CELLULOSE CHEMISTRY AND TECHNOLOGY

LABORATORY SCALE PRODUCTION OF HYDROXYPROPYLMETHYLCELLULOSE (HPMC) IN A GAS-TIGHT REACTOR UNDER PRESSURE AND ITS APPLICATION IN CEMENT PASTE

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Unfortunately, cellulose, which is the most abundant of natural polysaccharides in the world, and is found in high amounts in cotton and the waste/by-products of textile factories, cannot be recycled sufficiently. As an attempt to find a solution to this problem, in this study, a by-product of the towel production process, called "towel clippings" (TC), was used as a source of cellulose for obtaining HPMC. HPMC was synthesized for the first time from the reaction of cellulose, propylene oxide (PO) and chloromethane (CM) under pressure in a gas-tight laboratory scale reactor and then evaluated as an additive in cement paste. The HPMC was characterized by $^{1}H(^{13}C)$-NMR, FT-IR, XRD, DTA/TGA and SEM techniques. Additionally, the DS values were determined using the ^{13}C-NMR technique. The highest viscosity was obtained as 2740 cP in HPMC-5 with the highest DS value of 2.86. While the setting time of the standard cement paste, without any additives, started at the 140th minute and was completed at the 250th minute, with the addition of 0.5 grams of HPMC-1 to the cement paste, the starting time was extended by 180 minutes and the finishing time was extended by 260 minutes. In this way, it has been seen that problems such as low slip resistance and low setting time of cement paste, as well as negative effects caused by working conditions, will be avoided.

Keywords: waste recycling, HPMC, NMR, setting time

INTRODUCTION

Today, with the increasing population growth, unconscious use of natural resources increases the concerns for the future. One way to address these concerns, by considering concepts such as recycling, recovery and reuse, would be to increase the use of renewable resources with a sustainable policy. For our future, it is necessary to evaluate waste by reusing or transforming it into value-added products in order to bring waste into economy and reduce energy consumption. For example, by recycling used or useless cotton waste, that is, turning it into a raw material, this can contribute to preserving natural resources. Cotton and cotton yarn are used in the production of a wide variety of textile products, such as fabric, towels and the like. Textile factories producing towels have cellulose-containing towel clippings, which are a by-product of the towel production process and are considered as waste. Towel clippings (TC) represent very short fibers formed by shaving cotton fibers on the surface of towels during the production process.[1] Such towel waste, which is available in large quantities in textile producing countries, is frequently used as filling material in quilts, pillows and mattresses in many eastern countries.

Due to its hydrophilic nature and crystalline 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 the anhydrous glucose unit, cellulose derivatives with very different physical properties from those of crystalline cellulose can be synthesized.[3] Etherification and esterification

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are the most common methods used to improve the solubility and industrial use of cellulose. Cellulose ethers are typically synthesized from the nucleophilic reaction of hydroxyl groups of cellulose with electrophiles, such as alkyl halides or epoxides. Cellulose ethers are potentially becoming more usable in many industrial applications due to their increased solubility relative to cellulose.[4] Due to their advantageous properties, cellulose ethers can be used as thickeners, binders, lubricants, emulsifiers, rheology modifiers and film formers, in many different areas, such as in foods,[5,6] personal care products,[7] oil field chemicals,[8] construction industry,[9,10] paper,[11] adhesives,[12] textiles[13] and many more applications. Carboxymethyl cellulose (CMC) and hydroxypropylmethyl cellulose (HPMC) are among the most widely used commercial cellulose ethers worldwide. Then, methylcellulose (MC) and other cellulose derivatives have the second largest consumption by volume.[14]

In this study, we focused on the evaluation of cotton waste containing cellulose for HPMC synthesis. Towel clippings (TC), one of the waste textile products, were used directly as supplied from the factory. To provide optimum conditions, TC with high cellulose content were mercerized with a certain concentration of NaOH solution at different times and temperatures. HPMC was synthesized from mercerized cellulose in a pressure-resistant sealed reactor, in isopropyl alcohol (IPA) solvent medium, by the reaction with propylene oxide (PO) and chloromethane (CM) in different ratios. The structures of the synthesized HPMCs were characterized by ^{1}H(^{13}C)-NMR, FT-IR and XRD. Their thermal analysis was investigated by DTA/TGA, their surface morphology was examined by SEM and their viscosity was measured. In addition, after the DS values were determined by using ^{13}C-NMR spectra, the effects of HPMCs on the setting times of cement paste were investigated.

EXPERIMENTAL

Materials

Towel clippings (TC) containing cellulose available as cotton textile wastes were kindly supplied by towel producing factories in Denizli, Turkey. Portland Cement CEM I 42.5, propylene oxide (PO) and chloromethane (CM) were purchased. NaOH, isopropyl alcohol (IPA), methanol, ethanol and acetic acid were obtained from Sigma Aldrich. All the chemicals in this research were used as supplied by the producing companies, without any purification process.

Method

Synthesis of HPMC

TC were used directly as they were supplied from the factories, without any processing. HPMC was synthesized in three steps: mercerization, reaction with propylene oxide and chloromethane, and neutralization. In mercerization, 50 mL of 40% NaOH was added to 2 g of TC and thoroughly mixed at room temperature, and mercerization was allowed to occur while keeping the mixture in the refrigerator at -20 °C overnight. Then, after melting the frozen mercerized TC, the excess sodium hydroxide solution was filtered with the help of a vacuum pump. In HPMC synthesis, the reaction conditions, such as reactant amounts, reaction time and reaction temperature, were determined according to previous studies.[15-17] Considering the recommendations in the literature and preliminary experiments in our laboratory, the synthesis was carried out at a reaction time of 6.5 hours and a reaction temperature of 70 °C. HPMC was synthesized from the etherification reaction of 2 g of mercerized cellulose by changing the amount of propylene oxide and chloromethane in isopropyl alcohol solvent medium in a gas-tight reactor under pressure. The amounts of PO and CM added to the reactor are given in Table 1.

The PO was carefully added to the reactor through a closed system under cold ambient conditions. As CM is a gas, it was carefully weighed on a precision balance and added to the reactor in the same way.

Table 1
Amounts of reactants used in synthesis of HPMC

Sample	PO (g)	CM (g)
HPMC-1	5	5.25
HPMC-2	10	5.25
HPMC-3	15	5.25
HPMC-4	20	7.35
HPMC-5	25	7.35

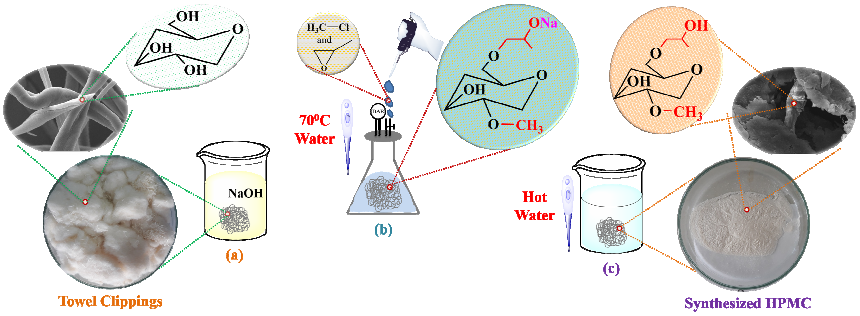

Figure 1: Mercerization (a), synthesis (b) and neutralization (c) of HPMC

After the reaction of etherification at 70 °C for 6.5 hours in the reactor was complete, the product brought to room temperature was filtered and poured into hot water containing acetic acid. It was washed quickly in hot water and precipitated again at the same time. Then, the resulting solid was washed with methanol and ethanol sequentially, dried in an oven at 50 °C, and then ground (Fig. 1).

Measurement of HPMC viscosity

Viscosity values of synthesized HPMCs were determined with a Brookfield Viscometer DV-I Prime. After taking 2 grams of HPMCs, they were mixed until dissolved in 100 mL of distilled water at 25 °C, and then the viscosity was measured as cP with spindle number 2.

Setting time of cement paste

Portland cement paste (PCP) used in the analysis was prepared from cement with a force of 42.5N according to CEM I/B standard, and the consistency of this paste was determined by the Vicat penetration method according to TS EN 196-3 standard.[18] The consistency measurement probe attached to the Vicat device was first lowered onto the base plate and the Vicat device indicator was set to zero. Then, 91 g of water was added to 300 g Portland cement (PC) within 5 to 10 seconds. It was made into a paste by mixing thoroughly for 4.5 minutes. This cement paste was placed in the Vicat chamber, filled completely and leveled (Fig. 2). The Vicat probe was lowered slowly onto the cement filled chamber surface and held steady for 1-2 seconds. The released Vicat probe was kept in 30 seconds until it remained stable at 6 (±1) mm between the base plate. Then, the same tests were repeated in the same way to determine the consistency of commercial HPMC (HPMC-C) and HPMC-69 added cement pastes; the results are given in Table 2.

The Vicat test is also an experiment to measure the setting time and the setting end time of cement paste. For this, first, 300 g of PC in the witness sample was mixed with water up to 30% of its own weight and turned into a paste. The test needle attached to the Vicat device was first lowered onto the base plate and set to zero. To start the test, this needle was lowered to the cement paste surface slowly for 1-2 seconds and then the needle, which was left to fall free, was fixed to the cement paste and the reading was started. Since the distance between the tip of the needle and the base plate is desired to be 4 (±1) mm, the time at this distance is recorded as the setting start time. The measurement was continued at 10-minute intervals at a distance of 10 mm from the previous measurement point and the results were record in Table 2.

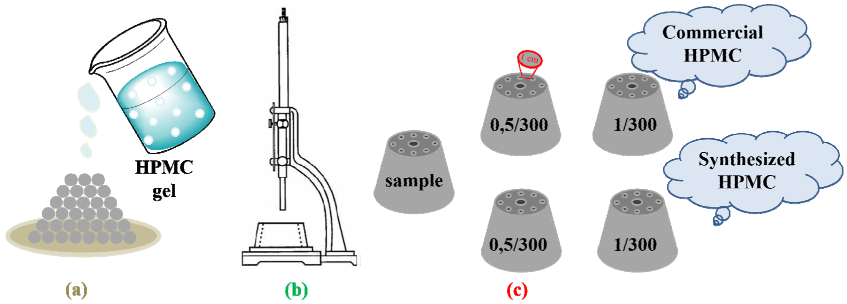

Figure 2: Preparation of cement paste with HPMC (a), performing the Vicat test (b) and measuring the setting time (c)

Table 2
Consistency and penetration values of HPMC-doped PCP

Consistency (consist.) of samples					
	PC	0.5 g HPMC/300 g PC		1 g HPMC/300 g PC	
		HPMC-C	HPMC-1	HPMC-C	HPMC-1
Consist. (mm)	5.5	34	21	36.5	33.5
Penetration time of HPMC-doped PCP samples					
Time (min)	Blank (mm)	HPMC-C (mm)	HPMC-1 (mm)	HPMC-C (mm)	HPMC-1 (mm)
140	4.5	-	-	-	-
150	5.5	-	-	-	-
160	6.5	-	-	-	-
170	8	-	-	-	-
180	10.5	-	5	-	-
190	14	-	11	-	-
200	19	4	23	4	-
210	27	6.5	24	16.5	-
220	34	10	35	18	-
230	39.5	16	38	20	-
240	40	19	40	26	4
250	40.5	27	40	33	7
260	-	38	40.5	39	11
270	-	39.5	-	40	14.5
280	-	40.5	-	40.5	20
290	-	-	-	-	22.5
300	-	-	-	-	25
310	-	-	-	-	39
320	-	-	-	-	40
330	-	-	-	-	40.5

The needle tip was thoroughly cleaned after each measurement. Secondly, since the Vicat needle was dropped on the cement paste every 10 minutes from the starting point of the setting, the moment when the Vicat needle penetrated the cement paste surface by 0.5 mm was recorded as the end of setting time (Fig. 2). The above-described start and finish setting time tests were repeated in the cement paste prepared by mixing PC, water and HPMC in the amounts listed in Table 2. 0.5 g, 0.75 g and 1.00 g of HPMC-69 and HPMC-C were added separately to this cement paste, and the setting starting and ending times were compared. After inserting the Vicat needle into the cement paste every 10 minutes, the distance from the base plate was measured, and the values were given in millimeters (mm).

RESULTS AND DISCUSSION

In this study, it has been intended to find a sustainable way of recovering towel clippings containing cellulose. For this, hydroxypropyl methylcellulose (HPMC) was synthesized (Fig. 3) from these wastes as a high value-added product, it was purified, and its structure was characterized by ^{1}H(^{13}C)-NMR, FT-IR and XRD spectroscopic methods. In addition, its thermal degradation was examined by DTA/TGA, surface morphology – by SEM and its viscosity was measured. Moreover, the effect of the obtained HPMC on the setting time of cement paste was investigated.

As will be seen further (Table 7 – DS and MS results of HPMCs), the viscosity values increased as the total DS value increased from HPMC-1 to HPMC-5 (Table 9). Since the DS value of the HPMC-1 was the lowest (1.15), it was compared with the commercial HPMC-C. Thus, the effects of HPMC-1 and HPMC-C on the starting and ending time of cement paste setting were investigated. With the addition of HPMC-1 to the cement paste, it was observed that the setting start and end times were extended and thus the hydration time. Since the DS value and the viscosities of other synthesized HPMCs are higher than those of HPMC-1, they will further extend the hydration time of the cement paste by retaining more water, as stated in the literature.[19-23] This means that such cement paste formulations will ensure a longer working time interval.

SEM analysis

SEM images of cellulose and synthesized hydroxypropylmethyl cellulose are given in

Figure 4. As can be seen from these images, a different surface morphology of hydroxypropylmethyl celluloses was observed caused by the degradation of the fiber structure of the cellulose. When the SEM images of HPMCs were examined, it was observed that they had different fiber sizes, were dispersed and had rough surface morphology. One of the reasons for the deterioration of the smooth surface of cellulose in HPMCs lies in the loose polymer chains formed by the penetration of a strong base, NaOH, into the more amorphous region of the cellulose and breaking the strong hydrogen bonds in the cellulose's structure. Therefore, due to the broken hydrogen bonds, the crystalline regions leave their place to the looser amorphous regions, and the smooth structure deteriorates and even collapses, cracks and uneven surfaces occur. In addition to this situation, the interaction of the OH groups with the PO and CM reagents in these degraded regions also contributes to the degradation of the cellulose.

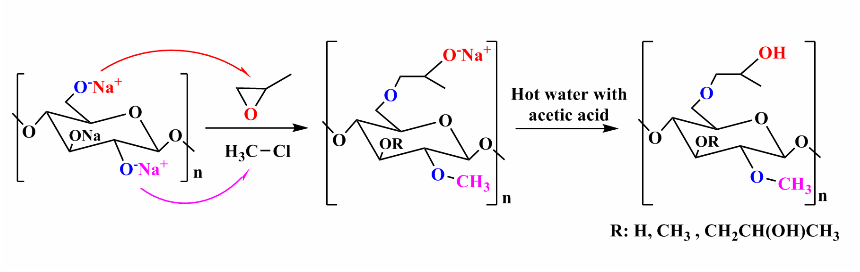

Figure 3: Synthesis mechanism of HPMC

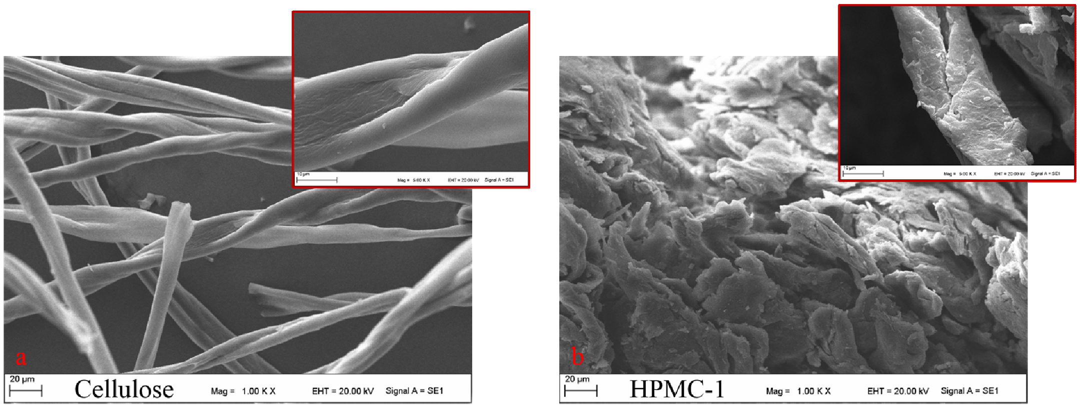

Figure 4: SEM images of cellulose (a) and HPMC-1 (b)

FT-IR analysis

The vibration bands of cellulose and synthesized HPMCs are given in Table 3, and the FT-IR spectra of cellulose, HPMC-C and HPMC-1 are given in Figure 5. From the FT-IR spectrum of cellulose, the (O-H) vibration band was observed to coincide with the vibration band of the adsorbed water molecule in the structure and was wide and broad at 3274 cm^{-1}. In the spectra of HPMCs, this band is seen between 3394 and 3455 cm^{-1}.[24-26] While the symmetrical vibration band of the -CH group in the aliphatic chains of the cellulose molecule was observed at 2895 cm^{-1}, this vibration of hydroxypropyl and methyl groups in the spectra of HPMCs was observed between 2895 and 2927 cm^{-1}.[24,26] Additionally, after hydroxypropylation and methylation, the new vibration bands seen at 2975 cm^{-1} can be attributed to the vibration bands of the C-H group, newly joined by the displacement of the hydrogen atom of the hydroxyl groups found in the anhydrous glucose unit (AGU). While the υ(C-O) stretching vibration in the glucose ring of cellulose is seen at 1621 cm^{-1}, it is seen in the range of 1646 to 1636 cm^{-1} in HPMCs.[26,27] In the υ(C-H) bonds of a methyl group, asymmetrical bending vibrations occur around 1460 cm^{-1} and symmetrical bending vibrations around 1375 cm^{-1}, both in-plane and out-of-plane.[27-29] The bands between 1400 and 1350 cm^{-1} can be attributed to the vibration bands of υ(C-O-C) cyclic anhydrides. The vibration between 1300 and 1250

cm^{-1} originate from the υ(C-O-C) cyclic epoxide group. The bands at 1047-1054 cm^{-1} can be considered to belong to the stretching of the vibration of ether υ(C-O-C) groups.[26,28] The bands between 1000 and 950 cm^{-1} are due to vibrations in the glucose ring.[30] It appears that the data in Table 3 and Figure 5 obtained from the FT-IR spectra of synthesized HPMCs are in agreement with those reported in the literature.[26,28,31-34]

Table 3
FT-IR vibration bands of cellulose and HPMCs

Sample	υ(O-H)	υ(C-H)	υ(C-O)	υ(CH_2)	υ(C-O)	υ(C-O-C)
Cellulose	3274	2895	1621	1427	1314	1027
HPMC-C	3426	2902	1644	1454	1313	1054
HPMC-1	3395	2895	1646	1452	1315	1049
HPMC-2	3452	2886	1638	1455	1309	1051
HPMC-3	3450	2905	1636	1455	1311	1049
HPMC-4	3449	2912	1642	1455	1307	1048
HPMC-5	3394	2895	1640	1450	1313	1047

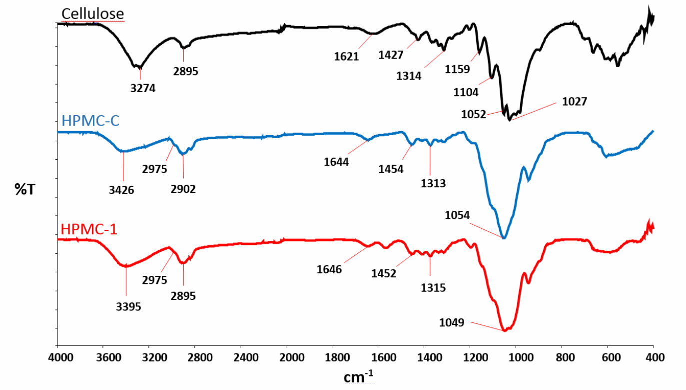

Figure 5: FT-IR spectra of HPMC-1, HPMC-C and cellulose

Table 4
Chemical shift values of ^{1}H-NMR spectra of HPMCs

Sample	H_1-H_5, H_8 (ppm)	H_6 (ppm)	H_7 (ppm)	H_9 (ppm)	H_{10} (ppm)
HPMC-1	3-5	3.47	3.82	1.03	3.29
HPMC-2	3-5	3.45	3.89	1.08	3.27
HPMC-3	3-5	3.44	3.81	1.01	3.27
HPMC-4	3-5	3.51	3.91	1.07	3.33
HPMC-5	3-5	3.43	3.79	1.01	3.25

^{1}H(^{13}C)-NMR analysis

Chemical shift values of the ^{1}H-NMR spectra of HPMCs synthesized from TC in D_2O solvent medium are given in Table 4. When examining the ^{1}H-NMR spectrum of HPMC-1 in Figure 6, the chemical shift values between δ=3-5 ppm can be attributed to the peaks of the anhydrous glucose unit of cellulose. However, these chemical shifts appear to overlap with the methyl groups of the methoxy substituent (H10) and the hydroxypropylate substituent (H7, H8).[35] In addition, the peak of the signal belonging to the methyl protons (H-9) of the hydroxypropylate group is clearly seen with a chemical shift value of δ=1.03 ppm. From here, it is seen that the proton NMR spectra are in harmony with other literature data.[34,36,37]

Chemical shift values of ^{13}C-NMR spectra of HPMCs in D_2O are given in Table 5.

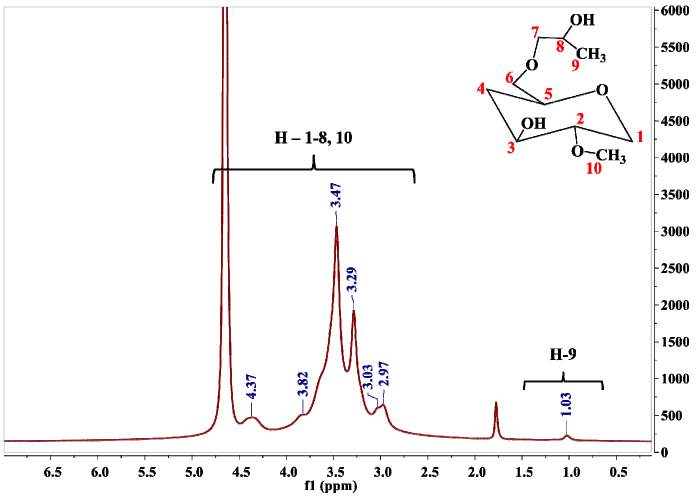

Figure 6: ^{1}H-NMR spectrum of HPMC-1

Table 5
Chemical shift values of ^{13}C-NMR spectra of HPMCs

C-atom	Cellulose*	HPMC**	HPMC-1	HPMC-2	HPMC-3	HPMC-4	HPMC-5
C-1	105.30	100	101.99	102.10	102.03	101.97	102.15
C-2 (–OH)	72.80	70–76	70–76	70–76	70–76	70–76	70–76
C-2 (–OR)	-	79	82.34	82.45	82.35	82.17	82.83
C-3 (–OH)	75.10	70–76	70–76	70–76	70–76	70–76	70–76
C-3 (–OR)	-	82	82.20	81.92	82.18	81.96	82.57
C-4	85	76	78.20	78.25	78.08	78.13	78.33
C-5	74.80	70–76	70–76	70–76	70–76	70–76	70–76
C-6 (–OH)	62.50	57	59.22	59.02	58.96	58.95	59.13
C-6 (–OCH_3)	-	68	69.70	68.38	69.61	69.53	69.89
C-6 (–OR)	-	70	70.06	69.52	69.84	70.16	72.64
OCH_3–C-2	-	56	58.11	58.14	58.22	58.03	58.53
OCH_3–C-3	-	56.50	59.40	59.20	59.18	59.26	59.52
OCH_3–C-6	-	58	60.17	60.23	60.13	60.20	60.35
CH (–OH)–int	-	73.50	74.72	74.93	74.91	74.43	74.94
CH (–OR)–ext	-	64–65	66.48	66.54	66.15	67.95	69.96
CH_2(–CHOH)–int	-	74	75.72	75.82	75.88	75.79	76.06
CH_2(–CHOR)–ext	-	72	73.34	73.26	73.46	73.17	73.53
CH_3(–CHOH)–int	-	16.50	17.86	22.31	21.29	20.62	19.84
CH_3(–CHOR)–ext	-	14	22.88	23.42	22.96	22.41	21.05

*T. Mori;[38] **R. N. Ibbett;[39] R: substitute, int: internal, ext: external

As can be seen from the spectrum of HPMC-1 in Figure 7, the chemical shift value of the signal belonging to the C1 atom of TC was observed at δ = 100.0 ppm, while it was observed at δ = 101.99 ppm in the synthesized hydroxypropylmethyl cellulose. While the chemical shift of the C4 atom of the cellulose molecule was observed at δ = 76 ppm, this peak of the C4 atom of the HPMC-1 sample overlapped with C2s and C3s at δ = 78.20 ppm. While the chemical shifts of the signals belonging to the C2, 3, 5 atoms of TC were observed between δ = 70-76 ppm, they overlapped with the signals of the methyl groups of the hydroxypropyl and methoxy groups, as well as the C2, 3, 5 atoms of the HPMCs. The peak of the C6 atom of TC was observed at δ = 57 ppm, however, this peak of HPMCs was observed to overlap with the methyl groups at δ = 59.22 ppm. In the ^{13}C-NMR spectra of HPMCs, signals belonging to the methyl carbon of the hydroxypropyl group were observed at δ = 22.88 and 17.86 ppm, unlike in cellulose.[39-41]

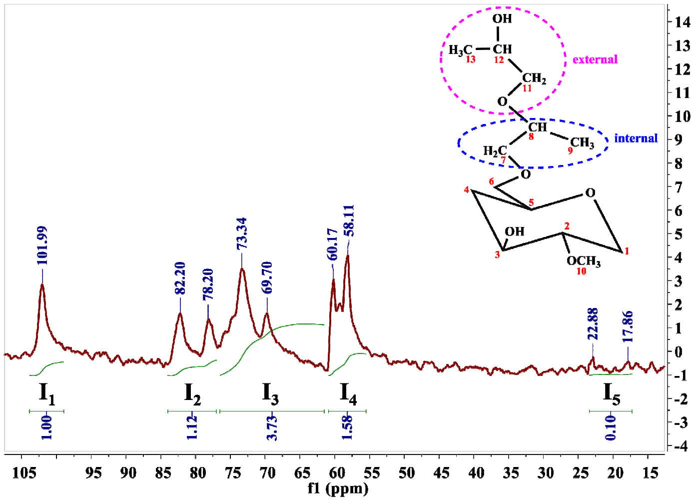

Figure 7: ^{13}C-NMR spectrum of HPMC-1

Table 6
Intensity of spectral regions of HPMCs in ^{13}C-NMR spectra

Sample	I_1	I_2	I_3	I_4	I_5
Cellulose*	1.00	0.85	3.59	0.74	-
HPMC-1	1.00	1.12	3.73	1.58	0.10
HPMC-2	1.00	1.20	3.70	1.68	0.11
HPMC-3	1.00	1.27	3.68	1.75	0.13
HPMC-4	1.00	2.08	4.11	1.81	0.13
HPMC-5	1.00	2.15	4.18	1.88	0.14

*S. V. Araslankin[40]

DS and MS values of HPMCs

Molecular substitution (MS) and degree of substitution (DS) calculations are based on the mathematical difference between the intensity of the specific spectral region in the ^{13}C-NMR spectrum of hydroxypropylmethyl cellulose and the spectral region density in the spectrum of the corresponding cellulose.[40] MS and DS values of the synthesized hydroxypropylmethyl cellulose were calculated as stated in Kostryukov's article.[41] The intensity of cellulose and synthesized HPMCs shown in the spectral regions are given in Table 6.

In the ^{13}C-NMR spectrum of HPMC-1 shown in Figure 7, the intensities in 5 different regions corresponding to the C atoms are shown. The molecular expression of the hydroxypropyl groups was calculated according to Equation (1):

$$ {}^{HP}_{HPMC}MS = \frac{2}{3}\sum_{i=2}^{n=3}\left({}^{HPMC}_{i}I - {}^{Cellulose}_{i}I\right) \qquad (1) $$

where ${}^{HPMC}_{i}I$ and ${}^{Cellulose}_{i}I$ are the densities of HPMC and cellulose, respectively. In the 5th region in the ^{13}C-NMR spectrum of HPMC, since it corresponds to the methyl signals of the hydroxypropyl groups, the degree of substitution was calculated according to Equation (2):

$$ {}^{HP}_{HPMC}DS = {}^{HPMC}_{5}I \qquad (2) $$

where ${}^{HPMC}_{5}I$ is the density in the 5th region of HPMC. The degree of substitution of the methyl groups of HPMC was calculated according to Equation (3):

$$ {}^{M}_{HPMC}DS = \sum_{i=2}^{n=4}\left({}^{HPMC}_{i}I - {}^{Cellulose}_{i}I\right) - 2\,{}^{HP}_{HPMC}DS \qquad (3) $$

The degrees of substitution of C-2,3 (${}^{C-2,3}_{HPMC}DS$) and C-6 atoms (${}^{C-6}_{HPMC}DS$) were calculated according to Equations (4) and (5), respectively:

$$ {}^{C-2,3}_{HPMC}DS = {}^{HPMC}_{2}I - {}^{Cellulose}_{2}I \qquad (4) $$

$$ {}^{C-6}_{HPMC}DS = {}^{HP}_{HPMC}DS + {}^{M}_{HPMC}DS - {}^{C-2,3}_{HPMC}DS \qquad (5) $$

The total degree of substitution for HPMC samples (${}^{Total}_{HPMC}DS$) was calculated according to Equation (6) with the sum of the substitution degrees of the groups in the C-2,3 and C-6 atoms:[42]

$$ {}^{Total}_{HPMC}DS = {}^{C-6}_{HPMC}DS + {}^{C-2,3}_{HPMC}DS \qquad (6) $$

In Table 7, the DS and MS results of the calculated HPMCs are given. In HPMC synthesis, as the amount of PO and CM increased, the MS and DS values also increased. While the amount of CM was kept constant as 5.25 grams, in the hydroxypropylation of these three samples coded HPMC-1, 2 and 3, when the amount of PO added to the reaction medium was increased from 5 grams to 20 grams, the MS value from 0.27 to 1.26 was proportionally increased. However, the DS (1.05-1.14) value remained almost unchanged with the addition of the PO amount. In HPMC-4 and 5 coded samples, when the CM amount was increased from 5.25 grams to 7.35 grams and the PO amount was increased from 15 grams to 20 grams, the MS values also increased from 1.16 to 1.26, respectively. Accordingly, the total DS value continued to increase.

XRD analysis

As can be seen from the XRD diffraction patterns of HPMCs and cellulose given in Figure 8, cellulose, like other polymers, has crystalline and amorphous regions, and thus has a heterogeneous structure. The reaction takes place over the hydroxyl (-OH) groups in the amorphous regions of the anhydrous glucose units in a cellulose chain, which are easy to reach.[31] The typical diffraction peak appeared at 2θ = 15°, 23°, and 34° in Figure 8, indicating the typical cellulose I crystalline form, which is in perfect accordance with the results of previous studies.[43,44] In HPMC synthesis, it can be said that the crystalline regions in cellulose disappear and a new crystalline region is formed at different intensities after hydroxypropylation and methylation.[32,45,46] It gave a different XRD diffraction pattern as the additives in commercial HPMC (HPMC-C) were unknown. However, when compared with the synthesized HPMCs, it is clearly seen that the peaks around 20° are in harmony with each other.

Table 7
DS and MS results of HPMCs

Sample	${}^{HP}_{HPMC}MS$	${}^{HP}_{HPMC}DS$	${}^{M}_{HPMC}DS$	${}^{C-2,3}_{HPMC}DS$	${}^{C-6}_{HPMC}DS$	${}^{Total}_{HPMC}DS$
HPMC-1	0.27	0.10	1.05	0.27	0.88	1.15
HPMC-2	0.30	0.11	1.18	0.35	0.94	1.29
HPMC-3	0.34	0.13	1.26	0.42	0.97	1.39
HPMC-4	1.16	0.13	2.56	1.23	1.46	2.69
HPMC-5	1.26	0.14	2.75	1.30	1.59	2.89

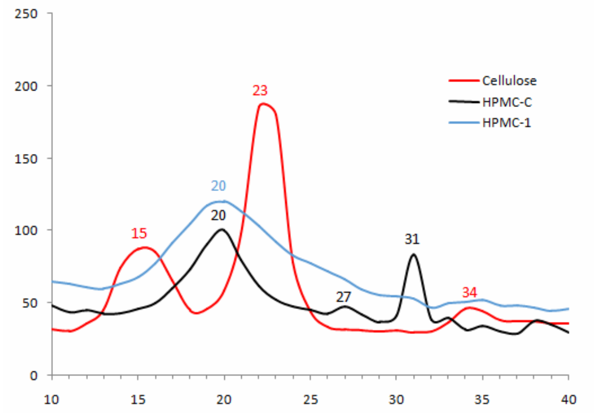

Figure 8: XRD diffraction patterns of HPMC-1, HPMC-C and Cellulose

DTA/TGA

For examining the thermal stability of cellulose and HPMC by TGA and DTA, a comparison of the thermograms is given in Figure 9, and the amounts of mass losses are given in Table 8. As can be seen from the thermograms, mass losses occur in three stages. A maximum initial mass loss of 3% at 30-100 °C, which can be attributed to intermolecular dehydration, namely, the desorption of free moisture in the hygroscopic matrix.[26,47,48] In a study by Feller and Wilt, it was reported that the lower the degree of substitution of cellulose ethers, the higher the equilibrium moisture.[49] From 100 °C to 200 °C, HPMCs were found to be thermally stable. In the second stage, thermal decomposition occurs at approximately 200-400 °C, when the highest mass loss was recorded – an average mass loss of 64% has occurred (Table 8). The second stage has been attributed to the oxidative decomposition of cellulose ethers, involving intramolecular dehydration and demethylation processes.[26,47,50] In the last stage, the mass loss at 400-600 °C was attributed to excess carbon and ash residues. As can be seen from the thermogram, the initial degradation temperatures of the synthesized HPMCs were lower than that of cellulose. In other words, the thermal stability of HPMCs synthesized from cellulose decreases. It should be noted that the thermal degradation data obtained for HPMCs in this work are compatible with those of previous studies.[33,51-54]

Table 8
Mass losses of cellulose and HPMCs

Sample	Mass loss between 30-100 °C (%)	Mass loss between 200-400 °C	
		Thermal degradation (°C)	Mass loss (%)
Cellulose	-	341	64.927
HPMC-C	3.091	355	60.427
HPMC-1	1.439	319	68.480
HPMC-2	2.935	365	87.980
HPMC-4	-	367	88.515

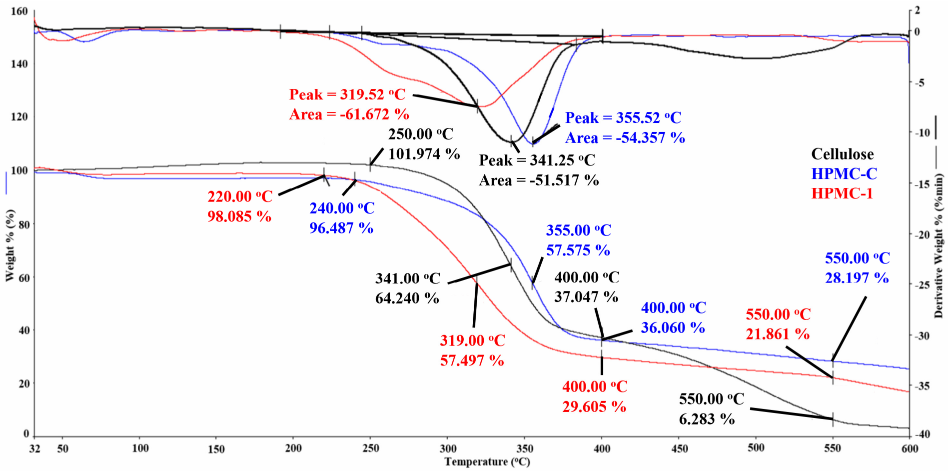

Figure 9: DTA/TGA thermograms of cellulose and HPMCs

Viscosity of HPMC-C and HPMCs

In this study, the viscosities of synthesized HPMCs were interpreted by comparing them with that of the commercial HPMC-C. In recent years, HPMC has been widely used in place of other cellulose ethers, such as carboxymethyl cellulose and methyl cellulose, which are used industrially, due to its gelling property, which enables it to retain more water, as a function of its increased DS value, increasing the viscosity and the thickness of the aqueous medium. The viscosity of HPMCs tabulated in Table 9 increases as the DS value increases, but decreases as the spindle rotation speed increases. At 2.5 rpm, an increase in viscosity was measured from HPMC-1, with the lowest DS and a viscosity of 380 cP, to HPMC-5 – with the highest DS and viscosity of 2740 cP. HPMC-C, at a spindle rotation speed of 2.5 rpm, had the viscosity of 3520 cP with 21% performance, while HPMC-5 measured 2740 cP with 14.5% performance. Commercial HPMC-C at 20 rpm reached 1730 cP with 80% performance, while HPMC-1, HPMC-2, HPMC-3, HPMC-4 and HPMC-5 recorded viscosities of 240, 308, 392, 1248 and 1457 (63.7% performance), respectively. Considering the commercial HPMC-C coded sample, one of the reasons for the low viscosity of the synthesized HPMCs, other than the DS value, could be that they do not contain additives. In order to be commercialized, HPMC should contain additives and some other mixtures, for adapting some of its properties according to the industrial requirements.

Table 9
Viscosity values of 2% HPMC solutions

Sample		2.5 rpm	5 rpm	10 rpm	20 rpm	50 rpm	100 rpm
HPMC-C	%	21	36	54	80	-	-
	cP	3520	2920	2170	1730	-	-
HPMC-1	%	0.7	1.5	2.8	5.6	14	30
	cP	380	300	260	240	160	140
HPMC-2	%	2.7	5.1	8.5	15.1	29	52.3
	cP	432	408	340	308	232	209
HPMC-3	%	3.9	6.5	11.5	20	35.9	60
	cP	640	520	457	392	287	239
HPMC-4	%	13	21.9	37.9	62.4	-	-
	cP	2080	1752	1516	1248	-	-
HPMC-5	%	14.5	23	40	63.7	87	-
	cP	2740	1980	1758	1457	1321	-

Effect of HPMC on setting time in cement paste

Although many theories have been put forward to explain the hardening and freezing of cement, almost all researchers agree that hydration and hydrolysis reactions occur during freezing. The solubility of hydration products in water is very low. The task of the water added to the cement mortar is to ensure that the mortar hardens and bonds within a certain period of time. The setting is the time between the moment when binding materials, such as cement, combine with water and the moment when the cement paste loses the water in its structure (chemical combination, evaporation *etc.*) and loses its plastic feature by solidifying. The setting time, which varies as a function of weather conditions (summer/winter), is required to be not less than 1 hour and not more than 10 hours under normal conditions. While the setting time decreases with increasing temperature, it is prolonged in low temperature or humid environments.

It is known that hydroxypropylmethyl cellulose retains water in its body and turns into a viscous structure, thus it is used in many industries. The effect of HPMC on the setting (hydration) time of cement paste would be important for the construction industry. In recent times, HPMC has been frequently used especially in construction chemicals, and has attracted much interest as it increases the adhesion strength of the mortar by increasing the slip resistance, facilitates the plastering process by improving the consistency of the mortar and adjusts the working time of the mortar.

A Vicat experiment was conducted to examine the effect of hydroxypropylmethyl cellulose on the setting time of cement paste. In the Vicat experiment, the times are given in minutes (Fig. 10). As can be seen from the Vicat test results, as the hydroxypropylmethyl cellulose ratio added to the cement paste increased, the setting start time and setting end time of the cement paste increased, compared to the witness sample. Therefore, many problems, such as low slip resistance, setting time and negative effects caused by working conditions, will be avoided and positive results will be obtained. The setting of the cement paste, without any additives, started at 140 minutes and finished at 250 minutes, but with the addition of 0.5 grams of commercial HPMC-C, the setting start time increased to 200 minutes and ending time to 280 minutes. With the addition of 0.5 grams of synthesized HPMC-1 (DS = 1.15) to the cement paste, the start of setting was extended to 180 minutes and the ending time to 260 minutes. It is clear from these results that these times can be extended depending on the amount of HPMC added. When the setting start and end times of the cement pastes with the addition of HPMCs synthesized in this study and the commercial ones were compared, it was concluded that HPMCs with different desired properties could be synthesized.

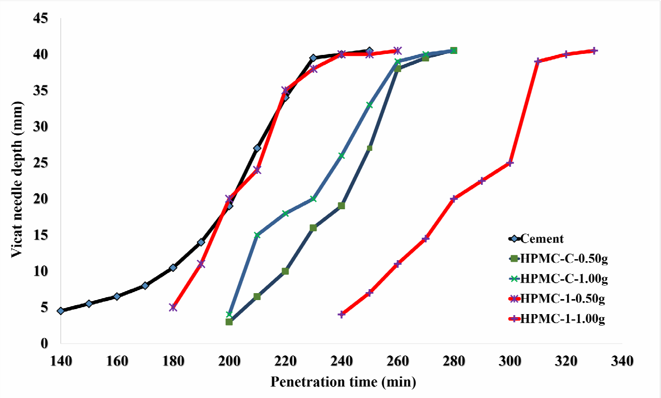

Figure 10: Setting start time and end time of cement paste with and without HPMC additives

CONCLUSION

Considering environmental issues, researchers and industry stakeholders should focus on zero waste projects, evaluating the possibility of recycling, recovering and reusing wastes. For example, in the industrial production of cellulose derivatives, to prevent deforestation, we need to turn to annual renewable plants and textile wastes containing cellulose as raw materials. In this context, in this study, hydroxypropylmethyl cellulose (HPMC), a cellulose ether, was synthesized from cellulose-containing cotton “towel clippings”, which are considered as waste in textile factories. The structure of the synthesized HPMC was elucidated with ^{1}H(^{13}C)-NMR, FT-IR and XRD, its thermal decomposition was investigated with DTA/TGA, its surface morphologies were examined with SEM and its viscosities were measured. The highest viscosity value and the highest DS value were obtained in the HPMC-5 coded sample – as 2740 cP and 2.89, respectively. In addition, the effect of HPMC, which has many industrial uses, on the setting (hydration) time of standard cement paste, which is one of the most common areas of use in the construction industry, was investigated. After adding 1 gram of HPMC-1, the starting time of the cement paste setting was extended up to 240 minutes and the finishing time – to 330 minutes, compared to the standard cement paste (without HPMC), which started to set at 140 minutes and ended at 250 minutes. As the HPMC ratio added to the cement paste increased, the setting start time and end time increased as well, compared to the reference sample. Therefore, it has been concluded that, in this way, many problems, such as low slip resistance, setting time and negative effects caused by working conditions, can be avoided, yielding positive results. Considering the structural characterization, the DS and viscosity values of the other HPMCs obtained in this study, it could be assumed that their addition to cement paste would lead to similar results as for HPMC-1. Although the DS value and viscosity of HPMC-1 were lower than those of the other HPMCs (HPMC-2, HPMC-3, HPMC-4 and HPMC-5), it contributed to a longer hydration time, compared to commercial HPMC-C, thus prolonging the range between the start and the end of the setting time. Thus, HPMC can be synthesized from cellulose-containing cotton “towel clippings”, and can be applied as an additive to cement paste to prolong its setting time, thus bringing benefits to the construction industry, due to its characteristic thickening and adhesive properties.

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