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Chemical Modification of Starch-Protein Material Performed in Order to Obtain a Half Product for Thermoplastic Processing

DOI: 10.5604/12303666.1221754

Abstract
This article presents the results of tests which were carried out on a starch-protein biomaterial produced from wheat. The research was performed in order to assess optimal conditions for performing the chemical modification (acetylation and oxidation reactions) and its influence on the physico-chemical properties of the new biomaterial. Modifying agents were acetic acid anhydride with the presence of NaOH and K_2CO_3 activators as well as hydrogen peroxide, whose effects were catalysed with Cu^{2+} ions. Modified polymers with a degrees of substitution from 0.38 to 2.45 and oxidation from 1.0 to 35% were obtained in the process. The polymers obtained were characterized with various levels of starch degradation, minimal when the acetylation reaction activated with the K_2CO_3 method was used, moderate to high when the acetylation reaction was activated by NaOH, and maximal starch degradation was observed when oxidation was catalysed with Cu^{2+} ions. The modified polymers showed minor thermal granulation abilities and did not achieve thermoplastic abilities. Evaluation of the modification effects was carried out with absorption spectroscopy in infra-red radiation with the Fourier transformation (FTIR) technique, DSC, scanning electron microscopy and determining the boundary viscosity value.

Key words: *chemical modification, starch, wheat, acetylation, oxidation, material properties.*

Introduction

Assumptions for conducting modification processes of starch-protein material were defined in preliminary laboratory tests. It was possible to develop a small batch of modified biopolymer. The quantity of material developed in the batch was insufficient for conducting further research, which aimed at developing new thermoplastic materials [1]. Obtaining modified biopolymers in quantities that would be sufficient for further research required to move from laboratory environment to large scale laboratory conditions, modification process optimization as well as making sure that the physico-chemical properties of the modifiers are repeatable. At this stage of the research, the most suitable starch-protein material designated for further testing [2] was the hydrothermally modified Q-Farin C1000. The raw material was prepared and provided by the Lubella Company (Lublin, Poland), which took part in the research.

Purpose and scope of the research

The goal of this research was to optimize and assure that the physico-chemical properties of the starch-protein material which was chemically modified (acetylation and oxidation) are repeatable in a big laboratory environment. Research was carried out with the use of initially hydrothermally modified (delivered by Lubella company), wheat origin, starch-protein material. The scope of the research was to evaluate modification effects and prepare an applicable quantity of the chemically modified biopolymer. During the further stage of the research, the modified biopolymer material was used for obtaining new innovative thermoplastic packaging materials. The effects of starch contained in the chemically modified material were evaluated with the following research: FTIR, DSC, SEM and the boundary viscosity value.

Research methodology

Optimization of the esterification processes for starch contained in the starch-protein material (Q-Farin C1000) was carried out according to the methods described by Mark and Mahltretter [3] (acetylation with acetic anhydride with NaOH acting as an activator) as well as Volkert [3] (acetylation with acetic anhydride with K_2CO_3 acting as an activator). Optimization of the oxidation process of the starch hydroxyl groups was carried out according to Zhang Y.R and the co-operatives method [4] (oxidation with hydrogen peroxide with the presence of copper (II) ions). For modification research, a Radleys Reactor Ready reactor was used [2]. The effects of the modifications were examined with the use of

the instrumental and analytical methods mentioned earlier in the publication.

For testing the acetylation of starch in starch-protein material, a Q-Farin product was used preliminary dried at 40 - 50 °C for 24 hours at 6% humidity. For oxidation tests it was not required to preliminary dry the material. Modification reactions were carried out with various dosages of the modifying substances. Once the reaction was completed the product was left to cool down, then cleansed and dried at 50 °C for 48 hours.

Esterification with acetic anhydride with sodium hydroxide as activator

A 47 g test sample of starch-protein material (containing 0.15 mol of starch) was placed in the reaction chamber of a chemical reactor. Acetic anhydride was added to the reactor chamber and both substances were mixed for 5 minutes. Subsequently a 50% solution of sodium hydroxide was added at 2 ml/min speed. Once sodium hydroxide dozing was completed, the reaction temperature was raised to 115 °C and kept for a specified time.

Esterification with acetic anhydride with potassium carbonate as activator

A 100 g test sample of Q-Farin C1000 (containing 0.34 mol of starch) was placed in the reaction chamber of the chemical reactor. Acetic anhydride was added to the reactor chamber and both substances were mixed for 5 minutes while simultaneously raising the reaction temperature to 90 °C, and then kept for 45 minutes. Subsequently a 0.29 mol of potassium carbonate was dosed, the reaction temperature raised to 115 °C, and then kept for 60 minutes.

Oxidation with hydrogen peroxide with copper (II) ions as catalyst

50 grams of starch-protein Q-Farin material (containing 25.85 grams of starch) were added to the reaction chamber containing 500 ml of distilled water and mixed for 30 minutes at room temperature. After 30 minutes, copper (II) sulphate solution was added (made by dissolving 0.39 g $CuSO_4 \times 5H_2O$ in 50 cm^3 of distilled water. The suspension temperature was kept at 50 °C and hydrogen peroxide solution was added to it in 1 hour time period. Afterwards the solution temperature was kept at 50 °C and the solution mixed for 15 minutes. Ethanol (99 - 96%) was added to the gruel received in order to precipitate the oxidised product.

Reagents

In the modification reactions, the following chemical reagents were used: acetic anhydride, 30% hydrogen peroxide, copper (II) sulphate 5 hydrate, Chempur company sodium hydroxide and anhydrous potassium carbonate from the POCh company. For biopolymer product cleansing operations, 96% ethanol was used, provided by the Blik Company.

Designation methods

Physico-chemical properties of the biopolymer products obtained were tested. Designated and tested with the following methods:

- The degree of substitution (DS) for hydroxyl groups with acetyl groups was designated with the titration method, as described by Li Xia and cooperatives, the degree of oxidation (DO) for starch hydroxyl groups, i.e. the number of carboxyl and carbonyl groups within the product was designated by conducting a reaction of the groups mentioned with sodium hydroxide and designating the amount of sodium hydroxide used with acid-based titration against phenolphthalein.

- Changes within the chemical structure of the product were checked with the use of absorption spectroscopy in infra-red radation with the Fourier transformation (FTIR); those within the crystal structure of the product were evaluated with scanning electron microscopy; thermal analysis was performed with differential scanning calorimetry (DSC), and the boundary viscosity value was evaluated with the use of the differential viscosimetric method [6].

Starch-protein raw material characteristics

The characteristics of the initially hydrothermally modified starch-protein material Q-Farin C1000 was presented in the publication [1].

Research results

The research performed allowed to optimise the material modification reactions in a large laboratory environment. Conditions of performing the modification reactions were determined in the course of preliminary tests. The influence of the components of the modification mixtures as well as that of process conditions on the degree of acetylation, oxidation and starch degradation within the biopolymer was also checked in preliminary tests. Initial evaluation of the biopolymer acquired was conducted by performing visual checks of their physical form, efficiency of eluting side products, results of designating the degree of substitution (DS) [5] and oxidation (DO) [4] as well as designating the boundary viscosity number. In order to verify the effects of the modification samples of the new materials, they were subjected to spectrophotometric tests (FT-IR), thermal analysis (DSC) as well as microscope scanning (SEM).

The influence of the proportion of the modifying factors (acetylating and oxidising) on starch contained within the starch-protein material as well as the amount of activators used and reaction times on the degree of substitution (DS) and oxidation (DO) and boundary viscosity number for each method of modification can be found in ***Tables 1 - 3***.

Acetylation in the presence of sodium hydroxide

Based on the results obtained (***Table 1***), it was concluded that the optimal amount of acetyl anhydride required for the modification of starch contained in the base material (Q-Farin) which will ensure proper consistency of the end product as well as good eluting of side products is at around 13 moles/moleAGU (counted in the ratio for starch in the biopolymer product). When esterification was performed with the use of acetyl anhydride below this value, the final product had a very high density which made removing the side products by eluting them with water very hard or even impossible in some circumstances. It was noticed that the degree of substitution of acetylated starch was increased when activator amounts used in the reaction were raised. The highest degree of substitution was achieved for the Q-Farin sample esterified with acetic anhydride and with 1.3 mole/moleAGU of NaOH used as an activator. The optimal time for this reaction was 5 hours. During the test, when the time of esterification was reduced by half, the products obtained had a lower degree of substitution compared to those esterified for 5 hours.

Table 1. *Esterification of the starch-protein product with acetic anhydride and presence of NaOH.*

Starch, mole	Amounts, mole/molAGU		Process conditions		DS	Boundary viscosity number
	$C_6H_5O_3$	NaOH	T, °C	t, min		
0.15	6.0	0.4	115	300	1.77	
	7.0	0.4			2.06	
	9.0	0.8			2.25	
	10.0	0.4			1.51	0.40
	11.0	0.7			2.10	
	11.0	0.7			1.97	0.42
	12.0	0.8			1.76	
	13.0	1.0			1.80	0.42
	13.0	1.3			2.45	0.54

Table 2. *Esterification of the starch-protein product with acetic anhydride with a K_2CO_3 presence.*

Starch, mole	Quantity, mol/mol AGU		Process conditions				DS	Boundary viscosity value
	$C_6H_5O_3$	K_2CO_3	T_1, °C	t_1, min	T_2, °C	t_2, min		
0.34	10.00	0.85	90	45	115	60	2.99	0.93
	12.00						2.18	0.70
	14.20						2.45	0.84
	22.65						1.84	0.86
	31.58						1.57	0.68

Table 3. *Oxidation of starch-protein material with hydrogen peroxide in copper (II) ions as a catalyst.*

Starch, mole	Quantities		Process conditions		DO, %	Boundary viscosity value
	H_2O_2, mole/moleAGU	$CuSO_4 \times 5H_2O$, %	T, °C	t, min		
0.16	3.60	0.39	50	75	14.00	0.14
	3.62				15.39	<0.10
	6.93				20.57	<0.10
	8.13				26.20	<0.10
	13.75				34.50	<0.10

For evaluation of changes within the chemical structure, once the acetylation process of the starch-protein material had taken place, infra-red light spectroscopy with the Fourier transformation method was used. A demonstrative graph showing three absorption spectrum curves can be found below. Three different samples are shown in ***Figure 1*** base Q-Farin material as well as the esterified products with DS values at 1.80 and 2.45.

Based on the absorption spectrum flow analysis (***Figure 1***), it can be noticed that unlike the Q-Farin C1000 spectra, the modified products are characterised by less intensity characteristic for vibrations responsible for stretching O-H bonds, occurring in the range 3700 - 2800 cm^{-1}, with an additional strand of vibrations responsible for stretching the C=O bonds occurring in the range 1749 - 1751 cm^{-1}. These types of changes within the IR spectrum may suggest a substitution of some of the OH groups from starch with acetyl groups.

Base material structure changes resulting from the chemical modification were examined with the use of electron scanning microscopy (SEM) techniques. ***Figure 2*** depicts sample photographs taken at a 500× zoom. It can be noticed that the crystal structure of the starch-protein material changes whilst undergoing a acetylation reaction with sodium hydroxide as an activator in an amorphous state. The researchers came to the conclusion that the structure is takes on an unorganized glomerular shape once the degree of the substitution value rises.

The chemical modification process (***Table 1***) caused a decrease in the boundary viscosity value of the products. Compared to the substratum (Q-Farin C1000), whose boundary viscosity was at 0.87, this value decreased to 46 - 62% of the nominal value. An increase in the amount of the activator from 1.0 to 1.3 mole/moleAGU (with the same amount of acetyl anhydride) caused a 30% increase in the boundary viscosity.

Thermal analysis of the products obtained as a result of the chemical modification of starch-protein biopolymer material in the presence of NaOH was conducted with the differential scanning calorimetry (DSC) method. Both dried and wet sample tests were performed within the temperature range -60 - 200/240 °C at a drying speed of 20 and 100 °C/min. Exemplary DSC curves (for Q-Farin with DS = 1.8 and 2.45) can be found in ***Figure 3***.

For all samples of the modified starch-protein product, irrespective of the degree of substitution a small endothermic effect was observed when both heating variants were used when scanning at 20 °C within the range of 140 - 157 °C. The exothermic effect was also observed when the samples were cooled and scanning was at a speed of 20 °C within the range of 128 - 150 °C (***Figure 3***). For the enthalpy of the processes, especially cooling and heating no. 2, every test sample matched each other, and the temperatures implemented when cooling were slightly lower than when heating took place. The conclusion is that this might be a reversible process similar to the melting – crystallization known from synthetic polymer behaviour. It is worth mentioning that the energy of the processes observed was significantly lower than in the case of synthetic polymers. Additional tests with scanning at 100 °C/min pointed out that if the test samples are subjected to high temperatures for less time, the events setup did not change and the process was still reversible. However, it was noticeable that

the increased scanning speed had an effect on the temperature dependent effects of the modifications. When subjected to heating, the peak temperature rose to around 15 °C, and when cooled the peak was reduced by 47 - 57°C. In the case of heating; the temperature rise might be explained by thermal delay (apparatus effect) or the overheating effect (known from synthetic polymer melting) and such a wide range of temperature shift once cooling was taking place might be explained by the kinetic effect – characteristic for crystallization. It might be concluded that the thermal effects observed are related to melting – crystallization, but final confirmation would have to be proven from changes within the crystal structure of the test sample during themodifications. In relation to the base test sample (Q-Farin C1000), a probable, residual gelatinization effect was noticed when the temperature reached 63 °C as well as an endothermic effect similar to that observed when heating up the test samples of the modified product.

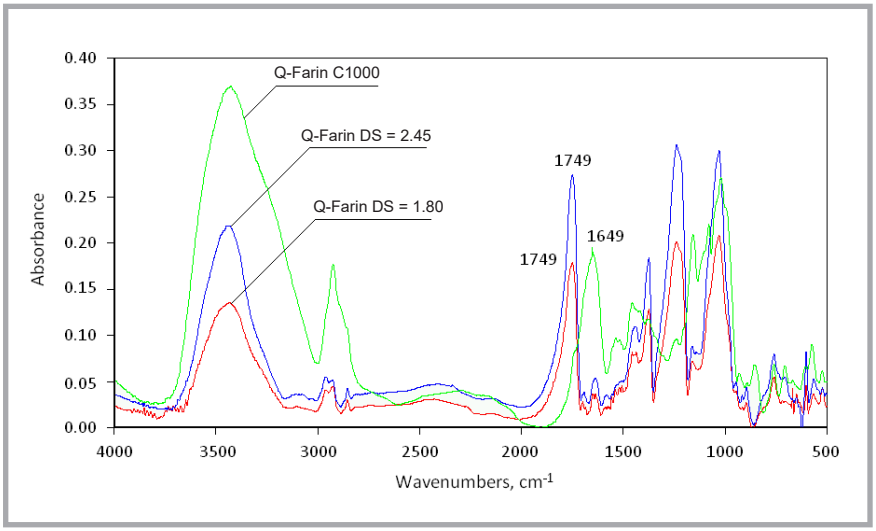

Figure 1. *FT-IR analysis of (Q-Farin C1000) test samples and esterified products Q-Farin DS = 1.80 and Q-Farin DS = 2.45.*

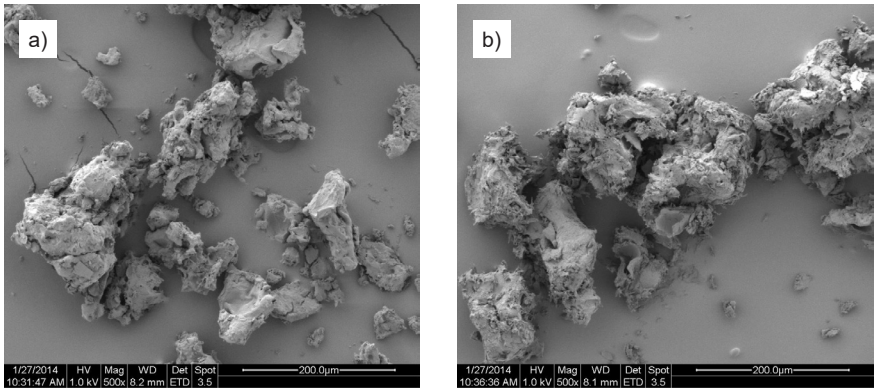

Figure 2. *SEM images of modified starch-protein products. a) Q-Farin DS = 1.80, b) Q-Farin DS = 2.45.*

Acetylation in the presence of potassium carbonate

Using potassium carbonate as an activator instead of sodium hydroxide speeded up the starch-protein material esterification reaction time by up to two times. The products obtained were characterized by a degree of substitution from 1.57 up to 2.99 (***Table 2***). A crucial influence on the degree of substitution was shown by the ratio of acetic anhydride to starch contained within the raw material. When the ratio of acetic anhydride was lower than the degree of substitution, the value was higher. The highest degree of substitution achieved was at 2.99 esterification performed with acetic anhydride in the amount of 10 moles/mol AGU. In the final phase of the process, difficulties were noticed that could lead to disrupting it. These were caused by the very dense consistency of the reaction products, which strongly disrupted the work of the mixing apparatus. Increasing the ratio of acetic anhydride to starch from 10 to

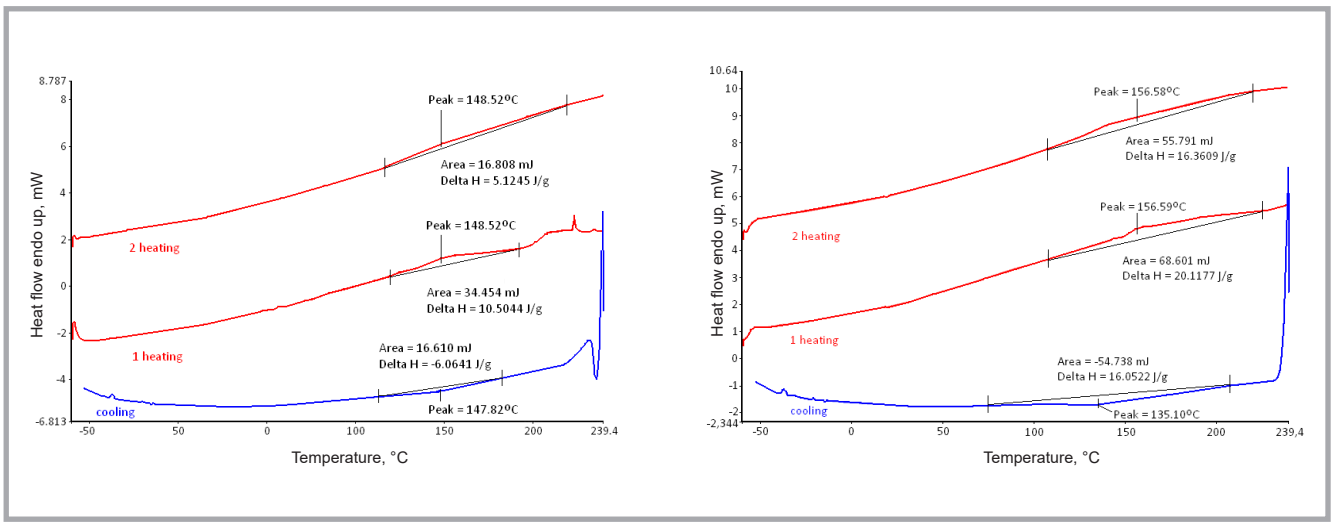

Figure 3. *Thermal analysis of modification products. a) Q-Farin DS-1.80, b) Q-Farin DS-2.45 (dried for 72 h at 55 °C/min, drying speed of 20 °C/min).*

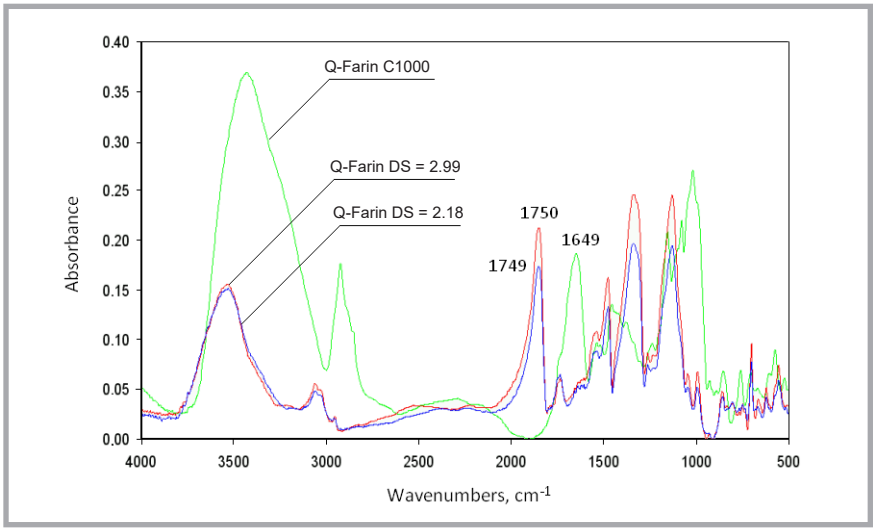

Figure 4. *FT-IR spectra of starch-protein material (Q-Farin C1000) as well as esterified Q-Farin DS = 2.18 and Q-Farin DS = 2.99.*

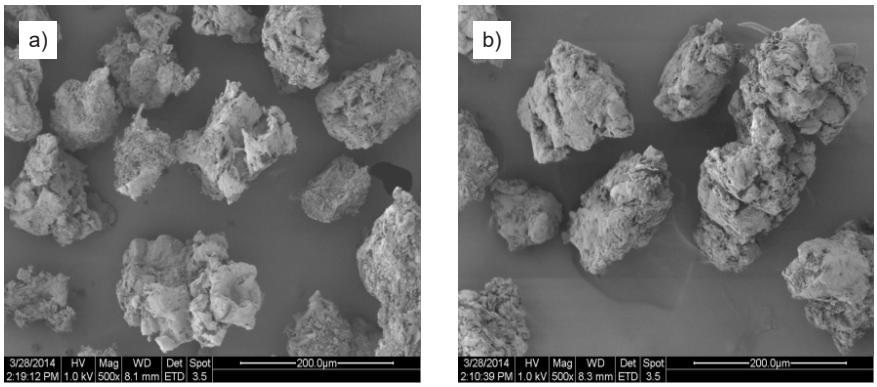

Figure 5. *Microscope images of modified starch-protein products. a) Q-Farin DS = 2.18, b) Q-Farin DS = 2.99.*

23 moles/mole AGU caused a decrease in the density of the final product up to the point where the reactor mixing apparatus's work was not disrupted. However, when the amount of acetic anhydride was superabundant, the esterification process was worse, and the degree of substitution for the product obtained was 1.84, being 1.5 times lower than that of the material esterified with smaller quantities of acetic anhydride.

For evaluating the changes within the chemical structure after the acetylation process of starch material with potassium carbonate similarly as in previous research series, the FT-IR method was used. ***Figure 4*** shows spectra for the base starch material (Q-Farin C1000) as well as esterified products Q-Farin DS = 2.18 and Q-Farin DS = 2.99.

Similar to the spectra of products obtained as a result of esterification with a sodium hydroxide presence, the FT-IR spectra obtained were characterized by a distinctly lower strand intensity in the range of 3700 - 2800 cm^{-1}, corresponding to vibrations stretching O-H bonds as well as an additional strand of vibrations stretching C=O, occurring in the range 1747 - 1750 cm^{-1}. This proves that the modification was a success and the OH groups were substituted within the starch molecule with acetyl groups.

Structure evaluation of the products obtained (***Figure 5***) was performed similarly as with the previous tests with the SEM imaging technique. ***Figure 5*** depicts exemplary photographs taken at 500× zoom. The microscope image obtained with this technique clearly showed that the crystal structure of the base material had undergone a transformation as an effect of acetylation reaction in an amorphous state. It was also concluded that the modified material with the degree of

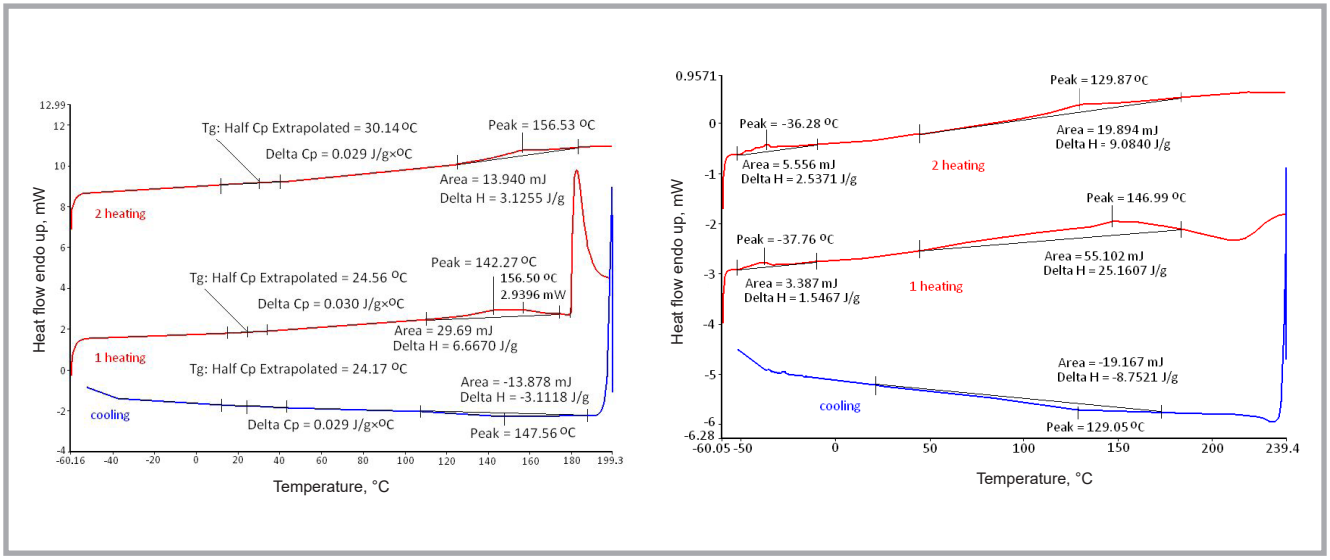

Figure 6. *Thermal analysis of modified starch-protein material. a) Q-Farin DS = 1.84 (dried for 72 h at 55°C/min in a vacuum), b) Q-Farin DS = 2.99 (dried for 72 h at a 55 °C/min, heating speed of 20°C/min).*

substitution at 1.57 to 2.99 had the same amorphous structure.

The esterified polymer degree of degradation (***Table 2***) evaluated based on the boundary viscosity value of the product designated before and after the esterification process turned out to be minimal. Values of the boundary viscosity number were at 0.68 to 0.93 when for the starch-protein base materials it was 0.87. It was also noticed that the amount of acetic anhydride used (10 - 32 mole/mole AGU) did not cause significant biopolymer degradation.

Exemplary DSC curves of the acetylation products for Q-Farin (with a degree of substitution DS = 1.84 and DS = 2.99) can be found in ***Figure 6***. As before, thermal analysis was performed with differential scanning calorimetry (DSC). Tests were carried out on dried samples in the temperature range -60 - 240 °C and at a eating speed of 20 °C/min.

All test samples behaved similarly, showing changes like vitrification, melting and crystallization. Samples suffered degradation in the temperatures range 179 - 199 °C, along with emitting aeriform substances (unsealed vessels). Minimal energy values were observed, which may suggest thermal crystallization potential. They may also be a good source of conditioning for the product to gain thermoplastic properties; however, because of their minimal values the test samples after the tests still had a granular form. In order to test the possibility of influencing the crystal state of the test samples

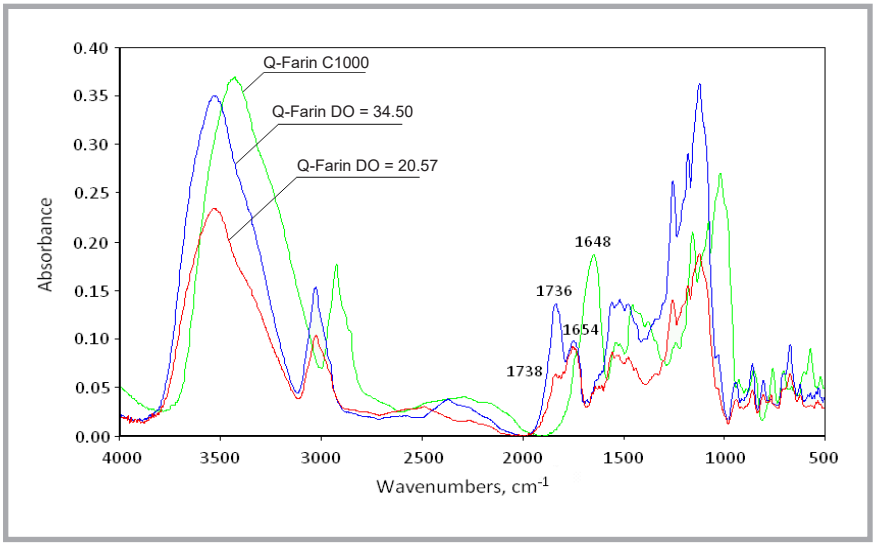

Figure 7. *FT-IR spectra of the Q-Farin C1000 as well as two oxidized products Q-Farin DO = 20.57 and Q-Farin DO = 34.50.*

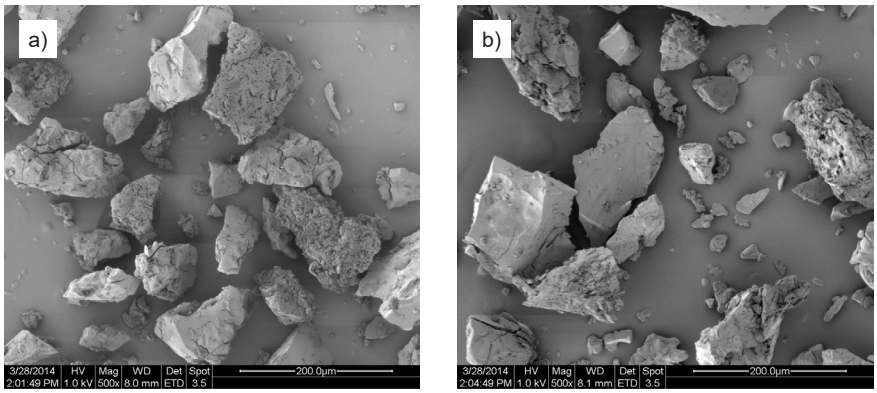

Figure 8. *Microscope images of oxidized starch-protein products. a) Q-Farin DO = 20.57, b) Q-Farin DO = 34.50.*

(in a reversible range), the crystal thermoplastic synthetic parts of the samples were subjected to additional heating for 4 hours at temperatures from 100 and 120 °C - that is between the vitrifacion and melting temperatures. Results of the analysis showed that the products tested did not gain higher crystallinity, as would

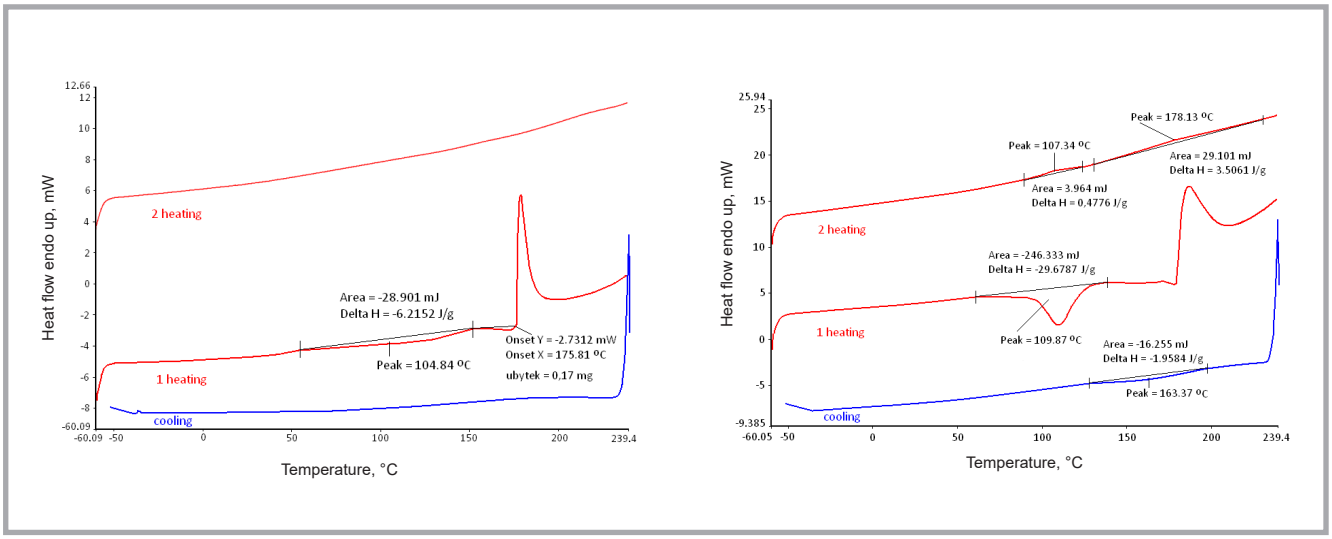

Figure 9. *Thermal analysis of oxidized test samples. a) Q-Farin DO = 20.57 (dried for 72 h 55 °C/min, b) Q-Farin DO = 34.50 (dried for 72 h at 55 °C/min, heating speed 20 °C/min), heating speed 20 °C/min)*

be expected for thermoplastic materials, with some of the changes being energetically weaker.

Oxidation with copper (II) ion presence

The results of the oxidation tests obtained allowed to formulate a conclusion that the ratio of hydrogen peroxide to starch with a constant quantity of the catalyst (copper (II) ions) exerts a noticeable effect on the oxidation. The highest degree of oxidation DO = 34.5% was obtained when a modification test sample was treated with 14 moles/mole AGU of hydrogen peroxide. Reducing the oxidiser by two times in the ratio to starch material caused a decrease in the degree of oxidation of 42%, and reducing the hydrogen peroxide by four times caused a drop in the oxidation degree of 56%.

Evaluation of the changes within the chemical structure caused by oxidation of the starch-protein material with copper (II) ions as a catalyst was conducted with absorption spectroscopy in an infra-red light with the Fourier transformation. ***Figure 7*** depicts exemplary FT-IR spectra of the starch base material Q-Farin C1000 as well as two oxidized products Q-Farin DO = 20.57 and Q-Farin DO = 34.50.

Spectra of the modified products obtained were characterized by lesser intensity of their spectrum than the raw material. The range was 3700 - 2800 cm^{-1}, matching the vibrations stretching the O-H bonds, as well as an additional strain within the wave length 1735 - 1738 cm^{-1}, which is characteristic for vibrations stretching C=O bonds. This may prove that the modification process conducted by oxidizing the hydroxyl groups to aldehyde and/or carboxyl groups was successful.

Research results of the starch material modification were evaluated using the SEM imaging technique. ***Figure 8*** depicts exemplary images obtained at 500× zoom. Thanks to the material obtained, it was possible to confirm that the oxidation was a success. The crystal structure of the starch-protein material underwent a partial transformation into an amorphous structure. Irrespective of the degree of oxidation, SEM images of the modified products were very similar to each other.

The degree of degradation for the oxidized polymer was evaluated by designating the boundary viscosity number value of the material after oxidation (***Table 3***). Analysis of the results obtained proved that the starch-protein material modified in these conditions undergoes drastic degradation. The boundary viscosity number value was near 0 in the highly oxidized products. Some of the highly oxidized polymers were degraded to the point that designating the boundary viscosity number was impossible. Designating the boundary viscosity number was possible only for products with a small value of the degree of oxidation i.e. 0.14, for such products the boundary viscosity number value was 0.14. DSC analysis for oxidized products was performed on products dried in the temperature range -60 - 240 °C at a heating speed of 20 °C/min. Exemplary DSC curves can be found in ***Figure 9***.

All modified products were characterized by a small thermal resistance irrespective of the degree of oxidation. When subjected to a temperature of 180 °C, decomposition took place along with the release of volatile substances. As a result of heating 1 and cooling with heating 2, endothermal and exothermal effects were observed. The effects observed were of marginal values, and hence they were deemed not credible. All curves obtained as a result of thermal analysis of the starch – protein material differed from the curves that are characteristic for thermoplastic materials.

Summary

In order to create innovative thermoplastic materials from starch-protein material, it is necessary to modify the physico-chemical properties of starch contained within it. The research performed allowed to establish a proper means of modifying the Q-Farin starch-protein material. Starch-protein material that was acetylated in the presence of the NaOH activator was greatly modified. The maximal degree of substitution with acetyl groups was DS = 2.45. Thanks to the acetylation reaction activated with K_2CO_3 , it was possible to obtain a product with a maximal degree of substitution - DS = 2.99. Oxidizing Q-Farin base material with Cu(II) ions as catalyst allowed to obtain a product with a maximum degree of oxidation - DO = 34.5%. FT-IR test results confirmed a proper process flow. FT-IR spectrum of the product obtained was observed in the range 1749 - 1751 cm^{-1}, the strain of vibrations responsible for stretching C=O bonds. Depending on the modification method implemented, the polymer degradation varied from low to severe. The most destructive influence was exhibited by oxidation with hydrogen peroxide. Products with the smallest degradation were obtained as a result of acetylation activated with K_2CO_3. Thermal tests of the products obtained showed only minor capabilities of having the thermal crystallization characteristic for synthetic polymers. Obtained biopolymer materials did not posses any thermoplastic properties.

Acknowledgement

The research work was carried out within the project "Modification and functionalization of biopolymer materials from the processing of grain and milling to developing a new generation of biomaterials" No PB1/A5/22/2012 supported by the National Centre of Research and Development in the Applied Research Program.

Editorial note

The above scientific description is related to the articuls listed in References (point 1, 2).

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Received 15.11.2016 Reviewed 12.12.2016