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Conversion of agricultural residues to carboxymethylcellulose and carboxymethylcellulose acetate

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ABSTRACT

In view of continuing interest in the utilization of agricultural by-products, we have converted cellulose, wheat straw, barley straw, and rice hull into carboxymethylcellulose (CMC), using both conventional heat and microwave-assisted synthesis. The application of microwave technology has enabled an improved synthesis of CMC to be conducted, with similar degrees of substitution as conventional heat (3 h) but reduced reactions times (30 min). The CMC obtained can be acetylated to form carboxymethylcellulose acetate (CMC acetate). The FT-IR and solid state ^{13}C NMR spectra of these materials have been characterized. With variations in the degrees of substitution of carboxymethyl and acetyl groups, a family of CMC acetate products can be made. The polymer may perhaps find applications as filtration membranes, functional fillers in polymers, and additives in commercial formulations.

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1. Introduction

There has been continuing interest in using agriculturally based raw materials for the synthesis of specialty polymers and biobased products (Mathers and Meier, 2011; Cheng and Gross, 2010; Yu, 2009; Belgacem and Gandini, 2008). The major advantages of agriculturally based materials are their availability, relatively low cost, and their favorable environmental profile. Thus, many publications have appeared on the conversion of agricultural products into cellulosic derivatives. As examples, cellulosic derivatives have been produced from agave fibers (Vieira et al., 2002). Carboxymethylcellulose (CMC) has been made from rice straw and wheat straw (Jahan and Rahman, 2006), sago waste (Pushpamalar et al., 2006), palm kernel cake (Bono et al., 2009), and from cotton byproducts (Cheng and Biswas, 2011). Cellulose acetate has been synthesized from corn fiber, rice hull, wheat straw (Biswas et al., 2006), from flax fibers, ears of corn, wheat straw (Vismara et al., 2009), and from cotton byproducts (Cheng et al., 2010). Mixed cellulose esters have been produced from cotton byproducts (Cheng et al., 2011). Acetates of wheat straw hemicellulose have been made with iodine catalysis (Ren et al., 2007). Methyl cellulose has been synthesized from wheat straw, barley straw and rice hull (Biswas et al., 2013a). Acrylic acid has been grafted onto wheat straw (Liu et al., 2009).

A particular focus of this work is CMC, a well known commercial product that has found many uses, e.g., as a thickener, water binder, film-former, suspension aid, and drilling fluid (Feddersen and Thorp, 1993). The synthesis of CMC from cellulose is well documented in the literature and usually entails the reaction of cellulose with sodium monochloroacetate under alkaline conditions (Cheng and Biswas, 2011; Heydarzadeh et al., 2009; Choi et al., 2007; Ruzene et al., 2007; Adinugraha et al., 2005; Togrul and Arslan, 2003; Dapia et al., 2003). In this work, we have made CMC from cellulose, wheat straw, barley straw and rice hull by both conventional and microwave-assisted methods. In addition, we have acetylated CMC to form CMC acetate using two different synthetic methods. As far as we know, the only previous reference to CMC acetate in the literature is a recent paper involving CMC acetate at high acetate content (degree of substitution 2.56) and low carboxymethyl (degree of substitution 0.3) for use in ultrafiltration membrane applications (Han et al., 2013).

The purpose of this work is two-fold: (1) to explore the use of microwave as a more energy-efficient method for CMC synthesis and (2) to convert agricultural waste materials such as wheat straw, barley straw, and rice hull into CMC and CMC acetate.

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2. Experimental

2.1. Materials

Sodium hydroxide pellets (97%), sodium monochloroacetate (98%), iodine (>99.8%), microcrystalline cellulose (20 μm powder), fibrous cellulose (cotton linters), and sodium carboxymethyl cellulose (average MW ~ 90,000 on label) were obtained from Sigma–Aldrich (Milwaukee, WI). Acetic acid (99.9%), acetic anhydride (99.4%), acetone (99.6%), isopropanol (99.9%), methylene chloride (99.9%), sodium thiosulfate (98.5%), ethanol (absolute), and chloroform (99.9%) were from Fisher Scientific (Pittsburgh, PA). Sulfuric acid (98.7%) was from J.T. Baker (Philipsburg, NJ).

Wheat straw was obtained from a farmer in Illinois. Barley straw was kindly supplied by Dr. Patrick Hayes, Oregon State University, Corvallis, OR. Rice hulls (rough grade) were purchased from Rice Hull Specialty Products, Inc., Stuttgart, AR. The wheat straw used in this study contained 32.0 ± 0% cellulose, 32.1 ± 1.3% hemicellulose, 11.2 ± 0.4% lignin and 6.5 ± 0.0% ash (moisture 5.5 ± 0.0%) (Saha et al., 2011). Barley straw contained 34.3% cellulose, 23.0% hemicellulose, and 13.3% lignin (moisture, 6.5%) (Saha and Cotta, 2010). Rice hulls used in this investigation contained 35.62 ± 0.12% cellulose, 11.96 ± 0.73% hemicellulose, 15.38 ± 0.20% lignin, 18.71 ± 0.01% ash, and 6.18 ± 0.05% moisture (Saha et al., 2005).

All these agricultural residues were pre-treated as described before (Biswas et al., 2013a); the pre-treatment entailed heating with weak sulfuric acid or alkaline peroxide. During pre-treatment most of the hemicelluloses was solubilized and degraded to monomeric sugars (e.g., xylose, arabinose, and galactose) and washed away. The pretreatment also increased the accessibility of cellulose for reactions.

2.2. Syntheses of CMC

Two procedures were employed in this work: conventional heat and microwave-assisted synthesis. Both procedures involved three steps: alkali cellulose formation, alkylation, and work-up. In the conventional synthesis (Cheng and Biswas, 2011), the alkali cellulose formation step entailed the swelling of 1 g cellulose in 20 mL isopropanol, 5 mL NaOH (6 M) overnight at room temperature; thereupon, the excess solvent was drained off. During alkylation, 1.08 g sodium monochloroacetate (MCA, in 10 mL isopropanol with ~2 mL water for dissolution) was added slowly over 30 min to swollen cellulose in isopropanol. The mixture was refluxed with nitrogen purge at 50 °C for 3 h. Later, in an improved alkylation procedure MCA was added directly as a solid to the cellulose/isopropanol and heated. In the work-up procedure, the reaction mixture was cooled and filtered to separate the solid product. The product was suspended in 70% ethanol/water, neutralized with glacial acetic acid, washed, and refiltered three times with 70% ethanol/water to remove excess reagents and salt, and finally washed with 80% methanol/water. The remaining material was then washed with 95% ethanol, filtered, and dried in a 70 °C vacuum oven overnight.

The microwave-assisted synthesis was initially adapted from a procedure used for methyl cellulose (Biswas et al., 2013b). In the alkali cellulose formation step, 1.0 g cellulose, 26.9 mL water, and 2.5 g NaOH were mixed together at room temperature for 1 h and then placed in a refrigerator at −20 °C overnight. The resulting frozen gel mixture was then thawed at room temperature and broken up. For alkylation, 20.6 mL water and 2.3 g MCA were added to the gel, and the mixture was subjected to microwave irradiation at 75 °C for 20 min. Later, in an improved process for alkali cellulose formation we used 1 g cellulose in 20 mL isopropanol and added 2 mL NaOH (25%) slowly over 5 min. Alkylation took place soon after that when we mixed MCA as a solid into cellulose/isopropanol and subjected the reaction mixture to microwave radiation at 45 °C for 30 min, or 82 °C for 5 min. For work-up, 50 mL of 10% acetic acid was added to neutralize the pH of the mixture. The precipitated CMC was washed with 70% ethanol/water, refiltered, and washed with 80% methanol/water. The product was finally washed with 95% ethanol, filtered, and then dried in a 70 °C vacuum oven overnight. Nitrogen analysis on CMC samples was conducted on a Perkin Elmer 2410 nitrogen analyzer (Waltham, MA). Standard operating procedures were used for nitrogen determination. Each analysis was done in triplicate; the data were reported as average ± standard deviation.

2.3. Syntheses of CMC acetate

The conversion of CMC to CMC acetate was carried out using two acetylation methods. In the conventional synthesis of cellulose acetate (e.g., Heinze et al., 2006), 2.0 g of starting material were added to 0.5 g acetic acid, 5.0 g acetic anhydride, 30 mL methylene chloride, and 0.04 g concentrated sulfuric acid in a 100-mL round bottom flask with stir bar. The reaction mixture was stirred and heated under reflux at ca. 80 °C for 4 h, then cooled to room temperature, and poured through a #60 Tyler screen to remove solid product. The solid product was dissolved in 60 mL chloroform at room temperature and poured through a #60 screen. The insoluble portion was discarded. The solvent was evaporated under vacuum at room temperature to give the acetylated product.

In the alternative, iodine-catalyzed acetylation (Biswas et al., 2009; Cheng et al., 2010), 0.57 g of starting material, 1.9 g of acetic anhydride, and 0.32 g of iodine were heated at 80–100 °C for 20–24 h. The reaction mixture was then cooled to room temperature and treated with 2 mL of a saturated solution of sodium thiosulfate while stirring. The mixture changed color from dark brown to colorless, indicating the transformation of iodine to iodide. The mixture was poured into 50 mL of ethanol and stirred for 30 min. The solid, which contained cellulose acetate, was filtered and washed with water and dried in a vacuum oven at 60 °C. Optionally, for further purification, the cellulose acetate was dissolved in methylene chloride and filtered. The filtrate was evaporated under vacuum at room temperature to remove methylene chloride.

2.4. NMR analysis

Solid-state NMR data were obtained on a Varian (Palo Alto, CA) Unity-Plus 200 spectrometer equipped with a Doty Scientific Supersonic 7-mm CP-MAS probe. 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. ^{13}C CP-MAS spectra were recorded at 50.3 MHz with a 1.2-ms contact time, a 4-second relaxation delay, and 33-ms acquisition time. Inverse gated decoupling was also used. The degrees of substitution (DS) was calculated from integrated peak areas. For CMC, the 45–110 ppm area = $6c + d$, where c = each carbon on the anhydroglucose unit in cellulose, d = carboxymethyl; the 160–185 ppm area = d. The carboxymethyl DS = d/c. For CMC acetate, the 45–110 ppm area = $6c + d$; the 160–185 ppm area = $a + d$; and the 14–22 ppm area = a, where a = acetyl. The acetyl DS = a/c.

Solution NMR spectra were obtained on a DRX400 spectrometer from Bruker Instruments (Carlstadt, Germany). Standard instrument conditions were utilized for ^{1}H and ^{13}C NMR with D_2O as the solvent. All chemical shifts were referenced to tetramethylsilane at 0 ppm.