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Investigation on the Structure and Properties of Modified Products from the Grain-Mill Industry for Use in the Preparation of Biopolymer Technical Materials

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Abstract
In the new century, the possible use of raw materials, half-products and materials derived from renewable resources is attracting growing attention. Green technologies come into play to exploit natural raw materials, including biopolymers such as cellulose, lignin chitin and chitosan, and starch. The company Lubella Sp. z o. o. S.K. (Lublin, Poland) is a manufacturer of innovative flour products of the Q-Farin series, which find use as starting materials in the preparation of new biodegradable and multifunctional biomaterials for packaging materials and paper processing. The preparation of innovative technology concepts opens ways toward the competitiveness and development of companies operating in the advanced sector of biodegradable packaging with the use of territorial renewable raw materials.

Key words: *grain-mill industry, functional biopolymers, bio-packaging thermoplastic bioresins, bio-glues.*

Introduction

Together with the strategy of consistent development aimed at slowing down the depletion of raw material resources and the irreversible changes in the natural environment, two model concepts have emerged for the development of human civilization. The first model presents a closed cycle of manufacturing and consumption which exchanges only energy with the environment. All consumer goods in the system are made of materials which after their life cycle are reused in a secondary processing. The other model assumes all construction materials to be from renewable resources and degradable in nature. Thus in ever-lasting cycles, nature provides raw materials for manufacturing and energy carriers for their processing. It is also nature that solves the problem of the accumulating post-use waste [2].

The enormous consumption growth of resins causes an equally fast increasing stream of waste. Any material and product is finally turned into waste. The very high share of packaging in the consumption profile of resins makes the life cycle of their 40 % part last merely one month. The vast majority of polymeric waste fills depots. The proportion between their volume and mass is rather high, causing considerable demand to the depot space and, in consequence, involving a high cost of disposal.

All this has triggered intensive investigation in the search for materials that maintain the valuable, useful properties of conventional resins and have the ability of returning to a biological cycle after their use. Such demands can be fulfilled by biodegradable polymers, which undergo processing to biomass in waste lagoons in a reasonable time [3].

Nowadays the sector of biodegradable resins belongs to the most innovative and dynamic industrial branches, offering solutions which in a long perspective would reduce the amount of waste delivered and accumulated. Ecology and the compulsion to find alternative resources for raw materials have been the most important factors influencing the sector in recent years [1].

The demands of environmental protection initiated in the mid - nineties of the XX century the implementation of innovative technologies for the manufacture of biodegradable resins based on renewable resources. The biodegradable polymers were, according to the association *European Bioplastics,* given the name bioresins [4].

Advances in research concerning the protection of the environment and the proceeding depletion of the world's crude oil resources have made scientists search for alternative streams of materials.

One of the research areas developed are works concerning the elaboration of technologies for the production of biodegradable polymers capable of replacing classical resins originating from crude oil and , at the same time, have similar useful and processing properties.

In comparison with the packaging of traditional resins, those made of biodegradable polymers present the advantage of

Table 1. Composition of flour and biopolymer raw materials Q-Farin C1000 and Q-Farin H501.

Raw material	Content of, %					
	moisture	starch	amylose in starch	protein	reduction sugars (DE)	fat
Wheat flour 500	5.42	65.1	42.0	13.8	0.59	1.30
Q-Farin H501	6.50	61.2	36.4	14.0	0.12	0.46
Wheat flour 1000	5.62	62.1	42.1	14.8	0.76	2.24
Q-Farin C1000	6.03	55.0	42.8	14.2	0.72	0.63

Table 2. *Solubility and water-binding capacity of the functional flours and Q-Farin C1000 & Q-Farin H501 raw materials.*

Raw material	Temperature, °C					
	20	60	80	20	60	80
	Solubility			Water-binding capacity (WBC)		
Wheat flour 500	5.94	10.7	15.4	1.11	1.94	5.91
Q- Farin H501	5.78	45.0	36.7	1.26	6.60	10.7
Wheat flour 1000	7.40	12.1	23.1	1.10	2.04	7.91
Q-Farin C1000	24.8	27.0	60.5	9.00	9.93	8.94

their post-use collection together with organic waste and of their composting in industrial waste-treatment plants [5, 6].

The aim of the work presented was the examination of starch-protein raw materials obtained from the milling of purified ordinary wheat (*Triticum aestivum L.*) and corn grain (*Zea mays*) subjected to an initial hydrothermal treatment with the view of their use in the preparation of biopolymer materials applicable in the preparation of biodegradable, multifunctional packaging materials, plasticized bioresins and environment-friendly glues for the production of corrugated paperboard.

The work encompasses a cycle of investigation on the characteristics of starch-protein raw materials and process of their chemical and biochemical modification on a laboratory scale. The work is aimed at the use of the materials prepared in injection moulding and extrusion.

From amongst the available methods of starch modification the following were selected for the research:

Table 3. *pH of aqeous solutions of flours and raw materials of the Q-Farin H501 and Q-Farin C1000 types.*

Raw material	pH
Wheat flour 500	6.49
Q-Farin H501	5.98
Wheat flour 1000	6.48
Q-Farin C1000	6.77

1. Esterification with acetic anhydride to starch acetate [7].
2. Oxidizing of the hydroxyl groups of starch to carboxylic- and/or aldehyde groups by hydrogen peroxide in the presence of cuprum sulfate (II) ($CuSO_4 \cdot 5H_2O$), according to the method by Zhang Y.R. *et al.* [8 - 10].
3. Esterification with fatty acids in the presence of the biocatalyst lipase [11, 12].

Examination of the structure and properties of starch-protein raw materials applied in chemical and biochemical modification processes

Materials

The starch-protein raw materials called Q-Farin (producer by Lubella Ltd., Lublin, Poland) presents a series of functional flours made from hydrothermally treated milled purified wheat grain. Depending upon the profile, processing degree and parameters applied, various biochemical transformations proceed, like the denaturation of proteins, dextrinization and saccharification, the hydrolysis of fats and the inactivation of amylolytic-, proteolytic-, and lipolytic enzymes. Functional flours made of first-class selected grain are submitted to a cycle of physical changes at elevated temperature and moisture.

Products of the Q-Farin series differ in physical-chemical properties like moisture, bulk density, viscosity, the ability to and degree of gelling, water absorption and granulation. The main representatives of the series are Q-Farin C (cold) and Q-Farin H (hot).

Q-Farin C

It undergoes cold gelatinization, producing consistent gels absorbing water in a proportion of up to 1.9. Selected parameters of the technology process yield an entirely instantinized product well assimilated by the human organism; hence it can be added to food products without any further thermal treatment [13].

Q-Farin H

Gelatinizes when hot; effectively thickens and stabilizes products which are additionally processed at high temperature (pasteurization, baking, cooking) [13].

The following grades of the Q-Farin family were used in the first step of R&D works:

- Q-Farin H 501 – of wheat flour (type 500), hot-gelatinizing; and
- Q-Farin 1000 of wheat flour (type 1000), cold-gelatinizing.

Methods

Characteristics of selected functional flours and starch-protein raw materials

The initial materials (functional flours and hydrothermally modified Q Farin's) were analyzed in respect of the following: the content of reductive sugars and estimation of glucose equivalent (DE) by the Schoorle-Regenbogen method [14], the content of starch by the polarimetric method using a Lippich triple-field polarizer [15], the content of amylose in starch by the Mahmood *et alii* [16] method, solubility in water and water-binding capacity acc. to Richter *et alii* [17], the content of protein by the Kjeldahla method [18], and the content of fats by the Soxhlet method. [19].

Characteristics of the initial flours and raw materials of the Q-Farin type are shown in ***Table 1***

Estimation of solubility in water and water-binding capacity of starch-protein raw materials

Testing of the solubility in water and water-binding capacity of Q-Farin C1000 and Q-Farin H501 raw materials was accomplished at 20, 60 and 80 °C according to Richter *et alii.* Results are presented in ***Table 2***.

Estimation of pH of aqueous solutions of starch-protein raw

The reaction pH was measured in 1% aqueous solutions of the preparations Q-Farin C1000 and Q-Farin H501 by means of a pH-meter - Lab 860 by Schott Instruments (Germany) equipped with a combined electrode - BlueLine 14pH. ***Table 3*** shows the pH measurements for all biomaterials examined.

Content of heavy metals in the starch-protein raw materials

The contents of heavy metals: Cd, Cr (total of all oxidation states), Pb, Hg and Zn were estimated in accordance with procedures implemented at the accredited Laboratory of Paper Quality at IBWCh by the method of Atomic Absorption Spectrometry (AAS) with the use of ContrAA 700 apparatus by Analytik Jena AG (Germany). The raw materials were mineralized the following way: samples of ca. 1g were put into a Teflon cell, 5 ml of 70% HNO_3 added, and the content was mineralized in a microwave oven - MDS 2000 by CEM Co at the following conditions:

- max. power of oven: 600 W
- max. pressure: 0.83 MPa
- mineralization time: 1 hour.

The mineralized samples were quantitatively transferred to a 50 ml measuring flask and analyzed by the spectrometric method.

Cd, Cr i Pb contents were AAS- estimated with electro-thermic atomization in a graphite oven. The main parameters of the estimation are shown in ***Table 4***.

The content of Hg was estimated by AAS with the generation of cold vapours.The main parameters of the estimation are shown in ***Table 5***.

The Content of As was AAS - estimated with electro-thermic atomisation in a graphite oven with the use of SCAN-1 apparatus by the Thermo Jarrell Ash Corporation (USA). The main parameters of the estimation are shown in ***Table 5***.

The raw materials were mineralised the following way: samples of ca. 0.5 g were put into a Teflon cell, 10 ml of 70% HNO_3 added, and the content was mineralized in a microwave oven - MDS 2000 by CEM Co.

Main parameters of the estimation are shown in ***Table 6.***

Table 4. *Parameters of the measurements of heavy metal contents in samples of Q-Farin C1000 and Q-Farin H501.*

Element	Wavelength, nm	Temperature of pyrolysis, °C	Temperature of atomization, °C	Modifier of matrix
Cd	228.8	600	1200	0.1% $NH_4H_2PO_4$
Cr	357.8	1300	2300	0.1% $Mg(NO_3)_2$
Pb	283.3	800	1500	0.1% $NH_4H_2PO_4$

Table 5. *Parameters of the measurements of Hg content in samples of Q-Farin C1000 and Q-Farin H501.*

Wave length, nm	Flame	Ionizing buffer 217
217.5	Acetylene/air	0.1% KCl

Table 6. *Parameters of the measurements of As content in samples of Q-Farin C1000 and Q-Farin H501.*

Element	Wave length, nm	Temperatur of pyrolysis, °C	Temperature of atomization, °C	Modifier of matrix
As	193.7	1100	2350	100 ppm $Pd(NO_3)_2$ + 200 ppm $Mg(NO_3)_2$

Table 7. *Contents of heavy metals in samples of starch-protein raw materials.*

Content of metals, mg/kg	Test results			
	Wheat flour 500	Q-Farin H501	Wheat flour 1000	Q-Farin C1000
Cd	0.065	0.062	0.069	0.091
Pb	<0.15	0.20	<0.15	< 0.15
Cr	0.230	0.20	0.29	0.29
As	<0.15	< 0.15	<0.15	< 0.15
Hg	<0.06	< 0.06	<0.06	< 0.06

Table 8. *Thermal analysis of raw materials Q-Farin C1000 and Q-Farin H501.*

Raw material	TG		DTG	DSC	
	t_i, °C	Δm, %	t_p, °C	t_o, °C	t_p, °C
Wheat flour 1000	44.1 247.3	7.77 61.12	88.0 295.9	57.6	103.7 (endo)
Q-Farin C1000	41.8 239.5	8.28 70.70	64.2 113.8 299.7	58.9 293.6 432.2	124.5 (endo) 406.9 (egzo) 476.2 (egzo)
Wheat flour 500	40.8 238.3	9.49 57.72	107.3 299.0	58.8	117.1 (endo)
Q-Farin H501	45.8 240.2	7.85 71.90	61.1 94.0 286.0 462.0	31.8 275.8 435.8	116.7 (endo) 345.8 (egzo) 463.0 (egzo)

Results of the measurements of heavy metal contents in the samples examined are shown in ***Table 7***.

It can be seen from the results that the contents of heavy metals are close to each other in all samples tested.

Thermal analysis TG-DSC of the starch-protein raw materials

A TG-DSC examination was made for samples of the functional flours and initial raw material Q-Farin with the use of a simultaneous thermal analyzer - STA409 C by Netzsch (Selb, Germany), Samples were heated in air at a temperature in the range of 25 - 500 °C at a temperature rate of 5 °C/min (Jan Dlugosz University in Czestochowa, Poland). Results of the TG-DSC analysis are presented in ***Table 8***.

The simultaneous thermal analysis TG-DSC revealed that the milling of the grain itself had caused partial damage to the starch structure, evidenced by the absence of the characteristic endotherm on the DCS curve, which is defined as the "starch melting temperature" or temperature of the start of its intensive decomposition.

Wheat starch was characterised by a high thermal stability; its endotherm appeared

Table 9. Spectrophotometric FTIR analysis of Q-Farin C1000 and Q-Farin H501.

Raw material	Wavenumber, cm^{-1}				
Wheat flour 1000	3334	2927	1157	1082	1020
Q-Farin C1000	3363	2927	1156	1082	1022
Wheat flour 500	3363	2930	1157	1082	1020
Q-Farin H501	3300	2928	1157	1081	1018

on the DSC curve only at 287 °C. The decomposition of starch started at 253 °C, accompanied by a mass loss of several tens of percent. The milling process also lowered the start of starch decomposition to a temperature of about 238 °C. Further thermal processing caused an insignificant improvement in stability and slightly increased the temperature at which decomposition begins.

Infrared spectrophotometric FTIR examination of flours and starch-protein raw materials

FTIR spectra were recorded using a Nexus Nicolet Spectrophotometer (Madison, WIS, USA). The powdered samples were mixed separately with analytical grade KBr and then pressed into discs. Their spectra were recorded in the region of 4000 – 400 cm^{-1} at 32 scans per sample. Prior to the recording, the baseline was adjusted against a KBr background (Jan Dlugosz Univeristy in Czestochowa). ***Table 9*** presents results of the IR-spectroscopic examination for both of the initial raw materials tested..

FTIR spectra of the modified starch-protein raw material and the initial flour 1000 are presented in ***Figure 1.a***. ***Figures 1.b - 1.e*** show FTIR spectra of the modified products.

The FTIR spectra of starch and Q-Farin are almost identical, with the same intensity of the relevant bands in Q-Farins being higher than that of the remaining ones, which may be explained by the loosening of the starch grain structure and impaired hydrogen bonds. Bands responding to vibrations of the individual groups were in fact identically positioned.

Examination of structure change in the starch-protein raw materials after chemical and biochemical modification

The initial biopolymer raw materials prepared by the milling and hydrothermal treatment of wheat grains were first characterised in respect of their physical-chemical and structural properties. Based on the results of the examination, Q-Farin C1000 and Q-Farin H501, showing the best properties, were selected for further chemical and biochemical modifications.

The character of the initial starch-protein raw material is a limiting factor in the preparation of new-generation biomaterials designed for technical uses (packaging, environmentally friendly adhesives), which was the reason why conferring of properties upon the raw material adequate to its further use was one of the assumed goals of the work. It included improvement of the hydrophobic, mechanical and thermoplastic properties.

The most popular hydrothermal treatments which modify the physical-chemical properties of starch are (a) the *annealing* (ANN) of starch in excess of water (> 60% w/w) or in a medium amount of water (40 - 55% w/w) at a temperature above the glass transition and below that of gelatinization at a time of 0.5 to 144 h, and (b) *heat-moisture treatment* (HMT) – the annealing of the starch at a low content of moisture (18 - 30 wt%) at a temperature higher than the gelatinization temperature (mostly at 90 - 130 °C) from 1 to 16 h.

The hydrothermal modification of starch does not disturb the size and shape of the starch particles; it increases the gelatinization temperature by 4 - 8 °C, or even by 10 °C if a multi-stage modification is applied and if there is a limited range of temperature at which the process runs. The thermal modification causes a decrease in the solubility and swelling of the starch products, improves thermal stability, reduces retrogradation and often increases the content of resistant starch, thus leading to materials suitable for the preparation of biodegradable film.

In the scope of R&D works, Q-Farin C1000 was modified on a laboratory scale by way of three methods leading to varied chemical properties of the products prepared.

Esterification by acetic anhydride in the presence of acetic acid as activator

The starch-protein raw material was subjected to esterification by acetic anhydride added in the amount of 0.5 mol on 1 mol of AGU. The mix was agitated, and a CH_3COOH solution was slowly introduced in the amount of 2.0 mol/1 mol of AGU. The temperature of the reaction was then increased to 115 °C and maintained at that level for 8 hours. Thereafter the mix was quenched and washed with distilled water. The supernatant was decanted and the residue was put into a crystallizer and dried at ambient temperature. An initial qualitative assessment of the product prepared included organoleptic estimation of its physical shape, effective leaching of side products and the degree of substitution by acetyl groups (DS). As a result of the trial, a product was obtained with DS = 2.84.

Oxidation by hydrogen peroxide in the presence of Cu^{2+} ions as catalyst

The oxidation of starch contained in the starch-protein raw material proceeds in its hydroxyl groups, which are turned to aldehyde and/or carboxylic groups. H_2O_2 in the presence of Cu^{2+} ions was used as the oxidation agent. The reagents were agitated at ambient temperature and a solution of $CuSO_4$ was added. The suspension was heated to 50 °C and the solution of H_2O_2 was added drop by drop for 1 hour. After that time, the mix was agitated for 15 minutes at 50 °C. A certain amount of ethanol was added to the gelatinous mass obtained to precipitate the oxidized product. The supernatant was decanted and the residue was put into a crystallizer and dried at 50 °C.

Enzymatic modification in the presence of lipase

Enzymatic modification of Q-Farin C1000 was accomplished in the presence of lipase - *Thermomyces lanuginosus.* Oleic acid in the proportion 3:1 (mol proportion of the acid to anhyroglucose AGU groups) was used as the donour of acyl groups The reaction was conducted in a water bath at 60 °C for 4 h in DMSO medium or in a microwave reactor for 1 minute (6 × 10 s repeated with 1 min intervals) in a 210 W field without solvent. The substitution degree of Q-Farin C 1000 oleate achieved was: water bath-0.01, microwave reactor - 0.06.

Results

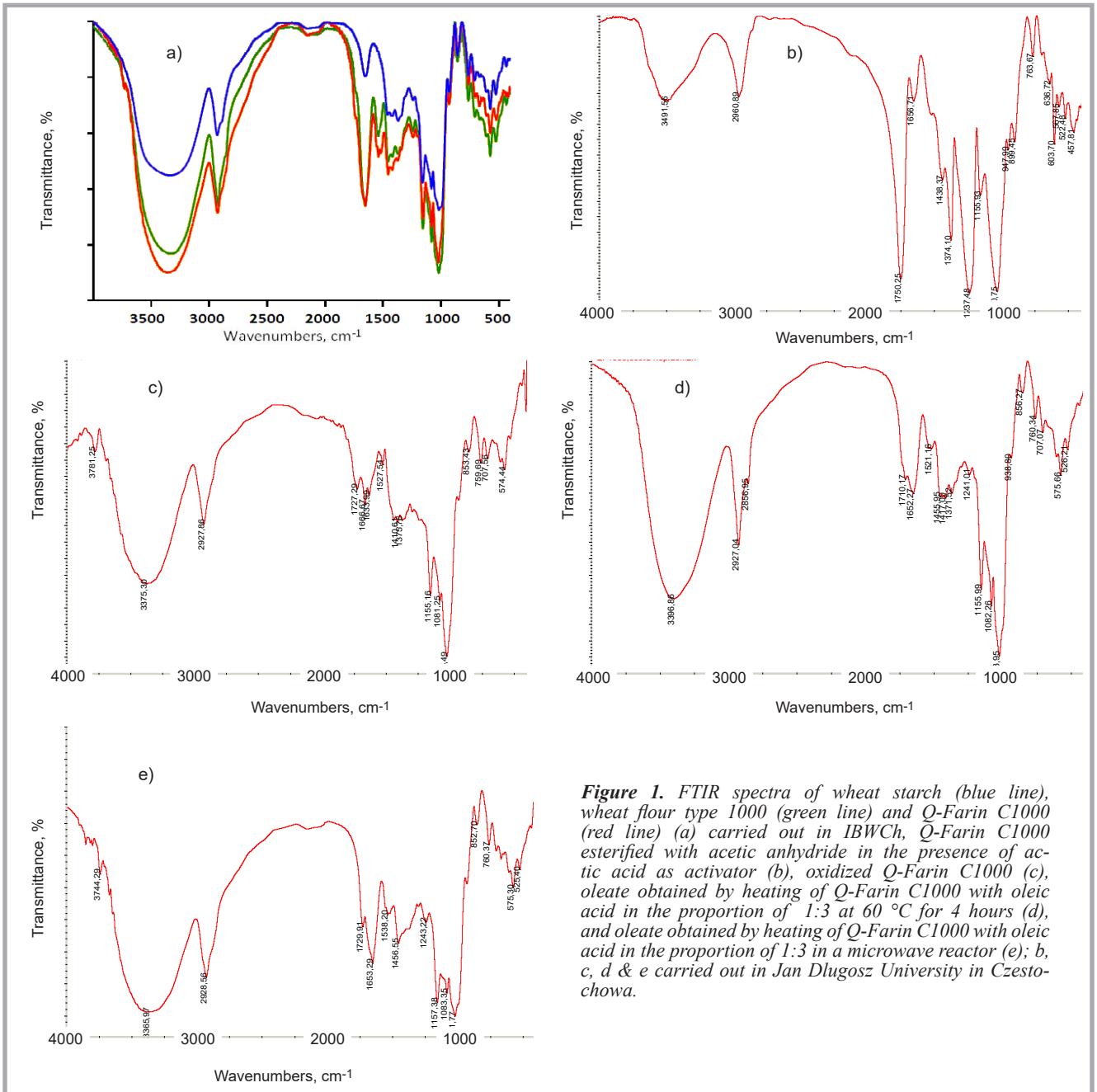

Figure 1. *FTIR spectra of wheat starch (blue line), wheat flour type 1000 (green line) and Q-Farin C1000 (red line) (a) carried out in IBWCh, Q-Farin C1000 esterified with acetic anhydride in the presence of actic acid as activator (b), oxidized Q-Farin C1000 (c), oleate obtained by heating of Q-Farin C1000 with oleic acid in the proportion of 1:3 at 60 °C for 4 hours (d), and oleate obtained by heating of Q-Farin C1000 with oleic acid in the proportion of 1:3 in a microwave reactor (e); b, c, d & e carried out in Jan Dlugosz University in Czestochowa.*

Examination by Fourier transform infrared spectroscopy (FTIR)

In the spectrum of Q-Farin C1000 esterified with acetic anhydride in the presence of acetic acid as an activator, bands were found which explicitly confirm the proceeding esterification reaction: 1237, 1374 and 1750 cm^{-1}. Very high intensity of the bands, particularly those which respond to the stretching oscillation of the C=O ester group, as well as a drastic decrease in the intensity of the bands which respond to the stretching oscillation of the hydroxyl groups unequivocally point to a very high degree of esterification (DS) of the polysaccharide chain with the acetic anhydride. It was confirmed by chemical estimation of the substitution degree DS = 2.84. The value indicates a close-to-complete esterification of the hydroxyl group with acetic radicals. The Q-Farin C1000 acetate prepared revealed strong hydrophobic properties, confirmed by the testing of solubility and water imbibition. In the spectrum of Q-Farin C1000 esterified with oleic acid in the DMSO medium, the presence of 1241, 1372 and 1710 cm^{-1} bands was observed, which confirm the proceeding of the esterification reaction. The intensity of the bands was low, indicating an insignificant degree of esterification. The observation was confirmed in the estimation of the substitution degree by potentiometric titration. The substitution degree of Q-Farin C1000 oleate prepared in a water bath amounted to barely 0.01.

In the FTIR spectrum of the esterification product made in a microwave oven, 1237 and 1374 cm^{-1} bands were also seen, evidencing the proceeding reaction. Their intensity was low, pointing to a low esterification degree. The chemically measured substitution degree of barely 0.06 confirmed the FTIR observation. The ^{1}H NMR examinations confirmed the possible use of the type of reactor in the process of enzymatic esterification.

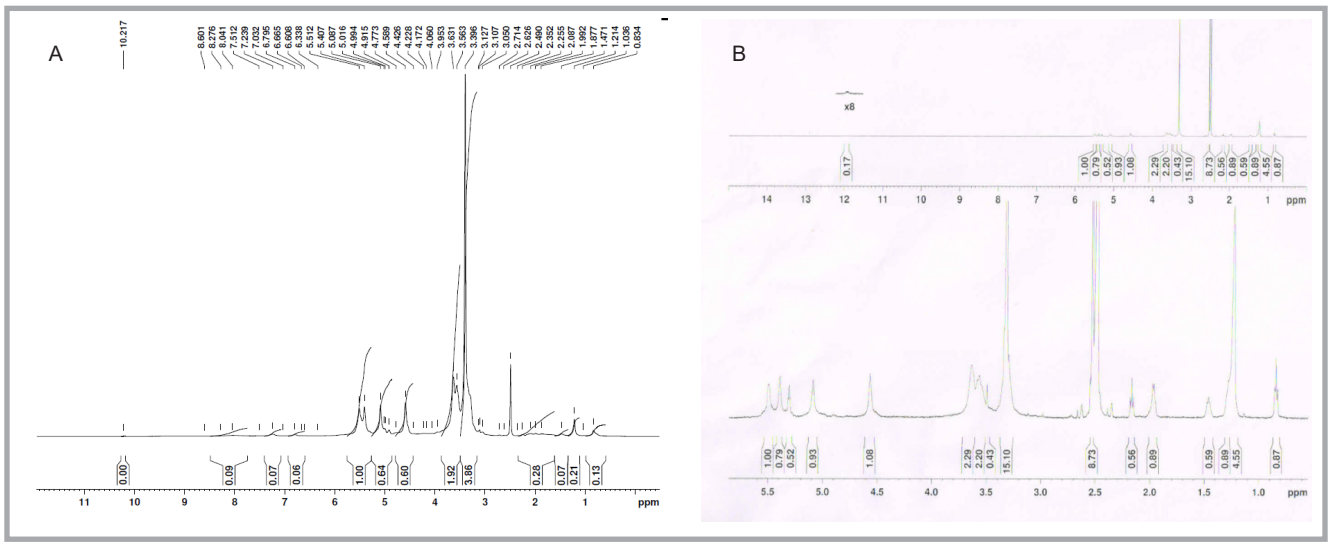

Figure 2. *^{1}H NMR spectrum of the initial Q-Farin C1000 (A) and product of Q-Farin esterification with oleic acid in the presence of immobilized lipase Thermomyces lanuginosus (B).*

Spectroscopic ^{1}H NMR examination of the strch-protein raw materials

The H NMR spectrum of Q-Farin C1000 was dominated by signals originated by polysaccharides, mainly starch, in the range of ca 3 to 6 ppm. The signals respond to protons of the anhydroglucose unit of starch. In the range of 0 to 3 ppm signals were seen from aminoacides and organic acids. Aromatic compounds and aldehydes generated signals in the range of 6 to 9 ppm. Signals in the range of 0 to 3 ppm are typical of isoleucine, valine, threonine, alanine, citric-and maleic acids etc. Signals from tryptophan could be seen in the region of 6 to 9 ppm.

In the ^{13}C NMR spectrum of Q-Farin 1000 C, signals were observed originated by carbon atoms of the anhydroglucose unit of starch: 60.46 ppm – C6, 71.67 ppm – C2, 71.97 ppm – C3, 73.25 ppm – C5, 78.74 ppm – C4 and 100.06 ppm – C1. Additional signals appeared at ca 29 ppm, which could originate from aminoacids: valine, metionine and lysine; 38 - 40 ppm from phenyloalanine, isoleucine, tyrosine, leucine, cysteine, arginine and proline.

In the ^{1}H NMR spectrum of the product of starch annealing with oleic acid (mol proportion 1:3) in DMSO in the presence of lipase *Thermomyces lanuginosus* in a water bath at 60 °C for 4 h, signals were observed from 3 protons of the terminal methyl group of the chain as a triplet at ca. 0.85 ppm. Signals in the ^{1}H NMR spectrum in the range from ca. 1.55 to 2.5 ppm were ascribed to protons of the methyl group in the chain. In the range of 3.5 to 5.5 ppm, a additional 7 signals were observed derived from protons of the anhydroglucose unit.

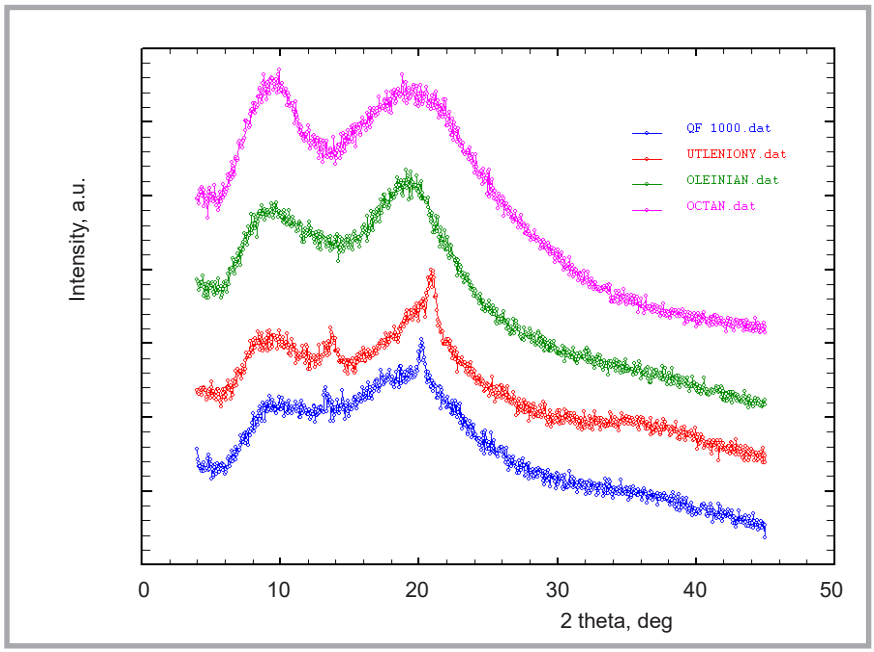

Figure 3. *Powder diffraction patterns of Q-Farin C1000 (blue line), the product of Q-Farin 1000 oxidation with hydrogen perhydrol in the presence of Cu^{2+} ions (red line), the product after the esterification of Q-Farin with oleic acid in the presence of immobilized lipase from Thermomyces lanuginosus in DMSO (green line) and the product after modification with acetic anhydride in the presence of acetic acid (purple line).*

X-ray analysis of the modified starch-protein raw materials

The molecular arrangement of the unmodified Q-Farin C1000 and Q-Farin after its molecular modification was X-ray analyzed. Powder X-ray diffractometry was applied to that end. The method renders the chance of determining the crystallographic type and degree of material tested; in other words, a quantitative determination of the content of crystalline and amorphous regions.

Figure 3 presents results of X-ray analysis of Q-Farin C1000 and the product of Q-Farin esterification with oleic acid in the presence of immobilized lipase from *Thermomyces lanuginosus* in DMSO.

It ensues from literature announcements that the diffraction pattern of wheat flour is almost identical to that of wheat starch. Relevant reflexes appear at 2θ, which reach values of 11.3, 15.2, 17.3,

18.1, 23.3 and 26.7°. Such a position of the diffraction signals is typical of starch, which reveals the crystallographic A type, namely grain starch. The diffraction pattern of both wheat flour and wheat starch indicates a semi-crystalline character and structure built up of alternate crystalline and amorphous layers. In the course of the hydrothermal treatment of Q-Farin C1000, a change occurred in the flour's structure, resulting in the transformation of the crystallographic type from A to V. Reflexes appeared in the diffraction pattern at 2θ equal to 21.0° and 13.0°. Moreover, a diffraction signal was observed at 2θ = 17.0°, which could indicate a residual crystalline structure of the A type in the wheat flour after its hydrothermal treatment. In the powder diffraction pattern of the oxidized Q-Farin, a diffraction reflex at 2θ = 17° was not observed. The post-oxidation product maintained the crystallographic V type. Esterification with oleic acid led to a complete disappearance of crystallinity and an entirely amorphous product. On its diffraction pattern emerged a wide diffraction signal at about 2θ = 9°, which may be ascribed to the forming of an inclusion complex in the interior of the amylose helix.

Investigation in the morphology of the modified starch-protein raw materials

The initial Q-Farins were inspected by scanning electron microscopy (SEM). ***Figure 4*** presents the SEM images.

On the grounds of SEM inspection made with the use of Quanta 200 apparatus of FEI Co. (USA), it was found that the hydrothermal treatment itself causes a destruction of the original granular structure, typical of starch as result of the combined action of temperature, pressure and high moisture content. The starch granules with a semi-crystalline structure were transformed into an almost homogeneous, amorphous material. Hydrogen bonds, which stabilize the starch structure, were probably broken in the course of the process.

The investigation results pointed to biopolymer samples of the raw material obtained from wheat flour marked Q-Farin C1000 (cold gelatinizing) and Q-Farin H501 (hot gelatinizing) having the best properties in respect of their use in further chemical and biochemical modification.

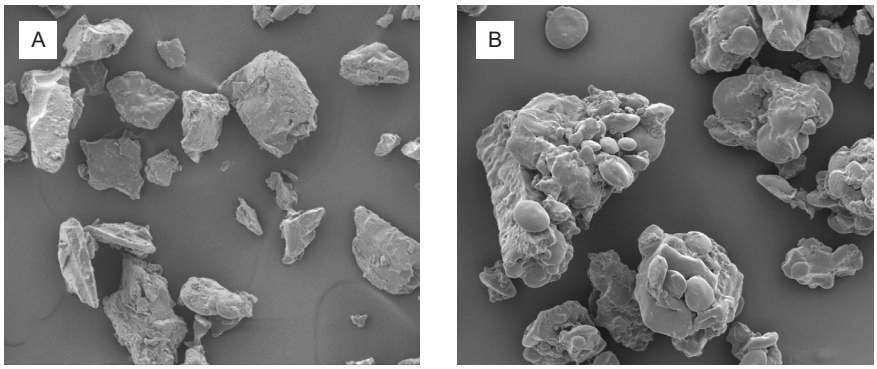

Figure 4. *SEM Q pictures of Farin C1000 (A) and H501 (B) (magnification 1000×).*

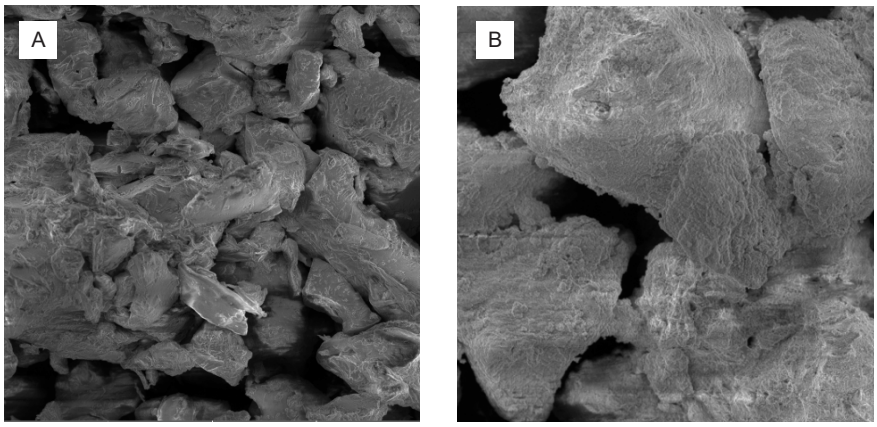

Figure 5. *SEM pictures of Q-Farin C1000 after its chemical modification by oxidizing with H_2O_2 in the presence of Cu(II) ions (A - magnification 1000×, B - magnification 2000×).*

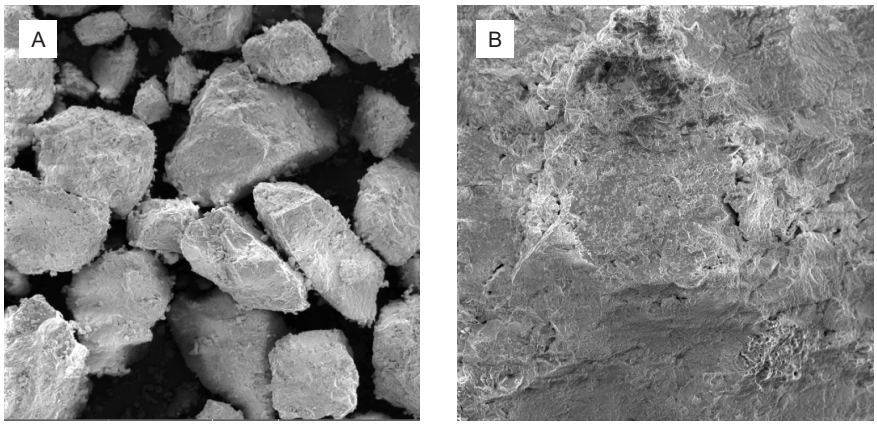

Figure 6. *SEM pictures of Q-Farin C1000 after esterification with oleic acid in the presence of immobilized lipase Thermomyces lanuginosus.*

Figure 5 shows SEM images of Q-Farin C1000 after oxidation with H_2O_2 in the presence of Cu(II) ions.

Chemical modification of Q-Farin C1000 by its oxidation with hydrogen perhydrol and by its esterification with acetic anhydride caused substantial changes in the structure of the end products in comparison to unmodified Q-Farin. By comparing the microscopic images it may be concluded that the chemical modification process is accompanied by a significant degradation of the starch polymer chain. In the case of the product of oxygenation, the microscopic image evidently pointed to dextrinization, which could prevail over the chemical modification process.

Figure 6 presents the results of the microscopic SEM observation of the product of Q-Farin C1000 esterification with oleic acid in DMSO in a water bath at 60 °C for 4 hours. The mol proportion in the process was 1: 3 of AGU to oleic acid; the process was run in the presence

of immobilized lipase from *Thermomyces lanuginosus*.

In the SEM images of the product of Q-Farin C1000 lipase-bio-catalyzed esterification with oleic acid, structures could be seen much bigger than those appearing in the images of the unmodified Q-Farin. It may be proof that the biochemical modification leads to an increase in molecular mass of the biopolymer and that the modification process itself did not cause the degradation of the polymer.

Summary

An investigation was conducted and optimal parameters were prepared for the manufacture of initial starch-protein raw materials designed for modification and functionalizing. Characteristics of the materials' physical-chemical properties were also established. It was documented that the best properties in respect of further chemical and biochemical modifications are featured by samples of the biopolymer raw material marked with the symbols Q-Farin C1000 (for packaging materials and thermoplastic compositions) and Q-Farin H501 (for bio-adhesives in the paper industry).

Trials of the chemical and enzymatic modification of the starch-protein raw materials conducted on a large laboratory scale allowed to optimize process parameters and conditions. Experimental lots of the biopolymers were prepared in amounts sufficient for further studies concerning properties and processing aimed at obtaining packaging materials, thermoplastic compositions and adhesives for use in the production of corrugated paper board in the paper industry. Experimental biopolymer materials were prepared with a degree of substitution (SD) from 0.7 to 2.45 and that of oxidation (DO) from 5.92 to 20.4 in amounts sufficient for further works. It was found that the starch-protein half products: that esterified in the presence of NaOH as catalyst with a degree of substitution DS=ca. 0.6-0.7, and the other oxidized with a degree of oxidation DO = ca. 12 lend themselves to processing into packaging materials.

The suitability was assessed of the modified biopolymer raw material for the preparation of functional adhesives for the paper industry primarily in the manufacture of multi-layer corrugated paperboard for the gluing together of the individual layers. A new glue recipe was elaborated with specific physical-chemical properties. It was documented that the starch-protein raw material investigated can be used in the joining of the individual layers of corrugated cardboard.

Editorial note

Related with this article are following titles published in Fibres&Textile in Eastern Europe (No 6, 2016):

I. Wietecha J., Kazimierczak J., Pałys B., Gutowska A. : Improving the Hydrophobic Properties of Starch-Protein Raw Material by Enzymatic Modification.

II. Janiga M., Stufka-Olczyk J., Milczarek A., Michniewicz M., Ciechańska D., Tomaszewski W., Gutowska A., Kapusniak J.: Chemical modification of the starch-protein raw material to obtain a half product for thermoplastic processing.

III. Sulak K., Gutowska A., Pałys B., Rychter P.: Heat plasticization of functional wheat flour by extrusion in the presence of plasticizers.

IV. Ciechańska D., Kaszuba L., Żakowska A., Sulak K., Kapuśniak K., Janiga M., Wietecha J., Gutowska a., Mik T.: Utylization of cereal and miling industry, products as raw materials for the manufacture of biopolymer technical products, 6/2016.

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19. PN-53/A-74039 Przetwory zbożowe. Oznaczanie tłuszczu.

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