REVIEW

Medium and high substituted carboxymethyl starch: Synthesis, characterization and application

Tadeusz Spychaj, Katarzyna Wilpiszewska and Magdalena Zdanowicz

Polymer Institute, West Pomeranian University of Technology, Szczecin, Poland

Carboxymethyl starch (CMS) could find application in many areas of industry. A review of synthesis methods of medium and high substituted CMS was presented. The influence of synthesis parameters on degree of substitution (DS) as well as reaction efficiency was described. The methodology of CMS physicochemical properties determination as well as the relation between CMS chemical characteristics (e.g. DS, amylose/amylopectin ratio) and its physicochemical properties was presented. Moreover, reported CMS applications were submitted.

1 Introduction

Products based on starch are potentially renewable, bio-degradable and environmentally friendly [1]. However, the shortcomings of native potato starch, such as the lack of free-flowing properties, insolubility in cold water, hardly controlled viscosity after gelatinization and sensitivity of cooked starch to shear substantially limit its use.

Due to the presence of hydroxyl groups in recurrent unit of the polysaccharide chain – starch could be modified chemically. Carboxymethyl starch (CMS) is a green polymer with great importance in pharmacy, medicine, cosmetics, food industry, environmental protection and many other industrial applications. The addition of bulky hydrophilic groups to polysaccharide chains resulted in reduced starch tendency to retrogradation (recrystallization), and cold water solubility. Moreover, it made the polymer less prone to damages caused by heat and microbial attack [2]. Solubility of CMS in cold water increases along with degree of substitution (DS) value increase, and the properties such as: water absorption, adhesiveness and film forming characteristics are improved simultaneously [3]. Similarly, paste and film clarity as well as paste and gel storage stability are significantly improved [4]. Carboxymethylated starch derivatives exhibited lower gelatinization temperature, specific changes in rheological properties and pH stability [5, 6].

In this paper, a review of synthesis methods of medium and high substituted CMS was presented. The influence of synthesis parameters on DS as well as reaction efficiency (RE) was described. Moreover, the methodology of CMS chemical characteristics (DS, amylose/amylopectin ratio, MW) as well as its effect on CMS physicochemical properties was given. Additionally, reported applications of CMS were collected. Finally, research gaps and challenges concerning CMS are formulated.

2 Synthesis of carboxymethyl starch

Carboxymethyl starch was first made in 1924 by reaction of starch in an alcoholic solution with sodium monochloroacetate [7]. From that time various production methods of CMS were carried out to optimize reaction conditions and improve applied properties of the product for various applications. The most important methods include aqueous

Correspondence: Professor Tadeusz Spychaj, Polymer Institute, West Pomeranian University of Technology, ul. Pulaskiego 10, 70-322 Szczecin, Poland
E-mail: tadeusz.spychaj@zut.edu.pl
Fax: +48-91-449-4247

Abbreviations: CMC, carboxymethyl cellulose; **CMS,** carboxymethyl starch; **DS,** degree of substitution; **ERF,** electrorheological fluid; **EtOH,** ethanol; **IL,** ionic liquid; **IPOH,** isopropanol; **MCA,** monochloroacetic acid; **MMT,** montmorillonite; **RE,** reaction efficiency; **SGF,** simulated gastric fluid; **SIF,** simulated intestinal fluid; **SMCA,** sodium monochloroacetate

method, dry method, extrusion technique and organic solvent slurry ways.

The DS is the average number of functional groups introduced into the anhydroglucose unit. CMS could be manufactured with rather wide range of carboxymethyl group substitution using various methods.

Carboxymethyl starch could be produced by wet method using water as the reaction medium [8]. Such a method is applicable for DS up to 0.07, above which starch started to gelatinize.

Basically, the methods performed using dry technique could give CMS with DS up to 0.5 [9, 10]. However, addition of small amounts of alcohols (ethanol, isopropanol) allowed to obtain CMS with DS up to ca. 0.7–0.8 [11, 12].

Recently, Li et al. [11] have obtained CMS with DS up to 0.8 with RE of 39%; carboxymethylation of potato starch was carried out in an electric blender. First, starch (15 wt% of water) and solid NaOH were added and mixed together to form an uniform powder mixture. A small amount of absolute ethanol (2 wt% based on starch) was added. The mixture was stirred for 1 h. Then powder sodium monochloroacetate (SMCA) was added and the reaction was carried out at ambient or elevated temperature (to 70°C) for desired time. Finally, product was washed with 85% aqueous solution of ethanol until no chloride in the filtrate was detected and filtered to remove the salts formed during process. Subsequently, the cake was dried at 313 K for 48 h. Similarly, relatively high DS (0.73) at the optimal reaction conditions (starch/SMCA 1:1, alkalization temperature 35°C, reaction time 60 min, etherification temperature 70°C, reaction time 2.5 h, with some amount of isopropyl alcohol – 1.4 mL/2.5 g NaOH) was reported (http://mt.china-papers.com/?p=164871). Solution viscosity (2 wt%) was higher than 20 000 mPa s. No data about RE was given.

Zhou et al. [12] synthesized CMS with DS up to 0.78 and high RE (up to 90%) using dry method. First, corn starch and fragmentlike NaOH were added to a blender. Then small amount of methanol was added and mixing agitation was conducted for 1.5 h. Next, certain amount of powder-like monochloroacetic acid (MCA) was added and the reactor was cooled if necessary. Finally, substances were allowed to react for various times at 50°C, according to the DS value of the final product; reaction was carried out for 1–5 h. CMS product was purified by filtration, washed with 85% aqueous methanol until Cl⁻ eliminations and dried at 40°C.

Mentioned dry method process allowed to retain granular CMS form thus side products could be easily washed out. The main feature of the dry process was its higher cost efficiency and eco-friendly character, especially in comparison with organic solvent slurry technique.

Reactive extrusion offered simple process with lower amount of solvents and shorter reaction time for preparing

highly substituted CMS than in a case of solvent slurry or dry methods. Bhandari and Hanna [13, 14] described production of CMS from corn starch with DS values up to 1.54 (the highest RE 0.42) in twin-screw extruder using ethanol/water 1:1 weight ratio [13]. Corn starch (8.8 wt% moisture) and SMCA were mixed with 50 wt% aqueous ethanol using planetary mixer. NaOH beads were added to the formulation immediately before extrusion (NaOH/SMCA weight constant ratio 0.74). The extruder was operated at screw speed of 70 rpm without the die. The extruder barrel temperature was set to 80–85–80°C. The configuration and number of kneading blocks were important to obtain the optimal values of DS and RE. CMS microstructure of the obtained product could be classified as: granule damage (without agglomeration or fusion), granule agglomeration and complete fusion (dependent on the experimental conditions).

In other work [14] CMS slightly crosslinked (with sodium tripolyphosphate, citric acid, or epichlorohydrin) designated for tablet disintegrant was synthesized by extrusion process for short residence time (2 min; DS 0.38, RE 81%).

Synthesis of CMS with high DS could be achieved with both MCA and SMCA in organic/aqueous slurries. Water content was the crucial factor for this reaction. In all the methods of CMS synthesis certain amount of water is required in order to swell the starch grains thus making them accessible for the reagents. An excess of water induces agglomeration of the starch particles during process. The most important factor determining technological meaning of the slurry methods is preservation of grain structure in starch derivative even if morphology of granules is changed.

The world production of starch is estimated as ca. 70 mln tons in 2010 [15, 16]. The most important types of starch, i.e. potato, corn, wheat and cassava are produced worldwide (respectively, in European Union) in large amounts (in mln tons): 2.49 (1.60), 45.8 (3.9), 4.9 (3.4) and 7.5 (0), respectively [16]. As the mentioned starches differ regarding their botanical as well as the physicochemical features (e.g. gelatinization temperature for potato: 60–65°C, corn: 75–80°C, wheat: 80–85°C, cassava: 65–70°C) [17] there are not universal carboxymethylation process parameters to perform modification of starch to its carboxymethyl derivatives using slurry methods.

The most representative examples of medium and high substituted CMS synthesis using potato, corn, cassava and wheat starches and slurry method are collected in Tables 1–4, respectively. No multi-step methods were concerned here because of their lower industrial meaning, even if such techniques allowed to obtain CMS with DS values above 2.0 [31].

Referring to Table 1 presenting potato starch modification into CMS one could conclude that: (i) carboxy-

Table 1. Synthesis parameters of carboxymethyl starch prepared by slurry methods in organic solvent/water systems from potato starch

No.	DS	RE (%)	(S)MCA/AGU (mol ratio; DS_t)	NaOH/(S)MCA (mol ratio)	Solvent (wt. %)	Temperature and time (°C/h or min)	Remarks on other experimental parameters and/or procedures	Ref.
1.	1.00	75	SMCA (1.66)	1.0	IPOH/water, 88/12	36/500 min	Optimization of the process conditions on a basis of experimental design; starch humidity not given; starch/solvent weight ratio 11.8/88.2.	[18]
2.	1.30	60	SMCA (2.4)	1.0	Optimal solvent: IPOH/water 90/10 also tested other alcohols	40/ng	Starch humidity: 10–15 wt%; (i) starch added to the solvent mixture, (ii) after 15 min NaOH added, (iii) heating to the reaction temp., left overnight, (iv) SMCA added.	[19]
3.	1.20	80	MCA	ng	IPOH/water, ng	40–60/5 h	Starch humidity not given; (i) MCA neutralized with aqueous NaOH in IPOH, (ii) starch addition, then dry NaOH and temperature increased to 40°C.	[20]
4.	1.36	88	MCA	1.94	IPOH	45/145 min	Starch humidity: 13–17%; IPOH/starch 4.0 cm^3/g; (i) starch alkalization 35°C/45 min, (ii) MCA in IPOH and NaOH added, (iii) etherification 45°C, 100 min.	[21]
5.	0.68	ng	MCA (1.54)	1.50	EtOH/water, 84.5/15.5	46/4 h	Starch humidity: 13–17 wt%; orthogonal experiments, sequence of effective factors for DS was in the order: etherification temp. > alkalization temp. = nNaOH/nMCA > V_2/m_3 > water content in solvent > nMCA/nAGU > mixing time of starch and solvent > charging time of NaOH (divided into two parts).	[22]

IPOH, isopropanol; EtOH, ethanol; ng, not given.

methylated starch with DS in a range of 0.7–1.4 could be obtained with maximum RE typically 60–88%, (ii) in majority cases isopropanol/water mixtures were used with the water content 10–15 wt%, (iii) MCA or its sodium salt SMCA were applied as etherifying agents, (iv) weight ratio of sodium hydroxide into etherifying agent was in a range 1.0–2.0, but higher ratios caused decrease of RE, i.e. higher content of undesirable by-products, such as glycolates, (v) typical range of etherification temperature was 35–50°C to preserve granular character of the product; reaction time could be changed in rather wide range 2.5–5 h. Process could be performed in one- or two-stages, and details of introducing particular reagents could differ (Table 1).

In comparison – carboxymethylation of corn starch offered CMS with DS 0.6 up to even 2.2 with similar maximum RE 55–92% (Table 2). Generally, higher temperature values (50–60°C) and consequently slightly shorter reaction times (2–4 h) were applied. It is a consequence of higher gelatinization temperature of corn

starch in comparison with potato starch (75–80 and 60–65°C, respectively).

In Table 2, process of CMS manufacturing in ionic liquid (IL) was also included even if it was not commercially important yet, and gave CMS which had to be precipitated from IL with ethanol. However, it was included here because of high potential of ILs as reaction media for modification of starch [34].

Cassava starch based CMS has been prepared with DS 0.8–1.4 and RE 56–74% in IPOH/water (10–19 wt%) or EtOH/water slurries at 30–55°C for 3–5 h. In one example of using ultrasonic irradiation [29] nanosized particles (100–400 nm) were produced (Table 3).

High substituted wheat starch based CMSs (DS 1.0–1.4) could be obtained (RE 60–82%) while keeping etherification temperature higher than for other starch substrates (gelatinization temperature of wheat starch is 80–85°C; Table 4). The process could be shortened from several hours to 10–30 min using microwave irradiation [32].

Table 2. Synthesis parameters of carboxymethyl starch prepared by slurry methods in organic solvent/water systems from corn starch

No.	DS	RE (%)	(S)MCA/AGU (mol ratio; DS_t)	NaOH/(S)MCA (mol ratio)	Solvent (wt%)	Temperature and time (°C/h or min)	Remarks on other experimental parameters and/or procedures	Ref.
1.	0.95–1.30	ng	SMCA	ng	EtOH/water	58/100 min	Starch humidity not given; (i) alkalization performed by mixing 40 g starch, 120 cm^3 EtOH and 28 cm^3 11.5 M NaOH at 25°C, (ii) after 20 min stirring SMCA was added and reaction system heated to 58°C and stirred 100 min.	[23]
2.	0.60	92	MCA	ng	IPOH/water	55–60/4 h	Starch humidity not given; one-step reaction: 30 g starch in 400 cm^3 IPOH, stirring 1 h at room temp. next 80 cm^3 30% NaOH was added, then MCA (36 g) was added step by step. Reaction was performed at 55–60°C/4 h.	[24]
3.	0.76	76	SMCA	1.20	Ionic liquid: 1-butyl-3-methyl-imidazolium chloride	90/3 h	Dry starch applied, heated in IL to 90°C then: (i) NaOH + SMCA added, (ii) heating through 3 h, (iv) gelatinized CMS precipitated in EtOH.	[25]
4.	2.20	55	MCA	2.50	IPOH/water	50/2 h	One step carboxymethylation; volume fraction of water to IPOH was 2.4%; details not accessible.	[26]

IPOH, isopropanol; EtOH, ethanol; ng, not given.

Basing on the examples mentioned above one could see that the cheapest and most often commercially applied processes are those realized by dry methods, however maximum DS values obtained for CMS produced are at medium range (0.5 up to 0.7) when some amount of alcohol (ethanol, methanol, or isopropanol) are used. RE could be high (up to 80%) with relatively low amount of NaOH used. The product could be additionally purified by extraction with alcohol/water mixtures. High productivity and proecological features are the main advantages of that technology.

On the other hand high substituted CMS (DS typically up to 1.2) could be effectively obtained using slurry methods, the most often in isopropanol/water or ethanol/water mixtures. However, slurry techniques exhibited lower productivity and necessity of operating with large amount of alcohol/water mixtures. This technique is also relevant when product purification is necessary (e.g. for pharmacy, cosmetics, or food industry).

Reactive extrusion as solely continuous process could be considered as potentially industrially applicable because offered similar quality product as dry methods. However, some amount of organic solvent was necessary to be performed smoothly. In addition, extrusion processing exhibits some advantages important from technological viewpoint as

compared with other methods, such as: (i) high productivity with constant product properties, (ii) energy efficiency, (iii) elimination or substantial limitation of organic solvent usage, (iv) eco-friendly character of the process. Some weak points of extrusion processed product are: lower purity than in case of product prepared by suspension modification method (some impurities removed with post-reaction liquor), the necessity of product grinding and sieving and irregular shape of CMS powder.

However, reactive extrusion processing optimization could be expected resulting in its wider industrial application than up to today.

3 Methods of structure and physicochemical properties of CMS determination

3.1 The degree of substitution

The DS value mainly determines the properties of CMS derivatives. However, to fully understand the structure–property relationship other parameters should be considered, such as: distribution of the carboxymethyl groups within repeating unit, CMS MW and others.

Table 3. Synthesis parameters of carboxymethyl starch performed by slurry methods in organic solvent/water systems from cassava starch

No.	DS	RE (%)	(S)MCA/AGU (mol ratio; DS_t)	NaOH/(S)MCA (mol ratio)	Solvent (wt%)	Temperature and time (°C/h or min)	Remarks on other experimental parameters and/or procedures	Ref.
1.	0.8–1.40	56, 74	SMCA (2.50)	1.0–1.5	IPOH/water, 90/10	55/300 min	Starch humidity not given; (i) IPOH + water and starch added and mixing at room temperature, (ii) heating to the desired temp. and NaOH pellets introduced, (iii) after 15 min mixing SMCA powder added (amount of starch 4–8 wt%).	[27]
2.	0.86	57	SMCA (1.1–1.5)	1.8–1.9	IPOH/water, 81–83/19–17	40/3 h	Starch humidity: 10 wt%; (i) starch dispersed in IPOH/water and mixed, (ii) NaOH added, (iii) heating up to 40°C, (iv) after 15 min of stirring SMCA added, (v) stirring at pH 5.5–6.5 (HCl correction) for 3 h.	[28]
3.	1.15	ng	MCA (0.5–1.50)	1.5–4.0	EtOH/water, ng	30–55/ng	Starch humidity not given; (i) starch dispersed in EtOH, (ii) aqueous NaOH added, stirring at 40°C/1 h, (iii) MCA solution added then ultrasonic irradiation, (iv) temp. adjustment between 25 and 55°C. Nanosized particles obtained (100–400 nm).	[29]
4.	1.24	ng	MCA (0.8)	0.8	EtOH/water, 90/10	50/2 h	Starch concentration: 35 wt%; other reaction details not accessible.	[30]

IPOH, isopropanol; EtOH, ethanol; ng, not given.

Table 4. Synthesis parameters of carboxymethyl starch performed by slurry methods in organic solvent/water systems from wheat starch

No.	DS	RE (%)	(S)MCA/AGU (mol ratio; DS_t)	NaOH/(S)MCA (mol ratio)	Solvent (wt%)	Temperature and time (°C/h or min)	Remarks on other experimental parameters and/or procedures	Ref.
1.	1.40	82	SMCA (1.70)	1.7	IPOH	55/5 h	Starch humidity: 14–19 wt%; (i) 50 g of starch suspended in 150 cm^3 IPOH and mixed for 60 min after addition aq. NaOH solution, (ii) SMCA 6 g was added and temp. raised to 55°C and then kept for 5 h.	[31]
2.	1.0	60	MCA	2.0	IPOH or IPOH/water 80/20	30/10–30 min micro-wave radiation	Starch humidity not given; (i) starch dispersed in IPOH/water, (ii) NaOH pellets added and mixing at 30°C/0.5 h, (iii) MCA added gradually while stirring, (iv) mixture subjected to microwave irradiation 180 W/10–30 min at interval of 1 min.	[32]
3.	1.15	ng	MCA (1.40)	1.8	EtOH/water	50–55/2–3 h	Starch humidity not given; (i) 4 g of starch, 6 cm^3 of water, 60 cm^3 of absolute EtOH, (ii) alkalization temp. 35–40°C/0.5–1.0 h, (iii) etherification temp. 50–55°C/2–3 h.	[33]

IPOH, isopropanol; EtOH, ethanol; ng, not given.

There are several techniques for determination of DS. Owing to simplicity and reproducibility the most common are classical titration methods, like direct titration, back titration and Cu salt precipitation [35, 36]. Additionally, modifications of the mentioned methods are reported, e.g. two step: titration and residue on ignition method [37].

In direct titration method, the acid form of CMS is dispersed in water (or aqueous NaCl solution) and titrated with sodium hydroxide solution of known molarity [23, 38, 39]. Mostly applied is the back titration method where preliminary free acid form of CMS is obtained by a treatment of CMS sodium salt dispersed in ethanol with concentrated hydrogen chloride [40] (acid–base back titration method is described in IS011216). Subsequently, aqueous sodium hydroxide is added and the excess of NaOH is back titrated with HCl using phenolphthalein as an indicator [23]. A salt precipitation method was adapted for CMS by Kessel [41]. It is assumed that 1 mol Cu ion interacts with carboxylic group. Sodium CMS salt is dissolved in water and precipitated by adding $CuSO_4$ solution. The excess of $CuSO_4$ is determined by titration with EDTA in the presence of an indicator (e.g. murexide) [23]. Stojanović et al. [23] compared the three methods mentioned above and concluded that back titration method was the most accurate one. Moreover, it should be stated that titration methods can be used for CMS samples with DS values up to 1.5 [40].

Spectroscopic (^{1}H NMR, ^{13}C NMR and ^{13}C CP/MAS NMR: Cross Polarization/Magic Angle Spinning/NMR) and liquid chromatographic methods could be applied over the whole DS value range and required complete hydrolysis of the polysaccharide into modified glucose units [42, 43]. NMR spectroscopy could be performed using intact polymer [44, 45], although the measurements of hydrolytically degraded sample approach gives the direct quantitative evaluation of the spectra [44]. Polymer dissolved in D_2O could give very viscous solution, however, using ultrasonic treatment partially degrades CMS without splitting of any carboxymethyl function and without occurrence of monomeric or dimeric components [39].

^{1}H NMR spectroscopy (CMS degraded with D_2SO_4) allows the evaluating of partial DS values at three positions of anhydroglucose unit and eventually the total DS [31].

HPLC (CMS hydrolysis in: e.g. H_2SO_4 or $HClO_4$) allows to quantify mono-, di- and tricarboxymethyl glucose, unmodified glucose, side product (sodium glycolate) as well as the regioselectivity and the total DS, which consequently gives additional information about the substitution pattern [42].

Recently Fourier transform mid-infrared spectroscopy coupled with partial least squares was used for DS determination, however it was applied only to low substituted CMS (up to 0.288) [46].

The introduction of carboxymethyl groups can be evidenced by FTIR spectroscopy (Fig. 1). The special pattern,
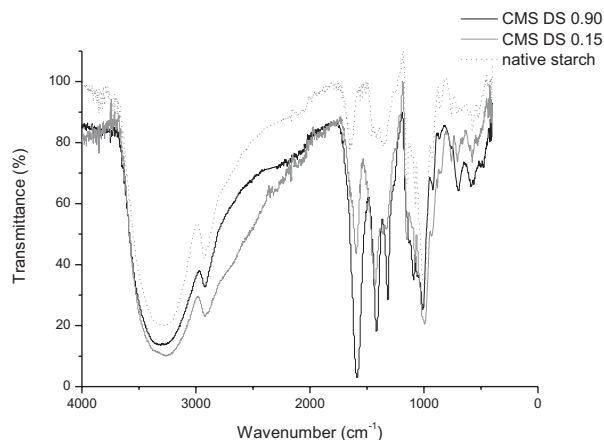

Figure 1. FTIR spectra of native potato starch and CMS derivatives with DS 0.15 and 0.9 (Wilpiszewska, K., Zdanowicz, M., Spychaj, T., submitted).

typical for native starch, in the region of 970 and 1200 cm^{-1} is preserved in CMS samples. The CMS carboxylate (–COO–) gives the strong bands at about 1600, 1440 and 1325 cm^{-1} [43]. Protonated carboxylic groups (–COOH) give a C=O band at 1735 cm^{-1} [47]. The broad band between 3600 and 3000 cm^{-1} is attributed to O–H stretching (due to hydrogen bonding involving hydroxyl groups on the starch molecules) and at 2900 cm^{-1} to CH_2 symmetrical stretching vibrations; by carboxymethylation the intensity of both bands decreases [35, 38, 43].

3.2 The degree of crystallinity

The degree of crystallinity of starch as well as CMS derivatives can be determined by XRD technique. Generally, CMS exhibits significantly reduced degree of crystallinity when compared to native starch – observed as reduced intensity of diffraction patterns [48, 49] (Fig. 2). The loss of crystallinity could be due to: (i) the rupture of starch granules caused by heat treatment together with the presence of water [47], (ii) the alkaline environment during chemical modification [37], (iii) breaking the hydrogen bonds that maintained the crystalline structure by replacing hydrogen atoms of OH by carboxymethyl groups [37], (iv) the presence of solvent during modification process, such as *n*-propanol or isopropanol (carboxymethylation using methanol as a solvent caused only slight crystallinity reduction) [49]. The loss of crystallinity is important in some applications, like preparation of hydrogels, as increase of amorphous region would mean enhanced ability of CMS to absorb water [38, 39].

3.3 Morphology observations

The most common tool of CMS morphology observation is SEM technique. It allows investigating the effect of
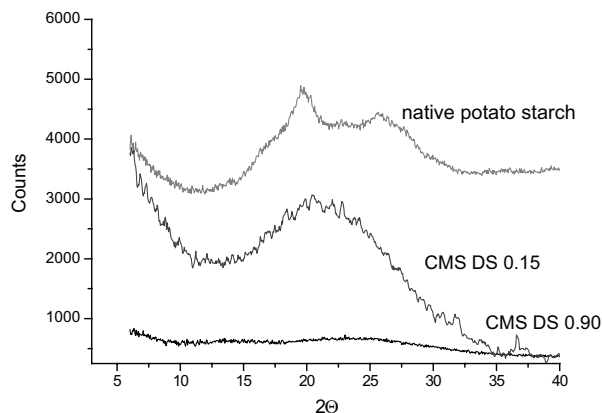
Figure 2. XRD patterns of native potato starch and CMS derivatives with DS 0.15 and 0.9 (unpublished results).

carboxymethylation and environment conditions on structural changes of starch (preserved/disrupted granules, size, shape, the presence of agglomerates) as well as suggesting possible changes of crystallinity [39, 43].

3.4 Thermal properties

For native starch DSC measurements allow to determine the onset temperature, peak temperature, conclusion temperature and the enthalpy of gelatinization. During gelatinization of starch due to the presence of water and heat the intermolecular bonds break down. The penetration of water decreases the number and size of crystal regions, which diffuse and the chains begin to separate into amorphous form – the randomness increases [35]. As the result no peak in DSC thermograms of CMS samples is observed, the gelatinization enthalpy could not be determined, which is an indication that amorphous region increased after carboxymethylation [49]. Thus, DSC thermograms of CMS correlate with the XRD results. This trend could be observed regardless of the DS value [39].

Thermogravimetry analysis provides important information about thermal stability of polymeric materials. TGA curves of native starch and CMS show usually a pattern of three-step weight losses (Fig. 3) [2]. The first one in a range of 60–120°C corresponds to the water evaporation [38]. The second and the third steps correspond to the decomposition of the starch material. Water is formed by inter- and intramolecular condensation of hydroxyl groups and is the main product of decomposition below about 300°C [2]. Further heating up to 500°C results in carbonization and ash formation, CO_2 is evolved [50]. The residual mass at 500°C for CMS could be higher than native starch because of the inorganic components formed during starch carboxymethylation [39].
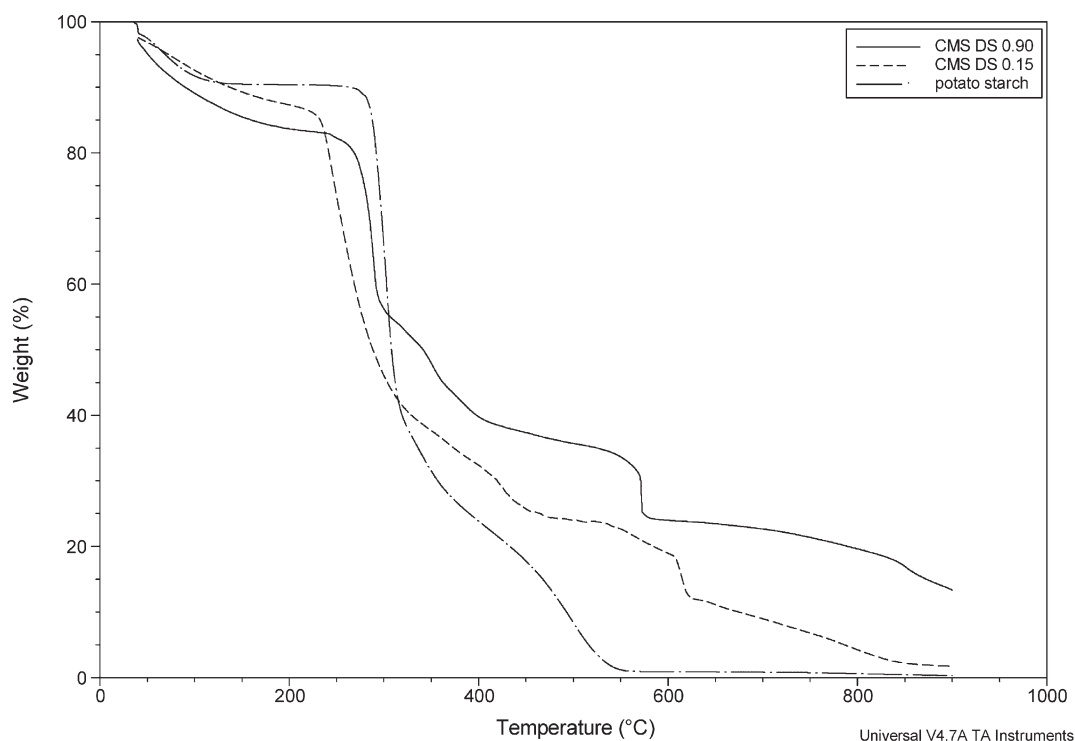

Figure 3. TG patterns of native potato starch and CMS derivatives with DS = 0.15 and 0.9 (Wilpiszewska, K., Zdanowicz, M., Spychaj, T., submitted).

The range of CMS maximum degradation depends on the source of starch as well as the DS and generally occurs within about 250–380°C. In this range 30–40% of the total mass was lost; for native starch it is about 60%. Since the main decomposition mechanism is the dehydration reaction between hydroxyl groups, it may be concluded that the lower amount of OH groups remained on the starch derivative (the higher DS value) the more stable it is [50]. Higher thermal stability of CMS is desired when its further processing is required.

3.5 Viscosity of CMS aqueous solutions

The CMS solubility in water is a complex phenomenon. It mainly depends on temperature and DS of starch derivative. Moreover, only Na-carboxylate form of CMS is soluble in water [51]. In general, higher substituted CMS exhibited higher cold water solubility [4]. Moreover, the amylose content in a starch source is important as Volkert et al. reported [52] lower solubility of waxy maize starch-based CMS than potato or corn-based CMS, ca. 95 and ca. 100%, respectively.

Similarly, the viscometric characteristics of CMS aqueous solutions mainly depend on temperature, CMS degree of substitution and MW [53]. CMS aqueous solutions are non-Newtonian liquids [28]. Generally, higher substituted CMS gave aqueous solutions of higher viscosities than low substituted derivatives [11]. This is possibly caused by higher density of negatively charged carboxymethyl groups and therefore greater electrostatic repulsion between high DS polysaccharide chains, molecules tended to exist in a more expanded state, resulting in higher viscosity value [4].

It is well known that viscosity of polysaccharide is a function of MW [28]. The CMS synthesis method requires alkaline conditions which at elevated temperature could cause carbohydrate molecules degradation. Thus, CMS with similar DS value could exhibit various viscosity patterns. Additionally, starch source also plays a role as amylose/amylopectin ratio seems important. Tatongjai and Lumdubwong [4] reported higher viscosity value for CMS (at similar DS level) with higher amylopectin content (5% w/v solutions). Volkert et al. [52] compared the shear viscosities of 2% CMS (DS 1.1–1.3) solutions prepared from potato, corn, wheat, waxy and high amylose starch at the shear rate of 2.55 s^{-1}. The values of potato, wheat and corn starch were similar (about 1000 mPa s), whereas the viscosity of waxy corn starch CMS was nearly ten times higher (9200 mPa s). On the other hand high amylose CMS exhibited very low viscosity (about 1 mPa s).

It is well established that polymer concentration affects the viscosity value. Yaacob et al. [54] reported that viscosity of CMS (DS 1.05) aqueous solutions increased exponentially as solid content increases. Moreover, at 8 w/v%

concentration reached ca. 83 mPa s, what fulfils the requirements of sprayable coatings applications.

The viscometric characteristics of CMS aqueous system could be modified by introduction of nanofiller, such as kaolinite [55] or montmorillonite (MMT; K. Wilpiszewska, M. Zdanowicz, T. Spychaj. submitted). The viscosity level of CMS/MMT systems depends on CMS degree of substitution, MMT type and concentration. Applying sodium MMT resulted in almost double viscosity increase at 1 rpm from 14 000 for pure CMS (DS 0.9) up to ca. 26 000 mPa s (2 phr MMT). In contrary, when organophilized MMT (with some hydroxyl groups in modifying ammonium alkyl substituents) was used only slight viscosity increase was noticed (little or no change of viscosity; K. Wilpiszewska, M. Zdanowicz, T. Spychaj. submitted).

3.6 Other methods

Beside the physicochemical properties evaluating techniques mentioned above there are more testing methods, such as: biodegradability [52], in vivo digestibility [56], light transmittance of CMS paste or solution [28], ζ-potential and absorption capacity [52, 57, 58], conductivity of CMS dispersions [59]. They are not the subject of this paper as are strictly related to specific CMS application.

4 Application of carboxymethyl starch

Carboxymethyl starch is cold water soluble material giving viscous, colourless and transparent solutions. It could be applied in food, medicine, pharmacy [60], textile [61] and paper sizing, printing, electrodes, ceramics (www.modifiedstarchproducts.com), drilling fluids [62], as corrosion inhibitors [63] or electrorheological fluids [55, 59]. However, they mostly correspond to CMS of low DS (below 0.4), as mainly such products are commercially available. In this paper, only the applications of moderate and high substituted CMS are presented.

4.1 Medicine, pharmacy, cosmetics and food additions

Non-toxic character and natural origin of CMS allow applying it in pharmacy, medicine, cosmetics and food industry.

In pharmaceutical industry, CMS is typically applied as tablets disintegrant; however, for that purpose mainly low substituted (DS ca. 0.3) polymer (partially crosslinked) under the name sodium starch glycolate is used [19, 64].

Sen and Pal [65] described using CMS (DS up to 0.6) for controlled release of acetylsalicylic acid from tablets containing poly(vinylpyrrolidone) as a binder. The rate of

model drug release increased with pH increase during in vitro tests. The usage of CMS allowed to release the drug in lower gastrointestinal tract (faster drug release in alkaline pH) thus minimizing undesirable side effects of acetylsalicic acid: ulcers and stomach bleeding at higher doses.

High amylose corn starch based CMS with DS up to 1.74 has been investigated as model drug (acetaminophen) release in simulated gastric fluid (SGF, pH 1.2) and intestinal fluid (SIF, pH 6.8) [66]. The polymer with DS between 0.9 and 1.2 could be used as delayed release excipient since drug release in SGF was driven by diffusion over a period up to 20 h and in SIF by fast erosion lowering to <3 h the complete release of the drug.

Hydrogels based on crosslinked potato starch modified with MCA and dichloroacetic acid with DS 0.4–0.5 have been synthesized, characterized and applied as slippery agents for ultrasonic medical examinations [1]. Stable etherified gel with a polymer content of 5 wt% exhibited the best accordance with rheological benchmark parameters and ultrasonic pictures.

Carboxymethyl starch has wide applicability in food industry due to high ranges of viscosity and stability. Generally, DS of CMS applied in food industry – by analogy with carboxymethyl cellulose (CMC) – could be in a range of 0.4–1.4 (as allowed for CMC according to respective regulations [67]). CMS could play a role of emulsifying, stabilizing and suspension stabilizing agent.

Its usage allowed keeping equality and stabilization of products, prevents albumen from agglomerating, and improves the quality of cream drinks. It could also act as fresh meat, vegetable and fruit preservative. CMS could be sprayed on food forming thin film which could keep food from decomposing [10]. Moreover, CMS exhibited fermentation stability when DS was above 0.4 [68].

It could be a replacement for fat in meat products [69]. Moreover, because of low glicemic index it could be applied in special products for diabetics [56].

It is used in noodles to improve consistency, reduce softening; in soups to reduce clouding; in bakery products to reduce retrogradation, prolong stability and anti-tensile force, in pie filling as stabilizer at high temperature, shear stress and pH; in ice cream to prevent ice forming [54]. CMS could be added to yoghurts and sauces as a stabilizer and thickener for snacks [70].

Highly substituted CMS could find an application as a colloidal agent in cosmetic industry or for replacing of non-biodegradable polyacrylates in detergents [13, 52].

Addition of CMS increased the suspending power and the overall washing efficiency of soap due to increased solubility [2]. CMS could be considered as thickening agent and surfactant for personal care [71].

According to other sources crosslinked CMS could be used as water absorbent [72, 73].

4.2 Environmental and technical applications

Radiation cross-linked CMS with DS 0.92 were tested for iron (ferrous sulphate) removal from aqueous solutions [58]. The iron removal capacity was almost independent of the pH of metal solution in the acidic range (pH 3–5); the adsorption capacity improved when pH approached neutral (but the iron showed complete precipitation at pH 7). High DS and crosslinking of CMS increased the metal-scavenging capability up to the level required for industrial applications [74].

The ability of binding or chelating metal ions by carboxyl groups of CMS could be used to produce pigmenting fillers in paper industry. CMS with high DS value (1.06) were used for insoluble CMS/metal cation complexes formulations [75]. These hybrid fillers with great particle size could affect optical and mechanical properties of paper sheet. Moreover, hybrid fillers exhibited good dispersability in water even after a few weeks of storage. Visual examinations showed that complexes of CMS with Ba^{2+} and Zr^{4+} could be well introduced into the paper as filler.

Radiation cross-linked CMS nanogels can be used in agriculture for growth of good Lactobacillus bacteria acted as a microbial biopesticides [45].

Zhou et al. [3, 12] reported using CMS as a shell–core main adhesive in a foundry. The CMS bonded shell–cores with the best properties (viscosity, flowability and specific adhesive strength) were obtained for DS ca. 0.5. The CMS bonded sand core as replacement of commonly used furan resins could reduce foundry industry pollution, reduce costs and improve casting quality.

Highly substituted CMS (DS 1.3) was applied as a thickener in reactive dye printing on textile [19]. The dye reacts with primary hydroxyl groups of the cellulose fibres of the textile and forms a chemical bond. Native starch contains also primary OH groups and these cause a loss of the dye. CMS could be an alternative to commonly used sodium alginate (which does not contain primary OH groups). The amount of primary hydroxyls of the thickener is a key factor; thus selective substitution of starch primary OH into carboxymethyl groups would prevent a loss of the dye. As primary OH groups are less reactive than secondary ones high DS is required.

Tatongjai and Lumdubwong [4] applied CMS as textile print paste. Print paste based on moderate DS CMS from rice starch was superior (higher cold water solubility, yield stress, apparent viscosity) to low substituted CMS (0.6 and 0.2, respectively). Moreover, at similar DS level (i.e. 0.6) samples printed using CMS with higher amylose content displayed better colour strength (equivalent to sodium alginate) than in case of using waxy starch based CMS. The explanation could be both high viscosity (a lack of penetration during colour fixation process) as well as cold

water solubility (facilitating of dye removal during the washing-off step) of the waxy rice starch based CMS.

CMS could be used as a dispersing phase for nanofilers, such as: kaolinite [76], or feldspar [77] in electrorheological fluids (ERF). CMS formed a coating on the surface of kaolinite/DMSO intercalate ensuring the high intercalation rate and enhancing the electrorheological effect. With the CMS DS value increase (up to 0.6) the electrorheological effect of ternary composite ERF was enhanced [76].

Carboxymethyl starch was successfully applied as water reducing agent for cement [58, 78]. The CMS (corn starch based, DS ca. 0.5) exhibited good dispersion capacity and stability. However, it is essential that the MW of modified starch product was ca. 10 000 g/mol.

Carboxymethyl starch was also added to mortar to improve the construction performance, such as water retaining, thickening, retarding and adhering (www.engpapers.com/73060.html). Two DS values of CMS applied were compared: high and low (0.8 and 0.2, respectively) for the same mortar test (CMS content 0.05–0.5 wt%). The results showed that using high substituted CMS gave better mortar considering water retention and consistency, lower apparent density, similar in retardation when compared to low substituted CMS. Moreover, applying CMS with higher DS could increase the adhesive strength of hardened mortar, thereby the mortar durability. Additionally, it could be compounded with other polymer with good prospects for development. Comparing other water soluble polymers, such as cellulose ethers or gum powder used for mortar applications, CMS with high DS was superior as its raw material was easily available, and not expensive exhibiting similar performance.

5 Conclusions

Carboxymethyl starch is biodegradable, and non-toxic polymer based on renewable resource. There are a few synthesis methods for medium and high substituted CMS, the most technologically effective seems to be dry (periodic as well as continuous processing) and slurry techniques. Physicochemical properties of CMS depend on starch source (amylose/amylopectin ratio), MW, carboxymethyl groups distribution, but most of all on the DS. Because of great variety of CMS products it could be used in wide areas of applications, from highly pure and sophisticated medical and pharmaceutical, via food, textile and paper industry, to more technical, like foundry binders.

Still some CMS research gaps and challenging fields exist, such as: (i) evaluation of an influence of synthesis parameters on CMS MW, (ii) relation between MW and some important utility properties (viscosity, stability of aqueous solutions), (iii) optimization of relation between CMS degree of substitution and synthesis RE, especially for more eco-friendly process like reactive extrusion, (iv) study on interaction between CMS and cationic (or nonionic) surfactants in aqueous systems, and an application of the formed complexes, (v) further research on sorption properties and application of the crosslinked CMS, (vi) study on physicochemical interactions between CMS chains and some nanoparticles, e.g. graphene or carbon nanotubes in aqueous dispersions, as well as evaluation of possible applications of such nanocomposite materials.

As an interest of using materials based on renewable resources, further development of CMS derivatives it is expected, including nanostructure (e.g. CMS-based nanocarriers), and environmentally responsive materials (e.g. in medical sensors).

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