CELLULOSE CHEMISTRY AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF CARBOXYMETHYL CELLULOSE (CMC) FROM DIFFERENT WASTE SOURCES CONTAINING CELLULOSE AND INVESTIGATION OF ITS USE IN THE CONSTRUCTION INDUSTRY

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This study aimed at the recovery of cellulose from abundantly available wastes and its sustainable application. Firstly, in the cleaning process, cellulose-containing wastes, such as "air particle vacuum powder" (APVD), "towel clippings" (TC), and "cottonseed delintation residues" (CD), were thoroughly washed, separately, with tap water to remove some organic and inorganic impurities. The cotton slurry was purified by 17.5% NaOH at 90 °C for about 4 hours, then filtered and washed with tap water. Afterwards, the resulting pulp was bleached by NaOH and H_2O_2, and washed with distilled water until neutralized. Secondly, for the synthesis of carboxymethyl cellulose (CMC) from the above-dried celluloses, optimum conditions were achieved by varying the concentrations of components and ambient conditions. In the sample coded TC_{CMC3}, a maximum degree substitution (DS) of 1.22, the highest consistency, the highest penetration time and the highest viscosity with 2520 centipoises (cP) were obtained from the reaction of towel clippings with 5.62 g sodium hydroxide and 13.12 g monochloroacetic acid (MCA) at 65 °C for 3 hours. Finally, the effect of these synthesized CMCs on the consistency and penetration time of a cement paste was investigated. The consistency of standard Portland cement (PC), without CMC addition, was 5 mm in the Vicat test, while the values measured for the cement pastes to which TC_{CMC3}, $APVD_{CMC3}$ and CD_{CMC3} were added reached 36.5 mm, 28.0 mm and 13.0 mm, respectively. While the setting time in the standard sample (Portland cement paste, PCP) was between 2.20-4.10 hours, this time shifted to 3.30-7.00 hours, with a maximum setting time recorded with the addition of TC_{CMC3}. Besides, while the penetration time for $APVD_{CMC3}$ started at 3.10 hours and was completed at 5.30 hours, for CD_{CMC3}, it ranged between 2.40 and 4.40 hours, leaving it without hydration in a higher time interval than in the case of standard Portland cement paste. As a result, it has been found that carboxymethyl cellulose synthesized by the etherification reaction of cellulose obtained from recycled wastes for industrial uses, in an aqueous alkali environment, can be applied as a thickener in the construction industry and other fields.

***Keywords**:* wastes, recycling, carboxymethyl cellulose, cement paste, setting time

INTRODUCTION

The production of new materials from wastes should become one of the most popular recycling processes, which can be simply described as the reuse of the wastes. In the textile industry, yarn is first produced by separating cotton from seeds, as raw cotton fibers, in cotton gin factories. These threads are used in the production of various textiles, such as fabrics, towels, and the like. Very short fibers, which are formed by shaving the cotton yarns on the surface of the towels to equalize their lengths, are called "towel clippings" (TC) waste.[1] Towel waste is the most widely found by-product in textile countries and is frequently used as filling material in quilts, pillows, and cushions in Eastern countries, as well as Turkey. Considering the common use of cellulose in different industries, cotton linters have also started to be used as raw materials in the production of cellulose derivatives. Because these linters contain approximately 95% cellulose, they play an important role as raw materials. Besides, the short fibers in the air and on the ground in the factory environment are pulled with a vacuum system and collected in a certain place. These wastes, which are also produced during the fabrication process, contain remarkable cellulose content and are called "air particle vacuum dust" (APVD).[2] Moreover, cottonseed separated from its fibers in gin factories has a sticky structure called "lint" that allows the seeds to stick to each other and many foreign substances. To get rid of this situation in cottonseed and to reuse the seed, improving it before planting it in the soil, the lint on it is removed with sulfuric acid in a certain concentration. This process is called "cottonseed delintation" (CD) and, after this, microcrystalline cellulose is obtained by breaking down cotton fibers in an acidic environment. As a result, cellulose remaining as waste can be used as "microcellulose" in the production of cellulose derivatives in the chemical industry.

Cellulose derivatives, such as carboxymethyl cellulose, differ from cellulose in many aspects (high viscosity, solubility, emulsifying, stabilizing, binding, thickening and suspending properties, hydrophilicity, bioadhesion, pH-sensitivity, non-toxicity, and gel-forming ability) and have many applications in different industrial areas, such as the textile industry, paper industry, detergents, pharmaceuticals, food industry, ceramics, cosmetics and others.[3-5] Moreover, CMC has become one of the most used, cheapest cellulose ethers, as it has been synthesized under atmospheric pressure using commercially available reagents, by simpler methods than most other cellulose ethers. CMC 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.[6-8] It has been synthesized from agricultural residues as cellulose sources, such as sago waste,[9] palm kernel cake,[10] orange peel,[11] sugar beet pulp,[12] sugarcane bagasse waste,[13] papaya peel[14] and water hyacinth.[15] However, no one has synthesized CMC from cellulose-containing wastes such as air particle vacuum dust (APVD), towel clippings (TC), and cottonseed delintation residue (CD) until now.

Within the scope of this study, different wastes, such as APVD, TC and CD, were recycled and turned into a higher value-added substance to be used in industrial applications. In this context, carboxymethyl cellulose was synthesized from these wastes. The structure of CMCs was characterized by spectroscopic methods (FT-IR, XRD, NMR), and surface morphologies and thermal properties were examined by SEM and DTA-TG analysis, respectively. The degree of substitution was determined by converting the polymer into its acid form in an acid-ethanol mixture. The viscosity of CMCs was measured using a rotational viscometer. In addition, the effects of CMCs on the setting time of cement paste were investigated.

EXPERIMENTAL

Materials and methods

Cotton wastes were kindly supplied by local factories, sodium hydroxide (NaOH) 99%, hydrogen peroxide (H_2O_2) 50%, hydrochloric acid (HCl) 37%, nitric acid (HNO_3) 65%, monochloroacetic acid ($ClCH_3COOH$), glacial acetic acid (CH_3COOH), phenolphthalein, isopropyl alcohol (IPA), ethanol and methanol were obtained from Sigma Aldrich. All chemicals used in this research were of analytical grade.

Purification and bleaching of cellulose-containing wastes

The wastes containing cellulose must be purified from impurities before synthesizing cellulose derivatives. In the cleaning process, air particle vacuum dust, cottonseed delintation residue and towel clippings were thoroughly washed, separately, with tap water to remove organic and inorganic impurities (Fig. 1). APVD[2] and TC[1] were purified according to previous studies in our laboratory. As regards CD, it has a very low pH, since it is a waste obtained from cottonseed delintation. During the delintation process, the short hairs on the cotton seeds have different characteristics compared to other wastes, as they are exposed to delintation with approximately 5 M sulfuric acid. Thus, the CD residue was first neutralized with sodium hydroxide and then it was boiled with 17.5% NaOH, according to the procedure described by Orhan.[2]

Synthesis of carboxymethyl cellulose

In this study, similarly to other numerous previous studies, the synthesis of CMC was performed in two stages: mercerization and etherification. In these processes, CMC is synthesized by treating cellulose with aqueous sodium hydroxide solution and then reacted with monochloroacetic acid (MCA) or its sodium salt.[15,16] Firstly, 5 g of cellulose was treated with 50 mL of 40% NaOH solution and mercerized at -5 °C overnight. The excess NaOH solution from this slurry brought to room temperature was vacuum filtered through a large pore diameter Gooch crucible. In a water bath, at room temperature, 200 mL of isopropanol and mercerized cellulose (Cellulose-ONa) were placed in a 500 mL glass flask under reflux. A solution of NaOH (3.78, 4.65, 5.62, 6.56 and 7.50 g) prepared by dissolving in a minimum amount of distilled water was added to this mixture. It was then alkalized with stirring for 60 minutes. After the alkalinization process was completed, the solutions of MCA (8.75, 10.93, 13.12, 15.31 and 17.50 g) dissolved in a minimum amount of distilled water were added to the reaction mixture and stirred at 65 °C for 3 hours for the etherification reaction (Table 1). The slurry in the reaction medium was filtered and suspended in 200 mL of 90% methanol and stirred for 12 hours. It was then neutralized with acetic acid and washed sequentially several times with 90% methanol, pure methanol, and pure ethanol to remove unwanted by-products. The resulting CMC was dried at 40 °C to constant weight. The reaction for the synthesis of CMC from cellulose is shown in Scheme 1.

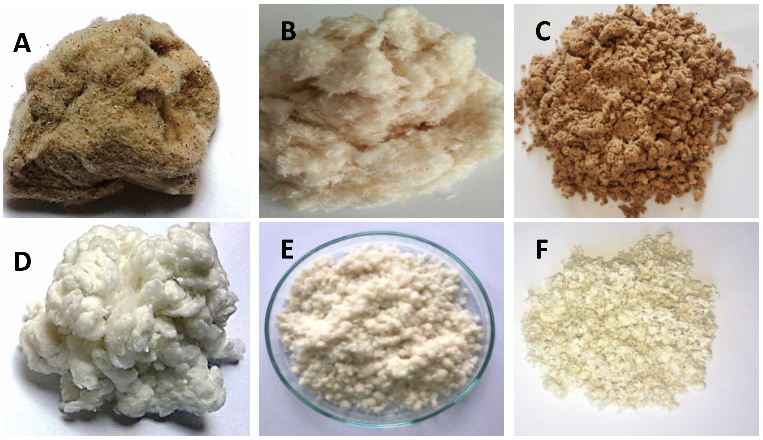


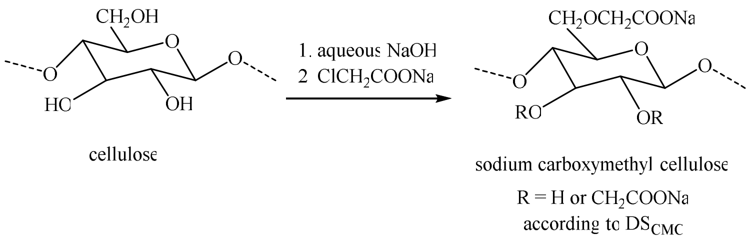
Figure 1: Cellulose-containing wastes: APVD (A), TC (B), CD (C); and bleached wastes APVD (D), TC (E), and CD (F)

Table 1
NaOH and MCA amounts used in the etherification reaction of cellulose and its DS values

Sample	mol (5 g) cellulose	mol (g) NaOH	mol (g) MCA	DS
APVD$_{CMC1}$	0.030	0.093 (3.75)	0.092 (8.75)	0.16
TC$_{CMC1}$				0.30
CD$_{CMC1}$				0.16
APVD$_{CMC2}$		0.117 (4.68)	0.115 (10.93)	0.13
TC$_{CMC2}$				0.45
CD$_{CMC2}$				0.13
APVD$_{CMC3}$		0.140 (5.62)	0.138 (13.12)	0.45
TC$_{CMC3}$				1.22
CD$_{CMC3}$				0.40
APVD$_{CMC4}$		0.164 (6.56)	0.162 (15.31)	0.26
TC$_{CMC4}$				0.31
CD$_{CMC4}$				0.26
APVD$_{CMC5}$		0.187 (7.50)	0.185 (17.50)	0.19
TC$_{CMC5}$				0.22
CD$_{CMC5}$				0.19

Determination of DS

DS was determined by the standard method (ASTM, 1961),[17] 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 CMC (weight on dry basis) was mixed with 75 mL of 95% ethyl alcohol and stirred.



Scheme 1: Carboxymethylation of cellulose

Then, 5 mL of nitric acid was added to the mixture and the suspension was stirred until boiling. This solution was stirred again for 10 min at room temperature. The precipitate was filtered and washed with 80 mL of 95% ethanol, and further washing 5 times by using 80% ethanol, which has been heated to 60 °C, until the acid and salts were removed. Finally, it was washed with pure methanol and dried in the oven at 105 °C for 3 h. After dried, it was cooled in a desiccator for an hour. Carboxymethyl cellulose (1-1.5 g) was weighed in a 250 mL Erlenmeyer flask and 100 mL of distilled water was added and stirred. The aqueous solution of CMC was mixed with 25 mL of 0.3 M NaOH solution and boiled for about 15-20 min. About 2-3 drops of phenolphthalein indicator were dropped into the solution (until a dark pink color was obtained) and titrated with 0.3 M HCl. DS was calculated based on Equations (1) and (2) (Table 1):[9]

$$DS = \frac{0.162xA}{1-(0.58)xA} \qquad (1)$$

$$A = \frac{BxC - DxE}{F} \qquad (2)$$

where A = milli-equivalents of consumed acid per gram of specimen; B = volume of NaOH added; C = concentration of NaOH added; D = volume of consumed HCl; E = concentration of HCl used; F = CMC in grams used; 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

The viscosity of CMCs (2% water solutions) was measured using a rotational viscometer (Brookfield Prime DV-I) at 25 °C, as described by Yang and Zhu,[18] varying spindle rotation from 10 up to 100 rpm. All measurements were performed in triplicate (Table 2).

Table 2
Viscosity values of CMCs

Samples	Rpm	APVD		TC		CD	
		Viscosity (cP)	Efficiency (%)	Viscosity (cP)	Efficiency (%)	Viscosity (cP)	Efficiency (%)
CMC1	10	70	0.7	1330	13.3	10	0.1
	20	75	1.5	850	17.0	10	0.1
	50	76	3.8	502	25.1	18	0.2
	100	81	8.1	324	32.4	20	0.2
CMC2	10	50	0.5	2000	20.0	20	0.2
	20	55	1.1	1290	25.8	25	0.5
	50	62	3.1	752	37.6	28	0.8
	100	71	7.1	515	51.5	37	1.4
CMC3	10	90	0.9	2520	25.2	30	3.0
	20	75	1.5	1780	35.6	36	3.2
	50	68	3.4	1038	51.9	42	4.0
	100	68	6.8	680	68.0	50	5.1
CMC4	10	25	2.5	430	4.3	25	2.6
	20	30	0.3	305	6.1	32	3.1
	50	54	1.7	210	10.5	40	4.0
	100	80	0.8	156	15.6	45	4.2
CMC5	10	23	2.3	270	2.7	20	0.2
	20	28	2.7	170	3.4	25	2.5
	50	33	3.3	110	5.5	27	2.7
	100	50	5.2	90	9.1	32	3.1

Table 3
Consistency and setting times of PCP and CMC-added PCP

Consistency of samples (mm)			
PCP	APVD$_{CMC3}$	TC$_{CMC3}$	CD$_{CMC3}$
5.0	28.0	36.5	13.0

Setting time of samples (mm)				
Time (h/min)	PCP	APVD$_{CMC3}$	TC$_{CMC3}$	CD$_{CMC3}$
2/20	0.6	-	-	-
2/30	1.0	-	-	-
2/40	1.2	-	-	1.0
2/50	2.2	-	-	3.5
3/00	6.0	-	-	4.9
3/10	6.5	3.0	-	6.3
3/20	13.0	5.0	-	10.5
3/30	17.0	9.5	0.1	16.0
3/40	22.0	11.0	0.4	21.0
3/50	35.0	14.0	2.6	27.0
4/00	39.0	17.0	4.0	33.0
4/10	41.0	23.0	6.5	37.0
4/20	-	26.0	9.0	39.0
4/30	-	27.0	14.0	40.0
4/40	-	32.0	18.0	41.0
4/50	-	34.0	21.0	-
5/00	-	38.0	21.0	-
5/10	-	39.5	22.0	-
5/20	-	40.0	23.0	-
5/30	-	41.0	25.0	-
5/40	-	-	25.0	-
5/50	-	-	25.0	-
6/00	-	-	26.0	-
6/10	-	-	32.5	-
6/20	-	-	36.0	-
6/30	-	-	38.0	-
6/40	-	-	38.0	-
6/50	-	-	39.0	-
7/00	-		41.0	-

Determination of cement consistency

The cement (PC) used in the present investigation was Portland cement CEM I 42.5 N, in accordance with EN 196-3 standard, and the consistency of this paste was determined by the Vicat penetration method.[19] A homogeneous mold was obtained by mixing 300 g of cement with 32.17% of its own weight of water in 4.5 minutes. Before starting the Vicat test, the probe at the end of the device was lowered to the baseplate to reset the indicator of the Vicat device. The Vicat compartment filled with the cement paste prepared above was placed on a non-porous glass plate by shaking several times to eliminate air and the upper surface of the paste in the compartment was completely flattened. The Vicat probe was then slowly lowered to the surface of the cement paste and left on this paste for 30 seconds until it remains fixed at a distance of 6 ± 1 mm from the base plate. In this study, after 30 seconds, the consistency of the paste was determined by fixing the Vicat indicator at a distance of 5 mm. Likewise, 95 mL of 2% CMC solutions were added separately to 300 g cement and the consistency of cement pastes containing CMC was determined by repeating the same procedures (Table 3).

Determination of cement penetration

The Vicat needle test measures the time taken for the cement-water mixture to harden, or in other words, for water to penetrate into the paste. The end of the rod used for measuring penetration has a straight steel removable needle, with a diameter of 1.00 ± 0.05 mm and 50 mm length. With this needle, the beginning of solidification (initial setting time) and end of solidification (final setting time) are measured. Initial setting time is defined as the time for the Vicat needle to penetrate the cement paste to a depth of 4 ± 1 mm. The final setting time is determined when the needle cannot penetrate the cement paste and leaves marks on the surface. In this context, after the molded cement paste was kept for 30 minutes, the Vicat needle was released onto the cement paste and waited for 30 seconds. This process was continued until the needle was inserted 4 ± 1 mm into the molded cement paste. When the needle inserted 4 ± 1 mm into the molded cement paste, this time was considered to be the initial setting time. Then, the process was continued every 10 minutes until the final setting time is reached. Each test was performed at a 10 mm distance from the beforehand tested place, *i.e.* the measurement point, and after each measurement, the needle tip was thoroughly cleaned. This process was continued until the needle could not penetrate the cement paste, that is, until it remained on the surface. In this way, the time passing until the needle remained on the surface of the cement paste was recorded as the final setting time. The setting times of PCP and PCP obtained after adding CMC were given in Table 3.

Scanning electron microscopy (SEM) analysis

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

Fourier transform infrared spectroscopy (FT-IR) analysis

The FT-IR spectroscopic method 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) analysis

^{1}H(^{13}C)-NMR spectra of CMCs were recorded at 30 ^{o}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

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

Thermal (TG-DTA) analysis

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

RESULTS AND DISCUSSION

In this study, the increase in the amount of the MCA+NaOH system used in the etherification reaction, not the increase in the amount of NaOH, was investigated. The increase rates were calculated according to the mole number of 5 grams of cellulose, taking into account the theoretical DS being a maximum of 3. These increases were set at a rate of 25% higher than the previous amounts. Therefore, there is an increase in the amount of NaOH to neutralize the increase in MCA at certain rates and even slightly more. In addition, in the mercerization stage, 40% NaOH solution was used to obtain alkalized cellulose. After the alkali cellulose has been filtered, there is enough aqueous NaOH in the medium. Experimental conditions are given in Table 1 in detail.

Degree of substitution (DS) and viscosity of CMCs

The physical and chemical properties of CMC are mainly dependent on its degree of substitution, distribution pattern, and degree of polymerization (DP). Especially, the degree of solubility is accepted to be a function of the degree of substitution. The monomer structure of CMC is shown in Scheme 1, where R stands for -H or $-CH_2CO_2Na$. The DS is the average number of carboxymethyl groups substituted per monomer unit, ranging from 0 to 3, with the remaining R=H.[20] Theoretically, the maximum DS value for cellulose/CMC is 3.0, but the range for commercially available CMC is generally between 0.4-1.5.[21] The DS value of CMC has good solubility in water above 0.6. 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.[22] The effect of various amounts of the MCA+NaOH system on DS and viscosity is shown in Figures 2-4. The amounts of NaOH (3.75-7.50 g) and MCA (8.75-17.50 g) were varied to 5 g of cellulose, while keeping the other etherification conditions constant. As can be seen from Table 1 and Figures 2-4, maximum DS values at 65 ^{o}C temperature, for 3 h reaction time, were reached for carboxymethyl cellulose synthesized from all three wastes at the amount of NaOH of 5.62 g and MCA of 13.12 g (DS = 0.45 for $APVD_{CMC3}$, DS = 1.22 for TC_{CMC3}) and DS = 0.40 for CD_{CMC3}). The DS value increased with the amount of MCA up to 13.12 g and thereafter it decreased. In this way, the increase in the amount of NaOH and MCA supported the etherification reaction up to a certain point and provided an increase in DS and viscosity. However, after a certain concentration, DS and viscosity decreased.

This can be explained as follows: during the carboxymethylation process, the NaOH provides the alkaline environment for the reaction, as well as serving as the swelling agent to facilitate diffusion and penetration of the etherifying agent to the cellulose structure.[23] However, the contact between MCA and cellulose was inhibited by the further increase in NaOH amount. Moreover, a further increase in NaOH concentration diverted MCA from the side reaction. At higher concentrations, glycolate formation may be higher, leading to a decrease of the reaction efficiency and therefore the DS.

One of the most important and most useful properties of CMC is that it can impart viscosity to its aqueous solutions, and the solutions can be prepared with a wide range of viscosities. CMC ranges from low molecular weight to high molecular weight. Viscosity is proportional to the average chain length or the degree of polymerization of the CMC molecule, and increases rapidly with an increasing degree of polymerization. The average chain length and degree of substitution determine the molecular weight of the CMC grade, and it can be dissolved or dispersed in water or alkaline solutions to form high viscosity solutions.[24,25] Under the same reaction conditions, in this study, the viscosity values were maximum for samples APVD$_{\text{CMC3}}$ (90 cP) and TC$_{\text{CMC3}}$ (2520 cP), but not for CD$_{\text{CMC3}}$ (30 cP). It is clear that TC$_{\text{CMC3}}$ has the highest viscosity, compared to APVD$_{\text{CMC3}}$ and CD$_{\text{CMC3}}$, and CMC from towel clippings is completely soluble in water, whereas CMC from APVD and CD is not completely soluble in water.

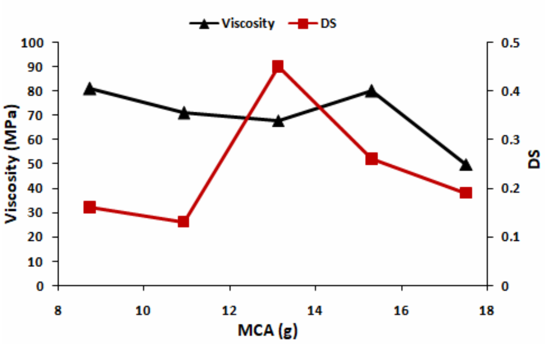


Figure 2: Effect of MCA amount on DS and viscosity of APVD$_{\text{CMC3}}$

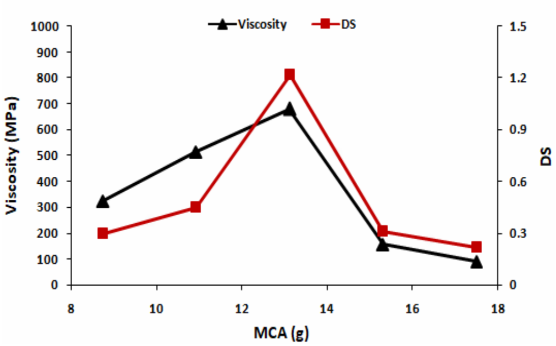


Figure 3: Effect of MCA amount on DS and viscosity of TC$_{\text{CMC3}}$

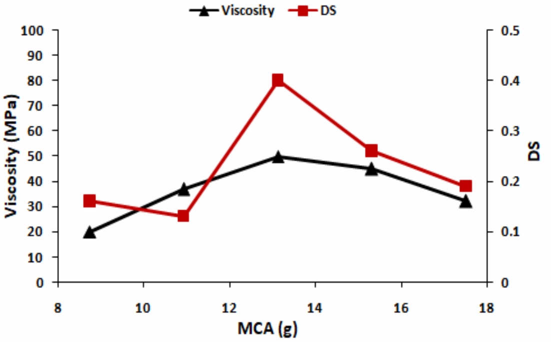


Figure 4: Effect of MCA amount on DS and viscosity of CD$_{\text{CMC3}}$

Consistency and penetration of cement

The consistency of the cement paste formed after mixing the cement with a sufficient amount of water depends on the water/cement ratio (w/c), cement fineness and composition, temperature, and the type of plasticizer/thickener.[26] The hydration of cement is a process that enables concrete to harden and in the first stages of hydration, concrete transforms from liquid to solid state. The consistency test is performed to estimate the amount of water needed to form a paste of normal consistency, namely defined as the percentage water requirement of the cement paste. When water is added to cement, the resulting paste begins to harden and gain compressive resistance. Cement paste acts as a separator for aggregates in a mortar, and a lack of sufficient mortar results in a mixture of limited flow. These mixtures tend to decompose and are limited in use. The setting time of the paste containing cement mortar varies according to the application area, and the quick setting and freezing of cement paste, which has a solid structure, limits its functionality. To extend this period, water-retaining agents, such as CMC, are added to the cement paste, so that the water held in the CMC penetrates into the cement paste for a long time and as a result, the freezing time of the cement paste is extended.

Generally, organic polymers behave as retarders and have distinct behavior towards the setting time of cement. The setting time may be varied according to the physical and chemical properties of organic polymers, like solubility, viscosity, chain length, polarity, and functional group(s).[27] CMC is a derivative of cellulose, which has a long chain polymer and is a member of the carbohydrate group. Organic setting retarding groups containing OH/COO- groups found in CMC molecules may retard the rate of absorption of H_3O+ ions on the cement universal surface and slow down the setting reactions.[28] As can be seen from the results of the Vicat experiment in Table 3, when the CMCs solutions were added to the cement paste, the initial setting time, final setting time, and consistency of PCP increased. While the PCP consistency was 5 mm, the consistency of the cement pastes to which $APVD_{CMC3}$, TC_{CMC3} and CD_{CMC3} were added was recorded as 28 mm, 36.5 mm 13 mm, respectively. For PCP, the initial setting time was found at 140 minutes, and the final setting time was 250 minutes. The setting time was completed within 110 minutes. Looking at the CMC examples, TC_{CMC3} has the highest penetration time – of 210 minutes. This time was recorded for $APDV_{CMC3}$ as 140 and for CD_{CMC3} as 120. Towel clipping has the highest DS and viscosity value, at the same time, it has the highest consistency and penetration time. The penetration time of PCP and PCP obtained after adding CMC was given in Figure 5.

Scanning electron microscopy (SEM) of CMCs

The surface morphology of cellulose obtained from wastes and of the synthesized CMCs was investigated by SEM. As can be seen in Figure 6, while cellulose fibers obtained from APVD, TC, and CD wastes have long, smooth surface, small cavity and no defects, as well as a regular fibrous structure of various thicknesses, the surface structure of CMC after carboxymethylation was loosened and turned into a defective structure. It can be said that NaOH penetrates the amorphous regions of the cellulose, causing partial disruption of the structure.[29,30] The thickness of the fibrils of TC_{CMC3} was reduced, as compared to other samples. This is because, during the alkali treatment, the intermolecular bond of cellulose is broken and a polyhydroxy group of polysaccharides results in the swelling of the fiber, which decreases fiber length. It was seen that, while the CMCs with low DS have only a few aggregates, TC_{CMC3} with higher DS has several aggregates due to the substituted chains.

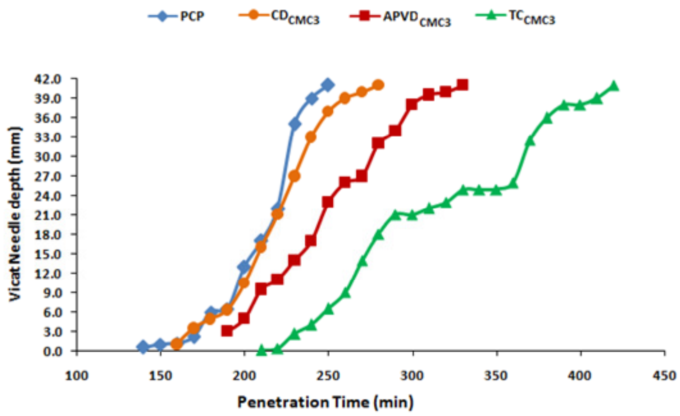


Figure 5: Penetration time of PCP and CMC-added PCP

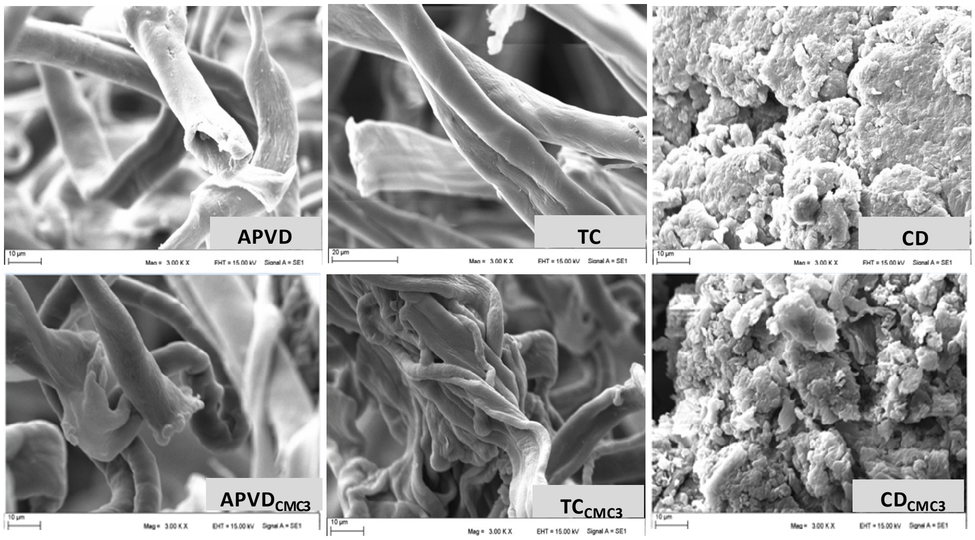


Figure 6: SEM images of (3.00 kx) $APVD_{CMC3}$ (DS = 0.45), TC_{CMC3} (DS = 1.22) and CD_{CMC3} (DS = 0.40)

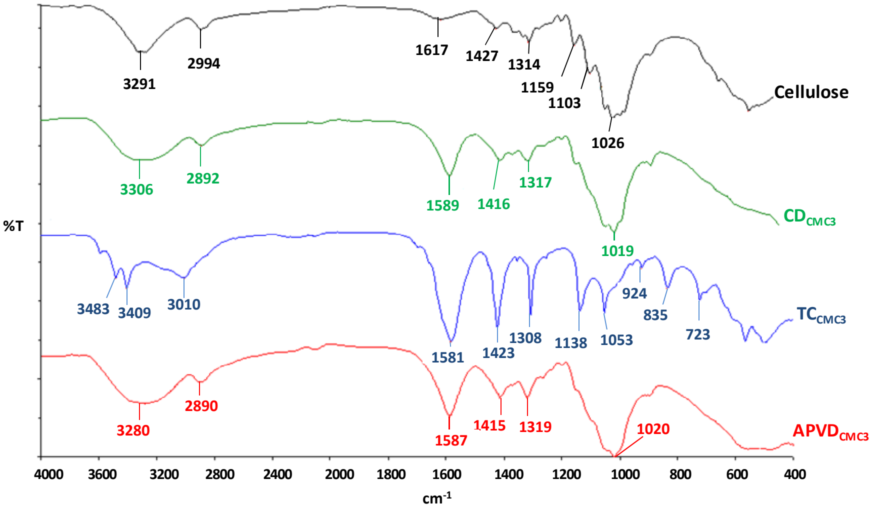


Figure 7: FTIR spectra of cellulose and CMCs

FTIR analysis of CMCs

As seen from the FTIR spectra of the CMCs in Figure 7, a broad absorption band located at around 3291-3409 cm^{-1} appearing for all CMCs is attributed to stretching of O–H groups and intra- or intermolecular hydrogen bonds. The bands at 2894-3011 cm^{-1} are due to C–H stretching vibration. The presence of a new and strong absorption band at 1581-1589 cm^{-1} confirms the presence of the COO^- group and the vibration band confirmed the successful carboxymethylation. The band is relatively stronger in TC_{CMC3} with DS = 1.22, due to the higher degree of substitution. The peaks at wave numbers of 1612 cm^{-1} (asymmetric) and 1425 cm^{-1} (symmetric) in the CMC sample are related to the C-O bond and the intensity of these peaks refers to carboxymethyl group substitution.

The bands around 1420 and 1320 cm^{-1} are assigned to $–CH_2$ scissoring and –OH bending vibration, respectively. The bands between 1198-1102 cm^{-1} and 1026-895 cm^{-1} are related to asymmetric bridge stretching (C-O-C) of cellulose and the β→4 glycosidic bonds between glucose units in the cellulose structure. The band at 1061 cm^{-1} is due to $CH–O–CH_2$ stretching. The weak bands around 770 cm^{-1} for TC_{CMC3} are due to ring stretching and ring deformation of α-D-(1–4) and α-D-(1–6) linkages. Similar results have been reported for CMC in previous literature.[9,21,22,31-34]

^{13}C and ^{1}H-NMR spectra of CMCs

The NMR is one of the most powerful and simple analytical methods for characterizing cellulose derivatives. The ^{13}C and ^{1}H-NMR spectra of TC_{CMC3} in D_2O are shown in Figures 8-9. In the ^{1}H-NMR spectrum, each AGU contains seven protons in the glucose ring, namely H1-H6 and additional methylene protons at the substituted carboxymethyl groups (Fig. 8). Numerous proton resonances from AGUs forming the CMC structure overlap in the narrow region between 4.8-3.1 ppm, which was in good agreement with previously assigned values by Kono.[21,35-37] Although the information about the structure of CMC could not be obtained from the ^{1}H-NMR spectrum, the behavior and signal range obtained in the ^{1}H-NMR of CMC is typical and similar to those reported in previous studies for CMC.[38,39]

In the ^{13}C-NMR spectrum (Fig. 9), which is no more complex than the ^{1}H-NMR spectrum, the carbonyl carbons of the substituent groups and C1 and C6 of the glucose ring appear at 176–179, 102–103, and 59–60 ppm, respectively, as previously assigned.[35,40] The peak with a chemical shift value of 178 ppm can be attributed to the signal of the carbonyl carbon atom (C8, C=O). The chemical shift value of the C1 atom was observed at 102 ppm. It can be said that the signal at 85 ppm originates from the C4 atom. The signal of the C2 atom can be attributed to the peak observed at 78 ppm. It is understood that the chemical shift values of C3, C5, and C7 carbon atoms overlapped and gave signals of 74 ppm, 73 ppm and 72 ppm, respectively, in the region close to each other. The clusters of resonances at 72.94 ppm are assigned to a methylenic carbon atom ($CO–CH_2–O–$), labeled as number 7.[41,42] The peak at 59 ppm can be said to be the signal of the C6 carbon atom.[43]

XRD patterns of CMCs

The crystallinity and crystallinity index of cellulose and CMCs were analyzed by X-ray diffraction and their XRD patterns were shown in Figure 10. The crystallinity of CMCs was compared with that of the cellulose wastes to clarify their crystalline structure and the changes produced in the polymer. TC_{CMC3} is characterized by higher DS and lower crystallinity than $APVD_{CMC3}$ and CD_{CMC}. This result can be explained by the fact that the proportional crystallinity of cellulose was increased by degradation of hydrogen bonds in the amorphous part of cellulose chains. According to Alemdar and Sain,[44] such an increase in the crystallinity index was expected after chemical treatment. This might also be due to the removal of lignin and hemicelluloses, because of their amorphous nature.

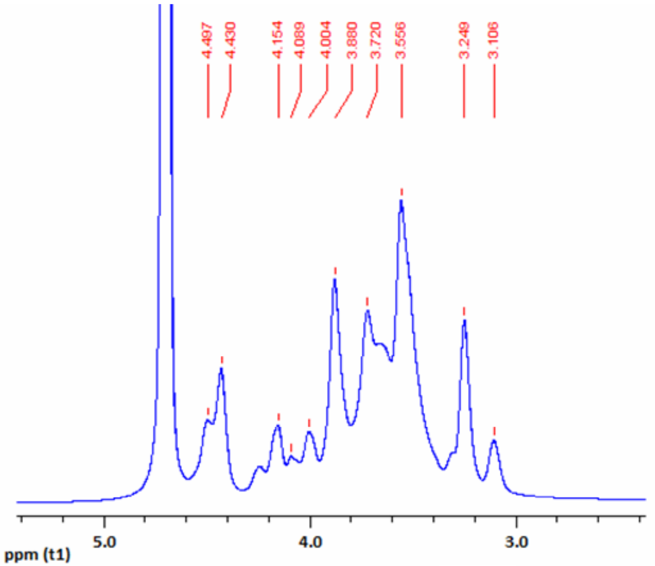


Figure 8: ^{1}H-NMR spectra of TC_{CMC3}

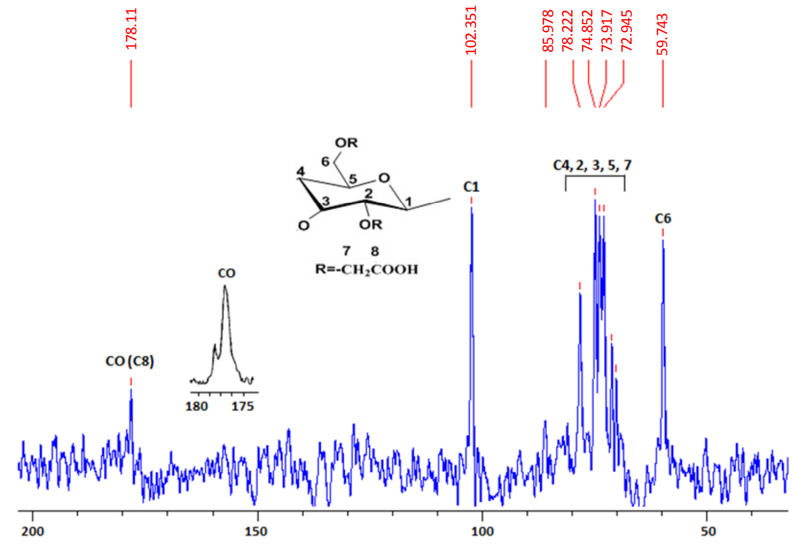


Figure 9: ^{13}C-NMR spectra of TC_{CMC3}

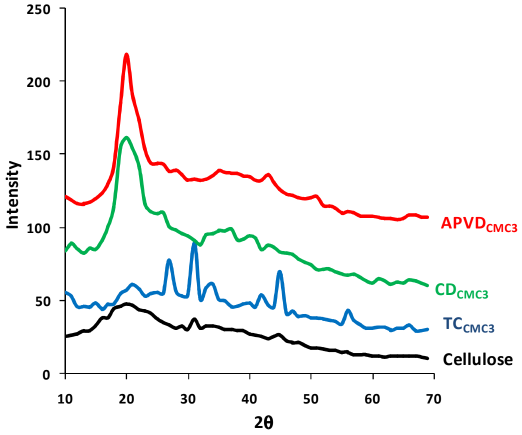


Figure 10: XRD patterns of cellulose and CMCs

Table 4
Crystalline index of cellulose and CMCs

Samples	2θ	$I_{110}{}^{a}$	2θ	$I_{AM}{}^{b}$	C_I (%)	DS
$APVD_{CMC3}$	20°	219	13°	116	47.03	0.45
CD_{CMC3}	20°	162	15°	85	47.53	0.40
TC_{CMC3}	21°	61	16°	44	27.86	1.22
Cellulose	20°	47	17°	38	19.14	-

[a] The highest intensity crystalline peak; [b] The lowest intensity peak in the amorphous area; (-): Not measured;
Note: All values were obtained from the raw XRD software program

Also, Adinugraha and Marseno[45] showed that, with decreasing crystallinity, the degree of substitution (DS) increased in carboxymethylation and higher DS of CMC resulted in a wider crystallinity peak and decreased crystallinity. The crystallinity index of CMCs was calculated based on the empirical formula proposed by Segal[46] and the results were given in Table 4. This formula relates the maximum intensity (the crystalline peak) at 2θ between 22° and 23° for cellulose and the intensity of the minimum (amorphous peaks, IAM) between 18° and 19° for cellulose.[1,32,47] The degree of crystallinity (the crystallinity index, CrI) in this method is determined in the following way:

$$CrI = 100 \times (I_{002} - I_{AM})/I_{002} \quad (3)$$

where I_{002} and I_{AM} correspond to the highest crystalline peak between 20° and 21°θ of the maximum intensity at 2θ and the lowest crystalline peak between 13° and 17° of the minimum intensity at 2θ, respectively.

TG-DTA thermograms of CMCs

Thermogravimetric analysis (TGA) is a process in which a material is decomposed by heat, which causes bonds within the molecules to be broken and has an important role in determining the thermal stability of the materials.[48] The remaining weight (%) and the thermal decomposition rate (dw/dt) were given as the decomposition function for cellulose and CMCs in Table 5 and Figure 11. The thermal decomposition processes of cellulose and CMCs were observed in two major steps. In the case of cellulose and CMCs, the initial weight loss occurred at 100 °C, which is due to the evaporation of physically bound water or the dehydration of the solvent.[49] In this stage, 2.3%, 9.2%, 8.1% and 10.5% weight losses were observed in cellulose, CD_{CMC3}, TC_{CMC3} and $APVD_{CMC3}$, respectively. This first weight loss was followed by the main decomposition stage between 200-400 °C, and the maximum weight loss was observed in the second stage. It was assigned to fragmentation associated with the degradation of the main chain and breaking of glycosidic bonds. At this temperature, the formation of aromatized units and the decomposition of the carbonaceous residues take place.[50-52] The weight loss of cellulose (74.4%), CD_{CMC3} (61.9%), TC_{CMC3} (43.2%) and $APVD_{CMC3}$ (56.4%) at 400 °C was the result of several coincident processes, such as dehydration, depolymerization, and decomposition.[53] At the final temperature (585 °C), the weight losses of CD_{CMC3}, TC_{CMC3}, and $APVD_{CMC3}$ were 72.8%, 54.8%, and 63.3%, respectively. As can be seen in Figure 11, at this temperature, cellulose was completely degraded. It was shown that the thermal stability of CMCs is higher than that of cellulose.[54] The conversion of cellulose to CMC has affected both the molecular structure and bonding energy, which causes the different thermal behavior of CMC.

Table 5
TG-DTA thermograms of cellulose and CMCs

Thermogram	TGA					DTA
	% Residual weight - % Weight loss					% Weight loss
Temperature	100 °C	200 °C	400 °C	500 °C	585 °C	286-297 °C
Cellulose	97.6-2.3	93.7-6.2	25.5-74.4	5.9-94.1	-	350 (60.2)
CD_{CMC3}	90.8-9.2	89.8-10.2	38.1-61.9	31.1-68.9	27.2-72.8	286 (43.21)
TC_{CMC3}	91.8-8.1	85.8-14.1	56.7-43.2	45.8-54.2	45.1-54.8	291 (39.7)
$APVD_{CMC3}$	89.4-10.5	86.7-13.3	43.6-56.4	38.7-61.3	36.7-63.3	297 (39.02)

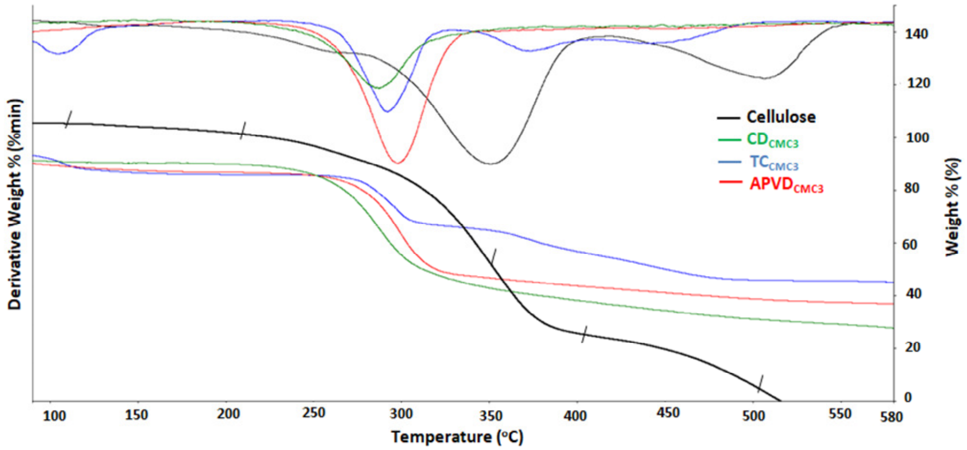


Figure 11: TG/DTA curves of cellulose and CMCs

The DTA curves of cellulose and CMCs (Fig. 11) reveal the endothermic peak at 286, 291, 297 and 350 °C for cellulose, CD_{CMC3}, TC_{CMC3}, $APVD_{CMC3}$ and cellulose, respectively.[51] The endothermic temperatures for CMCs shifted towards lower values than that of cellulose. This is due to the decomposition of the amorphous parts of CMCs during carboxymethylation. This could be confirmed by the crystallinity index (Table 4) – the crystallinity indices of CD_{CMC3} (47.53), $APVD_{CMC3}$ (47.03), and TC_{CMC3} (27.86) are higher than that of cellulose (19.14).[55]

CONCLUSION

Cellulose obtained from cotton wastes can be derivatized by chemical modification reactions, such as carboxymethylation. In this study, high-performance CMC (high DS, viscosity, and thickening property) was successfully produced from high cellulose content textile wastes and the effects of the CMC, with a high DS value, on the consistency and penetration time of cement paste were examined. The DS value of CMC increased with increasing of NaOH/MCA concentration and declined after synthesis with 5.62 g NaOH and 13.12 g of MCA concentrations. The viscosity and thickening properties are dependent on the DS of CMC. Therefore, the viscosity value increased proportionally to the DS value. Cement paste is thickened with water, but its setting time is quite short when obtained by this method. This is insufficient and undesirable in some application areas. In order to eliminate this deficiency and increase the consistency of the cement, it is desired to increase the setting time by adding thickening agents. The results from the Vicat tests showed that, because of its hydrophilic nature and the presence of hydroxyl groups on its surface, CMC increased the consistency and setting time of cement paste. It has been observed that CMCs synthesized from three cellulose sources increased the hydration time and consistency of cement paste. The prepared TC_{CMC3} can be an ideal thickener for the construction industry and other applications. Developing CMC with different properties by using cellulosic wastes can be a sustainable alternative, contributing to the production of important value-added products and to solving environmental problems caused by textile wastes.

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