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Effect of microwave radiation on physico-chemical properties and structure of cereal starches

G. Lewandowicz[a,*], T. Jankowski[b], J. Fornal[c]

[a]Starch and Potato Products Research Laboratory, ul. Zwierzyniecka 18, 60-814 Poznañ, Poland
[b]Department of Biotechnology and Food Microbiology, ul Mazowiecka 48, 60-623 Poznañ, Poland
[c]Institute of Animal Reproduction and Food Research Polish Academy of Sciences, ul. Tuwima 10, 10-817 Olsztyn, Poland

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Abstract

Wheat, corn and waxy corn starches of intermediate moisture content (30%) were subjected to microwave processing and the effect of microwave radiation on physico-chemical properties and structure of cereal starches was studied. The experimental starches were examined by the Brabender rheological method, light microscopy, X-ray diffractometry and differential scanning calorimetry. Microwave radiation was evidenced to cause a shift in the gelatinisation range to higher temperatures, and a drop in solubility and crystallinity. The extent and type of these changes depended on the variety of starch. Normal corn and wheat starches underwent pronounced changes, whereas under the same conditions waxy corn starch was almost unchanged. It was concluded that susceptibility of different starches to changes due to microwave irradiation depended not only on their crystal structure, but also on their amylose content. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Physico-chemical properties; Microwave radiation; Gelatinisation

1. Introduction

Microwaves are the nonionizing energy that causes a rise in the temperature within a penetrated medium as a result of rapid changes of the electromagnetic field at high frequency. Microwave irradiation seems applicable to starch processing, but it has not yet been used for this purpose on a commercial scale. Most of the experiments carried out on the interaction between starch and microwave irradiation pertained to the systems of high water content (Miller, Gordon & Davis, 1991; Rashed Khan, Johnson & Robinson, 1979; Zylema, Grider, Gordon & Davis, 1985). Very little research has been done on the dextrinisation and chemical modification of dry starches by microwave irradiation (Muzimbaranda & Tomasik, 1994; Sikora, Tomasik & Pielichowski, 1997a,b). In our previous work on tuber starches it was found that microwaves substantially affected physico-chemical properties of the irradiated starch with a strong correlation between the moisture content of irradiated starch and the extent of changes (Lewandowicz, Fornal & Walkowski, 1997). It was observed that microwave irradiation of tuber starches at a limited moisture content (<35%) caused a rise in the starch pasting temperature, a reduction of solubility, and changes in the crystalline structure. The extent of the changes was greater when the moisture content of the microwave-treated starch was greater. The most pronounced changes have been noted in potato starch, whose crystal structure changed from the B-pattern to the A-pattern.

Our observations on the modification of tuber starch by microwave irradiation were similar to those caused by the heat-moisture treatment of starch previously reported by other authors (Kulp & Lorenz, 1981; Lorenz & Kulp, 1982). Heat-moisture treatment typically employs prolonged heating of starch at a temperature range of 90–100°C at limited quantities of moisture insufficient to gelatinise the starch (Sair, 1967). To avoid gelatinisation at this temperature range, the moisture content of starch should be kept below 25–30% (Biliaderis, Mauricew & Vose, 1980).

It is known that the effect of heat-moisture treatment on cereal starches is less pronounced than on tuber starches (Donovan, Lorenz & Kulp, 1983). We have attempted, therefore, to examine the effect of microwave irradiation on the physico-chemical properties and structure of cereal starches. The most common cereal starches, i.e. wheat, corn and waxy corn, produced commercially, were investigated in this work.

* Corresponding author. Fax: +48-61-841-7610.
E-mail address: lewal@man.poznan.pl (G. Lewandowicz).

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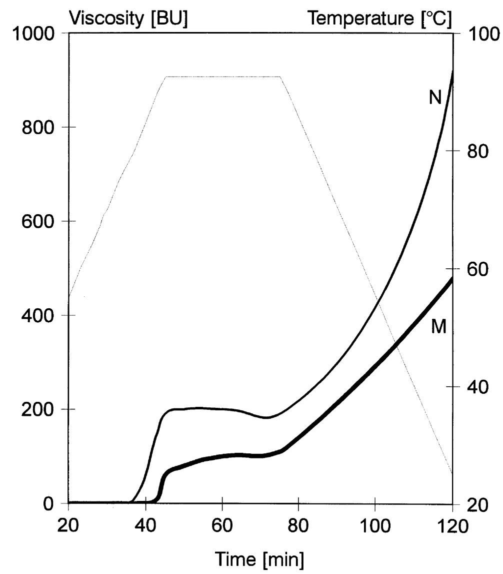

Fig. 1. Brabender viscosity curves for 8% solution of wheat starch samples, M = microwaved, N = native.

2. Experimental

2.1. Microwave irradiation of starch samples

Commercial wheat, corn and waxy corn starches were adjusted to a 30% moisture content by the addition of appropriate water amount to the starch samples of known moisture content. The moisture content of starches was determined by the oven-drying method according to ISO 1666 standard. Then moistened starch samples were placed in glass beakers, and sealed with a perforated polyethylene foil designed for microwave ovens. The experiments were limited to the moisture level at which the most significant effect of microwave heating on tuber starches had been observed (Lewandowicz et al., 1997). Irradiation was carried out for 60 min with a DeLonghi microwave oven (Italy) emitting a 2450 MHz microwave frequency and 0.5 W/g microwave energy.

2.2. Rheological properties

The course of gelatinisation 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.

2.3. X-ray diffractometry

X-ray diffractometry was carried out with a TUR 62 Carl Zeiss X-ray diffractometer type under the following conditions: X-ray tube CuKα (Ni filter); voltage 30 kV; current 15 mA; scanning from $\Theta = 2$ to 18°. To avoid the influence of relative humidity on relative crystallinity, starch samples were placed in desiccator and conditioned in the atmosphere of relative humidity of 92% for 48 h. To this end the desiccator was filled with sodium carbonate saturated aqueous solution.

2.4. Microscopic examination

The starch samples were prepared using the smear method. To this end starch suspensions were heated at the initial gelatinization temperature (as measured according to Brabender) and at 95°C. A drop of the resulting paste was placed on a microscope slide and, on cooling, the smear was stained with iodine and examined with a Nicon FX light microscope.

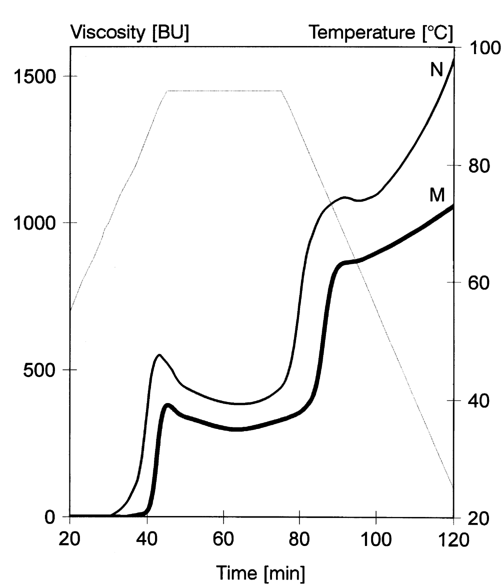

Fig. 2. Brabender viscosity curves for 8% solution of corn starch samples, M = microwaved, N = native.

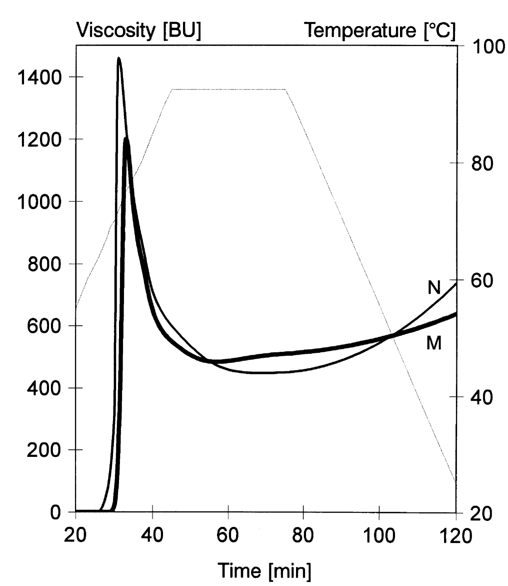

Fig. 3. Brabender viscosity curves for 8% solution of waxy corn starch samples, M = microwaved, N = native.

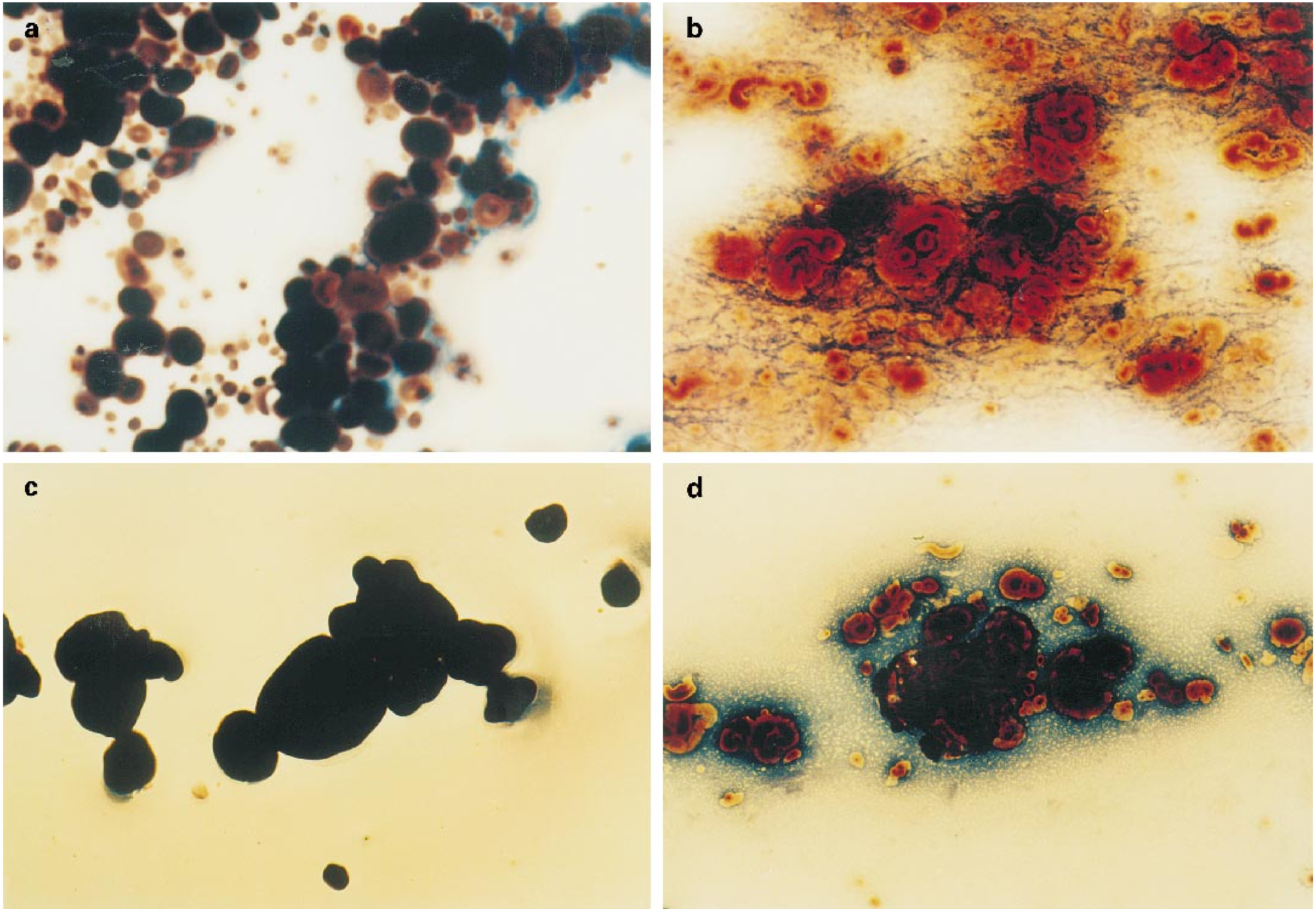

Fig. 4. Light microphotographs of the native and irradiated starch samples. Native wheat at 75°C (A) and 95°C (B), microwaved wheat at 75°C (C) and 95°C (D), native corn at 95°C (E), microwaved corn at 95°C (F), native waxy corn at 75°C (G), microwaved corn waxy at 75°C (H).

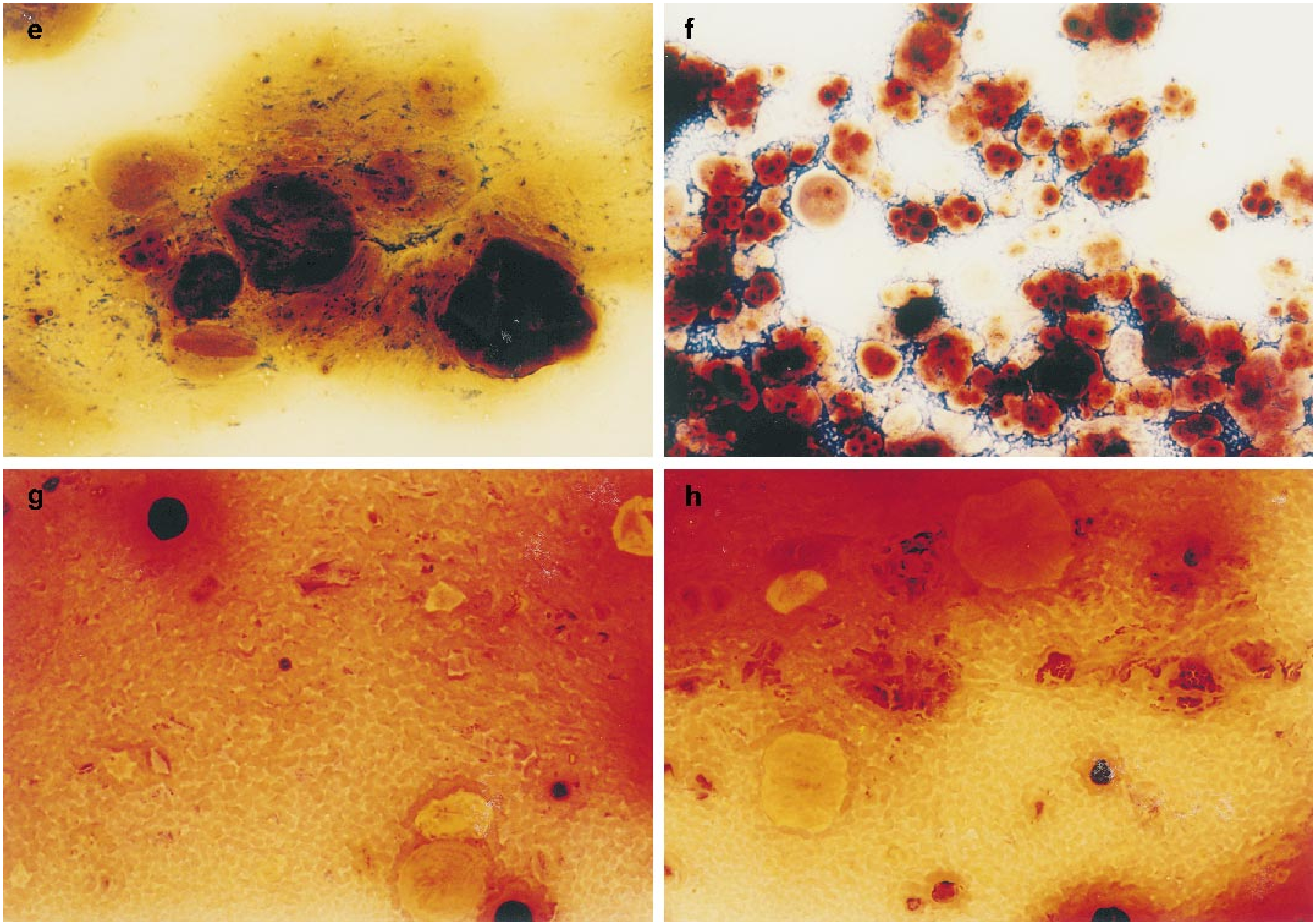

Fig. 4. (Continued).

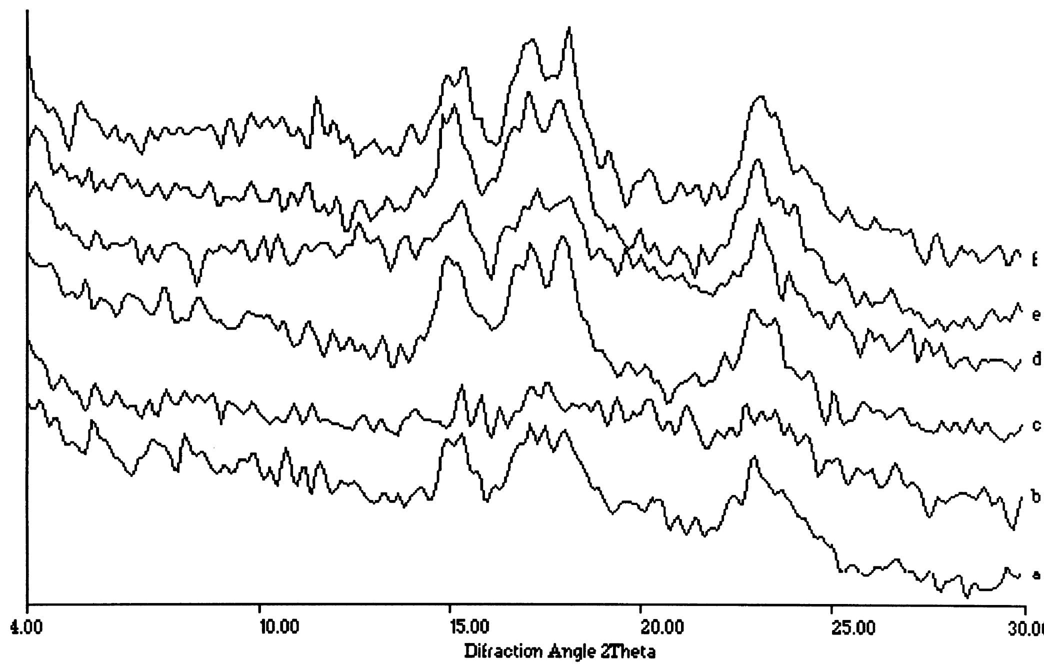

Fig. 5. X-ray diffraction patterns of microwaved starch samples as compared to native ones, a = native wheat starch, b = microwaved wheat starch, c = native corn starch, d = microwaved corn starch, e = native waxy corn starch, f = microwaved waxy corn starch.

2.5. Differential scanning calorimetry

The thermal transitions of native and microwave treated starches were investigated with the use of a Perkin Elmer DSC-7 (USA). A starch sample (2–4 mg) was weighed in a volatile aluminium pan and the excess water was added to obtain a starch/water ratio of approximately 1:3. The pan was then sealed, equilibrated for 3 h at 20°C, and heated from 20 to 100°C at the rate of 10 K/min. Characteristic temperatures of the transitions were onset gelatinisation temperature T_o and peak temperature T_p. Enthalpy of gelatinisation was related to the dry mass of the sample.

3. Results and discussion

The Brabender viscograph was used to study the effect of microwave heating on the pasting characteristics of cereal starches. A rise in pasting temperature and a drop in viscosity were observed as a result of irradiation of wheat and corn starches (Figs. 1 and 2). Medium type of swelling characteristic with a progressive rise in viscosity over a wide temperature range and the lack of a viscosity peak, typical of cereal starches, remained unchanged. This phenomenon was different from that of tuber starches, which changed their type of swelling characteristic from high, with a rapid increase in viscosity within a narrow temperature range and the occurrence of a viscosity peak to medium one (Lewandowicz et al., 1997). Different results were observed on the viscograph of the waxy corn starch. Its rheological properties, such as pasting temperature and high type of swelling characteristic, remained almost unchanged after microwave treatment (Fig. 3).

These observations were confirmed by microscope investigation. Native wheat starch suspension heated at 75°C (Fig. 4A) gave an image typical of early stage of gelatinisation. The granules were slightly swollen and a small amylose leakage from starch granules was observed. When the temperature rose to 95°C (Fig. 4B) the solubilisation process was advanced, starch granules were considerably swollen and an extensive amylose leakage were observed. In the case of microwaved wheat starch, the images were different. At 75°C (Fig. 4C) there were almost no symptoms of solubilisation which began at 95°C (Fig. 4D), mainly due to amylose leakage. Normal corn starch revealed a similar solubilisation behaviour (Fig. 4E and F). In both wheat and corn starches microwave treatment caused some structural changes which make solubilisation in water more difficult. Unlike wheat and normal corn starches, native waxy corn gave a different microscope image on heating. At temperatures as low as 75°C the solubilisation process was already advanced (Fig. 4G and H) and starch and water became an almost homogenous mixture. Only small remnants of starch granules could be observed. There were no significant differences between native and microwaved waxy corn starches in terms of their microscope appearance on heating.

Crucial differences of waxy corn starch behaviour due to microwave irradiation as compared to normal corn and wheat starches were also observed in X-ray diffraction studies (Fig. 5). After microwave irradiation, the degree of crystallinity of wheat and normal corn starch samples decreased, while that of waxy corn starch remained almost

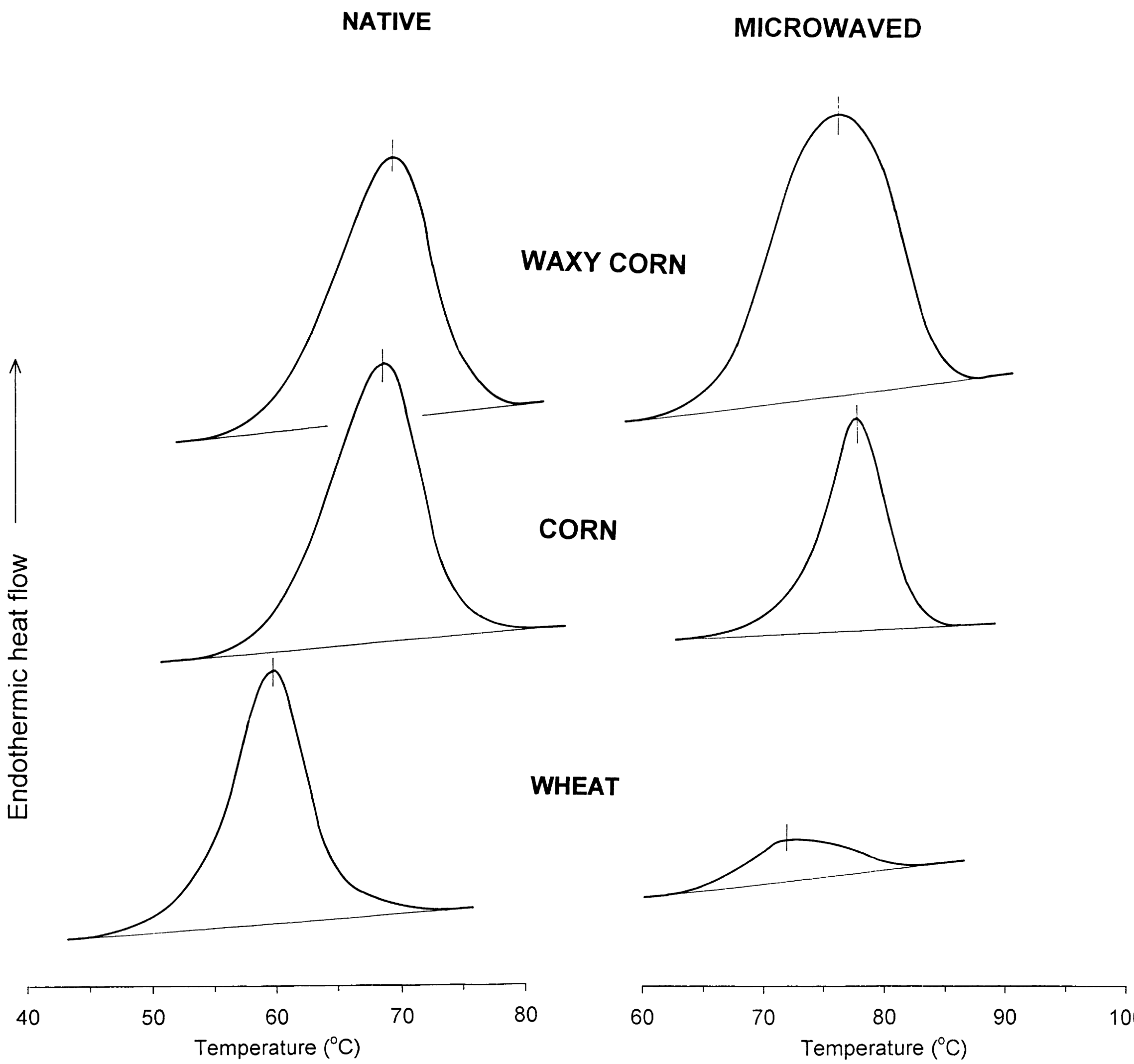

Fig. 6. Differential scanning calorimetry thermograms of native and microwaved cereal starches.

unchanged. In addition all starches retained the A type X-ray diffraction pattern.

The results of X-ray diffractometry were confirmed by differential scanning calorimetry. DSC thermograms of native and microwaved starches are given in Fig. 6. Single entothermic transitions were observed in all the samples when heated under similar water contents (74.4–76.0 w/w%). As measured with the calorimeter, the gelatinisation transition of microwave-treated cereal starches was shifted to higher temperatures, compared to untreated samples (Table 1). A rise of the onset gelatinisation temperature varied among the investigated starches from 13.8 K for wheat, and 11.3 K for corn, to 6.0 K for waxy corn starch. The total enthalpy change for the transition decreased substantially for the irradiated wheat and corn starches while that of waxy corn was insignificant. However, the decrease of ΔH was greater for wheat starch than for corn starch. Wheat starch has a lower initial gelatinisation temperature than the corn starch and it is possible that both the samples had been partially gelatinised by the microwave treatment, but to a different extent.

These observations prove that microwave treatment caused an alteration of the structure of the starch granules. The severity of the changes caused by microwave treatment represented by the increase of the gelatinisation temperature and the decrease in the degree of crystallinity of treated starches proceeded in the following order:

wheat $>$ corn $>$ waxy corn.

The changes in physico-chemical properties of cereal starches induced by microwave irradiation were less

Table 1
Differential scanning calorimetry values of native and microwave irradiated cereal starches

Starch sample	Native			Microwaved		
	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
Wheat	53.6	59.5	11.5	67.4	72.0	3.2
Corn	61.0	69.5	13.8	72.1	76.1	7.3
Waxy corn	60.4	68.6	14.7	66.4	75.1	13.6

pronounced than those of root starches reported previously (Lewandowicz et al., 1997). Similar differences were observed after the traditional heat-moisture treatment (Lorenz & Kulp 1982, 1983; Maruta, Kurashi, Takano, Hayashi, Kudo & Hara, 1998; Sair 1967). In general, it is believed that physical properties of starches, such as the gelatinisation temperature, swelling and pasting behaviour, are affected by the alterations of the crystal structure (Hoover & Manuel 1996; Kulp & Lorenz 1981). In fact the problem is more complicated, because the correlation between crystal structure of starch and its physico-chemical properties is not exact. Typically tuber starches reveal B-type of crystallinity and high type of swelling characteristic and cereal starches reveal A-type of crystallinity and medium type of swelling characteristic. In contrast to those, high amylose corn starch show B-type of crystal structure and restricted type of swelling characteristic (similar to medium type, but with higher pasting temperature and lower viscosity). Moreover waxy corn starch reveals high type of swelling characteristic and A type of X-ray diffraction pattern. Consequently in addition to the crystal structure, the amylose content of starch should be considered. The most distinguished property of waxy corn starch is the lack of amylose, while wheat and normal corn starches contain 28% of this component (Swinkels, 1985). Both cereal starches containing amylose revealed a relatively high susceptibility to microwave treatment and their swelling power and solubles were significantly reduced by this process. Moreover, the effect of the amylose content was also observed in our previous work, where potato starch (21% of amylose) showed greater alterations of its physico-chemical properties than tapioca (17% of amylose) (Lewandowicz et al., 1997). Our results confirm previous suggestion made by Donovan et al. (1983) that amylose associates or crystallises with portion of amylopectin molecules. It seems likely that association or changes in the amorphous amylose part of the starch granule rather than crystallisation occurs during microwave treatment applied in this work. This is evidenced by significant reduction of the swelling of the starch granule and the amount of solubles in the microwaved starches as seen in Fig. 4, resulting in different pasting characteristics (Figs. 1 and 2). A higher gelatinisation temperature of microwave irradiated starches (Fig. 6) may also indicate an association and a more stable configuration in a granular structure. These observations show a great importance of the amylose content on susceptibility of starches to microwave treatment.

The results presented show that microwave irradiation can be a convenient processing method for the modification of physico-chemical properties of starches similar to that obtained by the traditional heat-moisture treatment. Because of the penetrating power of microwaves, rapid and uniform heating occurs throughout the processed sample. This treatment in connection with a suitable choice of moisture content and time of treatment would produce starches of different structural properties.

4. Conclusions

Wheat and corn starches of an intermediate moisture content (30%) subjected to microwave processing showed alteration of their physico-chemical properties and structure, while waxy corn starch remained almost unchanged. Microwave irradiation was evidenced to reduce the crystallinity, solubility, and swelling characteristics of wheat and corn starches as well as to increase the gelatinisation temperature of all the investigated starches. The extent of the changes induced by microwave treatment depended not only on the crystal structure of starch, but also on its amylose content.

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