MODIFICATION OF SUGARCANE BAGASSE WITH ACETIC ANHYDRIDE AND BUTYRIC ANHYDRIDE IN IONIC LIQUID 1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE

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Bagasse acetate butyrates were prepared homogeneously in 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) ionic liquid from ball-milled sugarcane bagasse by acylation with acetic anhydride and butyric anhydride. The parameters, including reaction temperature, reaction time, feeding method of adding anhydrides, the dosage of total anhydrides to SCB, and the molar ratio of acetic anhydride to butyric anhydride, were considered, and the extent of acylation was measured by weight percent gain (WPG). The results showed the positive effects of reaction duration and total anhydride dosage on WPG and the negative effects of reaction temperature and molar ratio of AA/BA on WPG. The feeding method of acetylation after butyrylation resulted in the increased WPG compared with acetylation before butyrylation. FT-IR and ^{1}H–^{13}C correlation 2D NMR (HSQC) studies provided evidence for acylation. The bagasse acetate butyrates showed increased thermal stability after acylation. This study provides a new way for high value-added utilization of renewable lignocellulosic biomass.

Keywords: Sugarcane bagasse; Esterification; Ionic liquid; Anhydride

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INTRODUCTION

One of the major current challenges to the chemical industry is the efficient utilization of renewable resources for the production of performance materials, platform chemicals, and biofuels (Pandey *et al*. 2000; Orlando *et al*. 2002). Biomass is the most abundant renewable resource, with an estimated global production of around 1.1×10^{11} tons per year. Lignocellulosic biomass, such as agricultural residues, forestry wastes, waste paper, and energy crops represents a potentially sustainable source (Zhang *et al*. 2007; Ogaki *et al*. 2009). During the past few decades, much effort has been devoted to increasing the utilization of lignocellulosic biomass to create biofuels, biochemicals, biocomposites, and a host of other bioproducts to replace fossil-based products (Mohanty *et al*. 2000; FitzPatrick *et al*. 2010; Zhang *et al*. 2010).

Agricultural residues are mixtures of complex polysaccharides and lignin. The most abundant and reactive groups attached to these components are hydroxyl groups. A large number of modification reactions for hydroxyl groups in the isolated components

have been reported (Grondahl *et al*. 2003; Wu *et al*. 2004; Memmi *et al*. 2005; Potthast *et al*. 2006). The derived components with new functionality obtain increased value. During the past four decades, the heterogeneous chemical modification of lignocellulose has been extensively studied to improve the properties of lignocellulose-derived products, including dimensional stability, resistance to decay, photostability, hydrophobicity, and compatibility with thermoplastics. In this area, carboxylic (fatty) acid esters of lignocelluloses acylated with linear anhydrides have shown to be highly attractive derivatives (Hill *et al*. 2000; Cao *et al*. 2011; Papadopoulos and Tountziarakis 2012). Compared with heterogeneous modification, homogeneous modification results in the more uniform and stable products. However, to homogeneously process lignocellulose into the desired products is believed to be an impossible task in lignocellulose research and development because of the intrinsic lack of solubility of lignocellulose in water, organic solvents, and even organic solvent systems.

More recently, due to their unique physicochemical properties, such as chemical and thermal stability, non-flammability, and immeasurably low vapor pressure, ionic liquids (ILs) have been considered the most potential green solvents in the future, which has attracted a great deal of scientific attention in many fields (Forsyth *et al*. 2002; Turner *et al*. 2003). The application of ionic liquids (ILs) as alternative solvents and reaction media for a wide variety of synthetic processes of the isolated component cellulose have been reported around the world (Wu *et al*. 2004; Heinze *et al*. 2005; Guo *et al*. 2009). More importantly, alkylimidazolium-based ionic liquids were reported as green solvents for wood in 2007 (Fort *et al*. 2007; Kilpelainen *et al*. 2007). This breakthrough opened up new horizons in the chemistry of lignocelluloses and provided a possibility for homogeneous modification of lignocellulose. Homogeneous acetylation, benzoylation, and carbanilation reactions of wood-based lignocellulosic materials was accomplished to produce the highly substituted lignocellulosic esters under mild conditions (Xie *et al*. 2007). Compared with the monoester, the mixed ester exhibits great potential for use as biofilm, biomembrane, biocomposite and other bioproducts with a number of advantages, such as excellent solubility, structural stability, light resistance, good leveling, and transparency. In this work, the homogeneous acylation of ball-milled sugarcane bagasse with acetic anhydride and butyric anhydride to produce mixed ester in ionic liquid 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) was studied. The parameters, including reaction temperature, reaction time, feeding method of adding anhydrides, the dosage of total anhydrides to SCB, and the molar ratio of acetic anhydride to butyric anhydride were investigated. The resulting bagasse acetate butyrates were then characterized by Fourier transform infrared (FT-IR) and ^{1}H–^{13}C correlation 2D NMR (HSQC), as well as thermal analysis.

EXPERIMENTAL

Materials

Sugarcane bagasse (SCB) was obtained from a local factory (Guangzhou, China). It was dried in sunlight and then cut into small pieces. The cut SCB was ground and screened to prepare 40 to 60 mesh size particles (450 to 900 μm) and dried in a cabinet

oven with air circulation for 16 hrs at 55 °C. The dried SCB was further pulverized with a vibratory ball mill for 16 hrs in a stainless steel jar.

Ionic liquid [C_4mim]Cl was purchased from Cheng Jie Chemical Co., Ltd., Shanghai, China, and used as received. All other chemicals were of A.R. grade and purchased from Guangzhou Chemical Reagent Factory, China.

Dissolution of SCB in [C_4mim]Cl

Dried SCB powder was added to a three-necked flask containing [C_4mim]Cl, and the mixture was stirred at 140°C for 2.5 hrs under a nitrogen atmosphere to guarantee the complete dissolution of SCB. The complete dissolution of SCB in [C_4mim]Cl was monitored with the dark eyeshot of polarizing light microscope.

Homogeneous Acylation with Acetic Anhydride and Butyric Anhydride

Bagasse acetate butyrates were prepared in [C_4mim]Cl with acetic anhydride (AA) and butyric anhydride (BA) under various conditions in Table 1. To the SCB/[C_4mim]Cl solution, one anhydride was carefully introduced with agitation at the required temperature under a N_2 atmosphere. After the required time, the other anhydride was carefully added under vigorous stirring to the resulting solution. After the required time, the solution was slowly poured into ethanol with vigorous agitation. The solid residues were filtered out and washed thoroughly with ethanol to eliminate [C_4mim]Cl, un-reacted anhydrides, and by-products. The resulting products were freeze-dried for 48 hrs. The yield of the products was measured by weight percent gain (WPG) based on the dried SCB, according to the following equation:

$$WPG = ([\text{Mass of products} - \text{SCB mass}]/\text{SCB mass}) \times 100 \quad (1)$$

To reduce errors and confirm the results, each experiment was performed at least in duplicate under the same conditions; WPG represents the average value.

Characterization of the Native and Modified SCB

FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet 510) using a KBr disc containing 1% of finely ground samples. Thirty-two scans were taken for each sample, employing a resolution of 2 cm^{-1} in transmission mode in the range 4000 to 400 cm^{-1}.

The ^1H–^{13}C correlation 2D NMR (HSQC) spectra were recorded from 90 mg of modified SCB in 0.5 mL of DMSO-d_6 on a Bruker DRX–400 spectrometer with a 5 mm multinuclear probe. Acquisition time was 0.082 s. The delay time was 2 s.

Thermal analysis of the native and modified SCB was performed using thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) on a thermal analyzer (SDT Q600, TA Instrument). The sample weighed between 10 and 15 mg. The scans were run from room temperature to 700 °C at a rate of 10 °C per minute under nitrogen flow.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on WPG

The acetylation and butyrylation of hydroxyl groups in SCB with the acid anhydrides can attach the acetyl and butyryl groups onto SCB, resulting in the production of a lignocellulosic mixed ester. In the present study, bagasse acetate butyrates were prepared homogeneously by acylation of SCB with AA and BA in ionic liquid [C_4mim]Cl, as described in Fig. 1. The extent of acylation was measured by WPG. Table 1 gives the effects of various conditions such as reaction temperature, reaction time, feeding method of adding anhydrides, the dosage of total anhydrides to SCB, and the molar ratio of AA to BA on the WPG of the modified SCB.

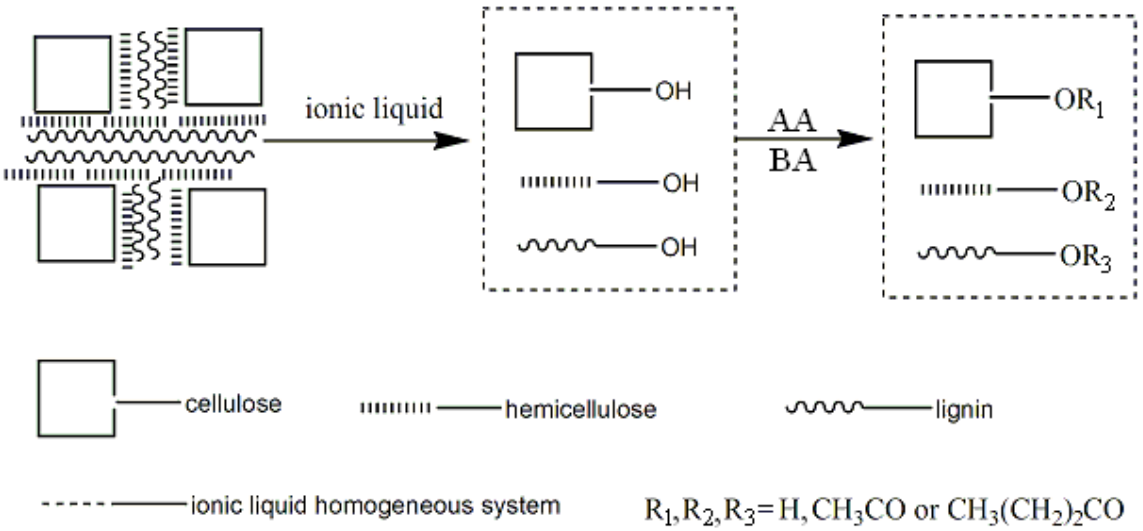

Fig. 1. Schematic representation of SCB dissolution and homogeneous esterification with acetic anhydride and butyric anhydride in [C_4mim]Cl

As can be seen from Table 1, holding the dosage of total anhydrides at 9.45 mL/g SCB, the molar ratio of AA/BA at 50/50, feeding method with acetylation before butyrylation, and reaction time for 60 min, an increase of the reaction temperature from 80°C (sample 1) to 90°C (sample 17), 100°C (sample 4), 110°C (sample 18), and 120°C (sample 7) resulted in a decrease in WPG from 19.75 to 17.72, 16.50, 13.55, and 9.30, respectively, indicating the detrimental effect of high temperature on acetylation and butyrylation of SCB in [C_4mim]Cl. Similarly, an increase of reaction temperature from 80°C to 100°C and 120°C led to a decrement in WPG from 26.60 (sample 2) to 21.25 (sample 5) and 13.15 (sample 8), respectively, with the molar ratio of AA/BA at 33/67 and the dosage of total anhydrides at 14.18 mL/g SCB, and a decrement in WPG from 30.60 (sample 3) to 25.80 (sample 6) and 17.25 (sample 9), respectively, with the molar ratio of AA/BA at 25/75 and total anhydride dosage at 18.90 mL/g. The decrease could be due to the reversible reaction of hydroxyl groups with anhydrides.

Keeping the molar ratio of AA/BA at 33/67, feeding method with acetylation before butyrylation, reaction temperature at 80°C, and reaction time for 60 min, increasing the total anhydride dosage from 5.70 (sample 10) to 8.55 (sample 11), 11.33

(sample 12), and 14.18 mL/g SCB resulted in an improvement of WPG from 3.10 to 18.05, 23.25, and 26.60, respectively. This favorable effect of anhydrides dosage on the bagasse acylation could be due to the greater availability of anhydride molecules in the proximity of the reactive hydroxyl groups in SCB at higher anhydride dosage.

Table 1. The WPG of SCB Acylated With Acetic Anhydride And Butyric Anhydride in [C_4mim]Cl under Various Conditions

Acylation conditions					Acylated SCB	
SCB/[C_4mim]Cl[a] (%)	T[b] (^{o}C)	Anhydrides/SCB[c] (mL/g)	Molar ratio[d]	Reaction time (min)	Sample No.[e]	WPG (%)
1	80	9.45	50/50	60	1	19.75
1	80	14.18	33/67	60	2	26.60
1	80	18.90	25/75	60	3	30.60
1	100	9.45	50/50	60	4	16.50
1	100	14.18	33/67	60	5	21.25
1	100	18.90	25/75	60	6	25.80
1	120	9.45	50/50	60	7	9.30
1	120	14.18	33/67	60	8	13.15
1	120	18.90	25/75	60	9	17.25
1	80	5.70	33/67	60	10	3.10
1	80	8.55	33/67	60	11	18.05
1	80	11.33	33/67	60	12	23.25
1	100	9.45	25/75	60	13	30.26
1	100	9.45	30/70	60	14	27.93
1	100	9.45	40/60	60	15	27.95
1	100	9.45	75/25	60	16	23.47
1	90	9.45	50/50	60	17	17.72
1	110	9.45	50/50	60	18	13.55
1	100	9.45	50/50	45	19	12.70
1	100	9.45	50/50	75	20	17.13
1	100	9.45	50/50	90	21	17.70
1	80	9.45	50/50	60	22	26.56
1	100	9.45	50/50	60	23	27.29
1	120	9.45	50/50	60	24	13.20

[a] SCB/[C_4mim]Cl by weight.
[b] Reaction temperature of acetylation and butyrylation of SCB in [C_4mim]Cl.
[c] Total anhydrides to SCB, expressed by acetic anhydride.
[d] Molar ratio of acetic anhydride (AA) to butyric anhydride (BA).
[e] Samples 1-21 were acetylated before butyrylation, and samples 22-24 were acetylated after butyrylation.

Data in Table 1 verified that prolonging the reaction duration had a positive effect on the WPG of acylated SCB. Keeping the reaction temperature at 100^{o}C, the molar ratio of AA/BA at 50/50, feeding method with acetylation before butyrylation, and the total anhydride dosage at 9.45 mL/g SCB (expressed by acetic anhydride), the WPG of bagasse acetate butyrate reached 12.70 within 45 min (sample 19), 16.50 within 60 min (sample 4), 17.13 within 75 min (sample 20), and 17.70 within 90 min (sample 21). This increment was a direct consequence of the favorable effect of reaction time on the

diffusion of anhydrides and the acylation of anhydrides with hydroxyl groups present in SCB.

The results of variation in the molar ratio of AA to BA are given in samples 13 to 16 in Table 1. Obviously, with the same dosage of the total anhydrides, the WPG of bagasse acetate butyrate decreased from 30.26 (sample 13) to 27.93 (sample 14), 27.95 (sample 15), and 23.47 (sample 16) with the increase in the molar ratio of AA/BA from 25/75 to 30/70, 40/60, and 75/25, respectively. This decrease could be due to the relatively higher net increase in the mass for butyrylation than acetylation. With the same total anhydride dosage, high AA/BA ratio indicated the high dosage of AA during acylation, suggesting that acetyl groups were more likely to be attached to SCB than butyryl groups, which resulted in the decreased WPG at the improved molar ratio of AA/BA.

A different feeding method of anhydrides also had important effects on the WPG of the mixed ester. As shown in Table 1, the WPG was 19.75 (sample 1), 16.50 (sample 4), and 9.30 (sample 7) with the feeding method of acetylation before butyrylation at 80, 100, and 120^{o}C, respectively. However, with the feeding method of acetylation after butyrylation under the same conditions, WPG was enhanced to 26.56 (sample 22), 27.29 (sample 23), and 13.20 (sample 24), respectively. The reason may be due to the relatively decreased efficiency of butyrylation with the increased chain length of anhydrides compared with acetylation. SCB was acetylated in the latter stage with the feeding method of acetylation after butyrylation, indicating that more hydroxyl groups were esterified, which resulted in the increased WPG.

FT-IR Spectra

Figure 2 shows the FT-IR spectra of unmodified SCB (spectrum 1) and bagasse acetate butyrate sample 1 (spectrum 2). The absorbances at 3488, 2872, 1748, 1637, 1508, 1462, 1421, 1375, 1237, 1166, and 1048 cm^{-1} present in spectrum 1 are associated with native bagasse. The strong band at 3488 cm^{-1} originates from the stretching of hydroxyl groups in unmodified bagasse. The absorption at 2872 cm^{-1} arises from C-H stretching. The band at 1637 cm^{-1} is principally associated with absorbed water. The small absorbances at 1508, 1462, and 1421 cm^{-1} correspond to the aromatic skeletal vibrations and ring breathing with C-O stretching in lignin. The bands at 1375, 1237, and 1166 cm^{-1} are attributed to the C-H bending, the symmetric stretching of C-O, and the antisymmetric stretching of C-O in ester. The strong peak at 1048 cm^{-1} arises from C-O-C pyranose ring skeletal vibration. In comparison, the spectrum of acylated SCB (spectrum 2) provides evidence of acetylation and butyrylation. The significantly decreased absorption of the band at 3488 cm^{-1} for hydroxyl groups indicated that the hydroxyl groups in SCB were acylated. The peaks at 1748 cm^{-1} for C=O stretching in ester, 1375 cm^{-1} for C-H bending, and 1237 cm^{-1} for C-O symmetric stretching in ester clearly increased. In addition, the absorption for C-H stretching appeared at 2969 cm^{-1}, indicating the new C-H was introduced into SCB. These changes suggested that the acetyl and butyryl groups were introduced into SCB, and the acylation reaction occurred, indicating the occurrence of acetylation and butyrylation reactions of SCB, as illustrated in Fig. 1. As expected, the absence of peaks at 1850 and 1780 cm^{-1} in spectrum 2 of the acylated SCB sample 1 confirmed that the products were free of the unreacted anhydrides.

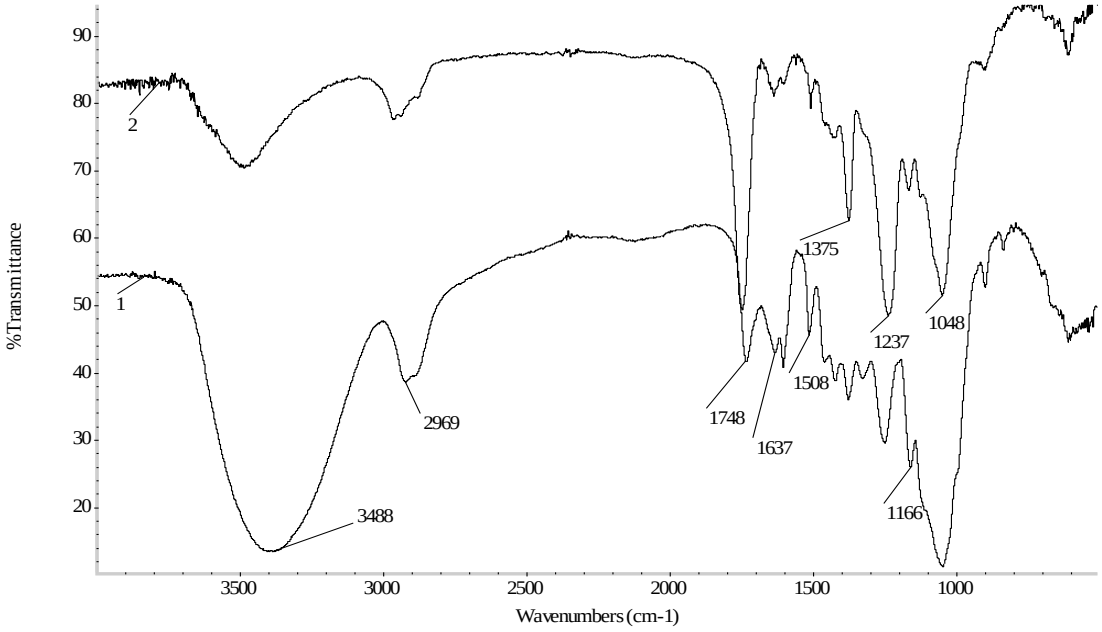

Fig. 2. FT-IR spectra of unmodified SCB (spectrum 1) and bagasse acetate butyrate sample 1 (spectrum 2)

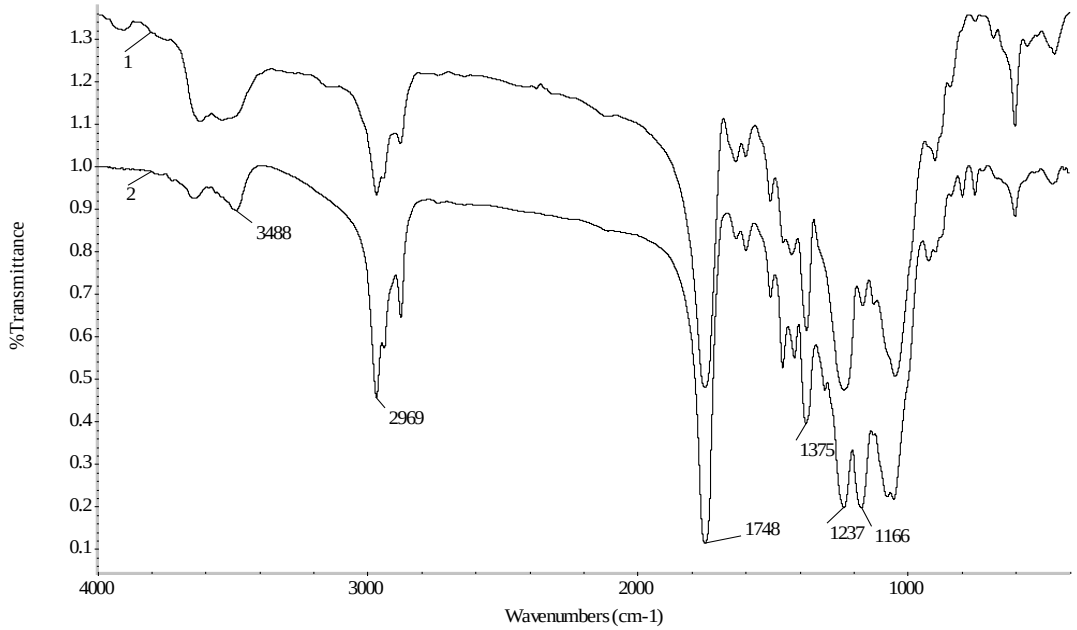

Fig. 3. FT-IR spectra of bagasse acetate butyrate samples 4 (spectrum 1) and 23 (spectrum 2)

The effects of reaction temperature, reaction duration, total anhydride dosage, and the molar ratio of AA/BA on the WPG were also investigated by the peak intensity of bagasse acetate butyrate samples (Figs. not shown). The intensities of the bands at 3488 cm^{-1} for O-H stretching, 2969 cm^{-1} for C-H stretching, 1748 cm^{-1} for C=O stretching in ester, 1375 cm^{-1} for C-H bending, and 1237 cm^{-1} for C-O symmetric stretching in ester changed corresponding to the WPG in Table 1, indicating the positive effects of reaction

duration and total anhydride dosage on WPG and the negative effects of reaction temperature and molar ratio of AA/BA on WPG. In addition, Fig. 3 shows the FT-IR spectra of bagasse acetate butyrate samples with different anhydride feeding method. As shown in Fig. 3, compared with spectrum 1 of acylated SCB sample 4 with the feeding method of acetylation before butyrylation, the intensity of the band at 3488 cm^{-1} for O-H stretching obviously decreased in spectrum 2 of sample 23 with the feeding method of acetylation after butyrylation; moreover, that at 2969 cm^{-1} for C-H stretching and 1748 cm^{-1} for C=O stretching in ester clearly increased, indicating that more hydroxyl groups in SCB were acylated with anhydrides with the feeding method of acetylation after butyrylation, which was paralleled to WPG in Table 1.

HSQC NMR

2D ^{1}H-^{13}C HSQC NMR is a powerful tool for qualitative and quantitative analysis of cell wall structure. It provides resolution of signals overlapping in the ^{1}H and ^{13}C NMR spectra and reveals the different linkages present in cellulose, hemicelluloses, and lignin (Villaverde *et al*. 2009). In the present study, the structure of bagasse acetate butyrate sample 7 dissolved in DMSO-d_6 was characterized with 2D ^{1}H-^{13}C HSQC spectroscopy. Bagasse acetate butyrate could be easily dissolved in DMSO-d_6, while native bagasse without modification could not be dissolved in DMSO-d_6. In order to avoid the overlapping of the primary signals, the 2D NMR spectrum is shown at high contour level to provide the well resolved correlations. Typically, methyl in acetyl group can easily be seen at δ_H/δ_c 1.95/19.08 ppm, and the strong correlations for C_α-H_α, C_β-H_β, and C_γ-H_γ in the butyryl group appears at δ_H/δ_c 2.31/34.10, 1.45/16.4, and 0.82/12.08 ppm, respectively. The presence of these correlations indicated that the acetyl and butyryl groups were successfully introduced into SCB.

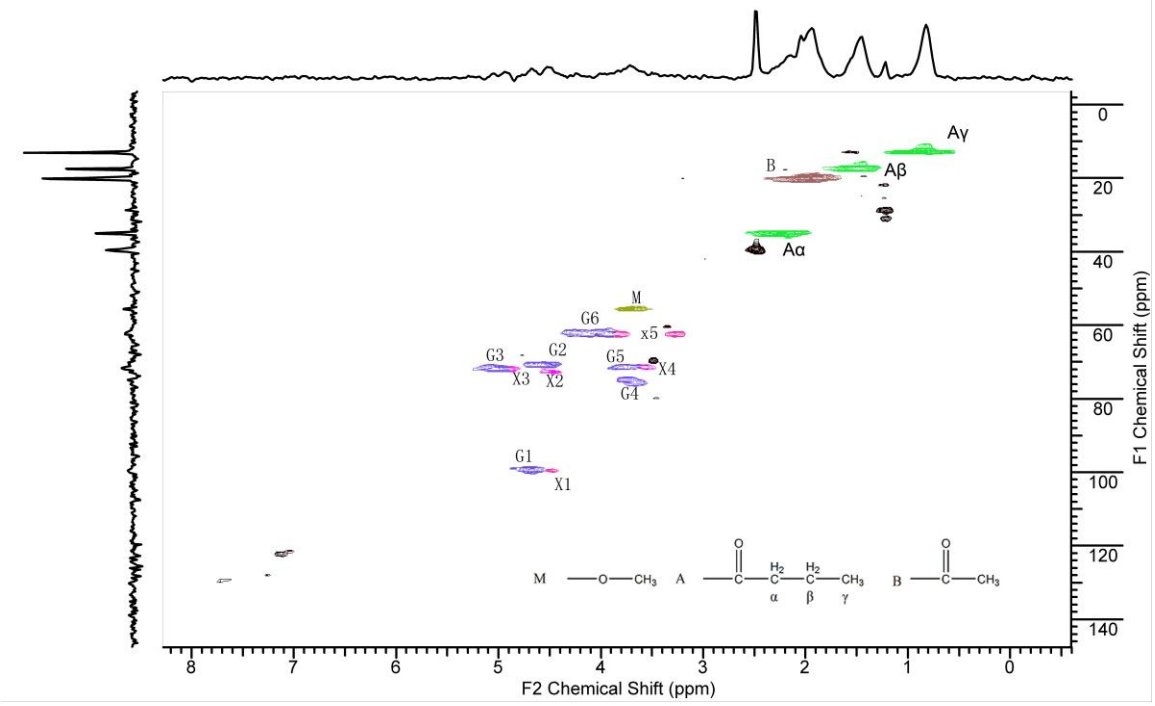

Fig. 4. HSQC spectrum of modified SCB sample 7

More importantly, many of the correlations in the range of δ_H/δ_c 2.5-5.5/50-120 ppm belong to the polysaccharide components. The anomeric C/H correlation for beta-D-glucosyl residues, which is mostly due to cellulose, appears at δ_H/δ_c 4.68/99.11 ppm (G1); that from beta-D-xylosyl residues in hemicelluloses appears at δ_H/δ_c 4.49/99.52 ppm (X1). Other anomeric C/H correlations are not detectable at present contour levels, which are observed at lower contour levels (not shown). Other correlations at δ_H/δ_c 4.51/69.50, 4.92/70.74, 3.75/74.03, and 3.82/70.53 ppm are assigned to H_2/C_2 (G2), H_3/C_3 (G3), H_4/C_4 (G4), and H_5/C_5 (G5) in beta-D-glucosyl residues, respectively, indicating the hydroxyl groups at C2 and C3 positions in cellulose were acylated. Those from H_2/C_2 (X2), H_3/C_3 (X3), and H_4/C_4 (X4) in beta-D-xylosyl residues in hemicelluloses appear at δ_H/δ_c 4.49/72.46, 4.88/71.47, and 3.74/74.68 ppm, respectively, indicating the hydroxyl groups at C2 and C3 positions in xylan were acylated. The signals at δ_H/δ_c 3.95 and 4.22/61.07 ppm are assigned to H_6/C_6 (G6) in beta-D-glucosyl (Glu) residues, indicating the hydroxyl group at C6 position in cellulose were acylated. Those at δ_H/δ_c 3.28 and 3.80/61.07 ppm relate to H_5/C_5 (X5) in beta-D-xylosyl residues in hemicelluloses. In addition, correlation for the lignin methoxyl group appears at δ_H/δ_c 3.68/54.69 ppm. The correlations for the aliphatic side chain in lignin are also detected and overlapped with those from carbohydrates at a lower contour level (Figure not shown).

In the aromatic region (δ_H/δ_c 6.0-8.0/100-140 ppm), the correlations for lignin are readily visualized in the spectrum. However, only 5- and 6-position correlations are detected at δ_H/δ_c 7.8/121.4 ppm at a high contour level because of the easier detectable correlations from carbohydrates and aliphatics.

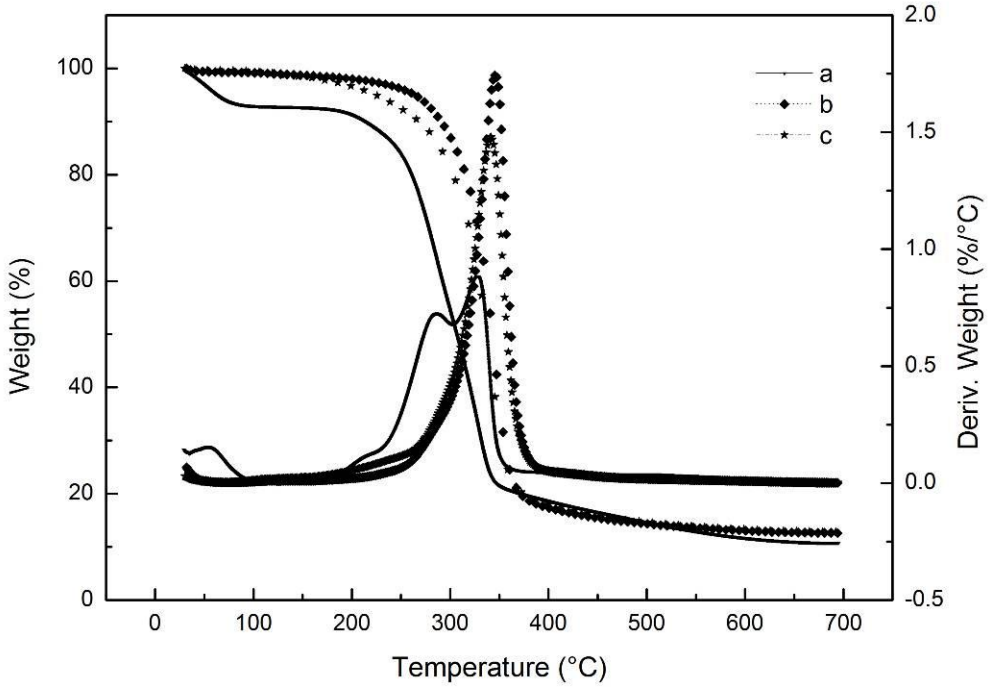

Fig. 5. Thermograms of unmodified SCB (a) and bagasse acetate butyrate samples 2(b) and 5(c)

Thermal Analysis

The effect of acylation with AA and BA on the thermal behavior of SCB was also studied by TGA in the range from room temperature to 700°C at a rate of 10°C per minute under nitrogen flow. Figure 5 shows the TGA and DTG curves of native bagasse and the acylated bagasse samples 2 and 5. Usually, the TGA curves are used to determine the weight loss of the samples as it is heated, cooled, or held isothermally. As shown in Fig. 5, a slight weight loss below 100°C was due to the elimination of absorbed water. The native bagasse started to decompose at 198°C, whereas the bagasse acetate butyrate samples 2 and 5 began to decompose at 202 and 207°C, respectively. At 50% weight loss, the decomposition temperature occurred at 292°C for native bagasse, 295°C for sample 2, and 315°C for sample 5. These increasing trends of decomposition temperature imply that the thermal stability of the bagasse was increased after acylation with AA and BA.

CONCLUSIONS

1. Bagasse acetate butyrate was homogeneously prepared from ball-milled SCB in ionic liquid 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) without any catalysts.

2. Under the conditions given, the WPG of acylated SCB ranged from 3.10 to 30.60. The WPG was improved with the increase of reaction duration and total anhydride dosage and was reduced with the increase of reaction temperature and molar ratio of AA/BA. The feeding method of acetylation after butyrylation resulted in increased WPG compared with acetylation before butyrylation.

3. The results from FT-IR and 2D ^{1}H-^{13}C HSQC NMR analyses confirmed the attachment of acetyl and butyryl groups into SCB.

4. The thermal stability of SCB increased upon homogeneous chemical modification with acetic anhydride and butyric anhydride.

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