

# SYNTHESIS, CHARACTERIZATION AND APPLICATION OF CARBOXYMETHYL POTATO STARCH OBTAINED FROM WASTE

SUMEYYE AKARSU\* and MUSTAFA DOLAZ\*\*,\*\*

\*Department of Food Engineering, Faculty of Engineering, Sakarya University,  
Sakarya 54187, Turkey

\*\*Department of Environmental Engineering, Faculty of Engineering and Architecture, Kahramanmaraş  
Sutcu Imam University, Kahramanmaraş 46100, Turkey

\*\*\*Research and Development Centre for University–Industry–Public Relations, Kahramanmaraş Sutcu  
Imam University, 46100 Kahramanmaraş, Turkey

✉ Corresponding author: Mustafa Dolaz, mdolaz@ksu.edu.tr, dolazmustafa@gmail.com

Received June 7, 2018

Waste potato starch (WPS) was obtained from the food industry during slicing, peeling and washing potatoes in the process of producing potato chips. After it was purified with H<sub>2</sub>O<sub>2</sub> and NaOH at the desired temperature, carboxymethyl potato starch (CMPS), with the DS in the range from 0.04 to 1.24, was synthesized in isopropanol (IPA) and NaOH solution by adding monochloroacetic acid (MCA). Considering all the studied conditions, the best results were achieved when IPA was used as solvent at 45 °C for 180 min and at a NaOH/MCA molar ratio of 2.2:1. CMPS-2, obtained under these conditions, reached a viscosity of 14200 mPa's (for 2% CMPS in water at 1 rpm) for the highest DS. The samples were investigated by determining their DS and by SEM, FTIR, XRD, NMR and thermal analyses. Moreover, the viscosity of the CMPS aqueous solutions was measured. 100% cotton yarns with different numbers (10/1, 20/1 and 30/1 Ne) were sized with CMPS-29, CMPS-27, CMPS-25 and CMPS-22, and then their tensile strength and elongation at break were measured. The tensile strength of the sized samples increased by 87.65%, compared with that sized with WPS. Also, CMPS with DS 0.04 exhibited considerably better sizing properties, compared to WPS.

**Keywords:** waste, carboxymethyl potato starch, FT-IR, XRD, sizing

## INTRODUCTION

Conversion of industrial food waste materials into useful products would facilitate a greener approach to manufacturing. Waste potato starch (WPS) is a by-product in the production of potato chips. It is a cheap, biodegradable, non-toxic and renewable natural polymer, available in great quantities on a global level.<sup>1</sup>

Brittleness and retrogradation are issues related to starch films after *e.g.* thermoplasticization. Starch has OH groups that can take part in many types of reactions characteristic of this functional group (*e.g.* etherification, esterification, oxidation, acylation).<sup>2</sup> In order to utilize starch in industrial applications, it must be converted into its derivatives. Hence, chemical modification proposes an interesting alternative to achieve new materials with biodegradation properties. Chemical modification of starch includes the

reaction of the hydroxyl groups on the anhydroglucose units (AGU), which have been used to generate starch derivatives based on carboxymethylation,<sup>3</sup> crosslinking,<sup>4,5</sup> oxidation,<sup>6</sup> hydroxypropylation<sup>7,8</sup> and grafting.<sup>9</sup> Among these derivatives, carboxymethyl starch (CMS) has attracted a lot of attention in industry.<sup>10</sup> In general, CMS is synthesized under alkali conditions by the reaction of MCA and starch. In the alkalization step, the hydroxyl groups on starch (St-OH) molecules are changed to the more reactive alkoxide form (Eqs. 1, 2):



Nevertheless, a side reaction takes place, producing sodium glycolate, with MCA and sodium hydroxide according to the following equation (Eq. 3):



Sodium carboxymethyl starch is an anionic, water-soluble, man-modified polysaccharide. Purified CMS is a white- to cream-colored, odorless powder. Some papers have reported the synthesis of CMS from various sources: cassava starch,<sup>11-13</sup> amaranth,<sup>14</sup> high-amylose corn,<sup>15</sup> potato,<sup>16-22</sup> wheat,<sup>23</sup> rice,<sup>24,25</sup> mungbean,<sup>26</sup> Chinese yam and Cassia tora gum,<sup>27</sup> kudzu root starch,<sup>28</sup> wastes from corn starch and potato flour,<sup>29</sup> sorghum,<sup>30</sup> arrowroot starch<sup>31</sup> and water yam (*Dioscorea alata*) starch.<sup>32</sup>

CMS is the most widely used starch with applications in pharmaceutical applications,<sup>17,33,34</sup> textile,<sup>35-38</sup> environmental,<sup>39,40</sup> paper and food industries.<sup>41,42</sup>

In this study, we used waste potato starch (WPS) from a chips factory to obtain carboxymethyl potato starch (CMPS). We investigated the size and shape of CMPS particles, the viscosity of CMPS aqueous solutions, as well as the degree of substitution, the crystalline characteristics and the thermal stability properties of CMPSs. The characterized CMPSs were then used as sizing agent in textile processing. This work aims to convert waste potato starch into a useful sizing material.

## EXPERIMENTAL

### Materials

Following the synthesis process, the viscosity of each CMPS obtained was measured by a Brookfield-Prime DV-I digital viscometer (ASTM D2364, USA). Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FT-IR, using KBr discs (4000-400  $\text{cm}^{-1}$ ). The morphological structures of WPS and CMPSs were investigated by a Jeol/Neoscope JCM-5000 SEM. <sup>13</sup>C-NMR spectroscopy (Bruker Superconducting FT-NMR Spectrometer Avance TM 300 MHz WB) and <sup>1</sup>H-NMR spectroscopy (Bruker Biospin 300 MHz NMR Spectrophotometer) were used. For this, the required amount of CMPS powder was dispersed in D<sub>2</sub>O in a tube at 25 °C under vigorous stirring. Measurements were carried out at room temperature. The thermal studies of WPS and CMPS were performed on a Perkin Elmer STA 6000 Simultaneous Thermal Analyzer under nitrogen atmosphere, at a heating rate of 10 °C/min. The XRD of each sample was conducted using a Philips X'Pert PRO MPD X-ray Diffraction System PW3040/60. Strength tests were performed on a Zwick Roell Z5.0 Universal Testing Machine according to TS EN ISO 2062:2009.

WPS was supplied by Seydisehir-Beysehir Torku Potato Chips Factory, Konya, Turkey. Cotton yarns (10/1 Ne, 20/1 Ne and 30/1 Ne 100% cotton yarn) were supplied by KİPAŞ Holding, Kahramanmaraş,

Turkey. Monochloroacetic acid (MCA), isopropanol (IPA), sodium hydroxide (NaOH), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), glacial acetic acid (CH<sub>3</sub>COOH), copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O), ethanol (C<sub>2</sub>H<sub>5</sub>OH), methanol (CH<sub>3</sub>OH), ammonium chloride (NH<sub>4</sub>Cl), hydrochloric acid (HCl), murexide and ethylenediaminetetraacetic acid disodium salt dihydrate (Na<sub>2</sub>EDTA·2H<sub>2</sub>O) were purchased from Merck. All the chemicals were reagent pure grade and were used without further purification.

### Preparation of CMPS

The reactions were performed in a glass batch reactor equipped with mechanical stirrer and thermocouple. The first process was the purification of the starches. WPS (50 g) and 3 g of NaOH in 15 mL water were suspended in a certain volume of IPA and heated to 45 °C. Then, hydrogen peroxide (5 mL, 30% w/w) was added and the mixture was stirred for 90 min. After cooling down to room temperature, the sample was neutralized with glacial acetic acid, washed with distilled water three times, and dried at 40 °C in vacuum. In the second step, the carboxymethylation of WPS was realized according to a reported method.<sup>43</sup> The sodium salt solution of monochloroacetic acid was dissolved in IPA in the glass reactor and an aqueous solution of sodium hydroxide was added. After 15 min, 10 g of starch (ca. 15 wt% moisture) and NaOH microgranules were slowly introduced (Table 1). The temperature of the reaction mixture was raised to 45 °C and allowed to react for 3 h under constant stirring. Then, the reaction mixture was cooled and neutralized with glacial acetic acid. The product was washed three times with 80% (v/v) methanol and pure methanol, filtered and dried in an oven at 40 °C in a vacuum (Fig. 1).

### Determination of DS

The degree of substitution by carboxymethyl groups was determined by quantifying the amount of carboxymethyl groups on the CMPSs (reported in Table 1) by using a previously described method.<sup>44</sup> Briefly, carboxymethyl potato starch was moisturized by 1 mL of ethanol and dissolved in 50 mL of distilled water, followed by adding 20 mL of 0.187 M NH<sub>4</sub>Cl buffer and adjusted to neutral pH. The whole mixture was poured into a flask with 50 mL of 0.039 M in copper sulphate salt (CuSO<sub>4</sub>·5H<sub>2</sub>O). After 15 minutes, bidistilled water was added to the slurry and the content was filtered. The filtrate was titrated with 0.05 M EDTA solution, using murexide as an indicator, by an SI Analytics TitroLine 6000 Titrator.

### Measurements of viscosity

An aqueous solution of carboxymethyl potato starch was prepared by adding CMPS to distilled water under stirring with a magnetic stirrer and mixed until homogeneous. After 30 minutes, the viscosity of the samples was measured (Table 2). The viscosity of a

2% water solution of CMPSs was measured in a rotary viscometer (Brookfield Prime DV-I) at 25 °C, varying spindle rotation from 1 up to 100 rpm.

#### Textile sizing

Pure cotton yarns (10/1, 20/1 and 30/1 Ne) were sized with WPS, CMPS-29 (DS = 0.04), CMPS-27 (DS = 0.14), CMPS-25 (DS = 0.39) and CMPS-22 (DS = 0.65). For this process, 5 g of CMPS samples were dissolved in 50 mL tap water for 10 minutes under slow stirring. The solution was heated at 90 °C for 30 minutes and the pH was adjusted to 7.5-8.5. Each yarn intended for sizing was immersed into the solution for 5 minutes and then squeezed out. The sized yarns were then dried for 5 minutes at 90 °C. Before the sized yarns (twenty-five specimens of 25 cm length) were tested for tensile strength (cN/tex) and tensile elongation (%), according to TS EN ISO 2062:2009, with a pulling speed of 250 mm/min and a preload of 0.5 cN/tex, they were conditioned for 24 hours (Table 3).

## RESULTS AND DISCUSSION

Carboxymethyl potato starch with the DS of 0.04-1.24 was synthesized under of a variety of reaction conditions. The molar ratio of NaOH/MCA was changed, and simultaneously the MCA/AGU molar ratio was also changed (0.01-3.0). The granular samples were investigated by DS determination, as well as by SEM, FTIR, XRD, NMR and thermal analyses. Moreover, the viscosity of the CMPS aqueous solutions was measured. The results revealed that NaOH and MCA affected the DS. As the amount of NaOH increased, the DS value also increased. However, the further increase in the amount of NaOH had a negative impact on the DS values. On the other hand, MCA has a positive effect on the DS, especially at a high NaOH amount.<sup>13</sup>

Table 1  
Measured DS of CMPSs

Sample	MCA/AGU	NaOH/MCA	DS
CMPS-1	3.0	2.4	0.96
CMPS-2	3.0	2.2	1.24
CMPS-3	3.0	2.0	0.79
CMPS-4	3.0	1.8	0.63
CMPS-5	2.5	2.4	0.73
CMPS-6	2.5	2.2	1.06
CMPS-7	2.5	2.0	0.90
CMPS-8	2.5	1.8	0.86
CMPS-9	2.0	2.4	0.70
CMPS-10	2.0	2.2	1.04
CMPS-11	2.0	2.0	0.82
CMPS-12	2.0	1.8	0.63
CMPS-13	1.5	2.4	0.86
CMPS-14	1.5	2.2	0.88
CMPS-15	1.5	2.0	0.68
CMPS-16	1.5	1.8	0.59
CMPS-17	1.0	2.4	0.63
CMPS-18	1.0	2.2	0.72
CMPS-19	1.0	2.0	0.67
CMPS-20	1.0	1.8	0.51
CMPS-21	0.9	2.2	0.69
CMPS-22	0.8	2.2	0.65
CMPS-23	0.7	2.2	0.57
CMPS-24	0.6	2.2	0.49
CMPS-25	0.5	2.2	0.39
CMPS-26	0.4	2.2	0.25
CMPS-27	0.3	2.2	0.14
CMPS-28	0.2	2.2	0.11
CMPS-29	0.1	2.2	0.04

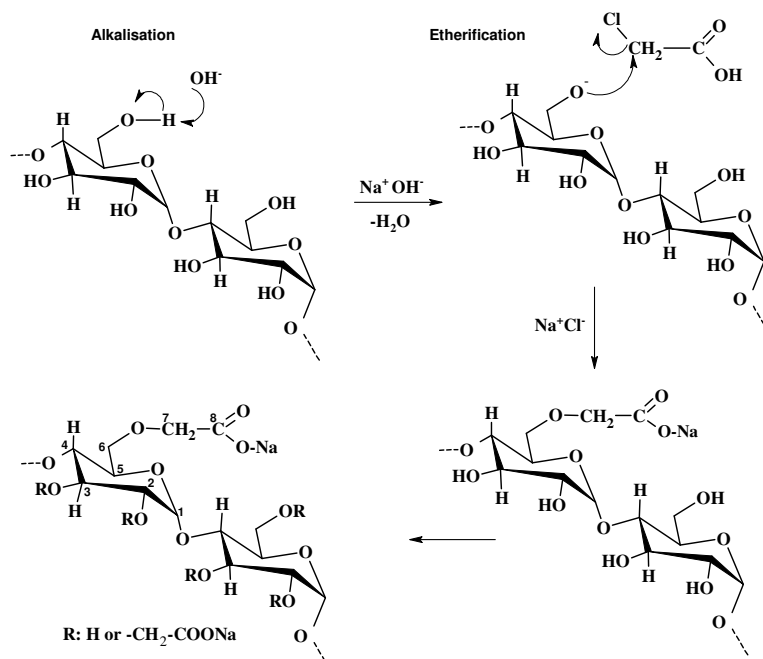


Figure 1: Synthesis of CMPS

Table 2  
Measured viscosity of CMPSs

Sample	Viscosity* of 2 wt% CMPS (mPa's)
CMPS-2	14200
CMPS-6	9900
CMPS-10	9500
CMPS-14	8200
CMPS-18	7200
CMPS-21	5000
CMPS-22	3400
CMPS-23	2300
CMPS-24	1200
CMPS-25	700
CMPS-26	100
CMPS-27	80
CMPS-28	50
CMPS-29	20

\*Viscosity measurement was obtained at 1 rpm

### Effect of various molar ratios of NaOH to starch

The influence of various molar NaOH:MCA ratios on the DS is shown in Figure 2. The molar ratios of NaOH to the anhydroglucose unit (AGU) were varied from 2.2 to 6.6, while the other reaction conditions were kept constant (45 °C for 180 min). The increase in the molar ratio of NaOH:MCA increased the DS until it reached 6.6

and a maximum DS of 1.24 was recorded. Figure 2 shows the DS ranging between 0.04 and 1.24. The DS of the CMPSs increased and reached the maximum DS of 1.24 at the NaOH/AGU molar ratio of 2.2. During the carboxymethylation process, the NaOH provides the alkaline environment for the reaction while also serving as swelling agent to facilitate diffusion and penetration of the etherifying agent to the granular

structure of the starch.<sup>45</sup> However, the starch then began to gelatinize and the contact between MCA and the starch was inhibited by the further increase in the NaOH amount. Moreover, further

increase in the NaOH concentration diverted the side reaction of MCA. These observations could explain the reduction in the DS at higher NaOH/MC ratios.<sup>45</sup>

Table 3  
Results for unsized and sized yarns with WPS, CMPS-29 (DS = 0.04), CMPS-27 (DS = 0.14), CMPS-25 (DS = 0.39) and CMPS-22 (DS = 0.65)

Yarn number (Ne)	Sample	Tensile strength (cN/tex)	Elongation at break (%)
10/1	Unsize	14.90	10.41
	WPS	26.41	12.37
	CMPS-29	27.96	13.23
	CMPS-27	27.72	12.27
	CMPS-25	23.78	10.20
	CMPS-22	23.43	13.48
20/1	Unsize	10.80	6.99
	WPS	15.71	8.04
	CMPS-29	16.88	7.71
	CMPS-27	16.51	6.26
	CMPS-25	16.19	6.10
	CMPS-22	14.18	8.85
30/1	Unsize	14.83	5.14
	WPS	21.13	8.14
	CMPS-29	23.25	7.72
	CMPS-27	22.42	7.54
	CMPS-25	20.35	7.09
	CMPS-22	20.17	6.27

### Effect of various molar ratios of MCA to starch

The results obtained by investigating the influence of the ratio of MCA to starch on the values of DS are presented in Figure 2. The reaction conditions during these experiments of the carboxymethylation of WPS were constant (45 °C for 180 min, NaOH:MCA = 2.2), but the molar ratio of MCA to AGU was varied from 0.1 to 3. Figure 2 shows CMPSs with varying DS. The DS values of CMPSs increased linearly with increasing MCA content in the reaction mixture. The increasing MCA/AGU ratio could lead to the usage of NaOH, so less NaOH can react with AGU, so higher MCA/AGU ratio leads to a lower DS. Also, this leads to sodium glycolate side reactions.

### Viscosity of CMPS aqueous solutions

The water solubility of CMPS is a complex phenomenon and depends on the degree of substitution and the temperature of the environment. The sodium carboxylate form of CMPS is soluble in water.<sup>46</sup> Generally, CMPSs with a high degree of substitution have high solubility in cold water.<sup>47</sup> Highly substituted

CMPS has higher viscosity than the low substituted one.<sup>48</sup> The electrostatic effect between polysaccharide chains with a high DS increases the viscosity by further widening the molecules.<sup>47</sup> It is also known that the viscosity of the polysaccharides depends on the molecular weight.<sup>13</sup> As the carboxymethyl derivatives of starch are synthesized, the temperature and the heavy alkaline conditions of the environment lead to the degradation of the carbohydrate molecules, resulting in variants with different viscosities and DS values. This situation also varies according to the starch source.<sup>40</sup>

In Figure 3, the influence of MCA content on the DS values and viscosity of the 2 wt% CMPS aqueous solution is presented. Significantly higher viscosity values can be observed in a low range of shear force (<10 rpm).<sup>40,46</sup> The viscosity of the 2 wt% CMPS aqueous solutions ranged between 20-14200 mPa·s and 25-1142 at 1 rpm and 100 rpm, respectively. It can be noted that the viscosity of the prepared CMPSs increased gradually with the increase in the DS values. The viscosity increased with upon the incorporation of carboxymethyl groups in the starch molecules.<sup>11,13</sup> When the hydroxyl groups are substituted by

carboxymethyl groups, the molecular weight of the starch increases, and as a result, the viscosity

of CMPSs increases.

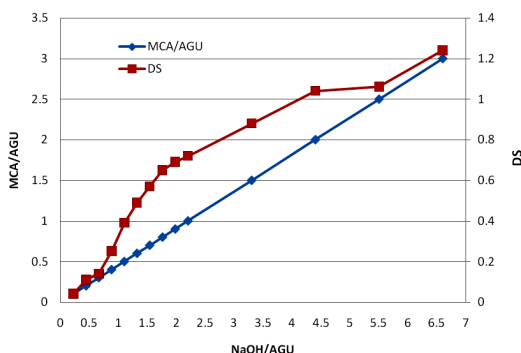


Figure 2: Effect of various NaOH/AGU molar ratios on DS and MCA/AGU

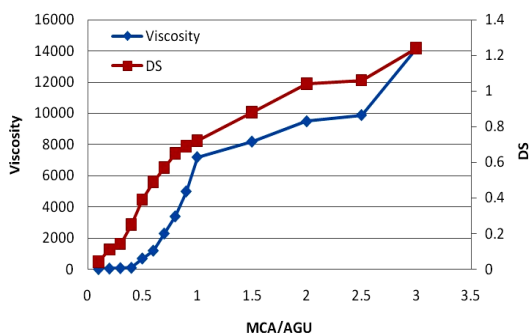


Figure 3: Influence of MCA to starch ratio (AGU) on DS and viscosity of CMPSs

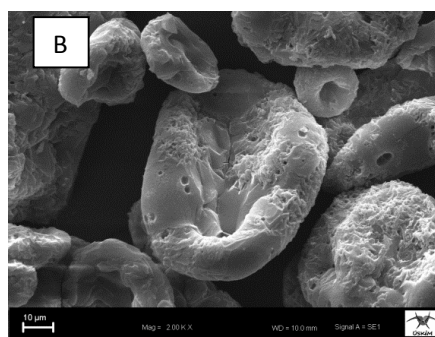
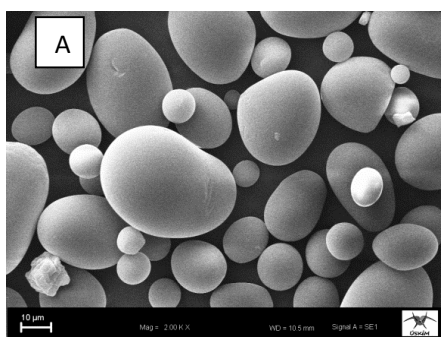


Figure 4: SEM micrographs of WPS (A) and CMPS-2 (DS = 1.24) (B)

### Granule morphology

The morphology of WPS and carboxymethylated starch granules was examined by a scanning electron microscope (JEAL/NEOSCOPE JCM-5000 SEM). The SEM micrographs of waste potato starch and CMPSs are shown in Figure 4. A smooth surface was observed for the elliptically shaped WPS granules. Comparing with waste potato starch, the granules of CMPSs had indented surfaces and some areas on the granule surface became shrunken and even fractured. After carboxymethylation, the granular shape was altered because of the alkaline conditions.<sup>13,18,40</sup> Strong alkaline conditions affected the changes on the starch granules, so the granules lost their crystalline structure. It is possible that carboxymethylation took place both on the surface and inside the starch granules. These findings prove the modification of starch. This result is in good agreement with those reported in the literature.<sup>13,18,40</sup>

### FT-IR spectroscopy

WPS, bleached WPS and carboxymethyl potato starch were characterized by Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer Spectrum 400). The FT-IR spectra of WPS and bleached WPS are closely similar to each other. The H<sub>2</sub>O<sub>2</sub>, which is a weak acid, did not cause a considerable change in the FT-IR spectrum. Some differences in relation to the functional groups in the carboxymethyl potato starch and the waste potato starch were detected on the FT-IR spectra presented in Figure 5. The broad band around 3273 cm<sup>-1</sup> assigned to the hydrogen bond corresponds to the hydroxyl groups on the starch molecules. The band at 2920 cm<sup>-1</sup> is assigned to the symmetrical stretching vibrations of -CH<sub>2</sub>.

When comparing the spectra of the CMPSs and WPS molecules, the vibrational band observed at 1642 cm<sup>-1</sup> in the spectrum of the waste potato starch disappeared in the spectra of the carboxymethyl potato starch. New peaks

occurred corresponding to the specific groups after the etherification reaction, which indicated the substitution of carboxylic groups. These strong absorption bands assigned to the asymmetric and symmetric vibration of  $\text{-COO}^-$  are located at  $1586$  and  $1415\text{ cm}^{-1}$ , respectively. These bands confirm the carboxymethylation of the starch molecules.<sup>18,49</sup> Table 4 shows the major FTIR peaks of the CMPS samples and WPS.

### XRD analysis

The crystalline characteristics of the samples were investigated by the X-ray diffraction method (XRD) (Philips X'Pert PRO). Diffraction patterns of waste potato starch, CMPS-26 (DS = 0.25),

CMPS-14 (DS = 0.88) and CMPS-6 (1.06) are shown in Figure 6. The diffractogram of WPS exhibits a typical B-type crystallinity pattern.<sup>50</sup> It can be observed that while the structure of waste potato was semi-crystalline, the crystallinity disappeared after the etherification reaction (*e.g.* DS = 0.25 and 0.88). The loss of crystallinity could be due to the effect of the alkaline environment during the modification.<sup>27,43</sup> The breakage of chemical bonds in the starch granules upon the heat treatment was also a possible reason of the loss of crystallinity.<sup>50</sup> On the other hand, when the DS value increased from 0.25 to 1.06, the structure turned again into a crystal one, with a typical B-type crystallinity pattern.

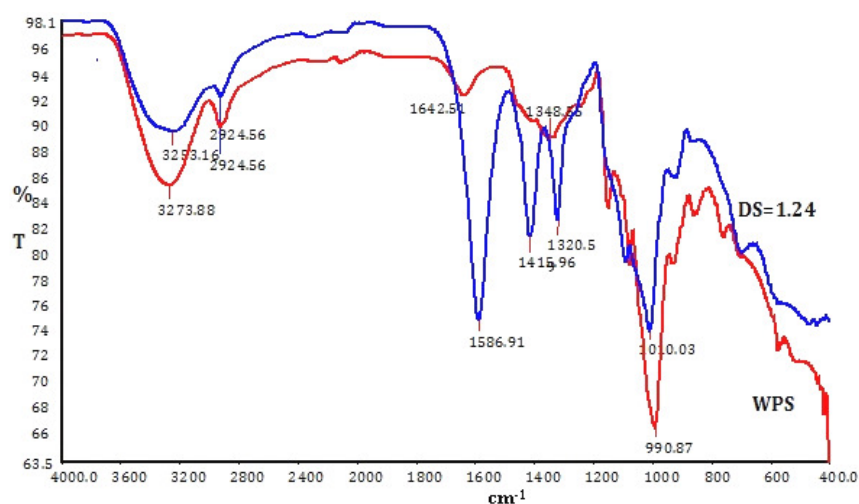


Figure 5: FT-IR spectra of WPS and CMPS-2 (DS = 1.24)

Table 4  
Major FTIR peaks of WPS and CMPS samples

Sample	$\nu(\text{OH})$	$\nu(\text{CH}_2)$	$\nu(\text{COO}^-)$
WPS*	3234	2923	-
WPS	3273	2920	-
CMPS-2	3275	2916	1586-1415
CMPS-6	3272	2901	1594-1417
CMPS-10	3252	2912	1587-1415
CMPS-14	3212	2916	1587-1411
CMPS-18	3230	2916	1586-1415
CMPS-21	3222	2912	1587-1411
CMPS-22	3230	2909	1589-1411
CMPS-23	3252	2916	1589-1411
CMPS-24	3274	2909	1591-1411
CMPS-25	3262	2920	1591-1416
CMPS-26	3249	2920	1590-1411
CMPS-27	3252	2924	1591-1416
CMPS-28	3274	2916	1591-1332
CMPS-29	3273	2920	1590-1334

\*WPS bleached by  $\text{H}_2\text{O}_2$



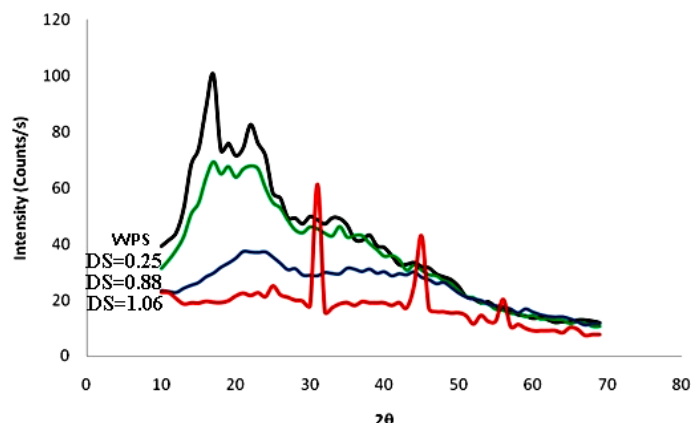


Figure 6: XRD patterns of WPS and CMPSs (DS = 0.25, DS = 0.88 and DS = 1.06)

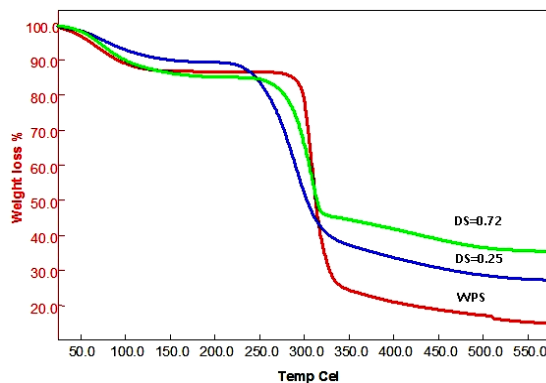


Figure 7: Weight loss for WPS and CMPSs (DS = 0.25 and DS = 0.72)

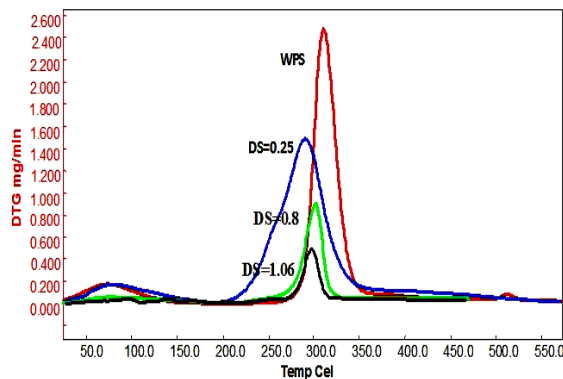


Figure 8: DTG curves for WPS and CMPSs (DS = 0.25, DS = 0.88 and DS = 1.06)

### Thermal properties

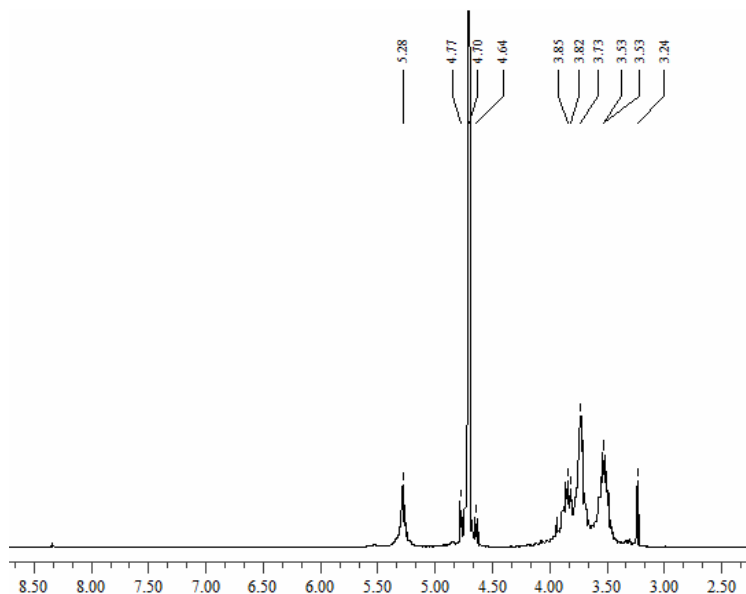
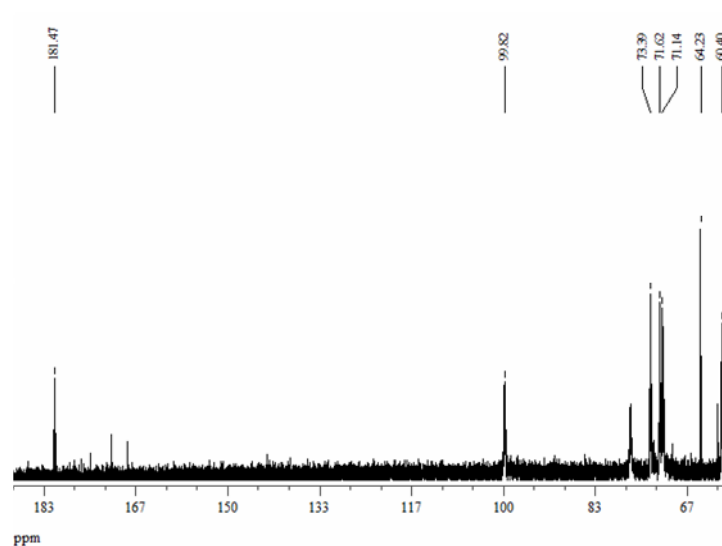
DTG measurements were performed by a SEIKO II TG-DTA. The polymeric materials were evaluated by thermogravimetric analysis to determine their thermal stability. The DTG and TG curves for the WPS and CMPSs are presented in Figures 7 and 8. According to the TG curves, the CMPSs start decomposing at a lower temperature than the WPS. As seen in Figure 7, the weight loss in the temperature range from 50 to 120 °C, which is the first step of degradation, was related to moisture (or free water) evaporation, while the second one corresponded to decomposition.<sup>51</sup> Comparing with WPS, which decomposed at 300 °C, the decomposition of CMPSs (DS = 0.25 and 0.88) started at 200 and 250 °C, respectively. The waste potato starch showed the fastest rate of decomposition as the temperature increased. On the contrary, the CMPSs with the DS values of 0.25, 0.88 and 1.06 exhibited lesser weight loss (Fig. 8). The residual

mass of CMPS could be higher than that of the waste potato starch due to the inorganic components produced during carboxymethylation.<sup>43,52</sup>

### <sup>1</sup>H(<sup>13</sup>C)-NMR analysis

<sup>1</sup>H-NMR spectroscopy of CMPS was carried out in D<sub>2</sub>O. The spectrum obtained for CMPS (DS = 0.88) and the signal assignment is shown in Figure 9. It was noted that the CMPS produced signals in the region of 5.28-5.33 ppm. The signals in the region of 4.64-4.67 ppm were assigned to the protons bound to the 2, 3, 6 positions of the AGU; the signals in the region of 3.73-3.85 ppm were assigned to the basic chemical shifts of the protons at carbon 6, 2, 3 of the glucose unit; and the signals in the region of 3.24-3.53 ppm could be chemical shifts of the proton at carbon 5 and 4 of the glucose unit, respectively.<sup>23,53</sup>



Figure 9:  $^1\text{H}$ -NMR spectrum of CMPS-14 (DS = 0.88)Figure 10:  $^{13}\text{C}$ -NMR spectrum of CMPS-14 (DS = 0.88)

The samples of CMPS were dissolved in  $\text{D}_2\text{O}$  (Fig. 10). Signals of  $-\text{COOH}$  (C-8) appeared at 180.47 ppm. This peak is associated with carboxymethylation. The signals of C-1 and C-4 appear at 99.82 and 76.99 ppm, respectively. The C-4 peak is attributed to the presence or absence of the carboxymethyl substituent on C-3. The peak at 73.39 ppm is assigned to C-2. Signals of C-3 and C-5 are detected at 71.62 and 71.14 ppm, respectively. The absorption peak at 60.40 ppm is

assigned to C-6, while that at 64.23 ppm corresponds to C-7.<sup>32,54,55</sup>

### Sizing of cotton yarns

Starch and its derivatives are among the sizing agents that are widely used in sizing of cotton-based textiles.<sup>56</sup> Different substituted CMPSs (DS = 0.04-1.24) were synthesized from waste potato starch (WPS). The sizability of WPS and CMPSs with low DS values (0.04-0.65) was assessed by

monitoring the tensile strength and elongation at break (Fig. 11). As seen in Table 4, the tensile strength of the 100% cotton yarns increases as a result of CMPS sizing. Moreover, the tensile strength of the cotton yarn sized with CMPS-29 (DS = 0.04) showed a higher value than in the case of WPS. Also, the tensile strength of the cotton yarn sized (30/1 Ne) with WPS and CMPS-29 was 21.13 and 23.25 cN/tex, respectively. Otherwise said, the percentage of the increase in the tensile strength was 14.30%.

Compared with waste potato starch, as the DS value of CMPSs decreased until 0.04, they exhibited much better sizing performance. On the other hand, the tensile strength of the unsized cotton yarn (10/1 Ne) and CMPS-29 was 14.90 and 27.96 cN/tex, respectively. The sizing efficiency of CMPS-29 of 87.65% evidences the suitability of the CMPS under study to be used as a sizing agent. Also, it can be observed that the CMPS with DS 0.04 had considerably better sizing properties compared to the WPS sample.

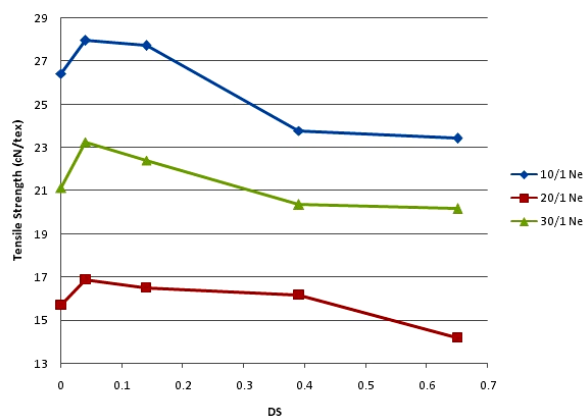


Figure 11: Tensile strength of sized cotton yarns

The results in Table 3 indicate that the cotton yarns of 10/1 Ne and 20/1 Ne, which were sized with CMPS-22 (DS = 0.65) and CMPS-29 (DS = 0.04), exhibited an increase in elongation at break, relative to that sized with WPS, and a slight change or decrease for CMPS-27 (DS = 0.14) and CMPS-25 (DS = 0.39). Also, the elongation at break for the cotton yarn (10/1 Ne) sized with WPS and CMPS-22 was 12.37 and 13.48, respectively. On the other hand, the elongation at break values for the cotton yarns (30/1 Ne) sized with WPS and CMPSs are almost equal.

## CONCLUSION

CMPSs were synthesized for the first time from waste potato starch, obtained from a chips factory, under heterogeneous conditions, as products of the reaction of WPS and MCA in the presence of NaOH. Considering all the studied conditions, it was established that the best results were achieved using IPA as a solvent at 45 °C for 180 min and a NaOH/MCA molar ratio of 2.2:1. Under these conditions, the obtained CMPS-2 showed a viscosity of 14200 mPa's (for 2% CMPS in water at 1 rpm) at the

highest DS. The 100% cotton yarns were sized using CMPS-29, CMPS-27, CMPS-25 and CMPS-22. It was noted that as the DS values of the CMPS decreased, the sizing efficiency increased. The sizing efficiency of CMPS-29 of 87.65% evidenced its suitability to be used as a sizing agent. Additionally, it can be observed that the CMPS with DS 0.04 had considerably better sizing properties compared to WPS.

**ACKNOWLEDGEMENT:** This work was supported by Kahramanmaraş Sutcu Imam University Scientific Research Project (BAP Project Number: 2014/3-12 YLS).

## REFERENCES

- 1 I. Vroman and L. Tighzert, *Materials*, **2**, 307 (2009).
- 2 H. Angellier, L. Choisnard, S. Molina-Boisseau, P. Dole and A. Dufresne, *Biomacromolecules*, **5**, 1545 (2004).
- 3 Z. Stojanovic, K. Jeremic and S. Jovanovic, *Starch/Stärke*, **52**, 413 (2000).
- 4 N. Nagasawa, T. Yagi, T. Kume and F. Yoshii, *Carbohydr. Polym.*, **58**, 109 (2004).
- 5 P. Chatakanonda, S. Varavinit and P. Chinachoti, *LWT-Food Sci. Technol.*, **33**, 276 (2000).

- <sup>6</sup> P. Tolvanen, P. Maki-Arvela, A. B. Sorokin, T. Salmi and D. Y. Murzin, *Chem. Eng. J.*, **154**, 52 (2009).
- <sup>7</sup> H. S. Kim, H. S. Choi, B. Y. Kim and M. Y. Baik, *Carbohydr. Polym.*, **83**, 755 (2011).
- <sup>8</sup> A. Gunaratne and H. Corke, *Carbohydr. Polym.*, **68**, 305 (2007).
- <sup>9</sup> S. Mishra, A. Mukul, G. Sen and U. Jha, *Int. J. Biol. Macromol.*, **48**, 106 (2011).
- <sup>10</sup> T. S. Anirudhan and J. Parvathy, *Int. J. Biol. Macromol.*, **67**, 238 (2014).
- <sup>11</sup> S. E. Barrios, J. M. Contreras, F. Lopez-Carrasquero and A. J. Müller, *Revista de la Facultad de Ingenieria U.C.V.*, **27**, 97 (2012).
- <sup>12</sup> H. Y. Qiu and L. M. He, *Polym. Adv. Technol.*, **10**, 468 (1999).
- <sup>13</sup> K. Sangseethong, S. Ketsilp and K. Sriroth, *Starch/Stärke*, **57**, 84 (2005).
- <sup>14</sup> D. Bhattacharyya, R. S. Singhal and P. R. Kulkarni, *Carbohydr. Polym.*, **3**, 167 (1995).
- <sup>15</sup> T. Nabais, F. Brouillet, S. Kyriacos, M. Mroueh, P. Amores da Silva *et al.*, *Eur. J. Pharm. Biopharm.*, **65**, 371 (2007).
- <sup>16</sup> C. J. Tijssen, H. J. Kolk, E. J. Stamhuis and A. A. C. M. Beenackers, *Carbohydr. Polym.*, **3**, 219 (2001).
- <sup>17</sup> P. N. Bhandari and M. A. Hanna, *Starch/Stärke*, **63**, 771 (2011).
- <sup>18</sup> Y. Bi, M. Liu, L. Wu and D. Cui, *Polym. Adv. Technol.*, **19**, 1185 (2008).
- <sup>19</sup> B. Zhang, H. Gong, S. Lü, B. Ni, M. Liu *et al.*, *Int. J. Biol. Macromol.*, **51**, 668 (2012).
- <sup>20</sup> Z. W. Wu and X. Y. Song, *J. Appl. Polym. Sci.*, **101**, 2210 (2006).
- <sup>21</sup> K. Kwon, J. H. Auh, J. W. Kim, K. H. Park and C. H. Park, *Starch/Stärke*, **49**, 499 (1997).
- <sup>22</sup> W. Lazik, T. Heinze, K. Pfeiffer, G. Albrecht and P. Mischnick, *J. Appl. Polym. Sci.*, **86**, 743 (2002).
- <sup>23</sup> T. Heinze and A. Koschella, *Macromol. Symp.*, **223**, 13 (2005).
- <sup>24</sup> S. Mohapatra, M. Asfer, M. Anwar, S. Ahmed, F. Ahmad *et al.*, *Int. J. Biol. Macromol.*, **115**, 920 (2018).
- <sup>25</sup> P. Rachtanapun, P. Simasatitkul, W. Chaiwan and Y. Watthanaworasakun, *Int. Food Res. J.*, **19**, 923 (2012).
- <sup>26</sup> O. S. Kittipongpatana, J. Sirithunyalug and R. Laenger, *Carbohydr. Polym.*, **1**, 105 (2006).
- <sup>27</sup> W. Yanli, G. Wenyuan and L. Xia, *Carbohydr. Res.*, **13**, 1764 (2009).
- <sup>28</sup> D. K. Raval, S. P. Patel, R. G. Patel and V. S. Patel, *Starch/Stärke*, **10**, 399 (1994).
- <sup>29</sup> D. Bhattacharyya, R. S. Singhal and P. R. Kulkarni, *Carbohydr. Polym.*, **4**, 247 (1995).
- <sup>30</sup> P. M. Ganorkar and A. S. Kulkarni, *Int. Food Res. J.*, **20**, 2205 (2013).
- <sup>31</sup> L. M. Kooijman, K. J. Ganzeveld, R. M. Manurung and H. J. Heeres, *Starch/Stärke*, **55**, 495 (2003).
- <sup>32</sup> O. S. Lawal, M. D. Lechner and W. M. Kulicke, *Int. J. Biol. Macromol.*, **42**, 429 (2008).
- <sup>33</sup> G. K. Bolhuis, K. Zuurman and G. H. P. Te Wierik, *Eur. J. Pharm. Biopharm.*, **5**, 63 (1997).
- <sup>34</sup> N. Huyghebaert, V. Snoeck, A. Vermeire, E. Cox, B. M. Goddeeris *et al.*, *Eur. J. Pharm. Biopharm.*, **59**, 273 (2005).
- <sup>35</sup> E. Csiszar, J. Borsa and S. K. Obendorf, *Arch. Environ. Contam. Toxicol.*, **35**, 129 (1998).
- <sup>36</sup> E. P. A. Kumbasar and M. Bide, *Dyes Pigments.*, **47**, 189 (2000).
- <sup>37</sup> K. M. Mostafa and M. S. Morsy, *Starch/Stärke*, **56**, 189 (2004).
- <sup>38</sup> A. A. Ragheb, H. S. El-Sayiad and A. Hebeish, *Starch/Stärke*, **49**, 238 (1997).
- <sup>39</sup> B. S. Kim and S. T. Lim, *Carbohydr. Polym.*, **39**, 217 (1999).
- <sup>40</sup> T. Spychaj, M. Zdanowicz, J. Kujawa and B. Schmidt, *Polimery (Warsaw)*, **7-8**, 503 (2013).
- <sup>41</sup> Z. Luo and Z. Xu, *LWT - Food Sci. Technol.*, **44**, 1993 (2011).
- <sup>42</sup> F. Cheng, J. W. Betts, S. M. Kelly, D. W. Wareham, A. Kornherr *et al.*, *J. Mater. Chem. B.*, **2**, 3057 (2014).
- <sup>43</sup> T. Spychaj, K. Wilpizewska and M. Zdanowicz, *Starch/Stärke*, **65**, 22 (2013).
- <sup>44</sup> V. H. Kessel, *Starch*, **37**, 334 (1985).
- <sup>45</sup> J. Liu, J. Ming, W. Li and G. Zhao, *Food Chem.*, **133**, 1196 (2012).
- <sup>46</sup> Z. P. Stojanovic, K. Jeremic, S. Jovanovic, W. Nierling and M. D. Lechner, *Starch/Stärke*, **61**, 199 (2009).
- <sup>47</sup> J. Tatongjai and N. Lumdubwong, *Carbohydr. Polym.*, **81**, 377 (2010).
- <sup>48</sup> S. Li, J. M. V. Mujiyambere and M. Liu, *Adv. Mater. Res.*, **233**, 306 (2011).
- <sup>49</sup> X. Li, W. Gao, L. Huang, Y. Wang, L. Huang *et al.*, *Carbohydr. Polym.*, **80**, 768 (2010).
- <sup>50</sup> X. D. Zhang, X. Liu and W. Y. Li, *J. Appl. Polym. Sci.*, **89**, 3016 (2003).
- <sup>51</sup> X. Li, W. Gao, L. Huang, Y. Wang, L. Huang *et al.*, *Carbohydr. Polym.*, **80**, 768 (2010).
- <sup>52</sup> K. Wilpizewska, M. Zdanowicz and T. Spychaj, *Adv. Polym. Technol.*, **32**, 21353 (2013).
- <sup>53</sup> D. Binh, P. T. T. H. Hong, N. N. Duy, N. T. Duoc and N. N. Dieu, *Radiat. Phys. Chem.*, **81**, 906 (2012).
- <sup>54</sup> W. Gao, X. Lin, X. Lin, J. Ding, X. Huang *et al.*, *Carbohydr. Polym.*, **84**, 1413 (2011).
- <sup>55</sup> L. F. Wang, S. Y. Pan, H. Hu, W. H. Miao and X. Y. Xu, *Carbohydr. Polym.*, **80**, 174 (2010).
- <sup>56</sup> A. Hebeish, A. Higazy, A. El-Shafei and S. Sharaf, *Carbohydr. Polym.*, **79**, 60 (2010).