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Chemical modification of cotton-based natural materials: Products from carboxymethylation[☆]

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ABSTRACT

The processing of cotton generates a number of byproducts, two of which are cotton burr and cottonseed hull. A proximate analysis indicates that they contain about 30–32% cellulose, 17–19% lignin and lesser amounts of protein and oil. They differ in level of hemicellulose with burr containing ~6% and hull containing ~20%. Both materials can swell in aqueous NaOH–isopropanol solutions in which state they become susceptible to reaction with monochloroacetic acid. The products of this reaction consist of a water-soluble fraction (observed weight yields ranging from 28% to 55%) and a water-insoluble residue. The water-soluble fractions produce clear films that dissolve slowly in water with viscosities that are somewhat lower than for carboxymethyl products generated from purified cellulose. The products were characterized by NMR and IR and were found to consist mostly of carboxymethyl derivatives of cellulose and hemicellulose.

1. Introduction

The two main products derived from the cotton plant are cotton fiber and cottonseed (Bailey, 1948; NCPA Publications, 2002; True, 1896). During processing to recover fiber and extract oil from the seed, a number of fibrous byproducts are generated. Harvesting of bolls with pickers or stripper results in some field trash being collected with the seed cotton (Agblevor, Batz, & Trumbo, 2003; Bailey, 1948; Mittal, Fornes, Gilbert, & Sasser, 1979). This trash is separated during the ginning of the cotton fiber, and it contains a significant amount of cotton burr (i.e., the exterior protective part of the boll). Cotton burr is known to contain inorganic nitrogen, phosphate, and potassium and has a carbon-to-nitrogen ratio of 22:1 (Cotton burr compost from Back to Nature Inc., 2010; Lofgren, 1982; Mittal et al., 1979; True, 1896). Separated gin trash is often used as fuel for boilers in cotton plants, and after composting, as a natural fertilizer or soil conditioner (Cotton burr compost from Back to Nature Inc., 2010).

After separating the fiber, the cottonseed, which is composed of linter, hull, and kernel components (Bailey, 1948; NCPA Publications, 2002; True, 1896), is often used for oil extraction. Linters are usually separated as a first step in preparing the seed for extraction and are recovered and used as a source of chemical cellulose. The seed is then cracked to separate the hull and kernel components. Although some hull material remains with the kernel during extraction, the bulk of the hull is separated as an additional coproduct. Hull is used as roughage in animal feed, mulch or soil conditioner, substrate for mushroom cultivation, and occasionally drilling mud in the oil industry.

As part of our efforts to develop expanded uses of cotton byproducts, we are conducting a series of reactions on cotton burr, cottonseed hull, and their various fractions to produce chemically modified polymeric materials (Cheng, Dowd, Selling, & Biswas, 2010). One reaction of interest is carboxymethylation. Carboxymethyl cellulose (CMC) is a well known commercial product that has many uses, e.g., as a thickener, water binder, film-former, suspension aid, and drilling fluid (Feddersen & Thorp, 1993). The synthesis of CMC from purified cellulosic sources is usually made by reaction of cellulose with monochloroacetic acid under alkaline conditions (Adinugraha, Marseno, & Haryadi, 2005; Baar, Kulicke, Szablikowski, & Kiesewetter, 1994; Edelman & Lindroos, 1990; Choi et al., 2007; Dapia, Santos, & Parajo, 2003; Heydarzadeh, Najafpour, & Nazari-Moghaddam, 2009; Ruzene, Goncalves, Teixeira, & Pessoa de Amorim, 2007; Togrul & Arslan, 2003). In this work, we have

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[☆] Product 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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found cotton burr and hull to swell in the presence of aqueous NaOH–alcohol solutions, and in these conditions these materials are susceptible to the monochloroacetic acid reaction. The process is amenable to scale-up, and the products may be of interest in selected applications.

2. Materials and methods

2.1. Materials

Cottonseed hull was produced in the laboratory by acid-delinting Upland (fuzzy) cottonseed and cracking the delintered seed with a Bauer mill. Hull was recovered by air classification. Cotton burr was part of a cotton gin trash sample collected with a harvesting cotton stripper. The trash sample had a high percentage of burr pieces but also containing other foreign matter (stem pieces, dried leaves, etc.) that were separated from the sample by hand. Purified cellulose power (20-μm), sodium monochloroacetate (MCA), isopropanol, sodium hydroxide, glacial acetic acid, xylan, and deuterated NMR solvents (e.g., $CDCl_3$ and D_2O) were also purchased from Sigma–Aldrich (Milwaukee, WI).

Hull and the burr samples were milled in a kitchen blender and separated on 7-mesh and 20-mesh sieves. Hull was more easily broken up and was separated into a fine powder that passed through the 20-mesh sieve (H1) and a medium-sized powder that passed through the 7-mesh sieve but was retained on the 20-mesh sieve (H2). Burr contained some fibrous material that was more difficult to mill; hence, it was fractioned into three samples. It was classified into a fine powder that passed through the 20-mesh sieve (B1), a medium-sized powder that passed the 7-mesh sieve but was retained on the 20-mesh sieve (B2) and a coarse fraction that was retained on the top of the 7-mesh sieve (B3).

2.2. Proximate analysis

Proximate analyses of the starting materials were carried out by Eurofins Scientific (Des Moines, IA). Conventional methods were employed for ash, crude protein (by combustion), crude fat (by ethyl ether extraction), crude fiber (through acid and alkaline digestion), and moisture (Proximate analysis, 2010). Nitrogen free extracts (NFE) was calculated by subtracting moisture, ash, crude protein, crude fat, and crude fiber from the initial weight of the sample. Acid detergent fiber (ADF) and neutral detergent fiber (NDF) were measured as per Van Soest fiber analysis (Van Soest & Wine, 1967, 1968; Van Soest, 1963). A separate determination was made of lignin content via the Ankom method (Ankom, 2005), also performed at Eurofins Scientific.

2.3. Carboxymethylation procedure

In our initial carboxymethylation, the hull and the burr samples were washed with hexane to remove the triglycerides prior to the exposure of concentrated base. ^1H NMR analysis indicated that the hexane extracts in both cases were mostly triglycerides. In later carboxymethylation, the hull and burr samples were reacted without hexane extraction.

The procedure consisted of three steps. Initially, 5 g of ground sample was suspended in 100 mL isopropanol and 25 mL of water into which 5–6 g of sodium hydroxide was dissolved. The mixture was stirred overnight at room temperature. An alkylation solution was prepared by dissolving 8–12 g of sodium monochloroacetate in 10 mL isopropanol with a minimal amount of water added to facilitate dissolution. The alkylation solution was added slowly to the cellulose/isopropanol sample over a 30-min period, after which the mixture was purged with nitrogen and maintained at 50 °C for 2–3 h. The reaction was then stopped and filtered to separate the solids. The solids was suspended in 70% ethanol/water, neutralized with glacial acetic acid, washed, and refiltered three times with 70% ethanol/water to remove unreacted reagent and salt. The remaining material was then dispersed in 200 mL water. For burr and hull samples, this resulted in soluble and insoluble fractions. The insoluble fraction was separated via filtration, washed with additional water, and dried in a vacuum oven. The soluble material was stripped of water on a rotary evaporator. In addition to the various cotton products, cellulose and xylan were also carboxymethylated, and the products were used as control materials.

2.4. Product characterization

Solid-state NMR spectra were obtained at Process NMR Associates, LLC (Danbury, CT, USA) on a Varian (Palo Alto, CA, USA) Unity-Plus-200 spectrometer operated at a ^{13}C resonance frequency of 50.2 MHz. Cross polarization (CP) was achieved with a variable amplitude cross polarization pulse sequence to reduce the effects of spin modulation on the quantitative nature of the experiment. Magic angle spinning (MAS) was employed at a rate of ~6 kHz. The CP-MAS experiments were performed with a 2-ms contact time and a 1-s relaxation delay.

Solution NMR experiments were carried out at the Department of Chemistry, University of New Orleans. ^1H NMR spectra were recorded on a Varian Unity 400 spectrometer operating at 399.939 MHz. ^{13}C NMR spectra were recorded on either the Unity 400 spectrometer (100.574 MHz) or a Varian Gemini 300 spectrometer (75.432 MHz). Chemical shifts were referenced externally to a sample of xylan in D_2O. For both spectrometers, 30° pulses were used with a 1-s pulse delay. All NMR spectra were acquired at ambient temperature (20–22 °C).

IR spectra were obtained on a Bruker Vertex 70 spectrometer. Samples were run in the ATR mode with a diamond anvil cell. A blank run was made prior to every sample run, and the spectrum from the blank was subtracted from the spectrum of the sample.

Nitrogen was determined on some of the derivatized products by combustion with a Leco TruSpec® instrument (St. Joseph, Michigan). The analyzer was calibrated with a corn gluten sample (11.49% nitrogen), and standard operating procedures were used.

Solutions were made of each soluble sample at concentrations of 1% (w/v). Brookfield viscosity was measured on a Model LVT DV-IICP viscometer fitted with a cone-and-plate configuration and CP-40 spindle and on a Model LVDV-II+ viscometer fitted with a ULA-31Y spindle operated at 30 rpm (at 22 °C). Four to five determinations were made for each sample and the results were averaged.

3. Results and discussion

3.1. Compositional analysis

Proximate analyses of cotton hull and burr have been recorded in a compendium by True (1896). In addition, some data for hulls are available from Bailey (1948) and the National Cottonseed Products Association website (NCPA, 2002). Recently, proximate analyses of hull were also reported by Munguti, Liti, Waidhacher, Straif, and Zollitsch (2006). Because we fractionated the sample and expected differences in composition among the fractions, proximate analysis was conducted on the H1, H2, B1, B2, and B3 samples (Table 1). Results for the whole hull and burr were then calculated from these data and the measured weight fractions (Table 1). In order to better gauge the extent of reaction of our materials, the levels of acid detergent fiber (ADF), neutral detergent fiber (NDF), and lignin were also measured (Table 1). This allowed for an estimation of the

Table 1
Proximate analysis of cotton hull and burrs and their milled fractions (all values in %).

Sample (ref.)	Wt. frac.	Moisture	Protein	Crude fat	Crude Fiber	Ash	NFE	ADF	NDF	Lignin	Cellulose	Hemicellulose
H1 (this work)	0.354	12.0	7.73	3.72	33.6	3.62	39.3	54.9	67.1	22.1	32.8	12.2
H2 (this work)	0.646	11.5	2.98	0.55	36.7	2.54	45.8	49.4	74.2	17.3	32.1	24.8
$\text{Hull}_{\text{calc,total}}$ (this work)	1.000	11.7	4.7	1.7	35.6	2.9	43.5	51.3	71.7	19.0	32.3	20.3
Hull (True, 1896)		7.3–16.7	2.8–5.4	0.8–5.4	35.8–66.9	1.6–4.4	12.4–41.2					19.3
Hull (NCPA, 2002)		10.1	5	1.9	48.6	2.8	31.5	67	86.9			
Hull (Munguti et al., 2006)		9.4	17.3	5.5	58.7	3.6	15.3					
B1 (this work)	0.545	12.0	9.92	2.12	26.1	8.72	41.2	45.4	52.4	17.2	28.2	7.0
B2 (this work)	0.284	11.7	6.03	1.34	37.9	5.28	37.7	50.5	55.6	16.9	33.6	5.1
B3 (this work)	0.171	12.2	4.82	0.83	37.6	5.7	38.8	50.9	57	18.5	32.4	6.1
$\text{Burr}_{\text{calc,total}}$ (this work)	1.000	11.9	7.9	1.7	31.4	7.2	39.8	47.8	54.1	17.3	30.5	6.3
Burr (True, 1896)		11.9	7.0	1.4	32.5	7.3	39.9					

amounts of cellulose and hemicellulose in the samples as follows:

$$\text{Cellulose} = \text{ADF} - \text{lignin}$$

$$\text{Hemicellulose} = \text{NDF} - \text{ADF}$$

Overall, the proximate compositions were in accord with earlier results. The value for hull crude fiber for our samples is near the low end of the range reported by True (1896), which most likely relates to the amount of linters present in the samples. Commercial hulls, even after delintering, will typically contain some residual linters. In contrast, the hulls prepared for this work were acid delintered to remove this component completely. Correspondingly, the hull's levels of nitrogen-free extract (NFE), which is calculated from all other measured components by difference, had values toward the high end of True's and National Cottonseed Products Association (NCPA, 2002) data (Table 1). True (1896) also reported values for empty boll material (i.e., boll minus the seed cotton) that were in very good agreement with the analyses of our burr material (Table 1).

In comparing the two cotton byproducts, burr had somewhat higher protein and ash content and lower hemicellulose content when compared with hull. The levels of cellulose were approximately equal in the two materials. Because of the differences in hemicellulose, one might expect that the yield of soluble carboxymethylated materials will be less for the burr samples (discussed below).

Some compositional differences were also noted among the milled fractions. In both burr and hull, the smaller particles (i.e., H1 compared with H2, and B1 compared with B2 and B3) had more protein, crude fat, and ash. The biggest difference in the fractions occurred between H1 and H2, with the H2 fraction having a greater level of hemicellulose compared with the H1 fraction.

3.2. *Synthesis of carboxymethyl derivatives*

Reaction of the defatted hull and burr samples generally yielded water soluble and insoluble fractions (Table 2), indicating that some components of the samples were recalcitrant to reaction. For comparative purposes, a purified cellulose sample was also treated as a control case (Table 2). As expected, this CMC product was entirely water soluble and was obtained in higher yield. The mass of insoluble material from the cotton products was about the same in most of the burr and hull fractions (35–45% of the initial mass), but the value depended somewhat on how thoroughly water extraction was done. The yield of the water soluble material was greater for the hull products compared with the burr products, and the H2 sample yielded more soluble material than did the H1 sample. These trends appeared to correlate with the increasing amounts of hemicelluloses in the hulls compared with the burrs and with the H2 fraction compared with H1 fraction.

3.3. *FT-IR spectra*

FT-IR spectra of H1 and B1 samples were representative of the results for the untreated samples (Figs. 1 and 2). The IR spectrum of unreacted hull has been previously published (Allen, Foulk, & Gamble, 2007; Foulk, McAlister, Himmelsbach, & Hughs, 2004; Himmelsbach, Akin, Kim, & Hardin, 2003; Himmelsbach, Hellgeth, & McAlister, 2006) and is consistent with our results. Many IR peaks have been assigned (e.g., Allen et al., 2007; Foulk et al., 2004; Himmelsbach et al., 2003, 2006); e.g., the peaks at 3200–3600 cm^{-1} correspond to O–H stretching, 2840–3000 cm^{-1} C–H stretching, 1650–1780 cm^{-1} carboxyl/carbonyl stretching, 1600–1650 cm^{-1} carboxylate anion stretching, 1640 cm^{-1} water, 1514 cm^{-1} tannin-type aromatics, 1504–1512 cm^{-1} lignin-type aromatics, and ca. 1000 cm^{-1} various C–O, C–O–H and C–O–C modes. Different cellulosic materials and sugars have been shown to have peaks at 1000–1500 cm^{-1} (Himmelsbach et al., 2006). Lignin has been shown to have IR bands that range from 1038 to 1717 cm^{-1} (Boeriu, Bravo, Gosselink, & van Dam, 2004). The spectrum of burr (Fig. 2) appears somewhat similar to that of a "rotor dust sample" (Foulk et al., 2004) or bract (Himmelsbach et al., 2006); it has the same peaks as hull but with different peak intensities. As expected, these spectra reflect the presence of cellulose,

Table 2
Yields of water-soluble and water-insoluble fractions from the carboxymethylation of cotton hull and burr fractions.

Sample	Starting wt (g)	Water soluble		Water insoluble		Total observed yield (%)	% Theoretical yield[a]
		Wt (g)	Obs'd wt (%)	Wt (g)	Obs'd wt (%)		
Cellulose	5.00	4.5	90	0	0	90	62
H1	5.00	1.8	36	2.2	44	80	68
H2	5.00	2.8	55	2.0	40	95	79
B1	4.64	1.3	28	1.7	36	64	56
B2	5.41	1.6	29	1.9	35	64	55
B3	5.00	1.7	35	2.2	45	80	69

[a] Theoretical yield is calculated on the assumption of total conversion of cellulose to CMC, sodium salt (DS 0.7), and xylan to CMX, sodium salt (DS 0.4). All hemicellulose is assumed to be xylan. All other components (lignin, lipid, protein, water, inorganics) are considered unchanged and not removed.

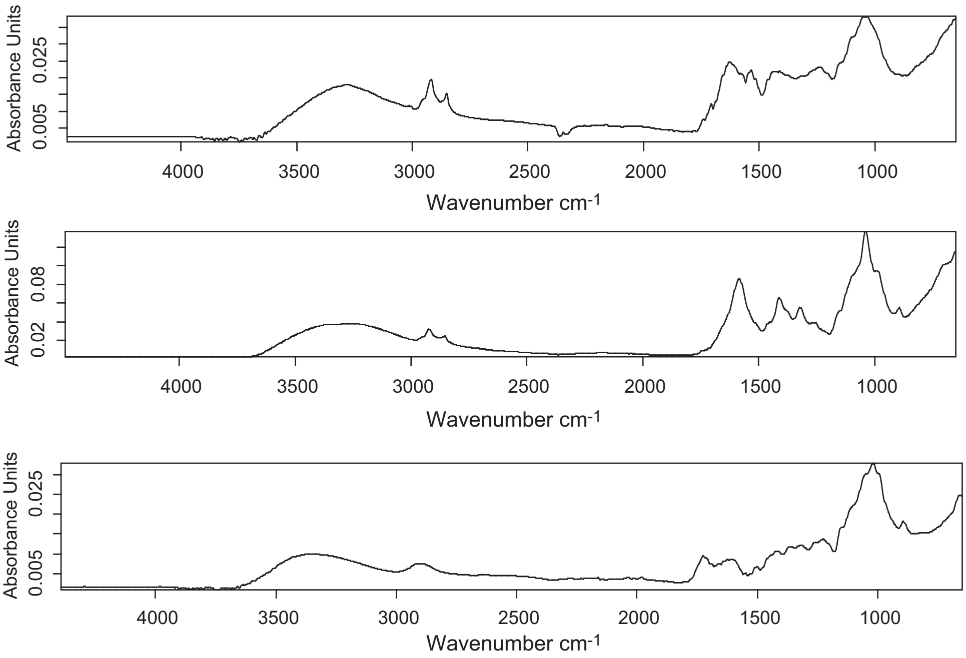

Fig. 1. FT-IR spectra of unreacted hull (top trace), reacted soluble hull (middle trace), and reacted insoluble hull (bottom trace).

hemicellulose, protein, lignin, and inorganics, but in different proportions.

The IR spectra of the carboxymethylation products are also shown in Figs. 1 and 2. The two soluble reacted hull and burr products had similar IR spectra, and indicated primarily the presence of CMC and carboxymethyl hemicellulose (CMX), the latter of which is believed to exist mostly as xylan (Agblevor et al., 2003). The IR spectra of the insoluble reacted hull and burr products can be interpreted to consist mainly of mixtures of cellulose and CMC.

3.4. ^{13}C NMR spectra

The ^{13}C NMR spectrum of cellulose is well known (Kono et al., 2002; Wickholm, Larsson, & Iversen, 1998). The cellulose peaks occur at 108 ppm (C1), 90 ppm (C4), 72–78 ppm (C2, C3, C5), and 68 ppm (C6). The ^{13}C NMR spectrum of xylan has also been published previously (Kobayashi, Wen, & Shoda, 1996; Sun, Fang, Tomkinson, Geng, & Liu, 2001; Sun, Sun, Lu, Xu, & Lin, 2002). Xylan peaks occur at 104 ppm (C1), 79 ppm (C4), 76 ppm (C3), 75 ppm (C2), and 65.5 ppm (C5). Likewise, the lignin ^{13}C NMR

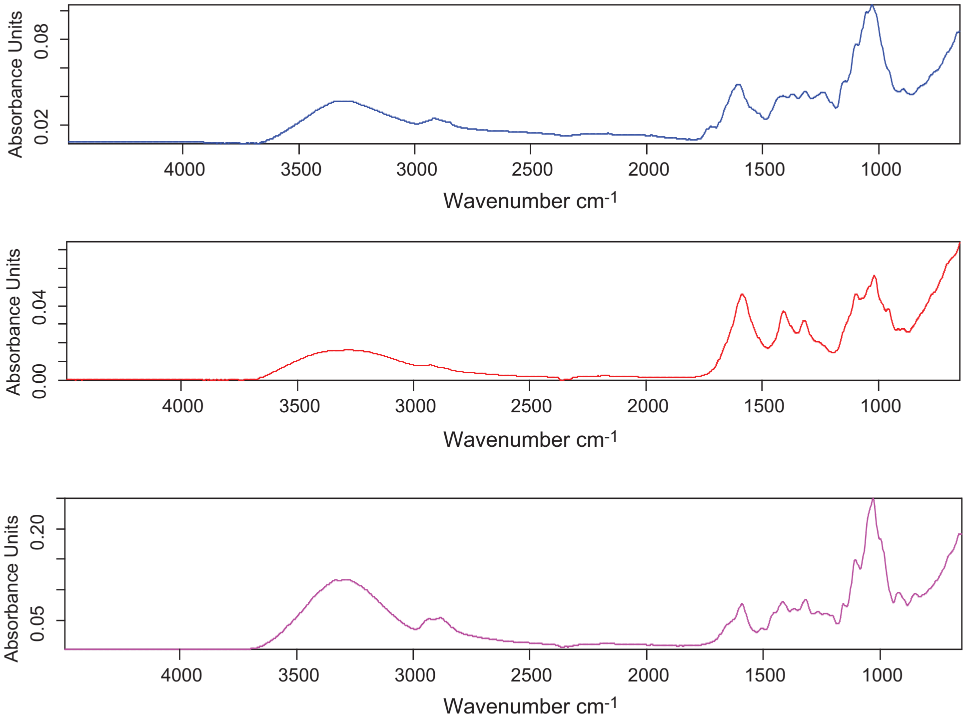

Fig. 2. FT-IR spectra of unreacted burr (top trace), reacted soluble burr (middle trace), and reacted insoluble burr (bottom trace).

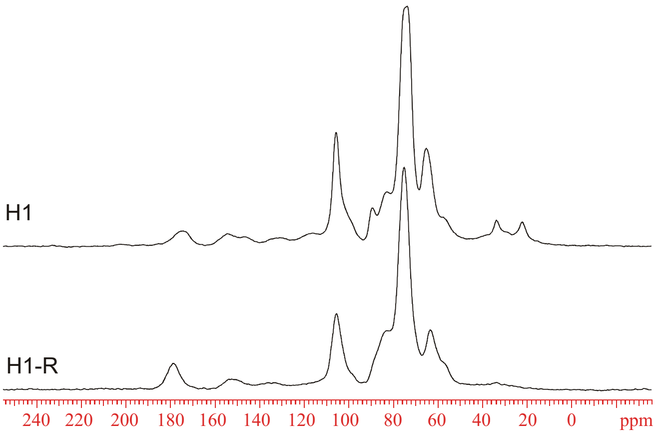

Fig. 3. Solid state ^{13}C NMR spectra of hull sample H-1: starting material (upper trace), and water-insoluble fraction of the reacted material (lower trace).

Table 3
Assignments of solid state ^{13}C NMR spectra for cotton burr and hulls.

^{13}C shifts (ppm)	Signal type	Assignment
195–190	C or quaternary	C=O in lignins
180–160	C or quaternary	C=O (in esters, acids) of lignin, and protein
160–141	C or quaternary	Oxygenated arom carbons in lignin (C-3, C-4)
160–150	C	Aromatic C–OH in tyr, ε-C in arg in protein
141–123	C or quaternary	C-1, C-5 condensed aromatic units in lignin
135–115	CH	CH carbons in phe, his, tyr in protein
123–105	C, CH	C-2, C-5, C-6 aromatic units in lignin
110–105	CH	C-1 of cellulose and xylan
90–58	CH, CH$_2$	C-α, C-β, C-γ units in lignin
89, 84	CH	C-4 in cellulose
78	CH	C-4 in xylan
75	CH	C-2 in cellulose
72–73	CH	C-3/C-5 in cellulose, C-2/C-3 in xylan
65	CH	C-6 in cellulose
63	CH	C-5 in xylan
65–50	CH, CH$_2$, CH$_3$	α-CH in proteins; β-CH$_2$ in Ser, Thr; OCH$_3$ in lignin
40–20	CH$_2$	Proteins

spectrum has also been studied (e.g., Landucci, 1991; Maciel, O'Donnell, Ackerman, Hawkins, & Bartuska, 1981; Xia, Akim, & Argyropoulos, 2001). Xia et al. (2001) assign the peaks as follows: 58.1 – 52.5 ppm (methoxy, C-β in β-β), 89.8 – 58.6 ppm (C-α,β,γ), 123.4–105.3 ppm (Ar–C2, C5, C6), 140.7–123.4 ppm (Ar–C1, C5 condensed), and 154.6–140.7 ppm (Ar–C3, C4). Wishart, Watson, Boyko, and Sykes (1997), Furie, Blumenstein, and Furie (1979), and Nigen et al. (1973) and others have reported ^{13}C data for protein, which is characterized by aliphatic peaks at 20–65 ppm, aromatic peaks at 115–160 ppm, and amide peaks at 160–180 ppm.

The solid-state ^{13}C spectra of the starting hull and burr samples (Figs. 3 and 4) resembled the spectra of wood (Baldock & Smernik, 2002; Johnson et al., 2005) and humic acid (Mao et al., 2000; Preston, 1996). The spectra indicate the presence of cellulose, hemicellulose, protein, and lignin. An approximate assignment scheme is shown in Table 3. Thus, cellulose and hemicellulose peaks can be clearly seen in the 60–110 ppm region. Lignin peaks can be seen in the 105–160 ppm region. Protein peaks are partly overlapped with cellulose, hemicellulose, and lignin peaks, but they are distinctive at 20–40 ppm. The 160–190 ppm region contain C=O peaks (e.g., from acids, esters, amides), which may include contributions from lignins, proteins, and oxidized cellulose and hemicellulose.

After carboxymethylation, the insoluble fractions produced simpler spectra (Figs. 3 and 4). The protein peaks were weak in insoluble reacted burr, whereas only a small amount of protein is seen in insoluble reacted hull. Weaker peaks in the 110–150 ppm range indicated that there was a reduced amount of lignin (Figs. 3 and 4) in the insoluble fractions compared with the starting material. The major components indicated by the spectra of the insoluble fractions were cellulose and CMC. The level of carboxymethylation was generally low, as was indicated by the relatively small peak at ca. 179 ppm. The carboxymethyl level was higher in insoluble reacted hull samples than in insoluble reacted burr fractions.

The water soluble carboxymethylated hull fraction (Fig. 5a) and burr fraction (Fig. 5b) were studied by solution ^{13}C NMR and compared with the spectra for CMC (Fig. 5c) and CMX (Fig. 5d). In contrast to the insoluble fractions, the NMR spectra of the soluble fractions consisted primarily of CMC and CMX. Peak assignments for CMC have been made by different groups (Baar et al., 1994; Capitani, Porro, & Segre, 2000; Chaudari, Gounden, Srinivasan, &

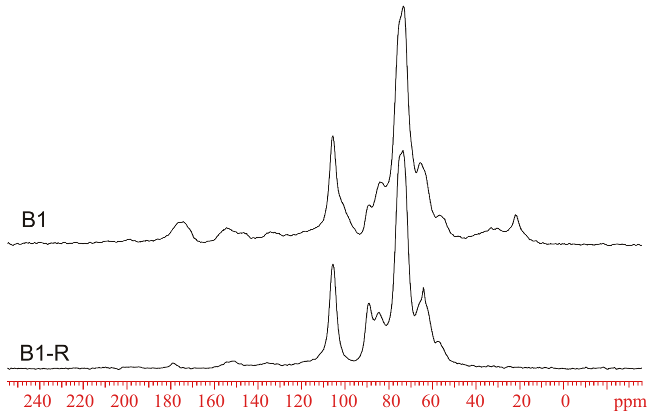

Fig. 4. Solid state ^{13}C NMR spectra of burr sample B-1: starting material (upper trace), and water-insoluble fraction of the reacted material (lower trace).

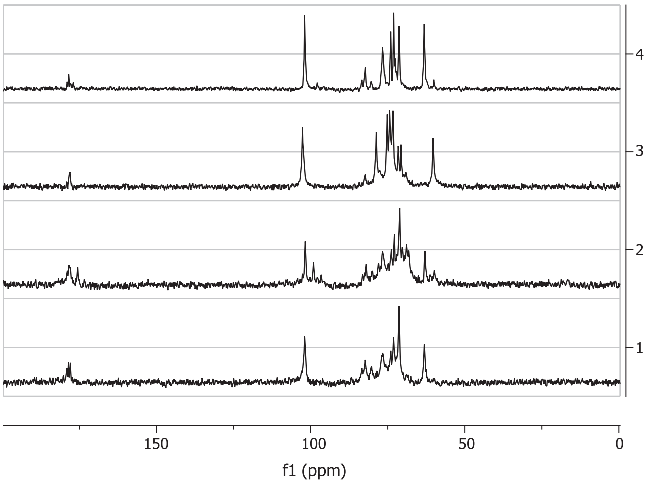

Fig. 5. ^{13}C NMR solution spectra at 75 MHz in D$_2$O: (a) bottom spectrum corresponds to the water-soluble fraction of reacted hull sample (H1); (b) second spectrum from the bottom corresponds to water-soluble fraction of reacted burr sample (B1); (c) third spectrum from the bottom corresponds to carboxymethyl cellulose (CMC); and (d) top spectrum corresponds to carboxymethylated xylan (CMX).

Ekkundi, 1987; Vieira, Heinze, Antonio-Cruz, & Mendoza-Martinez, 2002) with some variations in the assignments. The CMX spectrum has been only partly assigned (Petzold, Schwikal, Gunther, & Heinze, 2006; Ren, Sun, & Peng, 2008). A comparison of the intensities of the peaks at ca. 180 ppm (carboxy) and 102 ppm (C1) yields the overall degree of substitution (DS) for soluble reacted hull (about 0.5) and soluble reacted burr (about 0.7). Alternatively, an estimate of DS can be made by considering the intensities of the peaks at 102 ppm (C1) and 58–85 ppm (all other saccharide carbons plus methylene next to carboxy). Note that the C5 in CMX resonates at 63 ppm, but in CMC unreacted C6 resonates at 60 ppm and reacted C6 at 69 ppm (which partly overlaps with the other C–O peaks). Comparing the peaks at 63 ppm (C5 of CMX) and 102 ppm (C1 for both CMX and CMC), we can determine the approximate amount of CMX. Thus, the soluble hull product in Fig. 5 contained roughly 56 wt% CMX and 44 wt% CMC, whereas the soluble burr product in Fig. 5 contains 37 wt% CMX and 63 wt% CMC. In addition, the soluble treated burr contains several unidentified peaks (e.g., 96, 99, 172, and 177 ppm), which might be associated with minor hemicellulosic sugars, e.g., mannose, arabinose, or galactose, and perhaps other trace components.

Additional nitrogen analysis was conducted on the materials to confirm the partitioning of the protein component. A standard factor of 6.25 was used for the conversion of nitrogen to protein content. As shown in Table 1, the starting H-1 and B-1 samples have protein levels of 9.34% and 9.92%, respectively. The insoluble reacted H-1 sample has a nitrogen level of 0.54% (3.4% protein); the soluble reacted H-1 sample has a nitrogen level of 0.55% (3.4% protein). The insoluble reacted B-1 sample has a nitrogen level of 0.28% (1.7% protein); the soluble reacted B-1 sample has a nitrogen level of 0.55% (3.4% protein).

The Brookfield viscosity values for the CMC and water-soluble materials produced from hull fraction H-1 and burr fraction B-1 were 5.90 ± 0.43 cps, 3.45 ± 0.49 cps, and 2.81 ± 0.20 cps, respectively. The lower viscosities of cotton byproduct soluble fractions relative to CMC were due to the concentration of CMX, which has a lower molecular weight, and the presence of other unidentified components in reacted burr.

In summary, with relatively standard procedures, roughly 30% of cotton burr and 45% of cottonseed hull can be converted into soluble carboxymethylated products that consist mostly of CMC and CMX. These products are readily soluble in water and form films when dried. Perhaps these will be useful as low-cost replacements for CMC or for application where the properties of CMX are preferred. The insoluble burr and hull products were only slightly carboxymethylated, but they can still be used in conventional applications, such as a soil conditioner or fertilizer or as a source of roughage for animal feeds.

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