

DMAP-CATALYZED PHTHALYLATION OF CELLULOSE WITH PHTHALIC ANHYDRIDE IN [bmim]Cl

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It has been generally accepted that some ionic liquids are good media for homogeneous functionalization of cellulose. However, phthalylated cellulosic derivatives prepared in ionic liquids without any catalyst have lower DS as compared to the acetylated ones. In order to prepare the phthalylated cellulosic derivatives with higher DS, chemical modification of sugarcane bagasse cellulose with phthalic anhydride using ionic liquid 1-butyl-3-methylimidazolium chloride ([bmim]Cl) as a solvent and 4-dimethylaminopyridine (DMAP) as a catalyst has been examined. The results indicated that DMAP could enhance the reaction efficiency. The native cellulose and cellulose phthalates were characterized by FT-IR, solid-state CP/MAS ¹³C NMR, and thermogravimetric analysis. The results from FT-IR and solid-state CP/MAS ¹³C NMR analyses indicated that the phthalylation between cellulose and phthalic anhydride was successfully achieved. In addition, it was found that the thermal stability of the cellulose phthalates decreased upon chemical modification.

Keywords: Cellulose; Ionic liquid; Phthalylation; DMAP

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INTRODUCTION

In recent years, utilization and development of cellulose has drawn much attention around all over the world because of its excellent properties such as sustainability as a feedstock, non-toxicity, biodegradability, and functionality (Pandey et al. 2000; Focher et al. 2001; Richardson et al. 2003; Liu et al. 2007a). However, the full potential of cellulose has not been exploited (Zhu et al. 2006). One of the reasons is due to its insolubility in water or common organic solvents, a factor that is mainly responsible for its limited application.

Since Swatloski et al. (2002) found that ionic liquids including 1-butyl-3-methylimidazolium chloride ([bmim]Cl) could be used as a non-derivatizing solvent for cellulose, the research on ionic liquids as solvents for cellulose has been blooming. Now, some ionic liquids such as [bmim]Cl have been used as solvent for cellulose dissolution (Swatloski et al. 2002; Zhang et al. 2005; Heinze et al. 2005; Fukaya et al. 2008) and reaction media for cellulose modification (Liu et al. 2007a; Wu et al. 2004; Liu et al. 2006; Barthel et al. 2006; Schluffer et al. 2006; Erdmenger et al. 2007; Liu et al. 2007b; Fidale et al. 2009; Mormann et al. 2009; Zhang et al. 2009; Gericke et al. 2009). As reaction media for cellulose functionalization, ionic liquids provide a homogeneous phase for cellulose, which results in uniform and stable products (El Seoud et al. 2000; Liu et

al. 2009). At present, most researchers in the area of chemical modification of cellulose focus on the acetylation of cellulose in ionic liquids because of easier reaction of cellulose with acetic anhydride or acetyl chloride. Both Wu et al. (2004) and Fidale et al. (2009) successfully prepared the acetylated cellulose with higher DS ($DS > 2$) in ionic liquid 1-allyl-3-methylimidazolium chloride ([amim]Cl) and [bmim]Cl under mild reaction conditions without any catalyst. The order of reactivity of hydroxyl groups in cellulose was found to be $C6-OH > C3-OH > C2-OH$ (Wu et al. 2004; Schlufter et al. 2006). Barthel et al. (2006) prepared the fully substituted cellulose derivatives in [bmim]Cl with the presence of the pyridine. Moreover, ionic liquids can also be used as homogeneous reaction media for cellulose tritylation (Zhang et al. 2009), carbanilation (Barthel et al. 2006; Schlufter et al. 2006), and phthalylation (Liu et al. 2007b). Compared with cellulose acetylation, other homogeneous modifications of cellulose in ionic liquids only result in cellulose derivatives with low DS.

The monoester products of cellulose with cyclic anhydrides such as phthalic anhydride have been widely used in various applications such as water-absorbents for soil in agriculture, natural absorbents for the removal of heavy metal ions in waste water treatment, medicine for drug delivery systems, and thermoplastic materials (Hadano et al., 2003; Yoshimura et al., 2006). More importantly, they are key precursors to prepare derivatives by regioselective and quantitative chemical modification (Kurita et al. 2000; Liu et al. 2004). They provide a reactive site upon which further modification (Motawie and Sadek 1999; Nagaveni et al. 2005) for other potential utilizations such as in pharmaceutical industries is possible. In our lab, homogeneous phthalylation of cellulose were achieved without any catalyst (Liu et al. 2007b). However, cellulose phthalylation was more difficult than acetylation in ionic liquid, and the products with low DS were obtained under mild reaction conditions. Pyridine and 4-dimethylaminopyridine (DMAP) are outstanding nucleophilic basic catalyst for the acetylation of alcohols, amines, phenols and enolates (Höfle et al. 1978; Scriven 1983; Hill et al. 2000; Grondal 2003; Sakakura et al. 2007). Compared with pyridine, DMAP shows higher stability and stronger basicity. Connors and Albert (1973) found that DMAP had a specific catalytic activity about 10^4 times greater than that of pyridine. Because of the same function group (hydroxyl group) in alcohols and cellulose, we wonder whether DMAP is also a good catalyst for modification of cellulose. In this study, we have prepared cellulose phthalates with phthalic anhydride in ionic liquid [bmim]Cl in the presence of DMAP as a catalyst under various conditions. The modified celluloses were then characterized by DS, FT-IR, solid-state CP/MAS ^{13}C NMR, and thermogravimetric analysis.

EXPERIMENTAL

Materials

Sugarcane bagasse (SCB) was provided by a local factory (Guangzhou, China). It was dried in sunlight and then cut into piece to prepare 20-40 mesh size particles (450-900 μm). The cut SCB was further dried in an oven at 50 °C for 16 h before use. [bmim]Cl was obtained from the Chemer Chemical Co., Ltd., Hangzhou, China, and used

as received. All of other chemicals were of analytical-reagent grade and received from Guangzhou Chemical Reagent Factory, China.

Extraction of Cellulose from Sugarcane Bagasse

The dried SCB powder was first dewaxed with toluene-ethanol (2:1 v/v) in a Soxhlet apparatus for 6 h. Then the dewaxed SCB (100 g) was extracted with 2 L distilled water at 80 °C for 2 h. After filtration and drying, the insoluble residue was delignified with 100 g sodium chlorite in acidic solution (pH 4.0, adjusted by 10% acetic acid) at 75 °C for 1 h, and then 50 g sodium chlorite was added to further delignify for another 1 h. The residue (holocellulose) was subsequently washed with distilled water and ethanol, and then dried in oven. The holocellulose was further extracted with 10% KOH at 25 °C for 10 h to remove the hemicelluloses. After extraction, the residue (cellulose) was obtained by filtration, washed thoroughly with distilled water until the filtrate was neutral, then washed with 95% ethanol and dried in an oven at 50 °C for 16 h.

Preparation of Cellulose Phthalates in [bmim]Cl using DMAP as a Catalyst

For each trial, 0.2 g dried cellulose was added to 10 g [bmim]Cl in a three-necked flask. The mixture of cellulose/[bmim]Cl was purged with N₂ and stirred at 100 °C up to 10 h to guarantee the complete dissolution of cellulose. Then phthalic anhydride with or without DMAP was added to cellulose solution to synthesize the cellulose phthalate at the selected temperature for a specific period under N₂ atmosphere. After the required time, the mixture was slowly poured into isopropanol with stirring to stop the reaction. The solid was filtered out, washed thoroughly with isopropanol to remove contaminants such as ionic liquid, un-reacted anhydride, DMAP and by-products, and then dried in vacuum at 50 °C for 16 h.

Determination of the Degree of Substitution

The DS of cellulose phthalates was determined by the back-titration method (Stojanović et al. 2002). A certain weight of the sample was dispersed in 10 mL of NaOH by stirring at 50 °C for 30 min. Then 0.025 M HCl was used to back-titrate the excess of NaOH using phenolphthalein as the indicator. The titration was repeated at least three times, and the average value of the HCl volume was used for the calculations. The DS was obtained by using the following equation,

$$DS = \frac{162 \times n_{\text{COOH}}}{m - 148 \times n_{\text{COOH}}} \quad (1)$$

where 162 g/mol and 148 g/mol are the molar mass of an AGU and the net increase in the mass of an AGU for each phthaloyl substituted, respectively, m represents the weight of sample analyzed, and n_{COOH} is the amount of COOH calculated from the obtained value of the equivalent volume of known molarity HCl according to the following equation:

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

Characterization of the Native and Cellulose Phthalates

The FT-IR spectra of cellulose and cellulose phthalates were recorded on an FT-IR spectrophotometer (Nicolet 510) from finely ground sample (1%) in KBr pellets in the range $4000\text{--}400\text{cm}^{-1}$ with a resolution of 2 cm^{-1} in the transmission mode.

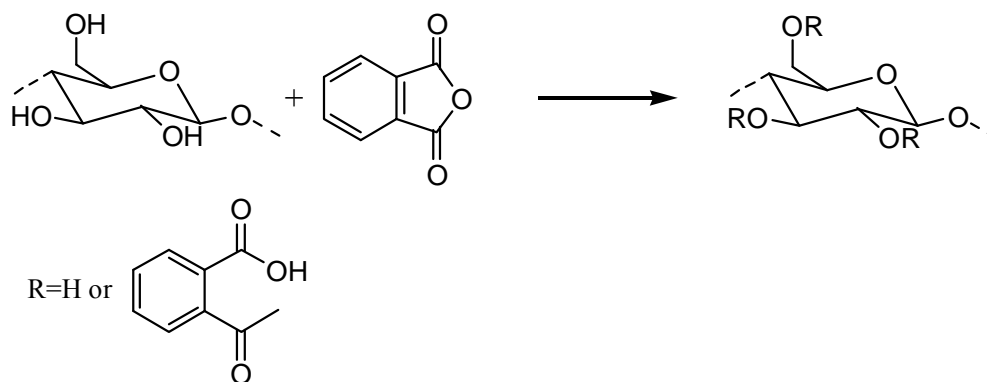
The solid-state CP/MAS ^{13}C -NMR spectra of unmodified cellulose and phthalylated cellulosic preparations were recorded on a Bruker DRX-400 spectrometer at the frequency of 100 MHz with 5 mm MAS BBO probe. Acquisition time was 0.034 s. The delay time was 2 s, and the proton 90° pulse time 4.85 μs . Each spectrum was obtained with an accumulation of 5000 scans.

Thermal stability of cellulose and cellulose phthalates were performed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (SDT Q600, TA Instrument). The sample weighed between 8 and 12 mg. The scans were run from room temperature to $550\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}$ per minute under nitrogen flow.

RESULTS AND DISCUSSION

Modification and the Degree of Substitution

Scheme 1 shows the reaction of phthalic anhydride with cellulose. In our previous work, phthalylation of cellulose was carried out in ionic liquid, which resulted in a much lower degree of substitution under mild reaction conditions (Liu et al. 2007b). Therefore, a suitable solvent or catalyst should be added to the reaction system to reduce the activation energy or enhance the accessibility of the reactive hydroxyl groups of cellulose to the reactants (Khalil et al. 1995). Pyridine and DMAP are common effective nucleophilic basic catalyst for the esterification of hydroxyl (Hill et al. 2000; Sakakura et al. 2007). Compared with pyridine, DMAP shows higher stability, stronger basicity and greater catalytic ability. Therefore, DMAP is chosen as a basic catalyst for cellulose. In the present study, we studied the phthalylation reaction of cellulose with phthalic anhydride in ionic liquid using DMAP as a catalyst to improve modification efficiency. Table 1 shows the various conditions of the phthalylation of cellulose.



Scheme 1. The reaction of phthalic anhydride with cellulose

Table 1. The Degree of Substitution (DS) of Cellulose Phthalate

Cellulose concentration	Phthalylation conditions			Cellulose phthalate	
	DMAP/phthalic anhydride (%)	Time (min)	Temperature (°C)	Sample no.	DS
2%	0	80	60	1	0.28
2%	1	80	60	2	0.88
2%	3	80	60	3	1.11
2%	5	80	60	4	1.31
2%	8	80	60	5	0.85
2%	15	80	60	6	0.69
2%	5	80	30	7	0.77
2%	5	80	45	8	0.97
2%	5	80	90	9	0.56
2%	5	80	120	10	0.44
2%	5	70	60	11	0.69
2%	5	90	60	12	0.75
2%	5	100	60	13	0.56
2%	5	110	60	14	0.36

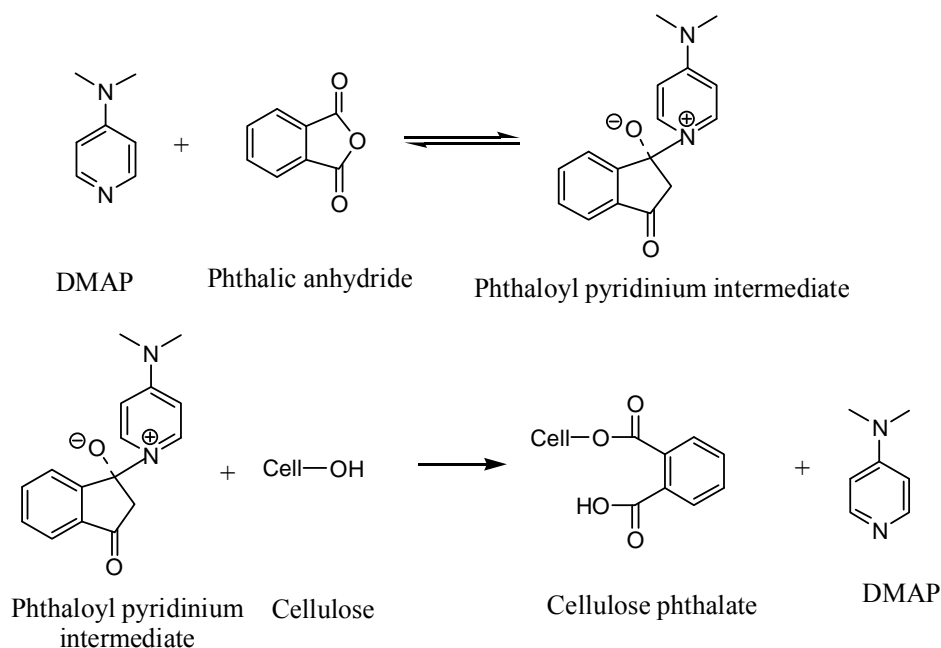
The molar ratio of phthalic anhydride to anhydroglucose in cellulose was 4:1.

The effect of DMAP dosage on DS of cellulose derivatives is given in samples 1-6 in Table 1. The reaction was conducted at 80 °C for 60 min with 2.0% cellulose and a molar ratio of phthalic anhydride/AGU 4:1. As shown in Table 1, the DS of cellulose phthalate obtained without any catalyst was only 0.28. However, with the increase of DMAP dosage (based on phthalic anhydride) from 0 to 1%, 3% and 5% led to a significant increment of the DS of products from 0.28 to 0.88, 1.11 and 1.31, respectively. Obviously, a certain dosage of DMAP is one of the most important factors for the reaction, which has great effect on the DS of cellulose phthalates. However, further increase in the DMAP dosage from 5% to 15% led to a decrement in DS from 1.31 to 0.69. This result indicated that 5% was the optimum dosage for catalyzed phthalylation under the conditions used.

The possible reaction of the DMAP-catalyzed esterification of cellulose with phthalic anhydride is shown in Scheme 2. The mechanism of cellulose phthalylation with DMAP as a catalyst is considered to be a nucleophilic substitution reaction (Bhandari et al. 2002). In the substitution reaction, phthalic anhydride reacts with DMAP to form phthaloyl pyridinium intermediate. This intermediate can attack hydroxyl groups of cellulose more easily than phthalic anhydride. Because of the tendency of hydroxyl oxygen of cellulose to link with carboxyl group, DMAP is eliminated for the next cycle of catalyzed reaction.

The reaction time and temperature also have important effects on the DS of products, as shown in samples 4 and 7-14 in Table 1. The DS of cellulose derivatives increased as the reaction time was raised from 30 to 60 min. It reached 0.77 within 30 min, 0.97 within 45 min, and 1.31 within 60 min. The reason for this increment of phthalylation by prolonging the reaction time was due to the favorable effect of time on absorption of the reactants between the phthalic anhydride and cellulose (Hill et al. 1998). However, as the reaction time further increased from 60 to 120 min, the DS of products decreased from 1.31 to 0.44, which indicated that a sufficient time did not result

in further increase in the phthalylation. The reason may be due to the cleavage of the ester bond with phthalic acid, by-product yielded during the reaction (Jayakumar et al. 2000). These results were in accordance with our previous study (Liu et al. 2007a). Therefore, 60 min was considered as optimum reaction time under the reaction conditions given.



Scheme 2. Proposed mechanism for the phthalylation of cellulose with phthalic anhydride in the presence of DMAP

The DS of cellulose phthalates increased from 0.69 to 1.31 with the increase of reaction temperature from 70 to 80 °C. This affect indicates that a higher temperature had a positive effect on the molecule motion and collisions of phthalic anhydride with hydroxyl, which led to the increase of cellulose macroradicals and thus enhanced the reaction rate (Yoshimura et al. 2006). However, further increase in the reaction temperature from 80 °C to 110 °C led to a decrease in the DS from 1.31 to 0.36, which probably was due to the formation of by-product and degradation of cellulose and cellulose derivatives at a relatively higher reaction temperature. This was a satisfactory result due to less energy cost and less degradation of cellulose derivatives under relatively lower temperature.

FT-IR Spectra

FT-IR spectroscopy is one of the most used technologies to prove the esterification of cellulose. The FT-IR spectra of unmodified cellulose (spectrum a) and cellulose phthalate sample 3 (spectrum b) are given in Fig. 1. Compared to spectrum a, the presence of the peaks at 1719, 1579, and 747 cm^{-1} in spectrum b provided evidence of the phthalylation. The band at 1719 cm^{-1} is due to the absorption of carbonyl group in carbonyl and ester (Gu et al. 1998). The peak at 1579 cm^{-1} is attributed to the antisymmetric stretching of carboxylic anions (Chang and Chang 2001). The absorption

at 747 cm^{-1} corresponds to out-of-plane C-H bending of the ortho disubstituted benzene. Moreover, the intensity of the absorption band at 1289 cm^{-1} for C-O symmetric stretching in ester and carboxyl also increased. These changes indicated that carboxylic groups and phthaloyl groups were introduced into the cellulosic molecules and esterification reaction occurred. In addition, the absence of peaks at 1850 and 1780 cm^{-1} in spectrum of cellulose phthalate confirmed that the product was free of the un-reacted phthalic anhydride (Gu et al. 1998).

Solid-State CP/MAS ^{13}C -NMR Spectra

To verify the chemical changes in the structure of the polymer, both native cellulose (spectrum a) and cellulose phthalate sample 4 (spectrum b) were further characterized by CP/MAS ^{13}C -NMR spectroscopy, and their spectra are illustrated in Fig. 2. The carbons of carbohydrate moiety are mainly shown in the region between 50 and 110 ppm. The signals at 101.9 (C-1), 85.9 (C-4 of crystalline cellulose), 80.3 (C-4 of amorphous cellulose), 71.9 (C-5), 68.6 (C-2 and C-3), 61.8 ppm (C-6 of crystalline cellulose) and 59.5 (C-6 of amorphous cellulose) are all observed in spectrum a (Fringant et al. 1996). Compared to spectrum a, the presence of the signals at 129.5 ppm for benzene ring and 170.6 ppm for carboxylic in spectrum b directly proved the evidence of phthalylation (Jeon et al. 1999). In addition, the absence of the signal at 85.9 ppm for C-4 of crystalline cellulose and the shift of the signal for C-6 from 61.8 ppm to 60.8 ppm in spectrum b indicated that the crystalline structure of the cellulose was disrupted during dissolution and modification.

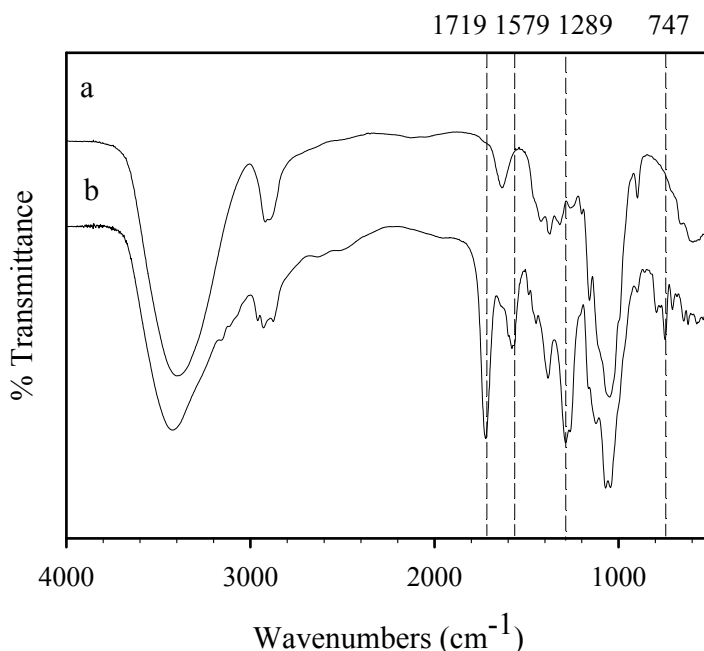


Fig. 1. FT-IR spectra of unmodified cellulose (spectrum a) and cellulose phthalate sample 3 (spectrum b)

Generally, the three free hydroxyl groups at C-6, C-2, and C-3 position are the main reactive sites in cellulose. As shown in Fig. 2, the intensity of the signals at 61.8

ppm for C-6 and 68.6 ppm for C-2 and C-3 decreased after phthalylation, which indicated that phthalylation reaction occurred at C-6, C-2, and C-3 positions.

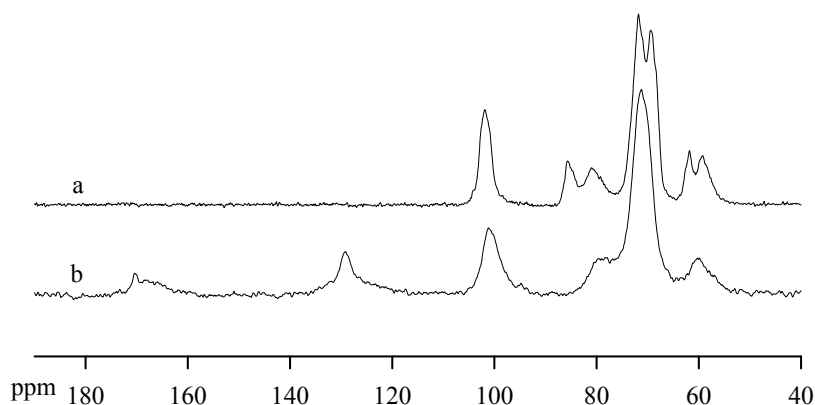


Fig. 2. Solid state CP/MAS ^{13}C -NMR spectra of unmodified cellulose (spectrum a) and cellulose phthalate sample 4 with DMAP as a catalyst (spectrum b)

Thermal Analysis

Thermogravimetry is one of the common techniques to characterize the thermal stability of polymers such as cellulose. The TGA and DTA thermograms of unmodified cellulose (a) and cellulose phthalate sample 6 (b) are given in Figure 3. Usually, the TGA curves are used to determine the weight loss of the products as it is heated, cooled or held isothermally. As shown in Fig. 3, unmodified cellulose and cellulose phthalate sample 6 started to decompose at 240 °C and 204 °C, respectively.

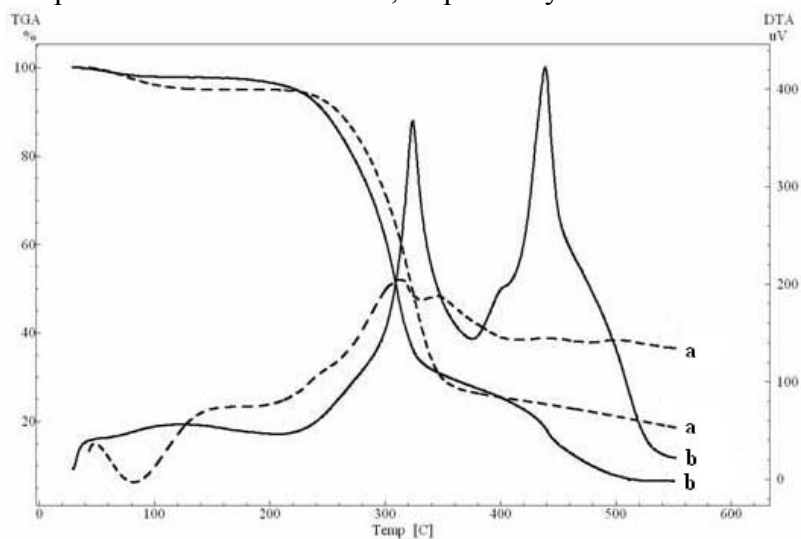


Fig. 3. Thermograms and their 1st derivatives of native cellulose (spectrum a) and cellulose phthalate sample 6 (spectrum b)

Beyond these temperatures, there was a sharp weight loss. Similarly, at 50% weight loss, the decomposition temperature occurred at 328 °C for native cellulose and 310 °C for cellulose phthalate sample 6, respectively. These data implied that the thermal

stability of cellulose phthalate decreased after dissolution and modification in ionic liquid. Similar result has been reported by Swatloski et al. (2002) and Liu et al. (2007a) during the dissolution and modification of cellulose in the ionic liquid. However, cellulose phthalate can still be used as novel and biodegradable absorbents for metal ions from waste water due to the thermal stability at 200 °C.

CONCLUSIONS

1. DMAP is an effective catalyst for cellulose phthalylation in the ionic liquid 1-butyl-3-methylimidazolium chloride. The DS of cellulose phthalates increased from 0.28 without any catalysts to the range of 0.36-1.31 under the catalytic conditions given.
2. Under the conditions given, the optimum reaction time, reaction temperature, and DMAP dosage (based on phthalic anhydride) is 60 min, 80 °C, and 5%, respectively.
3. The possible mechanism of DMAP-catalyzed phthalylation in ionic liquid is proposed as the formation of intermediate complex of phthalic anhydride with DMAP.
4. The FT-IR and solid-state CP/MAS ¹³C NMR spectra confirmed that phthalylation of hydroxyl groups in cellulose occurred at the C-6, C-3, and C-2 position. The thermal stability of cellulose phthalate decreased upon chemical modification.

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