COORDINATION OF CASSAVA STARCH TO METAL IONS AND THERMOLYSIS OF RESULTING COMPLEXES

Wojciech Ciesielski[1] and Piotr Tomasik[2,*]

[1]Institute of Chemistry and Environmental Protection, Pedagogical University, 42 201 Częstochowa, Poland
[2]Department of Chemistry, University of Agriculture, Mickiewicz Avenue, 21, 31 120 Cracow, Poland

ABSTRACT. Cassava starch formed Werner-type complexes with ions of metals from the transition groups. This was proven by conductivity and electron paramagnetic resonance measurements. The coordination of starch to central metal ions influenced the thermal decomposition of starch. As a rule complexes started to decompose at lower temperature than did starch. On the other hand, the decomposition proceeded at a lower rate than the decomposition of non-coordinated starch.

KEY WORDS: Cassava starch, Coordination of starch to metal ions, Thermal decomposition of starch, Electron paramagnetic resonance measurements, Conductivity

INTRODUCTION

Cassava (tapioca, manioq, yucca) starch is a common starch of wide regions of Africa, Asia, and Central America. Because of specific functional properties, it received a considerable attention as the nutrient and excellent texturising agent. Recently, more attention is paid to this starch variety as a source providing products for non-nutritive applications [1]. Experience collected in the research on modification of starches of other botanical origins not always directly applies to cassava starch. Several technical and chemical problems arise from the dimension of granules of this starch, their susceptibility to swelling, a ratio of amylose to amylopectin, molecular weight of both polysaccharides, level of mineral components included, and so on. These factors justify attention paid in this report to the complexation of cassava starch to metal ions and to the thermal properties of these complexes. Thermolysis of the complexes provides cassava dextrins. Thus, pasted cassava starch was coordinated to Co(II), Cu(II), Fe(III), Mn(II), and Ni(II) cations in the presence of chlorides, nitrates, and acetates as counterions. It has already been demonstrated that potato, corn, waxy corn, starches, amylose, and amylopectin formed Werner-type complexes with the non-transition [2] and transition [3] metal cations. The orbitals of the lone electron pairs of the oxygen atoms of the hydroxyl groups of starch polysaccharides ligated the metal cations. Metal salts influenced the thermal decomposition of starches [4, 5]. Thus, properly understood effect of coordination upon the course of thermolysis might lead to tailored dextrins of a wide range of application.

EXPERIMENTAL

Materials

Cassava starch was kindly provided by Centralne Laboratorium Przemysłu Ziemniaczanego in Luboń at Poznań (Poland). This starch contained 11% (w/w) of moisture. $CuCl_2.2H_2O$,

_____
*Corresponding author. E-mail: rrtomasi@cyf-kr.edu.pl

$Cu(NO_3)_2.3H_2O$, $Cu(OCOCH_3)_2.3H_2O$, $CoCl_2.2H_2O$, $Co(NO_3)_2.6H_2O$, $Co(OCOCH_3)_2.4H_2O$, $FeCl_3.H_2O$, $MnCl_2.4H_2O$, $Mn(OCOCH_3)_2.4H_2O$, $NiCl_2.6H_2O$, $Ni(NO_3)_2.6H_2O$,   and $Ni(OCOCH_3)_2.4H_2O$, all of analytical grade and ethanol, 96%, of analytical grade were purchased from POCh Gliwice (Poland).

Formation of complexes

Pasting of the starch was performed with 7% (w/w) of aqueous starch suspensions. One-hour heating and agitation at 90 ^{o}C was followed by precipitation with 96% ethanol. The precipitate was dried at 50 ^{o}C for 24 hours. Such preparation served also as a control sample.

   Blending with salts was performed on pasted starch (0.5 g of dry residue) agitated for 24 hours at room temperature with 0.1 M aqueous, anhydrous salt solution (10 cm^3). The metal complexes were precipitated with 96% ethanol (20 cm^3) then dried for 24 hours at 50 ^{o}C.

EPR spectra

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 x 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.

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

Thermal DSC-TG-DTG analysis was 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 was the standard. The heating was performed under the static conditions in the air in the range of 20-400 ^{o}C with the 5 K min^{-1} temperature rate increase. Measurements were duplicated. They provided the ±0.5 ^{o}C precision in the temperature reading.

Conductivity measurements

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 hours. Measurements were run in triplicates. Conductometer (inoLab, Pol-Eko-Aparatura, Poland) provided the precision of ±1% of recorded value.

RESULTS AND DISCUSSION

Comparison of the diagrams of differential scanning calorimetry for native, granular and pasted amaranthus, potato and cassava starch (Table 1) pointed to specific properties of cassava starch. The pasting of starches reduced their decomposition temperature. It is a consequence of decomposition of native complexes of granular starches. Pasting of cassava starch resulted in appearance of a series of initially endothermic transitions in the region up to 283 ^{o}C followed by another series of exothermic transition up to 400 ^{o}C. In native cassava starch only a single fairly

strong exothermic transition could be seen at 290 ^{o}C. This peculiarity might have interesting impact to the formation of metal complexes and their thermal properties.

Table 1. Effect of pasting upon thermal properties of starches measured by differential scanning calorimetry. Temperature of the peak maximum (minimum) T_m [^{o}C] and associated enthalpy changes, -ΔH [J/g].

Starch origin											
Amaranthus				Potato				Cassava			
Native		Pasted		Native		Pasted		Native		Pasted	
T_m	-ΔH	T_m	-ΔH	T_m	-ΔH	T_m	-ΔH	T_m	-ΔH	T_m	-ΔH
								43.1	70.5		
		70.6	485.7	71.3	242.1			73.1	61.8	78.0	374.5
78.0	374.5	92.2	195.6			91.3	572.1			89.9	268.9
262.3	41.2	267.0	-59.8	259.4	54.1	247.4	101.2			242.6	68.4
				265.0	48.7	262.2	18.1			254.3	120.3
										268.0	12.1
				285.3	34.2	291.9	21.2	290.1	-720.9	283.0	11.8
				293.7	11.8						
		316.3	-920.6							342.5	-211.5
370.9	78.4					369.3	30.7			354.7	-108.6
										388.6	-35.5
										399.6	-36.9

The starch macro-ligand might not offer any structural uniformity of the ligands around metal central atoms. It was likely that in different sectors of the macro-complex the arrangement of ligands could vary from tetrahedral into square planar. g-Factors for metal complexes of cassava starch (Table 2) being always close to 2.000 pointed to degeneration of orbitals of metal atoms caused by a weak delocalisation of spins to the starch ligand whenever it was possible, this is, when the arrangement of ligands around the central metal atom was spherical. However, changes in g-factor found in this study provided an evidence for the formation of the metal complexes.

Table 2. g-Factor in EPR spectra of salts and complexes with cassava starch.

g-Factor		
	Salt	Complex
Cobaltous salts		
Chloride	2.2448	2.0211
Nitrate	2.2423	2.2143
Acetate	2.0011	2.2436
Cupric salts		
Chloride	2.1073	1.9872
Nitrate	2.3148 ∥; 2.0946 ⊥	2.0012
Acetate	2.0231 ∥; 2.1652 ⊥	1.9976
Ferric salt		
Chloride	2.2109	2.2073; 2.1891
Manganous salts		
Chloride	1.9884	1.9941
Acetate	2.0125	2.0096
Nickelous salts		
Chloride	1.9876	2.0792
Nitrate	2.2201	2.0125
Acetate	2.2452	2.0925

Absolute values of the shift of *g*-factor for the majority of cobaltous, cupric, and nickelous complexes exceeded 0.2 unit but these shifts for $Co(NO_3)_2$, $Cu(OCOCH_3)_2$, and $NiCl_2$ were much lower resembling fairly negligible shifts noted for the examined ferric and manganous salts (below 0.1 unit). These differences might be associated with the structure of the inner coordination sphere of the central metal atoms. Simultaneously, the effect of anions was irregular and did not depend on whether they could act as mono- or bi-dentate ligands.

Evidence for the formation of the complexes of polysaccharides with the metal salts of the transition groups received support from the conductivity measurements (Table 3). The reduction in the conductivity of solutions of original pure salts was usually between 40 and 30%. Only in the complexes with $CuCl_2$ and $FeCl_3$ the decrease by 61 and 44.24% was noted. Thus, in the Cu(II) and Fe(III) complexes the chloride anions were to a highest extent incorporated into the inner coordination sphere of the complexes. The complexes of starch with nickelous nitrate and acetate held the accompanying anions mainly in the outer coordination sphere.

Table 3. Conductivity of aqueous suspensions of cassava starch and its metal complexes.

Conductivity [mS/cm][a]		
	Salt	Complex[b]
Cobaltous salts		
Chloride	16.58	-38.96
Nitrate	17.69	-23.35
Acetate	20.01	-37.24
Cupric salts		
Chloride	24.51	-61.00
Nitrate	23.58	-32.36
Acetate	21.54	-31.01
Ferric salts		
Chloride	22.56	-44.24
Manganous salts		
Chloride	23.54	-32.36
Acetate	18.95	-26.91
Nickelous salts		
Chloride	14.79	-35.23
Nitrate	18.25	-18.64
Acetate	19.46	-10.33

[a]Conductivity of cassava starch is 0.333 mS/cm.
[b]Given as decrease in conductivity resulting from complexation (in %).

Coordination of starch to the metal ions had an impact to the thermal decomposition of the starch ligand. The decomposition pathway of starch after its coordination entirely changed. In no case the patterns of thermogravimetric (TG), differential thermogravimetric (DTG) and differential scanning calorimetric (DSC) diagrams could be considered as a superposition of relevant diagrams for starch and the admixed salts.

Generally, there were two patterns of thermal behaviour of complexes if the course of the thermogravimetric line was taken as the criterion. Figure 1 presents the TG/DTG/DSC diagram of pasted cassava starch. In the initial temperature interval up to approximately 150 °C there was approximately 11% weight loss associated with evolution of the sorbed and included water. Relevant peaks on the DTG and DSC lines and endothermic character of the process confirmed this point of view. This course of the TG line was followed by a plateau up to the breakpoint at 250 °C from which a fast, apparently a one-step decomposition, reduced the weight of thermolysed sample almost by half. At this temperature interval dextrinisation into so-called

British gums (dextrins available from a roasting starch) took place. This step was followed by slower processes associated with deep degradation and carbonisation of resulting dextrins [5]. Because the DTG peak was narrow and symmetric, a fairly uniform decomposition of the starch could be assumed. Similar patter of decomposition was followed by complexes of starch with $CoCl_2$, $CuCl_2$, $MnCl_2$, $Ni(NO_3)_2$, and $Mn(OOCCH_3)_2$. However, the pattern of the DTG peaks not always confirmed that the dextrinisation mechanism was uniform. Figures 2 and 3 for the complexes of starch with manganeous chloride and acetate, respectively, well documented the complexity of the process in this stage.

The diagrams for starch complexes with ferric and nickelous chlorides, cupric, and cobaltous nitrates, and cobaltous, nickelous, and cupric acetates might be accounted to the second pattern of the thermal behaviour. After evolution of water and following short plateau on the TG line there was slow preliminary stage in which a weight loss associated with decomposition of either starch or the salt occurred. This preliminary step had a more or less visible impact to the subsequent fast step of the complex decomposition. As illustrated by diagrams for complexes with cupric and cobaltous nitrates as well as ferric chloride (Figures 4-6, respectively).
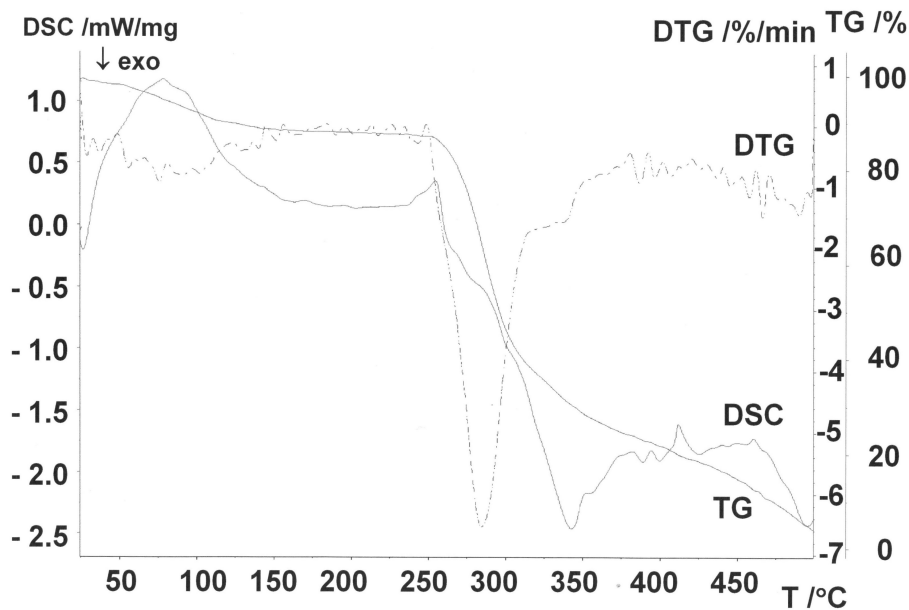

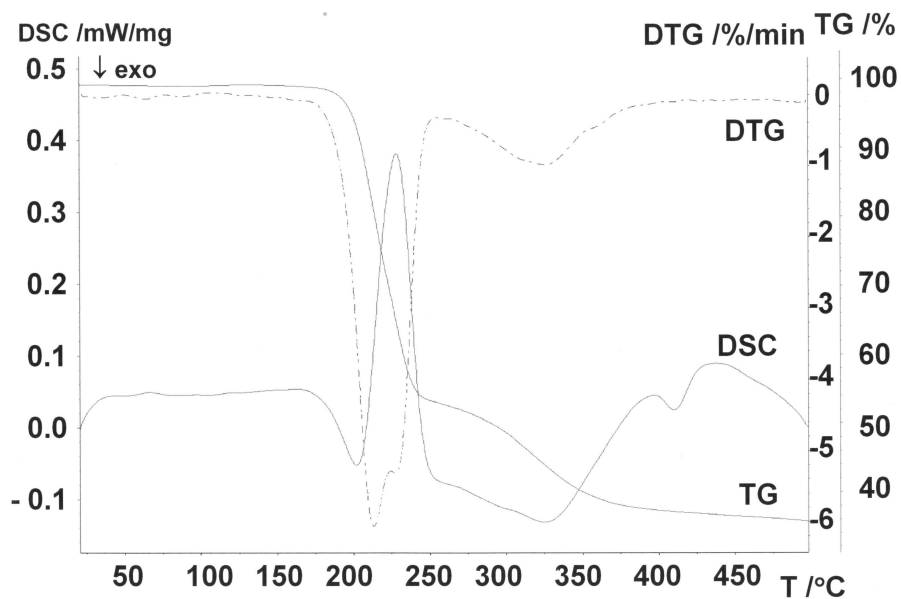Figure1. The TG/DTG/DSC diagram of pasted cassava starch.

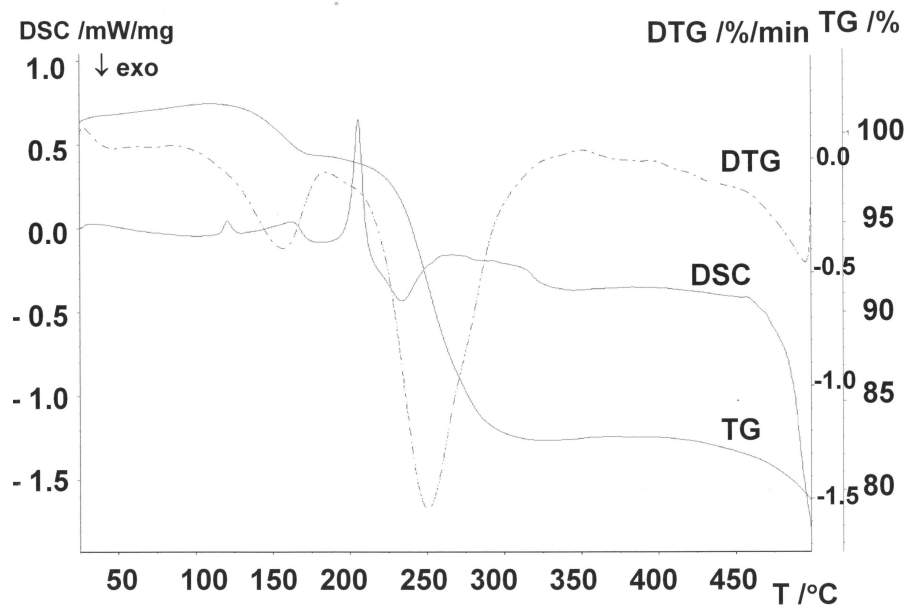Figure2. The TG/DTG/DSC diagram of the starch complex with MnCl$_2$.

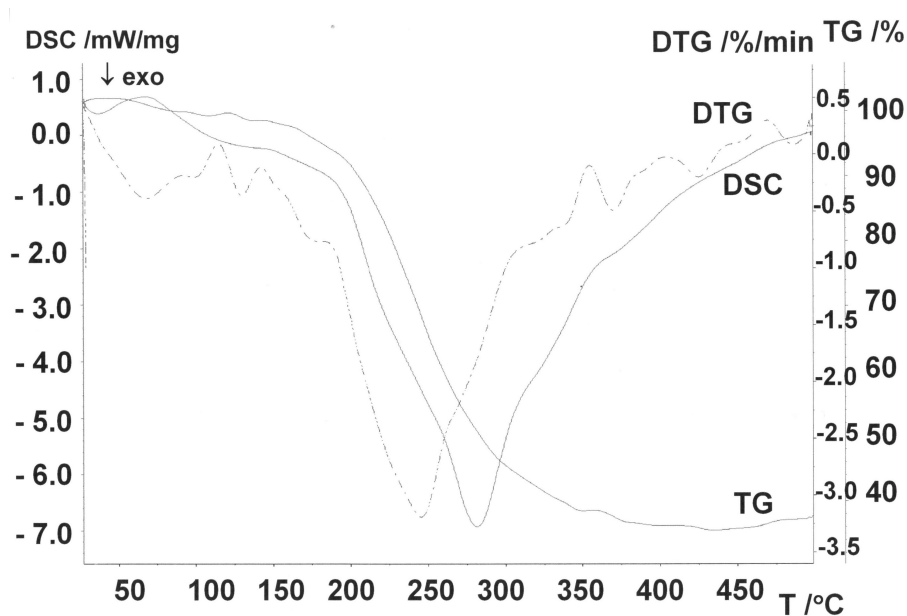Figure3. The TG/DTG/DSC diagram of the starch complex with Mn(OOCCH$_3$)$_2$.

Figure 4. The TG/DTG/DSC diagram of the starch complex with $Cu(NO_3)_2$.
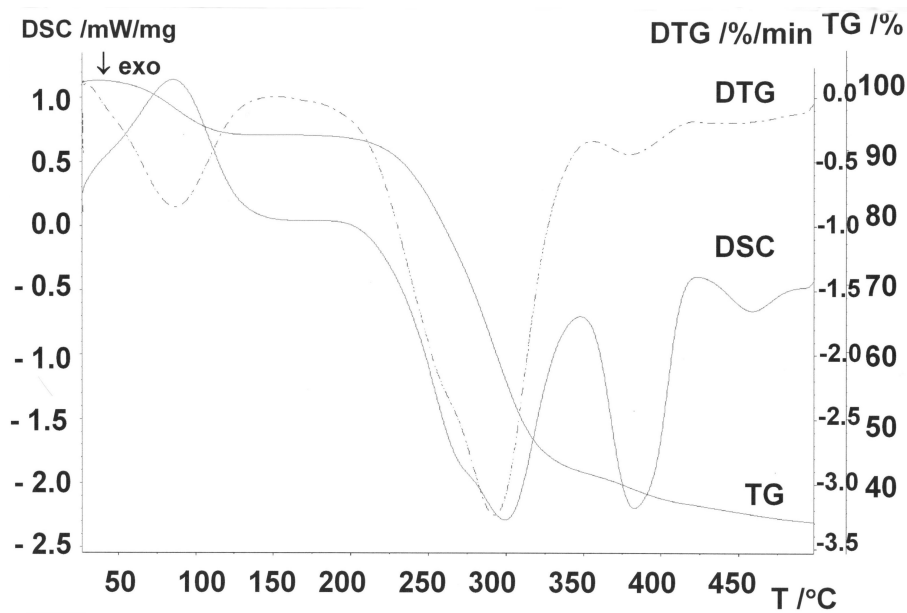

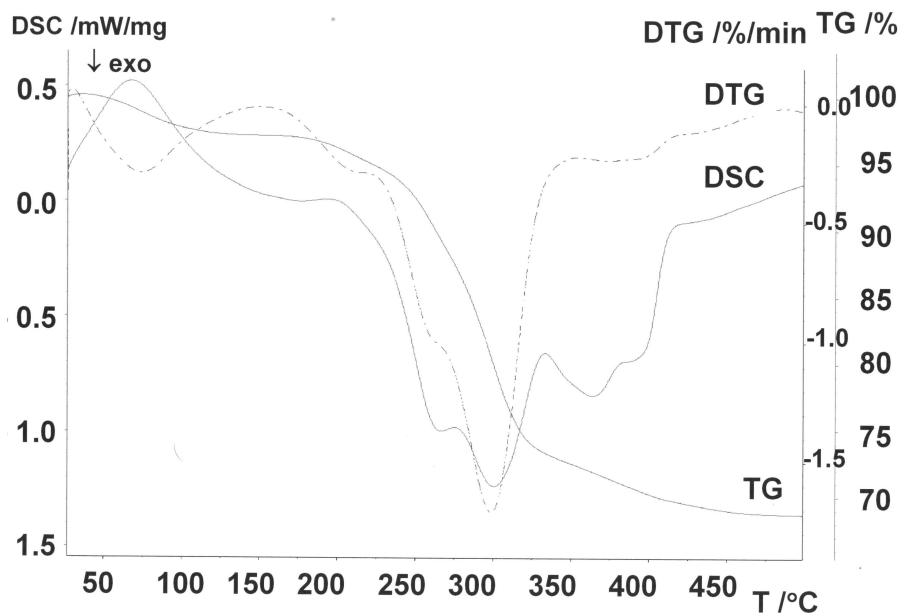Figure 5. The TG/DTG/DSC diagram of the starch complex with $Co(NO_3)_2$.

Figure 6. The TG/DTG/DSC diagram of the starch complex with FeCl$_3$.

Table 4 collects data on the thermal transformations of the starch complexes with particular salts.

Non-coordinated starch decomposed in three steps. The first step was relatively fast (tg α = 1.29) and the decomposition in two subsequent steps was much slower (tg α were 0.30 and 0.13, respectively). In starch coordinated to metal the first decomposition step was significantly slower. Only in the complex of Mn(OCOCH$_3$)$_2$ the rate of the first decomposition step was slightly slower than in pure starch (tg α was 1.09 and 1.29, respectively). The number of the recognisable decomposition steps varied from one metal complex into another showing a different effect of the coordination on the stability of dextrins. Majority of the salts stabilised dextrins by the complexation. Only Co(OCOCH$_3$)$_2$, MnCl$_2$, and NiCl$_2$ accelerated the decomposition of dextrins. Based on the major DTG effect the complexes of starch with Co(NO$_3$)$_2$, MnCl$_2$, and NiCl$_2$ were more thermally stable.

In all thermograms (TG) the dehydration stage was followed by a plane or almost plane section on the TG lines. This section was over at a breakpoint at which a significant weight loss begun. These points represented the decomposition point of the complexes. The point of the beginning of the decomposition for all complexes was lower from the decomposition point of starch itself. It could be caused by a hydrolysis of starch in acidic media of hydrolysing metal salts. Further steps represented the history of the decomposition of the complexes and the formation of the complexes of metal salts with dextrins. The extent and rate of the weight loss in these steps as well as related temperatures depended on the metal salt.

Table 4. Thermal studies of cassava starch and its metal complexes.

Salt	TG			DTG[a]		DSC	
	Temp. range	Weight loss[b]	Slope	Complex	Salt	Temp.	ΔH^c
	[°C]	[%]	[tg α]	[°C]	[°C]	[°C]	[J/g]
None	25-250	11				see Table 1	
	250-298	57.5	1.29	**284**[d]			
	298-350	71.5	0.30	340sh[d]			
	350-400	78	0.13	389, 394[d]			
Cobaltous							
Chloride	25-236	5.7			**107**, 148		
	236-293	37.5	0.86	**276**	191		
	293-400	63.9	0.25	325sh		354.6	-1971.2
Nitrate	25-177	3.10			130, 160		
	177-242	6.1	0.05	206sh	210	193	+8.7
	242-284	14.3	0.20	257sh	225, **248**	266	-431.2
	284-316	24	0.30	**299**	288	300	-512..5
	316-400	30	0.07	375		364	-112.7
						386	-18.1
Acetate	25-148	6.9			129		
	148-258	28	0.25	210	190	177	+39.4
						212	+29.8
	258-300	70	1.00	**283**	273	311	-786.6
	300-400	83.5	0.13		**332**		
Cupric							
Chloride	25-203	8.0			**117**		
	203-299	48.5	0.61	**257**		227	+198.7
	299-400	64	0.14	310sh		255	+19.7
						288	+11.2
						388	+12.1
Nitrate	25-169	2.5		157	150sh		
	169-227	3.5	0.02		179, **249**	182	+48.7
						206	+101.6
	227-279	15	0.22	250	**259**	233	-51.2
				275sh		265	+10.2
	279-400	15	0.00	370			
Acetate	25-149	5.3			152		
	149-200	20	0.29	187		133	+18.1
						184	+129.7
	200-257	30	0.18				
	257-300	68	0.88	**280**	**274**		
	300-400	80	0.12			366	+72.1
Ferric							
Chloride	25-146	1.8					
	146-167	2.3	0.02				
	167-208	9.8	0.18	175	**200**		
	208-263	43	0.60	**245**		261	-2859.5
	263-292	53.8	0.37	275sh			
	292-345	62	0.16	305sh			
	345-362	62	0.00	348sh			
	362-376	64	0.14	362			
	376-400	64.5	0.02				

Manganous							
Chloride	25-194	8.5			**129**, 150		
	194-277	30	0.45	260sh	207		
	277-316	56	0.65	**293**		299	-1050.1
	316-400	63	0.08	379		383	-728.1
Acetate	25-174	0.0			116		
	174-232	46	1.09	**212**, 229		228	+239.1
	232-287	49.2	0.06				
	287-350	61	0.19	325	**314**		
	350-400	62.5	0.03			397	+179.8
Nickelous							
Chloride	25-190		6.0				
	190-246	10.0	0.07	225sh		192	+8.5
	246-278	21	0.34	266sh		266	-241.2
	278-320	47.8	0.63	**297**		297	-387.2
	320-400	53	0.07			324	-287.7
					360	337	-99.2
Nitrate	25-234	9.4			**149**		
	234-303	61.3	0.73	**264**		288	-2288.3
	303-400	68.9	0.08	391		394	-301.7
Acetate	25-91	6.0					
	91-125	19.5	0.04	**115**		106	+720.9
	125-171	25.8	0.14				
	171-192	29.8	0.21	180		180	+38.4
	192-196	30.8	0.06				
	196-272	33.7	0.05	210sh		223	+12.4
	272-302	40	0.21	293		295	+67.6
	302-356	43.5	0.06	341	**311**	330	+11.8
	356-400	43.5	0.00	393			

[a]Main peaks are denoted with heavy print. "sh" denotes a shoulder. [b]Values report a total weight loss from origin. [c]Negative values denote exothermic processes whereas positive values point to endothermic processes. [d]These data relate to non-coordinated starch itself.

When the temperature passed over the breakpoint at 242 ^{o}C cassava starch decomposed in several subsequent steps (Figure 1). Up to 342 ^{o}C there were endothermic transitions related to the degradation. Starting from 342 ^{o}C the exothermic processes could be observed.

The thermolysis of the complexes of starch with $CuCl_2$, as well as copper, manganese and nickel acetates proceeded in endothermic manner, exclusively. The complex of starch with copper nitrate decomposed mainly endothermically although there was one of several steps being slightly exothermic. The complexes with cobaltous, ferric, and manganeous chlorides as well as nickelous nitrate decomposed solely in one or two exothermic steps pointing to the reactions of starch resulting in dextrins. After the preliminary endothermic step the complexes with cobaltous nitrate and acetate as well as nickelous chloride decomposed exothermically. Thus, one could assume that dextrins underwent exothermic reactions.

One might see that invariantly the coordinated metal atoms reduced the breakpoint temperature. An irregular, apparently the anion-dependent effect of salts could be interpreted in terms of the different thermal stability of particular salts and/or in terms of obviously different role of the anions in the building of the inner and outer coordination spheres of the complexes. These orders reflected a thermal resistance of the complexes under study regardless reasons of their instability. The different orders for amaranthus and cassava starch pointed to a different ability of both polysaccharides to form complexes and their different thermal stability.

The decomposition of cassava starch could be inhibited by certain metal cations. The effect of metal salts on the decomposition rate of the complexes, as a matter of fact, the decomposition rate of starch coordinated to the metal ion was as follows:

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

nitrates: none > Ni >> Co = Cu.

Jointly with inspection of data in Table 4 one might see that although acetates provided complexes of the highest thermal stability decomposition of complexes proceeded with the highest rate. Copper and manganese salts considerably accelerated decomposition of the polysaccharide ligand whereas cobalt and nickel salts but not acetates stabilised this ligand.

CONCLUSIONS

1. Acetates, nitrates, and chlorides of Co(II), Cu(II), Fe(III), Mn(II), and Ni(II) were ligated with cassava 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. Tomasik, P.; Schilling, C.H. *Adv. Carbohydr. Chem. Biochem.* in press.
2. Lii, C.Y.; Tomasik, P.; Yen, M.T.; Lai, V.M.-F. *Int. J. Food Sci. Technol.* **2001**, 36, 321.
3. Ciesielski, W.; Tomasik, P.; Lii, C.Y.; Yen, M.T. *Carbohydr. Polym.* **2003**, 51, 47.
4. Ciesielski, W.; Koziol, J.J.; Tomasik, P. *Pol. J. Food Nutr. Sci.,* **2001**, 10, 27.
5. Tomasik, P.; Wiejak, S.; Pałasinski, M. *Adv. Carbohydr. Chem. Biochem.* **1989**, 47, 279.