The quick heating and cooling during cavitation also provides a favorabe environment for many unexpected reactions. For example, it is stated that the heat from cavity implosion decomposes water (H_2O) into extremely reactive hydrogen atoms (H^+) and hydroxl radicals (OH^-), and during the quick cooling phase, hydrogen atoms and hydroxl radicals will recombine to form hydrogen peroxide (H_2O_2) and molecular hydrogen (H_2) (Suslick 1989). However, from Fig. 1, the brightness did not show an obvious increase if the unbleached pulp was only sonicated. So it is quite possible that the recombination of H_2O_2 is relatively minor, and since the lifetime of radicals is too short to survive until the addition of bleaching liquor, they perhaps help to degrade the lignin and other organic compounds. All of these theoretical possibilities prompt a question as to whether the interparticle collisions that result are capable of inducing striking changes in surface morphology, composition, and reactivity, and hence have an influence on bleaching.

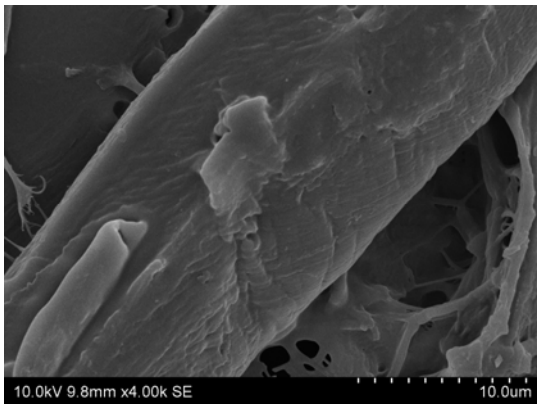
SEM Observation

The velocity of sound varies from medium to medium. At 0 ^oC, the velocity of sound in water is 1450m/s, while the sound velocity parallel to the grain of wood (poplar)

is 3993m/s (Liu 2004). So it can be estimated that the sound velocity in the pulp ranges from that of wood to that of water. If it is taken as 2000m/s, and the frequency of ultrasound is 20kHz, then it follows that the sound wavelength should be 10 cm, which is much longer than the size of a single cellulose molecule. So here the chemical effect of ultrasound does not matter at a molecular or atomic level directly (Tang 2000). Most researchers (Greenwood 2006; Csóka 2008; Xiao 2008; Zhao 2009) reported that it brought about variations only at morphological level, but greatly increased the accessibility and specific surface area of the material. The SEM micrographs of CMP that was either ultrasonically pretreated or untreated are shown in Figs. 2 through 5. The native material displays a regular, compact, and smooth surface structure (Fig. 2). After the ultrasonic pretreatment for different periods, significant differences were observed between the original material and even the sample that was pretreated for the shortest time. The surface of the latter (Fig. 3.) was no longer smooth and was covered with grooves and ridges. A few cracks caused by fierce impingement appeared, and the whole structure became loose.







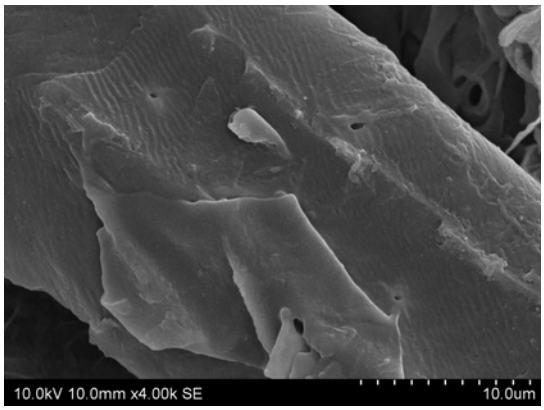


Fig. 2. SEM of control (left, top)
Fig. 3. SEM of Fiber with 5min ultrasonic treatment (right, top)
Fig. 4. SEM of Fiber with 20 min ultrasonic treatment (left, bottom)
Fig. 5. SEM of Fiber with 40 min ultrasonic treatment (right, bottom)

After longer ultrasonic preconditioning time, considerable damage to the fibers could be observed clearly (Fig. 4.). Both the cracks and grooves were more severe, and their shape was quite like the arrangement of S1 layer microfibrils. Besides, the surfaces were mildly layered, with the S2 layer exposed. If the sonication time was as high as 40 min, the phenomenon of layering was aggravated, and some damage to the fibers, such as flakes, holes, and shrinkage folds, are also apparent in the micrograph (Fig. 5). Also, the cracks were arranged in orderly fashion, most of them being parallel to the cell axis (angel of 10 to 30 degrees), which is consistent with the arrangement of S2 layer microfibril. So it could be concluded at least that the defibrillation resulting from ultrasonic pretreatment releases a large reactive area on the fiber surface, consequently improving the accessibility of bleaching agents and the bleaching efficiency.

AFM Measurement

Atomic force microscopy (AFM) can be used in monitoring the surface topography and surface roughness to reflect the surface pulp components of the original CMP and ultrasonically treated CMP. The phase lag is very sensitive to variations in material properties such as adhesion and viscoelasticity (Bastidas 2005). Hence, during the tapping mode scan, phase imaging goes beyond simple topographical mapping to characterize the components of composite materials.

To explore the fundamental changes in surface properties of the ultrasonic pretreated test sheets, samples were analyzed via AFM. It is known that lignin and extractives are rather hydrophobic in nature, showing up as dark areas in the phase imaging, while carbohydrates, i.e. cellulose and hemicellulose are hydrophilic, and show up as bright features in the phase imaging.

Figure 6 may be interpreted to consist mainly of non-carbohydrates, i.e. lignin and extractives, and only partly of hemicellulose. The isolated lignin has been found to be lamellar with irregular size and shape.

After ultrasonic treatment, it appears that in Fig. 7 most of middle lamella may have been degraded to granular form; some microfibrils are arranged arbitrarily, probably existing underneath the granular surface phase. This may be because the radicals that are produced by ultrasound help to degrade the lignin and the extractives. Another possible explanation is that some lignin and extractives are emulsified to accelerate the chemical reactions.

As shown in Fig. 8, with longer sonication period, the surface of the CMP appears to be clean, and most cellulose microfibrils are seen as having a high degree of orientation. And this picture is quite like the phase imaging of the S2 layer, as described by Gray's group (Pnag et al. 1998).

However, if the ultrasonic pretreatment process was too long, the lignin and extractives may have been deposited on the surface again, and the surface became more uneven (Fig. 9). In this way it was demonstrated that in ultrasonic irradiation, it was possible to partly get rid of the fibers' surface material-the fines and thus expose the main part of the fiber wall for a more efficient bleaching process.

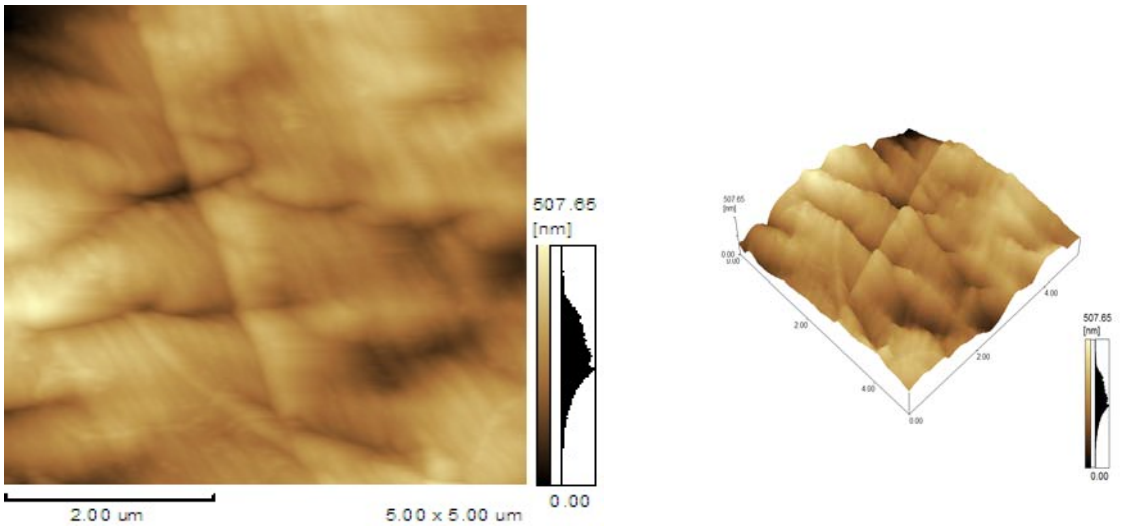


Fig. 6. AFM of Control

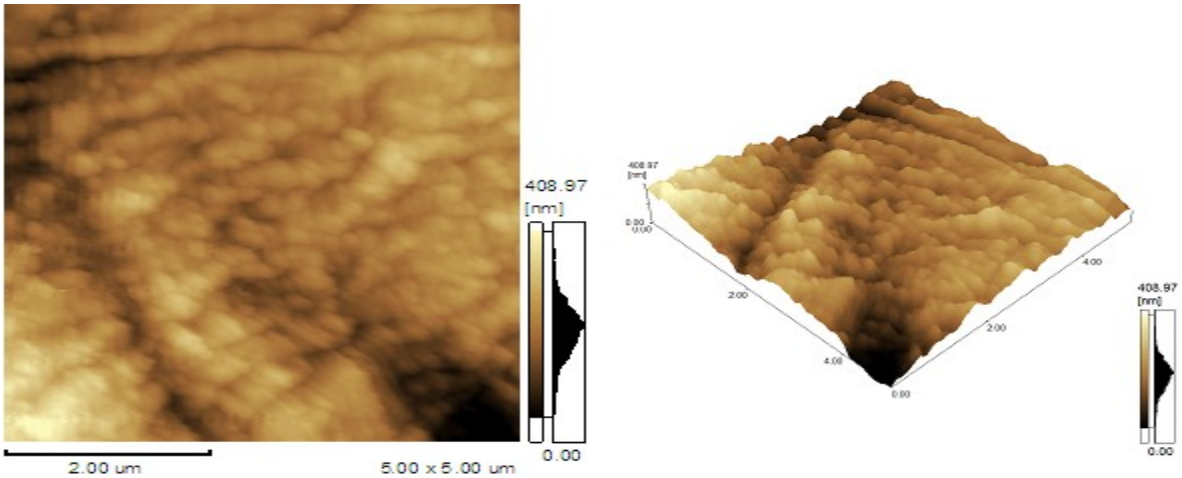


Fig. 7. AFM of fiber after 5min ultrasonic treatment

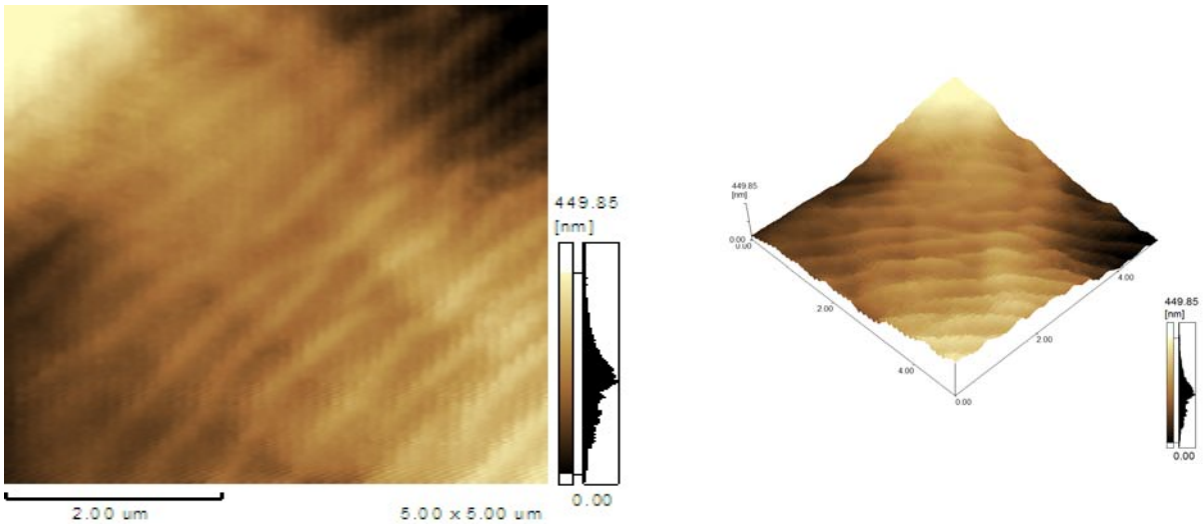


Fig. 8. AFM of fiber after 20 min ultrasonic treatment

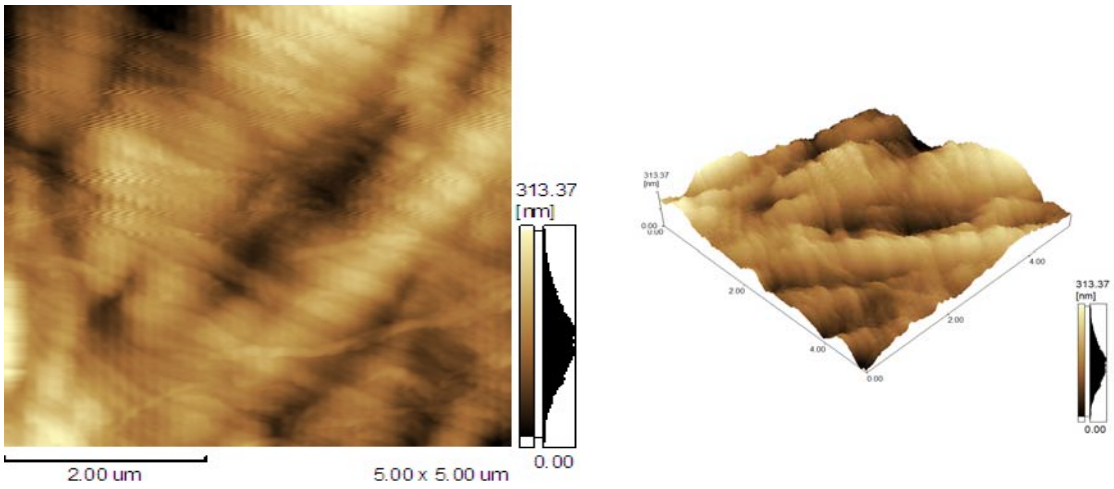


Fig. 9. AFM of fiber after 40 min ultrasonic treatment

FT-IR Spectral Analysis

The FTIR spectra of ultrasonically treated CMP were similar to that of the control CMP, but some significant difference should be observed (Fig. 10.). The broad absorption band at 3342 cm^{-1} is associated with H-bonded OH groups. With longer sonication period, the band became sharp, and it is attributed to the diminution of H-bonded OH groups, indicating that there was an augmentation of dissociative OH groups. Also, some bands (i.e.1600 cm^{-1}) had a trend to move to higher wavenumber, supplying evidence of the increase of dissociative OH groups. The decomposition of water to OH radicals is another possible reason for such an increase. Besides, a stronger band at 1740 cm^{-1} is assigned to the enhancement of ester absorbance (C-O-O-R). And there is an intense band at 1645 cm^{-1} due to the stronger absorption of carbonyl that is conjugated with phenyl. Both demonstrate an increase of the reaction from colored quinine to achromatous carboxylic or aromatic acid, which is the mechanism of hydrogen peroxide bleaching of CMP. Another great difference is a broad band at 1635 cm^{-1}. It is believed that the peak absorbance at 1635 cm^{-1} can be attributed to absorbed water in the isolated native hemicelluloses and non-crystalline regions of cellulose vibrations arising from absorbed water molecules. It is known that water cannot penetrate crystalline cellulose, but dry amorphous cellulose will absorb water and become soft and flexible. Such a phenomenon further explains the mechanism of the favorable effect of ultrasonic pretreatment on CMP hydrogen peroxide bleaching. In addition, compared to the spectrum of control pulp, no new band appeared in the spectra of ultrasound-treated pulp, providing evidence of that cavitation in the pulp did not produce new linkages or bonds.

XRD Studies

According to the conclusions discussed above, the ultrasound "cleaned" the surface of the CMP, even destroying the surface layer and exposing the main part of the fiber. Did it destroy the cellulose? To answer this question, the crystal structure and crystallinity was studied by XRD.

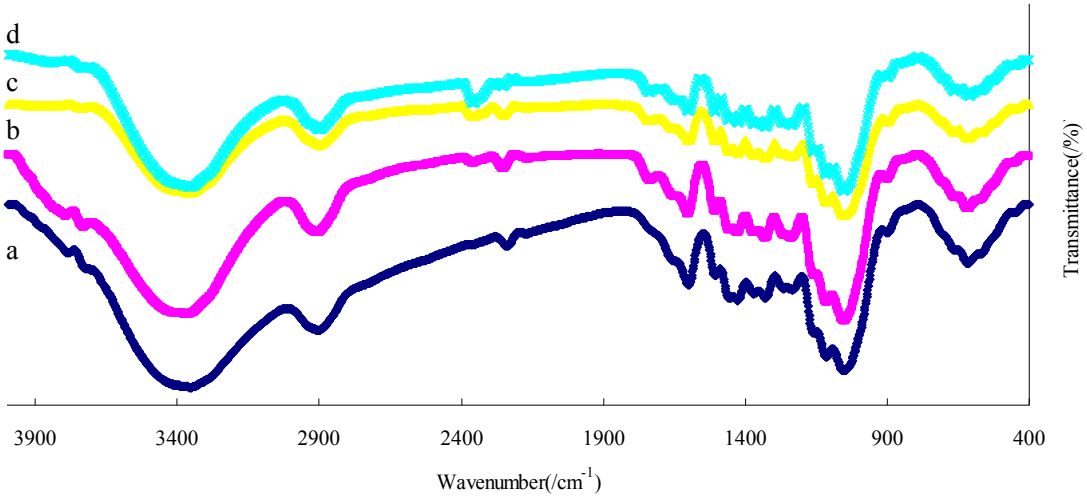


Fig. 10. FTIR spectra of ultrasonic treated CMP(a=Control ;b =CMP with 5min ultrasonic treatment ;c= CMP with 20 min ultrasonic treatment ;d=CMP with 40 min ultrasonic treatment)

As shown in Fig. 11, the characteristic X-ray diffraction patterns of all diffractograms showed the typical crystalline structure of native cellulose or cellulose I. As indicated by the similar curves and similar peaks in the figures, the whole structure of cellulose was not transformed by ultrasonic treatment. The crystalline and amorphous cellulose were still apparent after sonification. But from Fig.12 there were totally different trends between the crystallinity of bleached pulp and the crystallinity of unbleached pulp, both under ultrasonic pretreatment. If the pulp only was treated by ultrasonic irradiation, there was a decrease in crystallinity. This may be because the surface of crystalline cellulose was damaged by the impingement of microjets and shockwaves. Hence, when ultrasound is applied to cellulose without any other treatment, the ultrasound plays a part of reducing the crystalline area, which leads to a decrease in crystallinity, although the decrease is not very obvious. But if the pulp is treated by ultrasound and then bleached by hydrogen peroxide, the crystallinity will go up. A possible explanation is that after ultrasonic treatment, the fragments of crystalline cellulose and amorphous cellulose may react with hydrogen peroxide. This indicates that the structure of cellulose is accessible for the bleaching agent, hydrogen peroxide, which means the accessibility of bleaching agents and the bleaching efficiency is improved by ultrasonic treatment. As shown in Fig. 12, a difference of the crystallinity between unbleached and bleached CMP with the same ultrasonic treatment is evident ▲. The whole trend of the difference is consistent with the curve of brightness increase. This provides evidence that ultrasound could accelerate heterogeneous reactions by creating localized erosion on the solid surface, releasing larger reactive area, and consequently improving the accessibility of bleaching agents and the bleaching efficiency.

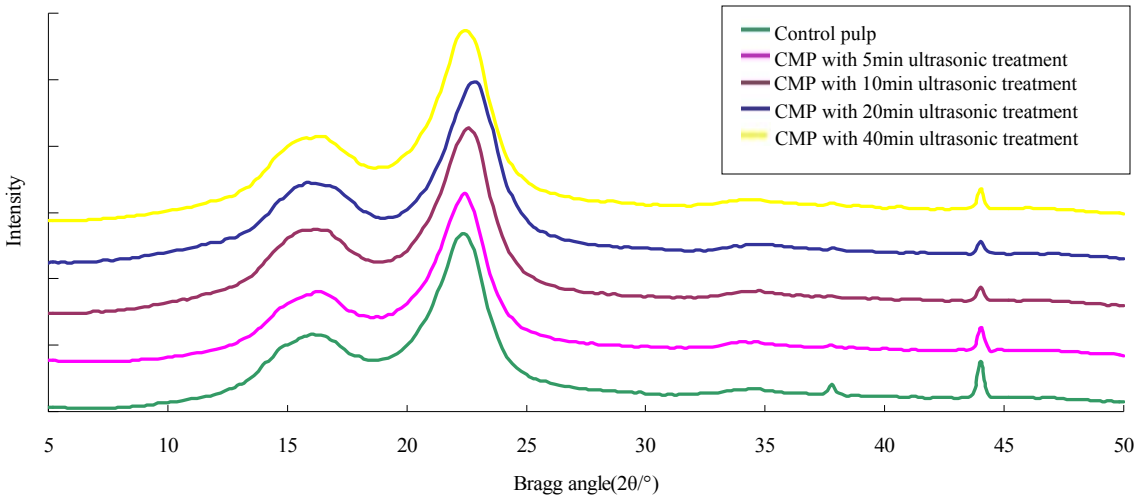


Fig. 11. XRD of CMP

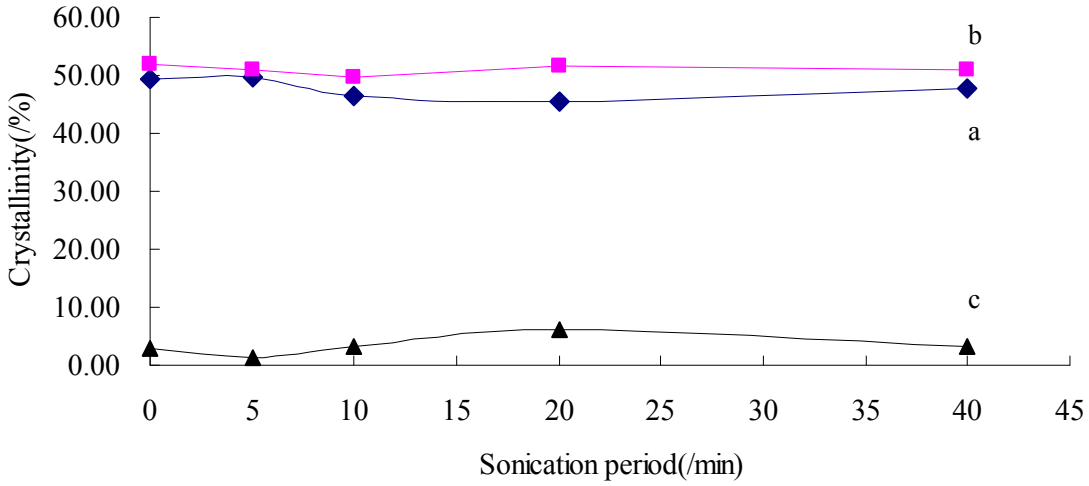


Fig. 12. Crystallinity changes of different treatment (a=unbleached CMP only with ultrasonic treatment; b=bleached CMP with ultrasonic pretreatment; c=the difference of both)

CONCLUSIONS

1. Ultrasound, which is able to clean the surfaces of objects and accelerate heterogeneous reactions, can be applied to bleaching. After hydrogen peroxide bleaching, ultrasonic pretreated CMP (using the following sonication conditions: 1.5% pulp consistency, 50°C, 20min, 90% amplitude, 20s pulse) was able to achieve an increase of 2.5% ISO brightness, reaching a value of 80.2% ISO.

2. Scanning electron microscopy (SEM) showed that after ultrasonic treatment, grooves and ridges and a few cracks appeared, and considerable damage to the fibers could be observed clearly. With longer sonication time, the surfaces were mildly delaminated, and the S2 layer was exposed.

3. Atomic force microscopy (AFM) showed that after ultrasonic treatment, most of the lamella lignin may have been degraded to granular form, and cellulose microfibrils were visible with a high degree of orientation.

4. The Fourier transform infrared (FTIR) spectra analysis of ultrasonic-treated CMP demonstrated the diminution of H-bonded OH groups and the increase of the reaction from colored quinine to achromatous carboxylic or aromatic acid. However, no new linkages or bonds were produced after ultrasonic pretreatment.

5. X-ray diffraction (XRD) studies showed that the crystalline structure of native cellulose was not transformed by the ultrasonic treatment. The crystallinity changes of unbleached pulp and bleached pulp showed different trends.

6. All of the analyses prove that there are striking changes in surface morphology, composition, and reactivity, which consequently releases large reactive area, improves the accessibility of bleaching agents, and increases the bleaching efficiency.

ACKNOWLEDGEMENTS

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