

# Characterization of starch and its mono and hybrid derivatives by thermal analysis and FT-IR spectroscopy

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**Abstract** Carboxymethylation of wheat starch and  $\alpha$ -cyclodextrin followed by ultrasonic treatment of carboxymethyl wheat starch afforded starch derivatives differing in molecular size. Their degree of substitution was estimated to be 0.6. Starch materials were further sulfated to give hybrid derivatives with carboxymethyl and sulfate groups. A series of wheat starch and  $\alpha$ -cyclodextrin derivatives were characterized by FT-IR spectroscopy and thermogravimetric analysis. Thermal analysis of starch and their derivatives revealed information concerning their thermal stability and decomposition. It has been found that carboxymethylation and sulfation decrease the thermal stability of starch materials. Similarly, their hybrid carboxymethyl-sulfate derivatives showed the same effect. Further, it has been found that the thermal stability of cyclic molecules was higher in comparison with linear ones.

**Keywords**  $\alpha$ -Cyclodextrin · Carboxymethyl starch · FT-IR spectroscopy · Hybrid derivatives · Sulfated starch · TG/DTG curves · Thermal analysis · Wheat starch

## Introduction

Polysaccharides are among the most widespread organic compounds in the plant kingdom. They are typically complex carbohydrate biopolymers composed of monosaccharide

units linked together by glycosidic bonds into linear or branched chains of different length, and are classified on the basis of their main building units, i.e. monosaccharide components, type of linkages and the anomeric configuration of glycosidic linkages. Polysaccharides play crucial roles in life processes of all plants. They can be divided into several broad groups according their functions i.e. structural polymers (cellulose), protective polysaccharides (pectin and hemicelluloses) and reserve polysaccharides (starch). Further, polysaccharides can form glycoconjugates with proteins and lipids resulting in biological macromolecules in the cell wall and cell wall membranes, and play important roles in many physiological and biochemical processes.

From an industrial point of view, one of the most important polysaccharides is starch. Native starch and its derivatives are used mainly in the food industry (as a main nutrient for humans), in pharmaceutical, medicinal, paper and pulp industries, printing and textile industries, etc. Starch is attractive as a raw material due to its low cost, biodegradability and simple chemical modification. Native starch is stored in plants in the form of insoluble rigid granules and is composed of two distinct components, amylose and amylopectin. Their ratio depends on the plant source and in general amylose content is higher than that of amylopectin. Amylose is a linear polymer composed of  $\alpha$ -(1,4)-linked glucose units, made up of several thousand glucose residues which are coiled into helical shape. It is insoluble or partly soluble in water. Amylopectin is a branched polysaccharide composed of  $\alpha$ -(1,4)-linked glucose units some of which are branched at C-6. Its molecular mass is higher in comparison with amylose and it is easily solubilized in water.

Low molecular weight fragments of starch can be found in cyclic form as cyclodextrins (or cycloamyloses). Typical

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cyclodextrins are composed of 6–8 glucose units linked by  $\alpha$ -1,4-glycosidic linkage. Moreover, larger cyclodextrins with 32 or even with 150 glucose residues are found as well. Cyclodextrins are produced from starch by means of enzymatic conversion and have found a wide range of applications in food, pharmaceutical (delivery of drugs), chemical, agriculture and other industrial contexts.

All carbohydrates, i.e. monosaccharides, oligosaccharides and polysaccharides upon heating undergo several physical and chemical transformations which can be studied by thermogravimetric analysis. There have been several reports of the thermal decomposition of native starches isolated from different plant origin: however, no significant differences in their thermograms were noticed [1–7]. It has been found that thermal treatment of dry starch leads to its depolymerization if the temperature does not exceed 300 °C [8]. Thermal properties of various starch derivatives with different degree of substitution have been studied in an inert atmosphere [9–14] as well as in air [15, 16]. Thermogravimetric studies showed characteristic degradation patterns of individual starch derivatives differing in thermal stability.

The aim of our work is to characterize the thermal behavior of wheat starch, its sulfate, carboxymethyl and hybrid derivatives as well as the low molecular weight  $\alpha$ -cyclodextrin, its carboxymethyl, sulfate and hybrid derivatives.

## Experimental

### Plant material and chemicals

Wheat starch (WS) was obtained from Duslo Šal'a (Slovakia),  $\alpha$ -cyclodextrin ( $\alpha$ CD), sodium salt of monochloroacetate and chlorosulfonic acid were purchased from Sigma-Aldrich (Germany).

### General methods

Solutions of polysaccharides were concentrated under reduced pressure at a bath temperature of 40 °C. Elemental analysis was performed by EA 1108 apparatus (FISONS Instruments, East Grinstead, U.K.). Sulphur content was determined by Schöniger [17].

The molecular size distribution pattern of polysaccharides was determined by Shimadzu apparatus using a tandem of two HEMA-BIO columns 1000 followed by HEMA-BIO 300 column and HEMA-BIO 100 followed by HEMA-BIO 40 column (Tessek, Prague, Czech Republic) of dimensions 8 mm  $\times$  250 mm. As a mobile phase 0.02 mol phosphate buffer pH 7.2 containing 0.1 mol NaCl

was used at a flow rate of 0.8 mL min<sup>-1</sup>. A set of pullulan standards was used for calibration of the column (Gearing Scientific, Polymer Lab., Hertfordshire, UK). Fourier transform infrared spectra (FTIR) of the samples were recorded with a Nicolet Magna 750 spectrometer (Nicolet, Madison, USA) with a DTGS detector (Nicolet, Madison, USA) and OMNIC 3.2 software (Nicolet, Madison, USA). The polysaccharides were measured in the form of KBr pellets with a sample/KBr ratio 1/200 mg.

Simultaneous TG/DTA curves have been acquired on T. A. I. sdt 2960 device, the sample mass was 20 mg, heating rate was 10 °C.min<sup>-1</sup>, ramping from ambient temperature to 500 °C in an air atmosphere. TG mass losses and DTA effects were analyzed using the T. A. I. Thermal Analyst package.

### Preparation of carboxymethylated derivatives of carbohydrates

Wheat starch and  $\alpha$ -cyclodextrin were solubilized in 20% sodium hydroxide solution for 1 h at room temperature [18]. Isopropyl alcohol and a sodium salt of monochloroacetic acid were added and the suspensions were stirred till reaction mixtures were completely homogeneous ( $\sim$  2 h). Reaction mixtures were subsequently neutralized with diluted hydrochloric acid and carboxymethylated starch (CWS) was recovered after dialysis by freeze-drying while partly carboxymethylated  $\alpha$ -cyclodextrin (C $\alpha$ CD) was desalted by gel filtration on a column of Bio-Gel P2 and freeze-dried.

### Estimation of carboxymethyl content

The carboxyl content in carboxymethylated products was determined by potentiometric titration. A sample of carboxymethyl derivative in sodium form was dissolved in deionized water, passed through cation exchanger (H<sup>+</sup>) and titrated with 0.1 mol potassium hydroxide solution, free of carbonate upon stirring. The degree of substitution of carboxymethyl derivatives was calculated according to the reported method [19].

### Depolymerization of carboxymethylated starch

Wheat carboxymethyl starch was dissolved in distilled water and partly degraded by ultrasound disintegration (Fischer Scientific Sonic Dismembrator Model 500, Germany) operating at a frequency of 20 kHz for 30 and 60 min. Both fractions were freeze-dried to give partly depolymerized fractions CWS<sub>30</sub> and CWS<sub>60</sub>.

## Sulfation of starch polysaccharides and $\alpha$ -cyclodextrin

Wheat starch, its depolymerized carboxymethyl derivatives, i.e. CMS<sub>30</sub> and CMS<sub>60</sub> and  $\alpha$ -cyclodextrin ( $\alpha$ CD), and its carboxymethyl derivative (C $\alpha$ CD) were suspended in DMF and pyridine and stirred at room temperature. Chlorsulfonic acid–pyridine complex [20] was added and the mixtures were stirred at 60 °C for 2 h. Reaction mixtures were cooled with ice and neutralized with sodium hydroxide solution to pH 7.0, dialyzed one day in tap water and 2 days in distilled water, concentrated and freeze-dried.

Sulfated and carboxymethyl-sulfated  $\alpha$ -cyclodextrins (S $\alpha$ CD and CS $\alpha$ CD) were recovered by gel filtration on a column of Bio-Gel P2. Ten mL fractions were collected and analyzed for carbohydrate content [21]. Desalted tubes were combined and freeze-dried.

## Results and discussion

Carboxymethylation of wheat starch with a sodium salt of monochloroacetic acid in sodium hydroxide-isopropyl alcohol suspension afforded hydrophilic carboxymethyl starch derivative (CWS). It was recovered from the reaction mixture after neutralization and dialysis by freeze-drying as a sodium salt. On HPLC it showed one dominant peak with  $M_w \sim 620,000$ . The degree of carboxymethylation in CWS, determined by potentiometric titration, was estimated to be 0.6. In order to depolymerize CWS into smaller fragments, it was treated with ultrasound for 30 and 60 min. Partly depolymerized CWS fractions, marked as CWS<sub>30</sub> and CWS<sub>60</sub>, were recovered after treatment by freeze-drying. Their molecular sizes, determined by HPLC, were estimated to be  $\sim 499,000$  (CWS<sub>30</sub>) and  $185,000$  (CWS<sub>60</sub>).

FT-IR spectra of all carboxymethyl derivatives (Fig. 1) showed the presence of band maxima at 1020, 1081 and  $1157\text{ cm}^{-1}$  characteristic for the starch moiety; the bands observed at  $1423$  and  $1599\text{ cm}^{-1}$  originated from resonances of carboxylic groups of carboxymethyl substituents and the bands at  $764$ ,  $860$  and  $929\text{ cm}^{-1}$  confirmed the  $\alpha$ -configuration of glycosidic linkage typical for starch [22].

Sulfation of the native wheat starch (WS) and its carboxymethyl derivatives CWS<sub>30</sub> and CWS<sub>60</sub> (DS  $\sim 0.6$ ) with chlorsulfonic acid–pyridine complex afforded sulfated starch products which were recovered from reaction mixtures after neutralization and dialysis by freeze-drying as the sodium salts. Sulfated products showed  $\sim 8\%$  (SWS),  $11\%$  (CSWS<sub>30</sub>) and  $12\%$  (CSWS<sub>60</sub>) of sulfur content. FT-IR spectra of the hybrid derivatives, i.e. sulfated and carboxymethylated, showed characteristic band maxima for

carboxymethyl starch at  $1433$  and  $1603\text{ cm}^{-1}$  and peaks due to sulfate groups at  $1262$ ,  $1228$  and  $824\text{ cm}^{-1}$  (Fig. 2).

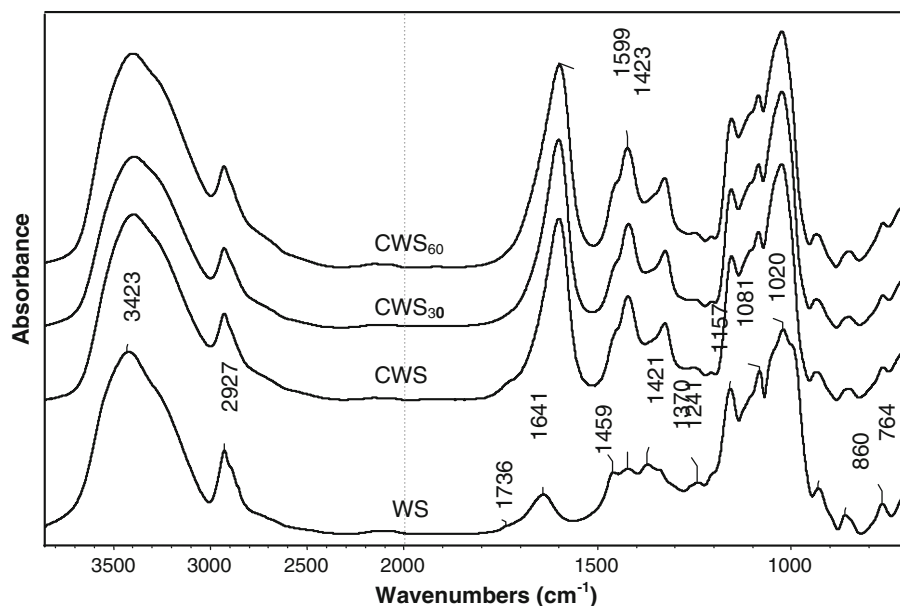
A similar procedure for carboxymethylation of  $\alpha$ -cyclodextrin was used. The carboxymethyl product of  $\alpha$ -cyclodextrin (C $\alpha$ CD) was purified by gel filtration after neutralization and recovered by freeze-drying in the form of its sodium salt. On HPLC it showed one peak with  $M_w \sim 1,200$  and its degree of substitution was estimated to be 0.6.

Sulfation of  $\alpha$ -cyclodextrin ( $\alpha$ CD) with a chlorsulfonic acid–pyridine complex yielded the sulfated product (S $\alpha$ CD) which was purified by gel filtration after neutralization and recovered by freeze-drying in the form of sodium salt. It had sulfur content  $\sim 9\%$  (DS  $\sim 0.6$ ). FT-IR spectra of  $\alpha$ CD and its both derivatives, i.e. carboxymethyl and sulfate are shown in Fig. 3. FT-IR spectrum of  $\alpha$ CD showed a similar pattern to the native starch (WS), while carboxymethyl derivative of  $\alpha$ -cyclodextrin (C $\alpha$ CD) showed characteristic bands at  $1418$  and  $1603\text{ cm}^{-1}$  due to carboxylic groups. FT-IR spectrum of the sulphated derivative (S $\alpha$ CD) showed characteristic bands for sulfate group at  $1235$  and  $818\text{ cm}^{-1}$ . The spectrum of the hybrid derivative (CS $\alpha$ CD) showed band maxima at  $1613$  and  $1428\text{ cm}^{-1}$ , and at  $1239$  and  $824\text{ cm}^{-1}$  thus confirming the presence of both carboxymethyl and sulfate groups in this molecule (Fig. 3).

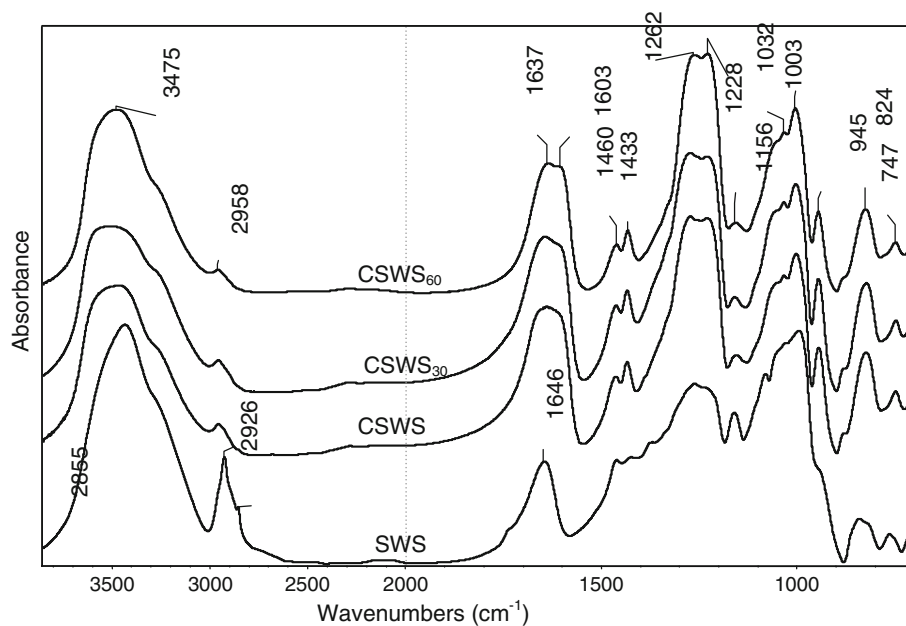
Wheat starch and  $\alpha$ -cyclodextrin are important raw materials for preparation of a large scale of industrial products. Thermogravimetric analysis could be a useful technique to determine the origin of starch and its derivatives in various blend products. The thermal properties of the tested compounds were investigated in the temperature range  $20$ – $500\text{ }^\circ\text{C}$  in order to find possible differences in their fingerprints.

As can be seen from Table 1, the native starch (WS) and its carboxymethyl derivatives CWS, CWS<sub>30</sub> and CWS<sub>60</sub>, differing in molecular sizes, showed some differences in TG and DTA curves. Thermal analysis data of WS, CWS, CWS<sub>30</sub> and CWS<sub>60</sub> initially showed uniform mass loss ( $\sim 10$ – $15\%$ ) connected with the endoeffect in the temperature range  $68$ – $70\text{ }^\circ\text{C}$ . According to literature data [23] these mass losses connected with appropriate DTA effects are due to dehydration of residual moisture in freeze-dried samples. The second mass losses were the largest ones ( $\sim 33$ – $55\%$ ) in all samples. WS exerted a typical endoeffect at  $305\text{ }^\circ\text{C}$ , which was in a good agreement with the literature data for corn, rice, potato and wheat starches [4, 23]. DTA curves of CWS–CWS<sub>60</sub> exhibited an extremely intense exoeffect in the temperature range  $281$ – $289\text{ }^\circ\text{C}$ . Additionally, less intense mass losses and exoeffects occurred from  $300$  to  $400\text{ }^\circ\text{C}$ . Two key differences in thermoanalytical traces of WS versus CWS–CWS<sub>60</sub> have been found: (i) an endoeffect at  $305\text{ }^\circ\text{C}$  for WS versus

**Fig. 1** FT-IR spectra of wheat starch (WS) and its carboxymethyl derivatives (CWS, CWS<sub>30</sub> and CWS<sub>60</sub>)



**Fig. 2** FT-IR spectra of sulfated wheat starch (SWS) and its carboxymethyl-sulfate derivatives (CSWS, CSWS<sub>30</sub> and CSWS<sub>60</sub>)

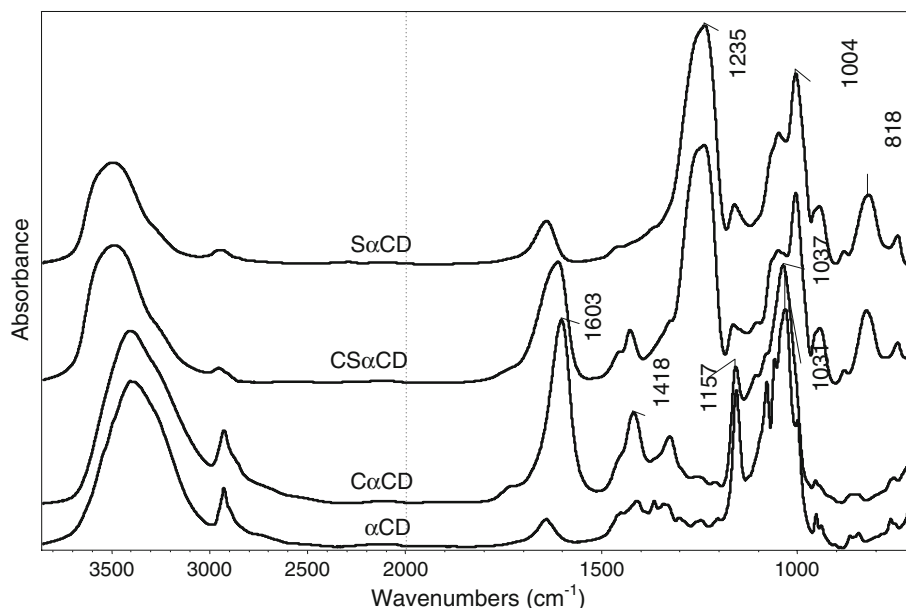


extremely intense exoeffects in the range 281–289 °C for CWS–CWS<sub>60</sub> and (ii) a residual mass ~8% for WS versus residual masses ~28–31% for CWS–CWS<sub>60</sub>. It has been reported that carboxymethylation impairs the thermal stability of starch [23]. From the results presented it is evident that the consequence of carboxymethyl substitution can be seen in the shift of the largest mass loss towards lower temperatures by 30 °C and in the change of endoeffect (305 °C) to an extremely intense exoeffect (281–289 °C). It is evident that the starch structure is destabilized in those parts where carboxymethyl substituents are located. Some differences in mass residues of samples after thermal

analyses are due to the presence of sodium salt of carboxymethyl groups.

Thermal analysis data (Table 2) of sulfated starch (SWS) and its hybrid derivatives with carboxymethyl and sulfate substituents (CSWS, CSWS<sub>30</sub>, and CSWS<sub>60</sub>) showed first uniform mass losses (~14–22%) connected with the endoeffect in the temperature range 57–75 °C due to dehydration of moisture occurring in tested samples [23]. The second, third and fourth mass losses were observed in the range ~22–29%, ~12–20% and ~9–22%, respectively, and the assigned exoeffects were found in the DTA curves at 195–224 °C, 329–334 °C, and 424–449 °C,

**Fig. 3** FT-IR spectra of  $\alpha$ -cyclodextrin ( $\alpha$ CD) and its sulfate (S $\alpha$ CD), carboxymethyl (C $\alpha$ CD), and carboxymethyl-sulfate (CS $\alpha$ CD) derivatives



**Table 1** Thermoanalytical characteristics of wheat starch (WS) and its carboxymethyl derivatives (CWS, CWS<sub>30</sub> and CWS<sub>60</sub>)

Composition	TG sequence of mass losses ( $\Delta m/\%$ ) and residue ( $m_{res}/\%$ )	DTA effects $T_{max}/^{\circ}C$ (for exo) $T_{min}/^{\circ}C$ (for endo)
WS	$\Delta m = 10.30$	80 (endo)
	$= 54.30$	305 (endo)
	$= 14.50$	352 (exo)
	$= 12.80$	
	$m_{res} = 8.10$	
CWS	$\Delta m = 15.20$	72 (endo)
	$= 49.50$	288 (exo)
	$= 6.80$	360 (exo)
	$m_{res} = 28.40$	
CWS <sub>30</sub>	$\Delta m = 14.80$	68 (endo)
	$= 48.70$	289 (exo)
	$= 4.90$	342 (exo)
	$m_{res} = 31.50$	
CWS <sub>60</sub>	$\Delta m = 15.30$	71 (endo)
	$= 33.10$	281 (exo)
	$= 12.40$	308 (exo)
	$= 7.70$	381 (exo)
	$m_{res} = 31.40$	

respectively. The key difference in the thermoanalytical traces of SWS versus CSWS–CSWS<sub>60</sub> was observed in the residual mass; estimated was  $\sim 15\%$  for SWS versus 34–36% for CSWS–CSWS<sub>60</sub>. A relatively high content of residues, similar to the case of carboxymethyl derivatives (Table 1), is due to the presence of sodium salts of carboxymethyl and sulfate groups. The shift of temperature interval ( $\sim 30^{\circ}C$ ) of the second mass loss in

CSWS–CSWS<sub>60</sub> ( $222\text{--}224^{\circ}C$ ) versus SWS ( $195^{\circ}C$ ) and the high level of the fourth mass change  $\sim 22\%$  in SWS versus 9–10% in CSWS–CSWS<sub>60</sub> are additional characteristics of this series.

The results reported in Tables 1 and 2 give a series of additional data to the knowledge of thermal stabilities of starch and its derivatives [4, 23, 24]. The consequence of organic functional substitution by the carboxymethyl group can be seen in the shift of the largest mass loss towards temperatures lower by  $30^{\circ}C$  and in the change of endo-effect ( $305^{\circ}C$ ) to the extremely intense exoeffect ( $281\text{--}289^{\circ}C$ ). Implementation of an inorganic sulfate group into starch macromolecules was accompanied by changes of characteristic mass losses and DTA exoeffects in several temperature ranges. In the DTA curves it is visible as the change of endoeffect ( $305^{\circ}C$ , in Table 1) to the exoeffect and its shift to lower temperatures ( $195^{\circ}C$  in SWS, or  $222\text{--}224^{\circ}C$  for CSWS series). Similarly, the most massive second mass loss ( $\sim 22\text{--}29\%$ ) is shifted to these temperatures in sulfated (SWS) and carboxymethyl-sulfated derivatives (CSWS). From the results presented it is evident that the sulfation contributes towards further destabilization of starch macromolecules. Our results supplement the earlier report on the effect of carboxymethylation on the thermal stability of macromolecules [23] and confirm the evidence of the same effects of sulfation and carboxymethyl-sulfation.

It has been reported that acylation leads to the stabilization of starch macromolecules [15]. This phenomenon is due to the different nature of the substituent (hydrophobic) in comparison with carboxymethyl or sulfate, which have hydrophilic character. It seems that hydrophobic functional groups can stabilize starch macromolecules while

**Table 2** Thermoanalytical characteristics of sulfate and carboxymethyl-sulfate derivatives of wheat starch (SWS, CSWS, CSWS<sub>30</sub> and CSWS<sub>60</sub>)

Composition	TG sequence of mass losses ( $\Delta m/\%$ ) and residue ( $m_{\text{res}}/\%$ )	DTA effects $T_{\text{max}}/^\circ\text{C}$ (for exo-) $T_{\text{min}}/^\circ\text{C}$ (for endo-)
SWS	$\Delta m = 14.08$	75 (endo)
	$= 28.75$	195 (exo)
	$= 20.0$	334 (exo)
	$= 21.70$	449 (exo)
	$m_{\text{res}} = 15.40$	
CSWS	$\Delta m = 20.00$	60 (endo)
	$= 23.00$	223 (exo)
	$= 12.70$	330 (exo)
	$= 9.30$	425 (exo)
	$m_{\text{res}} = 35.10$	
CSWS <sub>30</sub>	$\Delta m = 19.70$	58 (endo)
	$= 21.50$	222 (exo)
	$= 13.70$	336 (exo)
	$= 8.80$	424 (exo)
	$m_{\text{res}} = 36.30$	
CSWS <sub>60</sub>	$\Delta m = 21.60$	57 (endo)
	$= 22.10$	224 (exo)
	$= 12.60$	329 (exo)
	$= 9.85$	445 (exo)
	$m_{\text{res}} = 33.80$	

hydrophilic substituents exhibit an opposite effect on their thermal stability. However, the fourth mass losses ( $\sim 10\%$ ) and the DTA exoeffects at relatively high temperatures ( $440^\circ\text{C}$ ) indicate that a specific part of the structure of starch macromolecules can be stabilized by the hybrid hydrophilic substituents as well. These results suggest that both, i.e. the second and fourth mass losses, and the relevant DTA exoeffects may serve as the analytical indication of starch sulfation.

Thermogravimetric analysis of cyclic, low molecular weight  $\alpha$ -cyclodextrin ( $\alpha$ CD) and its carboxymethyl (C $\alpha$ CD), sulfate (S $\alpha$ CD) and hybrid carboxymethyl-sulfate (CS $\alpha$ CD) derivatives showed the first uniform mass losses ( $\sim 10$ – $17\%$ ) which are connected with the endoeffects in the temperature range  $56$ – $105^\circ\text{C}$  due to dehydration of the derivatives (Table 3).

The beginning of the second mass loss of  $\alpha$ CD is connected with the endoeffect at  $315^\circ\text{C}$  when, upon completion ( $\sim 76\%$ ), the exoeffect at  $363^\circ\text{C}$  occurs. The residues  $\sim 14\%$  for  $\alpha$ -CD versus  $\sim 34\%$  for S $\alpha$ CD,  $\sim 29\%$  for C $\alpha$ CD and  $\sim 40\%$  for CS $\alpha$ CD suggest changes of phase compositions due to sulfation and carboxymethylation of  $\alpha$ CD. The second, third and fourth mass losses, and the relevant DTA exoeffects may serve, similarly as for wheat starch derivatives, as the analytical indication of

**Table 3** Thermoanalytical characteristics of  $\alpha$ -cyclodextrin ( $\alpha$ CD) and its sulfate (S $\alpha$ CD), carboxymethyl (C $\alpha$ CD), and carboxymethyl-sulfate (CS $\alpha$ CD) derivatives

Composition	TG sequence of mass losses ( $\Delta m/\%$ ) and residue ( $m_{\text{res}}/\%$ )	DTA effects $T_{\text{max}}/^\circ\text{C}$ (for exo) $T_{\text{min}}/^\circ\text{C}$ (for endo)
$\alpha$ CD	$\Delta m = 10.40$	67, 105 (endo)
	$= 76.10$	315 (endo)
	$m_{\text{res}} = 13.50$	363 (exo)
S $\alpha$ CD	$\Delta m = 17.40$	56 (endo)
	$= 10.40$	201 (exo)
	$= 21.10$	253 (endo)
	$= 17.10$	324 (exo)
	$m_{\text{res}} = 34.05$	395 (exo)
C $\alpha$ CD	$\Delta m = 12.90$	62 (endo)
	$= 47.60$	279 (exo)
	$= 3.50$	338 (exo)
	$= 7.10$	358 (exo)
	$m_{\text{res}} = 28.90$	
CS $\alpha$ CD	$\Delta m = 10.97$	72 (endo)
	$= 27.48$	254 (exo)
	$= 10.72$	326 (exo)
	$= 11.09$	442 (exo)
	$m_{\text{res}} = 38.63$	

destabilization effects of both carboxymethyl and sulfate functional groups on  $\alpha$ CD molecules. The thermoanalytical traces of carboxymethylation can be followed in the temperature region  $250$ – $400^\circ\text{C}$  as the second (massive), the third and the fourth mass losses ( $\sim 48\%$ ,  $\sim 4\%$  and  $\sim 7\%$ ) with typical exoeffects ( $279^\circ\text{C}$ ,  $338^\circ\text{C}$  and  $358^\circ\text{C}$ ), while the sulfonation is characterized by values of mass losses  $\sim 10\%$ ,  $\sim 21\%$  and  $\sim 17\%$  and typical DTA effects at  $201^\circ\text{C}$  (exo), [ $253^\circ\text{C}$  (endo) +  $324^\circ\text{C}$  (exo)] and  $395^\circ\text{C}$  (exo). Both types of substitution destabilized those parts of the  $\alpha$ CD structure to which they were bonded.

The results presented enable a comparison of the effects of organic (carboxymethyl) and inorganic (sulfate) functional groups as well as their hybrid derivatives (carboxymethyl-sulfates) on thermal properties of starch and  $\alpha$ CD. Due to their similar degree of substitution, it is possible to exclude the influence of different degree of substitution upon TG and DTA effects, and thermal stability of investigated derivatives [24]. The DTA effects suggest only small difference of relevant starch-based versus  $\alpha$ CD-based moieties and their derivatives. However, TG data showed lower mass losses and higher residues in sulfated  $\alpha$ CD than that of starch (the second mass losses  $\sim 10\%$  vs.  $29\%$  and residues  $\sim 34\%$  vs.  $15\%$  for S $\alpha$ CD versus SWS). These different effects could be due to the cyclic structure of  $\alpha$ CD, where geometric effects contribute to bonding and lead to increased thermal stability.

## Conclusions

The thermal properties of starch materials (wheat starch and  $\alpha$ -cyclodextrin) were investigated in the temperature range 20–500 °C in order to find possible differences in their fingerprints. The results of thermoanalytical measurements revealed the significant destabilizing effects of organic (carboxymethyl) and inorganic (sulfate) functional groups as well as their hybrid organic–inorganic derivatives (carboxymethyl-sulfates) on starch macromolecules. It has been found that the thermal stability of cyclic molecules are higher in comparison with linear ones. It can be concluded that thermal characteristics may serve as the analytical indications of starch and  $\alpha$ -cyclodextrin substitutions.

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