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CARBOXYMETHYLCELLULOSE PREPARATION FROM TUNISIAN WHEAT STRAW; EFFECT OF DEGREE OF SUBSTITUTION ON RHEOLOGICAL PROPERTIES

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ABSTRACT

Tunisian Wheat Straw (TWS) is a raw material with a high content of cellulose (43%); this makes it a good potential for production of cellulose derivatives such as carboxymethylcellulose. The proposal of this study was to synthesize carboxymethylcellulose (CMC) from Tunisian wheat straw with different degrees of substitution (DS) and to study the rheology of the different prepared products. The carboxymethylation reaction was carried out with NaOH and monochloroacetic acid (MCA) as the reagent. We obtain different products with different degrees of substitution by varying the concentration of monochloroacetic acid. The functionalization of cellulose was checked using FTIR spectroscopy. The X-ray analysis showed that the crystalline structure of cellulose decreased when the DS increased.

KEYWORDS

Wheat straw; Cellulose; Carboxymethylcellulose; Rheological properties.

1. INTRODUCTION

Cellulose is a linear and high molecular weight polymer as well as natural, renewable and biodegradable material. However, due to its high crystallinity and strong inter- and intra-molecular hydrogen bond, cellulose neither melts nor dissolves in the most common organic solvents, therefore, reduces its applicability. In order to increase the cellulose applicability, an alternative pathway is to convert the cellulose to its derivatives such as carboxymethylcellulose (CMC) through chemical derivatization reaction.

CMC is important for its water-soluble properties where great applications are applied throughout the food industry, detergents, cosmetics, pharmaceuticals, textiles, paper…

The present work aims to prepare cellulose from Tunisian Wheat Straw and subjecting it to carboxymethylation (using different concentrations of the etherifying agent) and to investigate its chemical and rheological properties.

2. MATERIALS AND METHODS

2.1. Extraction of cellulose

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The cellulose from wheat straw was extracted according to the acidic method as reported by Sun, J.X. (Sun et al., 2004) with some modifications. The dried and sieved wheat straw (10g) was first treated with 200ml H_2O at 75°C for 2h. Further the water-soluble free sample was delignified with 1.7% sodium chlorite at pH 3.5-4.0, adjusted with 6M acetic acid, at 75°C for 2h. Finally the holocellulose obtained was treated with 10% potassium hydroxide for 16 h at room temperature.

2.2. Synthesis of carboxymethylcellulose (CMC)

The prepared cellulose pulp was subjected to carboxymethylation according the following procedure: In alkalization pre-treatment about 10g of unmodified material was weighed and added to 60ml of 40% aqueous sodium hydroxide followed by 60ml of isobutanol. Then the mixture was stirred for 12h at 60°C in order to convert the hydroxyl to alcoolate groups. After alkali treatment, etherification reaction was conducted by adding slowly the desired amount of monochloroacetic acid (MCA). The etherification reaction remains for 6h at 60°C.

The product thus obtained was suspended in 800ml of ethanol. The slurry was neutralized using glacial acetic acid. Then, the sample was washed using a 70% ethanol solution to remove undesired product.

Using the above general procedure, three different derivatives using 10, 20 and 30g MCA /10g cellulose pulp were prepared.

2.3. Determination of the degree of substitution (DS) of CMC

5g of CMC was added to 200ml HNO_3-Methanol (1:1 v/v). This solution was shaken and was kept for 3h. The excess of acid was washed with a 70% methanol solution. Subsequently, 2g of dried sample was dissolved in 200ml of distilled water and 30ml of 1N NaOH mixture. Then, the solution was titrated by 1N HCl. The DS of CMC was determined by following equations (Candido, Gonçalves, 2016):

$$DS = (0.162*A)/(1-(0.058*A)) \quad (1)$$

$$A = [(B*C)-(D*E)]/F \quad (2)$$

Where:

- A : equivalent weight of alkali required per gram of sample ;
- B : amount of NaOH solution (mL) ;
- C : normality of NaOH solution (N) ;
- D : amount of HCl solution (mL) ;
- E : normality of HCl solution (N) ;
- F : weight of sample (g)

2.4. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectroscopy has been extensively used in cellulose research, since it presents a relatively easy method of obtaining information on chemical changes that occur during various chemical treatments (Sun et al., 2004). The Spectra were measured in the region 400-4000cm^{-1} in a spectrophotometer (Perkin Elmer UATR Two).

2.5. X-ray diffraction (XRD)

The X-ray diffractograms of cellulose and CMC were recorded on a Rontgen Universal HZG 4/A diffractometer. The test conditions were Cu Kα, radiation with a 35-kV tube voltage and a 25-mA tube current.

2.6. Rheological measurements

Rheological measurements were carried out using a controlled speed rotating rheometer (rheotec RC30) operated with a cone-plate. All the measurements were conducted at a constant temperature of 25°C ± 1°C and the apparent viscosity (η) at various rates of shear was calculated from the shearing stress (ζ) and rates of shear (ɒ)as follows (Ragheb et al., 2012):

$\eta = \zeta / \text{ɒ}$

3. RESULTS AND DISCUSSIONS

3.1. Preparation of CMC from cellulose

In the present work, the cellulose was extracted from wheat straw and then subjected to carboxymethylation with monochloroacetic acid in the presence of sodium hydroxide. Cellulose can react with monochloroacetic acid as follows:

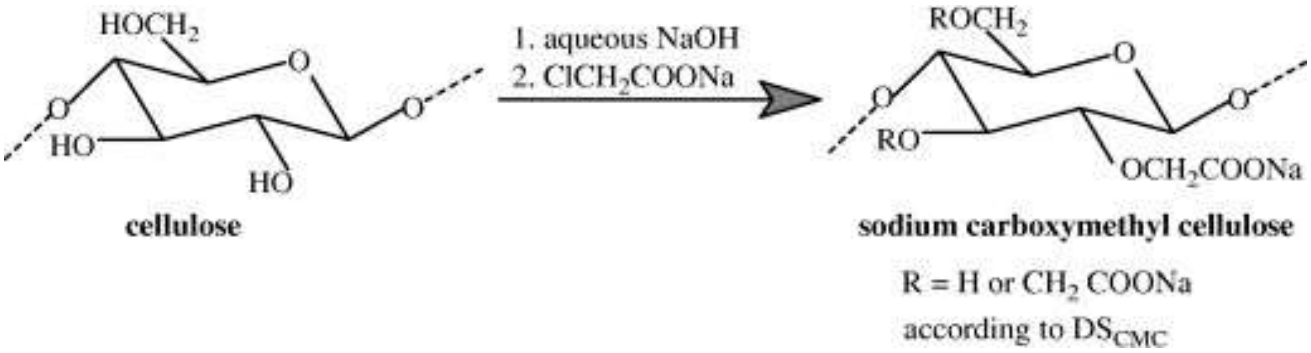

Figure 1: Reaction scheme of the carboxymethylation of cellulose (Pushpamalar et al., 2006)

The carboxymethylation reaction was carried out in non-aqueous medium using different concentrations of the etherifying agent to obtain carboxymethylated derivatives acquiring different degrees of substitution (DS) values. The effect of concentration of monochloroacetic acid on the extent of carboxymethylation reaction expressed as DS is shown in Table 1.

Table1: Effect of concentration of monochloroacetic acid on DS and solubility of carboxymethylcellulose derivatives.

Weight of cellulose (g)	Weight of $ClCH_2COOH$ (g)	Weight of NaOH (g)	DS	Solubility in water
Untreated	0.00	0.00	0.00	Insoluble
10	10	24	0.43	Partially Soluble
10	20	24	0.91	Soluble
10	30	24	1.37	Soluble

It is clear from the data of Table 1 that the extent of carboxymethylation reaction expressed as DS increases by increasing monochloroacetic acid concentration. For example, when the concentration of monochloroacetic acid was 10g/10 g of cellulose, the DS was 0.43, while the amount of monochloroacetic acid was increased to 30g/10 g cellulose; the DS was increased to 1.37. It is worthy to mention that untreated cellulose is insoluble in water. The current data indicates that modification of pure cellulose via carboxymethylation converts it into a water-soluble product. This holds true regardless of the DS value in the range studied.

3.2. FTIR analysis

Figure 2(A) shows the FTIR spectra of the cellulose extracted from Tunisian wheat straw and figure 2(B) illustrates the FTIR spectra of CMC with different DS values (0.43, 0.91, and 1.37)

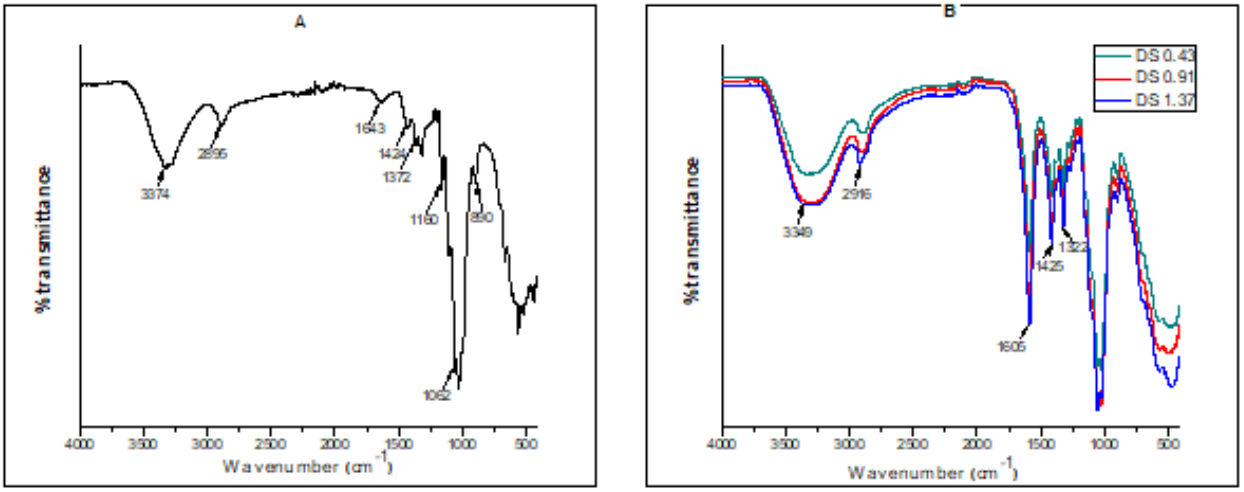

Figure 2: FTIR spectra of (A) untreated cellulose and (B) CMC samples prepared with different degrees of substitution

It is evident from figure 2 that the chemical modification of cellulose is successful. The presence of a new and strong absorption band at 1605 cm^{-1} confirms the stretching vibration of carboxyl group (COO-) (Yeasmin, Mondal, 2015).

The IR spectra of CMC with different degrees of substitution are recorded in figure 2(B) and they are almost the same. FTIR spectral data of cellulose extracted and different CMC prepared are listed in table 2.

Table 2: Assignment of main absorption bands in cellulose extracted and prepared carboxymethylcellulose

Wavenumber (cm^{-1})		**Assignment**
Untreated cellulose	**CMC prepared**	
3374	3349	OH stretching
2895	2916	CH stretching CH_2 and CH_3 groups
1643	-	H-O-H bending of absorbed water
-	1605	C=O region (indicated CMC)
1424	1425	CH_2 bending
1372	-	C-H deformation
1424	1425	OH in plane bending
1160	1164	C-O-C asymmetric bridge stretching
1062	1116	C-O symmetry stretching alcohol
896	899	β-Glucosidic linkages between the sugar units

3.3. XRD analysis

The X-ray diffraction patterns of the cellulose extracted from Tunisian wheat straw and of the synthesized carboxymethylcelluloses with different DS were recorded in figure 3.

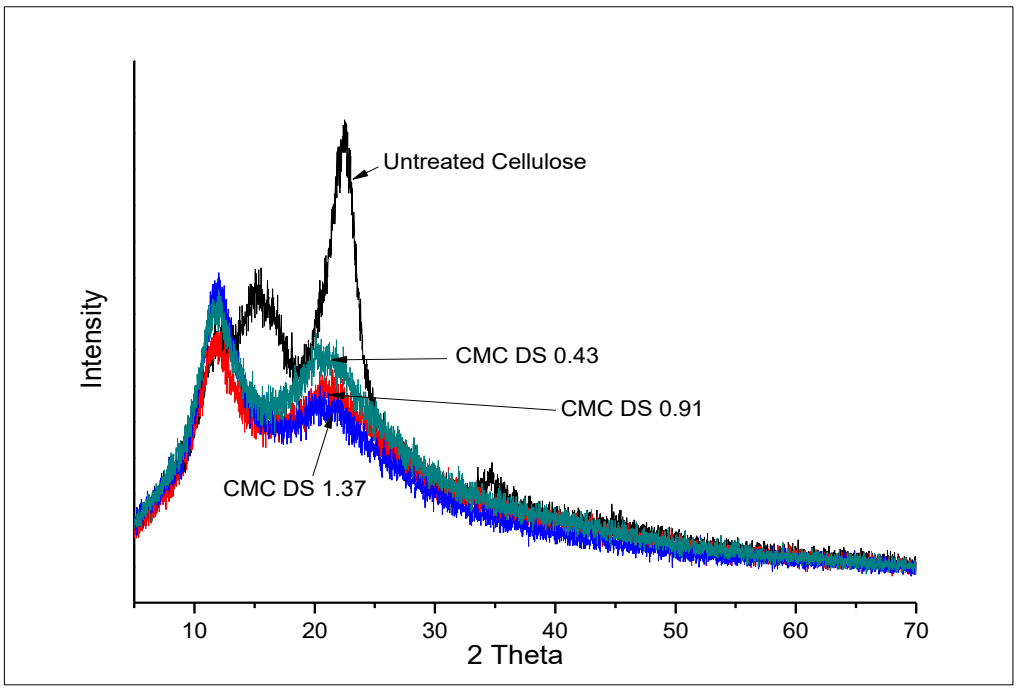

Figure 3: X-ray diffractograms of untreated cellulose and CMC samples with different degrees of substitution

It can be seen from figure 3 that cellulose extracted in this work present three typical peaks at diffraction angles of 15.48°, 22.4° an 34° appear; this confirms that the cellulose form is cell-I (Aguir, M'Henni, 2006).

It can be also noticed that crystallinity of CMC decreases with the increase of the degree of substitution from 0.43 to 1.37. This phenomenon may be due to broadening or cleavage of hydrogen bonds by carboxymethyl substitution at the hydroxyl groups of cellulose (Yeasmin, Mondal, 2015).

3.4. Rheological study of CMC with different degrees of substitution

Since carboxymethylcellulose derivatives are generally used in the form of viscous solutions, it seemed of interest to investigate the viscometric and rheological properties of their solutions.

The solutions of CMC with different degrees of substitution (0.43, 0.91 and 1.37) were prepared in 4% w/v concentration and their rheological properties were studied at 25 ± 1°C. The results obtained are shown in figure 4.

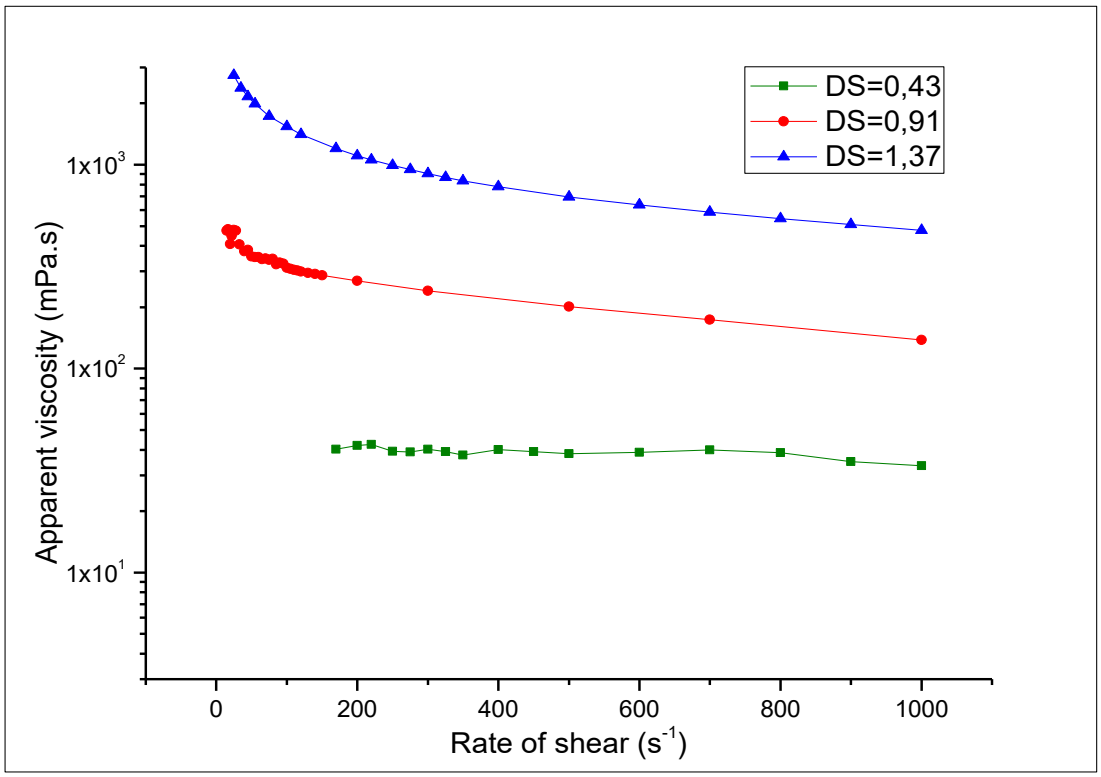

Figure 4: Apparent viscosity at different rate of shear of CMC samples

It is clear from the data shown in figure 4 that sodium carboxymethylcellulose solutions prepared are non-Newtonian and more specifically in the case of CMCs with degrees of substitutions 0.91 and 1.37. We can also shows that the location of the curves with respect to the rate of shear axis depends on D.S. of the carboxymethyl derivative. As the degree of carboxymethylation increases, the curve is located far from the rate of shear axis indicating an increase in the apparent viscosity

4. CONCLUSION

Carboxymethylation of cellulose extracted from Tunisian wheat straw was carried out with monochloroacetic acid (MCA) in the presence of alkali (NaOH) as a catalyst under heterogeneous conditions. The chemical and rheological properties of different samples were investigated.

The results obtained can be summarized as follows:

1. The extent of the reaction expressed as DS increases by increasing the etherifying reagent (MCA).
2. Modification of cellulose via carboxymethylation converts it into a water-soluble product, and decreases its crystallinity.
3. Regardless of the D.S. of these products, their aqueous solutions are characterized by non-Newtonian behaviour.

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