PREPARATION AND CHARACTERIZATION OF CARBOXYMETHYL CELLULOSE FILM FROM SUNFLOWER STALK

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Abstract- In this study, cellulose obtained from sunflower stalks was converted to carboxymethyl cellulose (CMC) by carboxymethylation reaction using sodium monochloroacetate (NaMCA) in order to obtain CMC films. Films were prepared by casting method. To investigate chemical structure of synthesized CMC and CMC films, Fourier transform infrared spectroscopy (FTIR) was performed. Film solutions were prepared by adding glycerol, polyethylene glycol (PEG) and canola oil separately as plasticizers. Thermogravimetric analysis (TGA) was performed and the degradation temperature of CMC21, CMC22 and CMC23 were found. Degree of substitution (DS) which is an important indicator of water solubility for CMC was calculated as 0.51.

Keywords- cellulose; carboxymethyl cellulose; film; plasticizer.

I. INTRODUCTION

Developing environmental, social and economic awareness, depletion of oil reserves, sustainability concepts and landscaping tend to encourage the studies on green materials compatible with environmental [1]. In recent years, there is growing interest in developing new biodegradable materials for use in various disciplines such as medicine, agriculture, packaging [2]. Biopolymers are polymeric materials in which at least one step in the degradation process is through metabolism of naturally occurring organisms [3]. Cellulose is the most abundant biopolymer in the world and is obtained from renewable resources [4]. Cellulose is linear, rigid, biocompatible and biodegradable macromolecule in which anhydroglucose units (AGU) are rotated 180° in connection with each other on account of β-linkage and AGU are linked by β-1,4-gluco-sidic bonds [2,5]. Three hydroxyl groups in the cellulose structure carry out esterification, etherification and similar chemical reactions. In the end of these reactions, cellulose derivatives occur. One of the most well-known cellulose derivative is CMC. CMC is linear, long-chain, soluble, odorless and white to cream colour and has been widely used in pharmaceutical, food industries, toothpaste, detergents and paper coating etc [6,7]. In the first step of carboxymethylation process is based on Williamson’s ether synthesis and alkalization between NaOH and hydroxyl group of the cellulose chains occurs as in (1). More reactive alkaline form is denoted by R [2].

\[
\text{ROH} + \text{NaOH} \rightarrow \text{RONa} + \text{H}_2\text{O} \quad (1)
\]

In the second step, etherification reaction occurs to obtain CMC as in (2) and a side reaction between NaOH and NaMCA takes place as in (3), which results in sodium glycolate [2].

\[
\text{RONa} + \text{CICH}_2\text{COONa} \rightarrow \text{ROCH}_2\text{COONa} + \text{NaCl} \quad (2)
\]

\[
\text{NaOH} + \text{CICH}_2\text{COONa} \rightarrow \text{HOCH}_2\text{COONa} + \text{NaCl} \quad (3)
\]

Edible films and coatings are used to form a barrier for oxygen, moisture and flavor on the food contact surface, to retard color change and decomposition, and to adhere one food component to another [8]. Polysaccharides such as CMC are accepted as good edible film candidates due to their good film forming property, good mechanical and gas barrier properties by comparison with other biodegradable materials [9]. Although there are many investigations on synthesis of CMC from various agricultural wastes, there is no information on the preparation CMC film from sunflower stalk. There are some investigations about antioxidant and antimicrobial activities of canola oil [10, 11]. Jahangrian et al. investigated the antimicrobial effect of phenyl fatty hydroxamic acid synthesized from canola oil. They found the antimicrobial activity on the Gram negative bacteria was higher than Gram positive bacteria [10]. Burt used canola oil as a coating for ham and searched the antibacterial activity of essential oils or their components in foods [11].

II. MATERIALS AND METHODS

Sunflower stalks were purchased from Eskisehir, Turkey. It was dried for 2 days in an oven at 55°C. All chemicals were used as they purchased from Sigma Aldrich Co. (Steinheim, Germany).

A. Extraction of Cellulose from Sunflower Stalks Powder

Dried sunflower stalks are ground into powder using a cross beater mill (Fritsch, Pulverisette 16). The
grounded powder was sieved through 0.25 mm² sieve. Then powder was dried on the same conditions again. 15 g of sunflower stalk powder was added into 500 mL, single-neck-round-bottom flask and was cooked in 8% NaOH at a ratio of cellulose:solvent 1:20 (w/v) for 3.5 h at 100°C. After the reaction, the dark slurry obtained was cooled down to room temperature and filtered. It was washed with 1 L of distilled water. Afterwards, product was bleached with 5% NaOCl for 2 h at 40°C until the odor of NaOCl could no longer be detected. Obtained cellulose was dried in an oven at 60°C overnight [2].

B. Synthesis of Carboxymethyl Cellulose

10 g dried cellulose powder was added to 150 mL of isopropyl alcohol as a solvent under continous stirring. Then, 10 mL of 25% NaOH (w/v) was added dropwise into the mixture and further stirred for 1 h at room temperature. When alkalinization process was over, carboxymethylation was started with adding 12 g NaMCA drop by drop. The temperature was increased to 45°C and the reaction was proceeded for 3 h. After the reaction was finished, the solution was cooled down to room temperature and then slurry was filtered. The slurry was suspended with 70% of ethanol for 40 minutes. Suspended slurry was neutralized with 90% of acetic acid and then filtered. The final product was washed with 70% of ethanol to remove undesirable by-product for 3 times and then, it was washed with absolute ethanol again. As the final product, CMC was obtained and was dried at 60°C overnight in an oven.

C. Film Preparation

2 g of CMC was dissolved in distilled water for each film. Dissolution was continued to achieve a clear solution at 70°C. Gycerol, PEG (50% v/w based on CMC weight) were added plasticizers and also canola oil was added as an antimicrobial agent. The solutions were stirred at 70°C for 15 minutes. A vacuum pulp was used to remove bubbles from the film solutions. The film solutions were cooled down to 30°C, casted onto petri dishes and left at 30°C for 48 h and CMC films were obtained. The composition of CMC film solutions is shown in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>CMCC1</th>
<th>Water</th>
<th>Gycerol</th>
<th>PEG</th>
<th>Canola Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMCC2</td>
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<tr>
<td>CMCC3</td>
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</tr>
</tbody>
</table>

III. CHARACTERIZATION

A. Measurement of CMC Yield

CMC yield was measured based on a dry weight basis and calculated as in (4);

\[
\text{CMC Yield} \times 100 = \frac{\text{Weight of prepared CMC}}{\text{Weight of dried cellulose}} \times 100 \tag{4}
\]

B. Determination of DS

The DS of CMC was determined by the standard method ASTM 1439-15. 1 g of CMC and 50 mL of 95% ethanol added into a 250 mL of beaker. Afterwards, 5 mL of 2 M nitric acid was added. Mixture was continuously stirred at room temperature for 10 minutes and heated to 83°C for 5 minutes. Next, it was agitated in a shaking incubator for 20 minutes and left to settle. Afterwards, it was filtered and residue was washed with 100 mL of 95% ethanol at 60°C and absolute methanol and filtered. The final product was dried in an oven at 105°C for 3 hours. About 0.5 g of CMC was weighted in 250 mL Erlenmeyer flask and 100 mL of water was added and stirred. Then 25 mL of 0.5 M NaOH added into the flask and boiled for 20 minutes. Obtained solution was titrated with 0.3 M HCl using phenolphthalein as an indicator. When the color changed from dark pink to colorless, titration was ended. The DS of CMC was calculated based on (5) and (6) below [12]:

\[
A = \frac{BC - DE}{F} \tag{5}
\]

\[
\text{Degree of Substitution} = \frac{0.162 \times A}{1 - (0.058 \times A)} \tag{6}
\]

where

- \(A\) = milli-equivalents of consumed acid per grams of specimen;
- \(B\) = volume of NaOH added;
- \(C\) = concentration of NaOH added;
- \(D\) = volume of consumed HCl;
- \(E\) = concentration of HCl used;
- \(F\) = specimen grams used;

162 denotes the molecular weight of the anhydrous glucose unit and 58 represents the net increase in the anhydrous glucose unit for each substituted carboxymethyl group.

C. Fourier Transform Infrared Spectroscopy (FTIR)

Samples were dried in an oven at 60°C for 24 h. FTIR spectra of the synthesized CMC and CMC films were recorded in a Perkin Elmer Frontier spectrometer. Pellets were prepared by grinding CMC samples with KBr.

D. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out at heating rate of 10°C/min under nitrogen atmosphere, using a Netzsch STA 449 F3thermogravimetric analyzer.

IV. RESULT AND DISCUSSION

A. Measurement of CMC Yield

Yield of CMC synthesis reaction was calculated as 70.33%.

B. Determination of DS
The DS of carboxylic group in CMC can be defined as the average number of hydroxyl group in the cellulose structure which was substituted by carboxymethyl groups at C2, C3 and C6. The DS of CMC was determined by the standard method ASTM 1439-15. DS of CMC was calculated as 0.51.

C. FTIR Analyses

FTIR spectrums of synthesized CMC and extracted cellulose are shown in Fig. 1. Peaks observed at 3241 cm\(^{-1}\) and 3368 cm\(^{-1}\) indicate the OH stretching bands for FTIR spectrums of synthesized CMC and cellulose, respectively in Fig. 1. Peaks at 2963 cm\(^{-1}\) and 2903 cm\(^{-1}\) arise from CH stretching of CH\(_2\) and CH\(_3\) groups in the structure of synthesized CMC and extracted cellulose, respectively [13-15]. Peaks observed at 1595 cm\(^{-1}\) are due to C=O region for FTIR spectrums of synthesized CMC and cellulose, respectively. Peak at 1413 cm\(^{-1}\) is attributed to CH\(_2\) bonding for FTIR spectrums of synthesized CMC [14]. C-O symmetric stretching of primary alcohol bands is observed at 1057 cm\(^{-1}\) for FTIR spectrums of synthesized CMC [13].

FTIR spectrums of CMC\(_{f1}\), CMC\(_{f2}\) and CMC\(_{f3}\) are shown in Fig. 2. The absorption bands at 3318cm\(^{-1}\), 3375cm\(^{-1}\) and 3341 cm\(^{-1}\) are due to the OH stretching. Peaks at 2933 cm\(^{-1}\), 2875 cm\(^{-1}\) and 2874 cm\(^{-1}\) are due to CH stretching. Peaks at 1600-1595 cm\(^{-1}\) are due to C=O region. Peaks at 1318 cm\(^{-1}\), 1349 cm\(^{-1}\) and 1328 cm\(^{-1}\) are due to C-H bending. The peaks observed at 1105 cm\(^{-1}\), 1038 cm\(^{-1}\) and 1034 cm\(^{-1}\) are attributed to the binding of C-O-C and C-C-H groups with PEG. Peaks at 918 cm\(^{-1}\), 835 cm\(^{-1}\) and 845 cm\(^{-1}\) are attributed to C-C stretching [16, 17]. Absorption bands indicating existence of canola oil in CMC\(_{f3}\) are observed at 2933 cm\(^{-1}\), 1800 cm\(^{-1}\) and 1134 cm\(^{-1}\)[18].

D. Thermogravimetric Analyses

TGA curves of synthesized CMC\(_{f1}\), CMC\(_{f2}\) and CMC\(_{f3}\) are shown in Fig. 3. The thermograms show that the films have a three staged degradation behavior. CMC starts to decompose at about 170°C and weight loss is outstanding in the range of 300-580°C. Degradation behavior of CMC films in given Fig. 3, is similar to reported results [19]. Temperatures below 170°C are due to evolution of absorbed moisture. The second step between 250-350°C may be related to decarboxylation and decomposition of cellullosic materials. Second stage can also be attributed to slow decomposition of the –CH2– linkages, H–bonding and other interactions between the polymers [20]. And the main chain of the films are degraded between 300-500°C as the third stage. Third degradation stage starts at 260°C, 300°C and 295°C for CMC\(_{f1}\), CMC\(_{f2}\) and CMC\(_{f3}\), respectively. The weight loss in third stage may be arising from the removal of non-cellulosic materials [9]. Total weight loss is 85.93%, 84.14% and 79.48% for CMC\(_{f1}\), CMC\(_{f2}\) and CMC\(_{f3}\), respectively. This result shows that incorporation of PEG in CMC film structure increases the thermal stability of the films.

Fig. 3. TGA curves of CMC/Glycerol/PEG/Canola Oil (CMC\(_{f3}\)), CMC/Glycerol/PEG (CMC\(_{f2}\)) and CMC/Glycerol (CMC\(_{f1}\))

CONCLUSION

FTIR analyses show that molecular structure of CMC synthesized in this work is quite similar to that of the commercial sample. TGA results showed that the synthesized CMC\(_{f1}\), CMC\(_{f2}\) and CMC\(_{f3}\) are thermally stable upto260°C, 300°C and 295°C respectively. Thermal stability of CMC films is improved with PEG incorporation into the film structure. Further studies can be done on biodegradability and antimicrobial activities of CMC films.

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REFERENCES

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