

Synthesis and Characterization of Carboxymethyl Cellulose from Sugarcane Bagasse

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Abstract

Various raw materials including plant biomass, bacteria, algae and the Tunicates (marine animals) have been used to produce cellulose. However, agricultural waste has rarely been utilized for this purpose. In this work, Sugarcane bagasse was used as raw material to produce cellulose. Cellulose was extracted from sugarcane bagasse through the elimination of lignin and hemicellulose. Cellulose was then converted to carboxymethyl cellulose (CMC_b) by using sodium monochloroacet (SMCA) and various sodium hydroxide (NaOH) concentrations. Fourier Transform Infrared Spectroscopy (FTIR) was applied to verify the effect of NaOH concentration on this property. The highest viscosity and degree of substitution (DS=0.78) were observed in 30 gr/100 ml NaOH of carboxymethylation. Maximum tensile strength of the films produced at these conditions was 37.34 Mpa. The addition of a various amount of glycerol (1 ml/ 100 ml, 2 ml/ 100 ml, 3 ml/ 100 ml) dramatically decreased the tensile strength. The highest level of water vapor permeability was also observed at the same NaOH concentration. Cellulose can be correctly extracted from sugarcane bagasse and converted to carboxymethyl cellulose. Based on the cellulose of the bagasse characteristic, proper amount of NaOH was found to get a high DS. CMC_b has considerable features for application on biodegradable coating materials.

Keywords: Sugarcane bagasse; Carboxymethyl cellulose; Edible film; Mechanical properties

Introduction

Nowadays huge quantities of plant wastes are produced globally. Although they are the most abundant and renewable resource for organic substances attainable today [1,2], still considerable amounts of these materials are not used in proper way. Thus, the conversion of plant wastes into valuable products can be helpful in reduction of the environmental problems [3]. Plant wastes consists of more than 90% (w/w) carbohydrate polymers which can be modified by both biochemical and chemical reactions to some products such as starch, cellulose, cotton linter, bagasse fiber etc. [4,5]. Sugarcane bagasse is a residue produced in large quantities every year by the sugar industries [6], and the most of this amount used as a fuel to supply the energy required for sugar mill [7]. Some reports reveal that bagasse is used as a raw material for industrial applications such as electricity generation, pulp and paper production, etc. New researches show the application of sugarcane bagasse to produce composites with bagasse linters [8]. However, the large quantities of sugar cane bagasse remain unused. Therefore, utilization of this huge agricultural waste for new applications has attracted growing interest because of their ecological and renewable characteristic. In general, each ton of sugarcane produces 280 kg bagasse. Sugar cane bagasse contains 40% to 50% cellulose (crystalline and amorphous structure), 25% to 35% hemicellulose (amorphous polymers usually composed of xylose, arabinose, galactose, glucose and mannose), 15% to 20% of lignin and the remainder lesser amounts of mineral, wax, and other compounds [9].

Cellulose is an important component for the application of new biomaterials obtained from agriculture wastes. Cellulose is usually found in the cell wall of plants and is generally associated with lignin and hemicellulose, which make it difficult to extract in pure form [10]. Cellulose is a high molecular weight and a linear homopolymer of repeating β -D-glucopyranosyl units joined by single oxygen atoms (acetal linkages) between the C-1 of one pyranose ring and the C-4 of the next ring. Because of their linearity and stereo regular nature, cellulose molecules associate over extended regions, forming polycrystalline, fibrous bundles. Large numbers of hydrogen bonds

together hold crystalline regions. They are separated by, and connected to, amorphous regions. Cellulose is insoluble because, for to dissolve, most of these hydrogen bonds would have to be released at once. However, Cellulose through substitution can be converted into water-soluble gums [11,12]. Cellulose can be applied in various form, its original fibers (used in textile and paper) or its derivative forms such as methyl cellulose and carboxymethyl cellulose.

carboxymethyl cellulose is a linear, long-chain, water-soluble, anionic polysaccharide. Purified CMC is a white- to cream-colored, tasteless, odorless, powder [13,14]. Sodium carboxymethyl cellulose is formed when cellulose reacts with mono chloroacetic acid or its sodium salt under alkaline condition with presence of organic solvent, hydroxyl groups substituted by Sodium carboxymethyl groups in C2, C3 and C6 of glucose, which substitution slightly prevails at C2 position [15,16]. Carboxymethyl cellulose (CMC) is extensively used as a food gum. It has many applications in various industries such as food, pharmaceuticals, detergent, lubricants, adhesives etc. [17-25]. However, Due to extensive use of CMC, many studies have been done to produce CMC from various resources such as durian rind [4], cotton linters [16], sugar beet pulp [26], cashew tree gum [27], Cavendish banana pseudo stem [28], sago waste [3], papaya peel [29], and Mimosa pigra peel [30]. Therefore, the purpose of this work was the production of carboxymethyl cellulose from bagasse (CMC_b) and study the effect of NaOH concentration on Characteristics of CMC synthesized from sugarcane bagasse and evaluation of this film.

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Materials and Methods

Materials

Required quantities of sugarcane bagasse was collected from the farms of Khuzestan, Iran. Sodium hydroxide, potassium hydroxide and glacial acetic acid were prepared from Merck Chemical Co. (Darmstadt, Germany). Ethanol and methanol were provided from the local market. Isopropanol and sodium mono chloroacetate were purchased from Daejung Co. (South Korea). Sodium chlorite (NaClO_2) used in the experiment was from Sigma-Aldrich, USA.

Extraction of cellulose

First of all, bagasse was milled and de-pitched, then the fiber was cooked at 370°C in digester prior to bleaching with Sodium hypochlorite and Chlorine gas and washing with KCL 5%. After this process bagasse fiber with 70-80 of Degree of whiteness (Euro standard) was obtained. Additional bleaching on the samples was carried out in two steps; with sodium chlorite 3% and then 1% (1:10) at $\text{Ph}=3.8-4$ [31]. Elimination of hemicellulose from the pulp was then done with 10 g/100 ml KOH (1:20) at 80°C for 2 h (after 12 h remaining in room temperature) after every step for elimination residual, pulp was washed with distilled water. Alpha-cellulose content was measured by following Equation 1 according to the TAPPI T 203 cm-99 standard.

$$\alpha\text{-cellulose (\%)} = \frac{w_2 - w_1}{w_1} \times 100 \quad (1)$$

Synthesis of carboxymethyl cellulose (CMC_b) from cellulose of sugarcane bagasse

The synthesis of Carboxymethyl cellulose followed the procedure described by Rachtanapun et al. [29]. Nine grams of Cellulose powder from sugarcane bagasse, 30 ml of NaOH (20 g/100 ml, 30 g/100 ml, 40 g/100 ml, 50 g/100 ml) and 270 ml of solvent (isopropanol, due to its good ability in cellulose etherification based on Pushpamalar et al. [3] study was stirred in the beaker and let stand for 30 min at ambient temperature. Then 10.8 g of sodium mono chloroacetate was added and mechanically stirred for 90 min in a beaker and covered with aluminum foil and keep in 55°C for 180 min. During this time, the reaction continued and the slurry divided into two phases. The upper phase's discarded and sedimentary phases suspend in 70% methanol (100 ml) and neutralized using glacial acetic acid and then, filtered and washed five times with 70% ethanol (300 ml) to remove undesirable salts. Afterward, it was washed again with absolute methanol and filtered. The obtained CMC_b was dried at 55°C in an oven. The yield of CMC_b was calculated by the following Equation 2:

$$\text{Yield of } \text{CMC}_b (\%) = \frac{\text{Weight of } \text{CMC}_b}{\text{Weight of cellulose}} \times 100 \quad (2)$$

Degree of substitution (DS)

DS value shows the average amount of hydroxyl group that was replaced by (sodium) Carboxymethyl group in the cellulose structure at C2, C3 and C6. The DS value of CMC from bagasse was measured by USP XXIII method described for Croscarmellose sodium, this method included 2 steps titration and residue on ignition.

Film preparation

Some quantities of powdered CMC from bagasse was dissolved in 100 ml distilled water at 80°C and stirred. Mixing was done until a homogeneous solution obtained. 1 ml, 2 ml and 3 ml of glycerol

were added to 100 ml of solution as a plasticizer. After obtaining a homogeneous solution, a film with a diameter of 10 cm (60 ml) was formed on glass plates by casting, then dried at 55°C within 24 hours.

Thickness

The thickness of the films was adjusted by the volume of film solution that cast on the plate (specific volume of solution poured on a plate with a fixed diameter) and measured by micrometers (model Mitutoyo, LIC.NO.689037, Japan). Measurements were done at ten different points on each sample and the average value was used to calculate mechanical properties.

Color

Colorimetry test was used to determine the color of samples with Chromameter CR-400 (japan). Three parameters which can be reached that in colorimeter is L (white=100, black=0), a (green=-60, red=+60) and b (blue=-60, yellow=+60). For each sample, at least three replications were done.

Mechanical properties

Measuring some mechanical properties of films was performed using tensile tester (M350-10CT, Testometric Co., Ltd., Rochdale, and Lancashire, England). Film samples were cut in 1×10 cm rectangles to be used as a test specimen, the samples preconditioned [32] at 53% RH for 48 hours in a desiccator containing magnesium nitrate. The initial grip separation and cross-head speed were set at 20 mm and 1 mm/min, respectively. Tensile strength and strain at break for specimen obtained using the curves of stress-strain. All measurement was done in triplicate.

Water vapor permeability

Water vapor permeability of the CMC_b films was performed based on modified ASTM (1995-method E96). According to this test, at first the films were cut into a circle (with 10 mm diameter), then placed on the glass cells with a specific diameter, and sealing completely with paraffin wax (anhydrous calcium chloride was poured into a glass cell that provides zero percent relative humidity). The glasses weight and was kept in a desiccator preserved at 75% RH with saturated sodium chloride at 25°C . Due to the Moisture differences on both side of the film (vapor pressure gradient), water vapor transmitted through the film specimen and absorbed by desiccant, evaluations were determined by measuring the weight gain. Changes in weight of the cells were recorded and plotted as a function of time. The slope of each line calculated using linear regression ($r^2 > 0.99$). Water vapor transmission rate (WVTR) (g/sm^2) calculated by Equation 3. And finally, the film permeability to water vapor (WVP) was calculated using the following equation (Equation 4):

$$\text{WVTR} = \frac{\text{slope (g / s)}}{\text{surface area (m}^2\text{)}} \quad (3)$$

$$\text{WVP} = \left[\frac{\text{WVTR}}{S(R_2 - R_1)} \right] \times D \quad (4)$$

Where S is saturation vapor pressure (Pa) at the test temperature (25°C); R_1 relative humidity at the desiccator; R_2 relative humidity inside the cell and D film thickness (m).

Viscosity

The viscosity of CMC samples was measured using rotational viscometer (LV model, Brookfield with ULA spindle). Samples were

prepared by dissolved of 1 gr CMC in 100 ml distilled water followed by vigorous mixing, then the solution was standing for a while to remove air bubbles. The viscosity of samples was measured by the ASTM D1439-94 at different temperature (30°C, 40°C, and 50°C). All measurements were performed in triplicate.

FTIR

The Functional groups of carboxymethyl cellulose were investigated using infrared spectroscopy spectrum (EQUINOX 55, BRUKER Germany). Pellets were made by CMC_b with KBr. Transmission levels were measured for wave numbers of 4000-400 cm⁻¹.

Statistical analysis

The collected data were analyzed by ANOVA and compared by Duncan's multiple range test ($p \leq 0.05$) with SPSS 18.

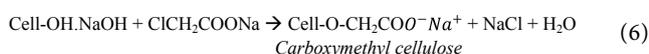
Results

α -cellulose

The alpha cellulose content was about 81% \pm 2%, which indicates sufficient purification of the sample from all impurities.

Degree of substitution (DS)

The Degree of Substitution (DS) is the average number of hydroxyl groups in the cellulose structure substituted by carboxymethyl or sodium carboxymethyl groups at the carbon 2, 3 and 6. Each anhydroglucose (β -glucopyranose) unit has three reactive (hydroxyl) groups so theoretically DS value can be in the range from zero (cellulose itself) to three (fully substituted cellulose). In general, the DS of carboxymethyl cellulose obtained by alkalization reaction of cellulose with sodium mono chloroacetate was in the range of 0.4-1.3. CMC is fully soluble at DS above 0.4 and hydro affinity of CMC increases with increasing DS, while this polymer is swellable but insoluble below 0.4 [33]. The DS of CMC obtained in this work was in the expected range of 0.45- 0.78, as figured in Figure 1A. As presented in this figure, the DS of CMC_b increased by adding NaOH concentration up to 30%, which shows the efficient concentration of alkali reagent in carboxymethylation procedure. Carboxymethylation of cellulose takes place by three simultaneously reaction as shown in equations 5-7:



According to Equation 5, Cellulose chains are swollen by Sodium hydroxide as an alkaline reagent (alkali cellulose), which provided the ability of substitution by sodium carboxymethyl groups in cellulose units. (Expose reactive site of anhydroglucose in compact cellulose chain to substitute by ether groups). The role of the solvent in the cellulose etherification is to provide miscibility and accessibility of the etherifying reagent (NaMCA) to the reaction centers of the cellulose chain rather than glycolate formation. Sodium mono chloroacetate (NaMCA) as an etherifying group participate in reaction and provide sodium carboxymethyl groups for substitution at C2, C3 and C6. As shown in Figure 1A, DS value augmented by adding NaOH concentration up to a maximum DS of 0.78 for 30% NaOH. At this level of NaOH concentration cellulose etherification (Equation 6) is

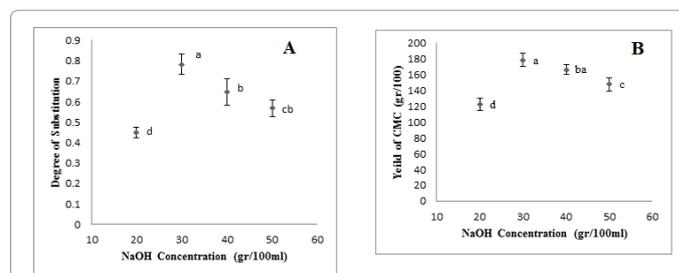


Figure 1: Effect of NaOH concentration on DS (A) and the yield of CMC (B) from sugarcane bagasse.

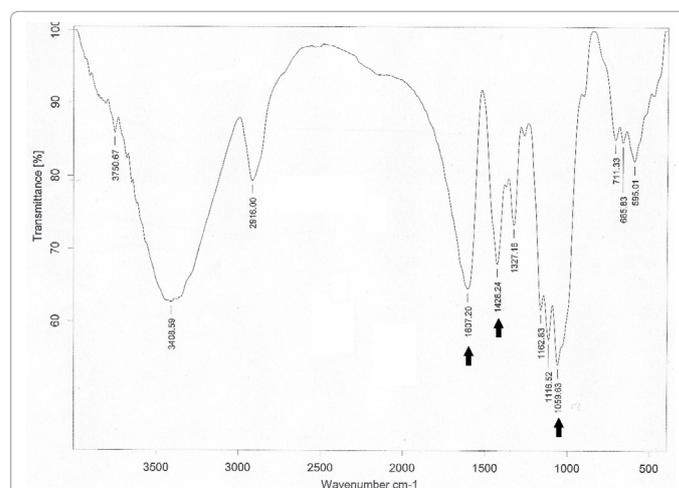


Figure 2: FTIR spectra of CMC made from cellulose of sugarcane bagasse with DS of 0.78 which was synthesized using 30% NaOH (the related peaks with substituted groups are marked with arrows).

predominating which produces CMC_b as a final product. Above 30% NaOH the DS value decreased. The reason for this observation is that an undesired side reaction happened which dominated the CMC_b production. Sodium glycolate was the product of such undesired reaction. With further increasing of NaOH concentration, more reduction in DS value was observed. It can be explained by degradation effect of high concentration of alkali reagent on CMC polymer chains. It must be noticed that DS value is affected by cellulose source. Crystallinity and regularity of cellulose structure according to its origin and considering the feasibility of substitution is more happened in an amorphous part of the cellulose structure [34,35]. Figure 1B shows the CMC_b yields from different experiments which indicated similarity with DS results. These results were in accordance with similar findings by several researchers.

FTIR

Fourier Transform Infrared Spectroscopy (FTIR) indicates chemical changes in the polymer structure. Cellulose and carboxymethyl have similar functional groups with same absorption bands in FTIR such as hydroxyl groups (-OH stretching) at 3200-3600 cm⁻¹, hydrocarbon groups (-CH₂ scissoring) at 1450 cm⁻¹, carbonyl groups (C=O stretching) at 1600 cm⁻¹ and ether groups (-O-) at 1000-1200 cm⁻¹, also C-H stretching vibration at 3000 cm⁻¹ [36]. Cellulose etherification with NaCMA causes the OH groups in cellulose replaced with CH₂COONa, which causes changes in the absorption spectrum of related bands. This lead OH groups to weaker peak and strengths or creates a new peak. However, from Figure 2, the differences can be observed in CMC_b

absorption bands, at 1059, 1426 and 1607 absorption bands which are relevant to -O-, CH₂- and -COO-, respectively. Pecsok [37] reported that the broadband at 1600-1640 cm⁻¹ and 1400-1450 cm⁻¹ is due to the carboxyl and its salts groups, which is confirmed substitution of carboxymethyl groups in cellulose structure. This peak doesn't exist in the FTIR spectra of cellulose from bagasse obtained in previous studies.

Viscosity

The viscosity of a solution is a measure of its resistance to gradual deformation by shear stress, which is due to intermolecular cohesive forces [37]. These forces are affected by some factors (CMC concentration, temperature, DS). Figure 3 shows the effect of NaOH concentration and temperature on viscosity of CMC_b solution. This figure indicates, as expected, the viscosity of samples decreases with increasing temperature. It can be explained by the fact that, during the heating to raising the temperature the energy of the molecules and molecular movement increased so intermolecular distances increase, which in turn, decreasing cohesive forces between molecules and causing lower viscosity. The viscosity of CMC_b samples increased with NaOH concentration (20% to 30%) at the constant temperature due to the presence of greater hydrophilic groups in polymer structure induced by greater DS, which gives more ability to the polymer to immobilize water in the aqueous system. As far as NaOH concentration raised above 30%, the viscosity fell down. This observation can be explained by decreasing of DS that provides less hydrophilic groups thereby ability of the polymer to bonding between water molecules reduced. Degradation effect of NaOH at a higher concentration on polymer chain also causes further declining in viscosity.

Water vapor permeability

Water Vapor Transmission Rate (WVTR) and Water Vapor Permeability (WVP) of the films obtained from CMC_b with different concentrations of sodium hydroxide is shown in Table 1. As tabulated,

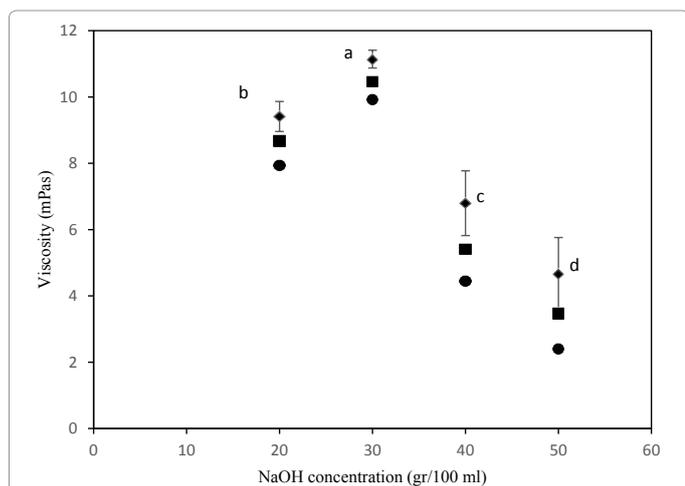


Figure 3: Effect of various NaOH concentration on viscosity of CMC from bagasse at different temperature (30°C, 40°C, 50°C).

Film type	WVP (g/msPa) × 10 ⁻¹⁰	WVTR (g/s.m ²) × 10 ⁻²
CMC _b -20 gr/100 ml NaOH	6.9632 ± 0.472 ^c	1.0477 ± 0.071 ^c
CMC _b -30 gr/100 ml NaOH	11.0795 ± 0.217 ^a	1.5025 ± 0.031 ^a
CMC _b -40 gr/100 ml NaOH	9.4524 ± 0.121 ^b	1.3510 ± 0.016 ^b
CMC _b -50 gr/100 ml NaOH	9.5868 ± 0.094 ^b	1.3270 ± 0.013 ^b

Table 1: Water vapor transmission rate (WVTR) of CMC_b films synthesized with various NaOH concentrations at 25°C, 75% RH.

Films type	a*	b*	L*
CMCb-20% NaOH	-0.595 ± 0.12 ^a	5.35 ± 1.87 ^b	58.465 ± 10.98 ^a
CMCb-30% NaOH	-0.685 ± 0.06 ^a	4.195 ± 0.66 ^b	59.755 ± 8.48 ^a
CMCb-40% NaOH	-0.34 ± 0.03 ^a	3.295 ± 0.62 ^{cb}	42.795 ± 1.27 ^a
CMCb-50% NaOH	-0.52 ± 0.04 ^a	6.845 ± 0.33 ^{ab}	57.24 ± 1.7 ^a

Table 2: Color values of cellulose and CMC synthesized with various NaOH concentrations.

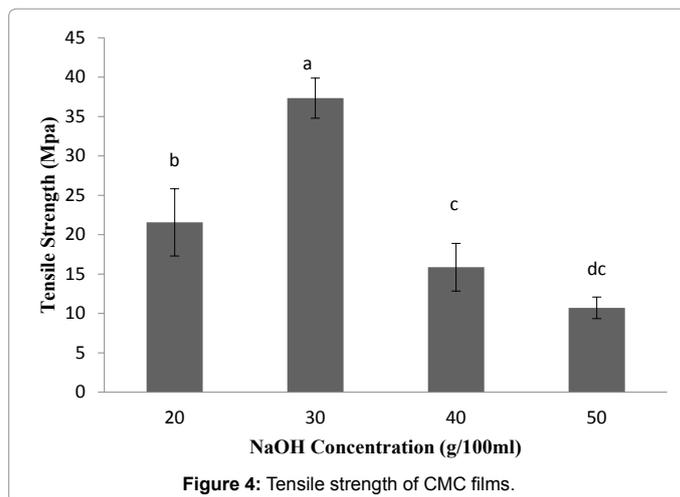


Figure 4: Tensile strength of CMC films.

when NaOH concentration increases, water vapor transmission rate significantly changes, and the highest WVP and WVTR values were observed for the films made with 30% NaOH. The Same trend was observed for DS of CMC_b meaning that higher DS values provided the polymer with greater hydrophilic groups which facilitate water molecules to easily pass through the films by dissolution-diffusion mechanism. It is obvious from different literatures that water vapor transmission rate through hydrophilic films depends on diffusivity and solubility of water molecules in the films Matrix [38,39]. In general, polymer polarities increased by conversion of cellulose to carboxymethyl cellulose also causes crystallinity reduction and changes in the granular morphology [40]. However, it can be observed from Table 2 that WVP of films with higher NaOH concentration (40%, 50%) reduced due to the reduction of hydrophilicity of films by declining polarity of the polymer.

Color

The result of color measurement of CMC_b films specimen is shown in Table 2. According to the values shown in this table, carboxymethyl cellulose from bagasse with different concentration of NaOH gives lighter, yellowish and slightly viridescent films. As can be seen, yellowness of samples decreased with increasing NaOH concentration up to 40%. It is probably due to the competitive reaction (Equations 2 and 3) to produce CMC or sodium glycolate. Beyond 40% NaOH yellowness increased which is most likely due to the intrinsic color of NaOH solution.

Mechanical properties

The results prove the effect of different concentrations of sodium hydroxide on mechanical properties of films. The tensile strength (TS) of film samples of carboxymethyl cellulose obtained under different conditions is given in the Figure 4. The TS of films increased with increasing NaOH concentration and maximum TS (37.34 Mpa) was observed in 30% NaOH, while TS decreased at higher concentration. With increasing the DS value due to the placement of more sodium

carboxymethyl groups in cellulose structure, the polarity of the polymer chains increased which promoted more intermolecular bonds between the polymer chains. On the other hand, at higher concentration of NaOH due to the formation of sodium glycolate as a reaction byproduct during CMC production (decreasing in polymer chains ionic characteristic), TS decreased. TS reduction was intense with degradation effect of high concentration of NaOH on polymer chains. Decreasing in the CMC content at high NaOH concentration provides a reduction in intermolecular forces [41].

Discussion

The effect of various NaOH concentrations on the percent elongation at break (EB) of CMC_b films is depicted in Figure 5 As can be observed, the EB of CMC_b film increased with increasing NaOH concentration, beyond the 40% NaOH concentration the EB of films dropped. This increase can be attributed to the fact that at high concentration of NaOH polymer chains get more swelled that declined the crystallinity and increase the flexibility of cellulose structure. Under higher concentration of NaOH, due to hydrolysis reaction on polymer chains, the flexibility of CMC_b films decreased. The mechanical properties of CMC_b films after applying plasticizer were also studied. Glycerol, as an external plasticizer, was added to CMC_b film in various amounts to improve the mechanical properties before casting. This was applied only to CMC_b films with 30% NaOH (with maximum TS). The results (Figure 6) showed that adding glycerol concentration lowers the TS of CMC_b films. Glycerol lessens the internal hydrogen bonds between polymer chains which effect on film resistance under tension. On the other side, the EB of CMC_b films increased at higher glycerol content. Glycerol positions between polymer chains and prevent the formation of further hydrogen bonds and reduce the intermolecular forces, thereby the chains are able to move and flexibility of them increased. Similar results have been reported previously.

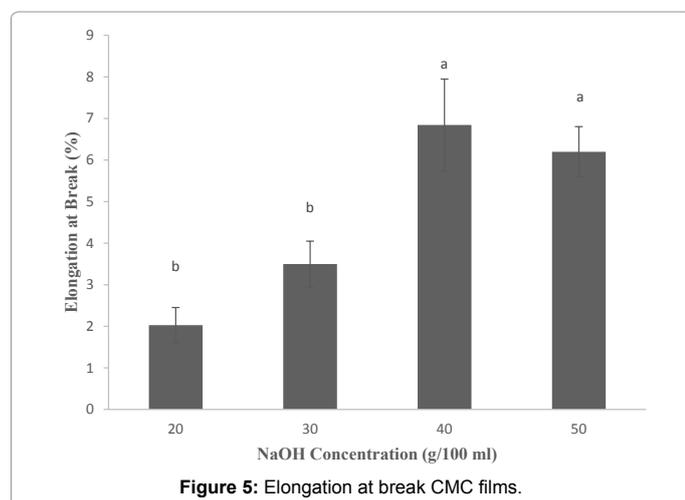


Figure 5: Elongation at break CMC films.

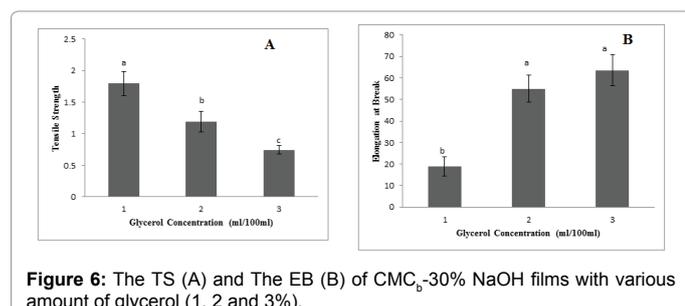


Figure 6: The TS (A) and The EB (B) of CMC_b-30% NaOH films with various amount of glycerol (1, 2 and 3%).

Conclusion

Sugarcane bagasse was properly used to extract cellulose and synthesis of carboxymethyl cellulose. The results showed maximum DS of CMC_b (0.78) at 30% of NaOH concentration. The viscosity, water vapor permeability, and mechanical properties are dependent to DS of CMC_b. Based on water vapor permeability and mechanical properties of CMC_b films, the possibility of its application on biodegradable coating materials is envisaged. Carboxymethylation of cellulose from bagasse was affected by various NaOH concentration, and crystallinity of cellulose sources is important for finding an appropriate concentration of NaOH. Carboxymethyl cellulose is one of most widely used cellulose derivatives in various industries like food, pharmaceutical, detergent, paper-making, oil drilling and Textile. Therefore, considering the methods that modified cellulose as cellulose derivatives, can help us to overcome environmental problems of agricultural waste (bagasse), which produced in large scale, and economical ways to use sugarcane bagasse.

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