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Carbohydrate Polymers 49 (2002) 449–456

Carbohydrate Polymers

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Effects of hydrogen, oxygen, and ammonia low-pressure glow plasma on granular starches

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Accepted 22 October 2001

Abstract

Cassava, corn, high amylose corn, potato, rice Indica, rice Japonica, sweet potato, waxy corn, and wheat starches were exposed to low-pressure ammonia, hydrogen, and oxygen plasma. In every case, depolymerization of the starch polysaccharides was noted. The extent of the depolymerization depended on the nature of the starch as well as the type of plasma applied. Among three fractions of polysaccharides distinguished by their molecular weight average, the fraction of the highest molecular weight suffered the most efficient depolymerization. The relative depolymerization for the middle- and low-molecular fractions of polysaccharides was found to be starch and plasma specific. The chemical character of the plasma had very little influence on the starch polysaccharides. Only subtle oxidation effects were observed in oxygen plasma. Low-pressure glow plasma treatment appeared to be a convenient tool for a waste-less dextrinization of starch. Manipulation of the plasma variety and the time of exposure resulted in a wide spectrum of dextrins of various molecular weights and paste-forming properties. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ammonia glow plasma; Hydrogen glow plasma; Oxygen glow plasma; Starch depolymerization

1. Introduction

Glow plasma is commonly used for etching, and cleaning of metallic and non-metallic inorganic materials (Korzec, Rapp, Theirich, & Engemann, 1994; Matsuoka, Sakaguchi, & Ihara, 1996; Panin, Slosman, & Matryonin, 1996; Rawles et al., 1997; Sun & Chao, 1995), but there is also a growing number of suggested applications of plasma for modification of organic materials. Thus, plasma has been applied for degradation of organic synthetic (Gilman, Drachev, Kuznetsov, Lopukhova, & Potapov, 1997; Koprinarov, Lippitz, Friedrich, Unger, & Woll, 1998; Weidner, Kuehn, Friedrich, & Schroeder, 1996) and semi-synthetic (Short, Munro, Ward, Chan, & Tan, 1994) polymers. It has been used to improve the performance of conducting (Oyama & Wightman, 1998) and superconducting films (Pang, 1998), sorption (Braznikova & Gerasimov, 1994), adhesion (Badey, Espuche, Jugnet, Chabert, & Duc, 1996; Brovikova, Abramov, & Menagarishvili, 1992; Brovikova, Menagarishvili, Rybkin, & Slabnova, 1996; Li, Netravali, & Sachse, 1992) and dyeing of synthetic (Mishra & Norton, 1993), and natural (Goto, Wakita, Nakanishi, & Ohta, 1992; Kaufmann, Herling, Thomas, Klausen, & Hoecker, 1993) fibers. Plasma treatment has been shown to increase reactivity of the surface of polymers (Lin, Ko, & Cooper, 1994; Xiang, Wu, Guo, & Xie, 1995). Other applications of glow plasma are as a source of energy for carrying reactions, for instance, graft polymerization (Girardeaux, Lefebvre, Le, Pireaux, & Caudano, 1995; Ratway & Balik, 1997; Wu, Gutowsky, Li, & Griesser, 1995; Zhao, Yao, & Liu, 1992; Zubaidi & Hirotsu, 1996). Applications of glow discharge plasma to biomaterials have been recently reviewed (Ratner, 1997).

Results of the treatment with plasma depend primarily on its energy, i.e. on the mode of its generation (low-pressure, radio frequency, microwave). The type of excited gas is also an important factor. Plasma may be generated by ionization of many gases, for instance, O_2, H_2, He, Ne, Ar, NH_3, CH_4, CF_4, and so on. Study of the action of some such plasmas on polysulfone (Hopkins & Badyal, 1996) revealed that chemical and topological modifications of the surface of that polymer were strongly dependent on the type of feed gas. Although plasma from each gas could physically modify surfaces (Mozetic, 2001), some plasmas might also cause

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PII: S0144-8617(01)00351-4

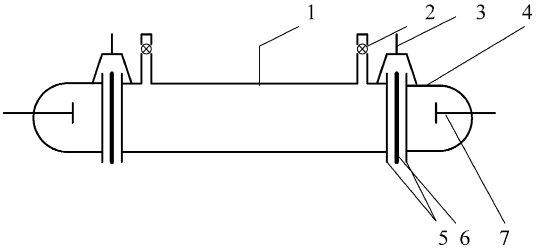

Fig. 1. Scheme of the plasma reactor. (1) Pyrex glass tube; (2) teflon valves; (3) clip; (4) adapter with electrode; (5) joints; (6) rubber O-ring; (7) stainless steel or platinum disc electrode.

chemical modifications. For instance, ammonia plasma defluorinated teflon (Pringle, Joss, & Jones, 1996). Under certain conditions, amination of polyglycidyl esters could be afforded in ammonia plasma (Brown, Chappel, & George, 1993). Because of its reducing properties, hydrogen plasma was utilized in the hydrocracking of higher hydrocarbons (Motallebi, Pernin, & Amouroux, 1991). Oxidative properties of oxygen plasma (Pastor Blas, Martin Martinez, & Dillard, 1998; Saha & Chang, 1992; Thompson, Tyler, & Minton, 1997) have found applications in the oxidation of alkylbenzenes to cresols (Ropero, Patino, Armas, Karam, & Iacocca, 1992), and antraquinone dyes (Ito, Nanba, Nomura, & Shiokawa, 1992) as well as for afterburning of gases (Boen, Vincent, Cartier, & Taupiac, 1994).

Water vapor is another factor influencing the action of plasma (Ratliff & Harrison, 1994). Water concentrations up to 5% were shown to be beneficial as water dissociated in the atmosphere of plasma and mediated ionization of gases. Higher water concentration had detrimental effect on gas atomization and ionization.

In a recent paper (Lii, Liao, Stobinski, & Tomasik, 2001), low-pressure glow plasma was suggested as a facile tool for a waste-less starch dextrinization. Results collected for air plasma prompted us to check the effects of hydrogen, ammonia, and oxygen plasma upon granular cassava, corn, high amylose corn, potato, rice Indica KSS7, rice Japonica TNu67, sweet potato, waxy corn, and wheat starches.

2. Materials and methods

2.1. Samples

Potato, corn, high amylose corn, and wheat starches were purchased from Sigma (St Louis, MI). Rice TNu67 Japonica, rice KSS7 Indica, sweet potato, waxy corn, and cassava starches were isolated in our laboratory using the method described by Yang, Lai, and Lii (1984).

All starches were exposed to glow plasma in the air-dried state. However, their humidity content was determined prior to experiment and after exposure. In one case, potato starch was exposed after overnight drying at 100 °C in a vacuum oven.

2.2. Gases

Ammonia of 99.99% purity was purchased from Conley Gas Ltd, Houston, TX. Hydrogen and oxygen, both of 99.99% purity, were the products of Far Eastern Gas Co., Hsin-Chu, Taiwan.

2.3. Exposure of starch to glow plasma

Samples of starch (1 g) were placed in a reactor made of a 10 cm Pyrex glass tube of 15 mm internal diameter with either stainless steel or platinum electrodes (Fig. 1). The electrodes were made of stainless steel rods sealed through the glass in both reactor ends with corresponding metal discs of 10 mm in diameter attached to these rods. The reactor was equipped with gas inlets and outlet pipes controlled by glass–teflon vacuum valves.

Starch samples were fairly evenly distributed within the horizontally positioned reactor and a home built vacuum system equipped with both turbo and rotary pumps, providing up to 10^{-7} Torr, was used to evacuate the reactor. The pressure was controlled throughout the period of experiment by means of an A-NET Crystal Gauge M-320XG (Anelwa, Japan). The valves of the reactor and the vacuum pump were installed in such a manner that, at any desired vacuum, there was a slow stream of a suitable gas from the tank passing through the reactor.

2.4. Plasma generation

After reaching a suitable vacuum in the reactor, a potential gradient was applied from the AC Induction Coil Power Supply (CENCO Central Scientific Company, Rochester, NY) operating at 65 kV and 0.25 A. In the first period of the experiments, approximately 5 min, the pressure within reactor was adjusted to a value which provided a filament discharge between electrodes. In this period, the plasma-killing water was evacuated from starch granules. When water was evacuated, the glow expanded to the whole volume of the reactor.

Uniform reaction conditions were applied to all starches after examination of the results of exposure of selected starches, using one of the two sources for 10, 20 and 30 min at 1, 10^{-1}, and 10^{-2} Torr. The reactor was mechanically shaken throughout the treatment. All exposures were duplicated. After the exposure was over, the samples of starch were collected in tightly closed vials and subjected to a series of tests.

2.5. pH in aqueous solution

pH was estimated for 0.5% aqueous solutions of starch.

2.6. FTIR spectrometry in KBr discs

The infrared spectra were run in KBr discs using a Perkin–Elmer FTIR spectrometer Paragon 1000 (Norwalk, CT), in the frequency range of 4000–400 cm^{-1}.

Table 1
HPSEC analysis of original and plasma exposed starches (data relate to starches exposed to plasma generated from a DC supply; M_w Av., η_{int}, and R denote molecular weight average, intrinsic viscosity (dl/g), and radius of gyration (nm), respectively; the data for the air plasma are taken from our earlier paper (Lii et al., 2001))

Starch	Plasma	M_w Av. × 10^7	Extent of changes[a] (%)	η_{int}	R
Cassava	None	9.35 ± 0.02	–	0.52 ± 0.04	75.68 ± 7.33
	Air	4.93 ± 0.06	47.3	0.45 ± 0.01	49.87 ± 1.34
	Hydrogen	5.79 ± 0.07	38.1	0.40 ± 0.01	58.15 ± 1.20
	Oxygen	4.52 ± 0.12	51.7	0.45 ± 0.02	45.44 ± 0.41
	Ammonia	1.59 ± 0.05	83.0	0.44 ± 0.02	31.91 ± 1.03
Corn	None	8.68 ± 0.11		0.31 ± 0.02	57.49 ± 6.51
	Air	5.34 ± 0.18	38.5	0.26 ± 0.04	25.49 ± 5.48
	Hydrogen	3.75 ± 0.34	56.2	0.33 ± 0.03	41.24 ± 3.18
	Oxygen	2.61 ± 0.14	69.9	0.31 ± 0.00	33.81 ± 0.58
	Ammonia	3.12 ± 0.25	64.1	0.35 ± 0.04	47.10 ± 4.37
High amylose corn	None	2.11 ± 0.02		0.30 ± 0.01	21.04 ± 1.17
	Air	1.74 ± 0.05	17.5	0.31 ± 0.01	21.76 ± 0.82
	Hydrogen	1.56 ± 0.05	26.1	0.29 ± 0.02	19.49 ± 0.65
	Oxygen	1.37 ± 0.09	35.1	0.15 ± 0.01	15.50 ± 0.41
	Ammonia	1.54 ± 0.07	27.0	0.37 ± 0.03	18.30 ± 0.64
Potato	None	7.73 ± 0.07		0.43 ± 0.08	53.11 ± 8.39
	Air	3.68 ± 0.23	52.4	0.34 ± 0.04	33.46 ± 3.00
	Hydrogen	5.63 ± 0.21	27.2	0.35 ± 0.02	46.18 ± 2.17
	Oxygen	2.72 ± 0.23	64.8	0.31 ± 0.02	38.67 ± 1.65
	Ammonia	1.95 ± 0.04	74.8	0.59 ± 0.05	47.52 ± 3.71
Rice KSS7	None	8.62 ± 0.08		0.30 ± 0.02	58.41 ± 0.78
	Air	6.87 ± 0.79	20.3	0.38 ± 0.02	59.61 ± 1.95
	Hydrogen	7.90 ± 0.01	8.4	0.34 ± 0.02	63.22 ± 1.88
	Oxygen	5.50 ± 0.15	36.2	0.26 ± 0.01	45.05 ± 4.25
	Ammonia	5.12 ± 0.10	40.6	0.33 ± 0.01	59.06 ± 0.22
Rice TNu67	None	13.70 ± 0.00		0.32 ± 0.01	76.45 ± 2.43
	Air	2.89 ± 0.08	78.9	0.25 ± 0.01	27.48 ± 0.90
	Hydrogen	7.99 ± 0.17	41.7	0.33 ± 0.01	60.06 ± 0.58
	Oxygen	6.00 ± 0.15	56.2	0.25 ± 0.01	54.26 ± 4.37
	Ammonia	3.21 ± 0.10	76.6	0.38 ± 0.02	46.98 ± 2.00
Sweet potato	None	5.45 ± 0.03		0.24 ± 0.01	38.12 ± 0.65
	Air	Not estimated			
	Hydrogen	4.22 ± 0.05	22.6	0.28 ± 0.01	40.54 ± 0.43
	Oxygen	3.59 ± 0.27	34.1	0.28 ± 0.02	36.07 ± 0.63
	Ammonia	2.70 ± 0.15	50.5	0.28 ± 0.00	38.31 ± 1.79
Waxy corn	None	14.34 ± 0.05		0.39 ± 0.01	72.66 ± 1.94
	Air	9.67 ± 0.73	32.6	0.25 ± 0.02	52.27 ± 4.43
	Hydrogen	9.12 ± 0.34	36.4	0.32 ± 0.02	70.97 ± 0.90
	Oxygen	4.53 ± 0.21	68.4	0.27 ± 0.01	54.13 ± 0.78
	Ammonia	4.92 ± 0.16	65.7	0.36 ± 0.05	60.31 ± 5.99
Wheat	None	7.09 ± 0.07		0.32 ± 0.03	52.13 ± 5.36
	Air	5.11 ± 0.61	27.9	0.42 ± 0.02	56.93 ± 2.28
	Hydrogen	4.22 ± 0.05	40.5	0.26 ± 0.01	40.49 ± 1.86
	Oxygen	3.85 ± 0.15	45.7	0.38 ± 0.02	40.80 ± 0.90
	Ammonia	3.96 ± 0.13	44.1	0.43 ± 0.02	50.54 ± 1.39

[a] The extent of reduction of average molecular weight in respect to non-exposed starch being the control sample.

2.7. Thermogravimetry (TG) and differential thermogravimetry (DTG)

The thermal characteristics were examined under a nitrogen stream using a Du Pont TGA 951 System (Willmington, DE) and scanned from 25 to 400 °C at scan rate of 10 °C/min.

2.8. High performance size exclusion chromatography (HPSEC)

Starch samples (1 g) were dissolved in 95% DMSO (50 ml) with stirring for 3 days at room temperature. The sample was then precipitated with ethanol (150 ml) and

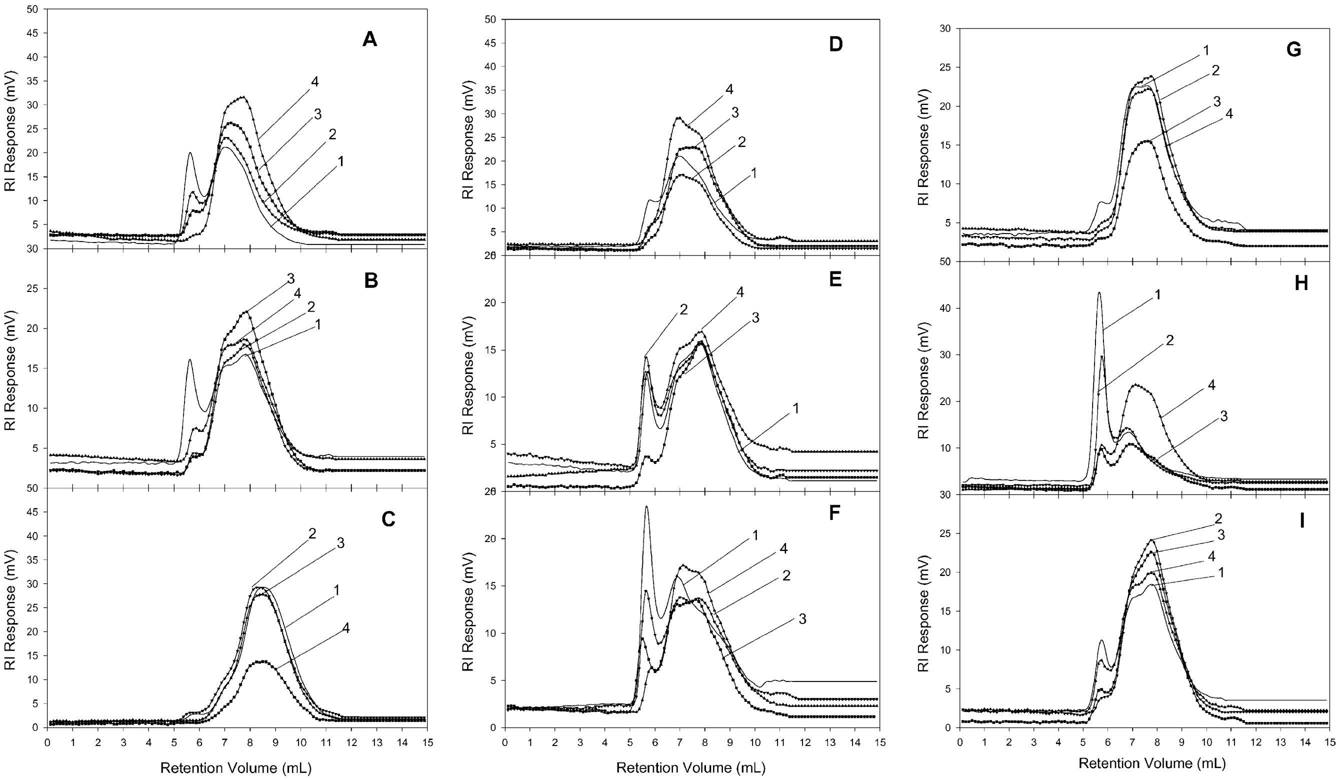

Fig. 2. Starch botanical origin-specific effect of plasma upon three fractions of starch polysaccharides in granular starches. (A) Cassava starch; (B) cornstarch; (C) high amylose cornstarch; (D) potato starch; (E) rice Indica KSS7 starch; (F) rice Japonica TNu67 starch; (G) sweet potato starch; (H) waxy cornstarch; (I) wheat starch. Plain lines (1) are for original starch, lines (2), (3) and (4) are for starches exposed to hydrogen, oxygen and ammonia plasma, respectively.

stored overnight at 4 °C. The precipitate was centrifuged in a bench centrifuge whilst with adding acetone (50 ml) and diethyl ether (50 ml). The precipitate was collected and finally dried in vacuum at room temperature for 24 h.

The mobile phase used for HPSEC was aqueous $NaNO_3$ solution (0.1 M) that had been filtered through 0.45 μm membrane filter and degassed by a vacuum pump before use. The HPSEC–MALLS–RI system consisted of a pump, an injector valve with a 500 μl loop, a guard column, a SEC column, a laser light scattering detector, and a refractive index detector. Column temperature and flow rate were 70 °C and 0.5 ml/min, respectively. The starch solution was filtered through 5.0 μm filters before injection into the HPSEC system.

Samples of concentration of 0.5 g/1 ml $NaNO_3$ were injected onto the column. Experiments were run in triplicates.

2.9. Powder X-ray diffraction

A Siemens D 5000 diffractometer (Germany) was operated at the Cu Kα wavelength of 0.154 nm, 30 mA and 40 keV. The spectra over the range of 4.0–30.0° 2θ were recorded at a scan rate of 0.02° 2θ/s. Percent of crystallinity was determined according to Gernat, Radosta, Anger, and Damaschun (1993).

3. Results and discussion

The energy necessary for the generation of low-pressure glow plasmas depends, amongst other things, on the nature of the gas being excited and/or ionized. Hence, energy of the generated plasma is its conjugated parameter. The lifetime and the chemical reactivity of excited and/or ionized molecules in a gas are, obviously, different for various gases. Therefore, one might anticipate that the effects of the action of low-pressure plasma generated in various gases would produce different effects on the material exposed to the plasma. Our former paper (Lii et al., 2001) on the treatment of granular starches with air plasma documented that results of the treatment depended on botanical origin of the starch.

Results in Table 1 show that particular starches exhibited varying affinities to different plasmas.

For all starches the polysaccharides could be separated into three fractions, distinguished from one another by molecular weight average (Fig. 2). In all nine starches, the effect of plasma on the polysaccharides from these three fractions was not uniform.

Differences in susceptibility of particular starches to air plasma were tentatively accounted for in terms of the structure of the granule as well as the effects of lipids and proteins non-uniformly distributed within the starch granules.

Based on their ability to depolymerize starch plasmas

Table 2
Crystallinity (%) of starches prior to and after exposure to plasmas (according to Gernat et al. (1993))

Starch	Applied plasma				
	None	Air	Hydrogen	Ammonia	Oxygen
Cassava	38.6	38.2	40.2	40.0	38.4
Corn	40.3		29.2	33.0	37.1
High amylose corn	33.7	33.7	36.6	23.9	32.5
Potato	46.8	41.3	36.6	43.2	44.6
Rice KSS7	38.7		36.7	35.2	36.4
Rice Tnu67	37.3	31.7	36.6	39.9	34.8
Waxy corn	43.6	32.6	46.3	44.7	45.1

could be grouped into two classes: less active (hydrogen and air plasma) and more active (ammonia and oxygen plasma). It should be emphasized that both air and oxygen plasma had oxidizing properties but both belonged to different classes. These differences might be associated, amongst other factors, with relative energies of both the plasmas. For the air plasma, part of the energy may be consumed on reactions between nitrogen and oxygen (Jennings, 1961). However, these reasons resulting only from the plasma property are more complex (Brown, 1958).

Cassava and rice TNu67 Japonica starches suffered the highest extent of depolymerization, whereas rice KSS7 Indica and high amylose cornstarches were the most resistant to depolymerization. In spite of evident depolymerization, the intrinsic viscosity of gels significantly decreased only in few cases. The chemical character of the acting plasma had fairly little effect on the results of exposure. The most drastic decrease could be noted for cassava, potato, and waxy cornstarches. Exceptionally, deep decreases in intrinsic viscosity were noted for high amylose cornstarch treated with oxygen plasma. In several cases, treatment with plasma resulted in an increase in the gel intrinsic viscosity. Generally, this effect could be accounted for by reaction of the plasma with non-starchy components of starch granules, e.g. proteins. The highest and almost regular increase in the gel intrinsic viscosity resulted from treatment of starch with ammonia plasma. This could be rationalized in terms of neutralization of acidic regions of these starches to form ammonium salts, and the effect of residual ammonia adsorbed in the starch granules. Such types of effects of ammonium salts and ammonium hydroxide on starch paste viscosity are known (Tomasik & Schilling, 1998). On the other hand, gaseous ammonia was shown to inhibit thermal dextrinization of starch (Sychowska & Tomasik, 1997). A noticeable increase in intrinsic viscosity was observed for gels from potato starch exposed to ammonia plasma. This could be caused by ammonium phosphate formed from phosphoric acid moieties and ammonia.

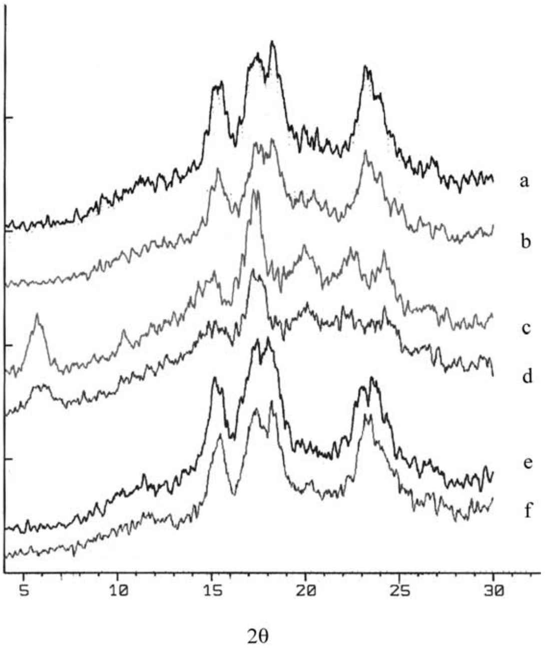

Fig. 3. X-ray powder diffractograms of native rice Japonica TNu67 (a) and after its exposure to ammonia plasma (b); native high amylose cornstarch (c) and after its exposure to ammonia plasma (d); native waxy cornstarch (e) and after its exposure to ammonia plasma (f).

Exposure of starches to plasmas had some effect upon the radius of gyration of starch gels. Particularly small changes were noted for high amylose cornstarch, rice KSS7 Indica and sweet potato starches. These findings related to the decrease in the degree of polymerization of those starches but they did not fit changes in crystallinity calculated from X-ray powder diffractograms (Table 2).

Assignment of crystallographic changes to areas of the starch granules was not uniform. It varied with the character of the plasma as well as the starch variety. Thus, for example, the most essential changes in waxy cornstarch and cornstarch exposed to ammonia plasma took place in the regions located at the closest to one another, e.g. at 2θ around 23° (Fig. 3).

The most essential crystallographic changes in high amylose cornstarch exposed to ammonia plasma could be observed around $2\theta = 6$ and 15°.

Interior of starch granules is composed of concentric layers of crystalline material. Between these layers, amorphous material is located (Gallant, Bouchet, & Baldwin, 1997; Tegge, 1984). Thus far, details of the composition of these layers as well as even distances between them, particularly, in connection with botanical origin of the starches, remain unknown. Because of its nature, plasma regardless of its type acted, first of all on the surface of granules. Plasma could also penetrate, to a certain extent, to the regions of the granule interior located closely to the surface. Changes in the diffractograms could throw a light on the interlayer distances in these regions of starch granules and relate these changes to starch varieties. Action of plasma resulted in certain cases in an increase and in the others, in decrease in the crystallinity (Table 2). The increase in the crystallinity could signalize the increase in

Table 3
Thermal properties of starches prior to and after treatment with plasma

Starch variety	Native		After plasma treatment					
			Hydrogen		Oxygen		Ammonia	
	TG[a] (%)	DTG[b] (°C)	TG[a] (%)	DTG[b] (°C)	TG[a] (%)	DTG[b] (°C)	TG[a] (%)	DTG[b] (°C)
Cassava	66.5	62	74	68	72	66	71.5	58
		287		287		275		287
		324		318		321		320
Corn	65	58	75.5	67	70	62	71	58
		291		290		279		292
		321		314		311		316
High amylose corn	63	68	65	64	68	70	67	58
		289		282		279		292
		314		309		310		310
Potato	56	66	66	60	66	65	63	63
						252		
		289		?s[c]		271		?s[c]
		314		305		302		313
Rice KSS7	63	58	74.5	62	68	64	69.5	62
		300		292		?[c]		?s
		332		319		323		320
Rice TNu67	66	58	70	65	71	66	69	57
		292		281		283		?s[c]
		321		309		319		317
Sweet potato	69	53	74	63	70	66	71	59
		274		281		265?		?s[c]
		315.5		311.5		316		316
Waxy corn	65.5	60	75	74	81	62	65.5	64
		300s		?s[c]		?[c]		300s
		325.5		320		323		326
Wheat	60.5	64	69	64	68	60	62	61
		?s[c]		?s[c]		?[c]		?s[c]
		315		309.5		314		310.5

[a] The weight loss in the range from 260 to 350 °C.

[b] The differential thermal gravimetry. The first value corresponds to water evolution, the second reflected the glass transition and the third the thermal decomposition.

[c] The shoulder.

the content of less branched polysaccharides resulting from splitting side chains of amylose. Such polysaccharides as well as fragments being split could organize into more crystalline domains. Such behavior was observed, for instance, on illumination of starches with white polarized light (Fiedorowicz, Lii, & Tomasik, 2001). Decrease in the crystallinity could be evoked by deeper depolymerization of polysaccharides as well as by a pattern of splitting which could occur beyond sites of branching of polysaccharides.

Thus, powder X-ray studies together with insights into the effects of plasma upon the three fractions of starch macromolecules might be useful in considerations on the structure of the interior of the starch granules. Generally, ammonia plasma was the most active and hydrogen plasma was least active. Particular plasmas differently decomposed the three fractions of polysaccharides in particular starches. The HPSEC profiles for different starches (Fig. 2) exposed to particular plasmas are shown to be different prior to and after exposure. All three plasmas depolymerized the highest molecular weight component of starch granules, presumably amylopectin, to the highest extent. Because the granule shells consisted of highly polymerized amylopectin this fact seemed to be well rationalized. Commonly, the middle-molecular weight fraction suffered the next level of extensive decomposition on exposure to plasma. Only in the case of rice Indica KSS7 starch, the ammonia plasma decomposed the low-molecular fraction more willingly than the middle-molecular fraction.

Quantitative results in Table 1 revealed that amongst all the starches exposed to plasmas, high amylose cornstarch appeared to be the most resistant to depolymerization. This was the botanical variety whose polysaccharides had the

Table 4
Changes in pH after exposure of starches to oxygen plasma

Starch	pH		ΔpH
	Original	Plasma exposed	
Cassava	5.97	4.48	1.49
Corn	6.05	4.38	1.64
High amylose corn	6.07	4.70	1.37
Potato	7.58	5.08	2.50
Rice KSS7 Indica	7.42	4.66	2.76
Rice TNu67 Japonica	6.95	4.44	2.51
Sweet potato	6.25	4.26	1.99
Waxy corn	5.89	4.45	1.44
Wheat	6.83	5.05	1.78

lowest molecular weight. Because the polysaccharides of waxy cornstarch with the highest molecular weight did not decompose more readily than, for instance, polysaccharides of cassava starch a conclusion that the extent of depolymerization increased with the molecular weight of polysaccharides only seemingly would be incorrect. The observed extent of the damage of starch polysaccharides is influenced not only by their molecular weight but also by their distribution in granules.

Thermogravimetric (TG/DTG) studies showed that plasma influenced the glass transition, and the decomposition point (Table 3). If the decrease in the glass transition temperature is taken as a criterion of damage due to the plasma on the starch than the oxygen plasma was the most active against the majority of the starches. However, hydrogen plasma the most effectively decreased the decomposition point of the starch in the majority of cases. This could be associated with the better penetrating ability of the hydrogen molecule and its ions into the granule interior.

Ionized gases of plasmas appeared to be fairly non-reactive with respect to starches. Only subtle chemical changes caused by reaction of the gas of the plasma could be observed in exposed starches. These changes manifested themselves as decreases in pH of the starches exposed to the air and oxygen plasma (Table 4) but could not be confirmed by any observable IR spectral changes.

Both rice and potato starches were the most sensitive to oxidation. The sensitivity of potato starch might be associated with chemically active exudations observed on the surface (Starzyk, Lii, & Tomasik, 2001) of this the most readily swelling starch variety. The behavior of both rice starches might support suggestion made above that proteins/lipids are incorporated within granule envelopes.

4. Conclusions

Low-pressure glow plasmas are convenient tools for waste-less dextrinization of starch. A variety of gases ionized under suitable potential gradients, together with the reaction time provide a wide spectrum of dextrins as products. The chemical character of the plasma has little effect on the changes to the starch polysaccharides. Results of exposure of starches to various plasmas can contribute to the knowledge of the structure of interior of starch granules.

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