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Carboxymethylcellulose from recycled newspaper in aqueous medium

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ABSTRACT

Recycled paper cellulose has some drawbacks, for example loss in mechanical strength, to use in paper industry alone. However, derivatives of cellulose can find applications in other industrial areas. Carboxymethylcellulose (CMC) is one of the most used cellulose derivatives and can be obtained by heterogeneous modification of cellulose. In general carboxymethylation of cellulose achieved in alkaline alcoholic dispersions. In this work modification of cellulose from recycled newspaper in aqueous alkaline solution was aimed. First cellulose was recovered from newspaper under oxidative alkaline conditions. Cellulose recovery was determined as 75–90% (w/w) of starting material. Carboxymethylation reactions were carried out to find optimum conditions for derivatization, changing concentrations of components and reaction temperature. Obtained CMC samples had a DS of 0.3–0.7% and 84–94% CMC content. As a result, carboxymethylation of cellulose from recycled newspaper was achieved in aqueous alkaline dispersion giving commercial grade CMC for industrial use.

1. Introduction

Cellulose is the most abundant renewable material resource in the world (Huda et al., 2005). Average production of cellulose via photosynthesis is estimated about 830 million tons per annum. This means annual bio-based cellulose production is about 200 million tons, because approximately 40% of dry-weight of crops is composed of cellulose. The world market for newsprint is growing over 2% per year. Virgin paper is made from highly compressed and heated cellulose fibers from soft woods, mainly grown and harvested as "paper pulp trees". Besides, recovery of cellulose from annual crop wastes to satisfy the need for paper is a popular research field (Bledzki, Reihmane, & Gassan, 1996; Lewis & McIlroy, 2008; Li, Shi, Wang, & Du, 2011; Sun, Fowler, Rajaratnam, & Zhang, 2010). Recycling of used paper is another way to obtain paper; however, recycling causes loss in mechanical strength of the paper due to changes in crystallinity of cellulose fibers (Gilbert & Kadla, 1998; Hubbe, Venditti, & Rojas, 2007). Thus, recycled paper is mostly used in production of low-quality paper products (e.g. paperboard, etc.) (Nazhad, 2005).

Cellulose derivatives, such as carboxymethylcellulose (CMC), hydroxypropylmethyl cellulose (HPMC), differ from cellulose in many terms (i.e. solubility) and have many applications in different industrial areas (Filho et al., 2008; O'Connell, Birkinshaw, & O'Dwyer, 2008; Talába, Sroková, Ebringerová, Hodul, & Marcinč in, 1997; Vieira, Klemm, Einfeldt, & Albrecht, 2005). Carboxymethyl cellulose synthesis is generally performed in alcoholic solutions or organic solvents like ionic liquids (Gericke, Liebert, Seoud, & Heinze, 2011; Ramos, Frollini, & Heinze, 2005; Togrul & Arslan, 2003). Although complete etherification can be achieved with these methods, use of organic solvents for the production can cause environmental pollution. Synthesis of CMC in aqueous solutions without organic solvent or alcohol has not been experienced frequently. However, recent studies in field of green chemistry mostly focuses on water as a solvent having the features of being cheap, easily accessible, and non-toxic. Carboxymethylation of cellulose in aqueous solution may yield low-substituted CMC samples, appropriate for use in different industrial fields, especially where low or medium DS numbers are required.

Aim of this work is to synthesize carboxymethylcellulose in aqueous solution using recycled newspaper cellulose as a raw material. Characterizations of obtained CMC have been made in terms of rheologic, thermal, physical, and spectral properties.

2. Materials and methods

Newspaper used in the study was obtained locally. Purification of newspaper was done using alkaline peroxide treatment. Newspaper was dispersed in aqueous $NaOH/H_2O_2$ solution and stirred. When reaction period was over pulp was filtered and washed with water. Obtained (recycled) cellulose **(1)** dried in air at first ambient temperature, then 60 °C.

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2.1. Synthesis of carboxymethyl cellulose

Carboxymethylcellulose (CMC) synthesis was done using **1** and monochloroacetic acid (MCA, **2**) in aqueous alkaline medium. **1** (2 g) was activated dispersing it in aqueous NaOH (50 ml, 20%, w/v) for 15 min using mechanical stirrer. Then the dispersion was diluted using isopropanol or water and stirred for an additional 15 min. Carboxymethylation was done adding **2** (2.5 g, 2.65×10^{-3} mol) to the dispersion. The reaction was carried out 2 h at 50 °C; then pH was adjusted to 5 with glacial acetic acid. Obtained product (CMC, **3**–**8**) was washed with 80% ethanol, then with absolute ethanol three times, and was dried first at ambient temperature, then 60 °C.

2.2. Determination of DS, moisture, CMC assay and NaCl content

Moisture content, degree of substitution (DS), CMC content, and NaCl content of obtained CMCs were determined according to literature (ASTM, 2008; Togrul & Arslan, 2003).

The DS was determined using methanol 108 ml of 65% HNO_3 was made to 1 l. The sample (0.1 g) was shaken with 20 ml of HNO_3–methanol mixture, was kept for 3 h and the surplus acid was washed with 70% methanol. Dried sample (0.05 g) was dissolved in 4.5 ml distilled water and 12.5 ml of 0.05 N NaOH mixture. Then the solution was titrated back with 0.05 N HCl. The DS of CMC was determined by following equations:

$$A = \frac{(BC - DE)}{F} \quad DS = \frac{0.162A}{(1 - 0.0058A)}$$

where A is the equivalent weight of alkali required per gram of sample; B (ml) and C are amount, and normality of NaOH solution; D (ml) and E are amount, and normality of HCl solution; F (g) is the weight of sample.

To determine assay of CMC, 0.025 g of sample was added to 20 ml of 80% methanol, stirred, kept for 10 min and filtered. Cake was washed with 80% methanol and dried.

$$\text{Assay of CMC, \%} = \frac{m_2}{m_1} \times 100$$

where m_1 (g) is the weight of dried sample and m_2 (g) is the weight of washed sample.

To determine NaCl amount, 0.025 g of sample was added to 10 ml of 65% methanol and kept for 5 h. Liquid phase was neutralized by diluted HNO_3 and titrated by 0.015 N $AgNO_3$ solution.

$$\text{NaCl \%} = 0.0147 \times \frac{V}{m}$$

where V (ml) is the amount of $AgNO_3$ and m (g) is the weight of dried sample.

2.3. Molecular weight and rheologic measurements

Molecular weight of CMCs were determined using Mark–Houwink equation as $[\eta] = 5.37 \times 10^{-4} M_V^{0.73}$ (dl g^{-1}) in 0.5 N NaOH at 25 °C (Eremeeva & Bykova, 1998).

Rheologic characterizations of the dispersions was determined with Brookfield DV–III low-shear rheometer using shear stress–shear rate measurements within 0–330 s^{-1} shear rates with SSA-18 spindle. The measurements were carried out in duplicate. Calculations of rheologic models were done using Python 2.7 with NumPy and SciPy modules. Measurements were done using 1% (w/v) aqueous samples, which were prepared using 0.5 N NaOH. Yield value (τ_B) and plastic viscosity (η_{Pl}) values were obtained from linear regression of shear stress–shear rate data in the range of 45–330 s^{-1}. Apparent viscosity (η_{125}) was calculated as shear stress/shear rate at 125 s^{-1}. Flow index calculated from linear regression of log–log plot of shear stress–shear rate data in the range of 45–330 s^{-1}. Hysteresis area was obtained from integration of up and down curves of shear stress–shear rate plot in the range of 0–250 s^{-1}.

2.4. Spectral and thermal characterizations

FTIR analyses were performed on Perkin Elmer Spectrum One FTIR spectrometer in the range of 4000–400 cm^{-1} using KBr pellets (1%, w/w). NMR analyses were performed on Agilent VNMRS (^{1}H NMR 500 MHz) and Bruker AC-3000 (^{1}H NMR 250 MHz) in D_2O operating at ambient temperature.

Thermogravimetric analysis (TGA) was performed on Perkin Elmer Diamond TG/DTA instrument with a heating rate of 10 °C min^{-1} under nitrogen flow (200 ml min^{-1}). TGA data was evaluated in order to calculate activation energy of decomposition following literature (Broido, 1969). Activation energy was obtained from the plot of equation:

$$\ln \ln \frac{1}{y} = \left(\frac{E_a}{R}\right) \frac{1}{T}$$

where E_a was activation energy in kJ mol^{-1}, R was gas constant in J mol^{-1} K^{-1}, T was temperature in K, and y was the fraction which was defined as

$$y = \frac{W_t - W_\infty}{W_0 - W_\infty}$$

where W_t, W_∞, and W_0 were weight at temperature t, end of decomposition, and beginning of decomposition respectively. Inverse absolute temperature was plotted against $\ln \ln 1/y$, then linear regression was applied and E_a was calculated from the slope of the linear function. Calculations were carried out using Python 2.7 with NumPy and SciPy modules.

2.5. Visual determination of surfactant class

Visual inspection for surfactant class was done using methylene blue and bromophenol blue tests (Snell, Hilton, & Ettre, 1972). 4 mg material dissolved in 20 ml water. Ten ml of the solution was mixed with 0.1 N HCl and 1 ml 0.02% aqueous methylene blue solution; then it was shaken with 5 ml $CHCl_3$. The other 10 ml of the solution was mixed with 0.1 N NaOH and 1 ml 0.002% aqueous bromophenol blue solution; then it was shaken with 5 ml $CHCl_3$. Color of the chloroform layer was dependent on class of the surfactant and indicator. For methylene blue, it was colorless for anionic surfactants and blue for cationic surfactants. For bromophenol blue, it was blue for anionic surfactants and colorless for cationic surfactants. Nonionic surfactants gave a faint blue color for both indicators.

3. Results and discussion

3.1. Recovery and characterization of cellulose from newspaper

Alkaline peroxide treatment is a method to fractionate crop wastes into cellulose, hemicellulose, and lignin (Sun, Tomkinson, Geng, & Wang, 2000). Hydroperoxide anion radicals and oxygen radicals are generated in the solution from H_2O_2 and NaOH; these radicals oxidize cellulose–hemicellulose and hemicellulose–lignin bonds to solubilize cell wall components. As newspaper was mainly composed of cellulose deinking and removal of solubilized impurities were done using oxidizing alkaline condition to obtain recycled cellulose from newspaper. Hydrogen peroxide concentration was kept constant at 1% while alkaline concentration was changed. Two different conditions were examined; higher alkali concentration and temperature were used for strong condition, while mild condition was achieved using less alkali at room temperature. Hydrolysis was performed for mild conditions as followed; 36 g newspaper