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Carbohydrate Polymers 49 (2002) 499–507

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Behaviour of granular starches in low-pressure glow plasma

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Accepted 2 November 2001

Abstract

Granular starches of nine botanical origins were exposed to low-pressure glow plasma generated in the air from either a high voltage DC supply or an AC inductor. Experiments with low energy air-plasma (10^{-2} Torr) and starches provided insight into some details of their surface structure. Starches were partly oxidized to carboxylic starches and partly depolymerized. Their affinity to plasma depended on their botanical origin. The structure of starch granules seemed to be a crucial factor, which determined the behaviour of starches in plasma. Lipids and/or proteins stabilized polysaccharides to plasma being preferentially decomposed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Air-plasma; Starch dehydration; Starch depolymerization; Starch granules; Starch oxidation

1. Introduction

Cold plasma can be generated in a gas-phase by electrical discharges: (i) between electrodes with involvement of either low-frequency discharges or high voltage DC discharges and (ii) electrodeless discharges developed by energy absorption from electric field at the resonance frequency (radio- or microwave-frequency). Low-frequency discharges usually require low-pressure, 10^{-1} to 10^{-3} Torr in the reactor. However, recently, stable glow plasma became available at atmospheric pressure using a source operating at 50 Hz (Okazaki, Kogoma, Uehara, & Kimura, 1993).

Apart from the chemistry of mono-atomic gases (Jennings, 1961) including industrial ozone formation, even on the industrial scale (Schmidt-Szalowski, 2000), plasma has been utilized in purification of gases from low molecular contaminations, such as methane, hydrogen sulphide, ammonia, lower ketones, and others (Bill, Wokaun, Eliasson, Killer, & Kogelschatz, 1997; Chang & Tseng, 1996; Chang & Chang, 1997a,b; Lee & Chang, 1998; Malik & Malik, 1999; Okazaki, Hirai, Nozaki, Ogawa, & Hijikata, 1997). Plasma can also induce polymerization (Sato, Iriyama, Cho, & Yasuda, 1989; Smirnova, Rumyantsev, Fayner, Akkerman, & Sysoeva, 1989), as well as depolymerize high molecular weight compounds (Puchkin, Baidarovtsev, Ponomarev, & Vasilets, 1983; Vasilets, Ponomarev, & Tikhomirov, 1981). Functional groups, such as amino, hydroxyl and carboxylic groups could be introduced into polymers as shown in the case of hyaluronic acid (Favia, D'Agostino, & Palumbo, 1997; Liedermann, Lapcik, & Demeester, 1997).

Evaporation of high-melting solids, such as silica (Gusev, Eliseev, & Kalinkin, 1986) and etching of the solid surface of various materials (Svettsov & Chesnokova, 1986), among them also organic polymers (Kuvaldina, Rybkin, Terekhina, & Titov, 1994; Wrobel, Kryszewski, & Gazicki, 1978) are major applications of glow plasma. Recently, such glow plasma was applied for etching semi-permeable biological membranes and the etching modified the membrane preferably in the points of already existing pores (Dmitrev, Kravec, Slepcov, Simakina, & Orelovich, 1997).

In all these processes, the energy of molecules of excited gases and molecules ionized even in a fairly unusual manner (for instance, the O^{5-} ion is formed from the oxygen molecule (Kumar, Rau, & Venkatasubramanian, 1981) are utilized before these species recombine. The efficiency of the treatment depends on the power input, as well as another factors of the plasma formation. In every case, it depends on the power input, as well as other factors amongst which impurities, for instance, water might positively influence the yield.

It was assumed that low-pressure glow plasma could provide a waste-less dextrinization of starch and could be

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PII: S0144-8617(01)00365-4

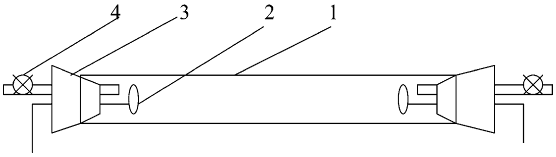

Fig. 1. Scheme of the plasma reactor. (1) Pyrex glass tube; (2) stainless steel disc electrodes; (3) polysilicone rubber stoppers; and (4) Teflon valves.

useful in the study of structural details of the surface of starch granules. In this study, investigation was carried out in air at 10^{-2} Torr using DC low-pressure generation of the low-energy glow plasma. In such a manner, the destruction of starch due to its depolymerization by electrons, ions, and radicals, local temperature increase, as well as oxidation by ozone and/or nitrogen oxides formed in the course of experiments, could be restricted. The native starches of cassava, corn, high amylose corn, oat, potato, Indica, and Japonica origin rice, waxy maize, and wheat were used as samples.

2. Materials and methods

2.1. Materials

Potato, corn, high amylose corn, waxy corn, and wheat starches were purchased from Sigma, St Louis, MO. Rice TNu 67 Japonica and rice KSS7 Indica and cassava starches were isolated in our laboratory using the method described by Yang, Lai, and Lii (1984). Oat starch was kindly provided by the Department of Carbohydrate Technology of the University of Agriculture in Cracow (Poland). All starches were exposed to glow plasma in the air-dried state, however, their humidity content was determined prior to the experiment and also after exposure. In one case, potato starch was exposed after 10-min drying at 100 °C in an vacuum oven.

2.2. Methods

2.2.1. 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 internal diameter of $\phi = 15$ mm. The tube was closed from both sides with polysilicone rubber stoppers in which electrodes made of stainless steel rod and a discs ($\phi = 10$ mm) of the same material, as well as Teflon–glass valves were mounted as shown in Fig. 1.

Starch samples were fairly evenly distributed in the horizontally positioned reactor and a vacuum system constructed in the laboratory and equipped with turbo and rotary pumps providing up to 10^{-7} Torr of was applied to the reactor. The pressure was always monitored throughout the whole period of experiment. Valves of the reactor and vacuum pump were installed in such a manner, that at any suitable vacuum, there was a slow stream of leaking air passing through the reactor. After reaching a suitable vacuum in the reactor, a potential gradient was applied from one of two sources. Firstly, a DC high voltage supply (Model 205B-20R, Bertan Associates, Hicksville, NY). It operated at 1–2 kV with constant current of 1 mA throughout the experiment. Secondly, an inductor (Spark Vacuum Leakage Probe, PIN-21, ZPAP, Warsaw, Poland) operating at approximately 15 kV and 27.2 MHz. In order to prevent this source from overheating, it was used in the pulse mode of 1 min on, 1 min off for cooling.

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.

2.2.2. Water content

This was determined by a Karl–Fischer titration method (Mitchell, 1951) using DL18 Fischer titrator (Mettler-Toledo AG, Switzerland). Solvent consisted of SO_2 and imidazole in methanol and iodine (RdH Laborchemikalien GmbH and Company, Seelze, Germany) was used as titrant.

2.2.3. pH in aqueous solution

pH was estimated for 0.5% aqueous solutions of starch.

2.2.4. Reaction with iodine reagent

Starch sample (40 mg) was dissolved in 10 ml of dimethyl sulphoxide containing 10% 6 M urea. The solution (1 ml) was placed in a 100 ml volumetric flask, to which an aqueous I_2–KI solution (2 ml) was added, followed by dilution with the deionized water to 100 ml. The I_2–KI solution was prepared by dissolving 200 mg of I_2 in 2% KI solution (100 ml). The sample solution was scanned from 400 to 800 nm using a Spectronic Genesys 5 Milton Roy Company, NY) spectrophotometer.

2.2.5. FTIR spectra

The infrared spectra were run in KBr discs using a Perkin Elmer FTIR spectrometer Paragon 1000 (Norwalk, CT), in the frequency range of 4000–500 cm^{-1}.

2.2.6. Thermogravimetry and differential thermogravimetry

The thermal characteristics were examined under a nitrogen stream using a Du Pont TGA 951 System (Wilmington, DE) scanned from 25 to 500 °C at 10 °C/min.

2.2.7. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements involved a Du Pont 910 PDSC Thermal Analyser (Wilmington, DE). Samples were blended with water at the ratio of 1:3 then hermetically sealed in aluminium pans. Temperature rose from 30 to 150 °C at a rate of 5 °C/min. The pressure was 3.5×10^6 Pa. The measurements were run in triplicates.

Table 1
Water content in starch samples prior to and after exposure to glow plasma from a DC supply (the measurements were duplicated. The differences in estimations did not exceed 2% of estimated values)

Starch exposed	Water content (%)	
	Original	After exposure
Cassava	12.6	8.7
Corn	11.1	10.4
High amylose corn	12.7	11.8
Oat	12.6	5.9
Potato	14.5	10.3 (9.65)[a]
Potato dehydrated at 100 °C	12.6	2.5
Rice Indica KSS7	12.1	8.7
Rice Japonica TNu67	10.9	8.2
Waxy corn	13.8	10.1
Wheat	9.7	5.3

[a] Water content after 30 min exposure to plasma generated from an AC inductor.

2.2.8. High performance size exclusion chromatography

Starch sample (1 g) was dissolved in 95% dimethyl sulphoxide (50 ml) with stirring for 3 days at room temperature. The sample was then precipitated with ethanol (150 ml) and stored overnight at 4 °C. The precipitate was centrifuged in a bench centrifuge with addition of acetone (50 ml) and diethyl ether (50 ml). The precipitate was finally dried in vacuum at room temperature for 24 h.

The mobile phase used for high performance size exclusion chromatography (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 (P580, Gynotek, USA), an injector valve with a 500 μl loop, a Tosoh PW_{XL} guard column, a TSK $GMPW_{XL}$ column (7.8 × 300 mm), a laser light scattering detector (Viscotek, Houston, TX), and a refractive index detector(Model 250, Viscotek). 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 into the column. Experiments were run in triplicates.

2.2.9. Scanning electron microscopy

A scanning electron microscope (SEM; JEOL TECHNICS LTD., Tokyo, Japan) operating at 20 keV was used.

2.2.10. 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 diffraction pattern over the range of 4.0–30.0° 2θ were recorded at a scan rate of 0.02° 2θ/s.

2.2.11. Electron paramagnetic resonance

X-band electron paramagnetic resonance (EPR) spectra were recorded for 15 mg samples at room temperature on a Bruker E 500 CW spectrometer (Billerica, MA).

3. Results and discussion

An almost uniform glow inside the reactor could be achieved even at 1 Torr, but calculations suggested a mean free path of the ionized species of the order of 1 cm at 10^{-2} Torr. Such a value corresponded to the diameter of the reactor and seemed to provide the highest density of the glow plasma at the surface of exposed starch. After reaching 10^{-2} Torr, the potential difference was applied and, for the first approximately 10 min period, there was only filament plasma formed between the electrodes. In this period of time an easy, fast removal of capillary and surface-sorbed water (Schierbaum, Taeufel, & Ulmann, 1962) took place. This portion of water vapour killed the plasma in the preliminary period of experiments. After that period of time, pinkish-blue plasma expanded to fill the whole reactor volume between the electrodes, suggesting that the starch samples were sufficiently dry. Within the whole exposure period, the temperature inside the reactor did not exceed 40 °C. Inspection of the electrodes, as well as the starch after exposure showed no visible changes to their surface.

Analysis of the water content revealed that exposure to the plasma at reduced pressure did not result in a complete drying of the starch samples (Table 1). It seemed to be an important result, because water has been reported to be crucial for the reactivity of starch (Muetgeert, Hiemstra, & Bus, 1958). However, action of the glow plasma on pre-dried (to a 2.5% water content) potato starch caused significant hydrolysis. The intensity of the absorption band of its blue complex with the iodine reagent was reduced by 62%.

It should be noted that a catalytic amount of water was beneficial for the yield of atomic gases in low-frequency discharges (Poole, 1937; Wood, 1920). Therefore, granular starch might be considered as a suitable source of traces of water in reactions carried out under low-frequency glow plasma.

Reaction of starch varieties with the iodine reagent also showed that waxy cornstarch was significantly changed by the plasma generated by the DC high voltage supply. There was observed to be a 46% decrease in the intensity of the UVVIS spectral band of the complex with the I_5^- ion (Table 2). Intensity of the corresponding band in the spectra of iodine complexes with the product resulting from exposure of rice Japonica TNu67 starch decreased by almost 31%. In terms of the order of susceptibility of starches towards plasma granular, potato starch took third place with over 28% decrease of the band under consideration and the decrease for exposed cassava starch was about 23%. Oat starch and high amylose cornstarch were much more resistant to plasma. After their exposure, the intensity of the

Table 2
Results of 30 min exposure of starch varieties to plasma, expressed as the shift and the intensity change in the absorption maximum of the starch–iodine blue complex after exposure to glow plasma (in calculations, dehydration of starch was taken into account. The measurements were run in duplicates. The differences in $\Delta\epsilon_{\max}$ did not exceed 0.1%)

Starch variety	Spectral changes[a]	
	$\Delta\lambda_{\max}$ (nm)	$\Delta\epsilon_{\max}$ (%)
Cassava	− 22	− 23.3
Corn	+ 3	+ 2.2
High amylose corn	+ 4	− 6.2
Oat	0	− 8.3
Potato	− 9[b]	− 28.1
	− 3[c]	− 18.9
Potato dehydrated at 100 °C	− 7[b]	− 62.0
Rice Indica KSS7	0	+ 31.6
Rice Japonica TNu67	0	− 30.9
Waxy corn	0	− 45.9
Wheat	+ 5	+ 21.7

[a] If not denoted, data are related to exposure to plasma generated from the DC supply.

[b] There was also an absorption band of equal intensity at 680 nm.

[c] Experiments with plasma generated from the AC inductor. There was also an absorption band of equal intensity at 674 nm.

absorption band of the iodine complex decreased only by 8 and 6%, respectively.

Changes in the band intensity in the UVVIS spectra of the blue complex of starch with KI_5 were either not assisted by any shift of the band (waxy cornstarch, rice Japonica, and oat starches) or they were accompanied by a hypsochromic shift of that band. Such a shift suggested that the amylose was less resistant to plasma than amylopectin and that this conclusion agreed with the former observation of Kerr (1950), who observed higher reactivity of amylose on exposure of starch to nitrogen dioxide. In the case of potato starch, the spectral changes were additionally reflected by the second band, which appeared at 680 nm. This band corresponded to the complex of higher molecular weight dextrins with the iodine reagent (Fig. 2).

Potato starch was also exposed to plasma generated from the AC inductor. For technical reasons, the use of this device was not convenient in the generation of plasma. In experiments with this kind plasma and potato starch, the intensity of the 600 nm band decreased by almost 20%. Also in this product, the longest wavelength band at 674 nm could be observed in the UVVIS spectrum of iodine blue complex of the exposed product, but it did not mean that the character of the starch damage was identical to that caused by plasma generated from the DC source.

After exposure to plasma, the iodine complexes of cornstarch, rice Indica KSS7, and wheat starches showed higher intensity of the longest wavelength UVVIS band than before exposure. This effect could not be accounted for by the dehydration of these starches on contact with plasma. It could result from decomposition of the polysaccharides. After decomposition of proteins and lipids, present in the starches in form of native amylose–protein and amylose–lipid complexes, respectively, the concentration of amylose available for complexation with iodine increased. A small bathochromic shift of the spectral band of the corresponding complexes with iodine suggested that the amylose engaged in the formation of complexes with proteins and lipids had slightly longer chains than free, non-complexed amylose.

Examination of starch granules under the SEM revealed some changes in appearance of the surface of starch granules. Surfaces of granules after treatment were covered with a kind of subtle, irregularly distributed deposit (Fig. 3). This could result from the oxidation of material usually present on the granule surface (Starzyk, Lii, & Tomasik, 2001).

It could be seen that neither prior to, nor after exposure to plasma no pores could be seen on the surface of potato starch granules. Lii, Tomasik, Hung, and Lai (2001) reported a SEM image of a sliced starch granule. Subtle tracks could be seen on the surface of the cut granule, which could be ascribed to subtle pores. This study did not support these observations or assumption.

The deposit observed on the granule surface was produced by the glow plasma generated by the DC supply,

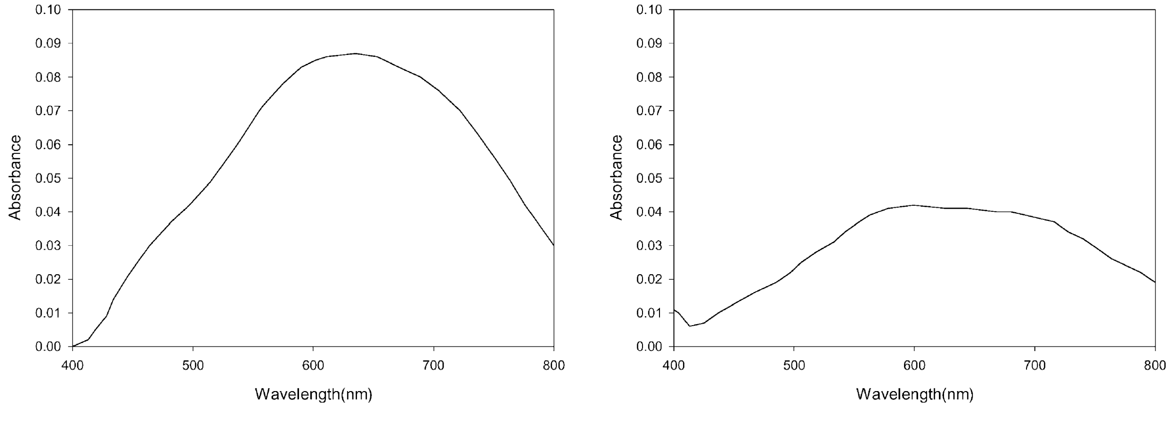

Fig. 2. The UVVIS spectra of the complexes formed between KI_5 and the original potato starch (left) and also the product of 30 min exposure of potato starch to plasma generated from the DC supply (right).

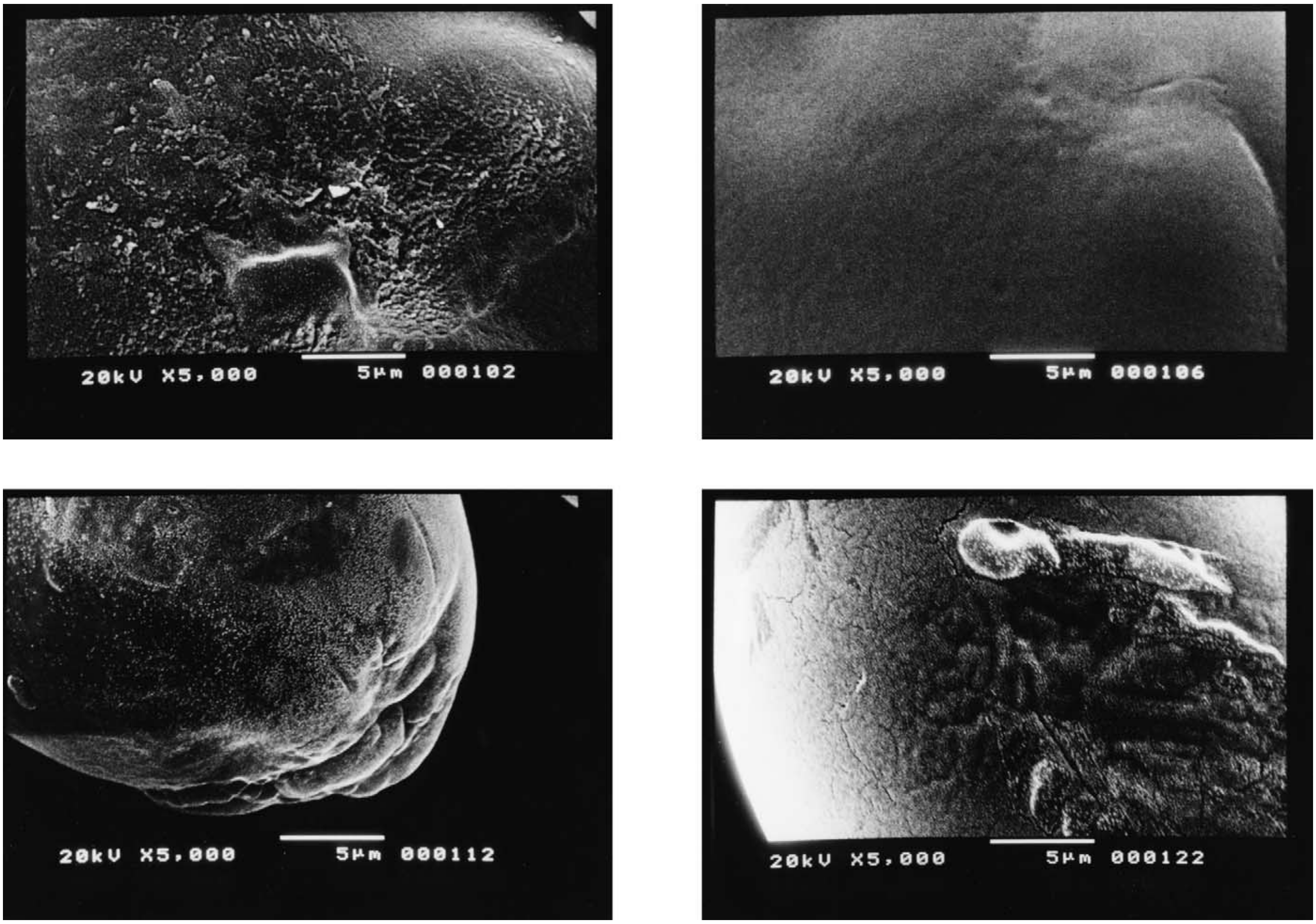

Fig. 3. SEM micrographs of a potato starch granule prior to (upper left) and after 30 min exposure to plasma generated from inductor (upper right), potato starch granule exposed for 5 min to plasma generated from inductor (bottom left) and granule exposed for 30 min to plasma generated from DC supply (bottom right).

as well as by the AC inductor. Contact of wheat starch with plasma resulted in extensive damage of the granules, but the deposit on the granule surface could not be observed. On the SEM picture of the original cornstarch and also on the waxy cornstarch, pores in the granules could be seen. Although the pores could not be observed in granules of both original rice starches, on exposure to plasma their granules, particularly these of KSS7 Indica starch, suffered extensive damage. The pattern of this damage could be considered as pores magnified by the plasma treatment. A deposit also developed on their granule surfaces. Granules of original oat starch were quite irregular. Therefore, apart from a random deposit on the surface of granules exposed to plasma any other symptoms of the action of plasma were difficult to evaluate.

Table 3
pH of aqueous solutions of starch varieties prior to and after exposure to plasma generated from the DC supply

Starch exposed	pH	
	Original	After exposure
Cassava	5.97	4.95
Corn	6.02	4.84
High amylose corn	6.07	5.08
Oat	7.04	5.33
Potato	8.29	7.38 (7.07)[a]
Rice Indica KSS7	8.15	7.12
Rice Japonica TNu67	6.95	5.40
Waxy corn	5.89	4.74
Wheat	6.83	5.62

[a] The value related to starch exposed for 30 min to plasma generated from the AC inductor.

Decrease in pH of aqueous solutions of exposed starches (Table 3) seemed to support the opinion that oxidation of the surface of granules took place on contact of the starch granules with the glow plasma and, simultaneously, that the oxidation proceeded to the formation of carboxylic acids. Either ozone and/or nitrogen oxides generated in the plasma could act as the oxidant. Solid-state oxidation of starch with such an oxidant to uronic acids (Kerr, 1950) and even to tri(carboxy)starch (Tihlarik & Kohn, 1988) has been previously described. No porous granules could be observed in high amylose cornstarch and cassava starch prior to, and after exposure to plasma. Similarly, as in other starches after exposure, granules were covered with a deposit.

Table 4
TG, DTG, and DSC analyses of starches prior to and after exposure to plasma presented in form of changes from the original values resulting from the plasma treatment (if not denoted shifts are related to experiments in which starch was exposed to plasma generated from the DC supply)

Starch variety	DTG		DSC[a,b]		
	Temperatures (°C)				
	Water loss	Glassy transition[c]	T_o	T_p	ΔH
Cassava	0	+	− 0.22	− 0.09	0.13
Corn	+ 3	+	0.97	0.65	0.77
High amylose corn	0	0			
Oat	0	+			
Potato (DC plasma)	− 6.5	+	0.85	0.87	− 1.96
Potato (AC plasma)	+ 3	0	0.71	0.78	1.35
Potato (only pumped)			0.17	0.43	− 1.78
Rice KSS7	+ 4	+	0.44	0.09	− 1.23
Rice TNu67	+ 1.5	+	0.22	2.38	0.18
Waxy corn	0	+	− 0.85	0.23	2.01
Wheat	0	0			

[a] Temperatures of the origin (T_o) and peak (T_p) of the effect are in °C, and enthalpy is in KJ/mol. The measurements were run in duplicates. The differences in ΔH did not exceed 5% of estimated values.

[b] All differences are insignificant.

[c] Since peaks were mostly observed as shoulders, the transition temperature for this effect could not be precisely determined.

The pattern of the damage of rice Indica and wheat starches suggested that in these native starches proteins could be incorporated into the external layer of the granules. Simultaneously, it should be noted that oat starch granules containing proteins and lipids survived contact with plasma without any strong damage. This could suggest either a different distribution of proteins and lipids in this starch, or additional stabilization in the form of a ternary polysaccharide–protein–lipid complex, which might be present in granules of this starch. This type of stability should not be related to the thermal stability, which amongst several starches was the lowest for oat starch (Ciesielski & Tomasik, 1996).

Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis delivered several parameters of potential interest. Thus, the amount of the humidity loss and the relevant temperature of the effect were available from the TG and DTG diagrams, respectively. Glass transitions were manifested by a small peak or shoulder preceding the main peak of starch decomposition and the temperature at the maximum of this peak was given by the DTG analysis. Table 4 contains this data for starch varieties in the form of the increments to values measured for non-processed, original starches. Thus, exposure to glow plasma had no effect on the glass transition in wheat and high amylose cornstarches. In other starches, the glass transition moved to slightly higher temperatures and was magnified. Thus, the result the peak of the glass transition could only be observed as a shoulder of the main endothermic peak (Fig. 4). A change in the glass transition suggested an increase in the crystallinity of such samples. TG/DTG analysis for potato starch subjected to vacuum and not exposed to plasma showed no effect of this operation on the glassy transition of the starch.

In all these cases, the glow plasma was generated from the DC supply. Potato starch was additionally exposed to a low-pressure glow plasma from the AC inductor. Such a plasma had no effect on the glass transition of this starch. This suggests that the two types of glow plasmas are not equivalent to one another.

Based on the observation of the history of residual water loss one could make deduction about the effect of the plasma on the granule macrostructure. Exposed cassava, oat, wheat, high amylose, and waxy cornstarches lost residual water in the same manner as granules not exposed to plasma. Rice Indica KSS7, rice Japonica TNu67, corn, and potato starch the latter after treatment with plasma from AC source, lost water at slightly higher temperatures (1.5–6 °C). In contrast potato starch, after treatment with plasma from the DC source, lost water at temperatures 6–7 °C lower than before treatment. Increase in the temperature at which water loss occurred could be interpreted in terms of closing of the channels in the starch granules suffered damage envelope through which water could escape. Thus, the envelope of potato starch granules after treatment with DC plasma. Simultaneously, a further argument for the different effects on granules of the DC and AC plasmas was obtained.

It has been reported that a mild roasting of starches did not produce any essential changes in the thermogravimetric patterns of the starches (Tomasik, Wiejak, & Baczkowicz, 1986). Close resemblance of the patterns of the thermograms of starches prior to and after exposure to plasma suggested that apart from low yield oxidation results of which could not be recorded either by the thermal analyser or the calorimeter a mild hydrolysis of starches took place. Similarly, powder X-ray diffractograms, as well as IR spectra for exposed starches did not show any essential changes.

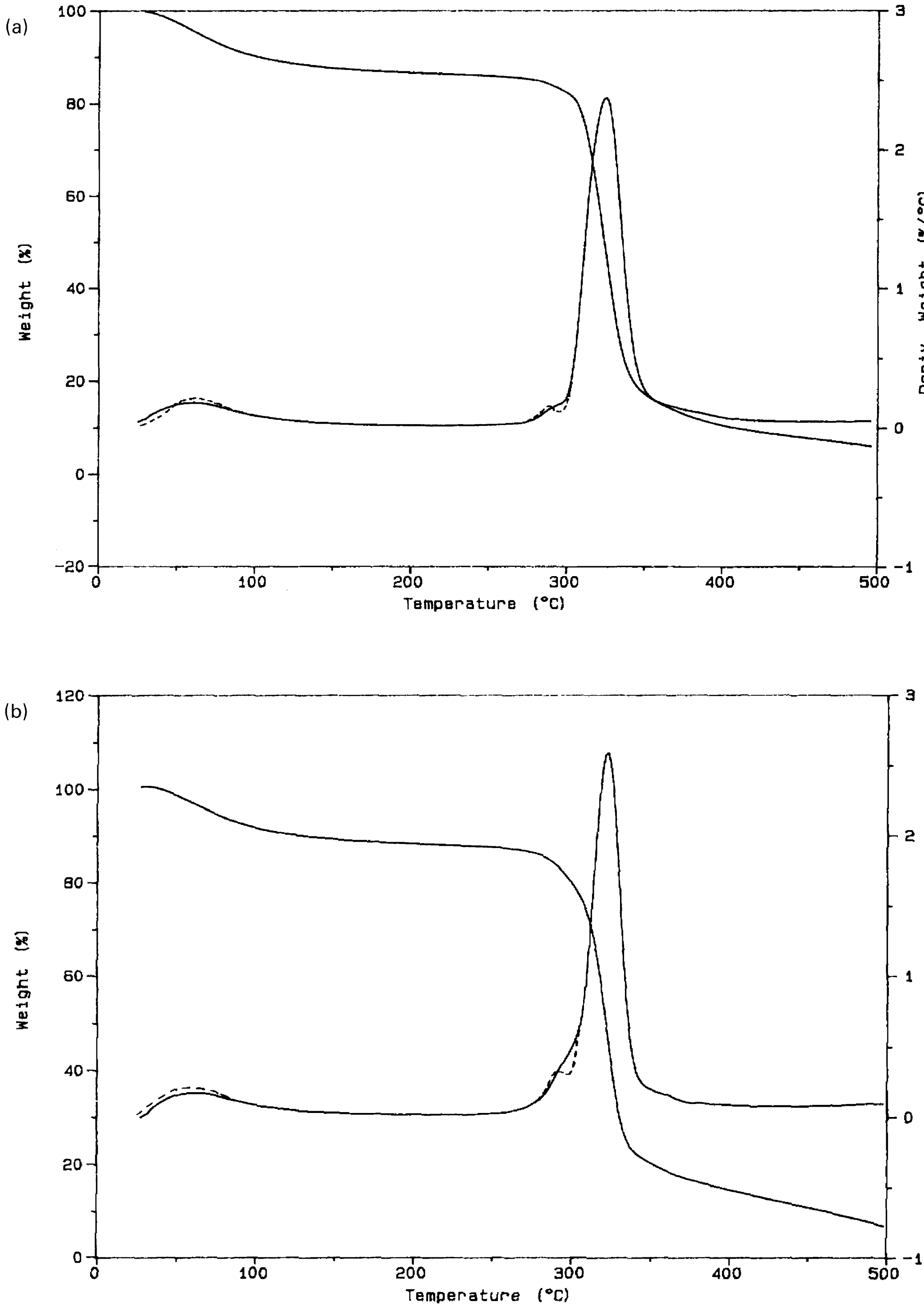

Fig. 4. Thermograms (TG/DTG) of original and plasma exposed starches. (a) Plasma exposed cassava starch. (b) Plasma exposed rice Japonica TNu67 starch. Dotted lines in the 50–100 and 300 °C regions in both thermograms present DTG lines in the thermograms of original starches.

Saccharide (Barabasz, Brzozka, Krzeczek, & Tomasik, 1990; Tomasik & Jane, 1995) and polysaccharides (Ciesielski & Tomasik, 1996) free radicals, even in the air exposure, are usually stable in time. Since EPR spectra of starches exposed to glow plasma never showed any detectable signal one might therefore assume that depolymerization of starch proceeded according to an ionic mechanism. Such mechanism is common for processes induced by glow plasma (Jennings, 1961).

The most convincing argument for destructive effect of plasma in respect to starches came from the HPSEC results, which are collected in Table 5.

The degree of damage of native starches expressed in terms of the decrease in molecular weight caused by

Table 5
HPSEC analysis of original and plasma exposed starches (data relate to starches exposed to plasma generated from the DC supply. M_w Av., η_{int}, and R are molecular weight average, intrinsic viscosity (dl/g), and radius of gyration (nm), respectively)

Sample	Starch					
	Original			Plasma exposed		
	M_w Av. $\times 10^7$	η_{int}	R	M_w Av. $\times 10^7$	η_{int}	R
Cassava	9.35 ± 0.17	0.52 ± 0.04	75.68 ± 7.33	4.93 ± 0.88	0.45 ± 0.01	49.87 ± 1.34
Corn	8.68 ± 1.17	0.31 ± 0.02	57.49 ± 6.51	5.34 ± 0.18	0.26 ± 0.04	25.49 ± 5.48
High amylose corn	2.11 ± 0.23	0.30 ± 0.01	21.04 ± 1.17	1.74 ± 0.05	0.31 ± 0.01	21.76 ± 0.82
Oat	9.18 ± 1.05	0.23 ± 0.01	45.45 ± 0.54	4.45 ± 0.46	0.47 ± 0.01	45.42 ± 1.72
Potato	7.73 ± 0.69	0.43 ± 0.08	53.11 ± 8.39	3.68 ± 0.23	0.34 ± 0.04	33.46 ± 3.00
Rice KSS7	8.62 ± 0.84	0.30 ± 0.02	58.41 ± 0.78	6.87 ± 0.79	0.38 ± 0.02	59.61 ± 1.95
Rice TNu67	13.70 ± 0.01	0.32 ± 0.01	76.45 ± 2.43	2.89 ± 0.08	0.25 ± 0.01	27.48 ± 0.90
Waxy corn	14.34 ± 0.48	0.39 ± 0.01	72.66 ± 1.94	9.67 ± 0.73	0.25 ± 0.02	52.27 ± 4.43
Wheat	7.09 ± 0.68	0.32 ± 0.03	52.13 ± 5.36	5.11 ± 0.61	0.42 ± 0.02	56.93 ± 2.28

exposure to plasma, did not quantitatively parallel results deduced from the reaction of starches with KI_5 (Table 2). The first estimation involved also high molecular weight products of oxidation, which did not react with KI_5. This analysis confirmed that the highest resistance of polysaccharides was for high amylose cornstarch, as well as rice Indica and wheat starches. There was the lowest decrease in the molecular weight of these starches due to contact with the plasma. An increase in the intrinsic viscosity of solutions of these starches, as well as oat starch was accompanied by an increase in the radius of gyration. These facts favour damage of the non-saccharide components of the granules in consequence of which ordering of polysaccharide–polysaccharide interactions in solutions lead to the formation of larger polysaccharide aggregates.

4. Conclusions

1. Low-pressure glow air-plasma oxidized starch producing carboxylic groups on the surface of granules. Additionally starch was depolymerized.
2. Exposure of anhydrous starch was beneficial.
3. Waxy cornstarch, as well as rice Indica and rice Japonica could have porous granules.
4. Potato starch granules are definitely non-porous.
5. Granular starch could be a source of a catalytic amount of water that activates reactions under low-frequency plasma.
6. The treatment with a glow plasma can be an alternative method of waste-less dextrinization of starches.

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