ELSEVIER

Thermochimica Acta 403 (2003) 161–171

thermochimica acta

www.elsevier.com/locate/tca

Thermal properties of complexes of amaranthus starch with selected metal salts

Wojciech Ciesielski [a], Piotr Tomasik [b,*]

[a] Institute of Chemistry, University of Education, Armii Krajowej 13/15, 42 201 Częstochowa, Poland
[b] Department of Chemistry, University of Agriculture, Mickiewicz Ave. 21, 31 120 Cracow, Poland

Received 2 July 2002; accepted 21 October 2002

Abstract

Metal cations (Cu(II), Fe(III), Mn(II), and Ni(II)) are ligated by amaranthus starch as proven by EPR spectra and conductivity measurements. The hydroxyl groups of starch are the coordination sites. The acetate and nitrate anions of the metal salts behave as bidentate ligands and reside in the inner coordination sphere of resulting polycenter Werner complexes. There is only a weak degeneration of orbitals of central metal ions caused by a shift of unpaired spin from the central atom to the ligand. The ligation of the central metal atoms resulted in a variation of the thermal stability, pathway, and rate of thermal decomposition of starch as proven by thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements.

Keywords: Dextrinisation; Polysaccharides; Waxy starch; Werner complexes

1. Introduction

Production of dextrins, and/or starch syrups is, perhaps, the most frequently met way of the starch processing. In both cases it involves either acid catalyst or thermal treatment and eventually enzymes. A thermal treatment of starch is widely applied for dextrinisation of starch into so-called British gums [1]. The latter are different in their properties from dextrins available by the acid-catalysed as well as enzymatic hydrolysis of starch. The role of parameters of the thermal treatment in the tailoring of properties of dextrins was subjected to numerous studies. Thermal treatment's parameters role in the modification of dextrinisation of starch received considerable attention. Thus, among others, it was carried out in the presence of various reagents such as alum, which hydrolysed with liberation of sulphuric acid [2–4]. Bryce and Greenwood [5,6] studied the effect of selected salts on the yield and composition of volatile products formed after the thermolysis of amylomaize starch. A deeper insight in the mechanism of such processes documented that the interaction of starch and starch polysaccharides with metal salts of the first non-transition group [7] involved penetration of starch granules by salt anions. This observation was in concordance with that of Samec [8] who reported that in aqueous salt solutions the salt anions interact with starch to a higher extent than cations did. In contrast to metal salts from the first non-transition group, the salts of other non-transition groups [9] and transition groups [10] formed the Werner-type complexes with starch polysaccharides. These circumstances prompted us to study effect of selected salts of copper(II), cobalt(II),

---

[*] Corresponding author. Tel.: +48-12-662-4335; fax: +48-12-662-4335.
E-mail address: rrtomasi@cyf-kr.edu.pl (P. Tomasik).

PII: S0040-6031(02)00509-9

iron(III), manganese(II), and nickel(II) upon the dextrinisation of amaranthus starch. Effects of sodium, potassium, and magnesium salts upon the course of thermal decomposition of starch were assisted by an effect of the accompanying anions [11]. Therefore, in this paper, effects of acetates, chlorides and nitrates of Co(II), Cu(II), Ni(II), and, additionally chlorides of Fe(III) and Mn(II) as well as acetate of Mn(II) upon thermal starch dextrinisation are evaluated. Results of such studies might be utilised in tailored preparation of novel dextrins and application of starch as biodegradable heavy metal traps.

2. Materials and methods

2.1. Materials

Amaranthus starch was kindly provided by Centralne Laboratorium Przemysłu Ziemniaczanego in Luboń at Poznań (Poland). $CuCl_2{\cdot}2H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(OCOCH_3)_2{\cdot}3H_2O$, $CoCl_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Co(OCOCH_3)_2{\cdot}4H_2O$, $FeCl_3{\cdot}H_2O$, $MnCl_2{\cdot}4H_2O$, $Mn(OCOCH_3)_2{\cdot}4H_2O$, $NiCl_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Ni(OCOCH_3)_2{\cdot}4H_2O$, all of analytical grade, and ethanol (96%) of analytical grade were purchased from POCh Gliwice (Poland).

2.2. Methods

2.2.1. Formation of complexes

Pasting of the starch was performed with 7% (w/w) of aqueous starch suspensions. The 1 h heating and agitation at 90 °C was followed by a precipitation with 96% ethanol. The precipitate was dried at 50 °C for 24 h. Such preparation was also taken as a control sample.

A blending with salts was performed with pasted starch (0.5 g of dry residue) agitated for 24 h at room temperature and 0.1 M aqueous anhydrous salt solution (10 cm^3). The preparations were precipitated with 96% ethanol (20 cm^3) then dried for 24 h at 50 °C.

2.2.2. EPR spectra

The EPR spectra were recorded for powdered samples in the X-band region (9.5 GHz, $l = 3.2$ cm) at room temperature. $CuSO_4$ was taken as the standard for the spin abundance (2.4×10^{21} spins/g) and diphenyl picrylhydrazide (DPPH) was the standard for the g-factor. The apparatus was manufactured by Politechnika Wrocławska (Poland). The spectral curves were processed using the 2.8 b MicroCal Origin program.

2.2.3. Thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC)

The thermal DSC–TG–DTG analysis were carried out with the NETZSCH STA-409 simultaneous thermal analyser calibrated with standard indium, tin, zinc, and aluminium of 99.99% purity. Samples of approximately 0.020 g were heated in corundum crucibles with non-hermetic lids. Corundum (SINGLE *R) was the standard. The heating was performed under static conditions in the air in the range of 20–400 °C with the 5 K/min temperature rate increase. The measurements were duplicated. They provided the ±0.5 °C precision in reading of temperature.

2.2.4. Conductivity measurements

The conductivity measurements were performed at room temperature on aqueous suspension of pasted starch (0.5 g of dry residue in 10 cm^3 of water), salt solutions (0.1 M calculated for anhydrous salt) and aqueous blends of starch with salts (0.5 g of dry residue of starch in 10 cm^3 of 0.1 M aqueous salt solution). Results were proven stable within 24 h. Measurements were run in triplicates. The conductometer (inoLab, Pol-Eko-Aparatura, Poland) provided precision of ±1% of the recorded value.

3. Results and discussion

Amaranthus starch is a waxy starch. In contrast to other starches processed thermally in the air it showed two exothermic processes included in its decomposition. This peculiarity had no visible consequences on its ability to generate thermally free radicals [12,13].

This paper confirms the formerly reported [10] formation of metal complexes with starches. Starch is a macro-ligand which in a pasted state dynamically changes conformation of its chains. Because of coordination, an admixture of metal salts stabilises to a certain extent, the structure of the macro-ligand but a full stabilisation of the structure was achieved on the precipitation of these complexes by addition of ethanol.

Table 1
The *g*-factor in EPR spectra of salts and complexes with amaranthus starch

	g-Factor	
	Salt	Complex
Cobaltous salts		
Chloride	2.2448	2.2601 $\parallel$; 2.0112 $\perp$
Nitrate	2.2423	2.0053
Acetate	2.0011	2.0115
Cupric salts		
Chloride	2.1073	2.0011
Nitrate	2.3148 $\parallel$; 2.0946 $\perp$	1.9917
Acetate	2.0231 $\parallel$; 2.1652 $\perp$	1.9978
Ferric salts		
Chloride	2.2109	1.8641
Manganous salts		
Chloride	1.9884	1.8641; 2.0015
Acetate	2.0125	1.9983
Nickelous salts		
Chloride	1.9876	1.8496
Nitrate	2.2201	2.0576
Acetate	2.2452	1.9976

It is likely that the arrangement of the macro-ligand as well as co-ligating anions around the given central atom might be non-uniform in various sectors of the macro-complex. Therefore, the shift of the *g*-factor (Table 1) on ligation of the metal ions under study depended not only on the central metal ion and the anion of the parent salt but also on the conformation of the ligand developed in the moment of precipitation of the complex. Thus, one might assume that there could be a spherical arrangement of the ligands around the central atom and, simultaneously, a square planar arrangement of the ligands around the same central atom in another sector of the macro-complex.

The value of *g*-factor in the complexes was close to 2.0000 what meant that degeneration of orbitals took place due to a weak delocalisation of spins to the starch ligand. The degeneration was possible only when the spherical ligand environment occurred in the complex. The overall shift of the value of *g*-factor increased in the following order:

$$\text{chlorides}: \text{Cu} < \text{Ni} < \text{Fe} = \text{Mn} < \text{Co}$$

$$\text{nitrates}: \text{Co} < \text{Ni} < \text{Cu}$$

$$\text{acetates}: \text{Co} < \text{Mn} < \text{Cu} < \text{Ni}$$

Table 2
Conductivity of aqueous suspensions of amaranthus starch and its metal complexes

	Conductivity (mS/cm)[a]	
	Salt	Complex[b]
Cobaltous salts		
Chloride	16.58	−26.7
Nitrate	17.69	−30.9
Acetate	20.01	−31.1
Cupric salts		
Chloride	24.51	−69.2
Nitrate	23.58	−46.7
Acetate	21.54	−36.2
Ferric salts		
Chloride	22.56	−20.9
Manganous salts		
Chloride	23.54	−22.5
Acetate	18.95	−41.5
Nickelous salts		
Chloride	14.79	−18.05
Nitrate	18.25	−40.9
Acetate	19.46	−51.4

[a] Conductivity of amaranthus starch is 0.372 mS/cm.

[b] Given as increase in conductivity resulting from complexation (%).

Except for the complex of starch with nickel acetate, the shifts in *g*-factor in the spectra of complexes formed with other metal acetates was the smallest suggesting the square planar-like structure of these complexes rather than tetrahedral.

An evidence for the formation of complexes of polysaccharides with metal salts of transition groups received support from the results of the conductivity measurements (Table 2). After addition of $FeCl_3$ and $MnCl_2$ pH of solutions decreased to 2.0 and 5.5, respectively. Thus, the hydrolysis of starch took place and, in consequence, a fast decrease in the viscosity of solution was observed [14]. Thus, the formation of complexes of these salts with dextrins and not with starch were more likely.

Analysis of data in Table 2 revealed that apart from $CuCl_2$, a combination of other chlorides with starch relatively slightly reduced the conductivity of solutions. The acetates as well as nitrates carrying bidentate anions produce deeper decrease in the conductivity of solutions. Thus, the central metal cations ligated by starch additionally held in their inner coor-

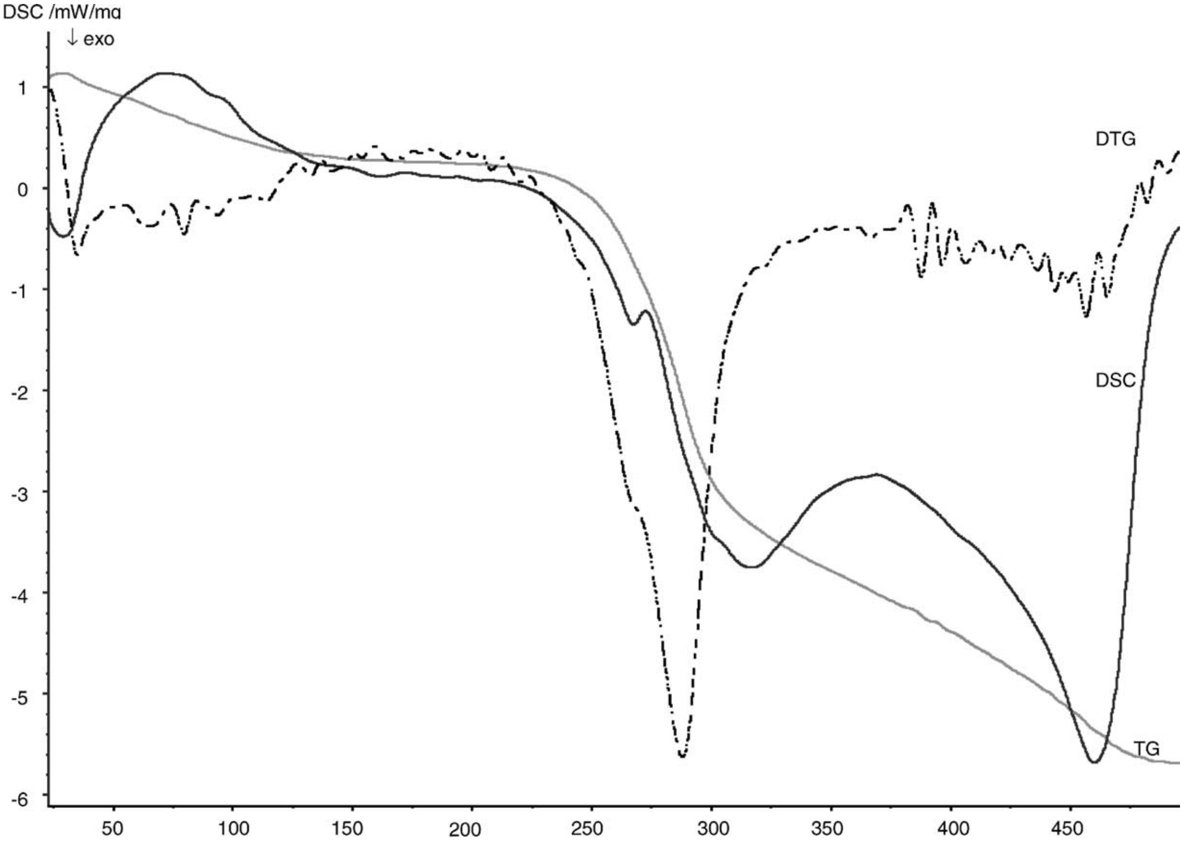

Fig. 1. The TG/DTG/DSC diagram for pasted amaranthus starch.

dination sphere the bidentate anions rather than monodentate chloride anions. Again, except the complex with nickel acetate, this observation corresponded to the effect of metal acetates upon the degeneration of orbitals of the central metal ions. Because a decrease in conductivity caused by the ligation was the largest in the case of the complex with nickel acetate. This irregularity could result from a change in the structure of the complex from octahedral (Oh) into square planar (D4h). The latter would result in a complete cancellation of degeneration of the e_g orbital and partial degeneration of the t_{2g} orbital. Such behaviour could result in increased delocalisation of spin to the ligand.

Coordination of starch with salts was also expressed by the differences in the thermal decomposition of the coordinated and non-coordinated salts. The coordination of starch to the salts entirely changed the course of the thermal decomposition of both components of the complexes. In no case the thermogravimetric, differential thermogravimetric and differential scanning calorimetric diagrams could be considered as a superposition of relevant diagrams for starch and admixed salt. Fig. 1 presents the TG/DTG/DSC diagram of pasted amaranthus starch.

One might see that after loss of approximately 14% water, reflected by a decrease of the TG line and peaks on the DTG and DSC lines (an endothermic effect) in the low-temperature part of the line, there is a plateau on the TG line. It extends up to a break point at which a significant weight loss begun. This point represents the beginning of decomposition of starch. Beyond this point there is a sharp, monotonous decline of the TG line followed by the step of a slower weight decrease. However, even when the course of the TG line suggested a one-step decomposition the pattern of the corresponding DTG peak showed that the process was

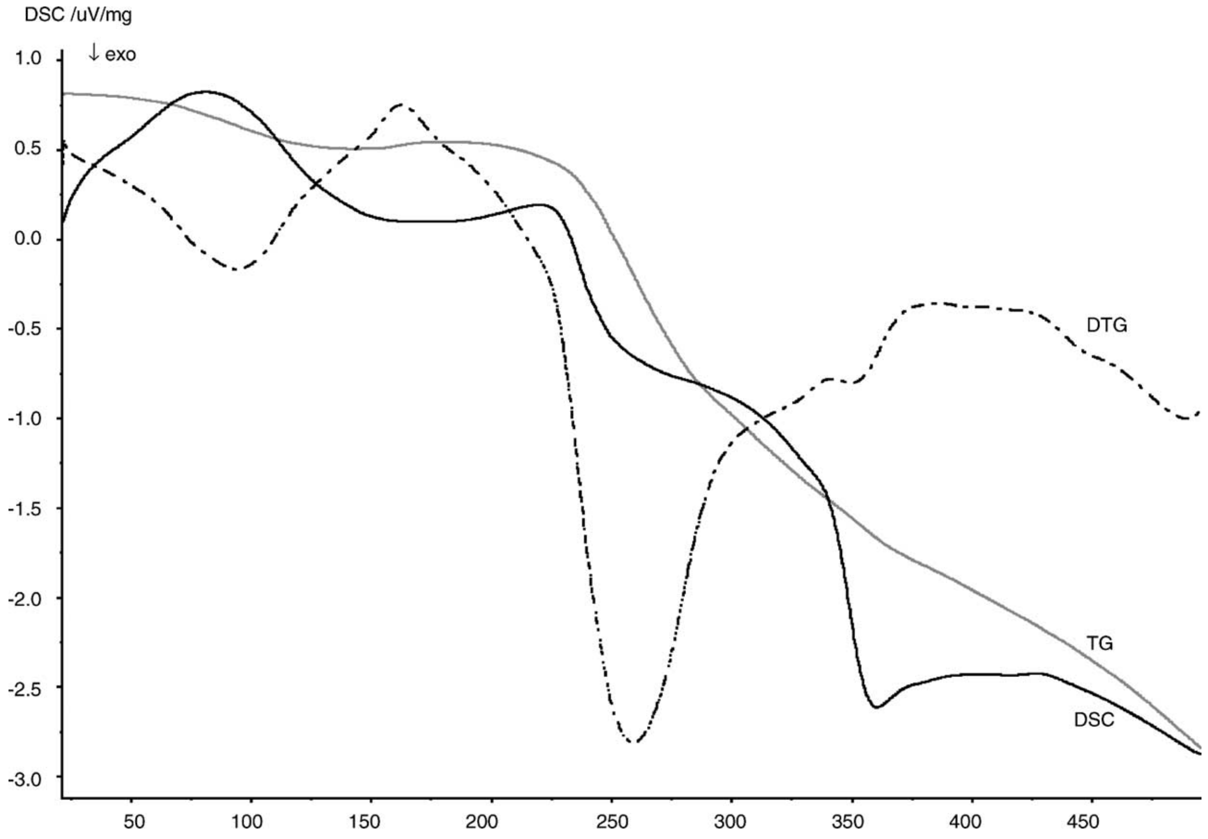

Fig. 2. The TG/DTG/DSC diagram for the complex of amaranthus starch with $CoCl_2$.

more complex. Analogous pattern was met in diagrams of starch complexes with $CoCl_2$ (Fig. 2), $Co(NO_3)_2$ (Fig. 3), and $CuCl_2$ (Fig. 4) and also with $Cu(NO_3)_2$ and $MnCl_2$. The DTG peaks are asymmetric and have shoulders either on its low- or high-temperature side.

The TG lines in diagrams for complexes of starch with all metal acetates and $FeCl_3$, $NiCl_2$, and $Ni(NO_3)_2$ show another pattern illustrated by the diagrams for the complex with manganous acetate (Fig. 5) and $FeCl_3$ (Fig. 6).

After a decrease of the TG line caused by the loss of sorbed water there was either well-separated step of a small weight loss (Fig. 5) or at least clear overlap of two effects (Fig. 6) confirmed by the patterns of the DTG and DSC lines. Also relevant DTG lines have complex structures.

Table 3 collects data on thermal decomposition of the starch complexes with particular salts.

It was striking that with exception of $Mn(OCOCH_3)_2$, the coordination resulted in a considerable change in the status of water in starch and in the coordination sphere of the salt cations. The amount of water in the complexes was significantly lower than in amaranthus starch after pasting. An analysis of diagrams strongly suggested that water in the complexes sorbed on starch rather than coordinated to the central metal cations. The peaks corresponding to dehydration of the salts were usually sharp and located at higher temperatures, than the broad peaks related to the drying of starch. Two salts exhibited specific properties. Copper nitrate, which sublimes in the range of 150–225 °C [15], evidently did not sublime from the complex with starch. There was no weight loss from the dry complex until 194 °C. Cobalt nitrate, known for decomposition to oxide at 74 °C [15], did not decompose at this temperature

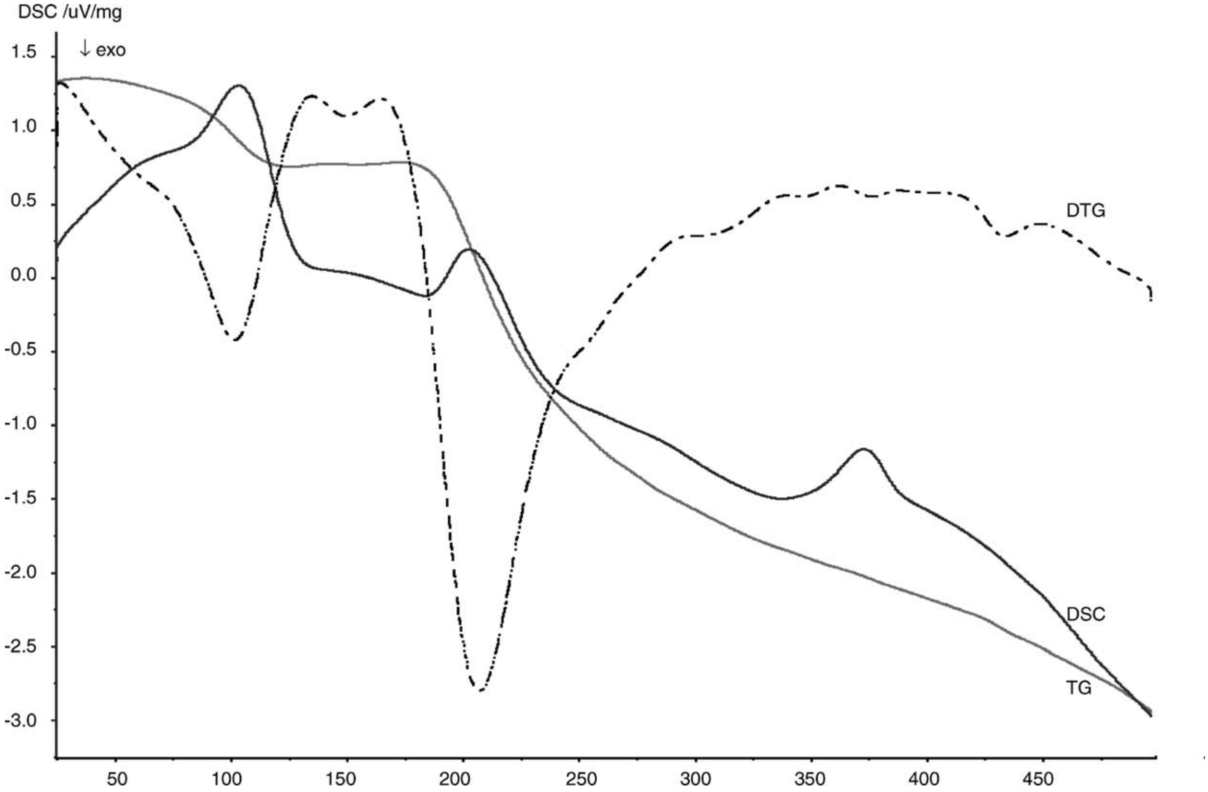

Fig. 3. The TG/DTG/DSC diagram for the complex of amaranthus starch with $Co(NO_3)_2$.

when complexed with starch. However, the decomposition of starch-ligated copper nitrate could be taken into account but it could be overlapped with other effects occurring within this temperature region. Only unusually high enthalpy changes for the corresponding endothermic processes could speak in favour of such suggestion. Nitrogen pentoxide resulting from decomposition of cobalt nitrate could act as an oxidant for starch. The oxidation of starch by nitrogen oxides is known [16,17] but such potential reaction could not be recognised in the thermograms recorded in this study. The oxidation of starch with Cu(II) salts under acidic conditions known as the Barfoed test for reducing sugars [18] seemed to be unlikely in course of thermal decomposition of the starch copper complexes because of anhydrous reaction conditions.

Inspection of the DTG diagrams revealed that main peaks for thermal decomposition of all complexes with metal chlorides and nitrates were located at lower temperatures than these for non-coordinated starch. Simultaneously, corresponding temperatures were always higher than these for pure salts. It suggested, among others, the acid-catalysed hydrolysis of starch assisting the complex formation. In the diagrams of complexes the peaks, which could be related to the decomposition of salts were absent. In the diagrams of complexes with metal acetates the main DTG peaks were located either at the same temperature (cobalt acetate) or at temperature higher than that for non-complexed starch. It could mean that the salts did not hydrolyse on the formation of complexes. The point of beginning of decomposition for all complexes except complexes with cobalt and nickel acetates were lower than the decomposition point of starch itself. It could be caused by a hydrolysis of starch in acidic media of hydrolysed metal salts. Further steps represent history of the decomposition of complexes and formation of complexes of metal salts with dextrins. The extent and rate of the weight loss in these steps as well as related temperatures depended on metal salt.

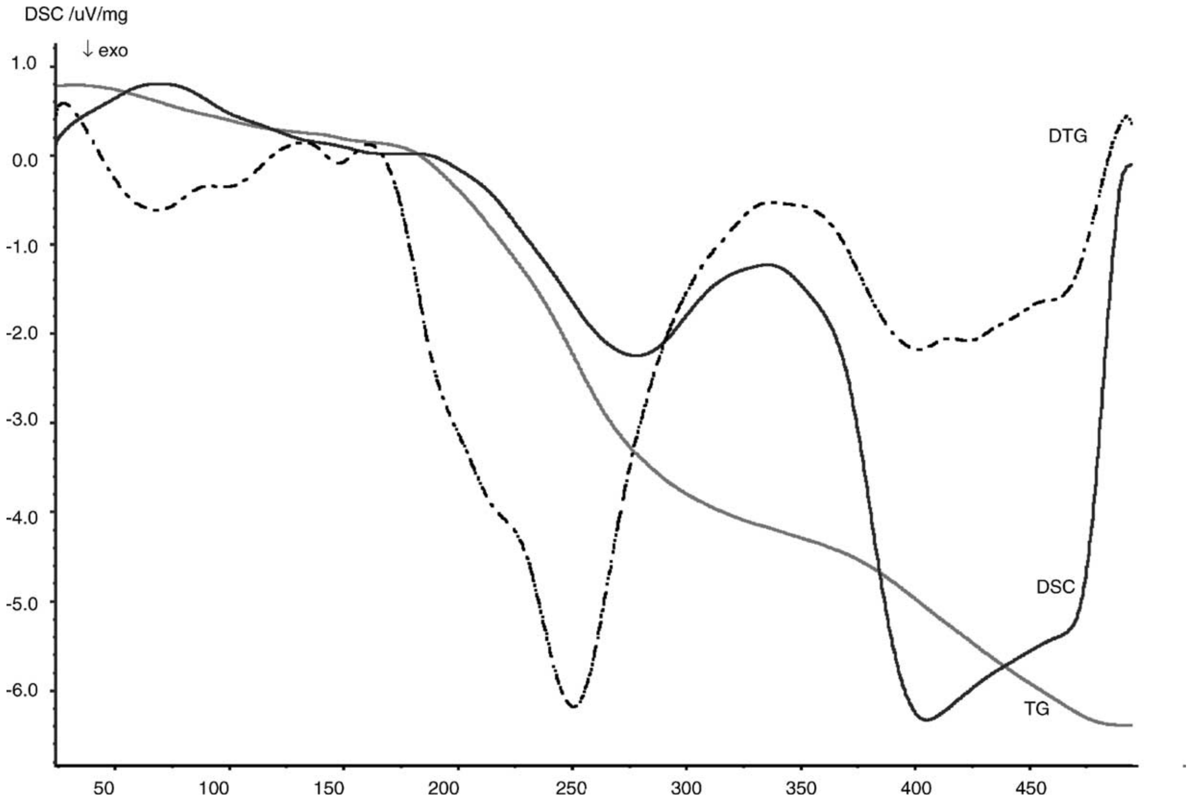

Fig. 4. The TG/DTG/DSC diagram for the complex of amaranthus starch with $CuCl_2$.

When the temperature passed over the breakpoint at 216 °C amaranthus starch decomposed in two steps (Fig. 1). The first step was fast with the slope of the TG line of 3.20 (the slope was defined as a weight loss in % per 1 °C). The DSC measurement showed that enthalpy change in this exothermic step was relatively low (−59.8 J/g). The second, also exothermic step, was slower (slope of 0.82) but it was associated with change in enthalpy of the process by over 1.5 orders higher than the preceding step. The main, always the fastest steps of decomposition of starch complexes, were preceded by one or two slower steps. The DSC measurements showed that in certain cases ($CuCl_2$, $NiCl_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Co(OCOCH_3)_2$ and $Ni(COCOCH_3)_2$) the main decomposition step was exothermic with a considerable enthalpy change. The main decomposition steps of complexes with $FeCl_3$ and $Cu(OCOCH_3)_2$ and $Mn(OCOCH_3)_2$ were endothermic with low enthalpy changes and decomposition of complexes with $CoCl_2$, $Co(NO_3)_2$, and $MnCl_2$ were considerably endothermic.

Effect of salts on the down shift in temperature of the breakpoint was as follows:

chlorides : none $>$ Co $>$ Cu $>$ Mn $>$ Ni $>$ Fe

nitrates : none $>$ Cu $>$ Co $>$ Ni

acetates : none $>$ Ni $>$ Co $>$ Cu $>$ Mn

An irregular, apparently anion dependent, effect of salts could be interpreted in terms of a different thermal stability of particular salts and/or in terms of obviously different role of anions in building inner and outer coordination spheres of complexes. These orders reflected a thermal resistance of complexes under study regardless reasons of instability.

The effect of salts upon temperature of the main DTG peak in thermograms of complexes varied

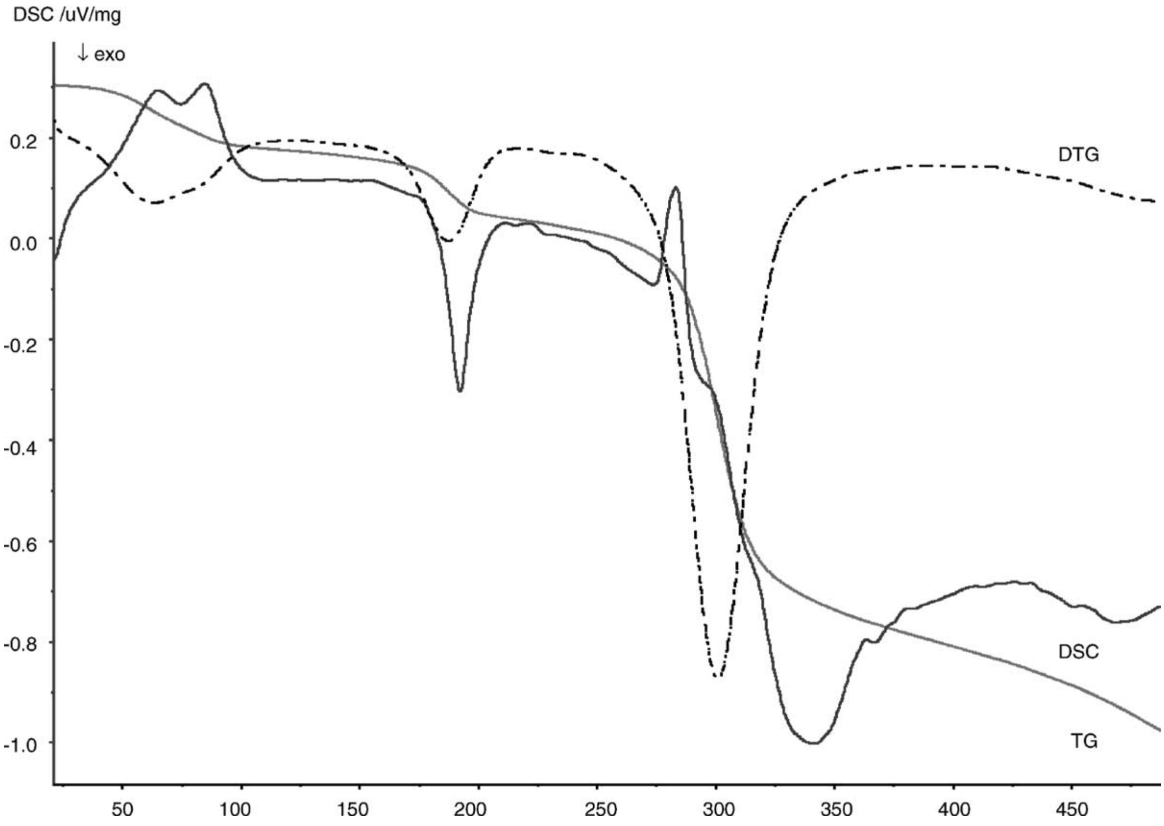

Fig. 5. The TG/DTG/DSC diagram for the complex of amaranthus starch with $Mn(OOCCH_3)_2$.

Table 3
Thermal studies of amaranthus starch and its metal complexes

Salt	TG		DTG[a]			DSC	
	Temperature range (°C)	Weight loss[b] (%)	Slope (tg α)	Complex (°C)	Salt (°C)	Temperature (°C)	DH[c] (J/g)
None	25–216	14		247sh		268	−59.8
	216–303	68.5	3.20	267		316	−929.6
Cobaltous							
Chloride	25–189	5.9		188sh	**107**, 148		
	189–285	33	1.41	225sh	191	220	+231.8
	285–362	53.5	1.33	**259**, 349		360	−438.6
	362–400	60	0.86				
Nitrate	25–173	5.9		149	130, 160		
	173–225	30.5	2.05	**207**	210	202	+321.4
	225–260	41.5	1.55	242sh	225, **248**		
	260–270	44	1.25				
	270–301	48	0.69	301	288		
	301–400	57.5	0.48	340, 375		372	+282.1

Table 3 (*Continued*)

Salt	TG		DTG[a]			DSC	
	Temperature range (°C)	Weight loss[b] (%)	Slope (tg α)	Complex (°C)	Salt (°C)	Temperature (°C)	D*H*[c] (J/g)
Acetate	25–219	9.2		155, 175	129, 190		
	219–246	12.5	0.95	200, 238			
	246–275	18	1.12		273		
	275–298	49	6.74	**287**		297	−752.3
	298–359	61	1.25	325	**332**	312	−598.7
	359–374	65	1.38	367			
	374–400	67.5	0.47				
Cupric Chloride	25–166	8.5		213sh	**117**		
	166–237	33	1.72				
	237–279	61	3.33	250		278	−1073.6
	279–375	71.6	0.55				
	375–400	77.5	1.20				
Nitrate	25–194	4.5		150sh			
	194–255	7.5		179, **249**			
	255–294	54.5	6.02	**274**	259	269	−499.5
	294–400	64	0.45	325sh		351	−797.6
Acetate	25–183	7.8			152		
	183–203	14.2	1.60			203	−20.1
	203–250	16.5	0.24				
	250–281	23	1.12	275sh	**274**	278	+31.2
	281–310	70	8.10	**298**		293	10.5
	310–400	80	0.56	328sh		329	−329.1
Ferric Chloride	25–132	6.6					
	132–155	8.6	0.43	150		140	+15.7
	155–209	19	0.96		**200**	182	+57.0
	209–275	60.5	3.14	**243**		230	+14.8
	275–350	70	0.63	318sh		325	−117.6
	350–400	74	0.40	398			
Manganous Chloride	25–141	5.0			**129**		
	141–210	12.5	0.55	149	150, 207		
	210–279	59	3.37	**240**		237	+1606.5
	279–350	65	0.77	275sh		351	−432.6
	350–380	67.5	0.42	366		370	−188.7
	380–400	70	0.63				
Acetate	25–170	11.3		116			
	170–198	20.8	1.70	187		192	−61.8
	198–285	25	0.24			283	+49.6
	285–317	74	7.66	**307**	**314**	295	+10.5
	317–400	81	0.42			342	−317.4
Nickelous Chloride	25–137	8.8					
	137–149	15.5	2.60				
	149–204	19	0.63	150		163	−199.8
	204–268	57.5	3.01	**227**		216	−372.2
	268–400	65	0.28		**360**	334	−117.6
						377	−43.1

Table 3 (*Continued*)

Salt	TG		DTG[a]			DSC	
	Temperature range (°C)	Weight loss[b] (%)	Slope (tg α)	Complex (°C)	Salt (°C)	Temperature (°C)	D*H*[c] (J/g)
Nitrate	25–138	6.4				134	−19.6
	138–270	24	0.68	152	**149**	160	−17.2
				182			
				211		270	−470.2
	270–342	53.5	2.05	275sh			
				302		306	−666.1
	342–400	60.5	0.60	375	367	374	−508.4
Acetate	25–223	7.8					
	223–250	10.1	0.43	239		246	−121.4
	250–264	13.1	1.33				
	264–300	61	6.63	**289**			
	300–400	73	0.60		**311**	319	−462.4

[a] Main peaks are denoted in bold.

[b] Values report a total weight loss from origin.

[c] Negative values denote exothermic processes whereas positive values point to endothermic processes.

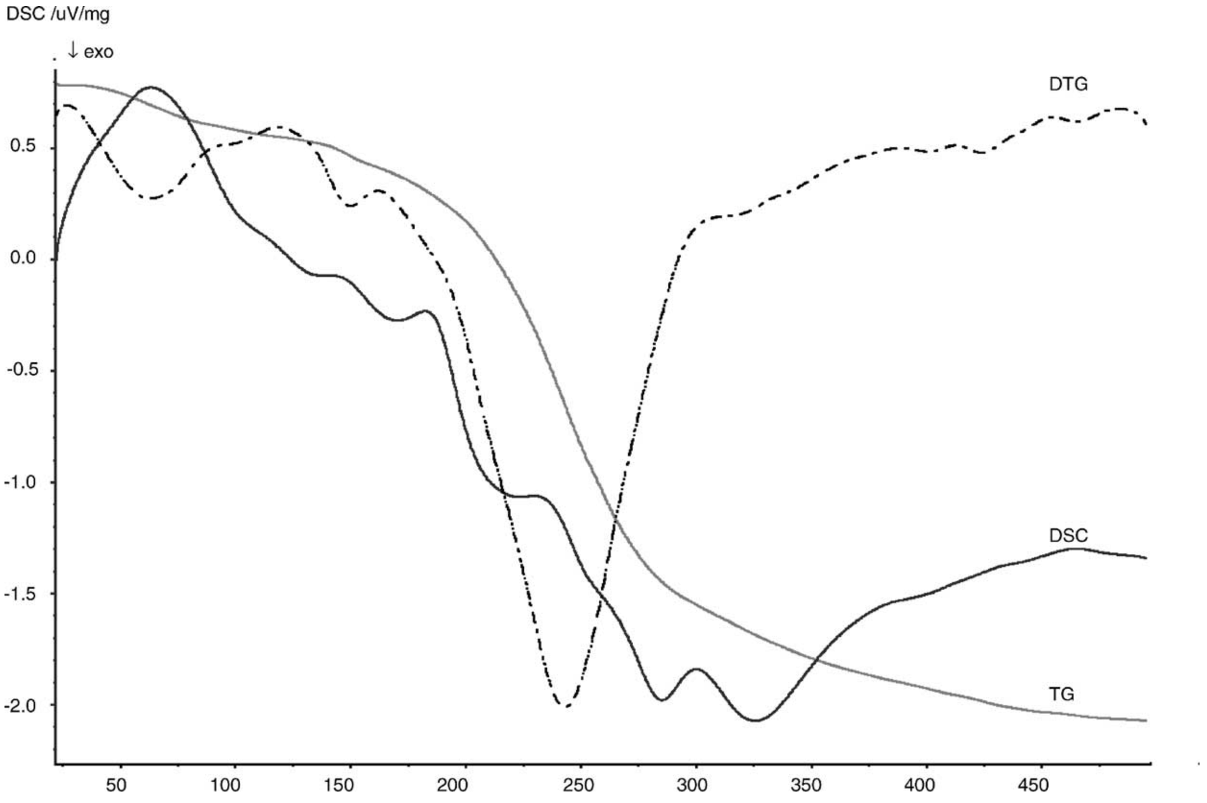

Fig. 6. The TG/DTG/DSC diagram for the complex of amaranthus starch with $FeCl_3$.

according to the following order:

chlorides : none $>$ Co $>$ Cu $>$ Fe $>$ Mn $>$ Ni

nitrates : none $>$ Ni $>$ Cu $>$ Co

acetates : none $>$ Mn $>$ Cu $>$ Ni $>$ Co

They also revealed irregularities resulting from former assumptions. These orders informed on the stability of metal complexes of dextrins regardless of their structure.

Effect of metal salts on the rate of decomposition of the complexes in their fastest step is as follows:

chlorides : Mn $\approx$ Cu $>$ none $>$ Fe $>$ Ni $\gg$ Co

nitrates : Cu $\gg$ none $>$ Co $=$ Ni

acetates : Cu $>$ Mn $>$ Co $>$ Ni $>$ none

These orders were different from the orders of effect of central metal ions upon the extent of degeneration of their orbitals.

Thus, one might see that although acetates provided complexes of the highest thermal stability the decomposition of complexes proceeded with the highest rate. The copper and manganese salts considerably accelerated decomposition of the polysaccharide ligand whereas cobalt and nickel chlorides and nitrates but not acetates stabilised this ligand.

4. Conclusions

1. Acetates, nitrates, and chlorides of Co(II), Cu(II), Fe(III), Mn(II), and Ni(II) were ligated with amaranthus starch. Lone electron pair orbitals of the hydroxyl groups of starch were sites of ligation. Polycenter Werner complexes were formed. In every case there was only a weak shift of unpaired spin from central metal ion to the ligand.
2. Coordination to central metal ion entirely changed pathway of starch decomposition. Well-distinguished multistep decomposition of starch potentially provides series of novel dextrins unavailable in classical roasting starch into British gums.
3. Stepwise decomposition of starch resulted from the formation of complexes of intermediary dextrins with metal salts.

References

[1] P. Tomasik, S. Wiejak, M. Pałasiński, Adv. Carbohydr. Chem. Biochem. 47 (1989) 277.

[2] L.S. Solomina, Izv. Vyssh. Uchebn. Zaved., Sakh. Prom., No. 10, 1979, p. 49.

[3] L.S. Solomina, E.A. Shtyrkova, N.N. Tregubov, Izv. Vyssh. Uchebn. Zaved., Sakh. Prom., No. 4, 1979, p. 40.

[4] L.S. Solomina, E.A. Shtyrkova, N.N. Tregubov, Izv. Vyssh. Uchebn. Zaved., Sakh. Prom., No. 4, 1979, p. 52.

[5] D.J. Bryce, C.T. Greenwood, Staerke 15 (1963) 285.

[6] D.J. Bryce, C.T. Greenwood, J. Appl. Polym. Sci. Pt. C 2 (1966) 159.

[7] C.Y. Lii, P. Tomasik, W.L. Hung, V.M.-F. Lai, Food Hydrocolloids 16 (2002) 35.

[8] M. Samec, Kolloidchemie der Staerke, Steinkopf, Dresden, 1927.

[9] C.Y. Lii, P. Tomasik, M.T. Yen, V.M.-F. Lai, Int. J. Food Sci. Technol. 36 (2001) 321.

[10] W. Ciesielski, P. Tomasik, C.Y. Lii, M.T. Yen, Carbohydr. Polym. 51 (2003) 47.

[11] W. Ciesielski, J. Kozioł, P. Tomasik, Pol. J. Food Nutr. Sci. 10 (1) (2001) 27.

[12] W. Ciesielski, P. Tomasik, Carbohydr. Polym. 31 (1996) 205.

[13] W. Ciesielski, P. Tomasik, M. Bączkowicz, Z. Lebensm, Untersuch Forsch. A207 (1998) 299.

[14] P. Tomasik, Y.J. Wang, J. Jane, Starch 47 (1995) 96.

[15] S. Budavari (Ed.), The Merck Index, XI ed., Merck & Co. Inc., Rahway, NJ, USA, 1989.

[16] R.W. Kerr, J. Am. Chem. Soc. 72 (1950) 816.

[17] K. Tihlarik, R. Kohn, Czech Patent 235,576 (1987) (Chem. Abstr. 109 (1988) 8322w).

[18] C. Barfoed, Z. Anal. Chem. 12 (1873) 27.