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Carbohydrate Polymers 56 (2004) 403–413
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Starch modification by iterated syneresis

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Received 8 September 2003; revised 8 September 2003; accepted 15 March 2004

Abstract

Potato, tapioca, corn and wheat starches were solubilised in water and isolated from the solution by iterated syneresis and the effect of this physical modification on the physicochemical properties and structure was studied. The experimental starches were examined by chemical analysis, the Brabender rheological method, scanning electron or light microscopy, X-ray diffractometry, infrared spectroscopy, and differential scanning calorimetry. Physical modification was evidenced to the change starch–water interaction and the structure of starches. Pasting temperature shifted to lower values and the gelatinisation mechanism changed. All modified starches had a B-type of X-ray diffraction pattern. The melting temperature of starch crystallites was typical of retrograded starch, but the enthalpy change was higher. The correlation between the resistant starch content of modified starches and their crystal structure was discussed together with the thermal properties.

Keywords: Physicochemical properties; Resistant starch; Starch; Physical modification; Structure

1. Introduction

Physical modification of starch is mainly applied to change the granular structure and convert native starch into cold water-soluble starch or small-crystallite starch. The major methods used in the preparation of cold water-soluble starches involve instantaneous cooking–drying of starch suspensions on heated rolls (drum-drying), puffing, continuous cooking–puffing–extruding, and spray-drying (Jarowrenko, 1986). The method for preparing granular cold water-soluble starches by injection and nozzle-spray drying was described by Pitchon, O'Rourke, and Joseph (1981). This type of starch could also be produced by physical processing accompanied by slight chemical treatments (Jane, 1992). These involve heating of starch in an aqueous alcohol solution (Eastman, 1987; Eastman & Moore, 1984a,b; Jane, Craig, Seib, & Hoseney, 1986a,b), alcoholic alkali (Jane & Seib, 1991), or polyhydric alcohol treatments at atmospheric pressure (Rajagopalan & Seib, 1991). Starches with submicron (less than 1 μm in diameter) crystallites have been applied as fat substitutes to provide a fat-like texture and mouthfeel (Jane, 1992). Small particle starch has been made from normal corn starch by a combination of acid hydrolysis and mechanical attrition of native starch (Jane, Shen, Wang, & Maningat, 1992).

Among the physical processes applied to starch modification, high pressure treatment of starch should also be mentioned as an example of 'minimal processing' (Stute, Klinger, Boguslawski, & Knorr, 1996). A process of preparing foods with starch pressurized at above 400 MPa was developed by Stute (1997). The effect of high pressure on starch is dependent on the environmental conditions (moisture content, pressure value, temperature) and the origin of the starch (Hibi, Matsumoto, & Hagiwara, 1993; Kudła & Tomasik, 1992a,b; Mercier, Charbonniere, & Guilbot, 1968; Stute et al., 1996; Vainionpää, Forsel, & Virtanen, 1993). As an effect of ultra high pressure (above 400 MPa) treatment, starches gelatinize but show very little swelling and maintain their granular character which results in quite different paste and gel properties of the UHP-gelatinised starches compared to the heat-gelatinised starches (Stute et al., 1996).

A distinct group of processing methods is comprised by those, which change the structure of starches, such as annealing, and heat-moisture or microwave treatments. Heat-moisture treatment changes the physical properties of starches such as gelatinisation temperature translucency, as well as swelling and pasting characteristics.

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doi:10.1016/j.carbpol.2004.03.013

The biggest changes occur in tuber and root starches. In the case of potato starch, the B-type X-ray diffraction pattern was found to change to the A-type (Donovan, Lorenz, & Kulp, 1983; Kulp & Lorenz, 1981; Lorenz & Kulp, 1982, 1983; Sair, 1967). Similar effects could be due to the application of annealing, but because of the lower temperature, this processing needs a much longer time (Stute, 1992). In contrast, the microwave treatment requires a shorter time at a lower temperature to create the same effects as the classic heat-moisture procedure (Lewandowicz, Fornal, & Walkowski, 1997; Lewandowicz, Jankowski, & Fornal, 2000).

The so called 'minimal processing' of starch has recently attracted considerable attention due to the promotion of healthy nutrition. Physical modification accomplished without any chemicals or even biological agents meets these requirements. The aim of this work was to establish the structure and physicochemical or functional properties of a new type of physically modified starches derived from the most popular commercial starches, i.e. potato-, tapioca-, corn- and wheat starch.

2. Experimental

2.1. Materials

Commercial potato (Poland's superior standard), tapioca (Thailand's super high-grade), corn (Franch Cerestar), and wheat (Polish) starches were used as raw and reference materials. Pregelatinised potato, tapioca, corn, and wheat starches (Polish) were used for IR studies as an amorphous reference material. The technological process for the production of these starches consists of rapid drying of starch suspension on hot drum dryers.

2.2. Physical modification of starch

Physically modified starch samples were obtained by solubilisation of native starch samples in water at concentration of 3%, and by their isolation from the solution without any non-solvents or complexing agents, according to the procedure described in Polish Patent specification (Lewandowicz, Soral-Śmietana, & Fornal, 1998). To this end commercial native potato, tapioca, wheat and corn starches were solubilised in water at a temperature of 90 °C for 4 h, then left at room temperature for 24 h and frozen to a temperature below −4 °C. The frozen samples were allowed to thaw at room temperature, then the liquid and solid phases were separated by filtration. The moist solid phase was frozen again and the frosting/thawing cycles were repeated until the moisture content of the solid phase was below 20%.

2.3. Analytical methods

The moisture content of starches was determined by the oven-drying method according to the ISO 1666 standard. The protein content was determined by the Kjeldahl method according to the ISO 5378 standard. The fat content was determined according to the ISO 3947 standard. The ash content was determined according to ISO 3593 standard.

The resistant starch (RS) content was determined by two different in vitro methods according to Akerberg, Liljenberg, Granfeldt, Drews, and Bjärck (1998) and Champ, Martin, Noah, and Gratas (1999).

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.

2.4. 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 Cu Kα (Ni filter); voltage 30 kV; current 15 mA; scanning from $\Theta = 2–18°$. To avoid the influence of relative humidity on relative crystallinity, starch samples were placed in a desiccator and conditioned in the atmosphere of relative humidity of 92% for 48 h. The desiccator was filled with a sodium carbonate saturated water solution.

2.5. IR spectroscopy

The FT-IR measurements were performed in solid state with a FT-IR Bruker IFS 113v spectrometer, under the following conditions: KBr pellet (200 mg/1.5 mg), resolution 2 cm^{-1}.

2.6. Microscopic examination

The starch samples were prepared for light microscopy examination using the smear method. The 8% starch suspensions were heated at 90 °C for 15 min. A drop of the paste was placed on a microscope slide and, on cooling, the smear was stained with iodine (I_2 in KI) and studied using an Olympus BX60 light microscope.

The starch samples analyzed by scanning electron microscopy (SEM) were prepared according to Fornal (1985) and studied using a Jeol JSM 5200 microscope at 5 keV.

2.7. Differential scanning calorimetry

The thermal transitions of starch samples were investigated with the use of a heat-flux Metler Toledo STAR® DSC-30 apparatus, calibrated by using a high purity indium standard. A starch sample (about 10 mg) was weighed in a high temperature Nimonic steel 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 25 °C, and heated from 25 to 220 °C at a rate of 3 °C/min. The characteristic temperatures of the transitions were onset

Table 1
Minor constituent content of native starches and experimental preparations

Starch preparation	Protein content (%)	Fat content (%)	Ash content (%)	Resistant starch content acc. to Akerberg et al. (%)	Resistant starch content acc. to Champ et al. (%)
Potato native	0.09	0.06	0.22	–	–
Potato amorphous	0.08	0.06	0.26	–	–
Potato modified	0.07	0.07	0.23	12.46	12.30
Tapioca native	0.08	0.05	0.16	–	–
Tapioca amorphous	0.07	0.05	0.25	–	–
Tapioca modified	0.06	0.06	0.15	16.26	10.63
Corn native	0.28	0.55	0.12	–	–
Corn amorphous	0.28	0.57	0.34	–	–
Corn modified	0.26	0.56	0.25	12.29	8.80
Wheat native	0.41	0.32	0.29	–	–
Wheat amorphous	0.40	0.34	0.33	–	–
Wheat modified	0.36	0.34	0.30	16.50	10.67

gelatinisation temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c). Enthalpy of gelatinisation was related to the dry mass of the sample.

3. Results and discussion

Low values for ash, lipid and protein content (Table 1), lower than those reported as typical of the native starches (Swinkels, 1985; Thomas & Atwell, 1997), indicated that the raw materials investigated were of high purity. The chemical composition of pregelatinised starch samples remained almost unchanged compared with the native starches. Also, the procedure of physical modification applied in the experiment did not change the chemical composition of the investigated starches, except the protein content, which insignificantly decreased.

SEM showed that the products obtained consisted of irregularly ripped and fragmentarily corrugated particles, which were formed as a result of the modification process (Fig. 1). The final shape and size of the modified starch particles was dependent on both the syneresis that

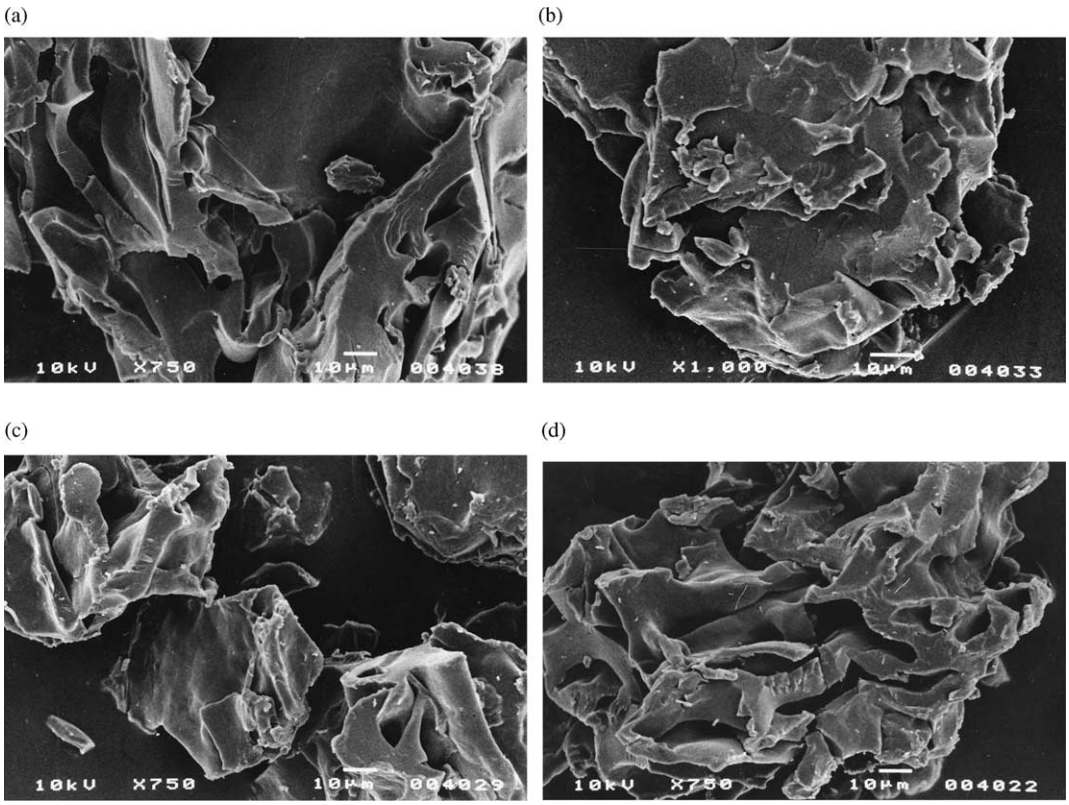

Fig. 1. Scanning electron microphotographs of physically modified starches: (a) potato, (b) tapioca, (c) corn, and (d) wheat.

Table 2
Thermal properties of native and modified starches determined by differential scanning calorimetry

Starch sample	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	Range (°C)
Native potato	58.5	64.1	72.2	15.0	13.7
Modified potato	44.7	55.3	71.5	9.5	26.8
Native tapioca	64.1	68.6	78.8	12.5	14.7
Modified tapioca	39.8	49.6	60.2	7.6	20.4
Native corn	64.2	69.7	76.4	11.0	12.2
Modified corn	43.8	50.2	61.7	9.5	18.9
Native wheat	56.1	61.0	66.6	9.2	10.5
Modified wheat	38.3	47.6	56.9	5.6	18.6

led to the isolation of starch from water solution, and the grinding method applied to the dry product. The SEM images of all the preparations did not show any significant differences in their structure related to the botanical origin of the starch. All the physically modified starches had a structure similar to the pregelatinised or extruded starch (Owsu-Ansah, van de Voort, & Stanley, 1983; Senouci & Smith, 1986; Śmietana, Szpendowski, Soral-Śmietana, & Świgoń, 1996). In spite of this, the physically modified starches did not solubilise in cold water. However, the modified starches started to solubilise in water at a lower temperature compared with the native starches (Table 2; Figs. 2–5). The modified potato- and tapioca starch, revealed a high type of swelling characteristics, similar to the native starch, but the viscosity of their cold solutions was significantly lower compared with the cold solution of the native starches (Figs. 2 and 3). The modified corn- and wheat starch maintained the medium type of swelling characteristics, and revealed a similar viscosity in cold solutions compared with the native starches (Figs. 4 and 5).

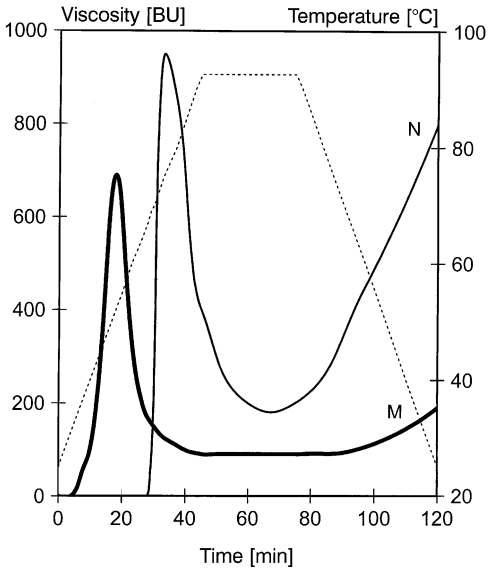

Fig. 3. Brabender viscosity curves for 8% solutions of tapioca starch: N, native; M, modified.

The differences in solubilisation of the modified starches were clearly visible on light microscopy images (Fig. 6). It is known that the amylose leakage from the starch granules is the initial phase of gelatinisation of the native starches and that the potato and tapioca starches are almost completely soluble at the 90 °C (Lewandowicz et al., 1997, 2000). The LM images of the investigated modified starches were different from those of their native counterparts. The solubilisation of potato starch was not complete and its paste consisted of different co-existing fractions of starch, i.e. retrograded amylose and solubilised amylopectin, which, on association, formed irregular particles of a colloidal system containing dispersed swelled but not solubilised starch granules (Fig. 6a). This observation

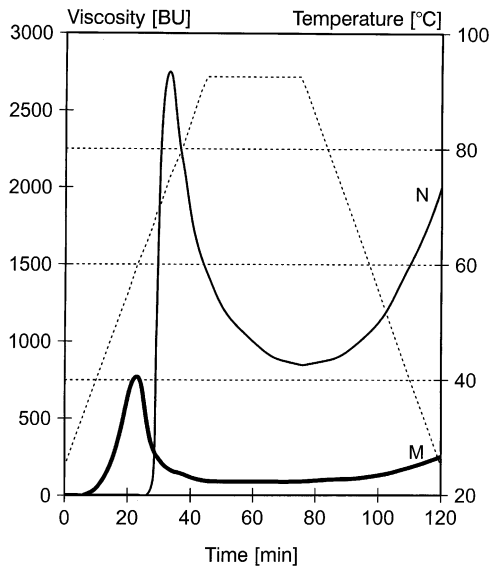

Fig. 2. Brabender viscosity curves for 8% solutions of potato starch: N, native; M, modified.

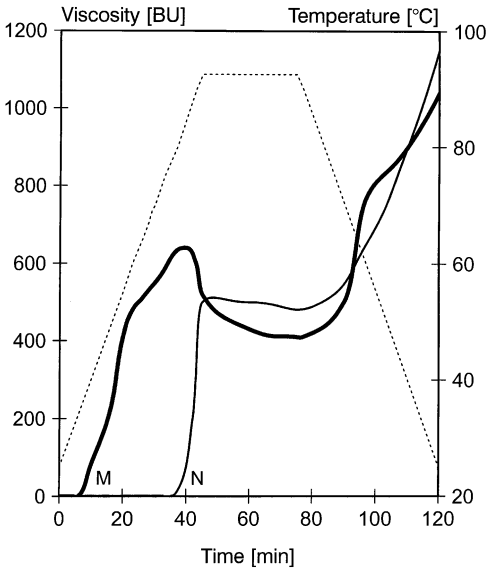

Fig. 4. Brabender viscosity curves for 8% solutions of corn starch: N, native; M, modified.

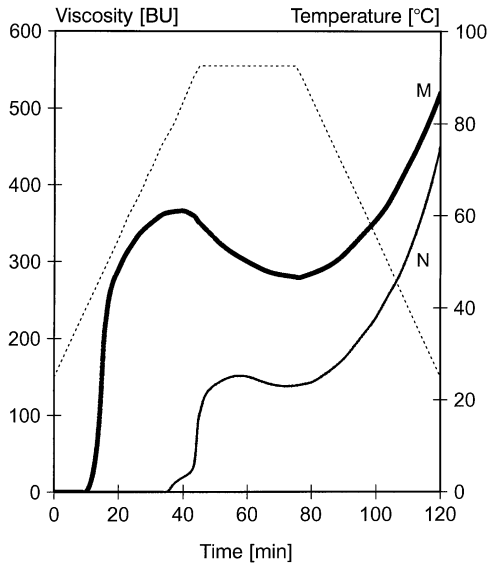

Fig. 5. Brabender viscosity curves for 8% solutions of wheat starch: N, native; M, modified.

proved that the physical modification process by iterated syneresis affected the solubility of the potato starch. As evidenced by LM microscopy, the extent of structural changes in the tapioca starch was lower compared with the potato starch. The modified tapioca starch solubilised well at 90 °C and the solubilised material consisted mainly of amylopectin with small drops of partially retrograded amylose dispersed in it (Fig. 6b). The native corn and wheat starch suspensions heated at 90 °C reveal an advanced solubilisation process: the starch granules are considerably swollen, and an extensive amylose and amylopectin leakage is observed (Lewandowicz et al., 2000). Both cereal starches modified physically (corn and wheat) solubilised in water with difficulty (Fig. 6c and d). The starch material consisted of highly swollen starch granules that co-existed with solubilised amylopectin and retrograded amylose.

Pasting properties and light microscopy studies pointed that the process of modification changed the starch–water interaction, probably due to different structural organization of starch particles. X-ray diffraction studies proved that the modified starches showed significant crystallinity (Figs. 7–10). The most vital information coming from the X-ray investigations seemed to be that all the modified starches had a B-type X-ray diffraction pattern independently of the botanical origin of the native starches and consequently crystal structure.

The changes in the crystal structure proved by the X-ray diffraction studies could be compared with infrared spectroscopy (IR) results. The region of the 1400–800 cm^{-1} is known to be sensitive to the conformation of polysaccharides in an aqueous solution as well as

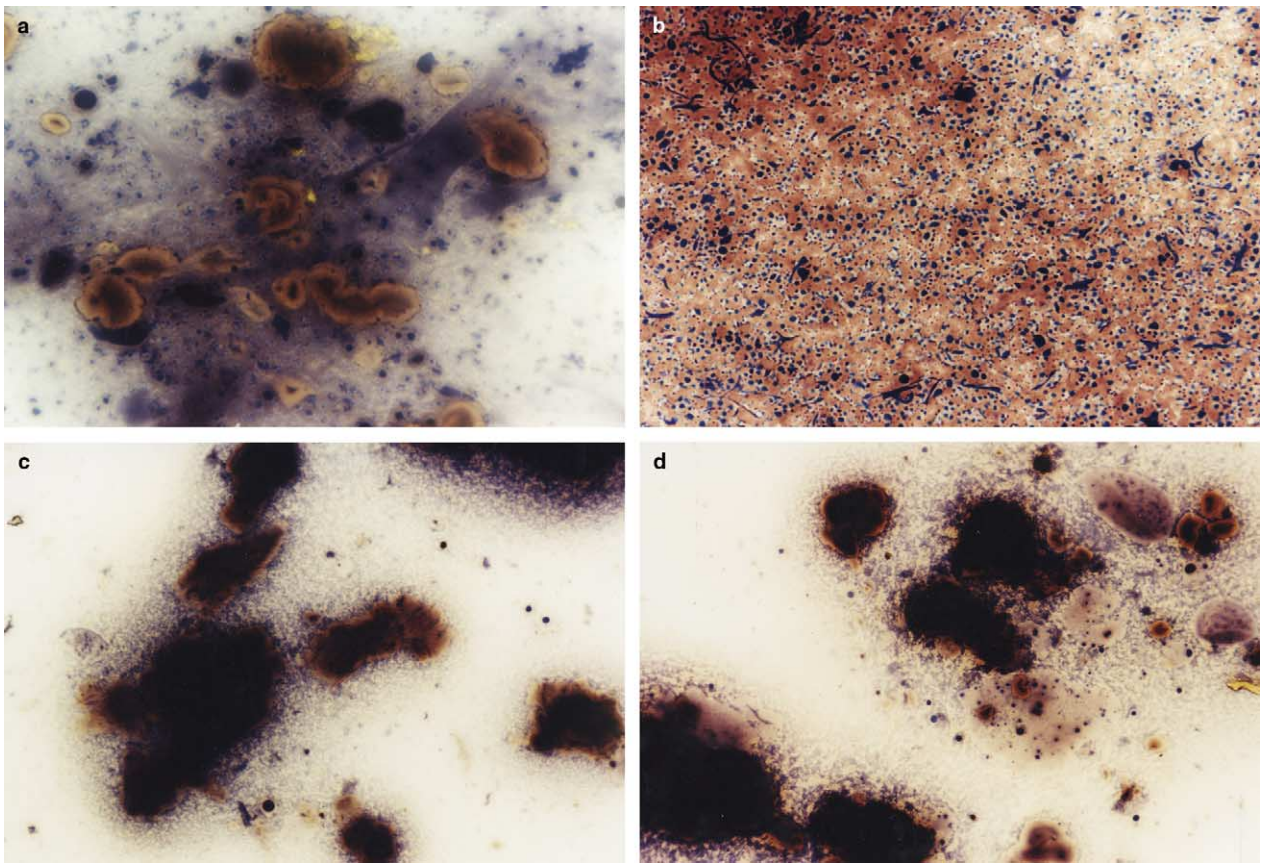

Fig. 6. Light microphotographs of physically modified starches: (a) potato, (b) tapioca, (c) corn, and (d) wheat.

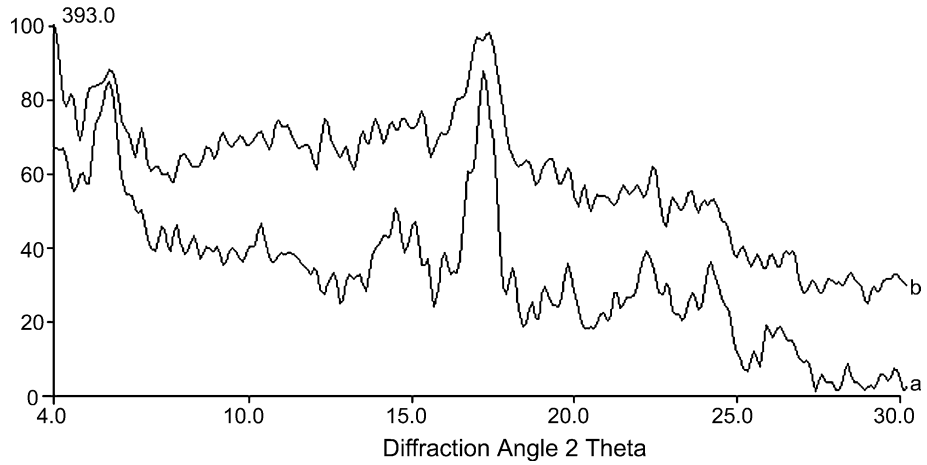

Fig. 7. X-ray diffraction patterns of potato starch: (a) native and (b) modified.

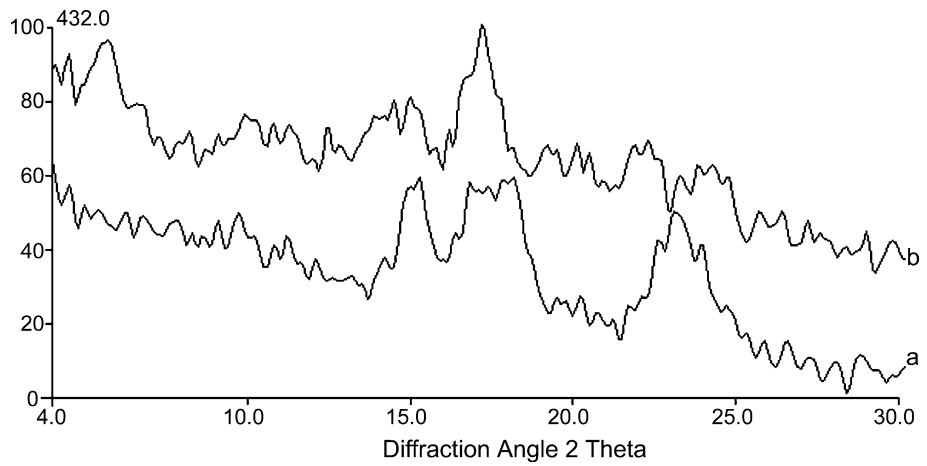

Fig. 8. X-ray diffraction patterns of tapioca starch: (a) native and (b) modified.

to the changes in the crystal structure of starch (Rindlav, Hulleman, & Gatenholm, 1997). However, most bands arise from highly coupled C–O and C–C vibrations and a precise assignment is difficult (Wilson & Belton, 1988). The most remarkable bands are 1019 and 1016 cm^{-1} that rise during the retrogradation of waxy corn and wheat starches (Wilson, Kalichevsky, Ring, & Belton, 1987). In case of native potato starch the bands located at 1047, 1018, and 994 cm^{-1} are reported as the most characteristic in this region by van Soest, de Wit, and Tourois (1994). According to

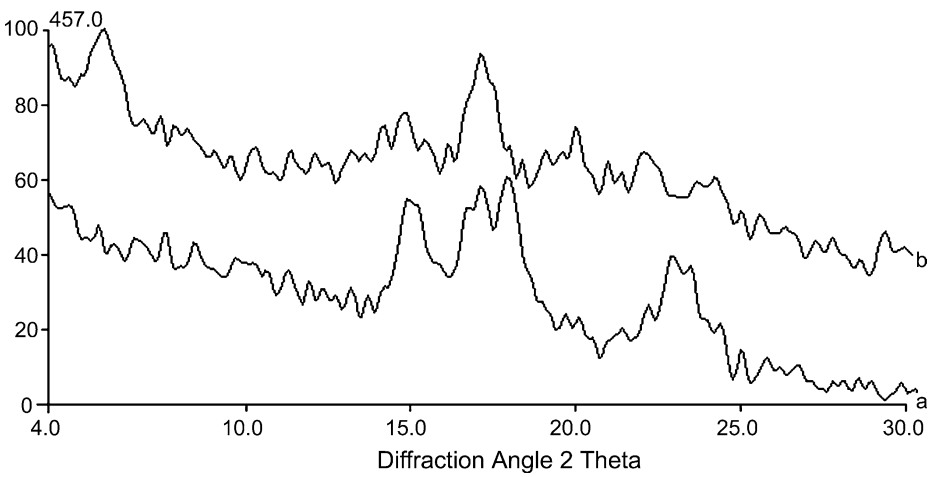

Fig. 9. X-ray diffraction patterns of corn starch: (a) native and (b) modified.

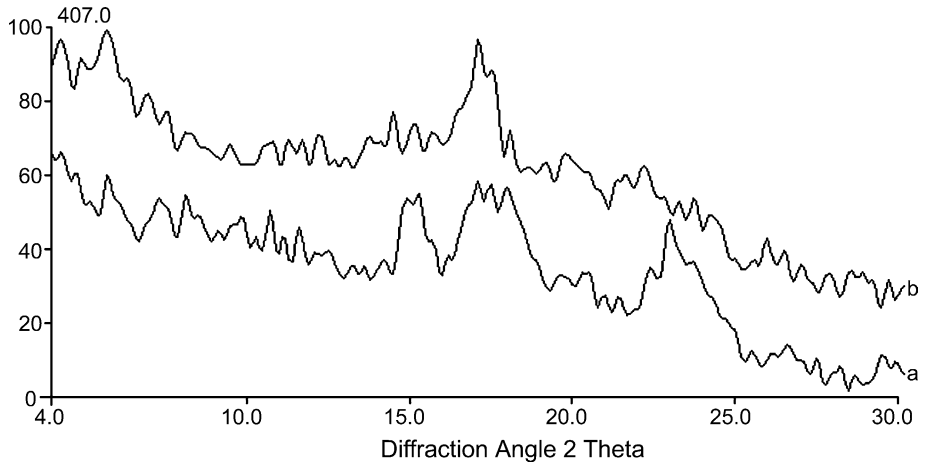

Fig. 10. X-ray diffraction patterns of wheat starch: (a) native and (b) modified.

these authors, the gelatinised starch shows an intense broad band at 1022 cm^{-1}, and three bands at 1053, 1022, and 1000 cm^{-1} after retrogradation. Our results (Figs. 11–14) confirmed the observation that the region of 1400–800 cm^{-1} is sensitive to the changes in the crystal structure of starch. IR spectroscopy, however, seemed to be less powerful tool in crystal structure investigation compared with X-ray diffractometry. In the IR spectrum of native potato starch (which had a B-type of X-ray diffraction pattern), the bands at 981, 1019, and 1046 cm^{-1} could be observed (Fig. 11). We noted that in the amorphous product obtained from this starch after gelatinisation and drum drying, the band at 981 cm^{-1} disappeared and the band at 994 cm^{-1} could be observed (Fig. 11). This change was also evident in the spectrum of the potato starch modified physically via iterated syneresis, which had a B-type of X-ray diffraction pattern similar that of the native starch (Fig. 11). Because of these observations no simple correlation between the presence of specific bands in the IR spectra and the type of X-ray diffraction pattern could be made. Moreover, significant differences in the IR spectra of the native starches (band at 994 cm^{-1} reported by van Soest et al. (1994) and band at 981 cm^{-1} observed in our investigation) suggest that some biological implications connected with the plant variety were the reason for the differences in IR spectra of the starches. Changes similar to those observed for the potato starch also affected the tapioca and corn starches (Figs. 12 and 13). In the IR spectra of the native tapioca starch (which had a C-type of X-ray diffraction pattern) and native corn starch (which had an A-type of X-ray diffraction pattern) the bands 986, 1019, and 1046 cm^{-1} could be observed (Figs. 12 and 13). In the amorphous starch or the iterated syneresis-modified starch (which had a B-type of X-ray diffraction pattern) the band at 986 cm^{-1} disappeared and the band at 994 cm^{-1} was present (Figs. 12 and 13). The relative intensity of the bands at 1019 and 1046 cm^{-1} changed with the crystal structure of the starch samples. The wheat starch (Fig. 14) showed deeper changes in the IR spectrum than the other investigated starches. The 1400–400 cm^{-1} region was found to be sensitive to the structure changes of the wheat starch, whereas in the case of the other starches the region was 1400–800 cm^{-1}. Some bands of the native wheat starch, i.e. 1154, 1078, 1046, 1019, 991, 859, and 570 cm^{-1}

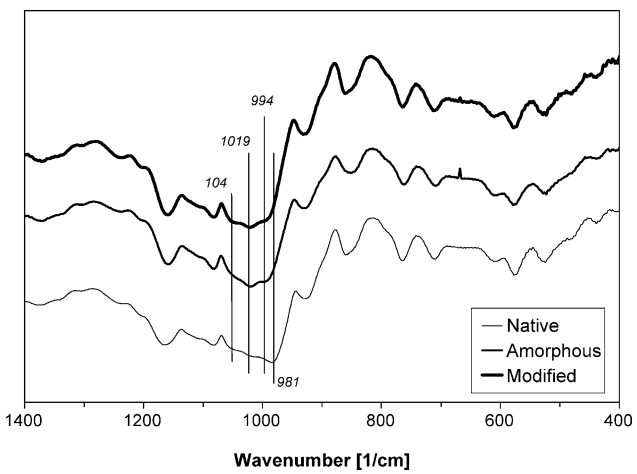

Fig. 11. Infrared spectra of potato starch.

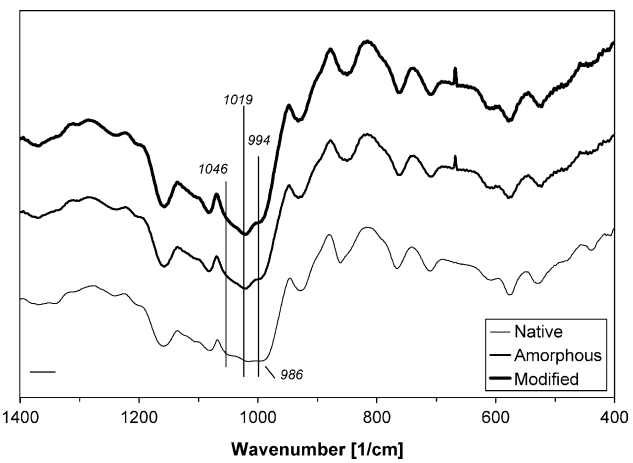

Fig. 12. Infrared spectra of tapioca starch.

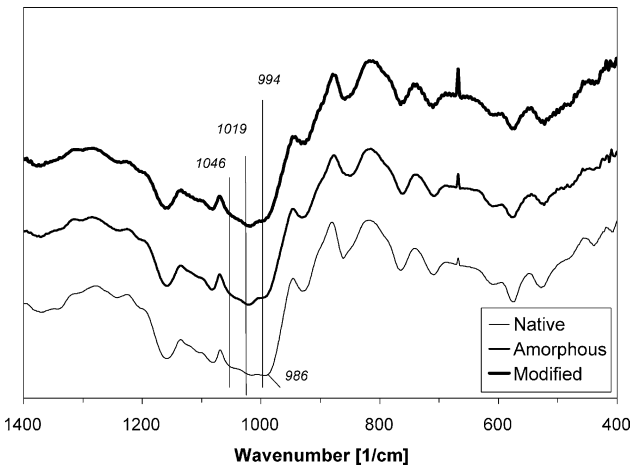

Fig. 13. Infrared spectra of corn starch.

were significantly less intense in the spectra of the amorphous or iterated syneresis-modified starches. On the other hand, the relative intensity of the bands: 762 and 446 cm^{-1} rose. Such deep changes for wheat, not observed by other research groups, could probably resulted from the biological diversification within the wheat species. These changes to some extent could be connected with relatively high level of minor constituents, especially the protein, content in wheat starch compared with other starch species (Table 1). Proteins could interact with carbohydrates and water, changing the conformation of starch in solution and in the solid state.

The X-ray and IR results suggest that a predominant mechanism of the process applied to physical modification was starch retrogradation, what is important from the technological point of view, because of the possibility of RS formation (Escarpa, Gonzales, Manas, Garcia-Diz, & Saura-Calixto, 1996; Russel, Berry, & Greenwell, 1989). The type of crystallites forming the RS fraction depends on the retrogradation conditions and the botanical origin of raw material. RS consisting mainly of retrograded amylose

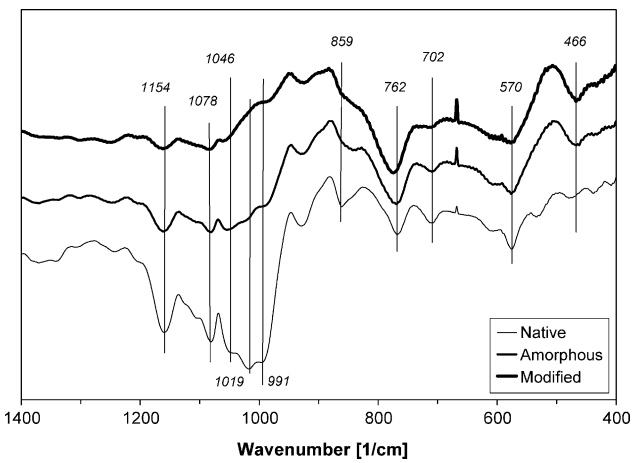

Fig. 14. Infrared spectra of wheat starch.

shows a B-type of the crystal structure and is formed at a temperature of 0–68 °C (Berry, I'Anson, Miles, Morris, & Russel, 1988; Czuchajowska, Sievert, & Pomeranz, 1991; Eerlingen, Crombez, & Delcour, 1993; Eerlingen, Deceunick, & Delcour, 1993; Gidley, Cooke, Darke, Hoffman, Russell, & Greenwell, 1995; Russel et al., 1989; Sievert, Czuchajowska, & Pomeranz, 1991; Siljeström, Eliasson, & Björck, 1989). A crystalline fraction in this type of RS has the melting endotherm peak of about 150–155 °C (Czuchajowska et al., 1991; Gruchala & Pomeranz, 1993; Sievert & Pomeranz, 1989, 1990). Crystallization at 100 °C gives the RS fraction that shows an A-type of X-ray diffraction pattern (Eerlingen et al., 1993a). Retrogradation of amylopectin, which needs even several days or weeks to be completed, gives a product with the melting endotherm peak at a low temperature of about 60 °C (Eerlingen, Jacobs, & Delcour, 1994). Gelatinisation properties of the native and iterated syneresis-modified starches are summarized in Table 2, which shows the values for differential scanning calorimetry (DSC) measurements. Single endothermic transitions were observed for all the samples. The melting endotherms of the modified starches were observed in the temperature range from 47.6 °C for wheat starch to 55.3 °C for potato starch. These temperatures were significantly lower compared to the characteristic melting endotherms of amylose and even of amylopectin (Czuchajowska et al., 1991; Eerlingen et al., 1994; Gruchala & Pomeranz, 1993; Sievert & Pomeranz, 1989, 1990). On the other hand, melting endotherms of the starches retrograded after storage at 4 °C for 7 days have been observed in the temperature range from 47.7 °C for wheat starch to 55.7 °C for potato starch, and are generally compatible with our results (Jane et al., 1999). The total gelatinisation enthalpy change of our physically modified starches varied from 5.6 J/g for wheat starch to 9.5 J/g for corn and potato starches, whereas the quoted values for retrograded starches are considerably lower, i.e. between 3.7 J/g for wheat starch and 7.5 J/g for potato starch (Jane et al., 1999). This observation indicates that retrogradation was a decisive process during repeated syneresis. The LM image (Fig. 6), showing amylopectin and retrograded amylose as the main leaching material, proved that amylose was the main starch fraction that underwent retrogradation. The differences between the values for enthalpy change probably resulted from a longer time of processing in our experiment. It should also be pointed out that the range values for gelatinisation of our physically modified starches varied from 18.6 °C for wheat starch to 26.8 °C for potato starch and were significantly higher compared with the native starches, for which they varied from 10.5 °C for wheat starch to 14.4 °C for tapioca starch (Table 2). A wider range of gelatinisation of modified starches indicated a less-arranged structure of modified starch particles compared with the native starch granules.

The examined preparations of modified starches contained certain amounts of the RS, a fraction not hydrolyzed by the pancreas alpha-amylase (Table 1). However, the real

amount of the RS is still a matter of discussion. The RS is defined in biological terms (Asp, 1992) and occurs as a combination of a pure RS fraction and a potentially digestible RS fraction. Indeed the RS collected in vivo in humans is composed of oligosaccharides (including glucose), high molecular weight alpha-glucans (starch granules) and a crystalline fraction, the size of which depends on the origin and treatment of starch (Champ, Kozlowski, & Lecannu, 2001). Consequently, the recommended and applied in vitro methods for RS content determination can give different results. The RS content of our modified starches determined according to Akerberg et al. (1998) was higher compared to the values obtained by Champ et al. (1999) method. A good conformity of values for the RS content was observed only in the case of the potato starch (Table 1). The procedure developed by Akerberg et al. (1998) mimics the physiological condition and involves chewing. The numbers obtained by this method may be higher because of the inclusion of non-digestible polysaccharides, which probably are high molecular weight dextrins, in higher amounts. The method proposed by Champ et al. (1999) raises the question about a possible 'overdigestion' of some resistant structures by alpha-amylase-amyloglucosidase cocktail, as was later commented (Champ et al., 2001). In fact, the RS is a special, non-nutritive fraction of dietary starch with health-promoting properties, which can be partly digested, but after a relatively long-time. The RS is digested 3–6 h, but a very low amount the RS is digested between 6 and 24 h, which makes it a good substrate for colonic bacterial fermentation, during its metabolisation to short chain fatty acids (Soral-Śmietana, 2000; Soral-Śmietana, Wronkowska, & Amarowicz, 2001). A simple correlation between the RS content of our physically modified starches and their thermal properties was not observed (Tables 1 and 2). The highest values for the total gelatinisation enthalpy change observed for the potato and corn starches were accompanied by the lowest RS content determined by Akerberg et al. (1998) method. The modified tapioca and wheat starches had almost the same values of the RS content (about 10% by Champ et al. (1999) method and of about 16% by Akerberg et al. (1998) method), but differed in the thermal properties. This would suggest on that the formation of non-digested starch fraction is more complicated than simple starch crystallization. The lower values for the RS content of the corn starch compared to the wheat starch could have resulted from a higher amount of fat in the former (Table 1). The formation of starch–lipid complexes has been suggested to be a competitive process to the RS formation (Czuchajowska et al., 1991). Moreover, the way the corn and wheat native starches are attacked by pancreas alpha-amylase is different: corn starch is hydrolyzed more easily by this enzyme (Soral-Śmietana, Wronkowska, & Świgoń, 2001). These results confirm that the formation of RS (which is a biological phenomenon) is difficult to describe in physicochemical terms. The physically modified starches containing certain amounts of the RS fraction had a B-type X-ray diffraction pattern, similarly like retrograded starch, but their melting endotherms had a relatively low temperature.

4. Conclusions

The process of iterated syneresis applied to the modification of potato, tapioca, corn and wheat starches resulted in a new type of physically modified starches that contained the RS fraction of unique physicochemical properties. The starch preparations obtained by iterated syneresis consisted of irregular ripped and fragmentarily corrugated particles significantly different from the native starches in the solubilisation/gelatinisation mechanism and their pasting properties. The modified starches contained similar amounts of minor constituents (protein, lipid, ash), gelatinised at a lower temperature than the native starches and had a B-type X-ray diffraction pattern, independently of the starch origin. The starch crystallites of the modified starches melted at temperatures corresponding to those for retrograded starches, but the enthalpy change was evidenced to be higher. IR spectra confirmed the changes in the starch–water interaction and, consequently, in the starch structure as a result of the modification procedure applied. The relationship between the starch structure and starch digestibility, and the development of proper methodology for the determination of the RS content still remains question for discussion.

Acknowledgements

This research was supported by grant no. PBZ-KBN/020/P06/1999/03 from the State Committee for Scientific Research (KBN).

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