SYNTHESIS, CHARACTERIZATION AND COATING PROPERTIES OF CARBOXYMETHYL CELLULOSE FROM SOCK PRODUCTION WASTES

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This study aims to evaluate and reuse defective products and cotton wastes resulting from factories producing socks in Bishkek, Kyrgyzstan, in order to solve the issues related to their disposal. For this purpose, microcrystalline cellulose (MCC) was obtained after isolating the cellulose from these wastes by treating them with sulfuric acid solutions. Then, under constant NaOH and monochloroacetic acid (MCA), CMC with the highest DS value of (0.65) was synthesized at 65 °C for 2 hours. When the reaction time was increased (3, 4 and 5 hours) at the same temperature, the DS value decreased by 0.39, 0.28, and 0.26, respectively. FT-IR, NMR, and XRD spectroscopic methods were used to characterize the structure of CMCs. SEM was used to investigate surface morphologies, and DTA-TG to examine thermal stability. In addition, the obtained CMCs were used as coatings for apples and tomatoes, and parameters such as mass loss, hardness, total soluble solids and ascorbic acid in fruits and vegetables, were investigated; also, microbial analysis, and sensory analysis were performed. These analyzed parameters were improved for tomatoes and apples coated with CMC, compared with those uncoated.

Keywords: recovery, carboxymethyl cellulose, NMR, storage quality, microbial load

INTRODUCTION

Due to the increasing population, unnecessary and unconscious use of resources raises concerns about the future. One way to reduce these concerns, by considering concepts such as recycling, recovery, and reuse, would be to increase the combined use of sustainable and renewable resources. With this awareness, waste should be re-evaluated or transformed into another form and re-introduced into the economy. Thus, energy consumption will decrease by preventing waste, and the factors causing global warming will also reduce in line with the principles of zero waste.

One of these wastes is cotton containing more than 95% α-cellulose, an essential textile industry resource. Cellulose is a hydrogen-bonding biopolymer with a linear polymer chain consisting entirely of glucopyranose monosaccharides (AGU) linked by 1,4-glycosidic bonds.[1] Due to its hydrophilic nature and crystal structure, cellulose is insoluble in water or a single organic solvent.[2] By adding different substituents to the hydroxyl groups in the 2-, 3- and 6-positions of AGU, cellulose derivatives with very different physical properties from those of crystalline cellulose can be synthesized.[3] The most common methods used to improve the workability and properties of cellulose are etherification and esterification. Carboxymethyl cellulose (CMC), one of the ethers of cellulose, is synthesized by the etherification of alkali cellulose, which is formed by sodium in the mercerization step with an aqueous NaOH solution, with either MCA as the free acid or NaMCA as a sodium salt in an alcohol-water-NaOH solution mixture. Due to the increased solubility of cellulose derivatives relative to cellulose, they are potentially becoming more usable in various applications in many industries.[4] Thus, due to their wide variety of properties, they can be used as thickeners, binders, lubricants, emulsifiers, rheology modifiers, and film formers, cellulose derivatives are used in food,[5] oilfield chemicals,[6] construction,[7] paper,[8] adhesives,[9] batteries,[10] and textiles.[11] Among commercial

cellulose ethers, carboxymethyl cellulose (CMC) is widely used, accounting for more than half of the total cellulose ether consumption worldwide.[12]

Food products are covered with a protective film to protect them from post-harvest physical and mechanical damage, thus extending their shelf life and quality. This coating increases the nutritional and sensory properties of foods, incorporating certain functional and bioactive compounds into the polymeric matrix, thus benefiting consumers' health. In addition, it provides shine to the coated fruit, helping to maintain the firmness of the products.[13] Moreover, by adding into the coating certain components that are not found in the natural product, it is possible to prevent spoilage, hair growth, the growth of pathogens, and the development of microorganisms.[14] For these reasons, a coating is considered one of the approaches of great interest to improve the quality of fresh horticultural products. Recently, it has been widely used in the food industry, as it extends the shelf life of fruits and vegetables and preserves their quality properties, especially in coatings made with cellulose derivatives derived from polysaccharides. CMC-based coating agents are generally odorless, tasteless, non-toxic and non-allergenic, water-soluble, transparent, and resistant to oils and fats. These polymers provide mechanical integrity as a barrier against moisture and gases. Such coatings provide benefits such as biodegradability and relatively low cost, and more importantly, they are suitable carriers for various bioactive agents.[15]

Socks are woven with cotton yarn, used to produce many different fabrics. The upper part of the collar of each woven sock is cut and takes the shape of the sock. Many of these cut cotton pieces and defective socks can be evaluated and reused. This study isolated cellulose from socks factory waste as microcrystalline cellulose (MCC) by treatment with H_2SO_4. Then, carboxymethylcellulose (CMC) was synthesized from the reaction of MCC with monochloroacetic acid (MCA) and NaOH, and its structure was characterized by FT-IR, NMR, and XRD spectroscopic techniques. SEM investigated the surface morphologies of the CMCs, and their thermal properties were investigated by thermogravimetric analysis (DTA-TG). The degree of substitution (DS) values was determined using potentiometric titration. In addition, the synthesized CMCs were used as coatings for apples and tomatoes, and the effects of the coatings on the shelf life and quality of the food products were investigated. For this purpose, coated and uncoated (control) apples and tomatoes were compared in terms of weight loss (WL), hardness, total soluble solids (TSS), and ascorbic acid (AC), at ambient temperature (25 °C).

EXPERIMENTAL

Materials

Sock wastes were supplied from socks-producing factories in Bishkek, Kyrgyzstan. Sodium hydroxide, hydrogen peroxide (H_2O_2) 50%, hydrochloric acid 37%, nitric acid 65%, monochloroacetic acid (MCA, $ClCH_3COOH$), glacial acetic acid, phenolphthalein, isopropyl alcohol (IPA), ethanol and, methanol was obtained from Sigma Aldrich. All chemicals were pure reagent grade and used without further purification.

Synthesis of carboxymethyl cellulose (CMC) from sock wastes

As it is more affordable than combed yarn, NE 20/1 colored carded 100% cotton yarn is generally used in socks production. Socks are normally produced with 2 yarns: an "outer" and an "inner" yarn. Cotton is used on the outer surface, and polyamide or polyester is used on the inner surface.[16] After the socks are produced, the cut parts of each sock and/or the defective socks are swept from the floor and stored in the waste area in bulk (Fig. 1). At these stages, particles, such as coarse-grained dust, originating from the factory environment, accumulate on these wastes.

The sock wastes obtained from the factory were washed several times with tap water and dried in batches to remove impurities.[17] Since the sock wastes contained both synthetic polymer yarn and cotton yarn, microcrystalline cellulose (MCC) was obtained by isolating cellulose with sulfuric acid.[18] For this purpose, the influence of sulfuric acid concentration, isolation temperature, and time was investigated in the isolation stage of MCC with H_2SO_4. The optimized conditions were the following: 20 g of cleaned and dried sock waste, treated with 500 mL of 15% sulfuric acid solution at 80 °C for 1.5 hours. The acidic product, brought to room temperature, was carefully neutralized with NaOH, passed through a 0.2 mm mesh sieve, and separated from the remaining unreacted synthetic polymers. Then, the precipitated MCC was filtered, washed sequentially with tap and distilled water, and dried in vacuum at room temperature.

The synthesis of CMC was conducted according to the method described by Celikci *et al.* (2021), but with a slight modification.[19] Firstly, 5 g of MCC was mercerized with 50 mL of 40% NaOH solution overnight at 4 °C

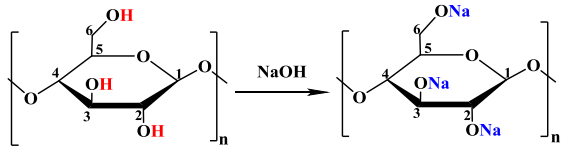
for the mercerization. Then, after melting the frozen mercerized MCC, the excess sodium hydroxide solution was filtered with the help of a vacuum pump (Scheme 1).

Afterwards, in a water bath at room temperature, 200 mL of isopropanol (IPA) and mercerized MCC were placed in a 500 mL glass flask under reflux and mixed. A solution of 3.78 g NaOH prepared by dissolving in a minimum amount of distilled water was added to this mixture. After stirring for 15 minutes, the sodium salt of monochloroacetic acid was added to the reaction mixture, affecting the amount of 3.70 g NaOH equivalent to 8.75 g of MCA, and stirring was continued. Reactions were performed at different times (2, 3, 4, and 5 hours) and temperatures (45, 55, 65, and 75 °C) to determine the effect of temperature and time on the carboxymethylation process (Table 1). After studying these parameters, the solid precipitated in the etherification reaction medium was filtered. This residue was suspended in 200 mL of 90% methanol and stirred for 12 hours. It was then neutralized in the same medium with CH_3COOH, filtered, and washed several times sequentially with 90% methanol, pure methanol, and pure ethanol to remove unwanted by-products formed in the reaction given below:

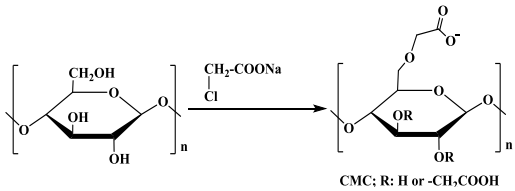
$$NaOH + Cl\text{-}CH_2\text{-}COONa \rightarrow HO\text{-}CH_2\text{-}COONa + NaCl \quad (1)$$

The resulting CMC was dried at 40 °C to constant weight (Scheme 2).

Figure 1: Cut parts of socks (A), MCC (B), and CMC-3 (C)



Scheme 1: Mercerized MCC



Scheme 2: CMC

Table 1
Effect of reaction time and temperature on viscosity and DS values of CMCs

Samples	Time (h)	Temp (°C)	DS	Viscosity (mPa·s)
CMC-1	2	45	0.41	6.57
CMC-2	2	55	0.48	4.64
CMC-3	2	65	0.65	6.43
CMC-4	2	75	0.34	4.68
CMC-5	3	45	0.26	4.68
CMC-6	3	55	0.38	5.84
CMC-7	3	65	0.39	4.28
CMC-8	3	75	0.38	4.68
CMC-9	4	45	0.43	4.83
CMC-10	4	55	0.29	4.5
CMC-11	4	65	0.28	9.14
CMC-12	4	75	0.52	14.7
CMC-13	5	45	0.32	5.18
CMC-14	5	55	0.51	5.83
CMC-15	5	65	0.26	5.84
CMC-16	5	75	0.49	6.01

Determination of DS value by titration

The DS values of CMCs were determined by the standard method ASTM (1961),[20] using potentiometric titration determined by converting the polymer into its acid form in a nitric acid-ethanol mixture, adding a known amount of NaOH and titrating with HCl using phenolphthalein as an indicator. 4 g of dried CMC powder was stirred in 75 mL of 95% ethyl alcohol. Then, 5 mL of nitric acid was added to the mixture, and the

suspension was stirred until boiling. The solution at room temperature was stirred for an additional 10 minutes. The resultant solution was filtered and washed 5 times with 80 mL of 95% ethanol, which was heated to 60 °C until the acid and salts were removed. The final product was washed with pure methanol, dried at 105 °C for 3 h, and kept in desiccators for an hour. For titration, 1-1.5 g of dried CMC powder was suspended in 100 mL of distilled water in a 250 mL Erlenmeyer flask and stirred continuously. Then, 25 mL of 0.3 M NaOH solution was added to the solution and boiled for about 15-20 min to dissolve the CMC. After cooling at room temperature, about 2-3 drops of phenolphthalein indicator were dropped into the solution (color until to be dark pink) and titrated with 0.3 M HCl. The titration was done in triplicate, and the average volume of HCl was recorded. DS was calculated based on Equations (2) and (3):[21]

$$\text{Degree of Substitution (DS)} = 0.162 \times A/1-(0.58) \times A \quad (2)$$

$$A = (B \times C) - (D \times E) / F \quad (3)$$

where A = milli-equivalents of consumed acid per gram of specimen; B = mL of NaOH used to titrate; C = concentration of NaOH; D = mL of HCl used to titrate; E = concentration of HCl; F = CMC amount (g); 162 is the molecular weight of the anhydrous glucose unit (AGU) and 58 is the net increase in the anhydrous glucose unit for each substituted carboxymethyl group.

Measurements of viscosity

Rheological measurements were carried out using an MCR-302 Rheometer (Anton Paar, Austria), equipped with a CC27 concentric cylinder. The viscosity (η) of 3% (w/w) aqueous solutions of CMC samples was measured at a shear rate of 15 1/s and at room temperature.

Gel permeation chromatography (GPC) analysis

Gel permeation chromatography (GPC) was performed at 40 °C using a Shimadzu LC-20 AD Instrument, with an internal differential refractive index detector, and an Agilent PLgel mixed-B column using HPLC grade N,N'Dimethylformamide (DMF) as the mobile phase at a flow rate of 1 mL/min. Calibration was performed with narrow polydispersity polystyrene (PS) standards.

Scanning electron microscopy

The images of the CMC granules were observed using a Scanning Electron Microscope (SEM) (JEAL/Neoscope JCM-5000) at EHT = 20kV.

Fourier transform infrared spectroscopy

The spectroscopic method of FT-IR was used for the characterization of cellulose and the CMC samples. The FT-IR spectra were taken from 4000 to 400 cm^{-1} using a Perkin Elmer Spectrum 400 Infrared Spectrophotometer with ATR apparatus.

Nuclear magnetic resonance (NMR) spectroscopy

$^{1}H(^{13}C)$-NMR spectra of CMCs were recorded at 30 °C using a Bruker-200 MHz Varian spectrometer (90^{o} pulse and 16 scans). The CMC sample was dissolved in deuterium oxide (D_2O) at a concentration of 25–30 mg/600 μL. Chemical shifts were reported as ppm and calibrated against the residual solvent signal of D_2O (δ 4.8 ppm) as an internal standard.

X-ray diffraction (XRD) analysis

X-ray diffraction patterns of the CMC samples and cellulose were analyzed using an XRD diffractometer (Philips X'Pert PRO) with CuKα radiation operating, the voltage of 40 kV, and the current of 30 mA at monochromatic radiation (λ = 154060 nm). All samples were scanned from 10 °C to 90 °C at a scan speed of 5° 2θ/min, with a step size of 0.02°.

Thermogravimetric analysis (TG-DTA)

The CMCs and cellulose thermal behaviors were measured using a TG-DTA (Seiko II, Japan). The sample (15 ± 5 mg) in a ceramic pan was heated from 30 °C to 600 °C, at 20 °C/min of heating rate under a nitrogen atmosphere (20 mL/min).

Application of CMC as coating

Preparation of the coating solution

The CMC coating solution was prepared by dissolving 6 g of CMC powder in 200 mL of water:ethyl alcohol mixture (3:1).[13] It was stirred at 80 °C with a magnetic stirrer for 10 minutes. Propylene glycol 2% (v/v) was chosen as a plasticizer and added to the CMC solution.[22]

Coating fruits and vegetables with CMC

Fruits and vegetables (apples and tomatoes) were purchased from a local market in Bishkek, Kyrgyzstan, on the day after harvest and were immediately placed in ambient storage (15 ± 2 °C). Then, they were coated by dipping them in the carboxymethyl cellulose solution at 20 °C for 1 minute. The fruits and vegetables coated with the CMC solution were stored together with the control samples (uncoated) at room temperature. Tomatoes were stored for 4 weeks and apples for 10 weeks. Physicochemical analyses were carried out every week after coating.

Weight loss

The weight loss of the fruits and vegetables was calculated by weighing them on day 0 and after weekly periods until the end of the experiment. The experiments were performed in 3 replicates for each sample. Results were expressed as the weight loss percentage relative to the initial value. Weight loss was determined according to the formula:

Moisture loss (%) = [(A-B)/A] x 100 (4)

where (A) indicates the fruit weight at harvest, and (B) means the weight after storage intervals.[23]

Firmness

Firmness was determined using a Koehler K95500 penetrometer as the maximum penetration force (N) reached during tissue fracture. The samples were sliced in half, and firmness was measured by introducing a straight needle into the center point of each half to 5 mm depth.

Total soluble solids

To measure the contents of total soluble solids in the samples, the fruits and vegetables were individually ground in an electric juice extractor for freshly prepared juice.[24] Soluble solids were measured using a digital refractometer (REF-113ATC, Hand Refractometer 0-32% Brix/ATC) at 20 °C. Results were expressed in %.

Ascorbic acid

The ascorbic acid content was measured using the iodometric titration method.[23]

Microbial analysis

10 grams of sample pulp was taken under aseptic conditions. The sample was then homogenized in a peptone salt solution (8.5 g/L sodium chloride + 1 g/L peptone) for 1 minute. After making a series of dilutions of the peptone solution, samples were introduced into different media as follows: (1) Plate count agar (PCA) – used to isolate total aerobic psychrotrophic microorganisms at 12 °C for 72 h and mesophilic microorganisms at 30 °C for 72 h; (2) Sabouraud agar (Oxoid CM41) – used to isolate yeasts and molds at 25 °C for 120 h. Colonies were counted, and results were given as CFg^{-1}.[25] Analyses were carried out periodically with random samples from fruits and vegetables.

Sensory analysis

The taste panels consisted of 8 semi-trained panelists. Each panelist was asked to assess the samples at the same session, and distilled water was used as a palate cleanser between samples. The sample's odor, skin color, appearance, and overall acceptance were assessed using a five-point hedonic scale (1 – bad, 2 – moderate, 3 – good, 4 – very good, 5 – excellent). The whole process was performed at ambient temperature and standard lighting.

RESULTS AND DISCUSSION

Microcrystalline cellulose (MCC) was isolated with sulfuric acid solution from the waste of a sock manufacturing factory in Bishkek, Kyrgyzstan. CMC was synthesized from the reaction of MCC with MCA, which was mercerized by sodium hydroxide solution. The surface morphology and thermal behavior of these CMCs, whose structures were characterized by spectroscopic methods, were examined, and DS values were determined. After the apples and tomatoes were coated with CMCs with three different DS values of $CMC_{DS=0.65}$, $CMC_{DS=0.39}$ and $CMC_{DS=0.28}$, the postharvest quality of these coated samples was examined.

Degree of substitution

DS plays an essential role in the water solubility of Na-CMC, and with an increase in DS, the hydro-affinity of CMC increases. It is the average number of carboxymethyl groups substituted per monomer unit, ranging from 0 to 3, with the remaining R=H.[26] When the DS value of CMC is above 0.6, it has complete solubility in water. However, when the DS is low, *i.e.* less than 0.2, the fibrous

character of the starting material is retained. Therefore, it is insoluble in water.[27] The DS values of synthesized CMCs are given in Table 1. When the DS values were compared, it was noted that the sample coded CMC-3 synthesized from the etherification reaction at 65 °C for 2 hours with 3.75 g NaOH and 8.75 g MCA had the highest DS value of 0.65. As seen in Table 1, the DS value decreased to 0.39, 0.28, and 0.26, respectively, when the reaction medium was kept at a constant temperature of 65 °C and the reaction times were increased to 3, 4, and 5 hours. This decrease in DS value can be attributed to the by-products formed, such as alcoholates in the complex environment. In CMC synthesis, with increasing reaction time and temperature, there were not too many differences in DS values and in the viscosities either. The viscosity at the highest DS value was found to be 6.43. Viscosity values were close, except for the 9.14 and 14.7 values. By its nature, the homogeneous distribution of microcrystalline cellulose in the aqueous medium reflected this feature in the synthesized CMCs and viscosity. Therefore, the viscosities of CMCs are concentrated between 4 and 6.

GPC analysis

GPC is a widely used technique to separate molecular compounds based on their shape, size, and weight.[19,28] The molecular weight distributions and average molecular weights of the MCC and CMCs are given in Table 2. The Mw/Mn ratio of microcrystalline cellulose is 2.65, while that of CMC with a DS of 0.65 is 1.78; that of CMC with a DS of 0.39 is 1.39; and that of CMC with a DS of 0.28 is 1.03. The XRD results showed that MCC was more amorphous than CMCs, as new crystal regions were formed in CMCs. These crystal structures result from the binding of monochloroacetic acid to the OH groups present in cellulose. However, monochloroacetic acid, which could not bind to the structure, also reduced the molecular weight due to hydrolysis of the amorphous regions of the MCC. Therefore, the molecular weight of CMCs is lower than that of MCC. The molecular weight of the synthesized CMCs increased with the DS value. This results from successfully substituting hydroxyl groups.[29]

SEM analysis

The surface morphology of cellulose and synthesized CMCs is presented in Figure 2. As can be seen, the fiber structure of native cellulose has a long, smooth surface, with no defects, and a stable fibrous structure. In contrast, the surface structure was disrupted after carboxymethylation and converted into a corroded structure. It can be said that NaOH penetrates the amorphous regions of the MCC, causing partial disruption of its structure. The alkaline environment during the modification process accounts for the structural changes and similar morphological changes have also been reported during the carboxymethylation of MCC.[30-32] While the fibrils of CMC-15 (DS = 0.26) with low DS were more prominent, as the DS value increased, the fibril structure of the cellulose deteriorated. This is because during alkali treatment, the intermolecular bond of cellulose is broken, and the polyhydroxy group of polysaccharides results in fiber swelling, which decreases fiber length.

Table 2
Molecular weight of MCC and CMCs

Samples	(Mn) g/mol	(Mw) g/mol	Mw/Mn g/mol
MCC	$1.12x10^4$	$2.98x10^4$	2.65
DS = 0.65	$3.01x10^4$	$5.39x10^4$	1.78
DS = 0.39	$5.53x10^3$	$7.70x10^3$	1.39
DS = 0.28	$4.70x10^3$	$4.89x10^3$	1.03

Mn: number-average molecular weight; Mw: weight-average molecular weight

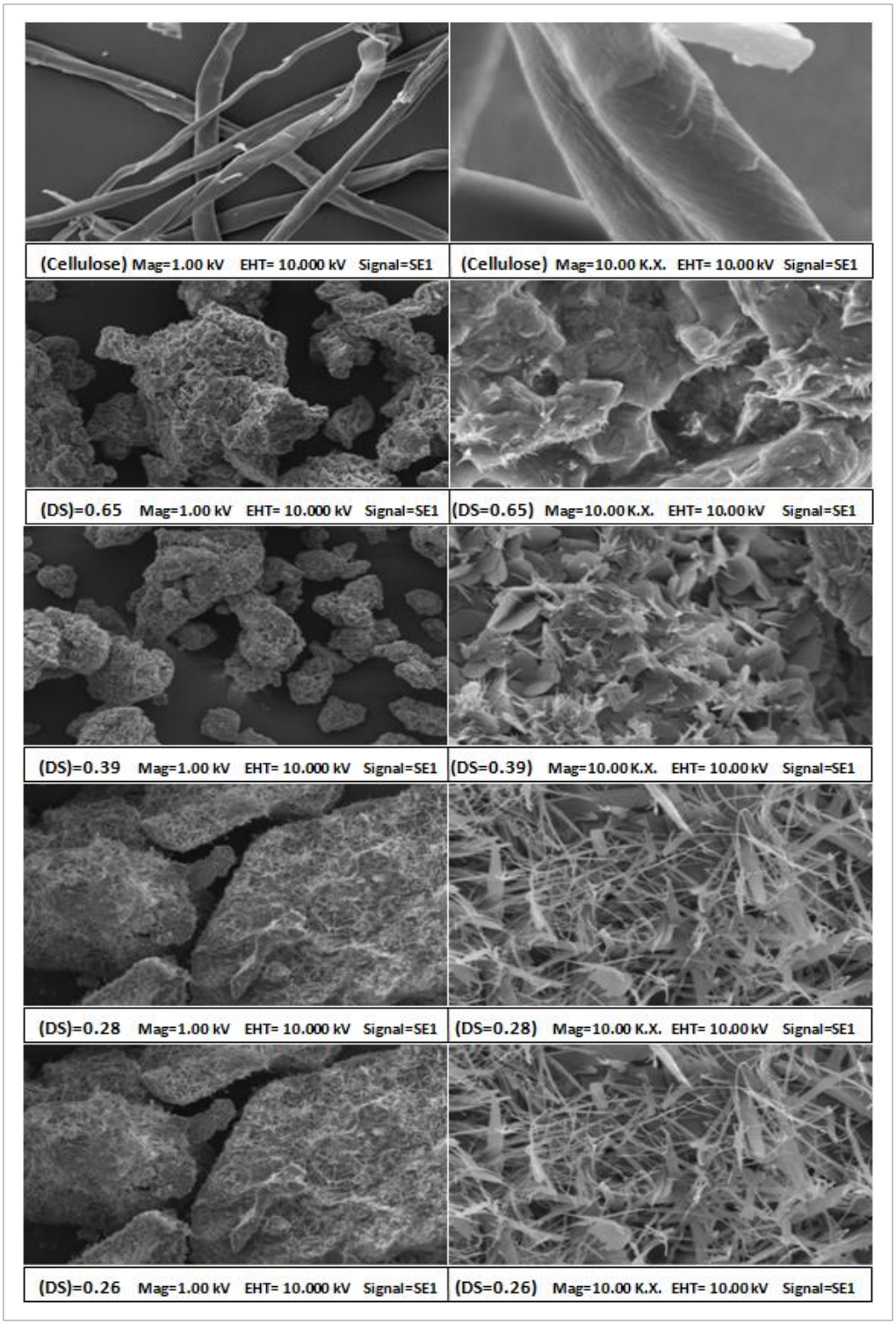


Figure 2: SEM images of cellulose (MCC) and CMCs

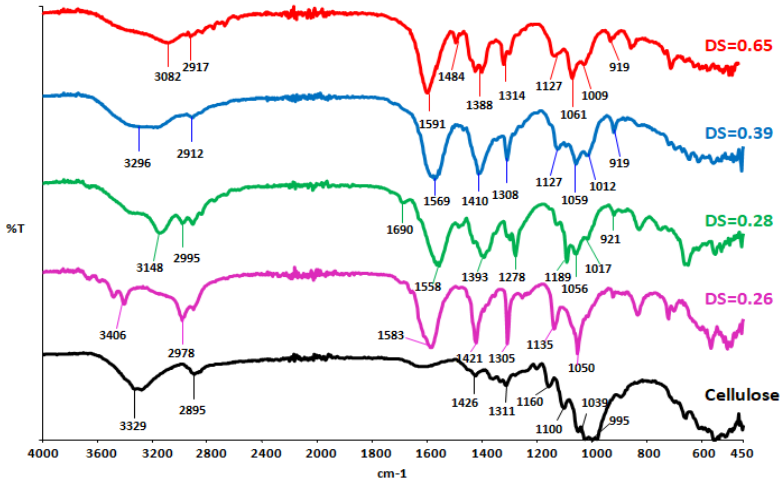


Figure 3: FT-IR spectra of cellulose (MCC) and CMCs

FT-IR spectroscopy

Figure 3 shows the FTIR absorption spectra of cellulose and CMCs. As seen from the spectra, specific absorbance of O-H stretching at around 3082-3406 cm^{-1}, weak C-H stretching vibration at 2912-2995 cm^{-1} (in addition to the vibration band of MCC at 2895 cm^{-1}, new vibration bands between 2995 cm^{-1} and 2912 cm^{-1} in CMCs can be attributed to the -CH groups formed as a result of carboxymethylation), $-CH_2$ scissoring and C-O symmetric stretching vibration between 1484 and 1278 cm^{-1} has appeared in all CMCs. The bands between 1189-1160 cm^{-1} and 1039-919 cm^{-1} are related to asymmetric bridge stretching (C-O-C) of cellulose and the β→4 glycosidic bonds between glucose units in cellulose structure. The band at 1061 and 979 cm^{-1} could be assigned to the C-O stretching of CH_2OCH_2 and O-H out-of-plane bending, respectively. A new and strong absorption band at 1558-1591 cm^{-1} confirms the presence of the COO^- group, and the vibration band confirms the successful carboxymethylation. Similar results were reported on the CMC in the previous literature.[27,33-37]

^{1}H- and ^{13}C-NMR spectroscopy

Since NMR spectroscopy is one of the most influential and straightforward methods in structure characterization, it is one of the most frequently used spectroscopic characterizations of cellulose derivatives. CMCs with a DS range of 0.65 to 0.26 were characterized by ^{1}H(^{13}C)-NMR spectroscopy. Their NMR spectra are given in Figures 4-7, and their chemical shift values are given in Table 3.

The ^{13}C-NMR characterization of CMC samples includes the distribution of carboxymethyl substituents at C-2, C-3, and C-6 positions within the anhydrous glucose unit (AGU) on the cellulose polymer. As seen in Figure 4, the eight-carbon structure containing the CMC chain and the distribution of substituents at the 2-, 3- and 6-positions in AGU was observed in the CMC-3 coded example with a value of DS = 0.65. A similar structure was obtained for CMC-7 (DS = 0.39), CMC-11 (DS = 0.28), and CMC-15 (DS = 0.26) (Fig. 5). The signals received in the range of δ 61.1–74.8 ppm, δ 102.3–102.5 ppm, and δ 177–178 ppm are the characteristic range of CMC as assigned earlier.[34,38-40] In Table 3, the chemical shifts at δ 60-61 ppm are assigned to C6 of the primary alcohol group. The peaks for the ring carbons of C2-C5 positions appeared as complex spectral lines in the region of δ 74.80-69.3 ppm and were attributed to the substituents' methylene groups.[41] The chemical shifts 102 ppm is associated with anomeric C1.[42] In addition, the peak that was observed in all CMCs, chemical shift value of δ 181-178 ppm can be attributed to the signal of the carbonyl carbon resonances (C8, C=O).[32,41]

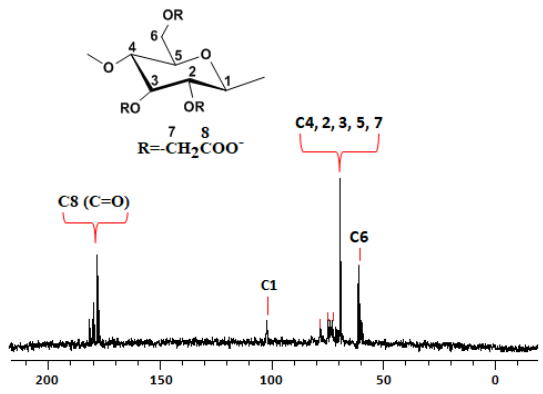


Figure 4: ^{13}C-NMR spectrum of CMC-3 (DS = 0.65)

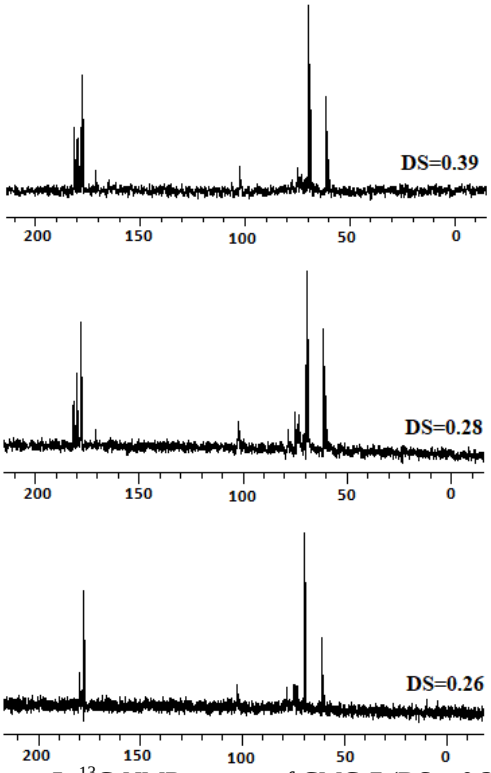


Figure 5: ^{13}C-NMR spectra of CMC-7 (DS = 0.39), CMC-11 (DS = 0.28) and CMC-15 (DS = 0.26)

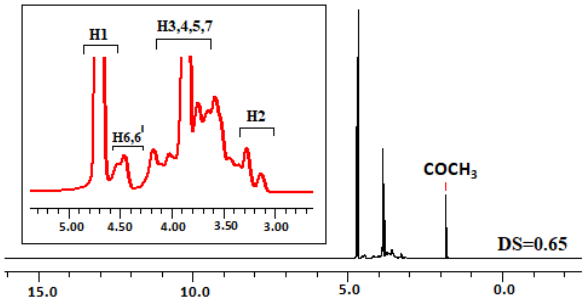


Figure 6: ^{1}H-NMR spectra of CMC-3 (DS = 0.65)

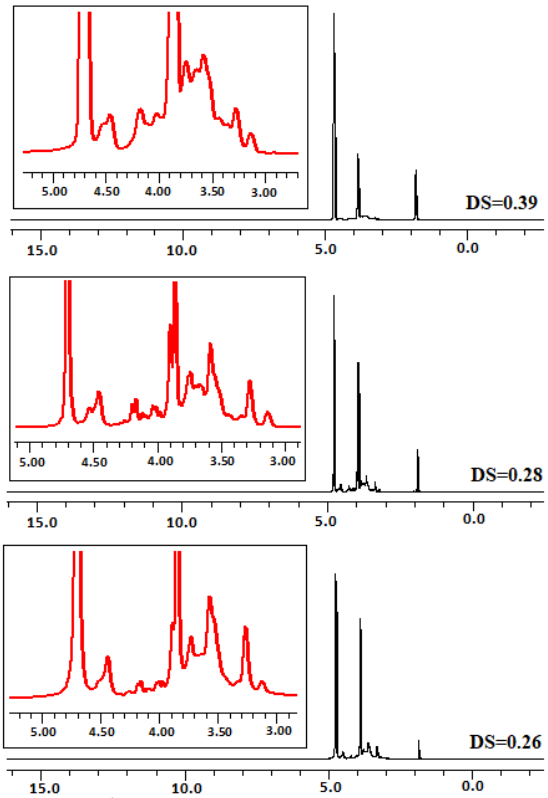


Figure 7: ^{1}H-NMR spectra of CMC-7 (DS = 0.39), CMC-11 (0.28) and CMC-15 (0.26)

Table 3
$^{1}H(^{13}C)$-NMR chemical shift (δ) of the AGU comprising CMC in D_2O

Sample	δ/ppm						
	C1	C2	C3	C4	C5	C6	C7
CMC-3	102.5	74.8	73.9	78.2	72.9	61.1	69.4
CMC-7	102.5	73.9	72.9	74.8	71.2	61.2	69.4
CMC-11	102.3	73.9	72.9	74.8	69.3	60.8	69.4
CMC-15	102.3	73.9	72.7	78.1	70.4	61.1	69.6
	δ/ppm						
	H1	H2	H3	H4	H5	H6	H6'
CMC-3	4.7	3.6	4.0	3.9	3.8	4.1	4.1
CMC-7	4.7	3.6	3.8	3.7	3.6	4.5	4.4
CMC-11	4.7	3.7	4.0	3.9	3.8	4.4	4.4
CMC-15	4.7	3.5	3.8	3.8	3.7	3.2	3.1

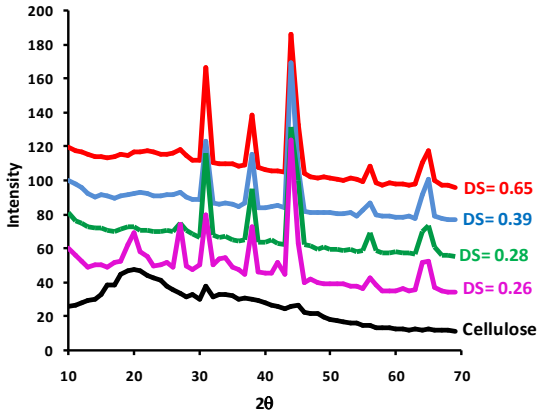


Figure 8: XRD pattern of cellulose (MCC), CMC-3 (DS=0.65), CMC-7 (DS=0.39), CMC-11 (0.28) and CMC-15 (0.26)

In the ^{1}H-NMR spectra shown in Figures 6 and 7, and as seen from the chemical shift values in Table 3, the resonance of the CMCs showed primarily seven protons, *i.e.*, H1-H6, corresponding to carbonyl and methylene carbons in the glucose ring and substituted carboxymethyl groups.[34] These resonances from the AGUs composing the CMC structure were seen to overlap in the narrow region between δ 4.7-3.1 ppm and were attributed to the protons of substituted monomeric glucose.[44] Also, it was observed in all CMC samples at 1.78 ppm, which was attributed to the chemical shift value of acetic acid remaining from neutralization during synthesis.[37]

XRD analysis

The crystallinity of cellulose and CMCs was analyzed by X-ray diffraction and the XRD patterns are shown in Figure 8. The pattern of MCC revealed its amorphous structure and showed a broad diffraction peak at $2\theta = 20^{o}$.[44] It was compared with those of the CMCs to clarify their crystal structures and the change in the polymer chains. After carboxymethylation, it was found that the proportional crystal structure of the MCC was reduced by breaking the hydrogen bonds of the cellulose chains in the amorphous region. It was observed that the crystalline areas of MCC did not form in CMCs, instead, new crystalline regions formed.[45] This might also be due to the removal of lignin and hemicelluloses because of their amorphous nature. Mainly, it was seen that the crystal structure increased in CMC-15 with a decreasing DS value. The new crystalline regions formed in CMCs changed inversely with the DS value, and the crystalline regions decreased as the DS value increased. This was an expected result for a low DS value, because this result means that fewer organic groups are attached to the cellulose structure.[46]

TG-DTA

The thermal behaviors of CMCs were investigated in the temperature range of 30-600 °C. As can be seen from the thermograms in Figure 9, the weight loss of MCC from 200 to 600 °C, with a

maximum degradation peak at 341 °C (second step, 55.27%), followed by a smooth degradation (third step, 19.10%), is attributed to decarboxylation and decomposition of Na–CMC and formation of carbonaceous char.[47-49] The first mass loss due to the evaporation of moisture and solvent in CMCs started at 100 °C.[47] The most pronounced decomposition in MCC and all CMCs was around 200-400 °C (Figs. 9-11). The intense weight loss of MCC around 200-400 °C was about 62.96%, and the remaining mass was 37.04% at 400 °C. At this stage, the residual group was recorded as 64.73% in CMC-3, 60.80% in CMC-7, 66.85% in CMC-11, and 53.80% in CMC-15. Mass losses of 27.6% in CMC-3, 19.3% in CMC-7, 20.75% in CMC-11, and 32.99% in CMC-15 were recorded. Endothermic peaks occurred at 271 °C in CMC-3, 271 °C in CMC-7, 273 °C in CMC-11, and 283 °C in CMC-15. Moreover, in this step, the mass loss was 13.94%, 9.97%, 10.78%, and 24.90%, respectively. MCC appeared to lose more weight than CMCs when the temperature rises above 400 °C. At the final temperature of 590 °C, the remaining mass of MCC, CMC-3, CMC-7, CMC-11, and CMC-15 was observed as 3.48%, 55.11%, 51.45%, 56.44%, and 45.94%, respectively. All these observations revealed the higher thermal stability of synthesized CMC.[50] The modification of MCC to CMC has affected both the molecular structure and bonding energy, which causes the different thermal behavior of CMC.

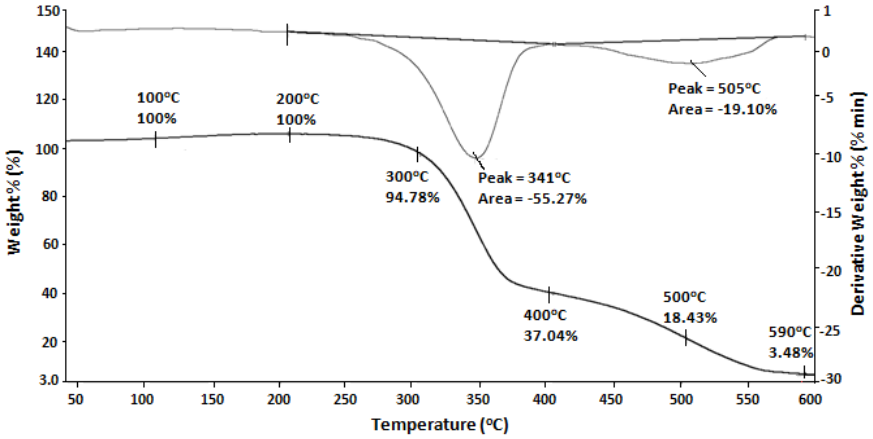


Figure 9: TG-DTA curves of MCC

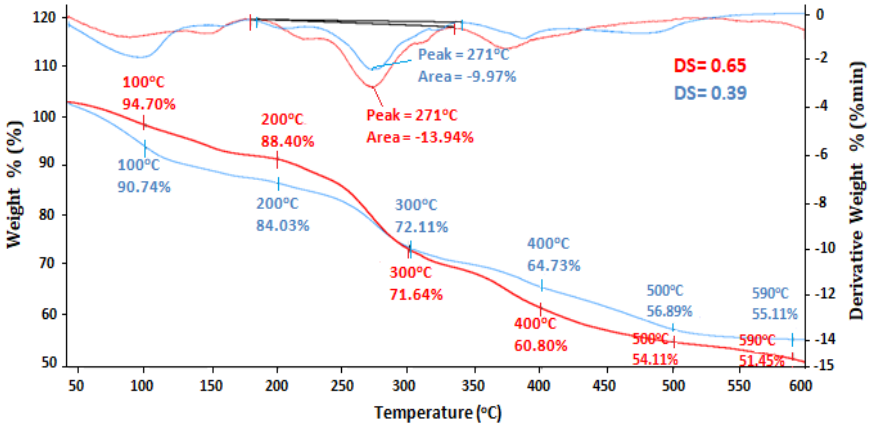


Figure 10: TG-DTA curves of CMC-3 (DS = 0.65) and CMC-7 (DS = 0.39)

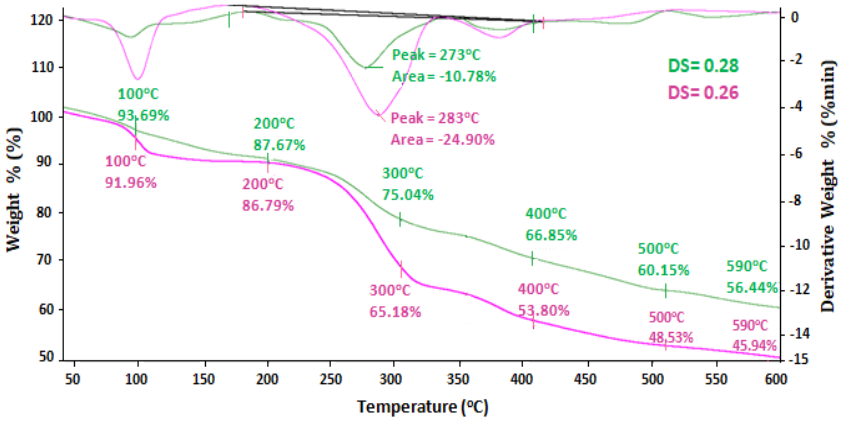


Figure 11: TG-DTA curves of CMC-11 (0.28) and CMC-15 (0.26)

Application of CMCs as coatings for fruits and vegetables

Weight loss

Weight loss in fresh fruits and vegetables is mainly due to dehydration caused by transpiration and respiratory processes, leading to visible symptoms, such as wilting and/or wrinkling. This is one of the primary reasons for the decrease in the quality of fresh horticultural produce after harvest.[51] Consequently, it leads to significant economic losses. The coating, made as a barrier in fruits and vegetables, prevents the transfer of water vapors, protects the fruit surface from mechanical injury, and thus prevents mass loss by reducing drying.[52] The effect of coating with CMCs on the post-harvest weight loss of tomatoes and apples is presented in Figure 12. As shown in Figure 12, the coated tomatoes and apples exhibited reduced weight loss during storage, compared with the control samples. The percentage weight loss after 4 weeks for the control and tomatoes coated with $CMC_{DS=0.28}$, $CMC_{DS=0.39}$, and $CMC_{DS=0.65}$ was obtained as 38.36%, 37.18%, 35.42%, and 30.25%, respectively (Fig. 12A). Also, the percentage weight loss for the control and coated apples was obtained as 2.81%, 2.67%, 2.34%, and 2.33%, respectively (Fig. 12B). As may be seen in Figure 12, there was no significant difference between the control and coated samples.[53-54] Since CMC is a hydrophilic compound (water-soluble) with moderate moisture permeability, it is unexpected for CMC to prevent water loss in coated fruit and vegetables significantly.[55] Weight loss is caused by the evaporation of moisture from vegetables and fruit.[56] The primary mechanism contributing to weight loss is the evaporation of moisture activated by a gradient of water vapor pressure at different locations in fruit.[57] However, compared with the control samples, the CMC coating has restrained the increase in weight loss.[58] Our results align with previous studies that reported the protective property of carboxyl group-containing coatings.[57,59-60]

Firmness

The effect of CMC coating on the firmness of tomatoes and apples is shown in Figure 13. As expected, the firmness parameter showed a decreasing trend for all the samples during storage. The control samples maintained their firmness during the first week of storage, but afterward it rapidly reduced. The firmness of the CMC-coated samples also decreased over time, but they kept their firmness better than the control. As seen in Figure 13A, at the end of 4 weeks, the observed penetration depth of the needle was 398 mm, 338 mm, 340 mm, and 362 mm in the control, and the tomatoes coated with $CMC_{DS=0.65}$, $CMC_{DS=0.39}$, and $CMC_{DS=0.28}$, respectively. For apples, the needle penetration depth was 53 mm, 32 mm, 41 mm, and 51 mm, in the control, and the apples coated with $CMC_{DS=0.65}$, $CMC_{DS=0.39}$, and $CMC_{DS=0.28}$, respectively (Fig. 13B). The CMC-based coatings had a significant influence on fruit firmness preservation. Carboxylic groups in the chemical structure of CMC cause hydrogen bonding inside the coating matrix and between the fruit/vegetable peel and the coating. This can increase its effectiveness in preserving fruit firmness.[51,59] Besides, O_2 deficiency in fruits and vegetables delays changes in the texture. The O_2 availability is restricted in the coated samples, and the inner gas composition is changed. Thus, oxidative metabolism is reduced, textural changes in coated fruit and vegetables are delayed, and the quality is preserved.[60-62]

Total soluble solids (TSS)

The TSS content in coated tomatoes and apples in all treatment groups is illustrated in Figure 14. The TSS value did not differ significantly for tomato or apple samples. The TSS of the coated samples was relatively stable during storage, but some differences can be seen across all coated groups, as shown in Figure 14. Initially, the TSS content in the control tomato sample was 4.5%, and the amount of TSS increased to 5.4% with a period of storage of up to 4 weeks (Fig. 14A). The TSS value for the control sample of apples was 13.7% on day 0 and 16.8% after 10 weeks of storage (Fig. 14B).

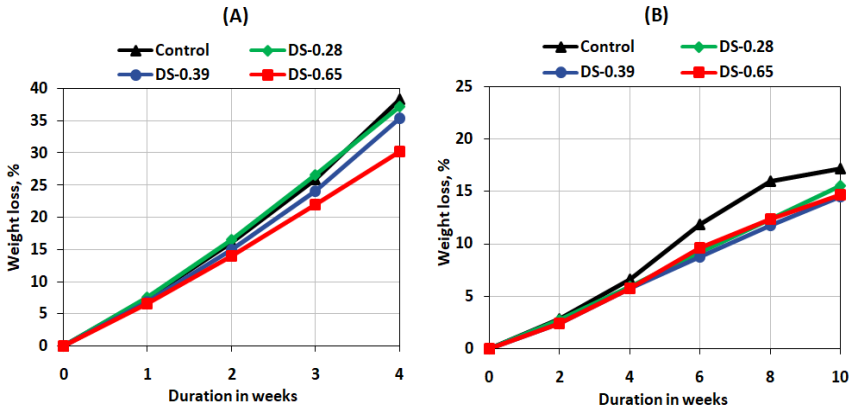


Figure 12: Effect of CMC coating on the weight loss of (A) tomatoes and (B) apples stored at ambient temperature (25 °C)

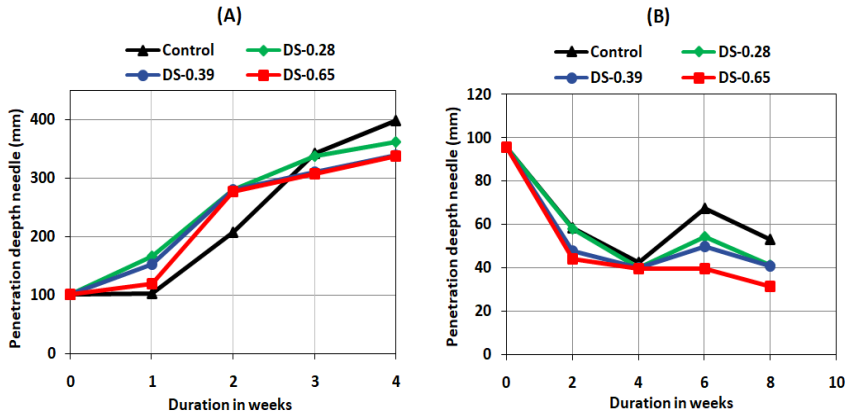


Figure 13: Effect of CMC coating on the firmness values of (A) tomatoes, and (B) apples stored at ambient temperature (25 °C)

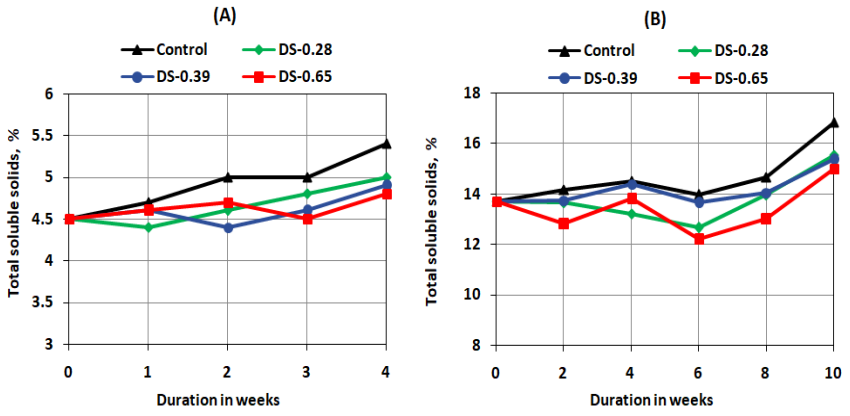


Figure 14: Effect of CMC coating on the TSS of (A) tomatoes, and (B) apples stored at ambient temperature (25 °C)

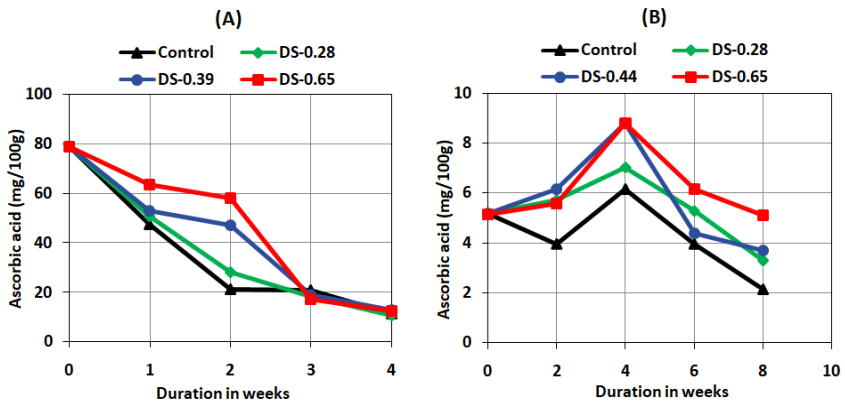


Figure 15: Effect of CMC coating on the ascorbic acid content of (A) tomatoes, and (B) apples stored at ambient temperature (25 °C)

The tomatoes and apples coated with CMC exhibited a lower TSS concentration increase than the controls. This might be because the coating material formed a thin layer on the surface of the fruit, which delayed the degradation process and reduced evaporation from the fruits.[63] Also, TSS concentration increases due to converting complex or bound sugars to simple units.[64] Increased water loss (fresh weight loss) also increases TSS concentration in fresh fruit.[65] The post-harvest coating can be attributed to the delay of the increase in TSS concentration of the samples by preventing the breakdown of complex sugars or starch.[64] Therefore, coating tomatoes and apples with CMC probably slowed the breakdown of sugars and reduced the increase in TTS in the coated samples compared to the control samples.

Ascorbic acid

The ascorbic acid (vitamin C) content in tomatoes and apples in all treatment groups is shown in Figure 15. The ascorbic acid content in tomatoes coated with CMC decreased more slowly than in the control sample. Therefore, it can be said that the coating preserves the ascorbic acid content of the tomatoes. The control tomato with an initial (day 0) ascorbic acid content of 78.8 mg/100 g significantly decreased after 4 weeks of storage to 11.44 mg/100 g. The percentage decrease in ascorbic acid content after 4 weeks of storage was of 67.3% in the control and 66.0-65.6% for coated tomatoes (Fig. 15A). All the coated apples accumulated comparatively high levels of ascorbic acid compared to the control. At the end of the 4th week, the ascorbic acid content in all the samples increased. However, after the apples were fully ripe (4-10 weeks), they started to be damaged, and the vitamin C content decreased accordingly (Fig. 15B). The percentage decrease in ascorbic acid content after 10 weeks of storage was 3.03% in the control and 1.89-0.05% in coated apples. The apples coated with CMC after 10 weeks of storage showed a higher amount of ascorbic acid than the control sample. Ascorbic acid tends to reduce based on auto-oxidation.[60] The oxidation-based decline is the leading cause of ascorbic acid reduction in various fruits and vegetables during storage.[63,66] The post-harvest coating on fruits and vegetables acts as a protective layer to limit oxygen uptake, thus leading to ascorbic acid degradation.[67] In our study, the coating of vegetables and fruits with CMC probably reduced oxygen diffusion, inhibiting the oxidation-based deteriorative reactions of ascorbic acid in the samples.

Microbial analysis

Figure 16 shows the total mesophilic aerobic counts, while storing the control and coated tomatoes and apples. The initial mesophilic microbial load in the control sample of tomato was 3.69 log CFU/g in the first week, while in the tomatoes coated with CMC (DS = 0.65, DS = 0.39, and DS = 0.28), it was 3.12, 3.25, and 3.30 log CFU/g, respectively. After 4 weeks of storage, the mesophilic aerobic count was recorded as 4.14 (control), 3.69 (DS = 0.68), 3.84 (DS = 0.39), and 3.90 (DS = 0.28) log CFU/g for tomatoes (Fig. 16A). For the apples, the control and coated apples recorded 3.19, 3.18, 3.15, and 3.15 CFU/g, respectively, in the first week. At the end of the 8 weeks of storage of the

apples, the microbial load was found as 4.20 (control), 3.50 (DS = 0.65), 3.60 (DS = 0.39), and 3.90 (DS = 0.28) log CFU/g (Fig. 16B).

The results of mesophilic aerobic counts showed the effectiveness of CMC as an antimicrobial agent. The results revealed that applying CMC coating reduced total microbial counts, compared to the control samples. The variation in the total number of yeasts and molds load in all the samples stored is shown in Figure 17. In the first week, the load of yeasts and molds in the control and coated tomatoes was observed as 3.51 (control), 3.20 ($CMC_{DS=0.65}$), 3.20 ($CMC_{DS=0.39}$), and 3.30 ($CMC_{DS=0.28}$) log CFU/g. After 4 weeks, it was found to be 4.26 (control), 3.63 ($CMC_{DS=0.65}$), 3.72 ($CMC_{DS=0.39}$), and 3.81 ($CMC_{DS=0.28}$) log CFU/g (Fig. 17A). For the apples, the initial yeasts and molds load was 3.31 (control), 3.17 ($CMC_{DS=0.65}$), 3.17 ($CMC_{DS=0.39}$), 3.20 ($CMC_{DS=0.28}$). After 8 weeks, it reached 4.44 (control), 3.22 ($CMC_{DS=0.65}$), 3.51 ($CMC_{DS=0.39}$), and 3.62 ($CMC_{DS=0.28}$), as shown in Figure 17B.

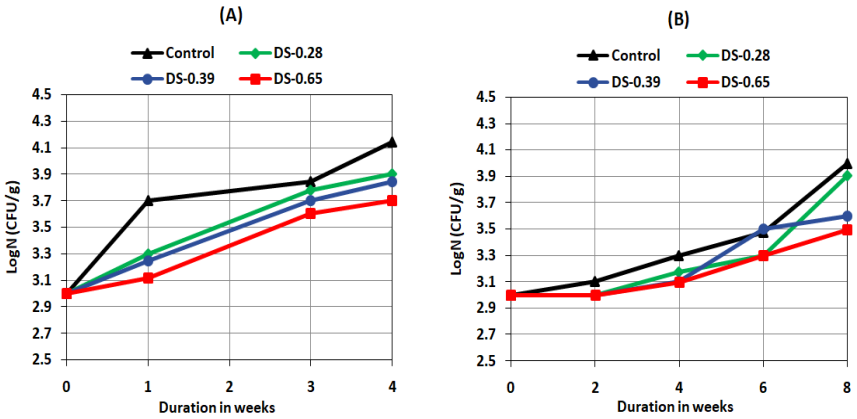


Figure 16: Effect of CMC coating on the mesophilic organisms in (A) tomatoes, and (B) apples stored at ambient temperature (25 °C)

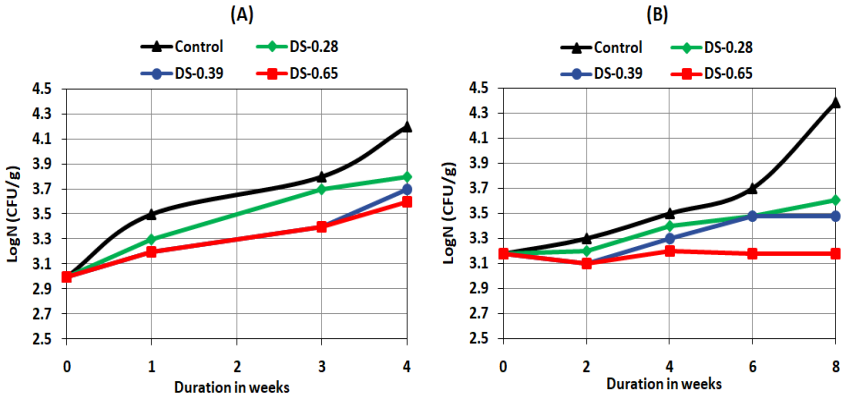


Figure 17: Effect of CMC coating on the yeast and mold organisms in (A) tomatoes, and (B) apples stored at ambient temperature (25 °C)

Sensory analysis

Sensory evaluation is a valuable technique for understanding consumers' expectations.[68] For this reason, sensory characteristics, such as taste, color, texture, and overall acceptability of the fresh fruits and vegetables were studied. All the samples were evaluated by the sensory panel of 8 semi-trained panelists. Sensory assessments were made over 4 weeks, with an evaluation covering color, aroma, odor, and flavor. Sensory acceptance was evaluated according to a 0–5 point scale, ranging from "very strong dislike" to "very strong like". Panelists did not reject any sample; in all cases, scores were higher than 3. The average results of the evaluations over the 4 weeks are shown in Figure 18. There was no significant difference between the samples in the first two weeks, but it decreased in the 3rd and 4th weeks. Among the coated samples, the best results were observed in those coated with $CMC_{DS=0.65}$.

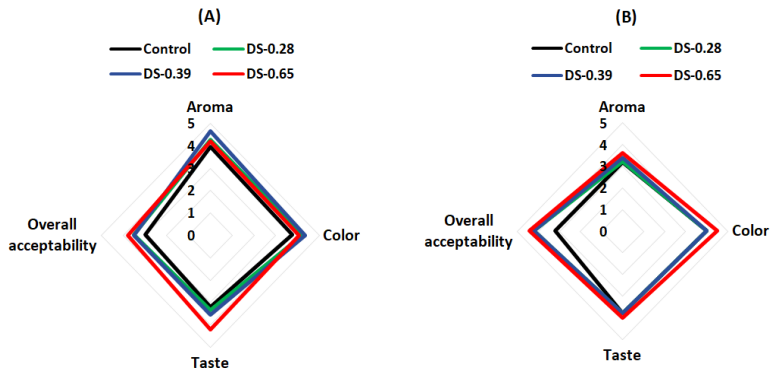


Figure 18: Effects of CMC coatings on the sensory analysis profile of (A) tomatoes, and (B) apples stored at ambient temperature (25 °C)

The control tomatoes and those coated with $CMC_{DS=0.65}$ were compared. The control sample's aroma, color, taste, and overall acceptability values were found at the end of 4 weeks as 3.95, 3.75, 3.20, and 3.00, respectively. For the sample $CMC_{DS=0.65}$, the corresponding values of 4.20, 4.10, 4.20, and 3.80 were recorded. The results of the sensory analysis showed that tomatoes and apples coated with CMC minimized the unwanted changes in the sensory characteristics.[69]

CONCLUSION

Chemical reactions, in many ways, can modify the biologically degradable, regenerative raw material cellulose. Cellulose ethers, one of the most common cellulose derivatives, are a common nomenclature for the cellulose derivatives soluble in an aqueous or organic medium. They serve primarily to control solution rheology and are used as additives in many formulations, due to their thickening, dispersing, emulsifying, film forming, suspension, adsorption, surface activity, moisture retention, and protective colloid properties. This study isolated microcrystalline cellulose by evaluating textile factory wastes resulted from the production of socks with high cellulose content. Since CMCs with low DS values are used in industrial applications, CMCs with a DS value in the range of 0.26 to 0.65 have been successfully synthesized from the reaction of microcrystalline cellulose with monochloroacetic acid.

Provided the amount of NaOH and MCA remains constant, CMC with the highest DS value of 0.65 was synthesized at 65 °C reaction temperature for 2 hours. When the reaction time increased to 3, 4, and 5 hours at the same temperature (65 °C), the DS value decreased by 0.39, 0.28, and 0.26, respectively. It has been concluded that CMCs synthesized from sock wastes can be an ideal source as a thickener in aqueous solutions. Thus, obtaining CMC with different properties from cellulosic sock by-products can be a way to produce critical value-added products and solve the environmental problems caused by the disposal of textile wastes at the same.

In the application of CMCs as coatings, it was observed that the weight loss of tomatoes coated with CMCs with DS values of 0.28, 0.39, and 0.65, after 4 weeks of storage, was 38.36%, 37.18%, and 35.42%, respectively, compared to the control (30.25%). The percent weight loss of apples coated with CMCs of the same DS was 2.81%, 2.67%, and 2.34%, respectively, compared to the control (2.33%). For tomatoes, after 4 weeks, the hardness parameter was 398 mm, 338 mm, 340 mm, and 362 mm needle penetration depth in the control, $CMC_{DS=0.65}$, $CMC_{DS=0.39}$, and $CMC_{DS=0.28}$, respectively. For apples, 53 mm, 32 mm, 41 mm, and 51 mm needle penetration depth was observed in the control, $CMC_{DS=0.65}$, $CMC_{DS=0.39}$, and $CMC_{DS=0.28}$, respectively. The value of total soluble solids (TSS) in fruits and vegetables did not differ significantly for both tomato and apple samples. The TSS of the coated samples was relatively stable during storage, but some differences could be seen across all coated groups. The control tomato sample, with an initial content of 78.8 mg/100 g ascorbic acid (vitamin C), showed a significantly decreasing ascorbic acid content to 11.44 mg/100 g after 4 weeks of storage. The ascorbic acid content of the tomato sample coated with $CMC_{DS=0.65}$ was 12.3 mg/100 after 4 weeks of storage. The ascorbic acid content for the control apple sample was 5.17 mg/100 at the beginning and 2.14 mg/100 at the end of 4 weeks. For apples covered with $CMC_{DS=0.65}$, this value was recorded as 5.12 mg/100 at the end of 4 weeks. The mesophilic microbial load in the control sample of uncoated tomatoes was 3.01 log CFU/g in the first week and 4.14 log CFU/g at the end of 4 weeks.

The tomato coated with $CMC_{DS=0.65}$ recorded a microbial load of 3.69 log CFU/g after 4 weeks, while the apples covered with $CMC_{DS=0.65}$ recorded 3.50 log CFU/g after 4 weeks. As a result of sensory analysis, it was concluded that the best results among the coated samples were noted in $CMC_{DS=0.65}$, similarly to other analyses (DS = 0.65). At the end of 4 weeks, the aroma, color, taste, and general acceptability values of the control sample were recorded as 3.95, 3.75, 3.20, and 3.00, respectively. For $CMC_{DS=0.65}$, the corresponding values were found as 4.20, 4.10, 4.20, and 3.80, respectively. Sensory analysis results showed that tomatoes and apples coated with CMC minimized undesirable changes in sensory properties. According to all these results, it can be stated that the coated apples and tomatoes are of higher quality than the control samples. Thus, it can be concluded that the synthesized CMCs can be used to coat fruits and vegetables, leading to better results in their shelf life, compared to uncoated ones.

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