

Application of Ultrasonic Waves in Activation of Microcrystalline Cellulose

Xianling Wang, Guizhen Fang, Chunping Hu, Tianchuan Du

Key Laboratory of Bio-Based Material Science and Technology, Northeast Forestry University, Heilongjiang 150040, China

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ABSTRACT: In this work, microcrystalline cellulose (MCC) was activated with ultrasonic waves. The influences of ultrasonic treatment on the changes of supramolecular structures and morphology structure were studied by WAXS and SEM. The accessibility of the MCC was characterized by water retention value (WRV) and specific surficial area. The influence of ultrasonic treatment on the reactivity of MCC was investigated through the reaction of MCC being oxidized into 2,3-diadehyde cellulose (DAC) by periodate sodium. The mechanism of the reactivity change of ultrasonically treated MCC was examined. The results showed that the degree of crystallinity of MCC decreased and the degree of polymerization showed little change after treatment with ultrasonic waves. The morphological varia-

tion of the treated MCC was significant when compared with the untreated MCC, which contribute to the improvement of accessibility. The aldehyde content of DAC prepared from ultrasonically treated MCC was improved from 64.19 to 85.00%, indicating that the regioselective oxidation reactivity of MCC was significantly improved. The aldehyde content was found to first increase with time of ultrasonic treatment to a point, and then decrease as time progressed. In addition, the aldehyde content was found to increase with an increase in ultrasonic power. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2762–2767, 2008

Key words: ultrasonic waves; supramolecular structures; morphology; WAXS; dialdehyde cellulose

INTRODUCTION

Cellulose is the most abundant and renewable natural source for synthetic materials. A variety of cellulose derivatives are produced by chemical modifications. Oxidation of cellulose with periodate sodium has been extensively investigated, since it leads to selective cleavage at the C-2 and C-3 vicinal hydroxyl groups to yield a product with 2,3-diadehyde cellulose (DAC).¹ DAC is an important functional polymer used in chromatography and medical applications such as antithromboresistance and oral adsorbents.^{2,3} However, the aldehyde content of DAC is usually low because of its insolubility, highly ordered structure, and crystallinity. Therefore, it is generally recognized that some types of activating treatments are needed to improve the accessibility and trends of heterogeneous reactions of cellulose.^{4,5} Traditionally cellulose is activated by milling, alkali swelling, and steam explosion.⁶ In recent years, scientists have become more interested in treatments without chemical reagents and pollution due to environmental concerns. As a new kind of energy, ultra-

sonic waves are now widely used in biochemistry, organic synthesis, environmental chemistry, photochemistry, and other areas of science. However, until now, the investigation of ultrasonic waves in cellulose activation has been rarely reported.

In our early research, ultrasonic waves were used to treat microcrystalline cellulose (MCC) to improve the accessibility and reactivity of cellulose. In this research, the influences of ultrasonic treatment on changes of supramolecular structures, morphology structure, and regioselective oxidation reactivity of MCC were investigated.

EXPERIMENTAL

Chemicals and apparatus

Chemicals

MCC was obtained from Huzhou Zhanwang Pharmaceutical (Zhejiang, China). Periodate sodium, ethylene glycol, sodium hydroxide, and sulfuric acid with analytical grade were provided by Tianjin Chemical (Tianjin, China).

Apparatus

The ultrasonic apparatus was a JY98-3D bio-cell disrupter (Ningbo Xin Zhi Scientific and Equipment

Correspondence to: G. Fang (Fanggz@public.hr.hl.cn).

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Institute, China). The instrument of specific surficial area was ST-2000 type (Beijing Analytical Instrumentation Technology, China).

Ultrasonic treatment

An ultrasonic apparatus that operated at 200–700 W and 20 kHz was used. Hundred milliliter of distilled water was added to the ultrasonic reactor vessel, 2 g MCC were then added and timing started. The time of ultrasonic treatment was between 5 and 20 min. The ultrasonic treatment was carried out in an ice bath, and performed in a way of treating for 0.5 s with 0.5 s cooling intervals. After the treatment, the MCC suspension was filtrated. The filtrated MCC was washed with distilled water, and the filter cake of MCC was dried in a vacuum oven at 45°C for 24 h in a vacuum of 0.09 MPa.

Characterization of treated MCC

X-ray diffraction

Wide angle X-ray diffraction was used to measure the crystalline structure of treated and untreated MCC. The instrument was RIGAKU D/MAX-B diffractometer (made in Japan) equipped with a Cu K target and β Ni filter. The wavelength was 1.5405 Å and the spectra were obtained with an accelerating voltage of 45 kV and electric current of 40 mA. The scanning angles were 0–70°. The crystallinity index was calculated by the method of peak separation and Scherrer's equation.⁷

Degree of polymerization determination

With copper ammonia as the solvent, the degree of polymerization (DP) of MCC was determined from viscosity measurements at $(25 \pm 1)^\circ\text{C}$ using a ubbelohde capillary viscometer according to the eqs. (1)–(3).^{8,9}

$$\eta_r = \eta/\eta_0 \quad (1)$$

$$[\eta] = \lim_{c \rightarrow 0} \ln \eta_r/c \quad (2)$$

$$\text{DP}^{0.905} = 0.75[\eta] \quad (3)$$

where the relative viscosity (η_r) is calculated by dividing the viscosity of MCC sample in copper ammonia solution (η) by the viscosity of copper ammonia solution (η_0); where c is the concentration of MCC in copper ammonia solution (g/mL). Intrinsic viscosity $[\eta]$ was calculated from the plot between $(\ln \eta_r/c)_{c \rightarrow 0}$ and c .

Scanning electron microscopic observation

To observe the morphological changes, dried MCC samples were observed by an American Quanta 200 scanning electron microscope (SEM).

Accessibility determination

The accessibility of cellulose can be measured by a variety of techniques. In this research, accessibility was determined by water retention value (WRV) and specific surficial area.

The WRV of cellulose sample was determined according to the method described in Ref. 7. Using this method, the MCC samples were centrifuged at $3000 \times g$ for 15 min. The samples were weighed in the wet centrifuged state, oven-dried for 24 h, and then weighed in the dry state. The WRV was calculated using eq. (4).

$$\text{WRV} = 100 \times (G_1 - G_2)/G_2 \quad (4)$$

where G_1 is the wet weight of MCC samples (g); G_2 is the dry weight of MCC samples (g).

The specific surficial areas were determined by nitrogen adsorption isotherm at the 77 K using a ST-2000 type instrument of specific surficial area. The specific surficial areas were calculated according to BET equation and adsorption quality of stand sample (Al_2O_3).

Preparation of 2,3-dialdehyde cellulose

DAC was prepared by suspending 1 g treated MCC and 2 g periodate sodium in 30 mL distilled water. The reaction mixture was kept at 35°C for 3.5 h in the dark. After decomposition of the excess periodate sodium by ethylene glycol,² the oxidized products were filtered, thoroughly washed with distilled water, and dried in a vacuum of 0.09 MPa at 45°C for 24 h. Finally, white powder of 2,3-dialdehyde cellulose was obtained.

The Fourier transform infrared (FTIR) spectra were recorded as potassium bromide pellets on a Magna-560 FTIR spectrometer.

Aldehyde content was determined by base-dissolving method¹⁰ according to the Cannizzaro reaction. DAC (0.15 g) was put in a conical flask and 10 mL 0.2 mol/L standard NaOH solution was added. When the sample was dissolved, the conical flask was heated at 70°C for 2 min and then cooled down. Fifteen milliliter of 0.1 mol/L standard H_2SO_4 solution was added in the conical flask, and the mixed solution was titrated with 0.2 mol/L standard NaOH solution. The aldehyde content (CHO) was calculated using eq. (5).

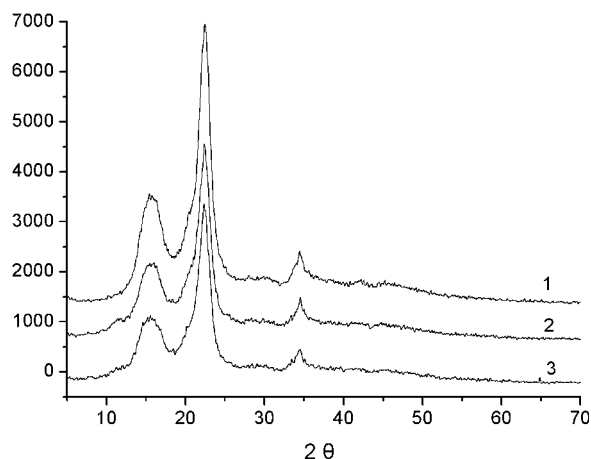


Figure 1 XRD spectra of MCC and MCC after ultrasonic treatment.

$$\text{CHO}\% = \frac{M_1(10 + V_1) - 2M_2V_2}{(G \times 1000)/160} \times 100 \quad (5)$$

where M_1 is the concentration of standard NaOH solution (mol/L); M_2 is the concentration of standard H_2SO_4 solution (mol/L); V_1 is the volume of standard NaOH solution used in titration; V_2 is the volume of standard H_2SO_4 solution; and G is the weight of DAC (g).

RESULTS AND DISCUSSION

Influence of ultrasonic treatment on supramolecular structures of MCC

Effects on crystal performance

The X-ray diffraction spectra of untreated and ultrasonically treated MCC under different conditions are shown in Figure 1. It was observed that the crystalline type of ultrasonic-treated MCC still kept type I. The intensities of the peaks of ultrasonic-treated MCC at 14.8° and 22.7° were lower than the untreated. As the ultrasonic power increases, the intensity decreases more obviously. This indicates that the hydrogen bonds in MCC molecules were destroyed and the degree of crystallinity of MCC decreased after ultrasonic treatment.

Table I shows the crystalline index calculated from the X-ray diffraction using Scherrer's equation. It can

be seen from Table I that the degree of crystallinity of MCC after ultrasonic treatment decreased from 62.42% to 61.36 and 54.56%, while the crystalline size showed little change. The degree of crystallinity of MCC treated at 700 W for 10 min was smaller than that of MCC treated at 200 W for 15 min. It is known that the degree of crystallinity depends on the extent of hydrogen bonds.¹¹ The lower degree of crystallinity of treated MCC than that of untreated MCC also shows that hydrogen bonds in the molecules were destroyed by ultrasonic treatment. The results could be due to the fact that ultrasonic cavitations disjoined the molecules in amorphous region and crystallite region, which induced the destruction of ordered packing of cellulose molecules and the decrease of crystallinity.¹² When the ultrasonic power increased from 200 to 700 W, the hydrogen bonds were more badly destroyed and the degree of crystallinity decreases more obviously.

Change in degree of polymerization

Table II shows the change in DP of ultrasonically treated MCC samples. The DP of untreated MCC was 130 and that of alkali activation was 108. It is shown from Table II that DP of ultrasonically treated MCC changed very little, while it was reduced to 108 after the treatment of alkali activation. This indicates that ultrasonic treatment can improve the reactivity of MCC without changing the performance of the MCC species material. The cleavage energy is 400–1000 kJ/mol for chemical bonds and 5–30 kJ/mol for hydrogen bonds.¹³ In this study, the power of ultrasonic waves was low (the maximal energy of ultrasonic waves was 600 kJ, others were less than 450 kJ), which could destroy the hydrogen bonds but not the chemical bonds. Thus ultrasonic treatment had little influence on the DP of MCC samples.

Influence of ultrasonic treatment on morphology structure of MCC

Figure 2 shows the SEM images of untreated and ultrasonically treated MCC under conditions of power 500 W for 15 min. It is observed that the particles of MCC without ultrasonic treatment are large and the surfaces are smooth, while the morphology structure is different after ultrasonic treatment. The

TABLE I
The Influence of Ultrasonic Treatment on Supramolecular Structures of MCC

Samples	Treating conditions	Crystal type	Crystalline size (nm)	Crystallinity (%)
MCC0	Untreated	Type I	4.915	62.42
MCC1-3	200 W/15 min	Type I	4.957	61.36
MCC4-2	700 W/15 min	Type I	4.896	54.56

TABLE II
The Influence of Ultrasonic Treatment on DP of MCC

Treating time (min)	Ultrasonic power (W)			
	200	300	400	500
5	129	131	120	131
10	129	133	127	129
15	129	129	130	131
20	127	131	127	125
Untreated			130	
Alkali activation			108	

large particles broke into small particles after treatment. Many concave pits and cracks were shown on the surfaces of treated MCC, which induced the increase of specific surficial area and the improvement of accessibility. These results agreed well with the previous researches.^{14,15}

Influence of ultrasonic treatment on accessibility changes of MCC

The changes of crystallinity and morphology structure contribute to some improvement of accessibility.

Change of specific surficial area

Figure 3 shows the results of specific surficial areas before and after ultrasonic treatment. The specific surficial areas of MCC increased dramatically after ultrasonic treatment. At a constant ultrasonic power, the specific surficial area was found to first increase with treating time to a point, and then decrease as time progressed. Generally, at a constant ultrasonic power the specific surficial area reached its peak value when the treating time was 15 min. When MCC was treated at 500 W for 15 min, the change of specific surficial area was significant, increasing from 0.2512 to 1.3461 m²/g.

Figure 4 illustrates the influence of ultrasonic power on the specific surficial areas of MCC. The specific surficial area was found to increase with an increase in ultrasonic power. This is due to the increase of smaller particles and deeper damage of surface structure caused by the increase of time and

power of ultrasonic treatment. When the treating time continually increased, the "hot-point effect" resulted from the collapse of ultrasonic cavitation bubble could cause the collision and aggregation between particles, thus resulted in a steadily decline of specific surficial area.

Change of water retention value

WRV, which can reflect the accessibility of agent to MCC, relies on the aggregation structure of MCC, the size, and the distribution of micropores. Table III shows the WRV changes of ultrasonically treated MCC samples. It can be seen that WRV increased with an increase in ultrasonic treating time. WRV of the untreated MCC was 130.5%. After MCC was treated by ultrasonic waves for 5, 10, 15, and 20 min at the power of 500 W, the WRV increased from 130.5 to 144.6, 157.0, 168.4, and 175.2%, respectively. The significant increase is mainly due to the morphological structure changes brought about by ultrasonic waves.

After ultrasonic treatment, both the specific surficial area and WRV were found to increase, which implies the improvement of accessibility.

Influence of ultrasonic treatment on reactivity changes of MCC

The reaction medium of MCC with periodate sodium is water. As a heterogeneous reaction, the increase of accessibility can contribute to an increase in contact area with reagents resulting in an improvement in reactivity. At the same oxidation condition, the aldehyde content of dialdehyde cellulose from ultrasonically treated MCC is improved from 64.19 to 85.00%. It indicates that the reactivity of MCC with periodate sodium is enhanced by ultrasonic treatment.

Effects of ultrasonic treating time and power

To obtain the optimum conditions for preparing DAC with high aldehyde content, the effects of ul-

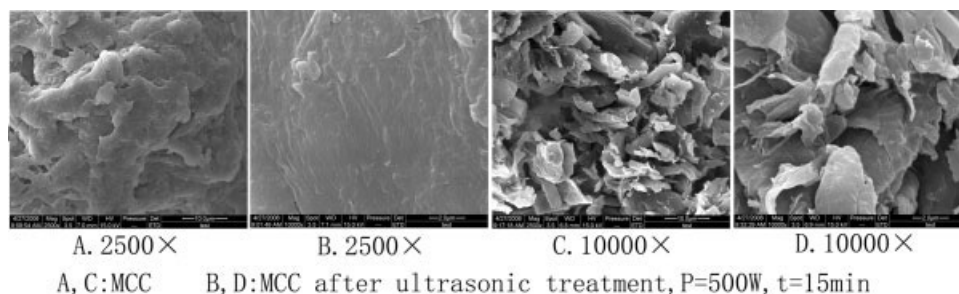


Figure 2 SEM micrographs of MCC and MCC after ultrasonic treatment.

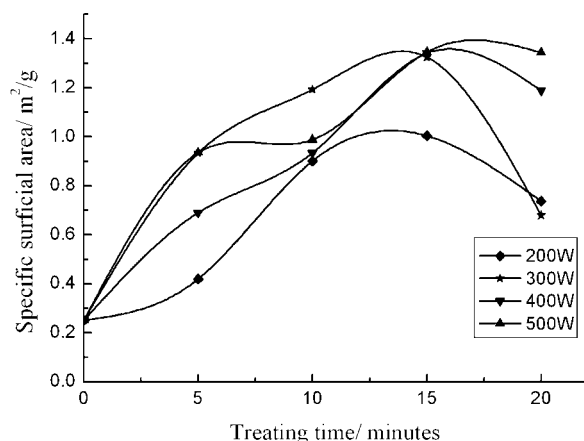


Figure 3 The influence of ultrasonic treating time on specific surficial area of MCC.

trasonic treating time and power on aldehyde content were examined. The results are shown in Figure 5. It can be seen from Figure 5 that as the treating time increased, aldehyde content first increased and then decreased. The increase of power improved the aldehyde content. However, there was no linear relationship between the aldehyde content and the ultrasonic power. Aldehyde content of the oxidized products showed the highest value of 85.00% as MCC was treated by ultrasonic waves at 700 W for 10 min.

Analysis of FTIR

MCC and its oxidized products DAC were characterized by FTIR. Figure 6 is the FTIR spectra of MCC and DAC. The characteristic carbonyl peak of DAC appeared at 1730 cm^{-1} , which showed the same result as the previous research.¹⁶ The intensity of O—H peak at 3360 cm^{-1} was greatly reduced when compared with that of MCC. Other than these differ-

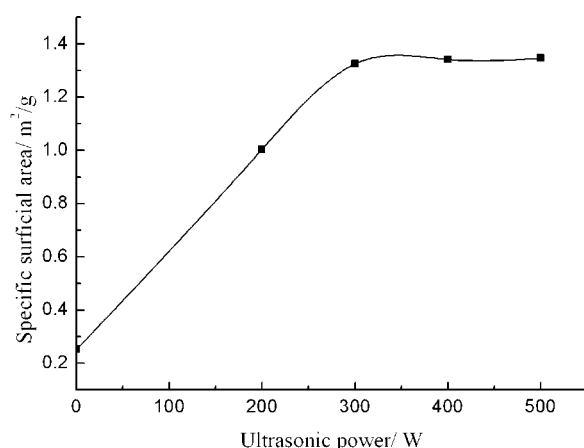


Figure 4 The effects of ultrasonic power on specific surficial area of MCC.

TABLE III

The Influence of Ultrasonic Treatment on WRV of MCC

Samples	Treating time (min)	WRV (%)
MCC ₀	0	130.5
MCC ₁	5	144.6
MCC ₂	10	157.0
MCC ₃	15	168.4
MCC ₄	20	175.2

ences, the spectra of DAC appeared similar to that of MCC. The intensity of the carbonyl peak was much smaller than expected as a result of the formation of hemiacetal linkages.¹⁷

Mechanism of the reactivity changes after ultrasonic treatment

The sonochemistry is a function of sound cavitation. When ultrasonic waves are used to treat MCC, ultrasonic cavitation can bring two functions to MCC. One is the dispersing effect resulted from the micro-wave jets of ultrasonic waves. The other is the breakage to the surface of MCC caused by the powerful shock wave. After treatment with ultrasonic waves, the particles of MCC become smaller, the smooth surface is damaged and the ordered packing of cellulose molecules is destroyed, which induce the increase of the specific surficial area and WRV. Furthermore, the hydrogen bonds in MCC molecules are destroyed and the degree of crystallinity of MCC decreases. As a result, the available contact area of MCC with reagents increases. The accessibility of reagents to MCC molecules is also improved, resulting in an improvement in the regioselective oxidation reactivity of MCC with periodate sodium. The aldehyde content of DAC prepared from ultrasonically treated MCC is higher than that prepared from

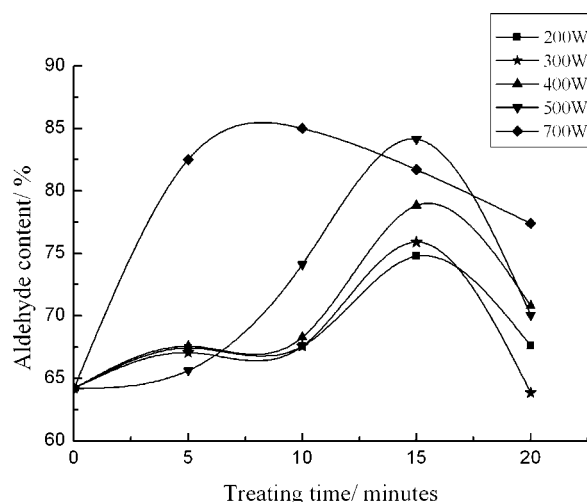


Figure 5 The influence of ultrasonic treatment on aldehyde contents of DAC.

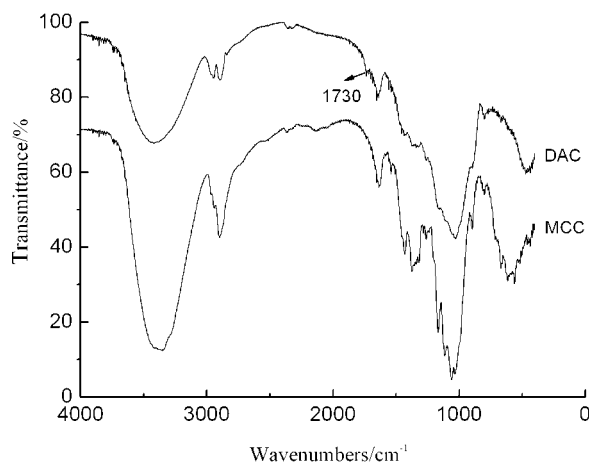


Figure 6 FTIR spectra of MCC and DAC.

untreated. At a constant ultrasonic power, the continual increase of treating time induces the decrease of regioselective oxidation reactivity, which is attributed to a "hot-point effect" resulting from the collapse of the ultrasonic cavitation bubble. The "hot-point effect" could cause the collision and aggregation between particles and the decrease of specific surficial area, which leads to the decrease of active hydroxyl and decline of regioselective oxidation reactivity of MCC.

CONCLUSIONS

After ultrasonic treatment, the hydrogen bonds in MCC molecules were destroyed and the degree of crystallinity of cellulose decreased. The particles of MCC became small and the surface was damaged after the treatment. All these contributed to the increase of accessibility in terms of specific surficial area and WRV. As a heterogeneous reaction, the reactivity of MCC with periodate sodium increased along with the increase of accessibility. The aldehyde content of dialdehyde cellulose prepared from ultra-

sonically treated MCC was much higher than that prepared from the untreated ones. DAC with higher aldehyde content of 85.00% was obtained when MCC was treated by ultrasonic waves at 700 W for 10 min.

As a green chemistry process, the ultrasonic treatment does not use any polluting chemical reagents. In addition, ultrasonic waves can improve the reactivity of MCC without changing the performance of the material. This ultrasonic treatment technique will be an effective and prospective means for the activation of cellulose.

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