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IONIC STARCH DERIVATIVES OBTAINED IN MICROWAVE ASSISTED REACTIONS – STRUCTURE AND FUNCTIONALITY

Abstract

Commercial potato and wheat starches were substituted to DS = 0.04 by cationic and anionic groups separately (to obtain cationic and anionic derivatives, respectively) and jointly (to obtain amphoteric derivatives). Microwave assisted processes were carried out in oven emitting radiation of 2450 MHz frequency and 0.5 W/g energy. Reaction products were examined by rheological methods, light, and scanning electron microscopy, and X-ray diffractometry. Nitrogen and carboxymethyl group contents were also determined.

Incorporation of ionic substituents into the starch molecules significantly changes its physicochemical properties related to starch-water interactions, results in the decrease of the gelatinisation temperature, changes of the swelling characteristics, solubilisation and iodine complexation. The extent of these changes depends on type of processing (microwave or traditional) and starch species. Crystal and granular structures of investigated starches were only slightly damaged on derivatisation.

Introduction

Microwaves are known to be capable of generating heat deeply inside the penetrated medium. As quite competitive in cost to other methods of heating it has been used for thawing of frozen foods, drying, baking, rendering, pasteurisation and sterilisation. Microwave radiation seems applicable to starch processing, but thus far, it has not been used on commercial scale, despite of the opinion that solid state reactions are the most promising area of applying microwave ovens instead of traditional heating methods [1]. The problem of the influence of microwave radiation on the reactivity of different substances still remains unsolved. It is believed that microwave radiation (2450 MHz) does not activate any specific bonds in molecules, and consequently this forms of treatment will not lead to any kinetic differences compared to other form of

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heating [1]. In spite of this, there has been a growing interest in the use of microwave heating synthesis, so called „MORE chemistry" (microwave oven induced reaction enhancement), and in some processes catalytic effect is claimed [2-7]. Our previous work on the application of microwave ovens to obtain inorganic starch esters proved that microwaves shorten reaction times and do not affect molecular and submolecular structure of the derivatives as compared to conventional technology [8, 9]. Promising results of using microwave ovens to esterification, suggest applying them to other starch modification reaction, for example etherification. These type reactions is conventionally applied in starch industry to produce derivatives of ionic type i.e. cationic starches, carboxymethylated (anionic starches) and amphoteric starches. Ionic starch derivatives of different degree of substitution reveal unique physicochemical properties, useful in many branches of industry, especially in papermaking, building and mining. The aim of this work was to examine the influence of microwave processing on structure and functionality of ionic starch derivatives.

Materials and methods

Preparation of ionic starch derivatives

Microwave assisted reactions

Microwave assisted processes were carried out according to the Polish patent description [15].

Cationic derivatives: Commercial potato and wheat starches were sprayed with the solution of N,N,N-trimethyl-2-epoxypropylammonium chloride to incorporate 0.34% of nitrogen (basis of starch dry mass), alkalised with 1% calcium hydroxide and 1% sodium metasilicate (basis of starch dry mass) and carefully mixed to unification. The moisture contents of the prepared blends were adjusted to 35%. Then, the starch samples were dried in a Panasonic microwave oven emitting radiation of 2450 MHz frequency and 0.5 W/g energy, to reduce moisture content level below 20%.

Anionic derivatives: 100 g of commercial potato and wheat starches were sprayed with the solution containing 3.5 g of sodium mochloroacetate, mixed carefully with 12 g of sodium metasilicate, then the moisture contents of the prepared blends were adjusted to 35%. Microwave processing was performed as described above.

Amphoteric derivatives: commercial potato and wheat starches were sprayed with the chemicals necessary both to cationisation and anionisation. Blends adjusted to moisture content of 35% were processed in microwave ovens as described above.

Reference samples

Cationic derivatives (suspension reaction): commercial potato and wheat starches were slurried in the water solution of 3-chloro-2-hydroxy-N,N,N-trimethylpropylammonium chloride (0.34% of nitrogen basis of starch dry mass). The suspensions were alkalised with the solution of sodium hydroxide (2 moles per 1 mole of cationisation agent) and the reaction were carried out at the temperature of 35°C during 6 hours. Then the reaction mixtures were neutralised with diluted hydrochloric acid, filtered, washed twice with water and air dried.

Anionic derivatives (rotating roaster process): 100 g of commercial potato and wheat starches were sprayed with the solution containing 3.5 g of sodium mochloroacetate and mixed carefully with 12 g of sodium metasilicate. Then the starch samples were pre-dried at room temperature to moisture content below 20% and heated in rotating roaster at the temperature of 120°C for two hours.

Amphoteric derivatives (rotating roaster process): commercial potato and wheat starches were sprayed with the chemicals necessary both to cationisation and anionisation. Starch blends were processed in rotating roaster at the temperature of 120°C for two hours.

Analytical methods

Rheological properties

The course of gelatinization was monitored with a Brabender viscograph under the following conditions: measuring cartridge 0.07 Nm; heating/cooling rate 1.5°C/min; thermostating 30 min.

Nitrogen content

Cationic starches obtained in microwave process were previously purified by with hydrochloric acid. To this aim, starch samples were suspensed in 5% solution of hydrochloric acid, filtered, and washed with water to remove chloride ions and air dried. The nitrogen contents was determined according to EN ISO 3188 standard.

Carboxymethyl groups content

Carboxymethyl groups content was determined according to ISO 11216 standard.

Microscopic examinations

The starch samples to be examined by light microscopy were prepared by the smear method. To this end starch suspensions were heated at the initial gelatinization temperature (as measured acc. to Brabender), and at 95°C. A drop of the resulting paste was applied to a microscope slide and, on cooling, the smear was stained with iodine acc. to Kaczyńska et al. [10], and observed with an Olympus BX60 light microscope.

The starch samples to be examined by scanning electron microscopy were prepared acc. to Fornal [11] and observed with a Jeol JSM 5200 microscope.

X-ray diffractometry

X-ray diffractometry was carried out with a TUR 62 Carl Zeiss X-ray diffractometer under the following conditions: X-ray tube CuKα (Ni filter); voltage 30 kV; current 15 mA; scanning from Θ = 2° to 18°.

Results and discussion

As it is shown in Table 1 microwave processing is a convenient way to obtain ionic starch derivatives of DS ≈ 0.04. Reference cationic starches obtained in a water suspension revealed lower degree of substitution in spite of relatively long reaction time (6 hours). Especially in case of wheat starch low reactivity was observed. Reference samples of anionic and amphoteric starches which were obtained in rotating roasters also revealed a lower degree of substitution as compare to microwave assisted product reactions.

Table 1

Degree of substitution of ionic starch derivatives obtained in microwave assisted and traditionally run reactions.

Starch origin	Reaction type	Nitrogen content [%]	Nitrogen degree of substitution	Carboxymethyl groups content [%]	Carboxymethyl groups degree of substitution
Potato	Microwave assisted	0.33	0.04	-	-
Potato	Suspension	0.30	0.03	-	-
Potato	Microwave assisted	-	-	1.47	0.04
Potato	Rotating roaster	-	-	1.39	0.04
Potato	Microwave assisted	0.33	0.04	1.49	0.04
Potato	Rotating roaster	0.27	0.03	1.08	0.03
Wheat	Microwave assisted	0.34	0.04	-	-
Wheat	Suspension	0.17	0.02	-	-
Wheat	Microwave assisted	-	-	1.46	0.04
Wheat	Rotating roaster	-	-	1.24	0.03
Wheat	Microwave assisted	0.34	0.04	1.42	0.03
Wheat	Rotating roaster	0.19	0.02	1.23	0.03

The incorporation of ionic substituents into the starch molecules significantly affected physicochemical properties related to the starch-water interactions. The substitution of cationic groups (DS = 0.02–0.04) resulted in a decrease of pasting temperature accompanied by a rapid increase in viscosity within a narrow temperature range and the occurrence of a sharp viscosity peak (Fig. 1, 2). The extent of these changes in microwave assisted ethers was more significant than that in products of suspension reaction, what could be a result of a higher degree of substitution [12].

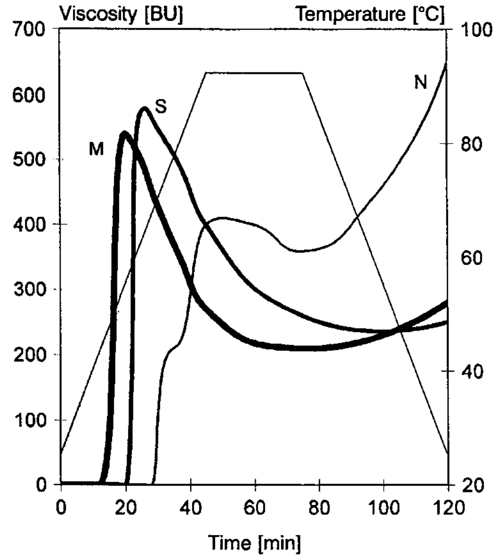

Fig. 1. Brabender viscosity curves (c = 3,3%) of potato starch cationic ethers as compared to native starch: N – native potato starch; S – suspension reaction product; M - microwave assisted reaction product.

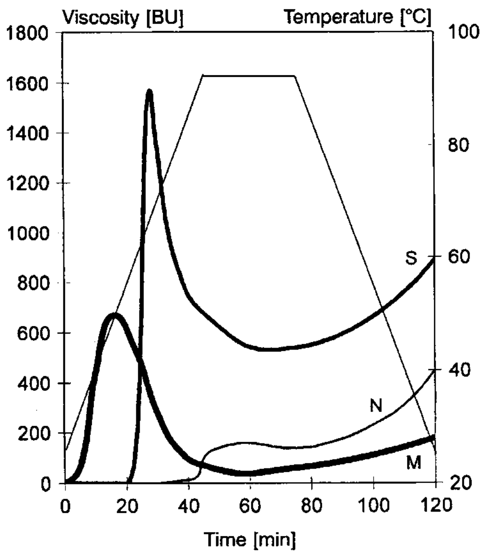

Fig. 2. Brabender viscosity curves (c=8%) of wheat starch cationic ethers as compared to native starch: N – native wheat starch; S – suspension reaction product; M – microwave assisted reaction product.

The substitution of anionic groups into the starch molecules also resulted in a decrease of pasting temperature. In case of potato starch it is accompanied by a rapid increase in viscosity within a narrow temperature range and the occurrence of a sharp viscosity peak, but extend of these changes were lower as compare to cationic derivatives (Fig. 3). In case of wheat starch, medium type of swelling characteristic was observed (Fig. 4). Rotating roaster reaction products revealed significantly lower viscosity than the derivatives from microwave assisted reactions. This observation could be explained by degradation phenomena accompanying the processing at relatively high reaction temperature (120°C).

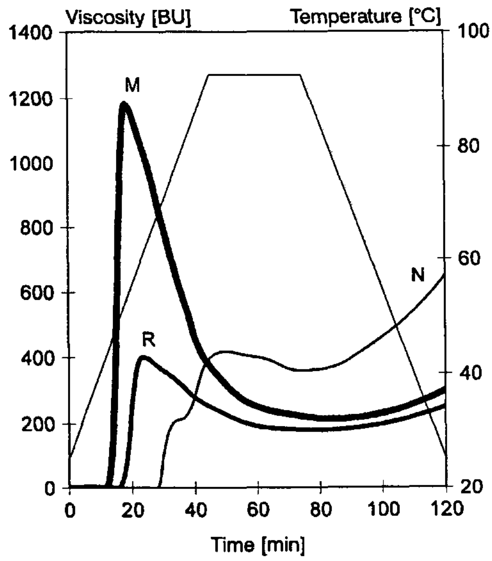

Fig. 3. Brabender viscosity curves (c = 3,3%) of potato starch anionic ethers as compared to native starch: N - native potato starch; R – rotating roaster reaction product; M – microwave assisted reaction product.

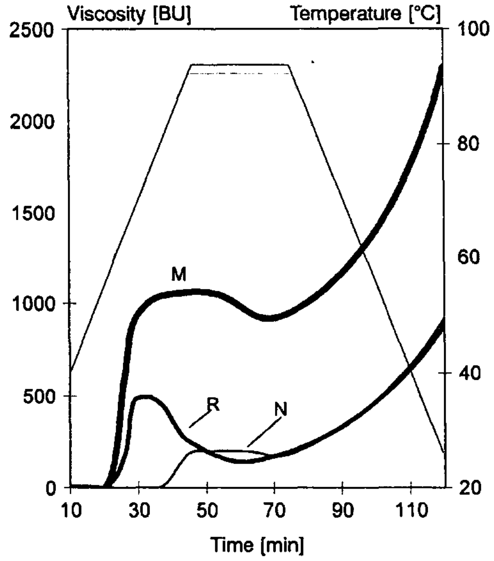

Fig. 4. Brabender viscosity curves (c = 8%) of wheat starch anionic ethers as compared to native starch: N – native wheat starch; R – rotating roaster reaction product; M – microwave assisted reaction product.

The incorporation of two types of ionic substituents into the starch molecules together, caused the decrease of pasting temperature, accompanied by different phenomena in case of potato than in case of wheat starch (Fig. 5, 6). In case of wheat starch an increase of the type of swelling characteristic was observed, whereas in case of potato starch a significant decrease in viscosity. As just as anionic, amphoteric derivatives obtained in rotating roaster, revealed lower viscosity than products of microwave reactions.

The above changes were confirmed by light microscopy. Native potato and wheat starches heated at pasting temperature give a characteristic behaviour – amylose leakage out of the starch granules [13, 14]. Cationic starches revealed similar solubilisation mechanism (pictures not shown) i.e. amylose leakage out of the starch granules. At the temperature of 90°C the solubilisation of native starches is advanced, amylose leaks completely out of granules, but amylopectin still forms aggregates which are the remnants of the granules [13, 14]. Cationic starches at the temperature of 90°C (pictures not shown) formed almost uniform mixture of soluble amylose and amylopectin. The colour of amylose and amylopectin – iodine complexes changed only a little as compared to native starches. Amyloses of different starch origin formed deep blue complexes, whereas amylopectins formed red-brown complexes, (pictures not shown). The differences between solubilisation behaviour of cationic derivatives obtained using microwaves and in water suspension were not observed.

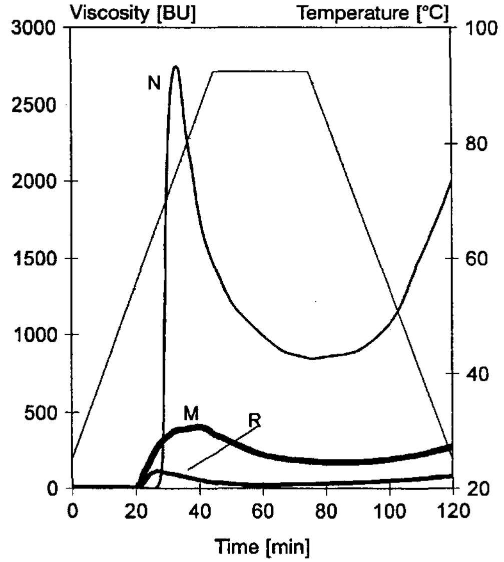

Fig. 5. Brabender viscosity curves (c = 8%) of potato starch amfoteric ethers as compared to native starch: N – native potato starch; R – rotating roaster reaction product; M – microwave assisted reaction product.

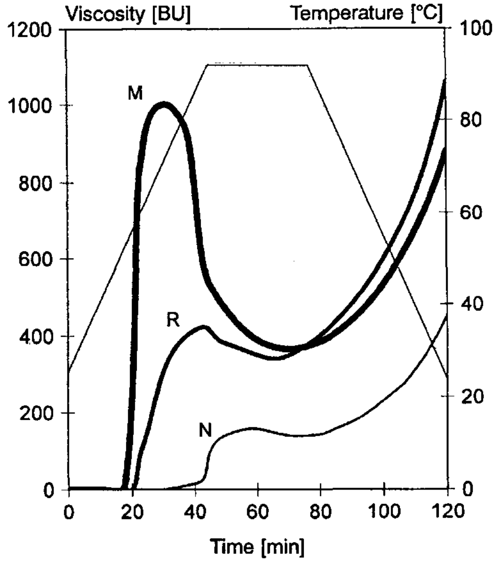

Fig. 6. Brabender viscosity curves (c = 8%) of wheat starch amfoteric ethers as compared to native starch: N – native wheat starch; R – rotating roaster reaction product; M – microwave assisted reaction product.

The substitution of anionic groups as well as together two types of ionic substituents into the starch molecules resulted in different phenomena in case of potato than wheat starches. Potato starch anionic derivatives, similarly to cationic ones, at the temperature of 90°C (pictures not shown) were almost completely soluble, what corresponded to their high type of swelling characteristics (Fig. 3). Amphoteric potato starch derivatives of restricted type of swelling characteristic (Fig. 5) at the temperature of 90°C (pictures not shown) revealed strongly limited solubilisation process – only part of amylose leached out of granules. The majority of the starch material remained insoluble. This observation pointed to the conclusion that cationic and anionic substituents probably formed amphions, which reduced solubility of starch.

Wheat starch anionic derivatives at the temperature of 90°C (pictures not shown) were only partially soluble, what corresponded to their medium type of swelling characteristics (Fig. 4). Amphoteric derivatives of wheat starch at the temperature of 90°C (pictures not shown) were better soluble than anionic ones, what corresponded to higher type of swelling characteristic (Fig. 6). LM pictures of anionic and amphoteric derivatives obtained in rotating roaster (pictures not shown) were coloured more red-violet as compare to microwave equivalent samples what pointed to degradation phenomena occurring during processing at the temperature of 120°C.

Deep changes in type of swelling characteristics could suggest some changes in the structure of starch granules as an effect of derivatisation. This hypothesis was not confirmed by X-ray and SEM investigations however. The type of X-ray diffraction patterns of native starches maintained unchanged after substitution of all types ionic substituents (Fig. 7-9). The type of processing (microwave, suspension and rotating roaster) also only slightly reflected on relative crystallinity of investigated starches. Even heating in rotating roaster at the temperature of 120°C during 2 hours did not affect crystallinity of investigated starches.

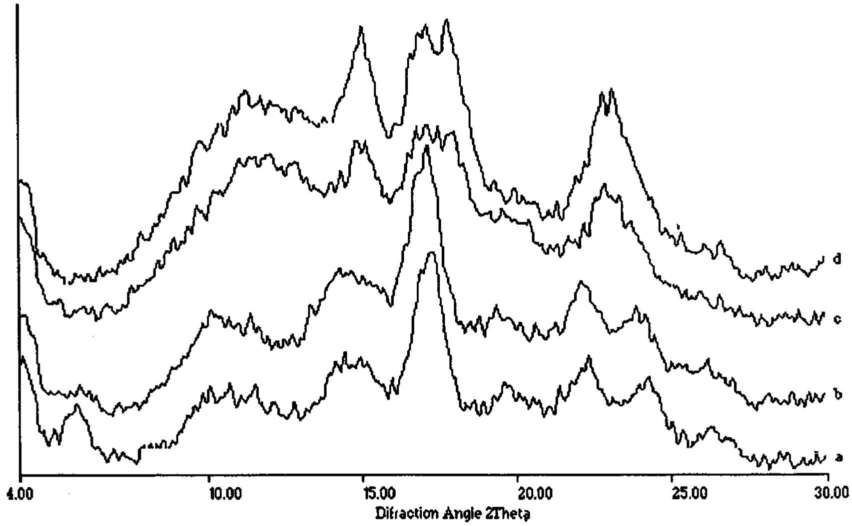

Fig. 7. X-ray diffraction patterns of the cationic starch ethers: potato starch microwave assisted reaction product (a); potato starch suspension reaction product (b); wheat starch microwave assisted reaction product (c); wheat starch suspension reaction product (d).

Scanning electron microphotographs of ionic starch derivatives proved that modification process induced only slight deterioration of starch granular structure (Fig. 10, 11). The strong alkaline conditions applied in all types of processing caused some gelatinization phenomena resulting in a leakage of starch material out of the granules. However, the extent of granules damages was the smallest in case of suspension reaction products. Solid state reactions (microwave and rotating roaster) occurring by local action of alkalis on starch granules caused more extensive leakage of starch material out of the granules.

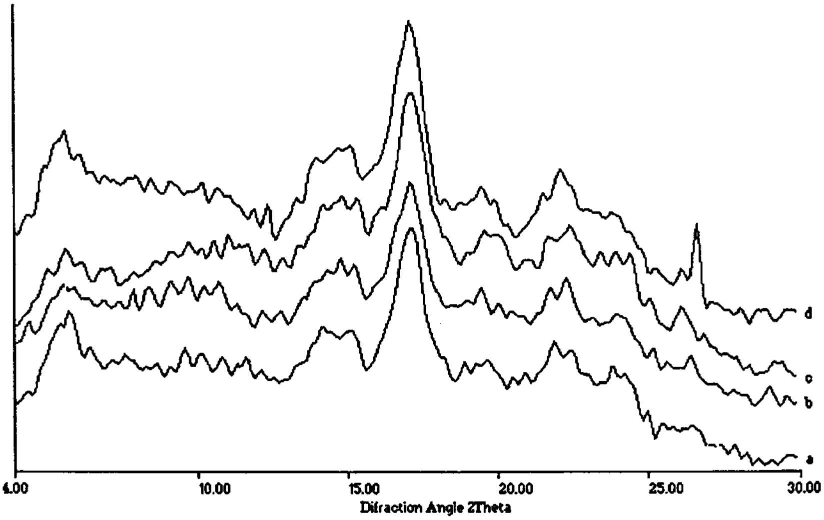

Fig. 8. X-ray diffraction patterns of potato starch ionic starch ethers: microwave assisted reaction amphoteric derivative (a); rotating roaster reaction amphoteric derivative (b); microwave assisted reaction anionic derivative (c); rotating roaster reaction anionic derivative (d).

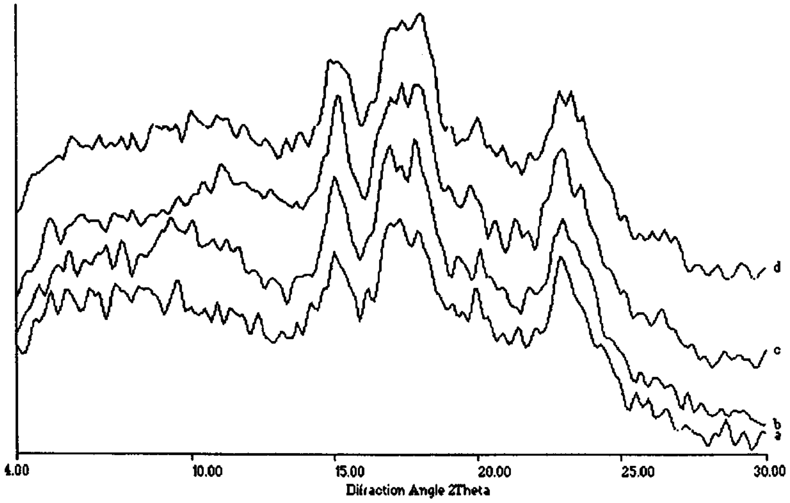

Fig. 9. X-ray diffraction patterns of wheat starch ionic starch ethers: microwave assisted reaction amphoteric derivative (a); rotating roaster reaction amphoteric derivative (b); microwave assisted reaction anionic derivative (c); rotating roaster reaction anionic derivative (d).

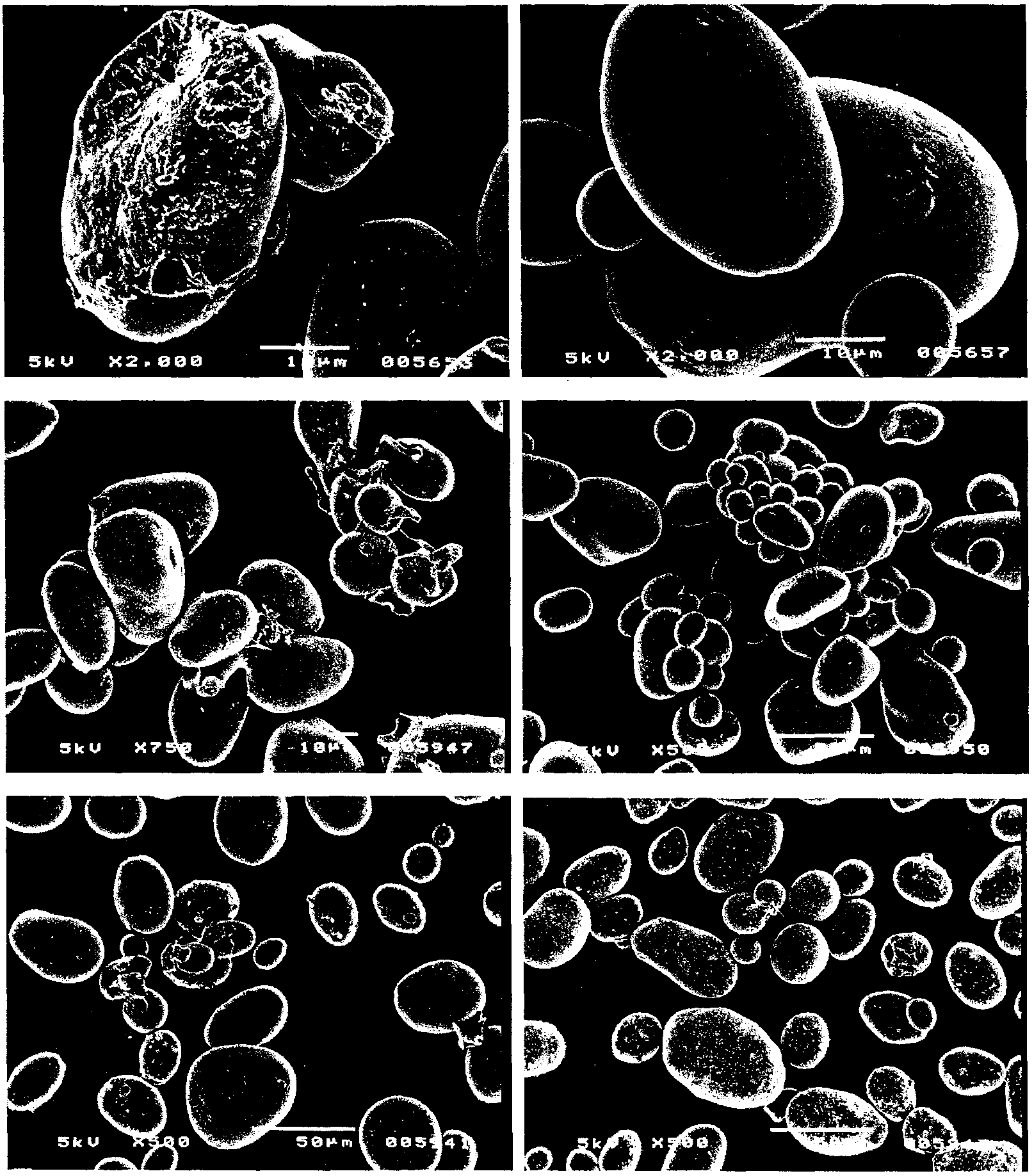

Fig. 10. SEM microphotographs of potato starch ethers: cationic derivative from microwave assisted reaction (A), cationic derivative from suspension reaction (B), anionic derivative from microwave assisted reaction (C), anionic derivative from rotating roaster reaction (D), amphoteric derivative from microwave assisted reaction (E), amphoteric derivative from rotating roaster reaction (F).

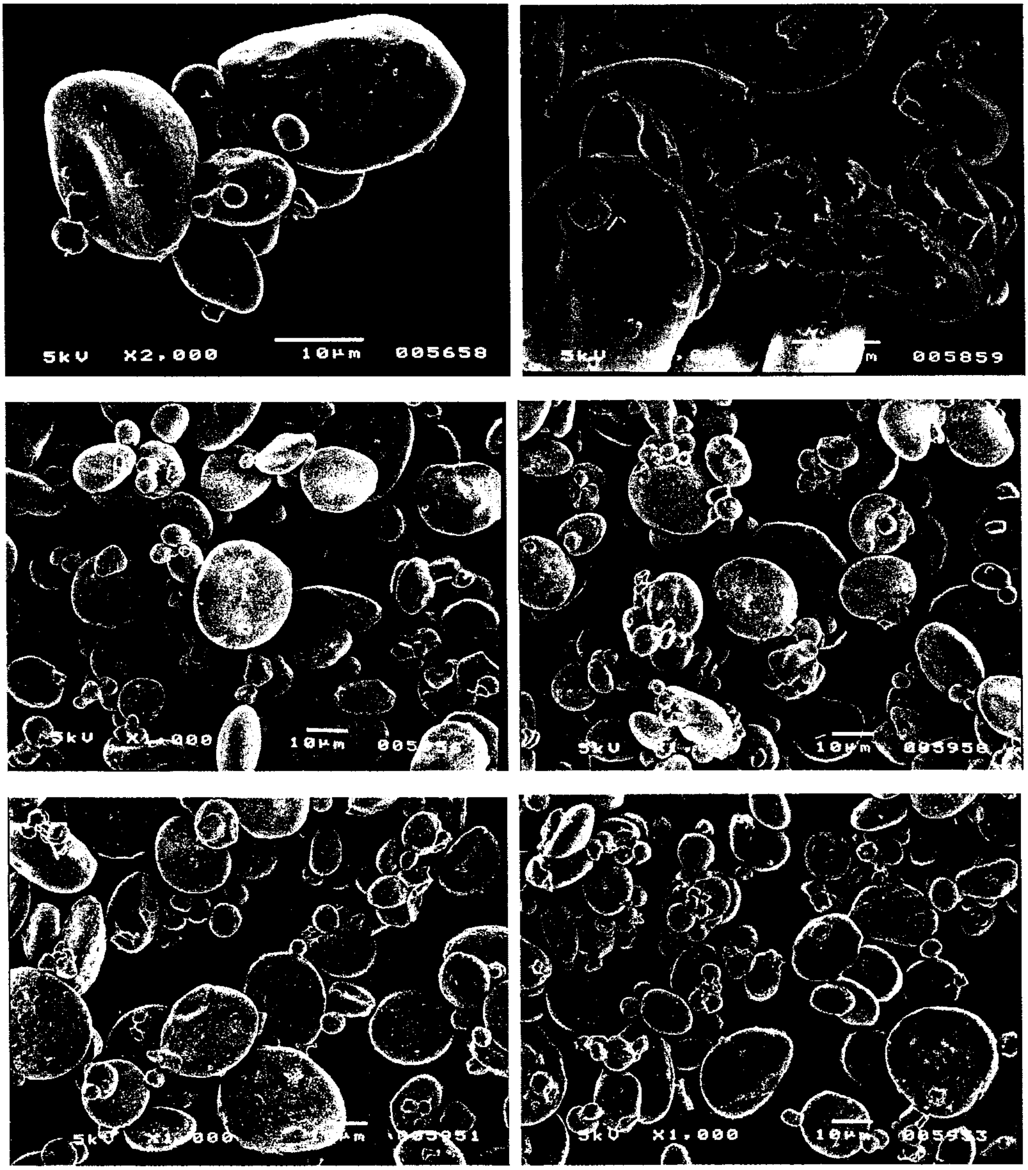

Fig. 11. SEM microphotographs of wheat starch ethers: cationic derivative from microwave assisted reaction (A), cationic derivative from suspension reaction (B), anionic derivative from microwave assisted reaction (C), anionic derivative from rotating roaster reaction (D), amphoteric derivative from microwave assisted reaction (E), amphoteric derivative from rotating roaster reaction (F).

Conclusions

1. Microwave processing is a convenient way to obtain starch ethers of DS ≈ 0.04.
2. The incorporation of ionic substituents into the starch molecules significantly affects their physicochemical properties related to starch-water interactions. These results in the decrease of the gelatinization temperature, changes of the swelling characteristics, solubilisation and iodine complexation.
3. The incorporation of ionic substituents into the starch molecules are not reflected in their crystal structure.
4. Microwave processing as well as suspenion reaction do not reveal degradation phenomena observed as changes in colour of starch-iodine complexes.
5. Rotating roaster processing causes some degradation phenomena observed as changes in colour of starch-iodine complexes.
6. Microwave processing caused deterioration in granular structure of investigated starches similar to those observed in rotating roaster produtcs.

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POCHODNE SKROBI JONOWYCH UZYSKANE W REAKCJACH W POLU MIKROFALOWYM. STRUKTURA I FUNKCJONALNOŚĆ

Streszczenie

Zbadano możliwości zastosowania energii pola mikrofalowego do otrzymywania skrobi kationowych (podstawionych grupami tetraalkiloamonio alkilowymi), anionowych (karboksymetyloskrobie) i amfoterycznych oraz wpływ takiego pola na strukturę i funkcjonalność produktów.

Natywne skrobie: ziemniaczaną i pszenną, podstawiono do DS = 0,04, stosując piecyk mikrofalowy 2450 MHz dający energię 0,5 W/g. Produkty badano za pomocą wiskografu Brabendera mikroskopowo (mikroskopy optyczny i SEM) oraz za pomocą dyfraktometrii proszkowej. Oznaczano też zawartość azotu w skrobiach kationowych według normy EN ISO 3188.

Stwierdzono, że zmiany spowodowane wprowadzeniem grup jonowych do skrobi zależą od sposobu dostarczania energii oraz od rodzaju skrobi.