

SYNTHESIS OF 2,4-BIS(4-SULFONATE PHENOXY)-6-CHLORO-1,3,5
 TRIAZINE AND ITS APPLICATION IN MODIFICATION OF
 CELLULOSE FOR HIGH GLUCOSE YIELD

YUANYUAN YIN,^{*,**} XIUZHI TIAN,^{*} FOQUAN WENG,^{*} XUE JIANG,^{*,**}
 HONGBO WANG^{*,**} and WEIDONG GAO^{*,**}

^{*}Key Laboratory of Eco-textiles of Ministry of Education, Jiangnan University, Wuxi,
 Jiangsu 214122, China

^{**}Jiangsu Province Functional Textiles Engineering and Technology Research Center, Jiangnan University,
 Wuxi, Jiangsu 214122, China

✉ Corresponding authors: Xue Jiang, jiangx@jiangnan.edu.cn
 Hongbo Wang, wxwanghb@163.com

Received February 26, 2016

A derivative of triazine, namely 2,4-bis(4-sulfonate phenoxy)-6-chloro-1,3,5-triazine (BSPCT), has been synthesized from the reaction between trichloride triazine and p-hydroxyl benzene sulfonic acid. Fourier transform infrared (FT-IR) spectra suggested the structure of BSPCT. Microcrystalline cellulose was modified with BSPCT and then hydrolyzed with 8 wt% H₂SO₄ at 130 °C for 5 hours. The yield of reducing sugar in the hydrolysis and the influence of the content of BSPCT in the modified cellulose were tested. The results showed that the yield of reducing sugar first increased and then decreased with increasing the content of BSPCT. A maximum yield of 12.42% was reached for 6.25% molar content of BSPCT. The probable mechanism was explained from the variation of the crystal structure of cellulose.

Keywords: microcrystalline cellulose, 2,4-bis(4-sulfonate phenoxy)-6-chloro-1,3,5-triazine, hydrolysis, crystal structure, yield of reducing sugar

INTRODUCTION

Because of environmental problems and the depletion of fossil energy resources, people have been seeking new clean energy resources.¹⁻⁴ Conversion of cellulose into ethanol has been the focus of researches in the field of biomass fuel.⁵⁻⁸ It is well known that cellulosic biomass is difficult to convert into ethanol, which is attributed to the high degree of polymerization and crystallinity of lignocellulose. In order to solve this challenge, proper pretreatment is an essential step for the conversion of lignocelluloses into ethanol.⁹⁻¹³

Compared with physical and biological

pretreatment technologies, neither special equipment nor extreme operating conditions are essential for the chemical methods. According to the studies of Borsa *et al.*, a substituent on the C6 position of cellulose could increase the hydrolysis of cellulose.¹⁴ In the field of dyeing and finishing, it has been found that reactive tendering of cotton fabric renders cotton fibers dyed with reactive dyes more easily hydrolyzable than the original fibers.¹⁵⁻¹⁷ Significantly, sym-triazine dyes have wide-ranging applications during reactive dyeing. This provides a new approach to the pretreatment of cellulose. Therefore, the derivatives of 2,4,6-trioctylthio-1,3,5-triazine are promising

candidates to pretreat lignocelluloses to obtain ethanol. Jiang *et al.*^{18,19} researched the influence of 2-chloro-4,6-diphenylamino-1,3,5-triazine (DACT) and 2,4-dichloro-6-phenoxy-1,3,5-triazine (PHCT) on the structure and hydrolysis of microcrystalline cellulose. They found that the crystalline structure of cellulose changed, the content of the amorphous region of the cellulose increased, and reducing sugar yield increased as well after the modification by DACT and PHCT.

In the current study, 2,4-bis(4-sulfonate phenoxy)-6-chloro-1,3,5-triazine (BSPCT) has been synthesized from the reaction between trichloride triazine and *p*-hydroxy benzene sulfonic acid to modify microcrystalline cellulose. The crystalline structure and the hydrolysis of cellulose were studied, and the possible mechanism of the change was also considered.

EXPERIMENTAL

Materials

Microcrystalline cellulose (J&K, Ph102), trichloride triazine (TCT) (J&K) *p*-hydroxy benzene sulfonic acid, sodium hydroxide, acetone, anhydrous sodium carbonate and sulfuric acid (AR) were bought from Sinopharm Chemical Reagent Co., Ltd. (SCRC).

Synthesis of BSPCT

BSPCT was synthesized from the reaction between trichloride triazine and *p*-hydroxy benzene sulfonic acid. *P*-hydroxy benzene sulfonic acid, trichloride triazine and sodium hydroxide (molar ratio of 2:1:4) were added to the solution containing water and acetone (volume ratio of 1:1). The reactive mixture

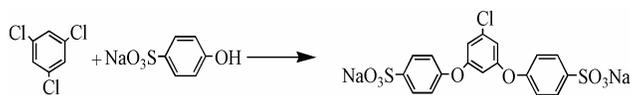
was kept under stirring for 2 hours at 0-5 °C, and then for 5 hours at 40 °C. After that, the mixture was filtered and washed with a small amount of acetone. Finally, the mixture was dried in a vacuum oven and the BSPCT was obtained.

Chemical grafting of BSPCT on microcrystalline cellulose

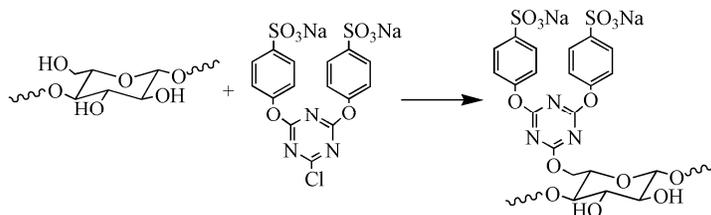
Grafting of BSPCT on microcrystalline cellulose was performed in a three-necked flask containing 2 g of MCC and 20 mL of deionized water. The suspension was adjusted to pH = 11 with 20 wt% sodium carbonate solution and stirred for one hour at 85 °C. Then, the solution containing a certain amount of BSPCT, 0.4 g sodium sulfate and 20 mL deionized water was slowly added dropwise into the reactive system. After the reaction mixture had been stirred for 2 hours, the mixture was filtered and washed with water until the pH of the filter cake reached a value of 7. Subsequently, the mixture was dried in a vacuum oven for 24 h at 50 °C.

Acid hydrolysis

An amount of 0.5 g of MCC was mixed with 10 mL of sulfuric acid aqueous solution (8 wt%) in a single-neck flask. The reactive mixture was kept under stirring for 5 h at 130 °C for hydrolysis, and then the pH of the mixture was adjusted to a value of 7. After that, the suspension was centrifuged for 3 min at 4000 rpm. The supernatant was transferred to a 100 mL volumetric flask, and the precipitate was washed with distilled water. The mixture was then centrifuged for 3 min at the same speed, and the centrifuged supernatant was collected in the previously mentioned flask in order to measure the yield of reducing sugar.



Scheme 1: Synthesis of DPHACT



Scheme 2: Grafting of DPHACT on microcrystalline cellulose

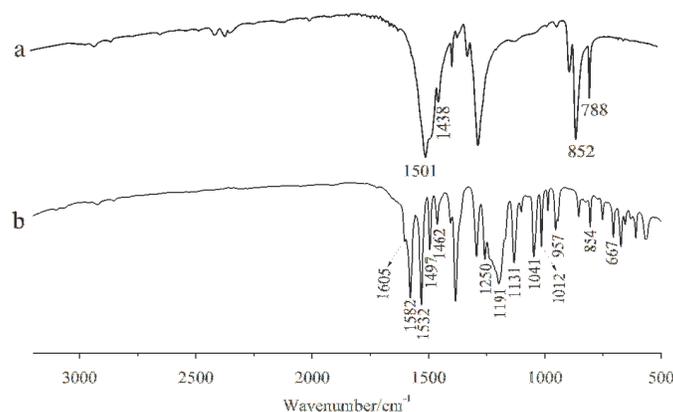


Figure 1: FT-IR spectra: (a) TCT and (b) BSPCT

Characterization

Infrared spectra were recorded at room temperature on a NICOLET IS10 Fourier transform infrared (FT-IR) spectrometer to characterize the surface modification of MCC. The samples were prepared by the KBr pellet method. The resolution of the spectrometer was 4 cm^{-1} , the wavenumber range was $400\text{--}4000\text{ cm}^{-1}$, and the samples were scanned 30 times. X-ray diffraction (XRD) patterns of raw MCC and the modified MCC were recorded on a Bruker Siemens D8 X-ray diffractometer operated at 3 kW with $\text{CuK}\alpha$ radiation ($\lambda = 0.154\text{ nm}$) in the range $2\theta = 3\text{--}60^\circ$ with a step of 0.02° . The yield of reducing sugar was determined using 3,5-dinitrosalicylic acid calorimetry (DNS).²⁰ The standard curve of glucose measured at 494 nm was calculated by the following Equation (1) and the yield of reducing sugar was calculated by Equation (2):

$$y = 1.07165x - 0.01356 (R^2 = 0.998) \quad (1)$$

$$y = \frac{0.9 m_1 \cdot V_0 / V_1}{m_0} \quad (2)$$

In equation (2), y is the yield of reducing sugar, m_1 is the weight of glucose (mg) obtained from the standard curve, m_0 is the weight of the sample (mg), V_0 is the total volume of the extracting solution (mL), V_1 is the volume used in measurement (mL).

The crystallite size of cellulose was calculated according to the Scherrer equation, as shown in Equation (3):

$$D = \frac{\kappa\lambda}{\beta \cos \theta} \quad (3)$$

where D is the crystallite size, κ is the Scherrer constant, $\kappa = 0.89$; λ is the wavelength of the ray, $\lambda = 0.15406\text{ nm}$; β is the largest width at half of the

characteristic diffraction peak, shown with radian; θ is the Bragg angle.²¹

Crystallinity index was calculated using Equation (4):

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \quad (4)$$

where I_{002} is the 002 plane diffraction intensity maxima and I_{am} is diffraction intensity in the range $2\theta = 18.3^\circ$.²²

RESULTS AND DISCUSSION

Synthesis of BSPCT and its grafting on MCC

The synthesis of BSPCT was investigated by FTIR analysis, as shown in Figure 1. Curves a and b are the spectra of TCT and BSPCT, respectively. The characteristic adsorption peaks of the triazine ring appeared in both spectra, while more adsorptions appeared in curve b, which suggested the benzene ring in the *p*-hydroxy benzene sulfonic acid. The adsorption peaks at 1605 cm^{-1} , 1582 cm^{-1} , 1532 cm^{-1} , 1497 cm^{-1} and 1462 cm^{-1} were attributed to the stretching vibration of the skeleton in the triazine and benzene ring. The adsorptions at $957\text{--}667\text{ cm}^{-1}$ were attributed to the bending vibration of C-H in the benzene ring, which contained the characteristic adsorption peak at 854 cm^{-1} . The peaks at 1250 cm^{-1} and 1041 cm^{-1} were attributed to the stretching vibration of C-O-C connecting triazine and the benzene ring, and the adsorption peaks at 1191 cm^{-1} , 1131 cm^{-1} , 1041 cm^{-1} and 1012 cm^{-1} were attributed to the stretching vibration of C-S-C.

The chemical grafting of BSPCT on MCC was

also investigated by FTIR spectroscopy, as shown in Figure 2. Curves a and b are the spectra of MCC and modified MCC, respectively. The characteristic adsorption peaks of cellulose appeared in both spectra, while more adsorptions appeared in curve b, which suggested triazine and the benzene ring. The adsorption peaks at 1618 cm^{-1} , 1541 cm^{-1} and 1405 cm^{-1} were attributed to the stretching vibration of the skeleton in the triazine, and the peak at 864 cm^{-1} was attributed to the bending vibration of C-H of the benzene ring.

Crystalline structure of cellulose modified with BSPCT

The variations of the crystalline structure of MCC modified with BSPCT were tested with X-ray (XRD) analysis. The XRD patterns of MCC modified with BSPCT with the dosage of 0, 3.23%, 3.85%, 6.25% and 16.69% are shown in Figure 3, with the curves marked as a, b, c, d and e, respectively. The diffraction peaks at 2θ of 14.8° , 16.4° , 22.5° and 34.5° appeared in the XRD patterns of all cellulose samples, which represent the crystalline structure of cellulose I of the polymorphous cellulose.²³⁻²⁵ However, there were several differences among the XRD patterns of the five kinds of cellulose samples. Starting with a dosage of BSPCT below 6.25% and along with its increase, the peak at 2θ of 18.5° was enhanced slightly, and the intensity of the diffraction peaks of the (021) plane gradually disappeared, while the (200) plane became weaker and wider.

As can be seen in Figure 3, the proportion of (110) and $(\bar{1}\bar{1}0)$ planes in the three main crystal planes in cellulose, which are (110), $(\bar{1}\bar{1}0)$ and (200), reached the maxima, which was conducive to the hydrolysis of cellulose, because the d-spacing values of (110), $(\bar{1}\bar{1}0)$ are much larger than that of (200). On the other hand, the peaks of modified cellulose at 34.5° were decreased, which revealed that the substitution reaction occurred not only in the amorphous regions, but also on the edge of the crystalline region. Therefore, the crystal structure of cellulose was impacted after modification, and was probably more accessible to hydronium ion, according to the previous study by Jiang *et al.*²⁶

The crystalline index and the grain size of MCC modified with BSPCT were calculated to intuitively characterize the crystalline structure of the samples, as shown in Figure 4. The crystalline index of unmodified cellulose was 85.48%, and the grain size was 9.410 nm. Along with the increase of BSPCT dosage, the crystalline index and the grain size of modified cellulose decreased, and then increased, when the dosage of BSPCT was over 6.25%. As shown in Figure 4, the crystalline index and the grain size of modified cellulose reached the minimum, when the BSPCT dosage was 6.25%. According to these results, it is clear that the crystal structure of MCC modified with BSPCT was impacted and the crystallinity of the modified MCC was diminished.

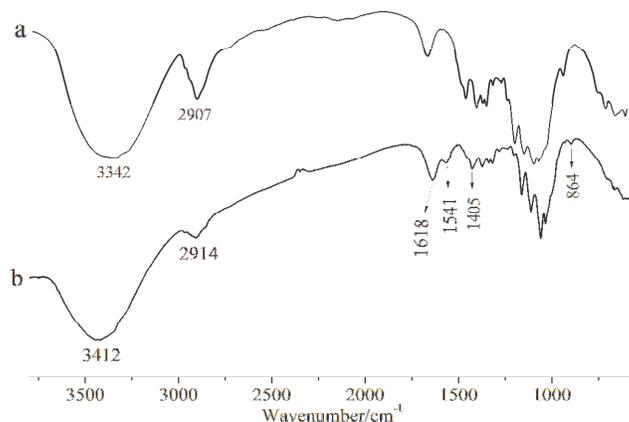


Figure 2: FT-IR spectra: (a) MCC; (b) BSPCT modified MCC

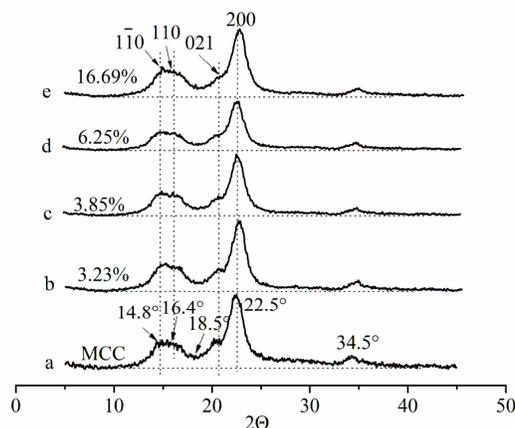


Figure 3: WAXD patterns of MCC and BSPCT modified MCCs

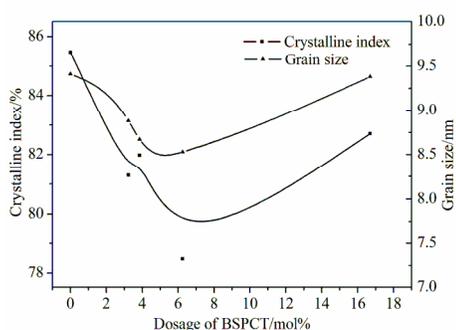


Figure 4: Crystalline index and crystalline size of MCCs as a function of loading with BSPCT

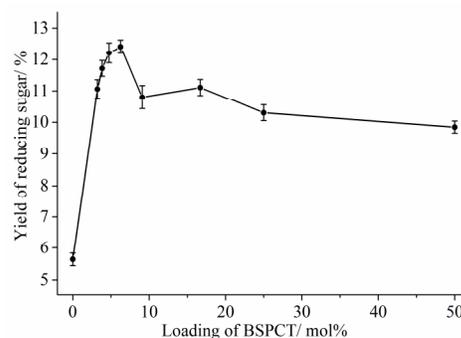


Figure 5: Yield of glucose in hydrolysis as a function of loading with BSPCT

Therefore, the pretreatment of BSPCT modification on MCC was meaningful to promote the conversion of lignocelluloses into ethanol.

Hydrolysis of cellulose modified with BSPCT

3,5-dinitrosalicylic acid colorimetry (DNS) was adopted to measure the glucose yield, and the influence of BSPCT dosage on the yield of reducing sugar in the hydrolysis of cellulose modified with BSPCT was investigated, as shown in Figure 5. According to the relationship between the yield of reducing sugar and the consumption of BSPAT, when the dosage of BSPCT was less than 6.25%, the yield of reducing sugar rose significantly along with the increase of BSPCT dosage, owing to the regularity of the amorphous region of modified cellulose being reduced, because of the space

broadening with the permeation of BSPCT into the amorphous area. The yield of reducing sugar reached the maximum (12.42%) when the dosage of BSPCT was 6.25%. On the other hand, hydrophilic sulfonic groups of BSPCT were conducive to the permeation of chemical reagents. When the dosage of BSPCT was beyond a certain limit, the gaps were restored with the increase of BSPCT dosage. That is the reason why the yield of reducing sugar was reduced when the dosage of BSPCT was more than 6.25%.

CONCLUSION

A derivative of triazine, namely 2,4-bis(4-sulfonate phenoxy)-6-chloro-1,3,5-triazine (BSPCT), has been synthesized from the reaction between trichloride triazine and p-hydroxyl benzene sulfonic acid and applied in the modification of

cellulose for achieving a high glucose yield. The substituent on the C6 position of cellulose promoted the hydrolysis of lignocellulose, which was attributed to the impact of BSPAT on the crystal structure and the decrease in the crystallinity of lignocelluloses. On the other hand, the introduction of hydrophilic sulfonic groups was conducive to the permeation of chemical reagents. Therefore, the pretreatment was meaningful to promote the conversion of lignocelluloses into ethanol. However, the mechanism of the promotion needs to be further researched. The study is in progress and will be presented in future work.

REFERENCES

- ¹ W. Zhang, R. B. Justin and R. Scott, *ACS Sustain. Chem. Eng.*, **3**, 413 (2015).
- ² M. Balat, H. Balat and C. Öz, *Prog. Energ. Combust.*, **34**, 551 (2008).
- ³ M. Wang, J. Wang and J. X. Tan, *Energ. Source. Part A*, **33**, 612 (2011).
- ⁴ P. Dwivedi, J. R. R. Alavapati and P. Lal, *Energ. Sustain. Dev.*, **13**, 174 (2009).
- ⁵ X. Fang, Y. Shen, J. Zhao, X. M. Bao and Y. B. Qu, *Bioresour. Technol.*, **101**, 4814 (2010).
- ⁶ C. H. Zhou, X. Xia, C. X. Lin, D. S. Tong and J. Beltramini, *Chem. Soc. Rev.*, **40**, 5588 (2011).
- ⁷ J. A. Geboers, S. V. de Vyver, R. Ooms, B. O. Beeck, P. A. Jacobs *et al.*, *Catal. Sci. Technol.*, **1**, 714 (2011).
- ⁸ H. Huang, N. Qureshi, M. H. Chen, W. Liu and V. Singh, *J. Agric. Food Chem.*, **63**, 2760 (2015).
- ⁹ H. Inoue, S. Yano, T. Endo, T. Sakaki and S. Sawayama, *Biotechnol. Biofuel.*, **1**, 1 (2008).
- ¹⁰ N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee *et al.*, *Bioresour. Technol.*, **96**, 673 (2005).
- ¹¹ X. B. Zhao, K. K. Cheng and D. H. Liu, *Appl. Microbiol. Biot.*, **82**, 815 (2009).
- ¹² M. J. Taherzadeh and K. Karimi, *Int. J. Mol. Sci.*, **9**, 1621 (2008).
- ¹³ H. Amiri and K. Karimi, *Ind. Eng. Chem. Res.*, **52**, 11494 (2013).
- ¹⁴ D. Karst and Y. Q. Yang, *Macromol. Chem. Phys.*, **208**, 784 (2007).
- ¹⁵ R. Haggerty, and M. Scalco, *IFI Fabricare News*, **20**, 9 (1991).
- ¹⁶ J. P. Luttringar, *Textile Chem. Color*, **25**, 25 (1993).
- ¹⁷ J. Fiegel, W. Reddig and J. Wolff, *Textile Asia*, **26**, 72 (1995).
- ¹⁸ J. Gu, X. Jiang and X. Tian, *J. Chin. Chem. Soc.*, **69**, 2975 (2011).
- ¹⁹ F. Weng, X. Jiang and X. Tian, *J. Cellulose Sci. Technol.*, **219**, 9 (2013).
- ²⁰ G. L. Miller, *Anal. Chem.*, **31**, 426 (1959).
- ²¹ S. J. Eichhorm, R. J. Young, R. J. Davies and C. Riekel, *Polymer*, **44**, 5901 (2003).
- ²² L. Segal, J. J. Creely, A. E. Martin Jr. and C. M. Conrad, *Textile Res. J.*, **29**, 786 (1959).
- ²³ X. L. Wang, G. Z. Fang and C. P. Hu, *Chem. J. Chinese U.*, **28**, 565 (2007).
- ²⁴ D. S. Zhao, H. Li and M. S. Liu, *Chem. J. Chinese U.*, **32**, 1629 (2011).
- ²⁵ S. Y. Oh, D. I. Yoo, Y. Shin, H. C. Kim and H. Y. Kim, *Carbohydr. Res.*, **340**, 2376 (2005).
- ²⁶ X. Jiang, J. Gu, X. Z. Tian, Y. L. Li and D. Huang, *Bioresour. Technol.*, **104**, 473 (2012).