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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.

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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:

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

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

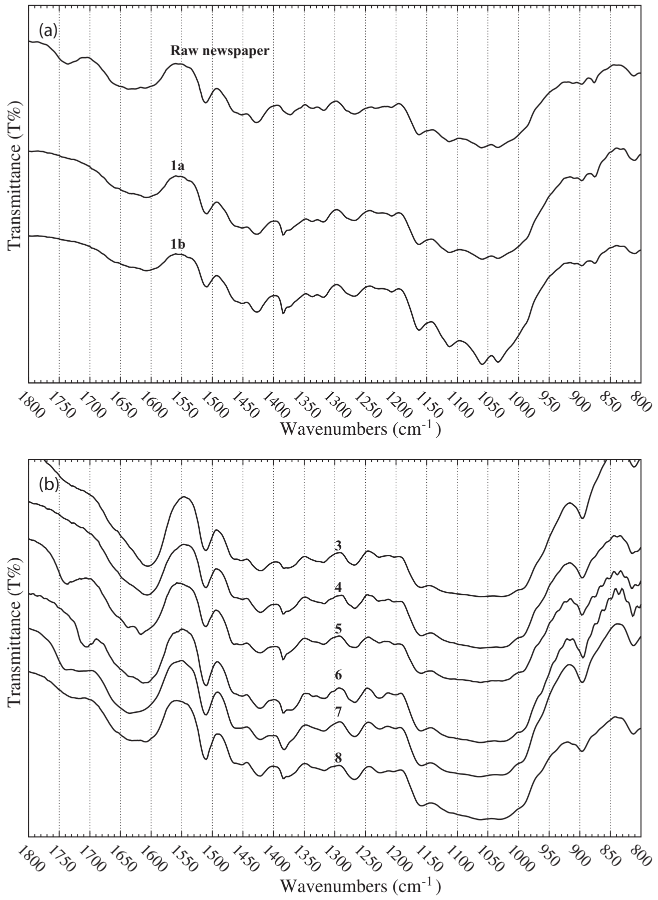


Fig. 1. FTIR spectra of (a) raw newspaper and recycled celluloses obtained using mild and strong conditions, (b) **3**–**8** in range of 1800–800 cm^{-1}.

was suspended in 1 l of water. Then 10 ml 1 N NaOH and 5 ml 35% (w/v) H_2O_2 were added to the dispersion. After 1.5 h of stirring at ambient temperature residual material was filtered, and washed with water several times. Same procedure followed for stronger conditions using 38 g newspaper, 25 ml 1 N NaOH, 3 ml 50% (w/v) H_2O_2 at 45 °C. Recovered cellulose (**1a** and **1b**) was 88 and 75% of starting material by weight for mild and strong conditions.

FTIR analyses were performed to characterize both starting and recycled materials. FTIR spectrum of starting material (newspaper) showed signals belonging to O—H stretching vibrations at 3350 cm^{-1}, C—H stretching vibrations at 2905 cm^{-1}, H—O—H deformation vibration at 1637 cm^{-1}, various C—C stretching, and C—O—H, H—C—H bending vibrations between 1500 and 1250 cm^{-1}, and various C—O stretching, C—O—C, C—C—O bending vibrations between 1250 and 900 cm^{-1} (Fig. 1a). Anomeric group vibration was observed at 897 cm^{-1}. Additional absorption bands were attributed to lignin fragments bonded to cellulose. Lignin-related vibrations were mainly those at 1730 cm^{-1} and 1620–1690 cm^{-1} (non-conjugated and conjugated carbonyl group), 1512 cm^{-1} (aromatic ring vibrations of phenylpropane skeleton) and 1250 cm^{-1} (aryl–alkyl ether linkage), and 810 cm^{-1} (C—O stretching of guaiacyl rings) (Filho et al., 2008).

After alkaline peroxide treatment, the most distinct change in spectra of recycled celluloses was disappearance of carbonyl stretching at 1735 cm^{-1}. This occurrence indicated that impurities of ester-type solubilized and removed from the recycled cellulose. Carbohydrates gave specific peak patterns in the range of 1300–950 cm^{-1} regarding to constituent sugar units (Kacuráková, Capek, Sasinková, Wellner, & Ebringerová, 2000). Change in the pattern of characteristic peak at 1050 cm^{-1} indicated the changes in conformational and crystal structure of cellulose as a result of the treatment. Proportion of signal intensities at 1430 and 900 cm^{-1} (A_{1430}/A_{900}) was an indicator of the proportion crystal to amorphous structures (Oh, Yoo, Shin, & Seo, 2005). Values for this proportion were found as 2.44, 3.89, and 2.76 for raw newspaper, **1a** and **1b**. This result indicated that crystal structure increased as a result of oxidative alkaline treatment; appearance of a weak intensity peak at 1385 cm^{-1}, which was also related to crystal structure of cellulose, was also supported this result.

Table 1
Results of carboxymethylation aqueous reaction (NaOH:fiber 125 mmol g^{-1}, MCA:fiber 13 mmol g^{-1}, 50 °C, 2 h).

Sample	[**1**], g l^{-1}	Gain	Assay	NaCl, % (w/w)	Moisture[a]	M_V, kDa
3[b]	20	95	84	0.28	5.8	274
4	20	89	88	–	5.9	70
5[c]	20	89	86	–	5.3	N/A[d]
6	13	90	94	–	5.6	270
7	10	88	94	–	5.6	80
8[e]	13	91	90	0.28	5.8	52

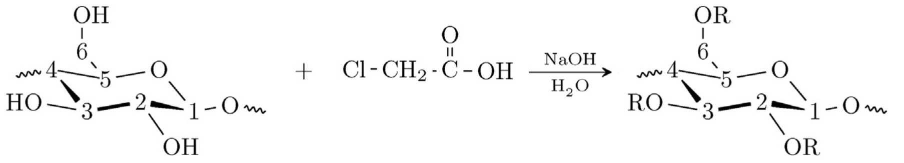
[a] Moisture content of cellulose = 6.3%.
[b] Solvent IPA.
[c] MCA:cellulose 18 mmol g^{-1}.
[d] Could not be determined due to solubility problem.
[e] Cellulose obtained under milder conditions (**1a**).

Cellulose was recycled from newspaper at moderate rate; changing recycling conditions affected purity and crystal structure of resulting product. The difference between two cellulose samples obtained under different conditions was probably due to residual lignin moieties which were bonded to cellulose. Complete removal of lignin could be probably achieved by stronger reaction conditions (i.e. increasing temperature, NaOH, H_2O_2 concentrations). However, residual lignin would not interfere with carboxymethylation, thus complete lignin removal was not attended.

3.2. Synthesis and characterization of carboxymethylcellulose

Regarding to the aim of the study carboxymethylation was done in aqueous alkaline medium using monochloroacetic acid (MCA, **2**) and use of alcohol was avoided (Scheme 1). Results of the selected experiments were summarized in Table 1. Initial reaction conditions were determined as 2 g of cellulose **(1)**, 125 mmol NaOH per gram fiber, 13 mmol MCA per gram fiber, 50 °C, 2 h, according to literature with some modifications (Heinze & Pfeiffer, 1999; Togrul & Arslan, 2003). Carboxymethyl celluloses (**3**–**8**) were obtained from reactions using water as solvent and **1b** as cellulose; but **1a** was also used for **8**. Water was the only solvent for all reactions except **3**, which was synthesized using isopropyl alcohol. **4** was obtained under identical conditions with **3**; only difference was use of water in reaction for dilution. Other reactions to obtain CMC samples from **5** to **7** were done using **4** conditions with some modifications. These modifications were changes in MCA:fiber ratio (**5**) and cellulose concentration (**6**, **7**). There was a decrease (about 10% by weight) for all CMC samples with respect to starting material. For all reactions, there was a loss in obtained material amount about 10% by weight with respect to the starting cellulose. This occurrence was probably due to degradation of cellulose resulting in formation of smaller chains.

Physical characterizations gave following results for **3**–**8**. CMC assay was determined as 84% by weight for **3**. Changing the reaction solvent to water caused an increase in the assay (**4**). The maximum assay was obtained for **6** as 94%. Sodium chloride was determined as 0.28% only for **3** and **8**, other samples gave no result for NaCl determination. Moisture content of cellulose was determined as 6.3% by weight. After carboxymethylation it was found as 5.6% (±0.2) CMC samples. Molecular weight of the samples varied regarding to the reaction conditions. **3** and **6** had the highest M_V as 274 kDa.



1 Cellulose from recycled newspaper

2 Monochloroacectic acid (MCA)

3–**8** $R = -H$ or $-CH_2COONa$ according to DS

Scheme 1. Simplified reaction scheme for derivatization of cellulose with monochloroacetic acid in alkaline medium.

5 was insoluble, thus its M_V was not measured. There were also some visual differences amongst starting material (recycled cellulose, **1**) and obtained CMCs (**3**–**8**) such as color (**1** was grey-brown while CMCs were greenish-yellow) and physical form (**1** was sheet-like while CMCs were small chips regarding to DS). Consequently carboxymethylation of newspaper cellulose in water as solvent achieved at optimum when reaction was carried out 2 h at 50 °C using 125 mmol NaOH per gram fiber, 13.3 mmol **2** per gram fiber, and 13.2 g l^{-1} fiber concentration.

Visual surfactant class determinations were also carried out for CMC samples. These inspections of surfactant class rely on salt formation between surfactant and indicator. Formed salt, having lipophilic groups, introduces into the organic phase coloring it. If a surfactant belongs to anionic class, it will form a salt with cationic indicator (i.e. methylene blue) and vice versa. Since CMC had negative charges due to carboxylate anions, they were expected to behave like anionic surfactants. Aqueous phase of methylene blue solutions faded, but chloroform phase remained colorless, however, CMC–methylene blue salt laid on the interface between aqueous and organic layers (Fig. 3). Carboxymethyl groups interacted with the indicator, however, they could not migrate into chloroform phase as CMC had no solubility in organic phase; thus they settled down on the interface fading the color of aqueous phase. Since CMC had no cationic group it was not interacted with bromophenol blue solution.

Degree of substitution (DS) of CMC samples was found using standard procedure which was explained above; but it could be also estimated using FTIR data (Yuen, Choi, Phillips, & Ma, 2009). Intensity of the 1426 and 1315 cm^{-1} bands was influenced to various extents by other vibrations, such as C—H stretching and anomeric skeleton, while the 1236 cm^{-1} band was affected by C—O—H vibrations. Although, it was difficult to find an IR band attributed only to the carboxymethyl groups, band intensities of signals at 1317 and 897 cm^{-1} could be used to estimate DS of the sample. FTIR estimated and traditionally found DS values were shown in Table 2. Both estimated and found DS results were consistent. Experimentally found DS values of samples were in the range of 0.3–0.7. CMC obtained using alcoholic dispersion (**3**) gave a DS of 0.72, which was the highest DS achieved. However, a DS value of 0.61 was observed for **6** using water as solvent. Other experiments showed slightly different results in water (for **4**, **7**, and **8** DS were 0.51, 0.59, 0.51); **5** had the worst DS value (0.35).

Table 2
Degree of substitution (DS) values of CMC samples.

Sample	I_{1317}[a]	I_{897}	Ratio	DS[b]	DS[c]
3	0.524	0.255	2.05	0.67	0.72
4	0.445	0.293	1.52	0.41	0.51
5	0.492	0.307	1.60	0.45	0.35
6	0.436	0.188	2.32	0.81	0.61
7	0.435	0.187	2.33	0.81	0.59
8	0.413	0.222	1.86	0.58	0.51

[a] Intensity values for 1317 and 897 cm^{-1}.
[b] Estimated using data of Yuen et al. (2009).
[c] Experimentally found.

FTIR analyses of samples showed also C=O stretching vibrations of carboxylate groups at 1606 cm^{-1} proving introduction of carboxymethyl moieties onto cellulose (Fig. 1b). Various C—O stretching and C—O—C, C—C—O bending vibrations were observed between 1250 and 900 cm^{-1} giving a unique pattern for polysaccharides (Kacuráková et al., 2000); this region was also very sensitive to side-groups and conformation changes. Since the carboxymethylation took place in basic medium, obtained CMC samples were in sodium salt form ($-$COO$^-$Na$^+$) rather than in acid form ($-$COOH). There were increases in two other IR peaks at 1426 and 1315 cm^{-1} in all CMC samples. These bands were attributed to C=O stretching in COO$^-$ ions. FTIR analyses proved that carboxymethylation reactions were done successfully and resulting product had carboxymethyl moieties at different ratios regarding to reaction conditions.

Additional spectral characterizations of CMC samples were also done using ^{1}H NMR spectroscopy. Signals belonging to lignin moieties appeared at aromatic (δ 7.2–7.7), aliphatic regions (δ 1.18–1.49, and δ 1.9), and at δ 3.9 as peaks having small intensities (Tejado, Pe na, Labidi, Echeverria, & Mondragon, 2007). Proton NMR spectra of obtained samples showed characteristic absorption signals of carboxymethylcellulose between δ 3.0 and 5.5. A representative NMR spectrum of **6** was presented in Fig. 2 as the CMC samples. Protons were labeled regarding to Scheme 1; anomeric protons (H_1) were observed at δ 5.13 and 5.21. Other protons of carboxymethylcellulose at positions at 2, 3, and 6 were observed as δ 3.41, 3.18, and 3.99; and H_4 and H_5 were at δ 3.69 as overlapped signals. Methylene protons of carboxymethyl moiety (H$_7$) were observed mainly at δ 4.33, a very weak signal also observed at δ 4.49. Spectral analyses confirmed the carboxymethylation reaction was performed successfully.

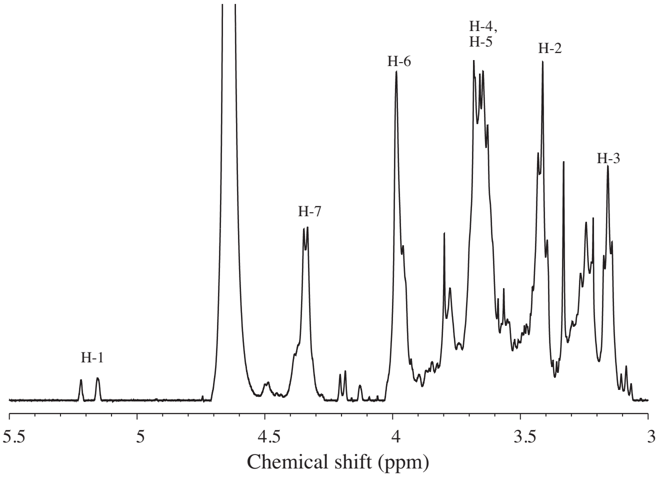


Fig. 2. Expanded ^{1}H NMR spectrum of **6**.

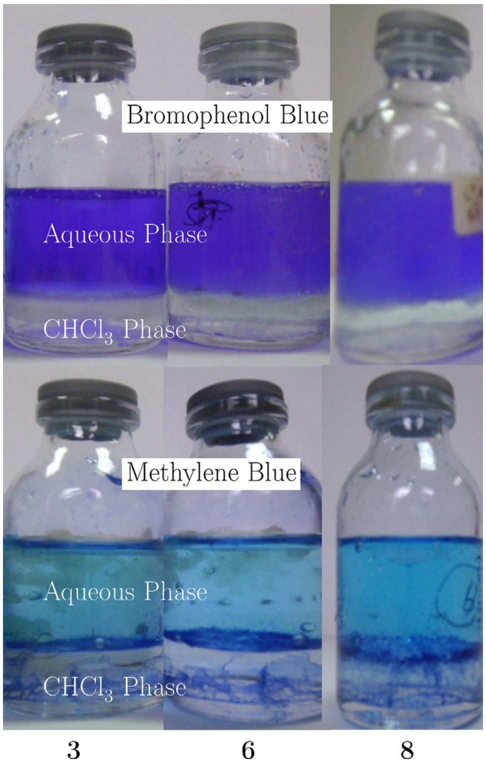


Fig. 3. Visual inspection of surfactant class for **3**, **6**, and **8**.

3.2.1. Thermal characterizations

Thermal characterizations of cellulose and CMC samples were done using thermogravimetric analysis (TGA). Maximum decomposition temperature (T_{max}) was identified using first order derivative of weight loss versus temperature plot. TGA analyses of the distinct samples (**1**, **3**, **6**, **8**) were summarized in Table 3 and TGA thermograms were plotted in Fig. 4. All samples showed a weight loss up to 150 °C about 5% attributed to adsorbed water; results were consistent with the results of ASTM method for moisture content.

Thermal degradation of the samples started after 150 °C and lasted about 500 °C; maximum degradation temperature (T_{max}) and activation energy (E_a) of the degradation were calculated between this range for all samples. Cellulose **(1)** showed maximum degradation at 376 °C; but CMC samples had different T_{max} values regarding to DS of the sample. T_{max} was found closer to **1** as DS was smaller; T_{max} for the sample **3**, whose DS was the highest as 0.72, was 314 °C while it was observed as 332 and 354 °C for **6** and **8** (DS were 0.61 and 0.51).

Activation energy of the thermal decomposition was calculated by manipulating weight loss data following Broido's method. Calculations displayed that **1** had different decomposition reactions involving different order of kinetics. There were three distinct slopes in 220–372 °C, 372–394 °C, and 394–450 °C ranges on ln ln 1/y versus 1/T plot of **1**. This result was an indicator of three kinds of decomposition reactions having E_a values of 86.3, 148.7, and 23.5 kJ mol^{-1}, which were obtained from linear regression with the highest regression coefficient. CMC samples had two distinct decomposition ranges separated approximately 380 °C; DS values affected also the E_a. Higher DS resulted in higher E_a, but the reaction took place in a narrow range; **3** had the highest DS, decomposition reactions were observed in two ranges separated at 340 °C having values of 96.8 and 25.4 kJ mol^{-1}. Decreasing DS caused higher upper limit of decomposition range and lower E_a; decomposition ranges of **6** split at 368 °C having E_a of 92.3 and 23.9 kJ mol^{-1} while they split at 380 °C for **8** having the E_a values of 90.5 and 25.5 kJ mol^{-1}. These results could be interpreted as the first part of the decompositions was regarding decarboxylation of the CMC samples and second part was related with main chain decomposition of the cellulose. Because higher DS indicated higher number of carboxymethyl moieties and decarboxylation reaction needed much energy to decompose these moieties; at the same time decomposed carboxylate groups left a back-bone of cellulose to decompose. Due to this occurrence last parts of the all decompositions (including **1**) showed similar E_a values (approximately 25 kJ mol^{-1}) because all of the samples had the same back-bone as they were only different at the amount of carboxylate groups.

Table 3
Summary table for thermal data of **1**, **3**, **6**, **8**.

Sample	DS	T_{max}, %	E_a, kJ mol^{-1}	
			220–380 °C	380–450 °C
1	–	376	86.3	148.7, 23.5 [a]
3	0.72	314	96.8	25.4
6	0.61	332	92.3	23.9
8	0.51	354	90.5	25.5

[a] Cellulose showed two different slopes between 372–393 °C and 393–450 °C.

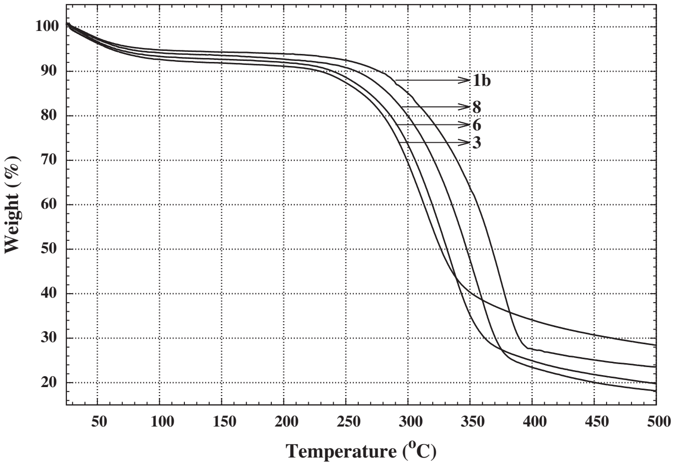


Fig. 4. TGA thermograms of **1** and the distinct samples (**3**, **6**, **8**) having the highest DS values.

3.2.2. Rheologic characterizations

Further analyses were made in terms of rheology to find flow properties of the samples. Results of rheological measurements were summarized in Table 4. Obtained results showed that all samples were obeying Bingham model. Cellulose from recycled paper **(1)** showed yield value (τ_B) and plastic viscosity values of 24.8 mPa and 1.21 mPa s. Flow index value (0.86) was very close to unity, this result showed that rheologic model of **1** was very close to Bingham plastic. Bingham model parameters of **3**–**8** had small but significant differences from **1**. Values of τ_B were generally slightly higher than

Table 4
Results of rheological measurements of CMC samples of 1% (w/v) dispersions in 0.5 N NaOH.

Sample	τ_B, mPa	η_{Pl}, mPa s	η_{125}, mPa s	Flow index	Hys.Ar., mPa s^{-1}
1	24.8	1.21	1.45	0.86	163.9
3	25.5	1.21	1.48	0.86	162.6
4	35.0	1.17	1.48	0.81	160.2
5	22.6	1.21	1.39	0.87	164.8
6	37.1	1.19	1.45	0.81	157.2
7	31.2	1.17	1.42	0.82	160.6
8	26.0	1.17	1.45	0.81	160.4

1; but **3** and **8** had almost same τ_B with **1**. Plastic viscosity (η_{Pl}) values were fairly different and had a value of 1.19 (±0.02) mPa s for all samples. Bingham coefficients (both η_{Pl} and τ_B) of **1,3** and **8** were almost same, this was probably due to presence of impurities like NaCl and sodium glycolate (1). Because these impurities prevents interactions between molecules resulting in a decrease in rheologic parameters. Apparent viscosity (η_{125}) values were quite consistent with η_{Pl}; they were measured as 1.45 (±0.03) mPa s. Flow indices and hysteresis area values of CMC samples were slightly lower than **1**. The lowest modification was observed for **5** and it gave fairly different results from **1**, while highly modified **6** gave the most distinct results of the series. These results showed that rheologic behavior of CMC samples were slightly affected from DS and M_V. Flow characteristics shifted slightly to pseudoplastic behavior and thixotropy of samples slightly decreased.

4. Conclusion

Cellulose was recovered from newspaper under oxidizing alkaline conditions. Obtained recycled cellulose was mainly cellulose with some extent of lignin. FTIR analyses indicated that crystallinity of cellulose increased after recycling. Changing recycling conditions was not removed lignin moiety completely. Remaining lignin was unimportant for carboxymethylation; thus complete removal of lignin was not attended.

Carboxymethylation of obtained cellulose was done in aqueous alkaline medium without using additional organic solvent. Obtained product had a DS changing between 0.3 and 0.6 with a high CMC content (above 85%). Weight loss indicated some degradation reactions took place during derivatization, however, acceptable amount of carboxymethylcellulose was obtained. Thermal analyses displayed that DS greatly affected thermal properties of obtained product. Rheologic characterizations showed that DS and M_V had very little effect on resulting product whose rheologic behavior was slightly thixotropic.

Finally carboxymethylcellulose was synthesized in completely aqueous medium; DS changed regarding to reaction conditions between 0.3 and 0.6. Obtained CMC would be used non-food applications in different fields such as civil engineering (e.g. concrete additive), coating (as thickener).

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