

Homogeneous Preparation of Cellulose Acetate Propionate (CAP) and Cellulose Acetate Butyrate (CAB) from Sugarcane Bagasse Cellulose in Ionic Liquid

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ABSTRACT: Cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) were prepared homogeneously in a 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid system from sugarcane bagasse (SB). The reaction temperature, reaction time, and molar ratio of butyric (propionic) anhydride/anhydroglucose units in the cellulose affect the butyryl (B) or propionyl (P) content of CAB or CAP samples. The ¹³C NMR data revealed the distribution of the substituents of CAB and CAP. The thermal stability of sugar cane bagasse cellulose was found by thermogravimetric analysis to have decreased after chemical modification. After reaction, the ionic liquid was effectively recycled and reused. This study provides a new way for high-value-added utilization of SB and realizing the objective of turning waste into wealth.

KEYWORDS: AmimCl ionic liquid, sugarcane bagasse cellulose, cellulose acetate butyrate, cellulose acetate propionate, recycling

INTRODUCTION

During the past few decades, much effort has been devoted to increasing the utilization of agro-industrial residues for several uses. These residues are regarded as abundant, inexpensive, and readily available natural organic resources. One of the most abundant residues is sugarcane bagasse (SB), which comes from the production of sugar and alcohol from sugarcane.¹ About 234 million tons of dry bagasse is produced annually throughout the world.² Most of the SB is burnt to generate energy for mills, but a considerable amount of it is still wasted, which causes serious environmental problems. Because SB contains about 45% cellulose, many studies were conducted^{3–6} aiming at the utilization of sugarcane bagasse cellulose (SBC) for production of several cellulose derivatives.

Due to its high crystallinity, cellulose is difficult to dissolve in common solvents. In most studies, cellulose derivatization was carried out in a heterogeneous system starting with cellulose activation.^{7–11} A major problem with the heterogeneous system, however, is the unequal accessibility among the OH groups in the amorphous and crystalline regions, leading to inhomogeneous substitution.

Over the past decades, with the discovery of cellulose solvents,^{12–15} such as *N,N*-dimethylacetamide/lithium chloride, dimethyl sulfoxide/tetrabutylammonium fluoride, and *N*-methylmorpholine-*N*-oxide, and some molten salt hydrates, such as LiClO₄·3H₂O, the homogeneous functionalization of cellulose has received increasing interest. However, the solvents above have some limitations in application because of their toxicity, high-cost, difficulty of recovery, and instability. Recently, ionic liquids (ILs) have been

shown to be green solvents that can dissolve cellulose and function as inert and homogeneous reaction media for this macromolecule. Many kinds of ILs, such as 1-butyl-3-methylimidazolium chloride, 1-allyl-3-methylimidazolium chloride (AmimCl), 1-ethyl-3-methylimidazolium chloride, 1-allyl-2,3-dimethylimidazolium bromide, 1-butyl-2,3-dimethylimidazolium chloride, and 1-(2-hydroxyethyl)-3-methylimidazolium chloride, among others, have been reported to be successfully used in cellulose derivatization.^{16–20} Some kinds of cellulose esters, such as cellulose succinates, cellulose phthalates, and cellulose sulfates, have been prepared in ILs using SBC as raw material.^{21–23}

However, the cellulose esters reported thus far are mostly monoesters, which have restrictions in some applications. The mixed ester can make up for the drawbacks of the monoester. Cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) are two of the most important mixed cellulose esters^{24,11} currently available. Compared to monocellulose esters, such as cellulose acetate (CA), CAB and CAP have a number of advantages, such as excellent solubility, structural stability, light and weather resistance, good leveling, high gloss retention, good transparency. They are widely used in the paint industry for top grade cars and furniture, as well as printing ink.²⁴ Recently, CAB has been successfully synthesized in AmimCl ionic liquid homogeneously by our group; however, the raw

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material used is still the microcrystalline cellulose with a relatively high price.²⁵ Bagasse from sugarcane is a very promising source of cellulose due to its availability and abundance. Chemical modification of SBC is an effective way of producing high-value-added cellulose derivatives and realizing the objective of turning waste into wealth. In this work, CAB and CAP were prepared homogeneously in the AmimCl ionic liquid using SBC as a cellulose source. The reaction conditions for the SBC derivatives, such as temperature, time, and the molar ratio of butyric anhydride or propionic anhydride/anhydroglucose units (AGU) in cellulose, were studied. The CAB and CAP samples were characterized by ¹H NMR and ¹³C NMR, as well as thermal analysis. Finally, the recycle and reuse of AmimCl are discussed.

MATERIALS AND METHODS

Materials. Sugarcane bagasse was obtained from Nanning Sugar Industry Co., Ltd., Guangxi Province, China. It was washed, dried in sunlight, and then dried in the oven at a temperature of 80 °C for 24 h. All other chemical reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., China.

Synthesis of AmimCl. The IL AmimCl was synthesized as described in our previous work.²⁶ 1-Methylimidazole and allyl chloride at a molar ratio of 1:1.25 were added to a round-bottom flask fitted with a reflux condenser for 8 h at 55 °C with stirring. The unreacted chemical reagents and other impurities, such as water, were removed by vacuum distillation, and the obtained product, AmimCl, was slightly amber.

Purification of Cellulose from Sugarcane Bagasse. The sugarcane bagasse was washed and dried at 70 °C for 3 h in a vacuum oven before use. Aqueous nitric acid solution (5 wt %) was added to the sugarcane bagasse (at 10 g of SB/mL solution), and the resulting mixture was heated to reflux for 3 h. The treated slurry was washed with water to remove the acid and then further heated to reflux for 1.5 h after the addition of 1.6% aqueous sodium hydroxide solution (at 10 g of SB/mL solution). When the temperature fell to 70 °C, 30% H₂O₂ (about 10 mL) was added to bleach the cellulose for 0.5 h. After bleaching, the cellulose was washed thoroughly with water. Finally, the SBC obtained was dried in a vacuum oven at 70 °C for 24 h.

The degree of polymerization (DP) of the obtained sugarcane bagasse cellulose and wood pulp were measured by Ubbelohde viscometer applying CUEN (cupriethylenediamine hydroxide solution) as solvent at 25 °C.²⁷ The cellulose sample of 20 mg (exactly weighed) was dissolved in 5 mL of CUEN solution mixed with 5 mL of distilled water under magnetic stirring for 1 h at room temperature. The DP value of the SBC sample was 860, which was quite close to that of wood pulp, with a DP of 990.

Dissolution of SBC in AmimCl. Dried cellulose (0.405 g) was dispersed into 9.6 g of AmimCl in a three-necked flask. The SBC/AmimCl mixture was stirred at 80 °C for 4 h to guarantee the complete dissolution of cellulose. The dissolution of SBC in AmimCl could be observed by polarized light microscopy with a hot plate (Linkam, THMS600) and digital camera (Olympus, BX51).

Homogeneous Synthesis of CAP in AmimCl. The temperature of the SBC/AmimCl solution was increased to 100 °C and held there for 30 min. A defined amount of propionic anhydride/AGU (M₁) was first added to the solution. After reaction for a certain amount of time (t₁) had been allowed, acetic anhydride/AGU (M₂) was carefully added. The reaction was stopped after the required time (t₂) had elapsed, and the product was reprecipitated from a 5-fold amount of distilled water and washed three times. The residue was dried under vacuum at 60 °C for 24 h. The filtrate was recycled IL (RPIL).

Homogeneous Synthesis of CAB in AmimCl. The SBC/AmimCl solution was heated to 80, 90, and 100 °C for 30 min. The required amount of butyric anhydride/AGU (M₁) was added to the

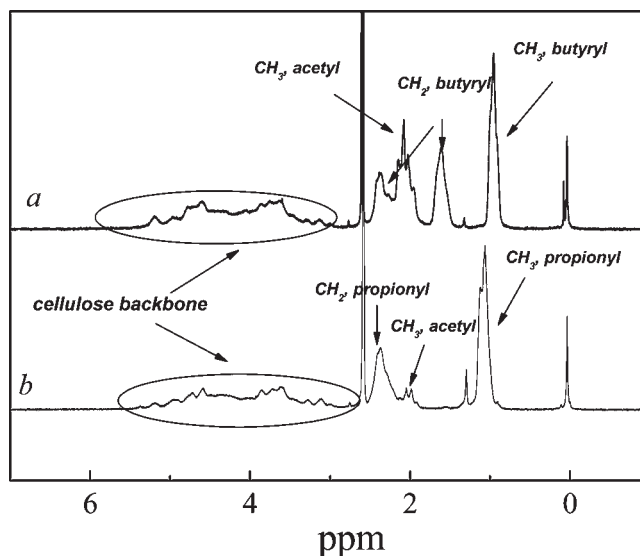


Figure 1. ¹H NMR of CAB and CAP: (a) CAB10; (b) CAP3.

solution. A few hours later (t₁), acetic anhydride/AGU (M₂) was carefully added under vigorous stirring. After the required time (t₂) had elapsed, the resulting product was precipitated with a 5-fold amount of distilled water and the mixture was separated by filtration. The solid was washed until it was free of the IL and then dried in a vacuum oven at 60 °C for about 24 h. The collected liquid (RBIL) could be recycled later.

Recycling of AmimCl. At the end of each experiment, the IL was collected from homogeneous synthesis of CAP and CAB, respectively, and was recycled by rotary evaporation of the filtrate and oven-drying at 95 °C. Its purity was determined by ¹H NMR spectroscopy. The RBIL and RPIL (the recycled IL) were used to prepare CAB and CAP, respectively.

NMR Analysis. The degree of substitution (DS) of CAB and CAP was determined by ¹H NMR spectroscopy (Bruker AV-400 spectrometer) after the addition of a drop of trifluoroacetic acid-*d*, which shifts active hydrogen downfield. The signal peaks of CAB in Figure 1 are described below:²⁸ δ 2.8–5.9 (protons of the cellulose backbone, 7H), δ 2.0 (methyl protons of acetyl of CAB, 3H), δ 1.0 (methyl protons of butyryl of CAB, 3H), δ 2.2 and 1.5 (two methylene protons of butyryl of CAB, 2H). Those for CAP were δ 2.8–5.9 (protons of the cellulose backbone, 7H), δ 2.0 (methyl protons of acetyl of CAP, 3H), δ 1.0 (methyl protons of propionyl of CAP, 3H), and δ 2.2 (methylene protons of propionyl of CAP, 2H).

The DS of CAB and CAP^{17,28} was calculated by eqs 1–9.

$$DS_A = \frac{I_{\text{acetyl}} \times 7}{I_{\text{AGU}} \times 3} \quad (1)$$

$$DS_B = \frac{I_{\text{butyryl}} \times 7}{I_{\text{AGU}} \times 3} \quad (2)$$

$$DS_P = \frac{I_{\text{propionyl}} \times 7}{I_{\text{AGU}} \times 3} \quad (3)$$

$$DS_{\text{totalB}} = DS_A + DS_B \quad (4)$$

$$DS_{\text{totalP}} = DS_A + DS_P \quad (5)$$

$$A_B = \frac{DS_A \times 43}{162 - (DS_A + DS_B) + DS_A \times 43 + DS_B \times 71} \times 100\% \quad (6)$$

$$B = \frac{DS_B \times 71}{162 - (DS_A + DS_B) + DS_A \times 43 + DS_B \times 71} \times 100\% \quad (7)$$

Table 1. Composition Analysis of Sugarcane Bagasse (SB) and Sugarcane Bagasse Cellulose (SBC)

	cellulose (%)	hemicellulose (%)	lignin (%)	moisture (%)	ash (%)
SB	46.3	30.6	21.8	0.5	0.5
SBC ^a	90.6	2.5	0.04	0.1	0.1

^a Failure to reach 100% of the total composition listed is mainly due to the experimental loss.

$$A_p = \frac{DS_A \times 43}{162 - (DS_A + DS_p) + DS_A \times 43 + DS_p \times 57} \times 100\% \quad (8)$$

$$P = \frac{DS_p \times 57}{162 - (DS_A + DS_p) + DS_A \times 43 + DS_p \times 57} \times 100\% \quad (9)$$

The distribution of the acetyl, butyryl, and propionyl moieties among the three OH groups of the AGU of CAB was calculated by integrating the ¹³C NMR spectrum of a solution of cellulose ester in DMSO-*d*₆ using a DMX-300 spectrometer (Bruker). Each spectrum was obtained with an accumulation of 10000 scans.

Thermal Analysis. Thermogravimetric analysis (TGA) was performed using a TGA/DSC instrument (TGA/DSC-1, Mettler Toledo) from 25 to 600 °C for all of the samples (sample weight is about 6.0–8.0 g), at a heating rate of 20 °C/min. The TGA measurements were carried out under nitrogen flow.

RESULTS AND DISCUSSION

Characterization of SBC and Its Dissolution in AmimCl.

The cellulose, hemicellulose, and lignin contents of the SB were 46.3, 30.6, and 21.8%, respectively. After SB purification, the contents of these three components were 90.6, 2.5, and 0.04%, respectively, as shown in Table 1.²⁹ The above analysis shows that this method can effectively remove the hemicellulose and lignin from SB and obtain SBC with high purity.

Optical microscopy of the SBC sample in AmimCl clearly demonstrates the disappearance of fibrous material within only 5 min at 100 °C. The full black field was observed at the end of dissolution, which means the full dissolution of SBC in AmimCl, despite the very small amounts of hemicellulose and lignin (2.5 and 0.04%) remaining in the purified SBC. This indicates that AmimCl can also dissolve a small amount of hemicellulose and lignin, which is in accordance with the report that AmimCl has excellent potential for dissolving woody biomasses.³⁰

Effects of Reaction Conditions on Propionyl/Butyryl Content of CAP/CAB. Cellulose esters can be synthesized by the reaction between the acid anhydride and the C6, C3, and C2 hydroxyl groups of cellulose. Table 2 gives the effects of various conditions such as reaction time, reaction temperature, and acid anhydride concentration on the DS of CAP/CAB.

The feeding method of adding acetic anhydride (Ac₂O) first and propionic anhydride (Pr₂O) later to the cellulose/IL solution was attempted, and the product obtained was coded CAP0. The propionyl content of CAP0 was only 22.51%, which is low for its industrial application.³¹ To obtain the excellent performance of CAP/CAB products with higher propionyl/butyryl content, we chose to add the Pr₂O/Bu₂O first and the Ac₂O later. Under this addition method, the OH group can react with Pr₂O/Bu₂O maximally, because there is only a propionylation/butyrylation step for cellulose in the system initially.

From Table 2, we can see that the propionyl/butyryl contents depended on the reaction time, temperature, and carboxylic acid anhydride content. At 100 °C, a 13:1 molar ratio of Pr₂O/AGU, a 5:1 molar ratio of Ac₂O/AGU, and a 6 h propionylation time, an increase in acetylation time from 1 h (CAP1) to 3 h (CAP2) to 4 h (CAP3) and finally to 5 h (CAP4) led to a decrease in propionyl content from 45.44 to 44.72 to 38.72% and, finally, to 36.33%, and an increase in acetyl content from 2.93 to 2.96 to 5.96% and to 9.62%, respectively. For CAB at 100 °C, a 9:1 molar ratio of butyric anhydride (Bu₂O)/AGU, a 5:1 molar ratio of Ac₂O/AGU, and a 3 h acetylation time, extending the butyrylation time from 1 h (CAB1) to 3 h (CAB2) and then to 5 h (CAB3), led to an increased butyryl content from 27.86 to 38.09 to 41.02% and a decreased acetyl content from 17.17 to 7.98 to 7.73%, respectively. Holding the butyrylation and acetylation time to 3 h, a reaction temperature of 100 °C, and a molar ratio of Ac₂O/AGU at 5:1, increasing the molar ratio of Bu₂O/AGU from 5:1 (CAB4) to 13:1 (CAB5) and then to 15:1 (CAB6) led to a decrease in acetyl content from 10.41 to 6.23 to 4.50% and a slight increase in butyryl content from 38.06 to 39.93 to 41.48%, respectively. All of these phenomena are taken as evidence of the strong steric hindrance effect between Bu₂O and Ac₂O. As there are two acid anhydrides in the solution, they will compete for the hydroxyl group of cellulose. If the reaction time is increased or one acid anhydride is added, the substituent of it will undoubtedly increase. However, it will certainly block the reaction of cellulose with the other acid anhydride and, thus, result in the relatively lower substituent of the other acid anhydride.

The results of variation in reaction temperature are given in samples CAB7–CAB9. The increase of temperature can accelerate the reaction rate and, consequently, increase both the butyryl and acetyl contents of CAB. For example, increasing the reaction temperature from 80 to 90 to 100 °C resulted in an increase in both butyryl content (from 26.53 to 34.30 to 46.00%) and acetyl content (from 3.55 to 3.66 to 4.04%) of CAB. Because the butyryl content of <35% at 80 and 90 °C (CAB7, CAB8) and a temperature of >100 °C will lead to serious cellulose degradation,²⁶ the desirable temperature for the reaction is 100 °C.

¹³C NMR Analysis. Elucidating the substituent distributions is important for a discussion of the functional properties of cellulose derivatives. At present, it is possible to obtain quantitative information on this problem by using ¹³C NMR methods.^{28,32,33}

Full-range ¹³C NMR spectra of the CAP and CAB samples are shown in Figure 2. From the figure, the shifts δ 160–180 are assigned to the signals of the carbonyl carbon region, δ 50–110 are assigned to the signals of AGU carbonate region, and δ 0–30 are assigned to the signals of the acyl carbon in CAB and CAP.

In the AGU carbonate region, the peaks at 102.5 and 80.1 ppm are attributed to C1 and C4 carbons bearing an unsubstituted hydroxyl group, respectively. A peak around 100.0 ppm (designated C1') is assigned to C1 carbons adjacent to C2 carbons bearing a substituted hydroxyl group, and a peak around 75.5 ppm (designated C4') is assigned to C4 carbons adjacent to C3 carbons bearing a substituted hydroxyl group. The resonance peaks of C2, C3, and C5 carbons in both of the samples heavily overlap as they give only a strong cluster around 70–75 ppm. The peak at 62.8 ppm is attributed to C6 carbons bearing a substituted hydroxyl group, and the disappearance of the peak at 59.0 ppm (designated C6) indicates full substitution of the hydroxyl group at the C6 position in both CAP and CAB.

A remarkable feature of the ¹³C NMR spectra of the CAP and CAB samples is that both acetyl and propionyl/butyryl carbonyl carbon signals appeared separately and were resolved into three

Table 2. Homogeneous Synthesis of CAP and CAB in AmimCl

no.	reaction conditions					reaction results				
	temp (°C)	M ₁	t ₁ (h)	M ₂	t ₂ (h)	DS _B /DS _P	P/B (%)	DS _A	A _P /A _B (%)	DS _{total}
CAP0	100	9	-5 ^a	5	1	0.93	22.51	0.51	9.31	1.44
CAP1	100	13	5	5	1	2.46	45.44	0.21	2.93	2.67
CAP2	100	13	3	5	3	2.39	44.72	0.21	2.96	2.60
CAP3	100	13	2	5	4	1.96	38.72	0.40	5.96	2.36
CAP4	100	13	1	5	5	1.88	36.33	0.66	9.62	2.54
CAP5 ^b	100	13	2	5	4	1.90	38.54	0.30	4.59	2.20
CAB1	100	9	1	5	3	1.14	27.86	1.16	17.17	2.30
CAB2	100	9	3	5	3	1.59	38.09	0.55	7.98	2.14
CAB3	100	9	5	5	3	1.80	41.02	0.56	7.73	2.36
CAB4	100	5	3	5	3	1.66	38.06	0.75	10.41	2.41
CAB5	100	13	3	5	3	1.67	39.93	0.43	6.23	2.10
CAB6	100	15	3	5	3	1.73	41.48	0.31	4.50	2.04
CAB7	80	13	5	5	1	0.86	26.53	0.19	3.55	1.05
CAB8	90	13	5	5	1	1.25	34.30	0.22	3.66	1.47
CAB9	100	13	5	5	1	2.07	46.00	0.30	4.04	2.37
CAB10	100	5	3	7	3	1.20	30.47	0.80	12.30	2.00
CAB11 ^b	100	5	3	7	3	1.20	30.47	0.80	12.30	2.00

^a Propionic anhydride was added into the system 5 h after acetic anhydride. ^b Using recycled ionic liquid AmimCl as the solvent medium.

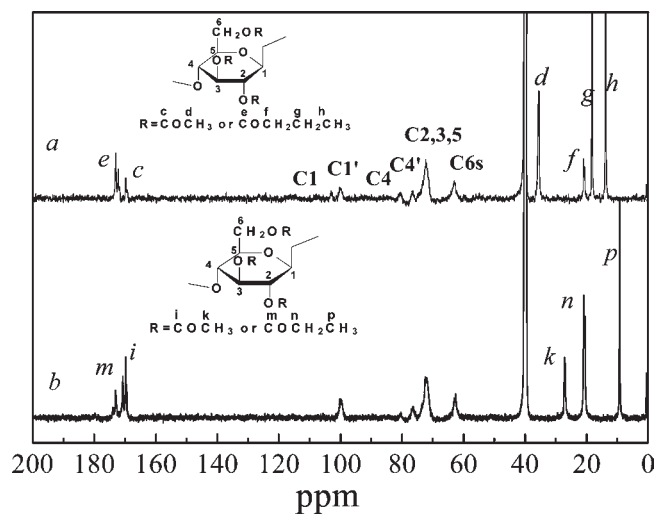


Figure 2. ¹³C NMR spectra of CAB and CAP: (a) CAB3; (b) CAP0.

peaks, which were previously assigned as C6, C3, and C2, respectively. The expanded carbonyl region spectra of CAP and CAB samples are shown in Figure 3. The shifts δ 172–175 (curve a) are assigned to the signal of propionyl carbonyl carbon in CAP, δ 171–174 (curve b) to the signal of butyryl carbonyl carbon in CAB, and δ 168–171 (curves a and b) to the signal of acetyl carbonyl carbon in both CAP and CAB.

For the CAB in curve a, the degree of butyryl substitution is larger than that of acetyl, and the degree of butyryl substitution at the C6 position is the largest, whereas the hydroxyl group at the C3 and C2 positions is substituted more than C6 for the acetyl group. This is because the first added butyric anhydride prefers the hydroxyl group at the C6 position. The acetic anhydride added later has to react with the less reactive hydroxyl group at C3 or C2.

As for CAP in curve b, acetic anhydride was added before propionic anhydride during the reaction, the degree of acetyl substitution is larger than that of propionyl, and the hydroxyl group at the C6 position of acetyl in CAP exhibits the highest

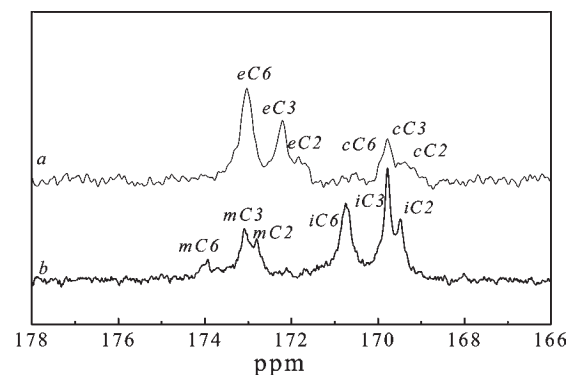


Figure 3. Carbonyl carbon region of CAB and CAP in ¹³C NMR: (a) CAB3; (b) CAP0.

reactivity. The hydroxyl group at the C3 position of propionyl in CAP exhibits the highest reactivity, which is just the opposite of CAB.

Overall, a different addition sequence of the reagent results in a different degree of substitution; thus, the structure and property of the product can be controlled by the reagent addition methods. However, the total partial substitution of the homogeneously synthesized CAB and CAP still satisfies the order of $C6_{total} > C3_{total} > C2_{total}$, which is similar to other cellulose esters synthesized homogeneously in IL,^{33,34} but different from the heterogeneously synthesized cellulose esters having a partial DS order of $C3_{total} > C2_{total} > C6_{total}$ ³⁵ because the whole heterogeneous process starts with the full substitution first and is followed by partial hydrolyzation.

Thermal Analysis. The thermal properties of CAB and CAP were studied by TGA in the range of 25–600 °C at a rate of 20 °C min⁻¹ under a nitrogen atmosphere. The results are shown in Figure 4.

As can be seen from the figure, the sugarcane bagasse cellulose sample starts to decompose at 373.6 °C, whereas the two mixed cellulose ester samples, CAP0 and CAB7, start to decompose at 358.5 and 356.6 °C, respectively. The maximum decomposition

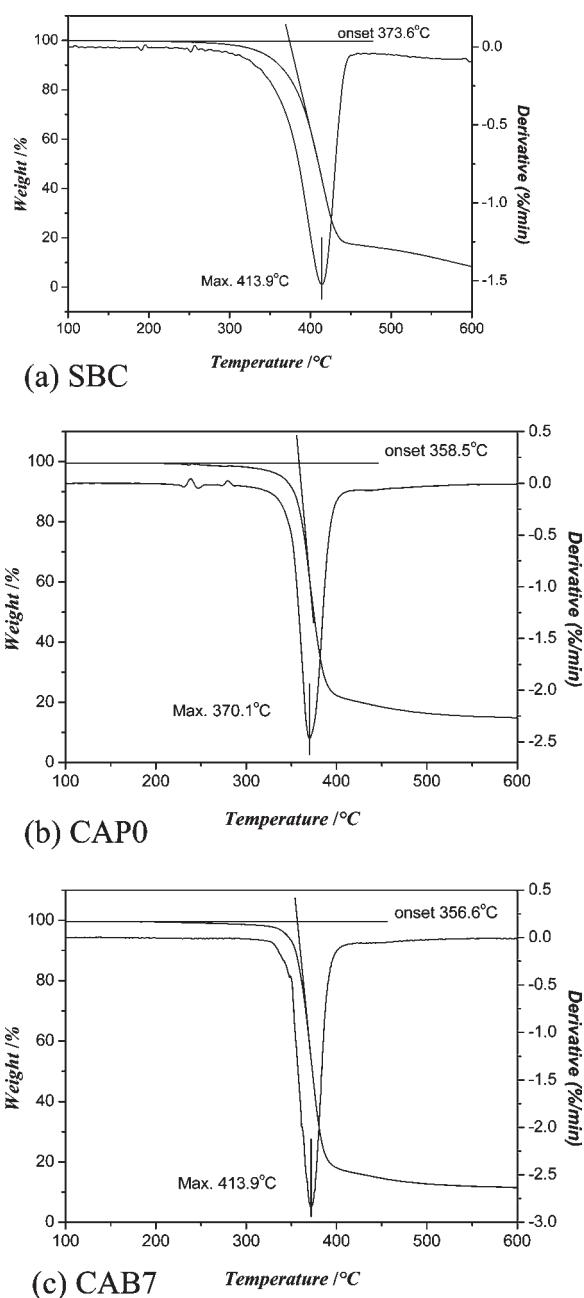


Figure 4. TGA thermograms of SBC, CAB, and CAP: (a) SBC; (b) CAP0; (c) CAB7.

temperature of sugarcane bagasse is 413.9 °C, and those of CAP0 and CAB7 are 370.1 and 371.9 °C, respectively. This indicates the thermal stability of sugarcane bagasse cellulose is slightly decreased due to the introduction of the acyl group, which is in accordance with the literature.^{17,33}

Recycling of the IL AmimCl. Due to the negligible vapor pressure and high thermal stability, AmimCl can be recycled easily by filtration and evaporation. The purity of the recovered AmimCl was confirmed by ¹H NMR spectroscopy, as shown in Figure 5. From Figure 5, no other impurities were detected except acetic acid (2.0 ppm) and butyric acid (1.0, 1.5, and 2.2 ppm) in RBIL and acetic acid (2.0 ppm) and propionic acid (1.0 and 2.2 ppm) in RPIL. These imply that no chemical reaction occurred during the recycling of AmimCl. The purities of RBIL

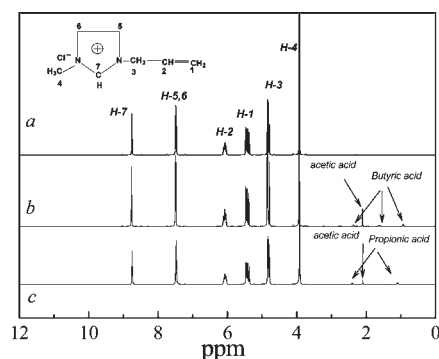


Figure 5. ¹H NMR spectra of IL, RBIL, and RPIL: (a) fresh IL; (b) RBIL; (c) RPIL.

and RPIL were 95 and 97%, respectively, as calculated from the area of integration of the corresponding signal peaks.

The recycled ILs were also used to synthesize CAB and CAP. The results are listed in Table 1. The DS values of mixed-cellulose esters obtained in the recycled ILs are in good accordance with that obtained in the fresh IL.

In this work, sugarcane bagasse cellulose was successfully utilized in the homogeneous preparation of CAB and CAP using AmimCl ionic liquid as solvent, in the absence of any catalyst. CAB (acetyl content of 3.6–10% and butyl content of 27–46%) and CAP (acetyl content of 2.9–10% and propionyl content of 23–45%) can be obtained by controlling the reaction conditions. The structures of CAB and CAP were confirmed by ¹H NMR and ¹³C NMR, which reveal the distribution of acetyl and butyl moieties in CAB and the acetyl and propionyl moieties in CAP. The thermal stability of SBC decreased after chemical modification. After reaction, the ionic liquid AmimCl was effectively recycled and reused. On the basis of the fact that the IL can be effectively recycled after each esterification, this study provides a procedure for the homogeneous one-step preparation of CAB and CAP without any catalysts using relatively cheap and abundant sugarcane bagasse as a source of cellulose.

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ABBREVIATIONS USED

CAP, cellulose acetate propionate; CAB, cellulose acetate butyrate; AmimCl, 1-allyl-3-methylimidazolium chloride; SB, sugarcane bagasse; SBC, sugarcane bagasse cellulose; CA, cellulose acetate; AGU, anhydroglucose units; RBIL, recycled IL from CAB; RPIL, recycled IL from CAP; DS_A, DS of acetyl moieties; DS_B, DS of butyryl moieties; DS_P, DS of propionyl moieties; A_B, acetyl percentage of CAB; A_P, acetyl percentage of CAP; B, butyryl percentage of CAB; P, propionyl percentage of CAP;

Ac₂O, acetic anhydride; Bu₂O, butyric anhydride; Pr₂O, propionic anhydride; I_{acetyl} , integral of methyl protons of acetyl moieties; $I_{\text{propionyl}}$, integral of methyl protons of propionyl moieties; I_{butyryl} , integral of methyl protons of butyryl moieties; I_{AGU} , integral of all protons of anhydroglucose units.

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