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Titanium (IV) starch complexes

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Potato and maize starch was titanated with titanium (IV) ethoxide. In both cases titanium was bound via the valence bond to the oxygen atom of the glucose unit 6-CH_2OH group, with insignificant coordination to other oxygen atoms present in these units, and the titanium reagent was partly complexed with starch. The amount of titanium bound to starch in both cases was dependent on the starch variety and not on the starch/titanium (IV) ethoxide ratio in the reaction. After the reaction potato and maize starch contained 37.5 and 42.0% of titanium, respectively. Titanium (IV) potato and maize 'starchates' fully decomposed and lost complexed titanium (IV) ethoxide at 470 and 450°C, respectively. Titanium (IV) oxide powder formed the residue in each case. © 1997 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

It is difficult to overestimate the role of metal ions and oxides in catalyzing chemical and biochemical processes. Their functions depend on several factors. The availability of metals for reagents and the type of interactions with reacting molecules are crucial points. Frequently the metal ions achieve their catalytic activity after prior complexation to specific ligands. Such ligation affects the catalyzing properties of the metal ions in both an electrical and a sterical way. It is obvious that ligation also influences the ligand reactivity (Houghton, 1979; Tomasik & Brzózka, 1987) and can be used in organic synthesis. In our previous papers we reported that starch offered interesting prospects as a ligand of metal ions. Thus, aluminium trichloride reacted with starch, by exchange of either one or two chlorine atoms, resulting in aluminum starchate, which was fairly stable to hydrolysis (Marusza & Tomasik, 1994). Starch ferrate appeared to be resistant to digestion with amylases (Tomasik *et al.*, 1995). Thus, using starch as the metal carrier, starch behaviour could be modified by these metal ions. In this paper the synthesis, structure and selected properties of titanium (IV) starchate are presented.

Titanium organics such as titanopolysiloxanes (Frazer, 1968), polysiloxanotitanoxanes (Andrianov, 1965) and copolymers of silicon and titanium monomers (Sikorski, 1981) are used as heavy duty greases and anti-adhesive lubricants. Blends of starch and either TiO_2 or titanyl sulfate, after processing at 130–135°C, formed starch films (Signaigo, 1951; Signaigo, 1952). Inorganic titanium (IV) compounds have application as a mordant in dyeing (sulfate and terachloride in combination with potassium bitartrate), in dermatological aids (sulfate), as polymerization catalysts (isopropylate) (Budavari, 1989) and as sensitizers in photodecomposition (oxide) (Gholap *et al.*, 1993).

Organic as well as inorganic titanium (IV) compounds form complexes with numerous organic ligands (Pruchnik, 1991) which, in combination with organoaluminium compounds, are known as the Ziegler–Natta catalysts of polymerization of alkene and alkyne monomers (Coates *et al.*, 1968; Tomasik & Ratajewicz, 1985; Bartecki, 1987). Titanium (IV) chloride ligated with pyridines promoted the Knoevenagel condensation of esters with ketones (Lehnert, 1973), polymerization of metanal to polyoxamethylene (O'Connor, 1959; O'Connor, 1962) and transformation of aldehyde oximes into nitriles (Lehnert, 1971). The coordination of alkyltitanium (IV) to alkenes also polymerized the ligand (Houghton, 1979). A separate group of titanium (IV) complexes is capable of nitrogen and carbon dioxide fixation (Coates *et al.*, 1968; Chatt, 1980).

There is little information in the literature on the biological role of titanium. It is possibly a bioelement

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for selected algae and cultivars (Kabata-Pendias & Pendias, 1979). For the human organism, titanium was recognized as a carcinogen (Vohora, 1983), although other sources (Doull *et al.*, 1980) report that all titanium non-hydrolyzing compounds are relatively non-toxic. Exceptions to this are titanic acid, which causes irritation of eyes and mucous membranes, and titanium (IV) oxide, which results in slight fibrosis of lung tissues. Doses of 5 mg/l of titanium were shown to affect rat reproduction and survival (Nikonorow & Urbanek-Karlowska, 1987). The limited number of studies on the biological role of titanium and the fairly insignificant biological effects observed for its compounds might be due to low solubility of the compounds.

The theoretical problem of bonding and/or coordination of the titanium (IV) ion to starch glucose units followed from earlier studies with other metal ions, for example studies on aluminium and arsenic (III) starchates (Marusza & Tomasik, 1994), iron (III) starchate (Tomasik *et al.*, 1995) and thallium (I) starchate (Baran *et al.*, 1997). Titanated starch could be used for further proof of the application of the X-ray photoelectron spectroscopy (XPS) technique for the structural studies of some modified starches. Moreover, one may suppose that starch as carrier of the titanium (IV) ions bound to it would be helpful in the administration and transport of the metal ions to some organs of living organisms. Furthermore, the titanium (IV) starchate might be useful as an industrial heterogeneous catalyst. One patent (Jasiński *et al.*, 1978) demonstrates that steel elements covered with solid metal complexes with pyridine ligands were effectively carbonized and alloyed when the element was rapidly heated by induction to 1000°C. Steel modification was observed on the surface and around a 1 mm layer under the surface. Based on this experience, titanium (IV) starchate might be useful in such processes.

MATERIALS AND METHODS

Materials

Potato starch was isolated in 1995 by the Potato Industry Enterprise in Glowno (Poland). Maize starch was provided by the Central Laboratory of the Potato Industry in Poznan (Poland). Titanium (IV) ethoxide, pure, was manufactured by Merck.

Methods

Synthesis and isolation of titanated starch

Starch was blended with titanium (IV) ethoxide, dry benzene (25 ml) was added and the mixture refluxed for 24 h under protection from moisture. Reagent proportions are given in Table 1.

After the reaction was over, the benzene (16 ml) was distilled off. Benzene (5 ml) was again added and the deposit was filtered off. The residue on the filter was collected and dried in a vacuum dessicator. The distillate was allowed to evaporate to dryness in air. The dry residue was then subjected to further studies.

Differential thermal analysis (DTA)

Samples (200 mg) were heated in a platinum crucible in air at a rate of 10°C per minute in the range 20–1000°C. Corrundum, $\phi = 8\,\mu m$, was used as the reference. The Paulik–Paulik–Erdey 1500Q (Hungary) apparatus was used.

X-ray photoelectron spectroscopic measurements

The apparatus and manner of taking spectra is described in our recent papers (Tomasik *et al.*, 1995; Baran *et al.*, 1997). All binding energies were corrected for sample charging. It was assumed that the most intense peak in starch belonged to the C–H bonds at 285 eV or that it was the lowest energy carbon peak with any intensity. By assigning this peak to 285 eV the charging shift in energy (about 3.6 eV in most cases) was determined. This charging shift was subtracted from all the spectra for the given sample.

RESULTS AND DISCUSSION

With metal salts and oxides starch can form capillary, surface sorption or inclusion complexes (Tomasik & Schilling, in press). Moreover, in potato starch metal atoms can be bound by the phosphoric acid moieties that randomly esterify glucose units via their 6-OH groups (Leszczyński, 1985). In this study the

Table 1. Proportion of reagents and the reaction product weight balance

$Ti(OEt)_4$	Starch	Insoluble matter	Weight (g) residue after evaporation	$Ti(OEt)_4$/starch ratio
		Potato starch		
9.236	1.496	1.154.	2.054	4.383
8.932	3.170	3.147	2.297	2.000
4.910	0.872	0.851	2.156	4.000
		Maize starch		
5.165	0.917.	0.910	1.779	4.000
4.848	1.732	1.112	1.011	2.000

preparation of metal derivatives of starch was undertaken in which the metal atom was chemically bound to starch without any involvement of phosphoric acid moieties. Based on experience with aluminium trichloride (Marusza & Tomasik, 1994), titanium (IV) chloride seemed to be a suitable reagent. However, the addition of this chloride to oven-dried starch resulted in the formation of a black solid (Muzimbaranda & Tomasik, 1994). This solid gradually turned yellow and readily dissolved in water with precipitation of colloidal titanium (IV) oxide. The initial black colour of the reaction mixture manifested the reaction with the evolution of hydrochloride, which formed an inclusion complex with starch (Costa, 1924). Further changes of colour and solubility were due to hydrolysis of starch with participation of hydrochloride which, although dry, dissociated under the influence of the starch hydroxy groups. For this reason, titanium (IV) chloride appeared to be an unsuitable reagent and the method used for starch thallation with thallium (I) ethoxide (Baran *et al.*, in press) was employed. In this case the starch variety was critical for the result of thallation because potato starch formed true thallium starchate whereas maize starch formed complexes rather than starchate (Baran *et al.*, in press).

Reaction of starch with titanium (IV) ethoxide gave mixtures which could be separated into unreacted starch and either titanium (IV) starchate additionally complexed with titanium (IV) ethoxide, when potato starch was reacted, or starch complexed with titanium (IV) ethoxide when maize starch was used. Product composition was independent of the starch to titanium reagent ratio. This ratio merely determined the yield of the product, i.e. the quantity of unreacted starch (Table 1). In the experiments with titanation, reaction products contained 37.5 and 42.0% titanium in potato and maize starch, respectively. These figures were calculated from the weight loss in the thermogravimetric analyses (TG curves in Table 2) in which the TiO_2 residue reached 37.5 and 29% in titanated products from potato and maize starch, respectively. Thus, the level of titanium uptake seemed to be a property of starch variety. Granular structure, as well as the presence of lipids in the maize starch, might be responsible for the observed difference. Extraction of lipids from the maize starch granules by reaction medium could open the granule interior to allow access for the titanium reagent.

Contact with titanium (IV) ethoxide ruined the suprastructure of starch, as suggested by the thermogram patterns of the insoluble portions. These were specific but at approximately 25 to 30°C below those found for unprocessed starches (Tomasik *et al.*, 1986). The content of titanium in the titanated portions of the reaction mixtures significantly exceeded the level calculated for the starch glucose unit with all three hydroxylic groups carrying the $Ti(OEt)_3$ moieties (20.3% of Ti). Thus, these products could be considered as starch carrying either titanium bound to the hydroxylic groups and, simultaneously, titanium (IV) ethoxide complexed to starch or exclusively titanium (IV) ethoxide in the complexed form. The comparison of thermograms of both soluble, i.e. titanated, and insoluble, i.e. titanium-free, portions of reaction mixtures from potato starch (Fig. 1 and Table 2) revealed their similar but not identical patterns.

After the evolution of either complexed ethanol from reacted $Ti(OEt)_4$ or complexed benzene from the reaction medium (the DTG peak at 85°C) destruction

Table 2. The thermograms of titanated starches

Sample	Thermal characteristics[a]
Potato starch + $Ti(OEt)_4$:	
titanted portion	TG: 20–105 (10%); 105–140 (15%); 140–190 (20%); 190–245 (30.5%); 245–280 (31.5%); 280–305 (34%); 305–420 (35.5%); 420–475 (37.5%). DTG: 85, 225, 290, 420 DTA: 100, 215, 280, 345, 385
titanium-free portion	TG: 20–110 (12%); 110–195 (12%); 195–235 (72.5%); 235–315 (80%); 315–355 (87%); 355–435 (100%) DTG: 75, 215, 345, 375 DTA: 85, 215, 265, 315
Maize starch + $Ti(OEt)_4$:	
titanated portion	TG: 20–100 (15%); 100–170 (22%); 170–220 (24%); 220–380 (27%); 380–450 (29%) DTG: 70, 170, 285, 330, 380, 420 DTA: 90, 170, 275, 345, 355, 370
titanium-free portion	TG: 20–110 (11%); 110–195 (12.5%); 195–250(66%); 250–420 (100%) DTG: 70, 235, 295, 345, 360, 395, 420sh DTA: 95, 195, 220, 275, 330, 360

[a] All figures are given in °C. Temperature intervals from one curve bend to another are complemented by the total weight loss from the origin (figures in parentheses). Consult also Figs 1 and 2.

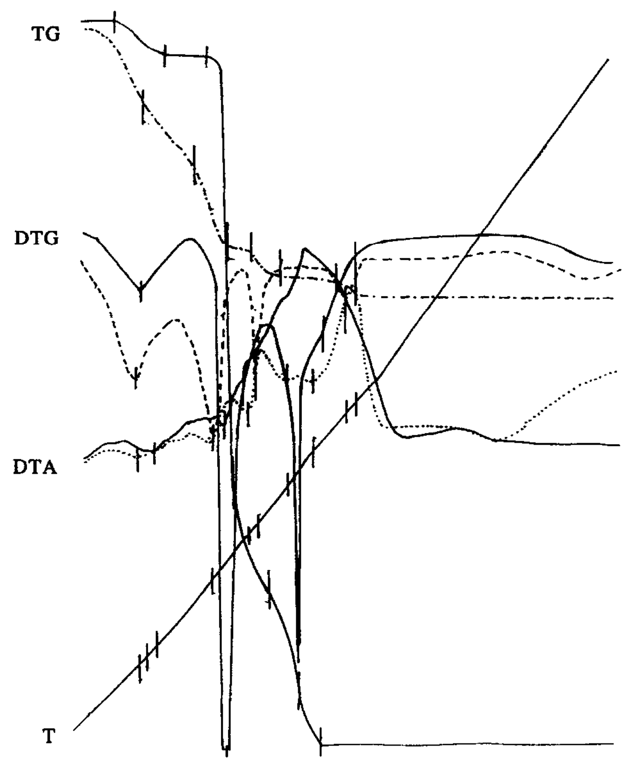

Fig. 1. Thermograms of titanated potato starch. Solid lines relate to the titanium-free portion of the reaction mixture and broken as well as pointed lines relate to the portion containing titanium. Consult Table 2 for temperatures (given in Table 2 in the same order as the vertical signs on each thermogram line).

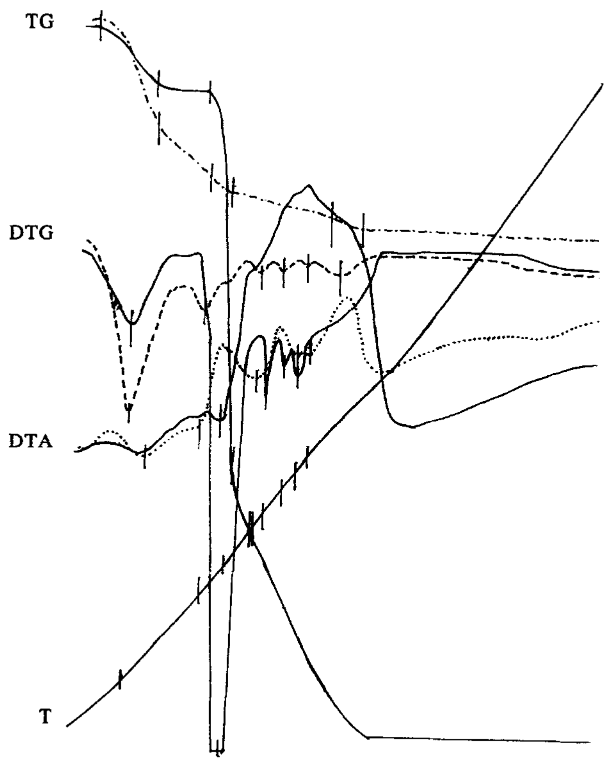

Fig. 2. Thermograms of titanated maize starch. Solid lines relate to the titanium-free portion of the reaction mixture and broken as well as pointed lines relate to the portion containing titanium. Consult Table 2 for temperatures (given in Table 2 in the same order as the vertical signs on each thermogram line).

of the starch matrix was accompanied by evolution of other species (8.5% of the overall weight in the range 105–190°C, 10% between 190 and 245°C, 1.5% over the next 35°C and the last 6% lost in three stages between 280 and 475°C (the TG and DTG curves)). This mode of decomposition suggests that the typical evolution of products (Tomasik *et al.*, 1986) for starch decomposition was accompanied by evolution of either titanium (IV) ethoxide (m.p. 28°C; b.p. 150–152°C at 10 mm Hg) and/or decomposition products of the $Ti(OEt)_3$ moieties. Similar comparisons for the products from maize starch were not so straightforward. Titanated product decomposed by 170°C whereas the titanium-free portion required 245°C for its decomposition, based on the DTG curves. The volatile products left the sample in five consecutive stages (Table 2 and Fig. 2).

Investigation of starch and its reaction products by means of XPS shed light on the mode of titanium bonding to starch. The spectrum of the physical blend of potato starch with TiO_2 taken in a routine manner is shown in Fig. 3. Figure 4 presents this spectrum in the regions of the binding energies of carbon and oxygen atoms at 284–296 and 530–542 eV, respectively, after expanding and Gaussian analysis. Table 3 collects the relevant data for processed spectra of titanated potato and maize starch.

The spectral pattern for the control sample preliminarily considered as the physical mixture of potato starch and titanium (IV) oxide differs from the pattern for original, unprocessed starch. It suggests that the control sample was in fact a complex of both components. The peaks of the binding energy for the electron at the carbon and oxygen atoms in the spectra of pure starch after Gaussian analysis contained four and three components, respectively. Blending of starch with titanium (IV) oxide reduced by one the number of components in the carbon peak and left the number of components in the oxygen peaks intact. However, the pattern of both peaks was slightly changed. In the XPS spectrum of potato and maize starch the carbon region (around 286 eV) contains three discrete components hidden within one intensive peak. They are situated at (1) 285, (2) 286.5, (3) 287.7 and (4) 288.5 eV. The peak areas decrease in the order (2) > (1) > (3) > (4). In the oxygen region of the spectrum (around 533 eV) the peak is composed of three discrete components at (1) 531.6, (2) 533.0 and (3) 534.2 eV. The peak areas decrease in the order (2) > (1) > (3). The control sample, which was nothing more than a sorption complex, is characterized by the peaks at 285, 285.7, 287.7 and

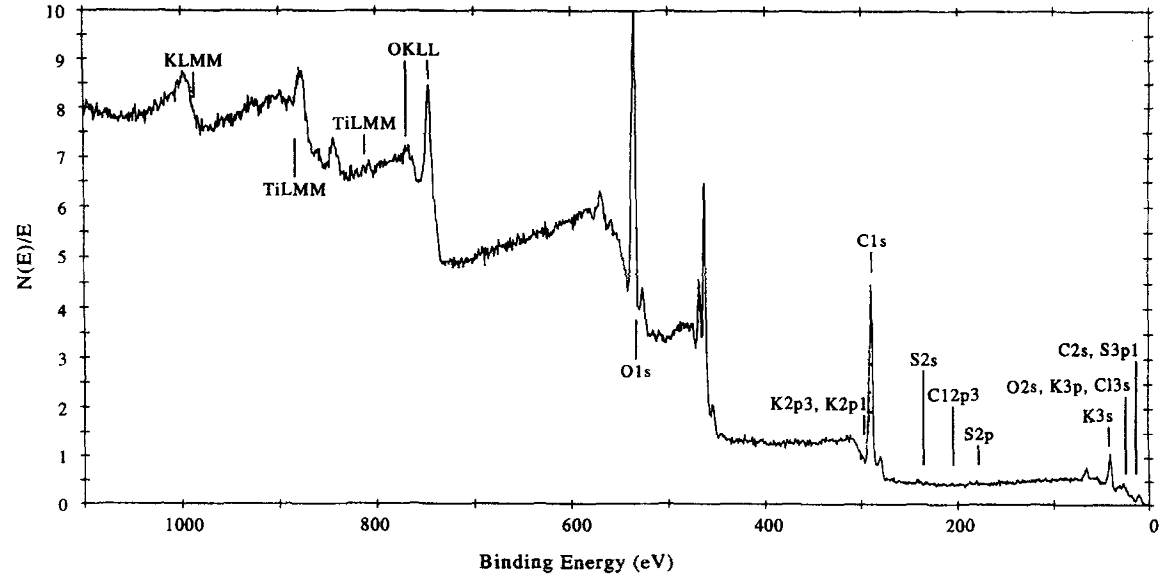

Fig. 3. The routine X-ray photoelectron spectrum of potato starch–TiO_2 blend.

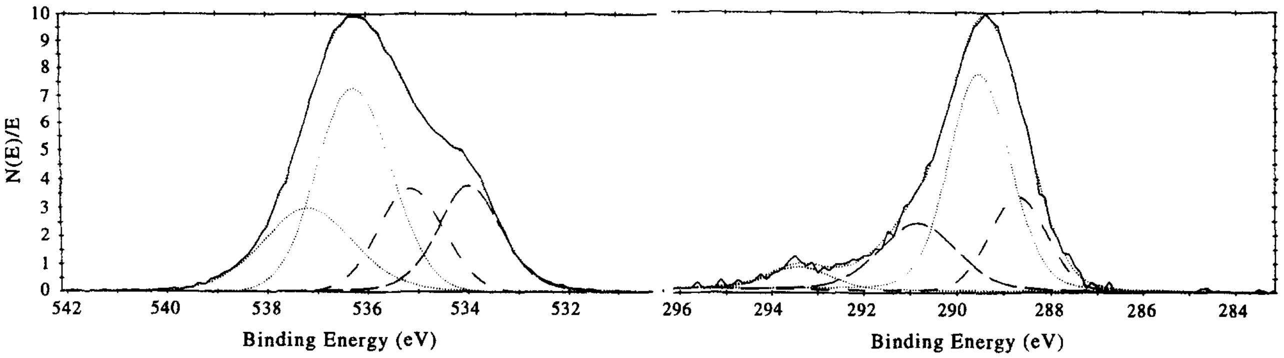

Fig. 4. The X-ray photoelectron spectrum of the potato starch–TiO_2 blend presented in Fig. 3 after expansion and Gaussian analysis.

288.5 eV in the carbon region and at 530.4, 532.3 and 533.4 eV in the oxygen region with the same orders of peak area decrease as above. Thus, the surface sorption of titanium (IV) oxide on starch is shown by the shifts of the peaks to slightly lower binding energies. In the spectra of titanium-free samples, which are probably starch with a damaged suprastructure, the shift of the bands to lower binding energies could be observed but this was accompanied by a change in the order of the peak intensities. Thus, in the carbon-binding energy region the order is (1) > (2) > (3) (one of four original peaks vanished) and in the oxygen-binding energy region the order is (3) > (1) > (2). Contrary to this, in the spectra of titanated products from potato starch the corresponding orders are (1) > (2) > (3) and (1) > (2) > (3), respectively, whereas in spectrum 12 of titanated products from maize starch the orders are (1) > (2) > (3) and (1) > (3) > (2), respectively. Again, as observed in thallated starch (Baran *et al.*, 1996), potato and maize starch accepted metal atoms in different ways.

Based on the experience with thallation (Baran *et al.*, 1996) and ferration (Tomasik *et al.*, 1995), it could be concluded that the titanium atom was present in the 6-CH_2OTi form (strong 530 eV band) as well as in the complexed titanium (IV) ethoxide form (strong 533 eV band). The negligible shifts of the bands suggest poor coordination of titanium to the hydroxy groups of the glucose units. This fact could readily be rationalized in terms of the steric effects. Similarly to titanium (IV) chloride, the arrangement of the ligands in titanium (IV) ethoxide should be tetrahedral. Therefore the sole coordination of the titanium atom of the 6-$CH_2O(TiOEt)_3$ group within the glucose unit might involve the pyranose ring oxygen atom. This would imply a coordination number of 5 for the titanium atom, which is essential for its catalytic activity. Limited stability of the products to oxygen and moisture was also anticipated and indeed such behaviour was observed. The points of complete decomposition of titanated products were 450 and

Table 3. Binding energies of the carbon 2s and oxygen 2s electrons in the XPS spectra of starch and its titanium (IV) derivatives

Sample	Binding energy[a] (eV)	Sample	Binding energy[a] (eV)
Potato starch	285.0 (28)	Potato starch + $Ti(OEt)_4$ (Ti: starch = 4.38)	285.0 (58)
	286.5 (51)		286.5 (35)
	287.7 (14)		288.6 (7)
	288.4 (7)		
			530.2 (44)
	531.6 (10)		531.4 (10)
	532.9 (83)		532.8 (46)
	543.2 (7)		
		Potato starch + $Ti(OEt)_4$ (Ti: starch = 2.00)	285.0 (61)
Maize starch	285.0 (33)		286.5 (32)
	286.5 (51)		288.4 (7)
	288.5 (5)		
			530.3 (52)
	531.6 (12)		531.7 (14)
	533.0 (80)		532.9 (34)
	534.2 (8)		
Potato starch titanium-free, insoluble	285.0 (76)	Potato starch – $Ti(OEt)_4$ (Ti: starch = 4.00)	285.0 (55)
	286.5 (35)		286.4 (38)
	288.6 (7)		288.3 (8)
	530.3 (52)		530.2 (28)
	531.7 (14)		531.7 (14)
	532.9 (34)		532.8 (49)
Potato starch – TiO_2 (control)	285.0 (26)	Maize starch + $Ti(OEt)_4$ (Ti: starch = 4.00)	285.0 (71)
	285.7 (46)		286.7 (20)
	287.0 (23)		288.4 (8)
	289.6 (6)		
			530.0 (52)
	530.1 (28)		531.4 (19)
	532.3 (54)		532.8 (29)
	533.4 (18)		
		Maize starch + $Ti(OEt)_4$ (Ti:starch = 2.00)	285.0 (68)
			286.6 (21)
			288.1 (11)
			530.1 (48)
			531.8 (23)
			532.9 (29)

[a] The numbers in parentheses are the relative peak areas.

470°C, as shown by the TG curves for the products from potato and maize starch, respectively. In every case the titanium (IV) oxide powder was left in the crucible. This implied a limited application of titanated starch in high temperature surface steel alloying and carbonation. The catalytic properties of titanium (IV) starchate will be reported in a separate paper.

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