CELLULOSE CHEMISTRY AND TECHNOLOGY

ULTRASOUND-ASSISTED MODIFICATION OF BEET PULP CELLULOSE WITH PHTHALIC ANHYDRIDE IN IONIC LIQUID

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Cellulose phthalates were synthesized from beet pulp cellulose and phthalic anhydride in ionic liquid (IL) 1-butyl-3-methylimidazolium chloride assisted by ultrasound. The parameters investigated included ultrasound time (from 15 to 60 min), temperature (between 95 and 120 °C), the molar ratio of phthalic anhydride/anhydroglucose units in cellulose (from 2:1 to 6:1), and reaction time (from 30 to 70 min). The results showed that the synergy of the combined use of ultrasound and IL successfully enhanced the degree of substitution of cellulose phthalates under the experimental conditions of the present study. After the chemical modification, the results of FT-IR and solid-state CP/MAS ^{13}C NMR showed the appearance of hydroxyl groups and reduction of OH bonds on the cellulose. The TGA data indicated that the cellulose phthalate showed lower thermal stability than native cellulose.

Keywords: ultrasound-assisted, cellulose, beet pulp, phthalation, ionic liquid (IL)

INTRODUCTION

In recent years, much attention has been focuse on the efficient utilization of agricultural residues,[1,2] which are regarded as readily available, renewable and biodegradable natural resources. However, serious environment pollution is caused by the huge quantities of agricultural residues burnt in the field every year. So, many countries have imposed regulations restricting field burning of agricultural residues, in order to reduce the emission of carbon dioxide, a major reason of global warming. This helped stimulate interest in the utilization of agricultural residues as renewable energy and for the production of a diversity of products, including bio-ethanol, functional polysaccharides and new-type materials.[3,4] One of the largest agricultural residues in China is sugar beet (*Beta vulgaris*) pulp (SBP), a by-product of the sugar production process. Except for use as pectin preparation, the SBP is a good source of cellulose due to its high content (23%, dry basis).[5]

Chemical modification of cellulose is a promisingmethod for the production of value-added products, which can be achieved by a series of reactions, such as sulfation, acetylation and succinoylation, for designing particular cellulose derivatives.[6,7] In particular, the cellulose derivatives with benzene ring not only serve as thermoplastic and optical materials, but also exhibit an excellent property of high chiral recognition, and thus can be used as chiral selectors directly for chromatographic separations absorption.[8-10] In most cases, chemical modification of cellulose starts from cellulose suspension in pyridine, and is carried out heterogeneously with an excess of the corresponding acid chloride.[11,12]

As a consequence, it was quite difficult to control the structure of cellulose derivatives because of the intermediate steps and uneven substitution. Generally, modification reactions carried out in a homogeneous phase could lead to more uniform and stable cellulose derivatives than those obtained from heterogeneous phases.[13] However, the intrinsic insolubility of cellulose in water and organic solvents is a major obstacle to homogeneous cellulose modification.[14] A number of solvents, such as DMAc/LiCl, DMF/N_2O_4, and N,N-dimethylformamide, have been developed for dissolving cellulose.[15,16] But these solvents have drawbacks, such as high toxicity, difficulty of solvent recovery and instability in processing.

The favorable properties of ILs, including extremely low vapor pressure, wide liquid ranges, and excellent thermal and chemical stability, have encouraged researchers to explore chemical reactions using ILs rather than the traditional organic solvents.[17] Some homogeneous cellulose derivations have been successfully performed in ILs with catalysis.[18,19]

Ultrasound technology has also been used in several ILs for improving yields, shortening reaction times and enhancing conversion of cellulose,[20,21] but there remains no report of ultrasound-assisted phthalation of SBP cellulose in ILs.

In the present study, the ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was studied as a reaction medium for modification of SBP cellulose with phthalic anhydride in the absence of any catalyst. The reaction was assisted by ultrasound, and the extent of phthalation was measured by the degree of substitution (DS) of cellulose derivatives. The modified cellulose was then characterized by FT-IR, solid-state CP/MAS ^{13}C NMR and TG-DTA.

EXPERIMENTAL

Materials

SBP was offered by Luyuan Sugar Industry Co., Ltd (Xinjiang, China). [Bmim]Cl (>98% purity) was purchased from Lanzhou Greenchem ILS, LICP. CAS., China. All other chemicals were of analytical grade, and purchased from Tianjin Chemical Reagent Factory, China.

Isolation of SBP cellulose

SBP cellulose was prepared as described previously[22] with slight modifications: the SBP was firstly treated with citric acid (80 °C, pH 2.0 and 2 h) to get pectin. The resulting solid was dewaxed with toluene:ethanol (2:1, v/v) for 6 h. The water-soluble free sample was delignified with sodium chlorite at pH 3.8-4.0, 75 °C for 2 h. After filtration, the solid residue collected was treated with 10% KOH at 20 °C for 10 h. The remaining solid was washed thoroughly with distilled water followed by 95% ethanol, and dried at 50 °C for 16 h to obtain SBP cellulose.

Phthalation of cellulose with ultrasonic assistance

Before the phthalation reaction, [Bmim]Cl was pre-melted in a three-necked flask agitated with a magnetic stirrer, and heated to 110 °C for 5 min in an oil bath. Then dried cellulose was dispersed into the pre-melted [Bmim]Cl (0.1 g cellulose/5 g [Bmim]Cl) under N_2 atmosphere to ensure complete dissolution of cellulose with continuous stirring for 3 h at 100 °C (N_2 can improve the dissolution based on our experience).

The cellulose phthalates containing free carboxylic acid groups were prepared by the reaction of cellulose with phthalic anhydride in [Bmim]Cl with ultrasonic assistance. To the cellulose/[Bmim]Cl mixture, 0.141, 0.211, 0.282, 0.312 or 0.422 g phthalic anhydride were added. The mixture was pretreated with a sonic power of 180 W for 0, 15, 30, 45 or 60 min in a HN1006 Ultrasonic Cleaning Bath (Huanan Ultrasonic Equipment Co. Limited, Guangzhou, China, 40 KHz). The mixture was then heated in an oil bath under N_2 atmosphere, with stirring, at the temperatures of 95-120 °C for 30-90 min. The resulting mixture was slowly poured into 50 mL of anhydrous ethanol with stirring to stop the reaction. The precipitate that formed was filtered and washed thoroughly with alcohol to eliminate ILs, unreacted anhydride and by-products. The material was then vacuum freeze dried for 16 h.

Determination of DS

The DS of cellulose derivatives was determined by direct titration.[23] A known weight of sample was dissolved in 10 mL of NaOH with stirring, at 50 °C for 30 min. After cooling to room temperature, 2-3 drops of phenolphthalein were added as an indicator, then, any excess of NaOH was back-titrated with standard 0.025 M HCl. The titration was repeated three times, and the average value of the HCl volume was used for calculations. The DS was calculated using the following equation (1):

$$DS=(162\times n_{COOH})/(m-148\times n_{COOH}) \qquad (1)$$

where 162 g/mol is the molar mass of an AGU, 148 g/mol is the net increase in the mass of an AGU for each phthalyl substituted, and n_{COOH} is the amount of COOH calculated according to equation (2):

$$n_{COOH}=(V_{NaOH}\times C_{NaOH}-V_{HCl}\times C_{HCl})/2 \qquad (2)$$

Characterization of cellulose phthalate

The cellulose phthalate was evaluated by FT-IR and solid-state CP/MAS ^{13}C NMR spectroscopy. FT-IR spectra were recorded on 1% finely ground samples in KBr pellets using an FT-IR spectrophotometer (Nicolet 510). Thirty-two scans were taken of each sample over the range of 4000-400 cm^{-1} at a resolution of 2 cm^{-1} in the transmission mode. The solid-state CP/MAS ^{13}C NMR spectra were obtained using a Bruker DRX-400 spectrometer at the frequency of 100 MHz with 5 mm MAS BBO probe. Acquisition time, delay time and proton 90^o pulse time were of 0.034 s, 2 s and 4.85 s, respectively. Each spectrum was recorded from an accumulation of 5000 scans. Thermal stability of cellulose phthalate was assessed using TG-DTA on a simultaneous thermal analyzer (SDT Q600, TA Instruments). The sample weighed between 6 and 10 mg. The scans were run from 25 °C to 500 °C at a rate of 10 °C/min under nitrogen flow.

RESULTS AND DISCUSSION

Synthesis of cellulose phthalate with ultrasonic assistance

As shown in Table 1, ultrasound has more favourable effects on the improvement of the DS of cellulose phthalate. Increasing the ultrasound irradiation time from 0 to 60 min led to an increase in DS from 0.76 to 1.41, which may be due to the efficient synergy of ultrasound and IL. The mechanism of cellulose dissolution in [Bmim]Cl involved hydrogen-bonding between the cellulose hydroxyl protons and the chloride ions of IL, weakening the intra- and inter-molecular hydrogen bonds of the cellulose chains.[21] Due to the non-volatility of the IL and cellulose, the cavitation bubbles generated by ultrasound contain only vapour of phthalic anhydride. In this case, the disadvantages of solvent vapour, such as retarding the sonochemical process, limiting the efficiency of cavitation and decreasing the selectivity, could be avoided. The cavitation bubbles in the reaction system increase the intensity of cavitational collapse of phthalic anhydride, then enhance mass and heat transfer, facilitating the reaction of cellulose and phthalic anhydride in IL. Similar results were obtained in the synthesis of 1,8-dioxo-octahydro-xanthene derivatives with the application of ultrasound.[24] These studies showed that the excellent yields could be explained by the 'hot spot' model of the cavitation phenomenon resulting in enhancing reaction rates, selectivity and yields of 1,8-dioxo-octahydro-xanthene derivatives. Raising the reaction temperature from 95 °C to 120 °C resulted in an increase in DS from 1.01 to 1.49, suggesting that a higher temperature would enhance the phthalation reaction. Increasing the molar ratio of phthalic anhydride/AGU in cellulose from 2:1 to 3:1 also led to a DS increment from 1.31 to 1.37.

Table 1

DS of cellulose phthalate using BmimCl as solvent

Phthalation conditions				Cellulose phthalate	
Ultrasonication time (min)	Temperature (°C)	Molar ratio[a]	Reaction time (min)	Sample no.	DS
0	105	3:1	50	1	0.76
15	105	3:1	50	2	1.18
30	105	3:1	50	3	1.29
45	105	3:1	50	4	1.37
60	105	3:1	50	5	1.41
45	95	3:1	50	6	1.01
45	100	3:1	50	7	1.16
45	110	3:1	50	8	1.47
45	120	3:1	50	9	1.49
45	110	2:1	50	10	1.31
45	110	4:1	50	11	1.48
45	110	5:1	50	12	1.49
45	110	6:1	50	13	1.49
45	110	3:1	30	14	1.01
45	110	3:1	40	15	1.23
45	110	3:1	60	16	1.52
45	110	3:1	70	17	1.56

[a] Molar ratio of phthalic anhydride/AGU in cellulose

However, with a further increase of molar ratio from 3:1 to 6:1, the DS of the product rose only slightly. Thus, excess phthalic anhydride had no significant effect on the phthalation rate of cellulose in [Bmim]Cl.

Prolonging the reaction duration from 30 to 70 min led to an increase in DS from 1.01 to 1.56. This was a direct consequence of the increased reaction time on the diffusion of phthalic anhydride and cellulose.

FT-IR spectra

FI-IR spectra of unmodified cellulose and cellulose phthalate with ultrasonic assistance are shown in Fig. 1.

Table 2

Relative intensity ratio of characteristic bands in FT-IR of modified cellulose with ultrasound treatment

Ratio of band absorption	Ultrasonication time, min		
	0	15	30
I1726/I1641	0.76±0.02	1.12±0.03	1.25±0.01
I1168/I1641	1.02±0.02	1.24±0.01	1.30±0.02

The characteristic peaks at 3411, 1641, 1070 and 892 cm^{-1} are attributed to hydroxyl groups, bending mode of the absorbed water, C-O-C pyranose ring and β-glucosidic linkages, respectively.[25]

Compared with cellulose, spectrum a of cellulose phthalate provides evidence of phthalation by showing the presence of two important peaks at 1726 cm^{-1} for carbonyl group in carboxyl and ester, and at 1168 cm^{-1} for C-O antisymmetric stretching.[26] An increase in ultrasound time from 10 min (spectrum b), to 20 min (spectrum c) led to an increment in the intensities of the bands at 1726 cm^{-1}, and 1168 cm^{-1}, indicating enhanced phthalation efficiency of cellulose with ultrasound irritation. The relative intensity ratio of characteristic bonds in the FT-IR of modified cellulose was also calculated in order to describe the effect of ultrasound treatment (Table 2). It can be seen that both ratios of band absorption (I1726/I1641 and I1168/I1641) increase with the increment of ultrasound time, which indicates enhanced phthalation efficiency of cellulose with ultrasound irritation.

Solid-state CP/MAS ^{13}C NMR spectra

In the present study, the ultrasound initiated phthalation reaction of cellulose was also studied by solid-state CP/MAS ^{13}C NMR spectroscopy, and the spectra of unmodified cellulose and cellulose phthalate are shown in Fig. 2. In spectrum a, the noticeable signals of carbohydrate moiety at 105.4 ppm (C-1), 89.1 ppm (C-4 of crystalline cellulose), 82.6 ppm (C-4 of amorphous cellulose), 74.7 ppm (C-5), 72.8 ppm (C-2 and C-3), 63.5 ppm (C-6 of crystalline cellulose), and 61.4 ppm (C-6 of amorphous cellulose) are all observed.[27]

In spectrum b, the signals at 89.1 ppm and 63.5 ppm disappeared, suggesting the complete disruption of the cellulose crystalline structure caused by dissolution and functionalization.[28] Apparently, the intensity of the signals of C-6, C-2 and C-3 decreased, which indicated the phthalation reaction occurred at free hydroxyl groups of C-6, C-2 and C-3. The presence of the signals of 171.5 ppm (carboxylic group) and 124.5 ppm (benzene ring) also provided evidence of phthalation, which indicated that the reaction shown in Scheme 1 did occur.

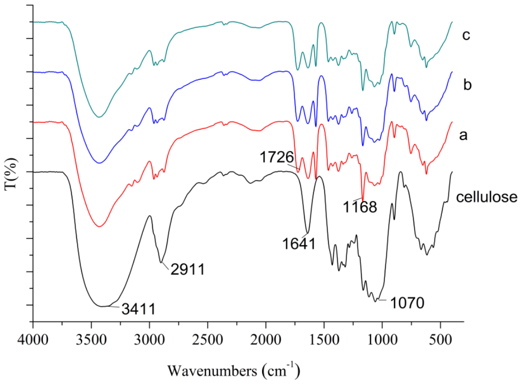


Figure 1: FT-IR spectra of cellulose, cellulose phthalate prepared at ultrasonication time of 0 min (spectrum a, DS = 0.74), 15 min (spectrum b, DS = 1.18), 30 min (spectrum c, DS = 1.29)

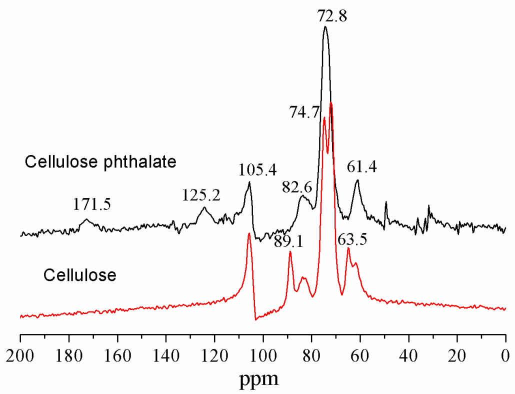
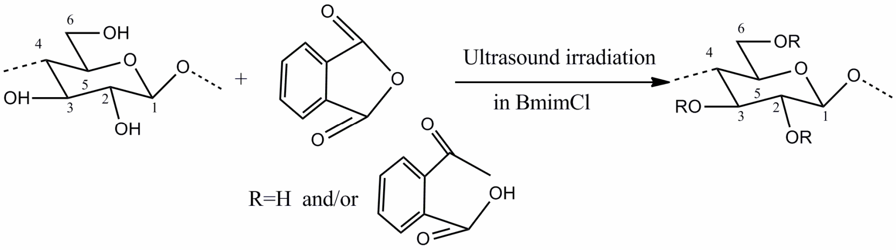


Figure 2: CP MAS ^{13}C NMR spectra of unmodified cellulose (spectrum a) and cellulose phthalate sample (spectrum b, DS = 1.01)



Scheme 1: Reaction of cellulose with phthalic anhydride in [Bmim]Cl under ultrasound irradiation

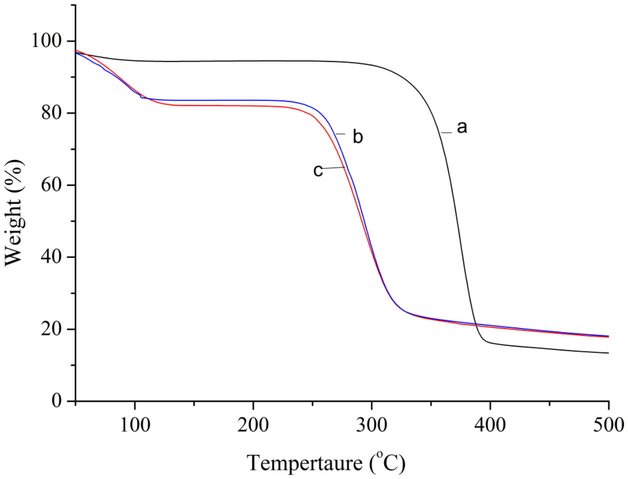


Figure 3: Thermal analysis of unmodified cellulose (spectrum a) and cellulose phthalate sample (spectrum b, DS = 1.29; spectrum c, DS = 1.37)

Thermal analysis

The effect of ultrasound-assisted phthalation in IL on the thermal behavior of cellulose was also studied by TGA under nitrogen flow (Fig. 3). The unmodified cellulose started to decompose at 304 °C, while the cellulose phthalates began to decompose at 255 °C (spectrum b) 243 °C (spectrum c), respectively. At 50% weight loss, the decomposition temperature occurred at 381 °C for unmodified cellulose, 306 °C (spectrum b) and 300 °C (spectrum c) for cellulose phthalate, suggesting the thermal stability of cellulose phthalate increased with decreasing value of DS, which was lower than that of native cellulose. The decrease of thermostability of cellulose phthalate could probably be attributed to free carboxyl groups attached to the cellulose derivative and partial degradation of macromolecular cellulose.

CONCLUSION

In conclusion, the cellulose phthalates were successfully synthesized in [Bmim]Cl with ultrasonic assistance. The DS of cellulose derivatives ranged from 0.76 to 1.56 and increased with the ncrement of ultrasonication time from 15 to 60 min, reaction time from 30 to 70 min, reaction temperature from 90 to 120 °C, and the molar ratio of phthalic anhydride/AGU in cellulose in a range from 2:1 to 6:1. FT-IR and solid-state CP/MAS ^{13}C NMR spectroscopies provided detailed evidence of phthalation. The thermal stability of cellulose phthalate decreased with chemical modification.

The present research focused on the efficient utilization of agricultural residues to reduce the environmental pollution caused by carbon dioxide emission. Typical cellulose, separated from SBP, was used as a material to study the combined effect of ILs and sonication on the phthalation of cellulose, for obtaining derivatives with special properties. It may be useful to researchers seeking more efficient ways of modifying cellulose, especially from less standard sources.

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