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Carbohydrate Polymers 41 (2000) 61–68

Carbohydrate Polymers

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Starch–lanthanum complexes

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Received 24 June 1998; received in revised form 2 March 1999; accepted 9 March 1999

Abstract

Starch–lanthanum complexes were produced by the reaction of soluble starch:lanthanum triisopropoxide [La(OPr-*i*)$_3$] using the proportions 1:1, 1:2, and 1:3. The reactions were performed by either of the two methods: (i) 48 h of reflux in dry toluene under argon and (ii) by heating for 20–30 min in a microwave oven at high energy. Starch dextrinization resulted from the microwave-induced reaction of starch with lanthanum chloride. Depending on the reaction method and reagent proportions, different starch–lanthanum complexes were formed according to thermogravimetric analysis, differential thermal analysis, and X-ray photoelectron spectroscopy. The latter method proved the chemical bonding of lanthanum to starch.

A product with intermolecular O–La(OPr-*i*)–O bridges was synthesized by reacting toluene with a 1:1 reagent blend. A starch–lanthanum complex with intramolecular O–La(OPr-*i*)–O bridges formed upon microwave heating the same blend. Increased concentrations of the lanthanum reagent resulted in products simultaneously having intra- and inter-molecular oxygen–lanthanum bridges. Excess, unreacted lanthanum reagent remained in the final product in the case of the 1:3 starch:lanthanum reagent blends. Starch–lanthanum complexes readily hydrolyzed in open air.

Keywords: Starch–lanthanum complex; Thermogravimetric analysis; X-ray photoelectron spectroscopy; Differential thermal analysis

1. Introduction

Previously, we demonstrated the syntheses of aluminum and arsenic (III) (Marusza & Tomasik, 1992), thallium (I) (Baran, Sikora, Tomasik & Anderegg, 1997), iron (III) (Tomasik, Jane, Spence & Anderegg, 1995), and titanium (IV) starch complexes (Tyrlik, Tomasik, Anderegg & Baczkowicz, 1997) having starch–O–metal bonds with additional coordination bonds to metal atoms.

Our motivation for synthesizing starch–lanthanum complexes originated from the observation of Tsubouchi and Bruice (1994) that lanthanum ions accelerate hydrolysis of phosphate ester bonds by 13 orders of magnitude. This suggests that phosphate diesters in DNA may also suffer such destruction. Thus, lanthanum should be situated among the class of highly toxic metal ions that are potentially effective against micro and higher organisms. Starch, to which lanthanum can be bonded, may be a good carrier for this ion in saccharide-metabolizing organisms. Another rationale for the synthesis of starch–lanthanum complexes originated from a recent observation of Schilling, Biner, Goel and Jane (1995) that saccharides and polysaccharides significantly improve rheological properties during the plastic molding of aqueous suspensions of metal oxide powders. In addition, dopants of lanthanum and other metal ions are critical to the control of various properties of oxide ceramics (e.g. porosity, mechanical strength) (Zaharescu, Parlog, Stancovschi, Crisan, Braileanu & Surdeanu, 1985; Kuo & Kriven, 1996, 1998; Cho, Harmer, Chan, Rickman & Thompson, 1997; Manor, 1997). We believe that the introduction of these dopants via starch–metal complexes during plastic molding may be beneficial from a manufacturing perspective.

2. Experimental

2.1. Materials

Lanthanum isopropoxide was manufactured by Gelest Inc., Tullytown, PA, USA and lanthanum chloride was

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0144-8617/99/$ - see front matter
PII: S0144-8617(99)00045-4

Table 1
Thermogravimetric analysis and comparison with theoretical calculations

Sample	Thermal effects (°C)
I	TG[a]: to 90 (− 6%), to 195 (− 10%), to 335 (− 33.5%), to 460 (− 50%), to 800 (− 60.5%), Residue: 39.5% and 22.5% before and after subtracting the toluene content, respectively. Residue calculated for the glucose unit having one La(OPr-*i*)$_2$: 40.55%. Calculated for two glucose units crosslinked with one LaOPr-*i*: 33.4%. DTA: 195 (shoulder), 300, 460, 550, 700
II (toluene insol.)	TG[a]: to 85 (− 6%), to 195 (− 9.5%), to 370 (− 39%), to 460 (− 49%), to 490 (− 48%), to 800 (− 60%). Residue: 40 and 34% before and after subtracting the toluene content, respectively. Calculated for glucose unit carrying one La(OPr-*i*)$_2$: 40.55%. Calculated for two glucose units crosslinked with one LaOPr-*i*: 33.4%. DTA: 190 (shoulder), 290 (shoulder), 305, 345 (shoulder), 450, 550, 750 (shoulder), 755, 790, 810
III (toluene insol.)	TG[a]: to 85 (− 5%), to 200 (− 7.5%), to 315 (− 33%), to 360 (− 40%), to 455 (50%), to 800 (− 63%). Residue: 37 and 32% before and after subtracting the toluene content, respectively. Calculated for glucose unit carrying one La(OPr-*i*)$_2$: 40.55%. Calculated for two glucose units crosslinked with one LaOPr-i: 33.4%. DTA: 260 (shoulder), 305, 355, 455, 465 (shoulder), 550, 760, 790 (shoulder)
III (toluene soluble)	TG[a]: to 120 (− 7%), to 205 (− 23%), to 830 (− 38%). Residue: 62% and 55% before and after subtracting the toluene content, respectively. Calculated for La(OPr-*i*)$_3$: 51.6% DTA: 205, 580 (shoulder), 580, 775
IV	TG[a]: to 330(− 28%), to 460(− 45%), to 810(− 55%). Residue: 45%. Calculated for glucose unit intracrosslinked with one LaOPr-*i*: 47.66%. DTA: 310, 415 (shoulder), 455, 465 (shoulder), 550, 700 (shoulder)
V	TG[a]: to 285(− 5%), to 315 (− 11%), to 485(− 21%), 830(− 31%). Residue: 69%. Calculated for two intracrosslinked glucose units carrying one LaOPr-*i* per one glucose unit additionally crosslinked by another LaOPr-*i* bridge: 56.6%. DTA: 300, 340, 395, 460, 550, 650 (shoulder)

[a] The weight loss reported is that calculated from the origin to the given point.

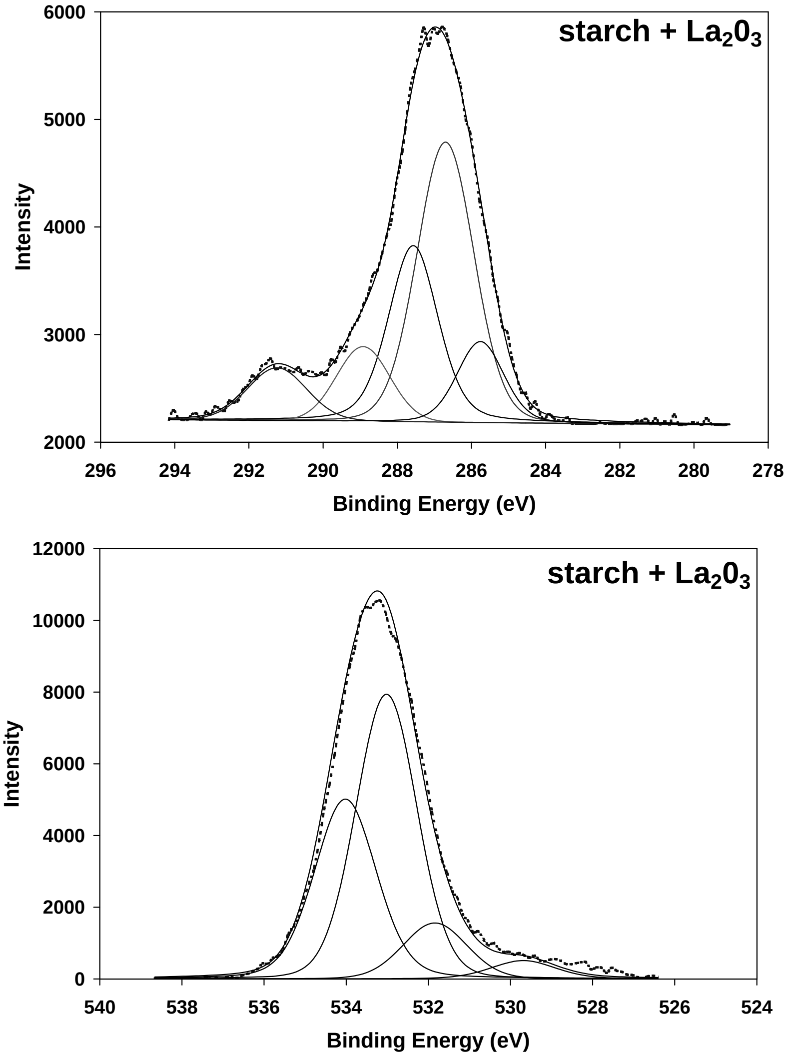


Fig. 1. XPS spectra of starch–La$_2$O$_3$ blend according to Table 2.

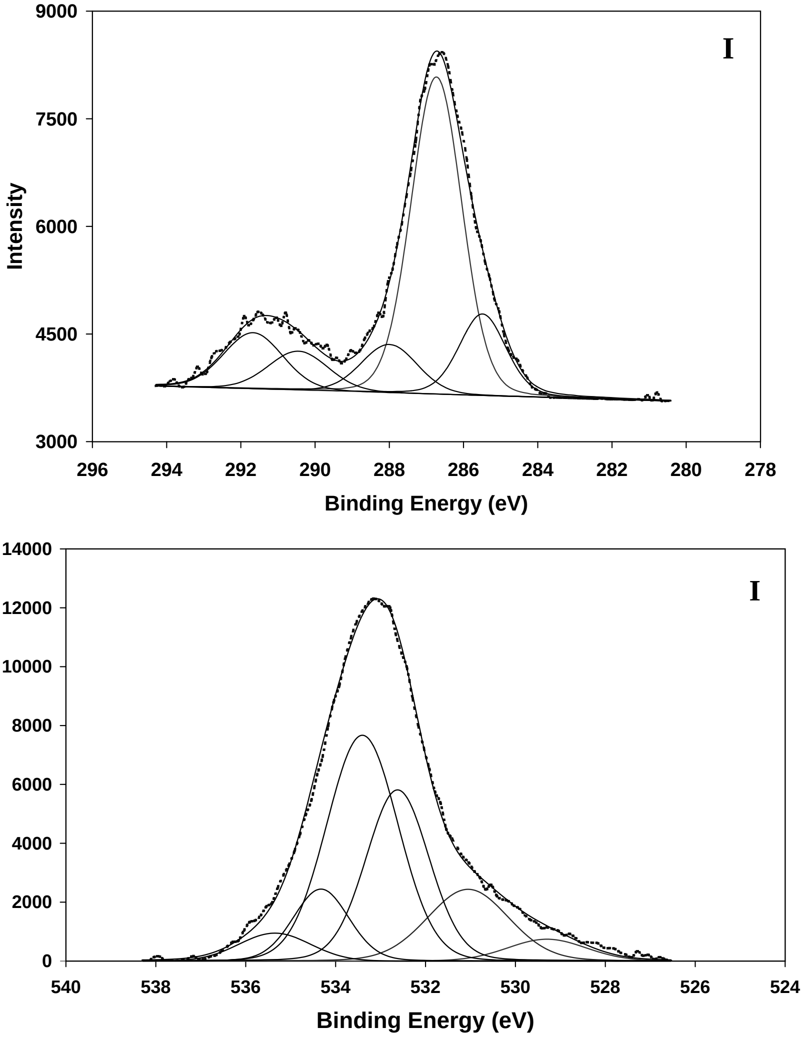


Fig. 2. XPS spectra of lanthanum starchate (I) according to Table 2.

produced by Pfalz and Bauer, Waterbury, CT, USA. Soluble starch and toluene were purchased from Fisher.

2.2. Methods

1. Soluble starch (1.80 g) was suspended in toluene (50 ml), and lanthanum isopropoxide was subsequently added at one of the three concentrations: (I) 3.16 g, (II) 6.32 g, and (III) 9.48 g. The reaction mixture was refluxed under dry argon for 48 h. The yellow liquid portion of the reaction mixture was subsequently decanted and evaporated on a rotary evaporator leaving a brown residue. The yellow, solid part of the reaction mixture (approx. 1 g) was also evaporated under dry argon to a dry condition. All samples were analyzed by simultaneous thermogravimetric analysis (TG) and differential thermal analysis (DTA). The structures of each sample were also investigated by X-ray photoelectron spectroscopy (XPS).
2. A second method involved blending soluble starch (0.6 g) and lanthanum isopropoxide in a mortar under a dry atmosphere using one of the two concentrations of lanthanum isopropoxide: (IV) 1.04 g and (V) 2.08 g. Each mixture was subsequently placed in a microwave oven set at maximum energy (90%) for 20 min (Sharp Carouselle R510-AK). The weight loss, after the reaction, was measured and it corresponded to the loss of two isopropoxide moieties (0.7 g).
3. A third method entailed blending soluble starch (1.79 g) with lanthanum chloride (2.46 g), followed by heating in the microwave oven set at 40% energy for 15 min, 60% energy for 2.5 min, and 90% energy for 3 min. In each of the five replicates a brown hygroscopic, acidic product with a typical odor of dextrin was obtained.

2.3. Thermal analysis

Simultaneous TG and DTA were performed in flowing air

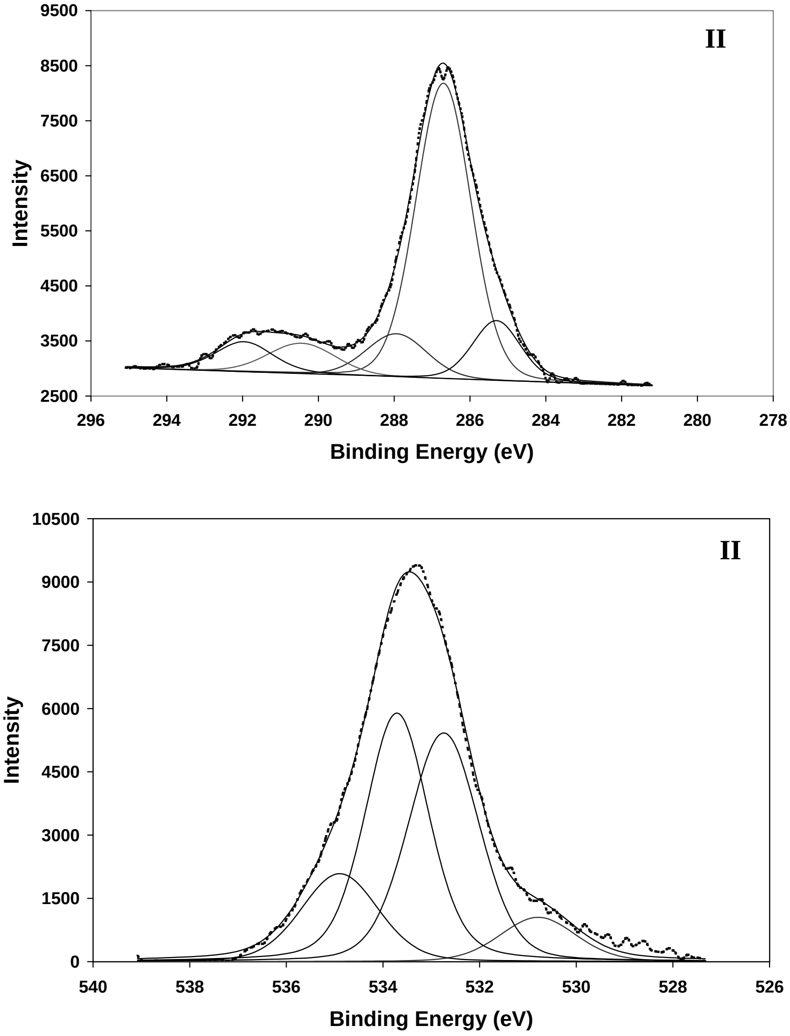


Fig. 3. XPS spectra of lanthanum starchate (II) according to Table 2.

(100 ml/min) during heating at 4°C/min from 20 to 500°C followed by heating to 1000°C at a rate of 20°C/min. SDT 2960 Simultaneous DTA–TG–TA Instrument and HIRES TGA 2950 TA instruments were used.

2.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded with a Physical Electronics Model 5000 Multitechnique Surface Analysis System. The pass energy was 29.350 eV using a Mg source at 300 W. Samples were mounted on double-sided adhesive tape. The positions of the peaks were normalized to the position of the main component of the C1s band at 286.7 eV.

3. Results

Thermal analysis (see Table 1) revealed that the toluene-soluble products in the reaction of method 1 mainly comprised impure, non-reacted lanthanum isopropoxide. In specimen (I), the lanthanum reagent fully reacted and nothing was isolated from the toluene supernatant after evaporation. Successively more non-reacted lanthanum isopropoxide was recovered when using higher concentrations of lanthanum reagent in samples (II) and (III). Sample (III) exhibited the presence of diisopropyl ether (16.1% weight loss), which was manifested by a sharp DTA peak with its maximum at 205°C. The total weight loss was reflected by two, broad, maxima in the DTA pattern. At 830°C, the weight loss reached 38% (a higher weight loss of 56.8% can be calculated by including the toluene present in the sample). DTA illustrated that the heating of lanthanum isopropoxide from 205°C up to 830°C consisted of three main features: (i) a distinct shoulder at 550°C, (ii) a peak at 580°C, and (iii) another peak at 775°C. TG did not show any significant weight changes associated with features (i) and (ii), however, a

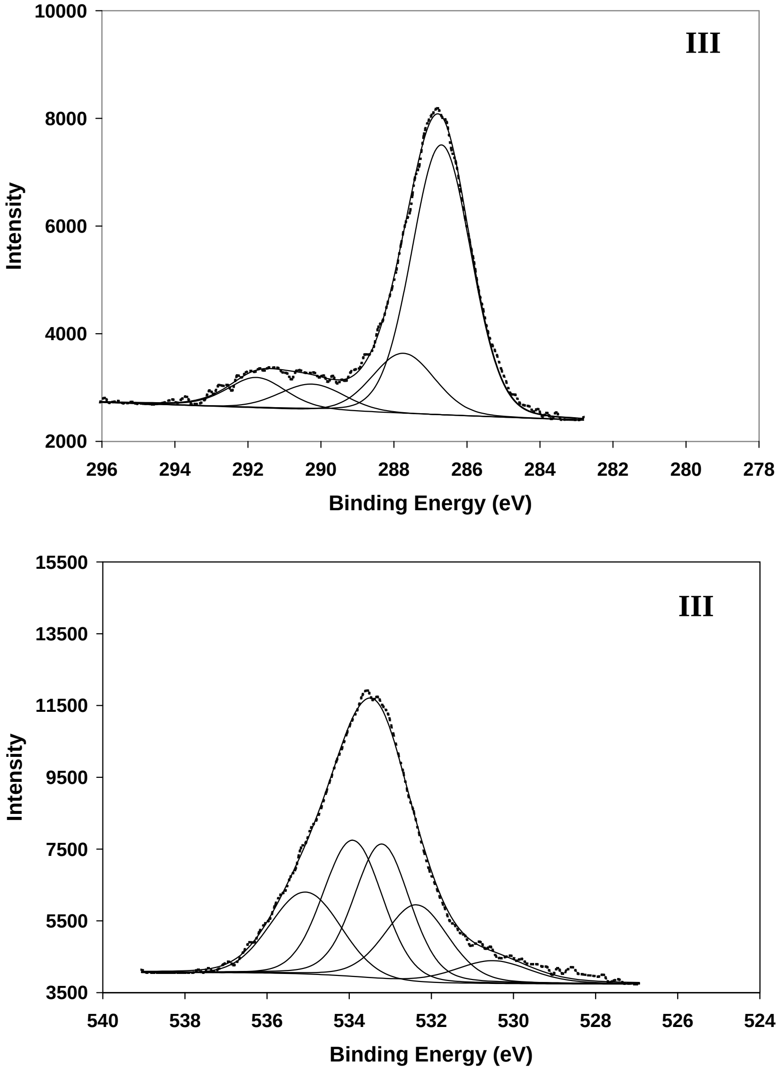


Fig. 4. XPS spectra of lanthanum starchate (III) according to Table 2.

12% weight loss corresponded with feature (iii). Table 1 reports the thermal analysis data and elemental analysis considerations of each sample. Table 2 reports XPS data for starch–lanthanum complexes, which are visualized in Fig. 1.

Table 2 and Figs. 1–6 illustrate differences in the spectral band shapes, maxima, and composition (in the sense of the Gaussian distribution) of the physical starch–lanthanum oxide blend and the starch–lanthanum complexes that were prepared by reflux in toluene. The hidden and overlapping bands for mutually non-equivalent carbon and oxygen atoms, as revealed by the Gaussian treatment of the spectra, changed their relative intensities as the result of bonding of the lanthanum atom and its coordination in starch–lanthanum complex. These differences are particularly visible in the part of the spectra associated with oxygen atoms. It is not surprising because these atoms are directly involved in bonding and coordination to lanthanum. One might also observe essential differences between the spectra of starch–lanthanum complexes that were prepared by reflux in toluene and also by microwave heating.

4. Discussion

The reaction of starch with lanthanum isopropoxide undoubtedly proceeded upon reflux in toluene and upon heating in a microwave oven. However, both methods provided slightly different results. Thermal analysis consistently showed that, in the case of reflux in toluene, only one intermolecularly crosslinked product formed independent of the reagent proportions. However, this result was not confirmed by corresponding DTA patterns. Because the entire amount of lanthanum reagent was consumed in the reaction associated with sample (I), one might assume

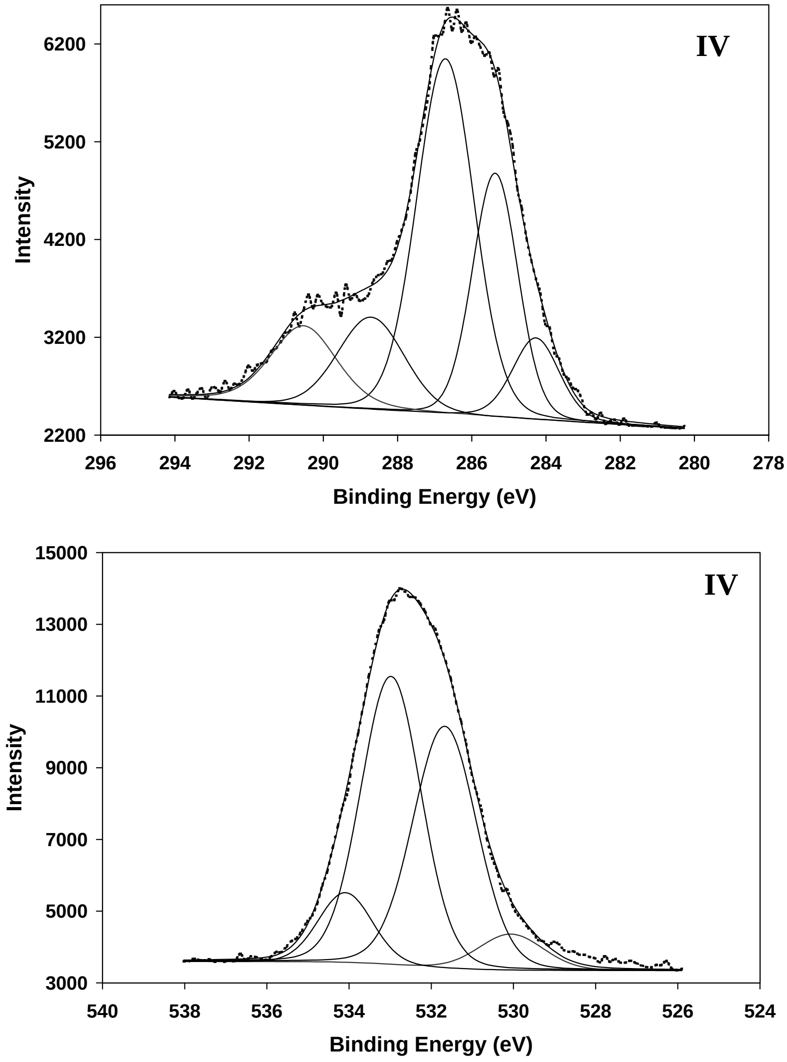
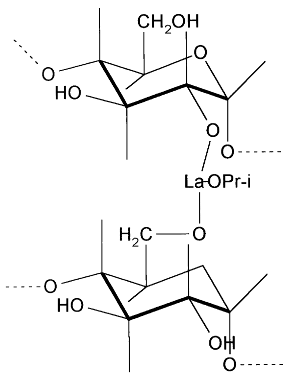


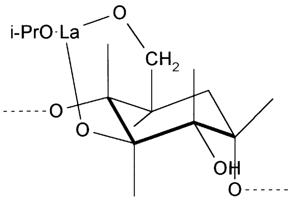
Fig. 5. XPS spectra of lanthanum starchate (IV) according to Table 2.

extensive intermolecular crosslinking with the LaOPr-*i* bridges between glucose units as shown below:



1

A product having a similar but not identical DTA pattern resulted upon heating a reaction mixture containing a similar proportion of reagents in the microwave oven. TG analysis indicated that the reaction product from sample (IV) had intramolecularly crosslinked glucose units with the same LaOPr-*i* bridges as shown below:



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The high amount of residue after burning the reaction product from sample (V) may be ascribed to a partly decomposed product formed of two intramolecularly bridged

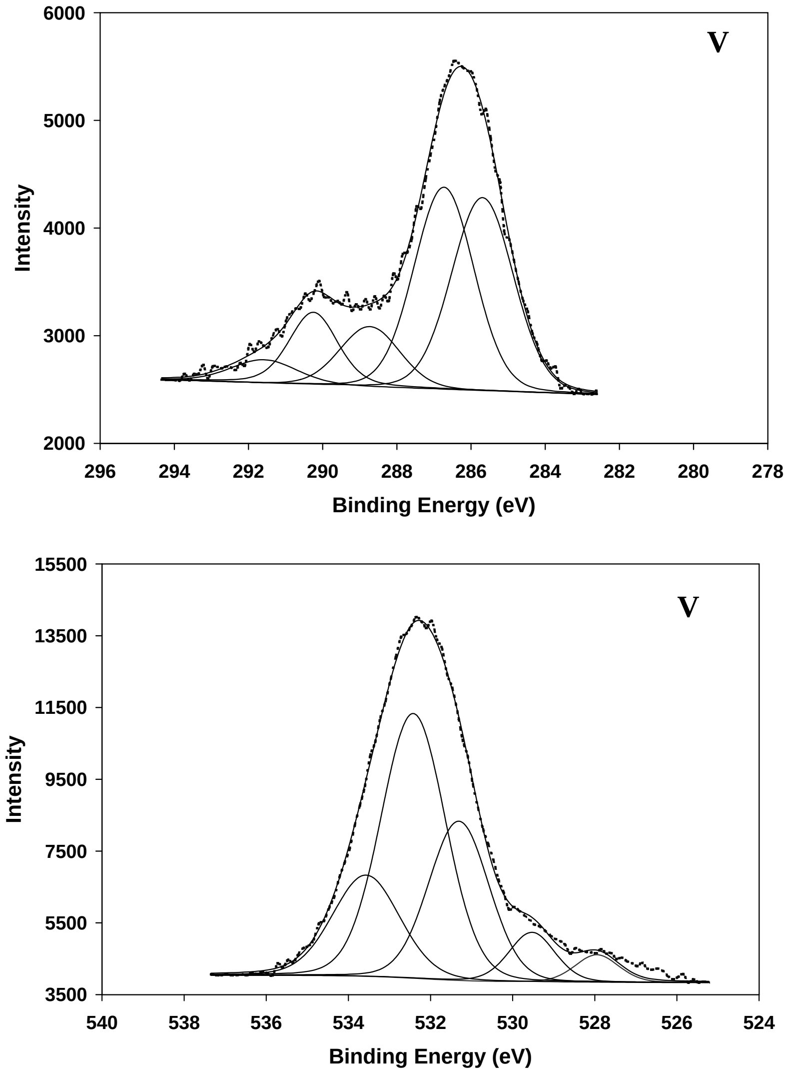
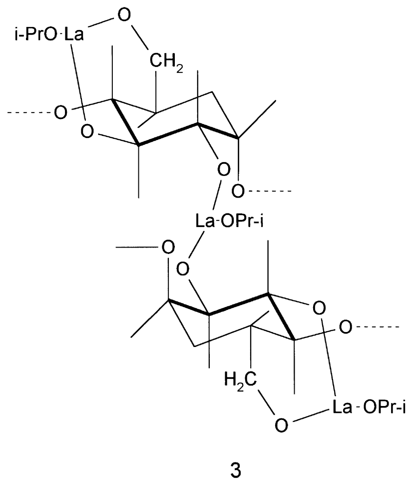


Fig. 6. XPS spectra of lanthanum starchate (V) according to Table 2.

glucose units that are intermolecularly connected by a LaOPr-*i* bridge as shown below:



3

The calculated amount of residue in the form of lanthanum oxide after combustion was 56.6%. Higher calculated concentrations of residue can be ascribed to lanthanum oxide formed by the decomposition of the compound in air.

XPS revealed close similarities between the carbon part of the spectra of the blank sample and the samples that were prepared from the reaction in toluene. The main peak of the blank sample spectrum has one main component. However, this part of the XPS spectrum for both of the microwave heated samples is broader and contains two main components. It is possible that this reflects a higher degree of substitution or partial destruction of the starch matrix by thermal decomposition. Undoubtedly, reflux of starch in toluene does not damage the starch structure. It is not surprising that the oxygen part of the spectra showed more essential differences after the reaction with lanthanum. Oxygen atoms are those which directly bind lanthanum by the valence bond, and eventually coordinate to it. The peak in the oxygen part of the spectrum of the blank sample

Table 2
XPS spectra of starch–lanthanum complexes

Sample	Binding energy (eV)		% of total area	
	C1s	O1s[a]	C1s	O1s
Starch + La_2O_3	285.81	529.69	10.53	2.22
	286.70	531.84	44.87	10.98
	287.57	*533.02*	25.62	52.37
	288.92	**534.02**	10.53	**34.44**
	291.24		8.45	
I (toluene insoluble)	285.54	529.33	12.65	3.33
	286.70	531.12	57.67	14.12
	287.93	532.59	9.88	26.87
	290.39	*533.42*	8.21	*40.04*
	291.71	**534.33**	11.59	**11.98**
		535.41		**3.65**
II (toluene insoluble)	285.30	530.73	10.66	7.92
	286.70	532.75	64.39	37.17
	287.94	*533.66*	9.37	*36.93*
	290.44	**534.84**	8.07	**17.98**
	291.96		7.52	
III (toluene insoluble)	286.70	530.50	69.07	5.00
	287.75	532.36	15.08	15.46
	290.21	533.20	7.53	31.87
	291.80	533.91	8.33	27.08
		535.06		20.60
IV	284.22	530.06	6.98	3.98
	285.32	531.67	23.46	40.64
	286.70	*532.98*	43.56	*46.03*
	288.69	**534.09**	13.45	**9.35**
	290.59		12.57	
V	285.69	527.95	34.22	1.74
	286.70	529.53	36.82	4.82
	288.76	531.31	12.00	25.59
	290.23	*532.42*	11.01	*50.12*
	291.58	**533.60**	5.95	**17.74**

[a] Mutually relevant bands in particular spectra are printed with the same, respective font.

consisted of two essential components, the component of lower binding energy being more intensive. In the spectrum of sample (I), the higher binding energy peak was the most intensive. Sample (IV) exhibited similar behavior of the peak components. In the spectra of sample (II) both components of the main peak are equal in intensity. In sample (II), the intensity of third peak, (i.e. the highest binding energy peak) grew. The spectrum of sample (III) showed the importance of the first component. Simultaneous increases of both the left and right side components were observed, suggesting in both samples (II) and (III) an increased role of the glucose unit oxygen atoms in bonding through the valence and coordination bonds. In the spectrum of sample (V), both main components of equal intensity and, additionally two lower but again equal in intensity components at higher binding energy. We suppose that the differences in the intensity are attributed to a decreased intensity of some composing peaks.

According to our previous point of view (Tomasik et al., 1995), the lowest energy peak should belong to the O6 atom followed subsequently by O2, O3, O4, O1, and $O_{pyranose}$. The interpretation of this part of spectrum is difficult because, apart from carrying chemically bound lanthanum, these oxygen atoms may also coordinate to the lanthanum atom. A comparison of these parts of the spectra led to the conclusion that samples (I) and (II) are very similar to one another and different from sample (III). Samples (IV) and (V) are entirely different from one another, and they are also different from Samples (I) to (III).

5. Conclusions

Three different starch–lanthanum complexes were prepared by varying the reagent ratio and the mode of applied heating. Chemical bonding of the lanthanum atom to the oxygen atoms of the glucose units was proven.

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