

OXIDATION-INDUCED CHANGES IN THE SURFACE STRUCTURE OF STARCH GRANULES

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Key words: starch, oxidation and surface structure

Native starches of potato, wheat, maize, and waxy maize were subjected to oxidation with: sodium chlorate(I), hydrogen peroxide in the presence of Cu^{2+} ions and sodium chlorate(III) in the presence of formaldehyde. Native starches and their modified preparations were determined for the content of carboxyl and aldehyde groups. In order to determine changes in the surface structure of starch granules, microphotographs (SEM) were taken and specific surface (S_{BET}) was determined. In the research performed sodium chlorate(I) and hydrogen peroxide were found more effective in the oxidation process as they induced greater changes in the surface structure of the investigated oxidised starches than sodium chlorate(III). The most remarkable changes in the specific surface area of the starches examined were caused by sodium chlorate(I), with an increase reported for maize starch and a decrease for wheat starch.

INTRODUCTION

Native starch occurs in the form of granules with species-specific morphological traits and physicochemical properties of a plant it was isolated from. Those properties can be modified by subjecting starch granules to the activity of physical, chemical or enzymatic factors.

One of the ways of chemical modification of starch is the oxidation process which results in the production of carboxyl and/or aldehyde groups in the starch. A number of those groups is determined by the type of the oxidative agent applied, reaction conditions as well as botanical origin of starch [Boruch, 1979].

Starches of different botanical origin are characterised with a different surface structure linked among others to the size and the shape of granules as well as the presence of pores and channels which affect the development of the specific surface [Fannon *et al.*, 1992, 1993; Huber & BeMiller, 1997; Achremowicz *et al.*, 1997; Juszczak, 2001].

The origin of pores may result from the botanical variety of starch or from the manner of starch isolation, disintegration and drying.

Pores are also formed during starch synthesis in the plant tissue and are a morphological trait of granules [Fannon *et al.*, 1992; 1993].

Fannon *et al.* [1992] claim that pores present on the surface of maize starch and sorghum granules facilitate the enzymatic modification of starch. They suggest that the pore depth in the starch granule may prove its reactivity and susceptibility to chemical modifications.

According to Aquilera [2000], morphology and topography are an important physical trait of solid bodies which in the case of food is of great importance not only to its sen-

sory attributes but also to the properties found crucial for processing and storing.

As the studies into starch oxidation address mostly the determination of its physicochemical properties and not changes proceeding in the surface structure and porosity of starch granules, the objective of this work was to determine the impact of the oxidation of starch on changes in the surface structure of starch granules.

MATERIAL AND METHODS

The experimental material consisted of starches of different origin, *i.e.* potato starch "Superior" and wheat starch produced at the ZPZ Niechlów as well as maize starch and waxy maize starch (National Starch & Chemical).

The above-mentioned starches were subjected to the oxidation process by means of three methods:

1. Modification with sodium chlorate(I) was performed according to Forsell *et al.* [1995]. Briefly, 400 g of starch was weighed and dispersed in water. The water solution of NaOCl (commercial, activity 100 g Cl/L, POCh) was slowly added to the obtained 40% suspension. Modification was performed at room temperature by mixing the starch suspension in alkaline medium (pH=10.0) for 50 min and subsequent neutralisation of the reaction mixture with 1 mol/L H_2SO_4 solution to reach pH=7.0.

The amount of the NaOCl reagent used in the oxidation was equivalent 40 g Cl/kg starch.

2. Modification with hydrogen peroxide (with the addition of 0.1% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was performed according to Parovuori *et al.* [1995]. Briefly 400 g of starch was dispersed in water to give 42% suspension. The reaction mixture was thermostated at a temperature of 40°C. Next, a 30% H_2O_2

(pure p.a., POCh) solution was added dropwise to the reaction mixture to reach its final concentration of 2%. The reaction mixture was thermostated once more for 60 min.

3. Modification of starch with sodium chlorate(III) in the presence of formaldehyde was performed according to the methodology of Hebeish *et al.* [1992]. Briefly 400 g of starch was dispersed in water to give 28% suspension. After the addition of 4 g of sodium chlorate(III) (pure p.a., Fluka) and 1.2 g of formaldehyde (pure p.a., Chempur) the suspension was mixed at a temperature of 50°C for 90 min.

Then, the modified starches were washed, dried, disintegrated, and sieved.

Starch oxidation was performed according to procedure which was optimized in previous trials.

Both native and modified starches were determined for: (1) the content of carboxyl groups, according to ISO norm 11214 [1996]; (2) the content of aldehyde groups, according to Potze [Potze & Hiemstra, 1963]; (3) the morphology starch granules – microphotographs were taken with a Jeol ISM 5400 scanning electron microscope (SEM); the samples were coated with gold before measurements [Fornal, 1985]; (4) the specific surface area using a multipurpose automatic apparatus ASAP 2010 (Micrometricis, USA), by measuring the adsorption of high-purity nitrogen [Fortuna *et al.*, 1998]. The measurement involved determining the isotherm of nitrogen adsorption at the temperature of liquid nitrogen (77.3 K) and calculating the monolayer capacity with the adsorption isotherm equation of Branauer-Emmet-Teller (BET) [Branauer *et al.*, 1938]. Prior to measurements, the samples were dried under vacuum conditions at a temperature of 30°C ($\pm 1^\circ\text{C}$) for 24 h, and next automatically desorbed at a degassing station and flushed with pure helium at a temperature of 22–24°C for 3 h. Before measurements the samples were checked for the presence of gas at a measuring station.

Chemical analyses were performed in triplicate.

To determine the significance of the differences between the contents of carboxyl and aldehyde groups, use was made of one factorial analysis of variance and Duncan's test, whereas standard deviation was determined for the measurements of the specific surface area.

RESULTS AND DISCUSSION

All the analysed types of starch (Table 1) oxidised by method based on sodium chlorate(I) were characterised

with a higher number of carboxyl groups compared to the starches modified by the other methods. The only exception was wheat starch in which the highest number of carboxyl groups was observed upon modification with hydrogen peroxide. The oxidation of starch by method based on sodium chlorate(III) in the presence of formaldehyde was found the least efficient, which was proved in literature data [Hebeish *et al.*, 1992; Parovuori *et al.*, 1995; Fortuna & Pietrzyk, 2002]. In addition, wheat starch appeared to be the most susceptible to oxidation by methods based on sodium chlorate(I) and hydrogen peroxide, whereas maize starch to the activity of sodium chlorate(III).

An analysis of the results compiled for the content of aldehyde groups (Table 1) enables concluding that potato starch was the most susceptible to hydrolysis with the oxidising agents applied, as it was characterised with the highest increment of aldehyde groups compared to the other starches. It confirms the results of a study by Kuakpetoon and Wang [2001]. Compared to the other methods, hydrogen peroxide caused the highest rise in the number of aldehyde groups, which confirms the results of our previous investigations [Fortuna & Pietrzyk, 2002].

Photos 1–4 present microscopic pictures of the granules of particular starch types before and after oxidation.

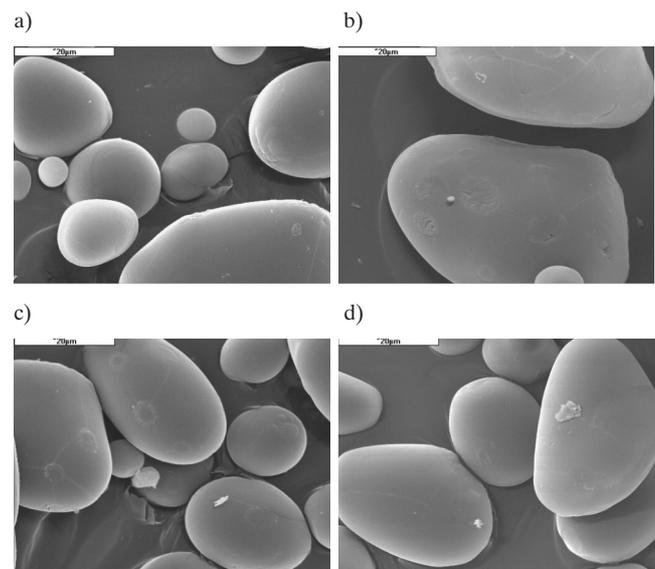


PHOTO 1. SEM pictures (2000x) of potato starch granules: a) native, and oxidised with b) sodium chlorate(I), c) hydrogen peroxide, and d) sodium chlorate(III).

TABLE 1. Content of carboxyl groups (%) and aldehyde groups (g CHO/100 g d.w.) in oxidised starches.

Starch	Carboxyl groups in starches oxidised with:			Aldehyde groups in starches oxidised with:		
	sodium chlorate(I)	hydrogen peroxide	sodium chlorate(III)	sodium chlorate(I)	hydrogen peroxide	sodium chlorate(III)
Potato	0.432	0.351	0.008	0.054 ^b	0.157	0.017 ^a
±SD	0.0155	0.0105	0.0006	0.0014	0.0027	0.0013
Wheat	0.226	0.325	0.056	0.014 ^a	0.113	0.001 ^c
±SD	0.0057	0.0155	0.0030	0.0012	0.0052	0.0001
Maize	0.380 ^d	0.301	0.061	0.053 ^b	0.102	0.002 ^c
±SD	0.0115	0.0176	0.0048	0.0015	0.0014	0.0001
Waxy maize	0.390 ^d	0.195	0.018	0.021	0.079	0.010
±SD	0.0291	0.0122	0.0015	0.0001	0.0040	0.0002

The same small letters indicate values that are not significantly different at $\alpha=0.05$.

Photos 1 (a, b, c, d) refer to the granules of potato starch and its modified preparations and show large and small oval granules with similar shape and a diameter less than $20\ \mu\text{m}$ which have been extensively described in literature. The surface of native potato starch (Photo 1a) demonstrated no cracks, scratches nor cavities. It confirms the theory of Fannon *et al.* [1992] who also observed a smooth surface of potato starch granules with a scanning electron microscope.

On the basis of SEM microphotographs, Juszczak [2001] observed a smooth surface of native potato starch granules with cracks and scratches formed most likely during sample preparation. The microphotographs were made in 500x magnification.

The presented Photos 1 (b, c, d) point out that the oxidation with the oxidising agents applied does not evoke any considerable changes in the surface structure of potato starch granules except for little cracks and wrinkles which were the most clearly visible in the starch oxidised with sodium chlorate(I) and hydrogen peroxide. It cannot be said definitely that those damages appeared as a result of the oxidation process as they were also likely to be formed either upon starch disintegration after oxidation or during drying. Nevertheless, a relationship between more apparent cracks and wrinkles caused by stronger oxidants, *i.e.* sodium chlorate(I) and hydrogen peroxide, compared to sodium chlorate(III) is evident.

Similar results were obtained by Boruch [1979] who – on the basis of microscopic pictures in natural and polarized light – found out that cracks visible in potato starch oxidised with sodium chlorate(I) were formed upon the activity of strongly alkaline solution of the oxidant. The presence of foldings and erosion on the surface of potato starch granules was also observed by Achremowicz *et al.* [2000] who oxidised potato starch with air. They reported an additional relationship between the increasing size of erosion on the granule surface along with an increasing aeration intensity.

Exemplary images of the granules of wheat starch and its modified preparations were shown in Photo 2. A typical bimodal size distribution of granules known from literature [Jane *et al.*, 1994] was observed in native wheat starch (Photo 2a). Diameters reported for large and small granules

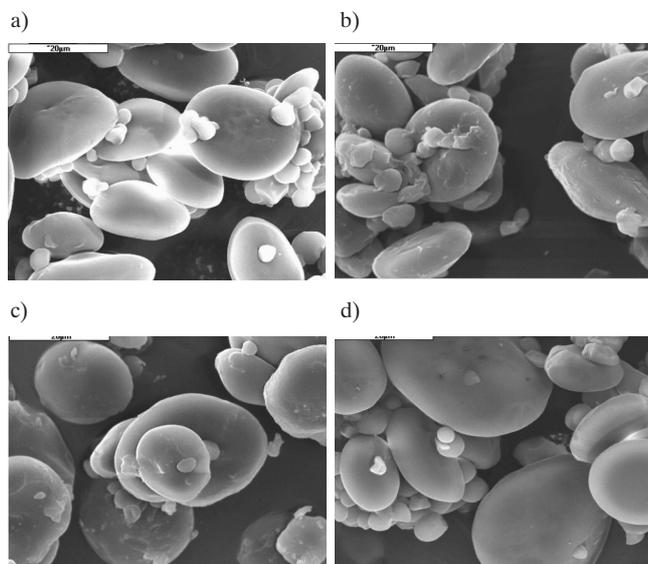


PHOTO 2. SEM pictures (2000x) of wheat starch granules: a) native, and oxidised with b) sodium chlorate(I), c) hydrogen peroxide, and d) sodium chlorate(III).

reached *ca.* $20\ \mu\text{m}$ and less than $4\ \mu\text{m}$, respectively, which was confirmed in literature data [Juszczak *et al.*, 2002]. The wheat starch granules were found to be characterised with a smooth surface. According to Fannon *et al.* [1992], pores present in wheat starch occur on large granules along parallel groove and are its natural trait. The presence of those pores was confirmed in the presented study (Photo 2a).

It was found that the oxidation with sodium chlorate(I) (Photo 2b) and hydrogen peroxide (Photo 2c) induced changes in the surface structure of wheat starch granules. Both oxidising agents affected the formation of foldings and wrinkles in the large granules as well as induced irregular wrinkles and even rags in the small granules. In addition, the modified preparations demonstrated delicate cracks and scratches which might have occurred as a result of the disintegration process.

In wheat starch oxidised with sodium chlorate(III), no changes in the surface were observed.

Photos 3 (a, b, c, d) present microscopic pictures of the granules of maize starch before and after oxidation. The granules of this starch were seen as having multilateral irregular shapes, sometimes with folded surfaces, which is confirmed by literature data [Jane *et al.*, 1994; Fannon *et al.*, 1992].

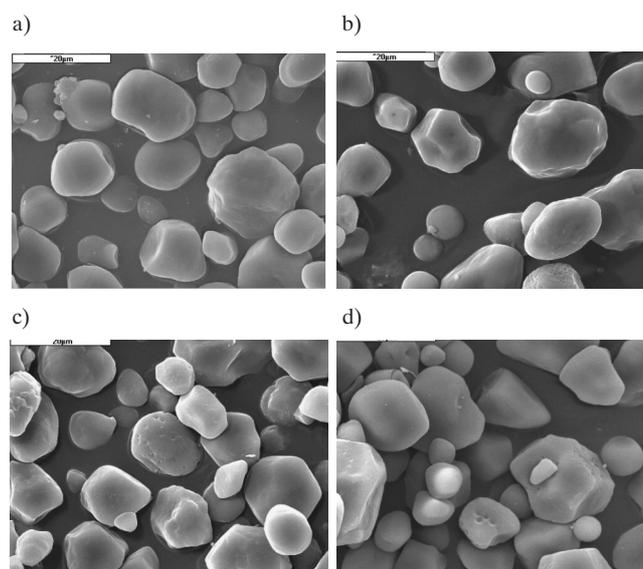


PHOTO 3. SEM pictures (2000x) of maize starch granules: a) native, and oxidised with b) sodium chlorate(I), c) hydrogen peroxide, and d) sodium chlorate(III).

As it was observed previously in photographs, oxidation with sodium chlorate (I) (Photo 3b) and hydrogen peroxide (Photo 3c) caused enlargement of foldings on the surface of starch granules. Those foldings are not however visible on all granules, they appear mainly on large granules. Similarly to wheat starch, oxidation of maize starch with sodium chlorate(III) did not result in any changes of the surface of starch granules. Still, single granules with regular pores were observed in Photos 3 (b, c, d). It is not, however, a consequence of oxidative agent's activity since similar pores were observed in maize starch by Juszczak [2001] and Pałasiński *et al.* [2000] who claimed that those regular pores were probably formed during granule growth as "imprints" of globular proteins of endosperm.

Photos 4 (a, b, c, d) present exemplary images of native and oxidised waxy maize starch granules. Similarly to maize starch granules, the granules of native waxy maize starch

(Photo 4a) were seen as having a folded irregular surface, however they demonstrated less sharp shapes.

All oxidising agents applied (Photos 4 b, c, d) resulted in larger foldings and additional wrinkles appearing on the granule's surface. It did not, however, refer to all grains. As in the case of maize starch, only larger molecules were subject to modification. A few granules were observed to possess small irregular pores (Photo 4b, c, d) the origin of which was identical as for maize starch.

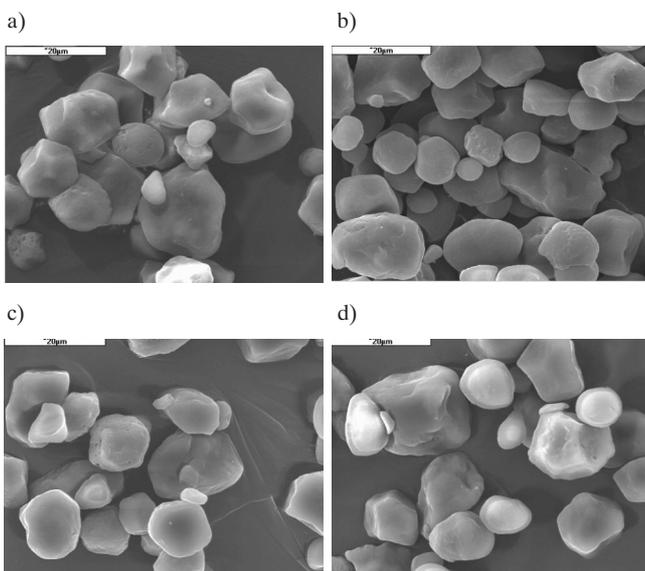


PHOTO 4. SEM pictures (2000x) of waxy maize starch granules: a) native, and oxidised with b) sodium chlorate(I), c) hydrogen peroxide, and d) sodium chlorate(III).

Summing up, it may be concluded that the pictures of starch granules obtained by means of a scanning electron microscope display not only differences in the shape and size of the granules but also those appearing on the starch granule surface. Those analyses indicate that the most remarkable changes in the surface structure of all starches appeared upon oxidation with sodium chlorate(I) and hydrogen peroxide. Whereas the oxidation with sodium chlorate(III) was found to affect the changes in the surface structure of potato and waxy maize starch only. The application of the scanning electron microscopy indicated that the surface structure of potato starch granules changed to the greatest extent (formation of additional wrinkles) upon the activity of all oxidising agents applied. It means that those granules are the least resistant to the activity of the oxidising agents used in the experiment, which proves the highest number of carboxyl groups in this starch.

In any of the grains studied, except for those of oxidised potato starch, neither cracks nor mechanical damages were observed on the granule's surface, which was contrary to observations of other researchers [Fannon, 1992; Juszczak, 2001]. However, one should be very cautious when forming explicit conclusion that they do not exist. Perhaps they are too small to be seen in the 2000x magnification.

Other results were reported by Kuakpetoon and Wang [2001] who observed, by means of an electron microscope, granules of potato, maize and rice starches modified with sodium chlorate(I), and did not observe any significant oxidation-induced differences in their structure and morphology.

In analysing SEM images, also Wing [1994] reported an

intact structure of the granules of maize starch oxidised with sodium chlorate(I).

Specific surface may be used as a measure of the reactivity of starches of different origin and their modified preparations. Its size is affected by the degree of granule disintegration (granule size) as well as its shape and porosity. The term of a specific surface of a body means the surface available to particles of gas or water which comprises both the outer and the inner surface of the body. The specific surface is a ratio of the total outer surface of a granule and surface of pores to their mass, and is most often expressed as m^2/g [Paderewski, 1999].

Figure 1 presents the results referring to the specific surface of native and oxidised starch granules.

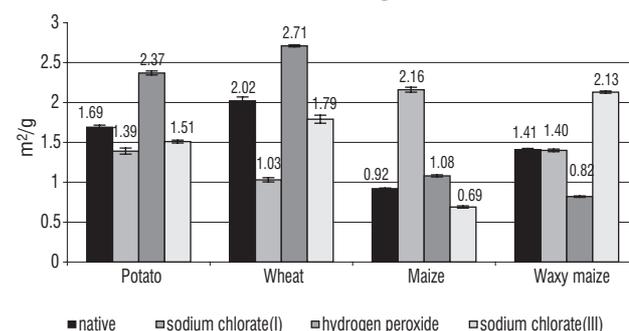


FIGURE 1. The specific surface area of starch before and after oxidation.

The results presented therein indicate that the specific surface area of native starches fluctuated from $0.92 m^2/g$ for maize starch to $2.02 m^2/g$ for wheat starch. Those values approximate the results obtained by other authors [Achremowicz *et al.*, 1997; Juszczak *et al.*, 2002].

The oxidation process of potato starch caused changes in its surface structure which was reported to increase upon the activity of hydrogen peroxide and was found relatively high (ca. 40%) compared to native starch. Whereas a decrease in the specific surface was noted in the case of the other oxidants and accounted for ca. 17% for sodium chlorate(I) and ca. 11% for sodium chlorate(III).

The same relationship was reported for wheat starch, namely the oxidation with hydrogen peroxide induced an enlargement of the specific surface of starch by ca. 35%, whereas the oxidation with sodium chlorate(I) and sodium chlorate(III) decreased it by ca. 50% and ca. 10%, respectively.

The oxidation of maize starch with sodium chlorate(I) resulted in almost twofold enlargement and that with hydrogen peroxide – in ca. 20% enlargement of its specific surface, compared to native starch. In contrast, a decreased specific surface area was observed in starch oxidised with sodium chlorate(III).

In waxy maize starch, unlike in the other starches, the oxidation with sodium chlorate(III) caused a substantial increase in the specific surface area (ca. 50%), whereas oxidation with hydrogen peroxide resulted in its decrease (ca. 40%). The oxidation with sodium chlorate(I) evoked no changes in the specific surface of that starch.

The data presented point to no relationship between oxidation-induced changes in the specific surface of starch. That property is determined to a high extent by the botanical origin of a plant, degree of its maturity, climatic and weather conditions, fertilisation and even cultivar.

Huber & BeMiller [2000] reported that immature granules of maize starch possess smaller cavities on the surface which tend to increase along with plant maturing. In their earlier study Huber & BeMiller [1997], those authors made an observation that starches differing in terms of surface structure demonstrate different susceptibility to water absorption, thus to its removal, which may also affect the specific surface. On the other hand, Achremowicz *et al.* [1997] claimed that large starch granules are characterised by a small specific surface and small starch granules by a large specific surface.

An enlargement of the specific surface upon the oxidation process may be explained by the adsorption of oxidising agents or catalysts on the surface of starch granules, which is in accordance with the results obtained by Achremowicz *et al.* [2000].

Whereas a decrease in the specific surface area of starch after oxidation may be explained by the fact that the oxidising agents or catalysts used were likely to either form complexes in the cavities on the granule's surface or to plug the pores, which finally decreased the specific surface area.

CONCLUSIONS

1. Potato starch appeared to be the most susceptible to oxidation with sodium chlorate(I) and hydrogen peroxide, and maize starch – to oxidation with sodium chlorate(III).

2. The modification of starch with sodium chlorate(I) and hydrogen peroxide caused the highest increase in the number of carboxyl and aldehyde groups, than the method based on sodium chlorate(III). The highest increase of aldehyde groups was observed after oxidation with hydrogen peroxide.

3. Changes in the specific surface of granules, analysed by means of scanning electron microscopy, were observed in starches oxidised with: sodium chlorate(I) and hydrogen peroxide.

4. The greatest changes in the specific surface compared to native starch were caused by sodium chlorate(I) which increased its area in maize starch and decreased it in wheat starch.

5. Of all the oxidised starches examined, the greatest specific surface (S_{BET}) was reported for wheat starch modified with hydrogen peroxide, whereas the smallest one was for maize starch oxidised with sodium chlorate(III).

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ZMIANY STRUKTURY POWIERZCHNIOWEJ ZIAREN SKROBIOWYCH WYWOŁANE PROCESEM UTLENIANIA

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Skrobie naturalne: ziemniaczaną, pszenną, kukurydzianą i kukurydzianą woskową poddano reakcji utleniania: chlo-
ranem(I) sodu, nadtlenkiem wodoru w obecności jonów Cu^{2+} , chloranem(III) sodu w obecności formaldehydu. W skrobi-
ach naturalnych oraz preparatach modyfikowanych oznaczono zawartości grup karboksylowych i aldehydowych. W celu
określenia zmian w strukturze powierzchniowej wykonano mikrofotografie (SEM) oraz wyznaczono powierzchnię właściwą
(S_{BET}). Chloran(I) sodu i nadtlenek wodoru w porównaniu z chloranem(III) sodu efektywniej utleniały skrobie. Działaniom
dwóch pierwszych utleniaczy towarzyszyły większe zmiany w strukturze powierzchniowej badanych skrobi (fot. 1–5).
Największą zmianę powierzchni właściwej spowodował chloran(I) sodu, w skrobi kukurydzianej zwiększając a w pszennej
zmniejszając tą wielkość (rys. 1).