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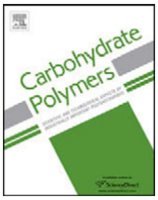

Conversion of cotton byproducts to mixed cellulose esters[☆]

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ABSTRACT

Cotton byproducts, such as cotton burr and cottonseed hull, can be used as low-cost feedstock for the production of specialty chemicals. The conversion of these cellulosic byproducts into mixed cellulose esters, e.g., cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB), was studied. Instead of using the conventional process for preparing these materials, which uses the appropriate anhydrides, sulfuric or perchloric acid, and methylene chloride as solvent, an iodine-promoted process was used that requires no chlorinated solvent in the reaction mixture. Product ester ratios and degrees of substitution were determined by ^{1}H NMR spectroscopy. At the conditions studied, acetic anhydride was only slightly more reactive than propionic anhydride in the formation of CAP, but acetic anhydride was noticeably more reactive than butyric anhydride in the formation of CAB.

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1. Introduction

Cotton is a valuable industrial material with an annual worldwide production of around 25.5 million metric tons (USDA, 2010). Cotton burr and cottonseed hull are two fibrous byproducts of cotton production (Dunning, 1948; NCPA Publications, 2002). Cotton burr is the outer part of the seed boll. While most of the burr is left on the field, some is collected with the fiber during harvesting, where it ends up as a component of either harvesting or ginning trash. At present, it is used as mulch or as a boiler fuel. Cottonseed hull is the outer husk of the seed. It is recovered as a byproduct of the oil extraction process and is used as feed roughage, mulch, and as a component of the medium for mushroom production. Both materials are readily available and inexpensive, and value-added products from these materials are of some interest.

Cellulose esters constitute a family of well-known commercial products (Bikales & Segal, 1971; Edgar et al., 2001; Heinze, Liebert, & Koschella, 2006). Esters with significant commercial value include cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB). CA is used commercially in plastics (such as tool handles, face shields, eyeglass frames), tapes, textile fibers, photographic films, and cigarette filters (Gedon & Fengl, 2004; Rustemeyer, 2004). CAP is used in printing inks, specialty coatings, toothbrushes, tool handles, and ophthalmic frames (Anon, 2006a; Rustemeyer, 2004). CAB is also used in plastics, such as brush and tool handles, automotive and furniture coatings, films and sheets (Anon, 2006b; Rustemeyer, 2004). Low-molecular-weight CAP and CAB are being studied as low viscosity binders and modifiers in coating formulations (Shelton et al., 2009). Other mixed cellulose esters of less commercial interest include cellulose acetate phthalate, and carboxymethyl cellulose acetate butyrate.

The conventional process for the preparation of cellulose esters uses the desired anhydrides with sulfuric or perchloric acid in solvents, such as methylene chloride (Edgar et al., 2001; Heinze et al., 2006; Larock, 1989; Rustemeyer, 2004). LiCl/*N*,*N*-dimethylacetamide (LiCl/DMAc) (McCormick & Callais, 1987), N-ethyl-pyridinium chloride (Deus, Friebolin, & Siefert, 1991), and ionic liquids (Abbott, Bell, Handa, & Stoddart, 2005; Barthel & Heinze, 2006; Wu et al., 2004; Zhu et al., 2006) have been used as alternative solvents, and superacids have been used as the acidification agent (Yan, Li, Qi, & Liu, 2006). Other reported methods for esterification include the use of reagents to enhance leaving group function, e.g., dialkylcarbodiimide or *N*,*N*-carbonyldiimidazole, or to improve the effectiveness of the acid catalyst, e.g., iminium chlorides (Heinze et al., 2006). Other approaches to esterification include base-catalyzed transesterification and ring-opening reactions (Heinze et al., 2006).

In earlier work, we found that the cellulose in cotton burr and cottonseed hull could be converted to cellulose acetate without

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[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standards of the products, and the use of the name USDA implies no approval of the products to the exclusion of others that may also be suitable.

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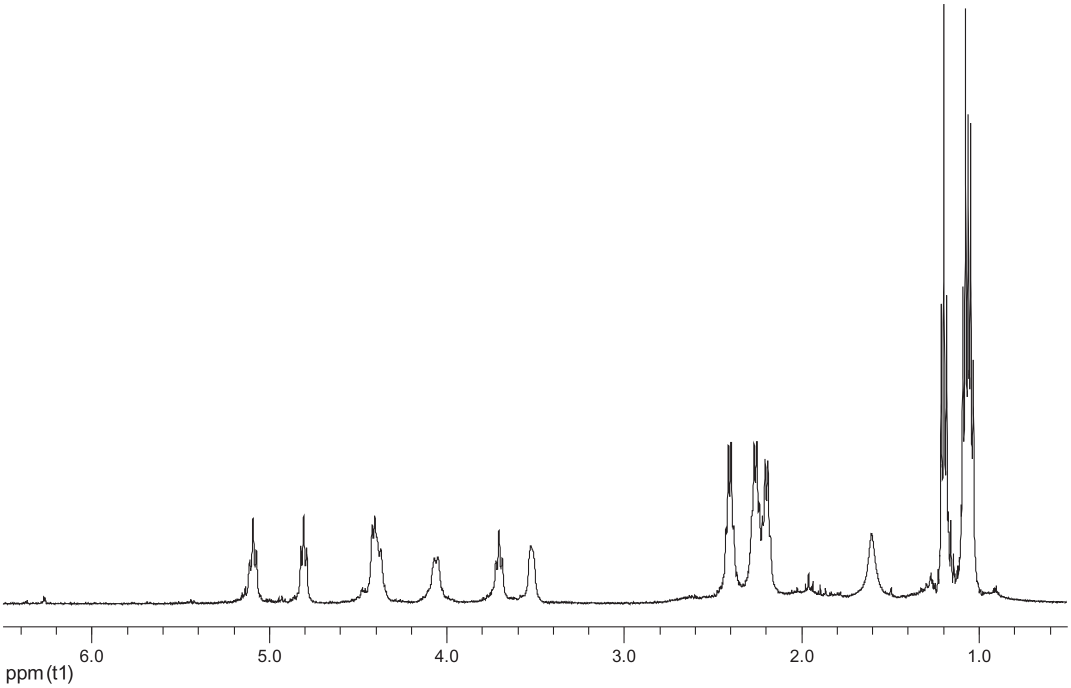

Fig. 1. ^{1}H NMR spectrum of cellulose propionate in $CDCl_3$ (sample CP-1).

prior chemical breakdown or physical separation of the burr or hull components (Cheng, Dowd, Selling, & Biswas, 2010). Iodine-promoted esterification was used for this work, following an approach reported by Biswas and others for esterification of a number of polysaccharides (Biswas, Selling, Appell, Woods, Willett, & Buchanan, 2007; Biswas, Selling, Shogren, Willett, Buchanan, & Cheng, 2009; Biswas, Shogren, & Willett, 2005; Li et al., 2009). This alternative promoter system generally produced high yields of cellulose acetate (up to 90%) (Biswas et al., 2007). Reported yields were not as high when preparing cellulose propionate (≤45%), and longer chain anhydrides were even less reactive under the same conditions (Biswas et al., 2007). Because of our interest in forming cellulose esters from byproduct materials, we re-examined this reaction with acetic, propionic and butyric anhydrides to derive mixed cellulose esters from cottonseed hull and cotton burr samples.

2. Experimental

2.1. Materials

Microcrystalline cellulose powder (20 μm), xylan from beechwood (>90%), chloroform, deuterochloroform, iodine, and the three anhydrides (acetic, propionic, and butyric) were all purchased from Sigma–Aldrich Chemical Co. All were used without further purification.

2.2. Sample preparation

To recover cotton hulls, whole seeds that had undergone acid delintering were cracked with a Bauer mill, and the hulls were separated from the kernels by air classification. Cotton burrs were collected as a component of the field trash recovered from a harvesting cotton stripper with the other debris (sticks, leaves, etc.) removed by hand. The burr and hull samples were pulverized with a hammer mill until they passed through a 16-mesh (1.18 mm openings) screen. They were then stored in capped bottles at room temperature.

2.3. Esterification procedure

The procedure was adapted from our earlier work (Cheng et al., 2010) and differed from the earlier report on the synthesis of cellulose propionate (Biswas et al., 2007) in that longer reaction times and more extensive product washing was used. In a typical reaction, 0.57 g (~3.5 mmol of anhydroglucose units assuming the sample was pure cellulose) of starting material, 0.32 g (2.52 mmol) of iodine, and 18–40 mmol of the single or mixed anhydride were heated at 100 °C for 20–24 h. The reaction mixture was then cooled to room temperature and treated with 2–4 mL of a saturated solution of sodium thiosulfate while stirring. With the addition of sodium thiosulfate, the mixture changed color from dark brown to colorless indicating the transformation of iodine to iodide, which stopped the reaction. The reaction mixture was then poured into 50 mL of ethanol and was stirred for 30 min. A solid phase was formed that was filtered and washed successively with water at 100 °C, and then washed successively with water and ethanol at room temperature. The remaining solids were then dissolved in chloroform at room temperature overnight and were filtered into a pre-weighted glass vial. The chloroform was removed with a rotary evaporator and the product was dried at 60 °C in a vacuum oven.

2.4. Product characterization

All products were characterized by ^{1}H NMR spectroscopy. Solution spectra were recorded on a Bruker DRX400 spectrometer at normal probe temperature with standard instrument settings. Deuterochloroform was used as solvent. All chemical shifts were referenced to tetramethylsilane at 0 ppm.

3. Results and discussion

3.1. Cellulose propionate and cellulose butyrate

In our earlier report (Cheng et al., 2010), cellulose acetate was made from cotton burr and cottonseed hull by heating ground material with acetic anhydride in the presence of iodine. The same

Table 1
Reaction parameters for the synthesis of cellulose derivatives.[a]

Item	Substrate	Initial wt (g)	Anhydride type, wt (g)			Product ID	Wt. yield (g)	Obsd yield (%)	% of Theoretical yield[c]
			Acetate	Propionate	Butyrate				
1	cellulose	0.57		2.42		CP-1	0.053	9	4
2	hull	0.57		2.42		CP-2	0.175	31[b]	44
3	burr	0.57		2.42		CP-3	0.389	68[b]	97
4	cellulose	0.57			2.94	CB-1	0.027	5	2
5	hull	0.57			2.94	CB-2	0.097	17	22
6	burr	0.57			2.94	CB-3	0.188	33	42
7	cellulose	0.57	1.08	1.08		CAP-1	0.091	16[b]	7
8	cellulose	0.57	0.25	4.5		CAP-2	0.054	10[b]	4
9	hull	0.57	1.08	1.08		CAP-3	0.080	14	21
10	hull	0.57	0.25	4.5		CAP-4	0.023	4[b]	6
11	burr	0.57	1.08	1.08		CAP-5	0.289	51	77
12	burr	0.57	0.25	4.5		CAP-6	0.220	39	56
13	cellulose	0.57	1.35		3.7	CAB-1	0.096	17[b]	7
14	cellulose	0.57	2.95		1.7	CAB-2	0.049	9[b]	4
15	hull	0.57	1.35		3.7	CAB-3	0.053	9[b]	13
16	hull	0.57	2.95		1.7	CAB-4	0.112	20	30
17	burr	0.57	1.35		3.7	CAB-5	0.229	32[b]	56
18	burr	0.57	2.95		1.7	CAB-6	0.349	61	92

[a] All reactions were conducted at 100 °C for 24 h.

[b] Average of duplicate experiments.

[c] % of theoretical yield was calculated by dividing the observed yield by the yield expected for complete reaction of the cellulose in the material. In the case of hull and burr, these were assumed to contain 30% cellulose based on prior proximate analysis of these materials (Cheng & Biswas, 2011).

procedure was used with different anhydrides to esterify cellulose, hull, and burr materials to produce cellulose propionate (CP) and cellulose butyrate (CB) products (Table 1, items 1–6). For the purified cellulose sample, observed yields of CP and CB were 9% and 5%, respectively. As expected, yields from these reactions were relatively low. The low yields appeared to be due to the reduced activity of the propionate and butyrate anhydrides compared with the activity of acetic anhydride, and to the occurrence of some polymer degradation that was more prone at the higher temperature used for this series of reactions (discussed below). Product yields were higher for the hull and burr samples with the cotton burr producing the highest yields (Table 1).

The CP products had a ^{1}H NMR spectrum typical of cellulose esters. The spectrum for CP-1 was typical (Fig. 1). Peak assignments for cellulose acetate and cellulose propionate have been previously reported (Buchanan, Hyatt, & Lowman, 1987; Kowsaka, Okajima, & Kamide, 1988; Oliveira & Glasser, 1994; Shuto, Murayama, Azuma, & Okamura, 1988). Peaks at 3.6–5.2 ppm correspond to the protons resonances on the anhydroglucose unit, i.e., H-3 at 5.06 ppm, H-2 at 4.78 ppm, H-1 and H-6a at 4.40 ppm, H-6b at 4.05 ppm, H-4 at 3.70 ppm, and H-5 at 3.52 ppm. The methyl protons of the propyl moieties esterified at the ring 2- and 3-positons resonate at 1.06 ppm, and the methyl protons of the propyl moieties esterified at the ring 6-position resonate at 1.18 ppm. The propionate methylene protons from the ring 2-position resonate at 2.24 ppm, the propionate methylene protons from the ring 3-position resonate at 2.18 ppm, and the methylene protons from the ring 6-position resonate at 2.39 ppm. All of the expected peaks were apparent in the CP samples. In addition, the peak observed at 1.6 ppm (Fig. 1) was due to a small amount of water in the CP-1 sample. An estimate of the DS of the CP products was made by dividing 1/3 of the combined propionate methyl peak area by 1/7 of the combined anhydroglucose peak area. These calculations indicated that the substitutions of the CP products were between 2.8 and 3.0 indicating essentially complete esterification.

Proton spectra for the CB products were only slightly more complicated (spectra not shown). Peaks resonating between 0.85 and 1.1 ppm correspond to the three methyl protons of the butyrate moieties. Calculation of the DS for these products was similar to the DS for the propionate products. Again, the calculations indicated that the substitution of the CB products was essentially complete (2.7–3.0).

3.2. *Cellulose acetate propionate*

Because the results for CP were encouraging, synthesis of a CAP was attempted. Two formulations were tested with the same reaction conditions. One sample was prepared with equal weights of acetic and propionic anhydride corresponding to a 56:44 molar ratio of acetic anhydride to propionate anhydride. The second sample was prepared with a 7:93 molar ratio of acetic anhydride to propionic anhydride, equal to the ratio of the two esters present in the Eastman Chemical Co. commercial product CAP-482-0.5 (which has an acetic ester weight of 2.5% and a propionic ester weight of 45%) (Anon, 2006a). The reaction with hull gave product yields as high as the yields obtained for the reaction with purified cellulose (Table 1, items 9–10). As for the preparation of CP and CB, the burr material produced the highest yields of CAP.

The proton NMR spectra for mixed ester samples were more complicated than for samples prepared with a single anhydride; see, e.g., the spectra for CAP-5 (Fig. 2). As was previously noted (Buchanan et al., 1987; Cheng et al., 2010), the acetate methyl proton resonates are found around 2 ppm (viz., 2.12 ppm for the acetate at the 6-position, 2.00 ppm for the acetate at the 2-position, and 1.94 ppm for the acetate at the 3-position). The methyl and the methylene protons from the propionate resonate at ~1.1 and ~2.3 ppm, respectively.

Individual ester and total DS were also calculated from the ^{1}H peak areas, although the calculations were more complicated. The peaks observed between 3.6 and 5.2 ppm again correspond to the seven anhydroglucose protons; the peaks observed between 1.0 and 1.2 ppm correspond to three methyl protons of the propionate moieties; and the peaks observed between 1.9 and 2.4 ppm correspond to the acetyl methyl protons plus the two methylene protons

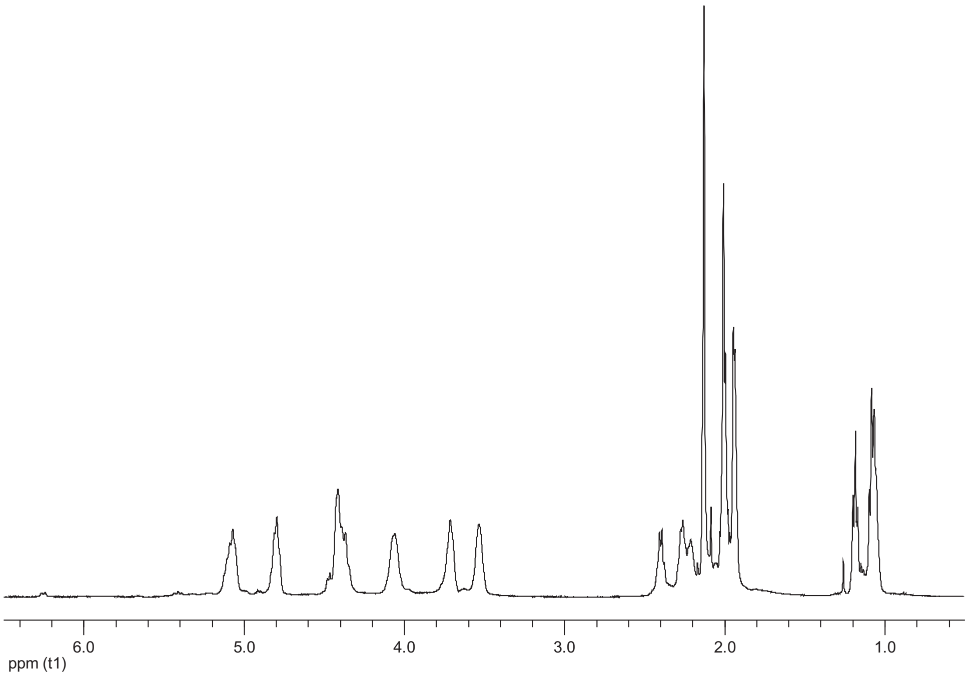

Fig. 2. ^{1}H NMR spectrum of cellulose acetate propionate in $CDCl_3$ (sample CAP-5).

of the propionate ester. Hence, 1/3 of the propionate methyl peak area divided by 1/7 of the anhydroglucose peak area provides an estimate of the DS for the propionate ester. Subtraction of 2/3 of the propionate methyl peak area from the 1.9–2.4 ppm region gave the signal corresponding to the acetate methyl protons. The 1/3 of this peak area divided by 1/7 of the anhydroglucose peak area gives the DS for acetate. (Note: if the spectral resolution is good enough to isolate separate acetate and propionate methyl peaks, then these could be separately integrated to make the calculations more direct.)

From the NMR data, the acetate/propionate ratio ranged between 57:43 and 63:37 for the CAP-1, CAP-3, and CAP-5 products (Table 2). For the CAP-2, CAP-4, and CAP-6 samples, the acetate/propionate ratio ranged between 7:93 and 13:87 (Table 2). Thus, the reactivity of acetic anhydride was only slightly greater than the reactivity of propionic anhydride at the conditions used in this work. In addition, the relative reactivity did not appear to vary with the source of the cellulose. For CAP-5 (Fig. 3), the DS for acetate ester was ~1.8, and the DS for propionate ester was ~1.0. The total DS samples for the CAP samples (Table 2) was between 2.8 and 3.0, again indicating essentially complete esterification of the recovered products.

3.3. *Cellulose acetate butyrate*

The same reaction was carried out to produce CAB, again with two anhydride compositions. One composition had a higher butyric anhydride anhydride/acetate anhydride ratio that was meant to produce a product with the composition of Eastman Chemical Co. product CAB-381-20; the second composition had a higher acetate anhydride/butyrate anhydride ratio that was meant to mimic the composition of Eastman Chemical Co. product CAB-171-15 (Anon, 2006b). Product yields were similar to those observed during the syntheses of CAP (Table 1, items 13–18). Once again, the burr material produced the highest product yields.

^{1}H NMR peak assignments for CAB were similar to those of CAP, except for the peaks corresponding to the butyrate moieties; e.g., the spectra for CAB-6 (Fig. 3). Thus, the peaks between 0.85 and 1.1 ppm correspond to three methyl protons of butyrate; the peak between 1.5 and 1.7 ppm corresponds to the butyrate ester β-methylene protons (which might overlap the peak associated with water at 1.6 ppm); and the peaks between 1.9 and 2.4 ppm correspond to the three acetyl protons and the butyrate ester α-methylene protons. The molar ratio of acetate ester to butyrate ester was calculated from the areas of the acetate and butyrate peaks; 1/3 of the butyrate methyl peak area divided by 1/7 of the anhydroglucose peak area gave the DS for the butyrate ester. Subtraction of 2/3 of the butyrate peak area from the 1.9 to 2.4 ppm region gives the area of the acetate protons. The ratio of 1/3 of this area to 1/7 of the anhydroglucose area yields the DS of the acetate ester. (The butyrate β-methylene peaks were not used in the calculation because of their possible overlap with water peak at 1.6 ppm.) For CAB-6 in Fig. 4, the DS for acetate was ~2.5, and the DS for butyrate was ~0.5.

From this analysis, the CAB-1, CAB-3, and CAB-5 products, which were formed from the anhydride mixture containing 36 mol% acetic anhydride and 64 mol% butyric anhydride, had an ester content that was 47–50 mol% acetate ester. For samples CAB-2, CAB-4, and CAB-6, which were formed with a starting mixture containing 73 mol% acetic anhydride and 27 mol% butyric anhydride, the ester content was 80–81 mol% acetate ester. Thus, a noticeably higher reactivity of acetic anhydride was observed relative to butyric anhydride. Similar ester ratios were observed regardless of the source of the cellulose. DS values for the CAB samples also indicated that the esterification reaction was essentially complete (Table 3).

3.4. *Xylan esters*

Proximate analysis indicates that cottonseed hulls contain about 20% xylan and cotton burr contains about 6% xylan (Cheng & Biswas, 2011). The xylan in these samples would most likely have undergone esterification and contributed to the recovered products. To estimate their potential contribution to the products, acetylation was conducted on a purified xylan sample isolated from beechwood (>90% xylan). With similar procedure and conditions as used above (0.28 g xylan, 0.16 g iodine, 0.95 g acetic anhydride, 80 °C

Table 2
Comparison of mol% of starting anhydride, ester ratios and degree of substitution for cellulose acetate propionate (CAP) products.

Sample	Starting mol% of anhydride		Mole % of ester in product		Degree of substitution[a]		
	Ac	Pr	Ac	Pr	Ac	Pr	Total
CAP-1	56	44	57	43	1.6	1.2	2.8
CAP-2	7	93	7	93	0.2	2.7	2.9
CAP-3	56	44	62	38	1.8	1.1	2.9
CAP-4	7	93	13	87	0.4	2.6	3.0
CAP-5	56	44	64	36	1.8	1.0	2.8
CAP-6	7	93	13	87	0.4	2.6	3.0

[a] The experimental error for calculating DS was around ± 0.1 units.

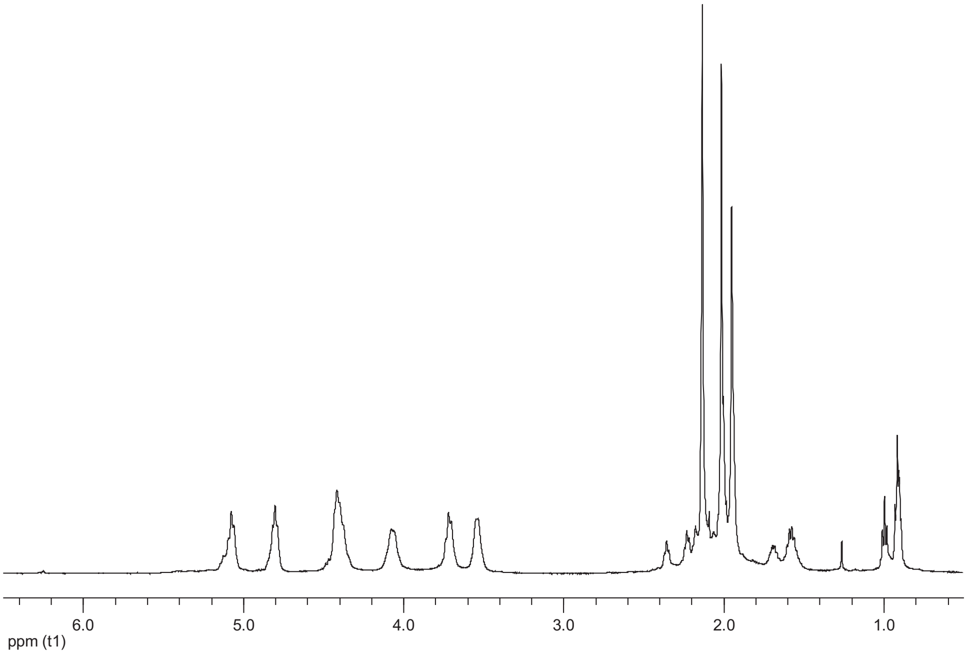

Fig. 3. ^{1}H NMR spectrum of cellulose acetate butyrate in $CDCl_3$ (sample CAB-6).

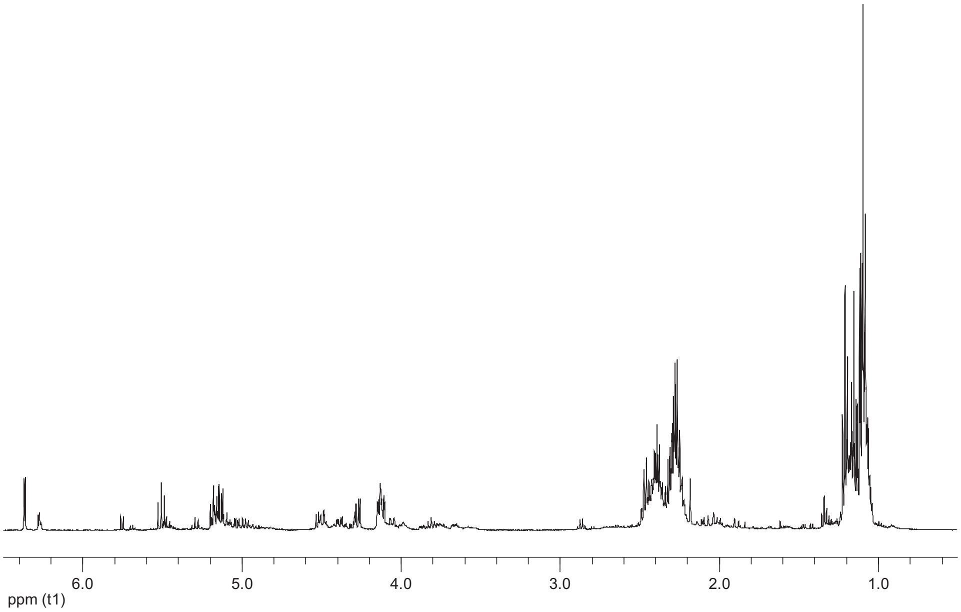

Fig. 4. ^{1}H NMR spectrum in $CDCl_3$ of the material recovered from the wash solvents used in the formation of CP-1 (sample CP-1s).

Table 3
Comparison of mol% of starting anhydride, ester ratios and degree of substitution for cellulose acetate butyrate (CAB) products.

Sample	Starting mol% of anhydride		Mole % of ester in product		Degree of substitution[a]		
	Ac	Bu	Ac	Bu	Ac	Bu	Total
CAB-1	36	64	50	50	1.5	1.5	3.0
CAB-2	73	27	80	20	2.4	0.6	3.0
CAB-3	36	64	50	50	1.5	1.5	3.0
CAB-4	73	27	80	20	2.4	0.6	3.0
CAB-5	36	64	52	48	1.5	1.4	2.9
CAB-6	73	27	83	17	2.5	0.5	3.0

[a] The experimental error for calculating DS is around ± 0.1 units.

Table 4
Data on the polymers recovered from the wash solvents. Reaction temperature was 100 °C and reaction time was 24 h.

Substrate	Initial wt (g)	Anhydride type, wt (g)		Product ID	Wt. yield (g)	Obsd yield (%)	% of Theoretical yield[a]
		Acetate	Propionate				
cellulose	0.57	0	2.42	CP-1s	0.525	92	39
cellulose	0.57	1.08	1.08	CAP-1s	1.005	176	81

[a] % of theoretical yield was calculated by dividing the observed yield by the expected yield of 100% reaction of cellulose to cellulose derivatives.

reaction temperature, 24 h reaction time), acetylation resulted in a 6% observed weight yield of xylan acetate. Assuming similar reactivity and recovery of the xylan in the cotton byproducts, esterified xylan would be expected to contribute about 1.2% of the weight yield of the hull product, and around 0.4% of the weight yield of the burr product.

^{1}H NMR spectrum of xylan acetate and its assignments have been previously reported (Hori & Nakatsubo, 2001; Lundquist, Simonson, & Tingsvik, 1979). Resonates were found at 5.03 ppm (H-3), 4.72 ppm (H-2), 4.46 ppm (H-1), 3.9 ppm (H-5eq), 3.75 ppm (H-4), and 3.3 ppm (H-5ax). Because xylan acetate was a minor component in the samples produced in this work, the corresponding peaks for xylan acetate were small and often were buried in the noise in the observed spectra.

3.5. Low molecular weight materials

Relatively low yields were obtained in the reaction with the purified cellulose used as a control. On reviewing the possibilities, it was found that considerable material was removed during the various washing steps used to recover the product. Consequently, the wash solvents (ethanol and water) were collected from two of the cellulose trials (CP-1 and CAP-1) and the solids from these fractions were recovered by drying (Table 4). From the CP-1 reaction, 0.525 g of extra dry matter were recovered. From the CAP-1 experiment, 1.005 g of extra material were obtained. Accounting for the added ester weight and assuming that these materials were entirely cellulose esters, the added masses correspond to theoretical yields of the starting mass of 39% for CP-1 and 81% for CAP-1.

The ^{1}H NMR spectrum of the material recovered from the wash fraction of sample CP-1 (Fig. 4) bore some resemblance to spectra reported for low-molecular-weight cellulose acetate (Einfeldt, Gunther, Klemm, & Heublein, 2005) and low-molecular-weight starch acetate (Elomaa et al., 2004; Laignel, Bliard, Massiot, & Nuzillard, 1997). As expected, the H-1, H-2, H-3, H-4, H-5, H-6a and H-6b ring protons of the cellulose propionate polymer are found around 4.38, 4.78, 5.07, 3.68, 3.51, 4.35 and 4.03 ppm, respectively. At the reducing ends, H-1α resonates between 6.2 and 6.4 ppm, H-1β resonates between 5.6 and 5.7 ppm, H-3α resonates at ca. 5.4 ppm, H-3β resonates at 5.2 ppm, and H-2α and H-2β resonate between 4.9 and 5.0 ppm. At the non-reducing ends, peaks for H-3 and H-4 are found at 5.1 and 5.0 ppm, respectively (Einfeldt et al., 2005). Spectra for the material recovered from the water and ethanol washings of CP-1 (Fig. 4) showed the presence of peaks between 5.0 and 6.4 ppm, indicating that low-molecular-weight cellulose esters were present.

The iodine promoted formation of esters appeared also to promote hydrolysis of the cellulose polymer, and the low yields obtained from the methylene chloride fraction were partly due to the loss of some of the product to the wash fractions. If needed, these low-molecular-weight fractions can be recovered, thereby increasing the polymer yield. Further optimization of the iodine level in the reaction mixture may also be warranted to minimize polymer degradation. Alternatively, recent work indicates that these low molecular weight products may also have useful properties (Shelton et al., 2009), and their characterization may be of future interest.

4. Conclusions

The cellulose in cottonseed hull and burr can be converted to higher alkyl and mixed cellulose esters by way of an iodine-promoted esterification reaction. Cellulose propionate, cellulose butyrate, cellulose acetate propionate and cellulose acetate butyrate were prepared and characterized. Under the current reaction conditions, acetic anhydride is only slightly more reactive than propionic anhydride in the formation of CAP, but acetic anhydride is noticeably more reactive than butyric anhydride in the formation of CAB.

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