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Air oxidation of potato starch over vanadium (V) catalyst

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Abstract

The air oxidation of potato starch over ammonium vanadate (V) is presented. Contrary to the effect of oxidation described for corn starch, oxidised potato starch produced less viscous gels. Optimum quantity of the catalyst applied was about 4% (w/w). Oxidation proceeded at the granule surface level as proved by polarised light and electron microscopies. © 1999 Elsevier Science Ltd. All rights reserved

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1. Introduction

Starch oxidation as a process, as well as starch oxidation products, has attracted considerable attention because of several practical and potential nutritive and non-nutritive applications. Several oxidation methods have been elaborated upon and a variety of products described (Tomasik and Schilling, 1998a). Catalytic air-oxidation has achieved only moderate attention. Among the methods published, the total decomposition of starch into carbon dioxide and water is a trivial one. Such deep decomposition is usually facilitated by ultraviolet irradiation and eventually promoted by metal oxide sensitisers (Tomasik and Zaranyika, 1995). As reported by Gilbert (1958) passing a stream of oxygen through aqueous suspensions (to which 1% KCl was added), resulted in cleavage of the amylose and amylopectin and oxidation at the C2 and C6 as well as C3 atoms, i.e. it did not proceed selectively. Tapioca starch was air oxidised in 3% suspension of hydrochloric acid at 48°C (Dao Tuy Lam et al., 1978). Sunlight has assisted in the air-oxidation of starch and sometimes sensitisers such as zinc oxide have been used (Palit and Dhar, 1928 Palit and Dhar, 1930a Palit and Dhar, 1930b). When the air oxidation was carried out over either Ce(IV) or Fe(III) hydroxides the total decomposition of starch to carbon dioxide and water was achieved (Palit and Dhar, 1925Palit and Dhar, 1926). However, in alkaline medium (pH 9) using metal catalysts from the VIII transition series as well as copper and/or silver, the oxidation did not cause such total destruction and oxidised starch products with applications as ink thickeners, coatings, and detergent builders could be obtained (Conca and Brussani, 1992). Preferably, metal ions should be chelated. Silver in combination with either sodium or ammonium persulfate resulted in the oxidation to carbonyl products rather than to carboxylic acids, although persulfate alone also catalysed the oxidation (Harmon et al., 1971). Carbon supported Pd/Bi and Pd/Pb catalysts were useful in the preparation of polyhydroxypolycarboxylic acids (Fuertes and Fleche, 1987).

There is a report in the literature describing the air oxidation of corn starch over vanadium (V) catalyst (Harmon et al., 1971a). The authors claimed the oxidation of starch for carboxyl and carbonyl compounds with a preference to the latter. They also observed that the oxidation products gave more viscous gels than unprocessed starch.

It is essential that the oxidation products retained their granular structure. In such type reactions the penetration of air might be strongly dependent on specific structure of starch granules i.e. their ability to swell and be penetrated by the oxidant. This paper describes the course and result of the air oxidation of potato starch following the method described by Harmon et al. (1971a).

2. Materials and methods

2.1. Materials

Potato starch was isolated by Pila Potato Enterprise in Poland in 1995, and ammonium vanadate (V), [NH_4VO_3], was obtained from POCH Gliwice (Poland).

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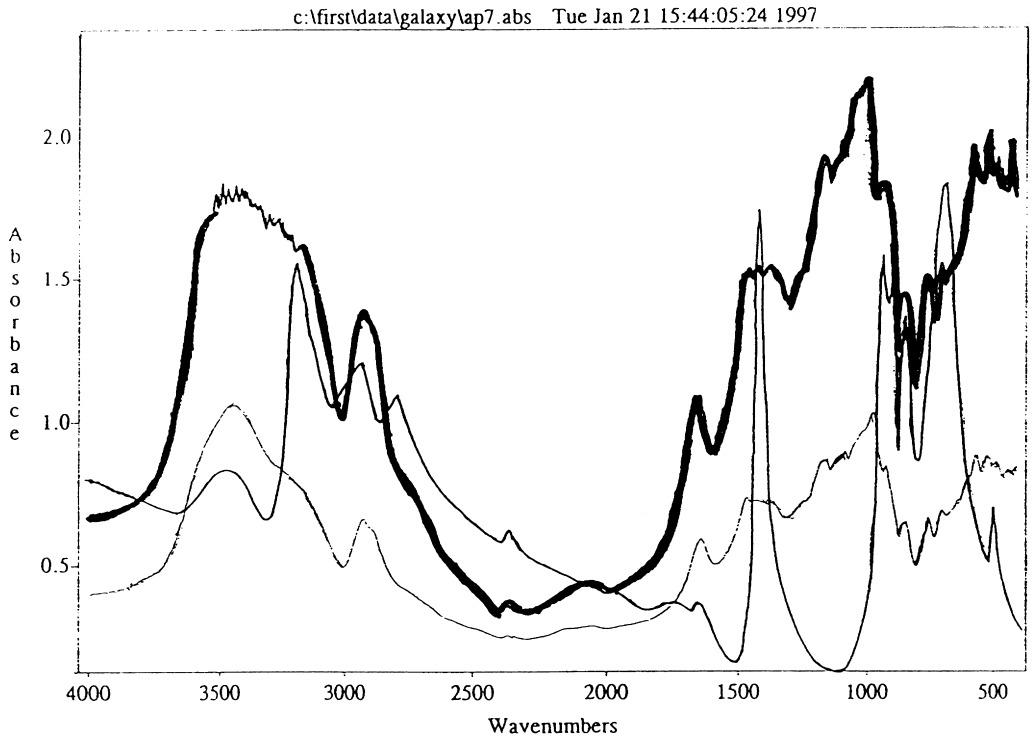

Fig. 1. IR-absorption spectra of original starch. Thin line spectrum belongs to untreated starch, Bold line spectrum belongs to starch oxidised in the presence of 10 g of ammonium vanadate, and spectrum of pure ammonium vanadate is given in medium bold line.

2.2. Methods

2.2.1. Oxidation

Suspensions of air-dried potato starch containing 12% moisture (50 g) in distilled water (500 ml) was supplemented with ammonium vanadate (V) (either 1, 2, 5, 10 or 20 g). A marine blue colour appeared. The pH of each blend was adjusted to 9.0 by addition of 10% aq. NaOH. Each continuously stirred reaction mixture was maintained at 35–40°C and was aerated for 48 h with a slow air stream. After the reaction was over and its colour turned yellowish, the reaction mixture was filtered through a sintered glass filter and the filtrate washed with ice cold water to remove the catalyst. The products were dried in a desiccator over molecular sieves. The control samples were prepared by 2 h stirring of non-aerated reaction mixtures prepared as above.

2.2.2. Analyses

Characteristics of gelation were recorded for 7.2% aqueous product suspensions using a Rheotest-2 instrument following the standard program. Nitrogen contents were determined by Dumas semi-micro combustion analysis. Infrared spectra were recorded using KBr discs. Thermal analysis [thermogravimetry (TG), differential thermal gravimetry (DTG), and differential thermal analysis

Table 1
Characteristics of gelation of potato starch air-oxidised over vanadium (V) catalyst and pH

Catalyst amount (g)	Initial gelation temperature (°C)[a]	η_{max} (cP)[a]	Temperature at η_{max} (°C)[a]	η after 20 min at 96°C (cP)[a]	η_{min} (cP)[a]	Temperature at η_{min} (cP)[a]	η_{25} (cP)[a]	pH[a]
0	65.5	1250	96.0	850	830	87.0	1330	6.30
1	64.0	540	96.0	500	490	91.5	1040	7.06
	(64.0)	(940)	(88.5)	(660)	(650)	(92.5)	(1360)	(7.02)
2	65.5	320	96.0	280	275	90.0	570	8.15
	(63.5)	(950)	(76.5)	(600)	(580)	(91.5)	(1180)	(7.12)
5	62.5	510	75.0	290	280	87.0	540	7.60
	(59.5)	(1090)	(69.0)	(490)	(480)	(93.0)	(970)	(6.40)
10	61.5	680	77.0	330	320	90.0	600	6.77
	(60.0)	(1290)	(62.5)	(470)	(465)	(94.0)	(930)	(6.92)
20	59.5	465	71.5	210	205	89.5	395	7.87
	(60.0)	(480)	(68.0)	(200)	(190)	(91.0)	(320)	(6.62)

[a]The upper values are for oxidised starch and lower values in parentheses are for nonoxidised starch–vanadate blends.

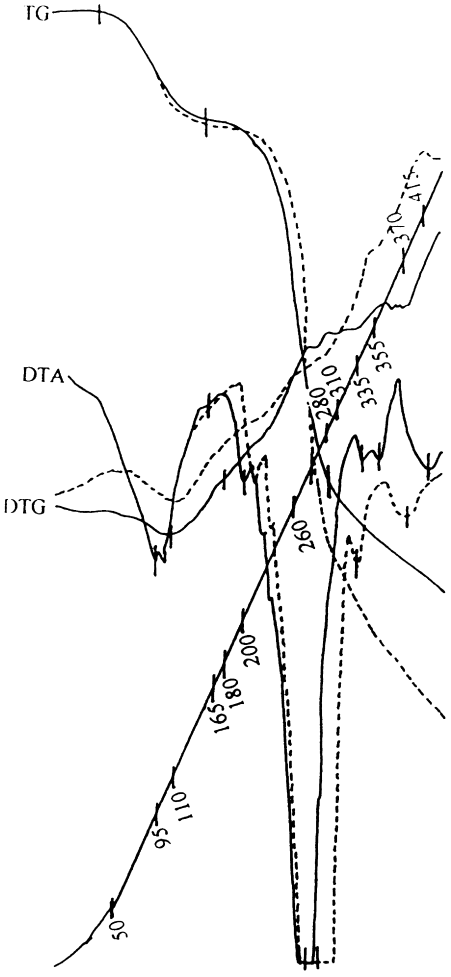

Fig. 2. Thermograms (TG, DTG and DTA functions) of starch oxidised in the presence of 2 g (solid lines) and 20 g (broken lines) of ammonium vanadate.

(DTA)] were run on 200 mg samples in air over a 20–500°C range with a temperature gradient of 10°C min^{-1}. Corundum, 8 μm, was the standard. Quantitative determination of the carbonyl groups was carried out according to Krajcinovic (1948), and carboxylic groups were determined according to Boruch (1970).

Granularity changes were determined using a sedimentation Sartorius balance. Aqueous suspensions were measured.

Observations of starch granules under the polarised light were performed with a polarised-interferential microscope Biopolar-PI, manufactured by PZO Warsaw, Poland. Electron micrographs were taken with a JEOL 5400 instrument equipped with a LINK ISIS 300 Oxford Instruments electron probe energy dispersive microanalyser. Samples were fixed to the holder with two-side carbon tape and covered with gold. The granule morphology was studied up to $\times 10^4$ magnification employing secondary electrons at an accelerating gradient of 20 kV.

3. Results and discussion

Table 1 presents the gelation characteristics of air oxidised starch prepared with increasing addition of the catalyst. One can see that application of catalyst applied above 4% (w/w) essentially resulted in a change in the temperature of the viscosity maximum, leaving all other characteristic parameters only slightly affected.

As a rule, a decrease in all of the characteristic parameters, except in the temperature of the viscosity minimum, was always observed. The temperature at the viscosity minimum slightly increased. This effect is opposite to that observed by Harmon et al. (1971a) who oxidised corn starch in the same manner. In Table 1, pH of the reaction mixtures are given. One might see that all non-aerated blends of starch with catalyst, after the blank isolation procedure,

Table 2
Aqueous solubility (AS, %) and water binding capacity (WBC, g/g of dry substance) of oxidised starches[a], pH of 1% aq. solutions and amount of the carbonyl and carboxylic groups, mval 100 g^{-1} of dry sample

Amount of vanadate (g)	25°C		40°C		60°C		Groups[a]		
	AS[a]	WBC[a]	AS[a]	WBC[a]	AS[a]	WBC[a]	pH[a]	C = O	COOH
Control	0.91	0.87	1.79	0.90	7.55	12.91	6.30	2.32	4.11[b]
1.0	8.88	2.53	8.27	2.72	28.50	24.93	7.06		
	(3.65)	(2.08)	(4.09)	(1.97)	(20.44)	(28.17)	(7.02)		
2.0	5.84	2.04	5.28	1.99	39.20	22.34	8.15	31.7	1.16[c]
	(2.31)	(1.77)	(2.59)	(1.65)	(20.69)	(38.09)	(7.12)	(8.71)	
5.0	6.50	2.32	7.59	2.37	48.56	38.62	7.60	74.0	
	(4.35)	(3.73)	(4.85)	(3.52)	(28.07)	(49.06)	(6.40)	(21.7)	
10	3.67	2.57	3.51	1.86	34.43	36.39	6.77	13.6	1.83
	(3.97)	(1.75)	(2.29)	(1.55)	(26.75)	(53.97)	(6.92)	(67.37)	
20	14.79	3.85	16.29	3.87	59.20	47.86	7.87	46.0	1.97[d]
	(8.05)	(3.97)	(9.09)	(4.19)	(28.47)	(42.33)	(6.62)	(53.32)	
	[31.19]	[0.79]	[30.29]	[0.57]	[37.30]	[46.51]			

[a]The upper values are related to oxidised starch and lower values in parentheses are related to aqueous starch–ammonium vanadate blends maintained for 48 h at room temperature without oxidation. The figures in brackets on the bottom of the table are these determined for starch–ammonium vanadate blend maintained dry for 48 h.

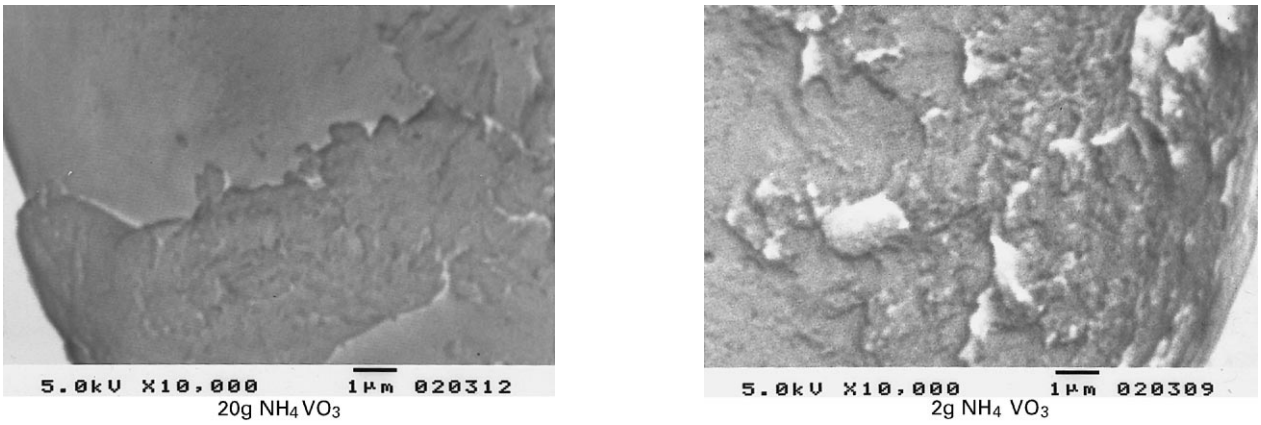

Fig. 3. Electron micrographs of starch granules oxidised over 2 g ammonium vanadate (left) and 20 g of ammonium vanadate (right) ($\times 10^4$ magnification).

gave material being either neutral or slightly acidic. This meant that the majority of the catalyst and alkali could effectively be removed from starch. Indeed the elemental analysis showed residual content of nitrogen in the oxidised samples (0.33 and 0.71% N in the samples processed with 2 and 20 g catalyst, respectively). However, the oxidised starch samples after the same procedure retained basic properties. It could suggest that starch was oxidised to carboxylic acids, salts of which captured sodium cations from the reaction medium. Corresponding sodium carboxylates being salts of weak acid and strong base hydrolysed in aqueous solution increasing the pH above 7. The elements of the vanadate spectrum could not be recognised in the IR spectrum of the oxidised product (Fig. 1).

The 2500–4000 cm^{-1} range of the spectrum points to some essential changes in the hydroxyl group pattern of the glucose units. Significant changes can be observed in the shape of the intensive band of stretching frequencies of these groups and their intensity with respect to the aliphatic CH stretching frequencies at 2900 cm^{-1}. Moreover, all KBr spectra of original starch run at concentrations varying from 0.0281 to 0.0067 g/1 g of KBr had the ratio of the bands at 1465 and 1383 cm^{-1}, slightly above unity. In the spectra of the oxidised products this ratio was slightly below unity. In the latter region vibrations of the carboxylic group may appear.

Table 2 reports further physicochemical characteristics of the oxidised products. Their aqueous solubility and water binding capacity, particularly at 25 and 40°C, increased with respect to the control, but this increase was not linearly related to the amount of the catalyst used.

The solubility of starch in the presence of ammonium vanadate prior to oxidation varied similarly. This observation might be rationalised in terms of the complex formation. The complexation of starch with inorganic salts has been observed several times (Tomasik and Schilling, 1998).

Table 2 shows that the oxidation of starch to carbonyl starch has a priority over its oxidation to carboxylic starch.

Comparison of the thermal properties of starch oxidised in the presence of 2 and 20 g of catalyst; the latter being more oxidised than the previous one, is given in Fig. 2.

One can see that the matrix of both samples retained the same amount, 10.5% of water. The less oxidised sample revealed a glassy transition at 215°C and the main decomposition peak at 275°C. The fast weight loss started at 165° and lasted up to 310°C. Up to this temperature the sample lost 60% of its weight. The more oxidised sample was less thermally stable. Its glassy transition and main decomposition occurred 15°C lower, but at the same time the interval of the fast weight loss was over at 280°C with only 44.5% weight reduction. A 60% weight loss, as in the case of the former sample, was achieved just at 415°C. The course of the DTA curves in the thermograms of both samples also differed from one another. The more oxidised sample had more well defined, but still weak, peaks. The lower thermal stability of the more oxidised sample might be accounted for by the reduced number of inter- and intra-molecular

Table 3
Changes in the particle size distribution of granules as a function of oxidation

Sample	% contribution to total		
	$< 21.7\ \mu m$	21.8–30.6 μm	$> 30.7\ \mu m$
Original	28.7	23.9	47.4
Oxidised with:			
2 g of vanadate	26.0	23.9	50.1
5 g of vanadate	23.4	28.7	47.9
10 g of vanadate	27.1	24.5	48.4
20 g of vanadate	28.2	23.9	47.9

hydrogen bonds and a disorder of the starch matrix after processing. The higher stability of the decomposition products from the more oxidised sample might be due to the presence of crosslinked residues which could be formed by a participation of the carboxyl and carbonyl groups.

Table 3 shows that oxidised starch retained its granularity and almost negligible changes could be observed in the proportion of the granular fractions after oxidation. A very similar distribution of granules of particular sizes suggests that granules did not swell as a result of processing. The microscopic observations under polarised light showed a six-arm star instead of usual cross of polarisation but typical shining of the granules retained.

These results are also confirmed by electron micrographs (Fig. 3). A clear erosion of the granule surface was observed after the oxidation demonstrating that the process occurred on the surface and not in the granule interior.

4. Conclusions

Contrary to the effect of oxidation described for corn starch, oxidised potato starch produced less viscous gels. The optimum quantity of the catalyst applied was about 4% (w/w). Oxidation proceeded at the granule surface level.

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