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Heat Plasticization of Functional Wheat Flour by Extrusion in the Presence of Plasticizers

DOI: 10.5604/12303666.1226223

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Abstract
Innovative functional flours with the trade name Q-Farin were used in the preparation of biopolymer materials with properties adequate to the production of biodegradable multifunctional packaging. To meet the assumed goal, it was necessary for the modification and functionalization of starch-protein material derived from the milling of purified wheat grain to confer hydrophobic, thermoplastic and barrier properties upon it. Unmodified and modified functional flour with the tradename Q-Farin C1000 was plasticized by pressure-thermal treatment in a mixture with typical plasticizers: glycerol, sorbitol & ethylene glycol. The modification of starch was accomplished by its esterification with acetic acid, enzymatic esterification with oleic acid or by oxidation with hydrogen peroxide. Mechanical and viscoelastic properties of the granulated thermoplastic compositions were examined. Their structure (microscopic and SEM observation), thermoplastic and processing properties as well as their susceptibility to biodegradation and phytotoxicity were also assessed. Selected thermoplastic compositions with adequate properties were processed into film and shapes. The materials obtained were examined for their physical properties like grammage and strength. Parameters of the technology processes involved were also prepared.

Key words: *thermoplastic starch, starch-protein material, plasticizing, film, starch profiles.*

Introduction

Polymeric materials are commonly used in everyday life and in the modern economy. The ever increasing production of polymers causes the fast depletion of fossil fuels and mounting quantities of waste materials, of which only a part is recycled or utilized. Problems in the protection of the environment arising out of the massive production of traditional petrochemical resins necessitated a search for new environmentally-friendly polymers, which is the reason for the recent growing interest in the use of raw materials, as well as half and side products derived from renewable resources. One such material is flour of various grains, a starch-protein material valuable for the food industry.

These products, due to their high bioavailability, microbiological purity, durability and other advantages are a high quality product intended for human consumption. However, this does not should limit the possibility of their use for other purposes, especially when those are cheap and their capacity exceeds the demand of foodstuffs applications. Starch contained in flour is unstable in respect of rheology, which makes it unsuitable for processing typical to thermoplastic polymers. Due to its poor solubility and mechanical properties, and strong hydrophilic character, unmodified (native) starch has a much limited range of practical uses. Therefore starch is subjected to various modifications which modify its properties to confer adequate consistence, durability and stability in storage and use, as well as specific physical-chemical properties desired in thermoplastic processing. Chemical, enzymatic and physical-chemical methods can be harnessed to modify starch. [1, 2]. Chemical modification prevails in industrial uses of starch. In respect of reagents and reaction conditions applied, chemical modification is accomplished by esterification, etherification, cationization or oxidation. However, the simplest way of conferring thermoplastic properties upon starch materials is their physical modification by extrusion with the addition of plasticizers [3]. Plasticizing destroys the granular structure of starch; due to having a semi-crystalline structure, starch granules are by thermomechanical energy transformed into a homogeneous, amorphous material.

Plasticized starch materials reveal properties adequate to processing in equipment commonly used with typical thermoplastic resins. Plasticizing agents play a crucial role in the plasticizing of starch by influencing its structure and properties [4]. They have the ability of attracting water molecules, reducing intermolecular forces between the biopolymer chains, and increasing the elasticity of the material obtained. Without the addition of a plasticizer, a film of starch is prone to destruction; it is torn to fragments,

Sulak K, Gutowska A, Pałys B, Rychter P. Heat Plasticization of Functional Wheat Flour by Extrusion in the Presence of Plasticizers.
FIBRES & TEXTILES in Eastern Europe 2016; 24, 6(120): 202-209. **DOI:** 10.5604/12303666.1226223

particularly when dried at elevated temperature. Hydroxyl groups are the active centres both in starch and the plasticizer. Therefore, polyols like glycerol, sorbitol and ethylene glycol are preferred plasticizers in the production of starch film [5]. The presence of plasticizers (water, ethylene glycol, glycerol, urethane, sorbitol) causes a drop in the glass transition temperature (T_g) of the starch, thus preventing its decomposition during extrusion. Regardless of the kind of starch, the plasticizer's influence rises with its increasing concentration [6, 7]. With a content of the plasticizer below 10 wt%, its interaction with starch is faint; at contents above 20 wt%, the elasticity and elongation of the materials obtained go up [8].

A number of works can be found in literature concerning the plasticization of native starch derived from potatoes or corn [9, 10]. In this work, a hydrothermally pre-modified starch-protein raw material (functional flour with trade name Q-Farin) was subjected to plasticization. Apart from starch, it contains protein, fat, mineral and organic components [11]. The material was not investigated earlier in respect of its use as an alternative to classical resins.

The optimal conditions of modification of the raw material may therefore entirely differ from those reported in literature for native starch.

It was an aim of the work to prepare a method to produce thermoplastic granulated material from starch –protein raw material. A further goal was to define the possibilities and methods of their processing into shapes and functional packaging in the form of film.

Materials and methods

Materials

Starch-protein material was supplied by Lubella Ltd, Poland. It is a product obtained in the controlled hydrothermal treatment of wheat flour. The hydrothermal treatment consists in the forcing-through-of classical wheat flour with the addition of 8 – 12 wt% of water at 80 – 150 ºC under a pressure of 8000 – 13000 kPa for 40 – 70 seconds. Depending upon the route, the degree and parameters of the processing, various biochemical transformations proceed like the denaturation of proteins, dextrinization and saccharification, as well as the hydrolysis of fats and the inactivation of amylolytic-, proteolytic-, and lipolytic enzymes. The hydrothermally processed wheat contains 54 – 64% of starch, 13 – 15% of protein, 17 – 23% of cellulose, 0.5 – 1,5% of fat and reducing sugars, 0,5 – 1,0% of ash and about 6% of water. Thanks to its nutrient availability, microbiological purity, durability and other advantages, the material is intended for alimentary uses [11]; however, not limiting its other application. Production capacity surpassing actual market demand may favour a non-food application.

Submitted to plasticizing were the functional flour Q-Farin C1000 and products of its chemical modification: oxidised with hydrogen peroxide in the presence of copper ions Cu^{2+}, and esterified with acetic anhydride either in the presence of acetic acid (Kakuszke and Rapthel method) or catalysts (NaOH or K_2CO_3). Q-Farin C1000 enzymatically esterified with oleic acid was also plasticized. The medium substitution degree was 0.7 to 2.5 in the case of Q-Farin esterified with acetic anhydride, and the oxidation degree was 35 - 38 for oxidized Q-Farin [12] The substitution degree in the enzymatically esterified sample was SD = 0.04 [13]. Anhydrous glycerol (POCH S.A Poland), glycerol monostearate (Brentag Poland), sorbitol (POCH S.A. Poland) and polyethylene glycols (Aldrich) were used plasticizers.

Methods

Plastification

The starch-protein raw materials were plasticized in the following steps:

i) first blending of the starch material with the plasticizer,
ii) airtight conditioning of the mix for at least 24 hours,
iii) extrusion by degassing and granulation.

The starch-protein material was first blended at 75 °C for 30 minutes in a laboratory mixing tank equipped with a heated mixing chamber to complete absorption of the plasticizer by the starch. The blend was then quenched to the ambient temperature and conditioned for 24 hours in airtight containers. The starch-protein material mixed with the plasticizer was subjected to pressure-thermal treatment by a traditional method commonly applied in the processing of resins i.e. extrusion by means of a double-screw extruder (Zamak Co, Poland). The extruder is designed for the processing of thermoplastic and composite materials. The concurrent arrangement of the double-screw extruder provides intensive and uniform mixing of the components and adjustment of the characteristic of the work zones to the processed materials, thus ensuring proper quality of the product. The segmented cylinder divided in the horizontal plane enables observation of the homogeneity at any time of the process.

Extrusion was accomplished with a simultaneous degassing of volatile components in the sixth plasticizing zone. The temperature of the plasticizing zones was changeable in the range of 90 to 150 °C. The screws rotated at 50 r.p.m. and the pressure did not exceed 5000 kPa; the torque moment of the screws was in the range of 10 to 12 Nm. The content of the plasticizers (glycerol, sorbitol) in the compositions prepared was in the range of 15 to 30 wt %.

Preparation of film and shapes

A selected thermoplastic material in granulated form was processed into biodegradable film and shapes. Plasti-Corder® 330 apparatus (Brabender Messtechnik Gmbh&Co, Germany) equipped with a single-screw extruder with a extrusion head and take-up device was used for the casting of film. The following process parameters were applied:

- Temperature profile of the plasticizing section: 125/125/140/140/135 °C
- Size of the slot in the extrusion head: 100 mm × 0.35 mm
- Temperatue of guide rollers: 80 °C
- Film take-up speed: 0.5 m/min.

The shapes were made with the use of a single-screw injection moulder with a plasticizing section based on an extruder with the proportion of length to diameter of the screw L/D = 28 and controlled temperature in the chute. The injection pressure was 80000 kPa and injection cycle - 7 sec.

Analytical methods

Biodegradability assessment

The testing of biodegradability in compost medium was accomplished by the method of mass loss according to the procedure "Estimation of the decomposition degree of resins and textiles under simulated composting condition on a laboratory scale". "Method of mass loss meas-

urement "(PN-EN 14045:2005, PN-EN 14806:2010 PN-EN ISO 20200:2007) in the Laboratory of Biodegradation[1]. The samples examined were subjected to the action of the compost medium under conditions that simulated intensive aerobic composting. Certified compost taken after its fiery ripening from the industrial municipal compost prism in Lodz served as inoculum. Reactors with the samples tested were put into a thermal chamber with a constant process temperature of 58 ± 2 °C and humidity in the range of 40 to 70%.

Crucial in correct biodegradation testing was estimation of the total number of microorganisms (biological activity), which should amount to no less than 10^6cfu/ml. It was estimated at the accredited Laboratory of Microbiology at IBWCh[2].

Phytotoxicity assessment

The impact of the film upon the sprouting and growth of higher plants was tested in the vegetation hall of the Biochemistry Department of Jan Długosz University, Częstochowa. Testing procedures[3] were applied in the testing of phytotoxicity. Monocotyledons-oats (Avena sativa) and dicotyledons-radish (Raphanus sativus) were used in the experiments. In the phytotoxicity method, the impact of the biopolymers tested upon the sprouting and early growth of various land plants is assessed. Seeds of the plants selected were planted in bowls with soil to which the material tested was added, as well as being put in bowls with reference soil. The bowls were incubated under conditions optimal for the plants selected. The sprouting and mass (dry or green) were compared to the sprouts of the tested and reference plants. In assessing the toxicity, the lowest concentration of the material tested was defined at which an evident impact could be observed upon the sprouting and growth of the plants in comparison to the reference (LOEC). Also defined was the concentration at which observable effects do not occur (NOEC). A visual assessment was also made of any defects in the plants like growth inhibition, chlorosis and necrosis both in the reference and tested bowls. Uting was expressed as a percentage of seedlings that sprouted in comparison to thise in the reference bowls. The impact upon growth was expressed as the difference in the above-soil mass between the plants with materials tested and the plants in the reference bowels.

Scanning electron microscopy (SEM)

SEM images were taken with the use of a scanning electron microscope - Quanta 200 delivered by FEI Co (USA). The examination was accomplished in a low vacuum in natural conditions without spraying.

Thermal properties

Thermal properties were measured by means of DSC model Diamond (Perkin Elmer, USA) apparatus equipped with an Intercooler II and standard software Pyris-Diamond. Samples of 10 − 12 mg were examined in the cycle: I heating → cooling → II heating at a heating rate of 20 °C/min. Thermal stability was estimated by the thermogravimetric method with the use of the thermo-scale TGA HI-REST V5.4A. Measurements were made in the temperature range of 20 to 400 °C at a heating rate of 10 °C/min in nitrogen.

Rheological properties

Rheological and processing properties were estimated by the method of thermal extrusion and pressing in the temperature range 80 - 200 °C. A plastometer - a type II RT Dynisco Co, USA equipped with a 2 mm (dia) spinneret and laboratory hydraulic press was used for the purpose.

Mechanical properties

Physical-mechanical properties of the granulated material, film and shapes were measured. The maximal draw strength, tenacity and elongation were estimated with the use of an Instron machine in accordance with adequate Polish standards: breaking strength, elongation at break, tenacity, elasticity module of the granulated material according to Standard PN-EN ISO 527-3:1998 and the compressive strength of the granulated material according to Standard PN-EN ISO 604:2006.

Assessment of film's hydrophobicity

The hydrophobicity of the film was assessed by analysing its static wetting angle. It was measured by the method of sitting drop in accordance with European Pharmacopoeia 8.0 p. 2.9.45. Apparatus STFI of AB Lorentzen-Wettre Co ,Turkey was used for the purpose. The shape of the drop is registered by a digital camera, and the picture is then transferred to a computer, where it is magnified and analysed by means of suitable software.

Measurement of the drop's height and width serves to estimate the wetting angle. Distilled water was used as measurement liquid.

Results and discussion

Thermal and rheological properties of the initial starch-protein materials

Thermogravimetric (TGA) measurements revealed that the thermal composition of the starch-protein raw material oxidized by hydrogen peroxide in the presence of copper as catalyst starts at as low a temperature as 40 °C. The mass loss of the material estimated at 150 °C amounted to 6.38%, while intensive decomposition began at 170 °C. The starch-protein raw material esterified with acetic anhydride is thermally much more resistant; its mass loss at 150 °C was merely 1.24%, while intensive decomposition began at 200 °C. For the raw materials examined, ***Table 1*** gives values of their mass loss after 1 hour of heating at 180 °C.

Assessment of the rheological properties of the modified Q-Farin C 100 evidenced that the biopolymers do not melt below 200 °C. Moulded pieces were prepared by thermal pressing, and at 120 °C of the process intensive degradation proceeded, disclosed by a colour change (browning). Regardless of the lack of suitable rheology properties, it was attempted to press the modified starch-protein raw materials through a double –screw extruder. Under a shearing force at a temperature up to 180 °C, the samples examined did not acquire plasticity sufficient for extrusion. Very high resistance (torque above 50Nm) and pressure (above 15 000 kPa) made the processing impossible. The DSC thermograms prepared also indicate a lack of thermoplas-

Table 1. *Mass loss in the starch-protein raw materials after 1 hour of isothermal heating at 180 °C.*

Symbol of sample	Mass loss, %
Q-Farin C1000 esterified	4.05
Q-F arin C1000 esterified by method K and R	2.11
Q-Farin C1000 oxidized	9.20
Q-Farin C1000 unmodified	5.59

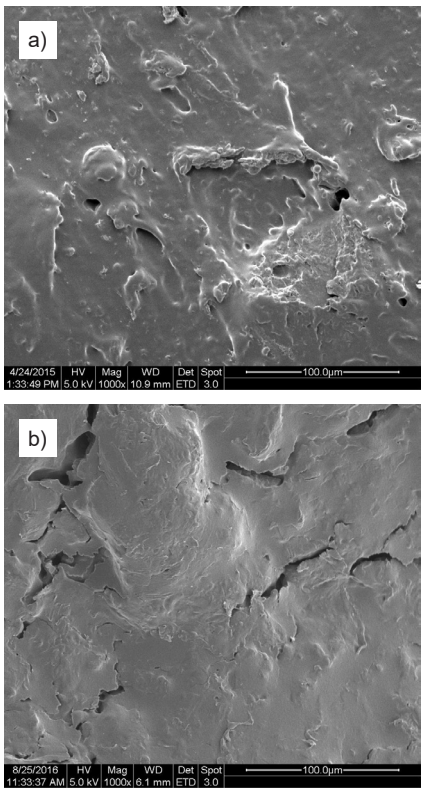

Figure 1. *SEM images of chemically modified Q-Farin C1000 (a - oxidized, b - esterified) and that plasticized with glycerol 25 wt%. Magnification 1000×.*

tic properties. Both in Q-Farin C1000 esterified by methods K and R and the oxidized one, small, endemic peaks could be observed at a temperature of about 40 and 107 °C [12]. The thermal effect observed does not exceed a value of 15 J/g, indicating that the starch-protein raw materials undergo a much limited melting; only some components of the material melt, most probably sugars.

The products of chemical modification Q-Farin C1000 selected without the addition of a plasticizer do not reveal processing behaviour adequate to classical processes applied for resins.

Influence of selected plasticizers on the processing and thermoplastic properties of modified starch-protein materials

Several compositions were prepared of the modified biopolymers investigated with plasticizers like sorbitol, glycerol, glycerol monostearate and polyethylene glycols with the aim of defining the impact of the singular plasticizers upon the thermoplastic and processing properties of the starch-protein raw materials. The content of the plasticizers in the samples examined was from 15 to 40 wt%. The compositions prepared were subjected to pressure-thermal processing. High pressure and resistance appeared in the course of extrusion trials of the starch-protein raw materials containing sorbitol, glycol monostearate and polyethylene glycols. The torque of the screws exceeded the allowable value of the extruder. The resistance rendered the trials with such blends impossible regardless of the process temperature.

The highly substituted esterified (SD ≥ 2.01) starch-protein material caused high resistance as well; the addition of glycerol did not provide plasticity in that case, and a polymer string could not be formed through the head of the extruder. Esterification of the starch causes a remarkable increase in starch hydrophobicity, particularly at a high substitution degree [14]. The high hydrophobicity after extensive esterification (SD ≥ 2.01) impedes the incorporation of glycerol into the structure of the polymer chains. This is the reason why the presence of glycerol does not limit the interaction between the starch chains and does not confer a higher mobility upon them. Probably for that reason most of the commercial starch esters are featured by a low substitution degree SD in the range of 0.01 to 0.2 [15].

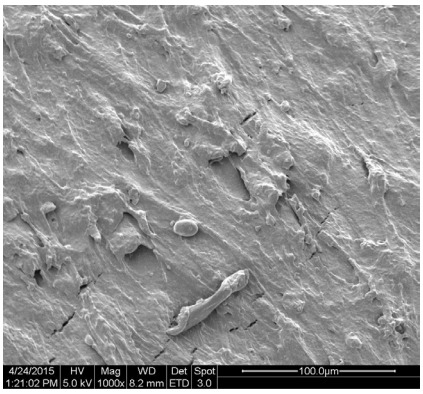

Figure 2. *SEM image of Q-Farin C1000 chemically unmodified and plasticized with glycerol 25 wt%. Magnification 1000×.*

Good processing behaviour was characteristic of the biopolymer compositions containing oxidized and unmodified Q-Farin C1000 and glycerol in the amount of 25 wt%. A remarkable thermal decomposition evidenced by turning a deeper brown shade proceeded at 130 °C. The intensive brown colour is an indication of caramelization and reaction between aminoacides and reducing sugars (Maillard reaction). The reaction usually proceeds at elevated temperature, comprising a series of chemical processes, and like carmelization counts in the reaction of the non-enzymatic browning type. Hundreds of various compounds reponsible for a range of colours and odours are formed in the reaction. The compounds formed undergo further transformation to a similar kind of substances [16].

Inconsecutive trials, the processing temperature was lowered to 95 °C. A sample prepared at that temperature underwent insignificant thermal decomposition and showed good thermoplastic properties. The thermoplastic compositions prepared were SEM-inspected. SEM images are shown in ***Figures 1*** and ***2***.

Table 2. *Physical-mechanical properties of the granulated starch-protein raw materials.*

Kind of granulate of starch-protein material/ plasticizer	Max. drawing force, N	Tenacity, MPa	Elongation at max. stress, %	Elasticity modulus, MPa	Diametral compressive strength, MPa
Q-Farin C unmodified/glycerol	4.2	0.80	104	1.4	1.4
Q-Farin C oxidized/glycerol	0.7	0.29	20	2.2	2.8
Q-Farin C esterified (DS = 0.9)/glycerol 25 wt%	12.0	1.40	16	13.9	8.5
Q-Farin C enzymatically esterified (DS = 0.04)/glycerol 20 wt%	27.2	4.40	74	31.0	11.2

Table 3. *Properties of film made of plasticized starch-protein raw materials.*

Starch raw material	Film thickness, mm	Surface density, g/m²	Elongation at max. stress, %	Tenacity, MPa	Max extension strength, N	Modulus of elasticity, MPa
Q-Farin C1000 unmodified plasticized with glycerol 25 wt%	0.37	528	103	2.16	12.0	7.5
Q-Farin C1000 oxidized plasticized with glycerol 25 wt%	0.33	391	202	0.24	1.2	2.2
Q-Farin C 1000 esterified – acetic anhyd, plasticized with glycerol 25 wt%	0.46	563	22	0.94	6.8	7.8
Q-Farin C 1000 enzym. esterified with oleic acid, glycerol cont. 20 wt%	0.34	500	96	-	15.8	8.3

Table 4. *Properties of shapes prepared from plasticized starch-protein raw material.*

Starch raw material	Max. extension force, N	Tenacity (extension), MPa	Extension at max. stress, %	Modulus of elasticity, MPa	Average initial shrinkage (linear), %
Q-Farin C unmodified/ glycerol 25 wt%	32.4	2.7	114	3.32	1.1
Q-Farin C oxidized/glycerol 25 %wt	2.3	0.24	121	0.94	1.0
Q-Farin C esterified with acetic anhydride DS = 0.7/glycerol 25 %w	16.9	1.5	44	6.64	1.2

The SEM images point to Q-Farin C1000 esterified with acetic anhydride with the addition of glycerol plasticizer as the material with a most uniform structure. The internal structure is slightly less uniform in the oxidized Q-Farin C1000 plasticized with glycerol. The least uniform structure was revealed by the unmodified Q-Farin with glycerol. Mechanical properties of the plasticized materials are shown in ***Table 2***.

Results shown in ***Table 2*** evidence that the best physial-mechanical properties are characterised by the esterified starch-protein raw material. The result accords with conclusions from the SEM observation of the granulated material tested. The chemically unmodified material has a good characteristic. The lowest resistance to extension appeared in the oxidized starch-protein raw material, with the extensive degradation of starch in the oxidadtion process being the assumed reason. The oxidadtion of starch is always accompanied by the depolymerization of polysaccharide chains, leading to a decrease in molecular mass and change in the surface structure of granules [3]. As a result of the oxidation in the starch glycoside units, carbonyl and carboxylic groups are formed in amounts depending upon the kind and concentration of the oxidizing agent, process parameters and on the botanical origin of the starch [17]. A high degree of degradation is observed in starch with a low content of water. Viscosity is high in such a blend and the rotational speed of the extruder screws causes high shearing stress. The residence time of such a blend in the extruder ought to be as short as possible. On the other hand, a high content of moisture promotes hydrolytic degradation of the polysaccharide chains [18]. For these reasons, parameters of the extrusion are adopted not only in respect of the kind of starch, type of extruder and air humidity at which the product is exploited but also in respect of its intended use. In the case of industrial use, milder process conditions are usually applied to minimalise the degradation of the polysaccaride.

Preparation and properties of films and shapes

Selected biopolymer compositions were processed into films and shapes, for which optimum process conditions were adopted. The film casting process ran best at the following temperature profile of the plasticizing zone: 125/125/140/140/135 °C for oxidized Q-Farin and 120/145/155/155/151 °C for esterified Q-Farin. The temperature of the guide roller was 80 °C. Properties of the film obtained are compiled in ***Table 3***.

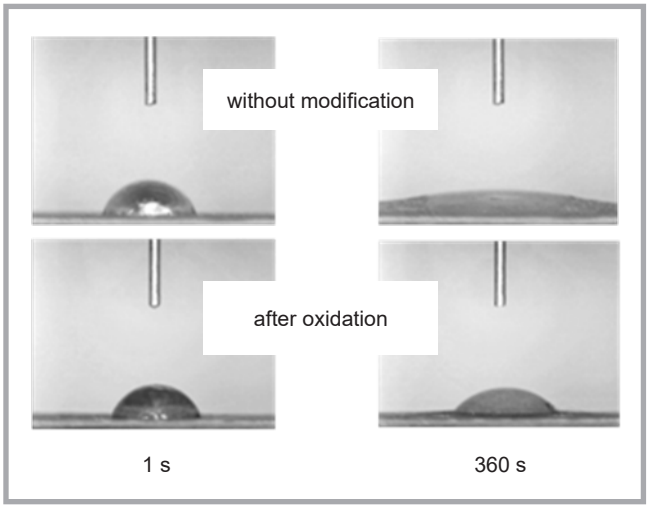

Figure 3. *Shape of a water droplet on the surface of film made of oxidized and unmodified starch material.*

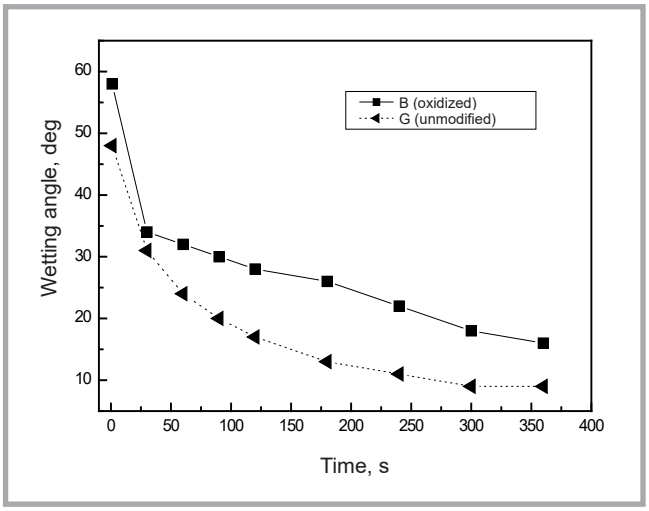

Figure 4. *Dynamics of the wetting angle of film made of oxidized and unmodified starch material.*

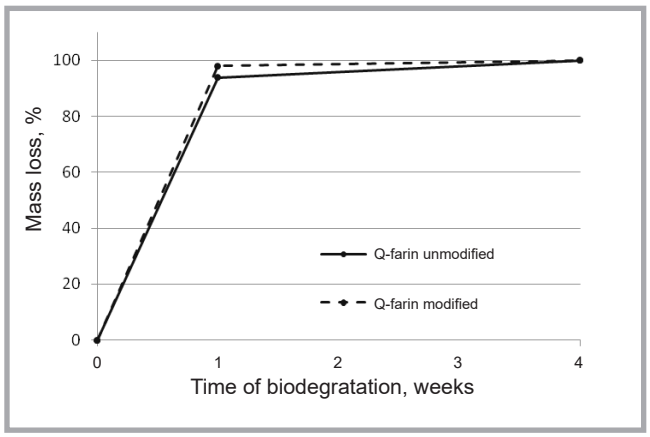

Figure 5. *Process of biodegradation in the compost medium of the initial granulated starch-protein raw materials Q-Farin with the addition of 25 wt% of glycerol.*

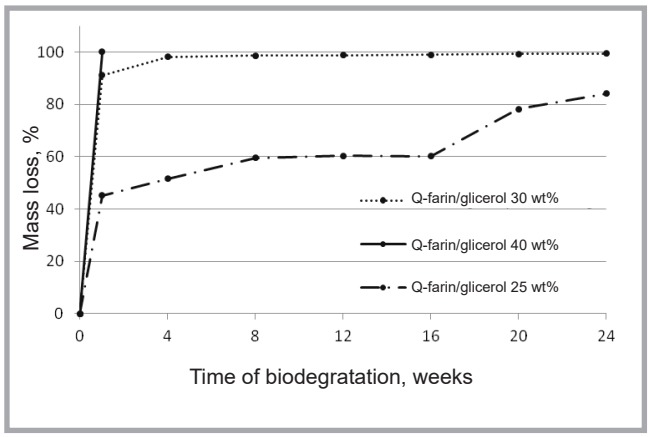

Figure 6. *Process of biodegradation in the compost medium of film samples with a varied content of glycerol.*

Results compiled in ***Table 3*** indicate the best physical-mechanical properties of the film made of Q-Farin, enzymatically esterified (SD = 0.04). Film made of unmodified plasticized starch-protein raw material shows similar properties. Most probably, degradation occurs in the differently modified starch (high SD), which is confirmed by a significant drop in the limiting viscosity number of the starch-protein material after its modification [12].

The granulated material was also processed on laboratory injection moulders to prepare universal shapes. ***Table 4*** presents physical-mechanical properties of the shapes. The initial shrinkage of the shapes (S_1), which indicates the decrease in a dimension in a given direction, is calculated from the equation:

$$S_1 = (L_1 - L_2)/L_1 \times 100\%$$

where, L_1 – selected dimension in the mould in m, L_2 – the same dimension measured in the ready shape at a given temperature and pressure in m.

The initial shrinkage was measured for shapes prepared at the following temperature profile of the plasticizing zone of the extruder: 145/145/150/150 °C.

As in in the film manufacture, good physical-mechanical properties appear in shapes made of the unmodified starch-protein raw material.

Assessment of film hydrophobicity

In ***Figure 3*** a photo is shown illustrating the shape of a water droplet after being deposited on film made of the plasticized starch-protein raw material after 1 and 360 seconds. The shape of the droplet deposited on film from unmodified starch-protein raw material indicates a better wettability of the material surface than that of the film made of oxidized material.

The time-dependent change in the wetting angle deposited on film of oxidized and unmodified starch material is presented in ***Figure 4***.

Results shown in ***Figure 4*** prove that film made of the oxidized starch-protein raw material reveal a weaker hydrophylicity in comparison to that prepared from the unmodified raw material.

Biodegradability assessment

Figure 5 illustrates the results of testing of the bio-decomposition of the granulated starch-protein raw material Q-Farin oxidized and unmodified with the addition of 25% of glycerol.

Samples of both granulated Q-Farins underwent a complete degradation in the medium applied as soon as after 4 weeks. The mass loss measured was 100%. ***Figure 6*** presents the kinetics of the biodecomposition process of film samples with contents of glycerol of: 25, 30 and 40 wt%.

As can be seen in the graph, the content of plasticizer influences the biodegradation of the film. The film with a 40 wt% content of glycerol was entirely decomposed as soon as after 1 week. In samples with a 25 and 30 wt% content of glycerol, the mass loss after 24 weeks amounted to 84.1 and 99.5 wt% respectively.

Based on the analysis, it may be concluded that the modification process of the film samples prepared does not influence the biodegradation. The samples tested are entirely biodegradable in the medium used.

Table 5. *Impact of the concentration of test materials in the soil on the sprouting and mass of the above-soil part of the plants for radish seedlings.*

Results of examination, mg/kg of soil	Denotation of sample					
	granulated Q-Farin/oxidized/ glicerol 25 wt%		granulated Q-Farin unmodified/glycerol 25 wt%		film Q-Farin unmodified/glycerol 25 wt%	
	% crop on reference	% mass on reference	% crop on reference	% mass on reference	% crop on reference	% mass on reference
REFERENCE	100	100	100	100	100	100
200	93	93	100	91	94	90
400	100	78	107	83	88	88
800	93	81	100	73	88	83
1000	100	77	93	65	94	82

Table 6. Impact of concentration of the test materials in the soil upon the sprouting and mass of the above-soil part of oat seedlings.

Results of examination, mg/kg of soil	Denotation of sample					
	granulated Q-Farin/oxidized/ glycerol 25 wt%		granulated Q-Farin unmodified/glycerol 25 wt%		film Q-Farin unmodified/glycerol 25 wt%	
	% crop on reference	% mass on reference	% crop on reference	% mass on reference	% crop on reference	% mass on reference
REFERENCE	100	100	100	100	100	100
200	95	98	100	95	100	96
400	95	96	100	92	95	96
800	90	93	95	91	95	92
1000	100	91	95	87	95	88

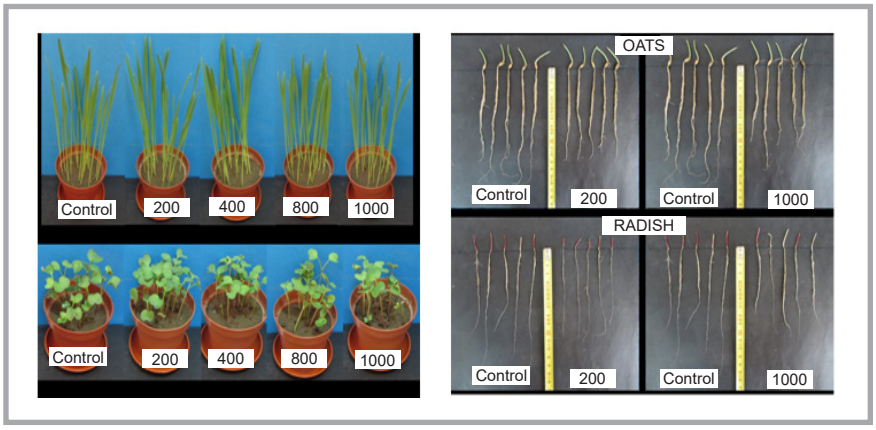

Figure 7. Photographic documentation of the assessment of phytotoxicity of granulated oxidized Q-Farin C1000.

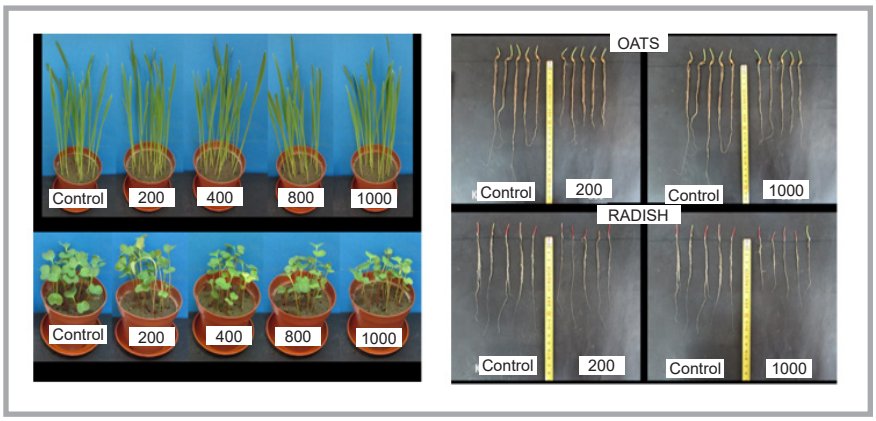

Figure 8. Photographic documentation of the assessment of phytotoxicity of granulated unmodified Q-Farin C1000.

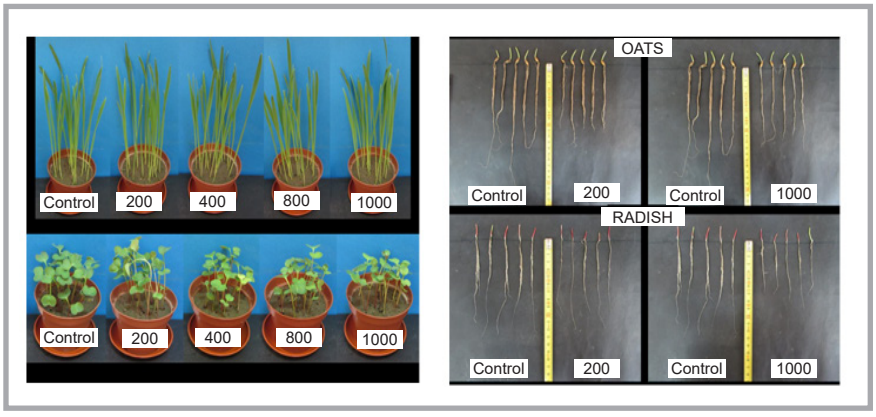

Figure 9. Photographic documentation of the assessment of phytotoxicity of film made of unmodified Q-Farin C1000.

Phytotoxicity assessment

Films obtained using the thermoplastic starch-protein material are provided to be widely used in agriculture and horticulture. They can be appied as mulch and starting material for the production of biodegradable seedling pots. Biodegradable pots are very useful in agriculture and wood nursery. They are applied in greenhouses for seedlings that after the initial growth period are replanted to the soil. Transplantation to the soil without the need to remove the pots is a valuable advantage of the biodegradable products which are put to decomposition in the soil. For these reasons, the materials developed were evaluated in terms of their phytotoxicity.

Phytotoxicity was tested for selected samples of the granulated starch raw materials and film cast from modified and unmodified functional flours of Q-Farin. Tests were conducted with monocotyledon- (oats) and dicotyledon (radish) plants. ***Table 5*** shows the impact of the concentration of the samples upon the sprouting and above-soil mass of radish seedlings. Changes in the main parameters of the phytotoxicity test for radish were observed when an exactly defined amount of the biopolymer material tested was admixed to the soil.

Table 6 presents results of the impact of the prepared samples concentration on the sprouting and mass of the above-soil part of oat seedlings.

Figures 7 - 9 present photographic documentation which shows the phytoxocicity in radish and oats after putting suitable amounts of the test material into the soil in mg/kg per dry mass. The sprouting and growth (fresh mass) of the seedlings was analysed. The development of roots was also observed.

The inhibition degree of the plants' sprouting and growth expressed by values of NOEC *(no effect of concentration observed) and* LOEC *(lowest effect of concentration observed)* for the sub-

Table 7. OEC & LOEC values calculated from the results of phytotoxicity examination.

Sample	OATS		RADISH	
	NOEC	LOEC	NOEC	LOEC
No 1	1000	-	200	400
No 2	800	1000	200	400
No 5	800	1000	200	400

stances tested are presented in ***Table 7***. More susceptible to the action of the substances tested was the plant from the dicotyledons family: radish *(Raphanus sativus)*.

The results obtained prove that the material tested in respect of phytotoxicity at a concentration of 200 - 1000 mg/kg of the dry soil mass exerts an evident influence on the sprouting and growth of both plants. A visible difference between the images of the plant was not observed. Neither growth inhibition nor chloro-or necrotic changes were noticed. Results of the phytotoxicity examinations are proof that the initial raw bio-material made of glycerol-plasticized Q-Farin C1000, and the film prototype made of it do not exert any toxicity upon higher land plants. The highest concentration of the samples tested which does not limit the sprouting and growth (NOEC) of oats remarkably is at the level of 400 and 800 mg/kg of the dry soil mass. Radish, which counts as a dicotyledon, is more sensitive to the action of the samples placed in the soil. Here the largest differences in the toxicity tests were observed at concentrations of 200 & 400 mg/kg of the dry soil mass.

Conclusions

The plastification of both unmodified and chemically modified functional flour calls for the use of proper plasticizers. The composition – modified material/ plasticizer requires thermal-pressure processing by extrusion.

Biopolymer compositions based on plasticized Q-Farin C1000 are suitable for processing by methods that are typical for classical resins i.e. extrusion moulding and film casting. Compositions which contain Q-Farin C 1000 esterified with acetic anhydride with a high substitution degree (SD $\geq$ 2.01) are insufficiently plasticized, thus causing high resistance in extrusion. Good rheological properties are characteristic of biopolymer compositions which contain glycerol and Q-Farin C1000 esterified by means of acetic anhydride to the substitution degree of SD = 0.7 and 0.9. Materials obtained from the chemically modified starch-protein raw material reveal lower hydrophylicity in comparison to the unmodified substance.

Examination of phytotoxicity and biodegradability showed that the materials tested made of plasticized starch-protein raw materials are readily susceptible to biodegradation and do not exert toxicity upon higher land plants.

Editorial notes

1) *Biodegradation was tested at the accredited laboratory of the Institute of Biopolymers and Chemical Fibers. Certificate; accreditation-AB 388*
2) *Microbiological testing was accomplished at the accredited microbiology laboratory of the Institute of Biopolymers and Chemical Fibers. (Certificate of accreditation- AB 388) according to the procedure: "Estimation of the total number of microorganisms in compost and soil".*
3) *Phytotoxicity was examined in accordance with 208 OECD GUIDELINES FOR THE TESTING OF CHEMICALS Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test and Standard PN-ISO 11269-2 titled: "Quality of soil. Estimation of the impact of impurities on the soil flora".*

The problems discussed in this article were presented on the 9th International Conferenceson Modification, Degradation andStabilisationof Polymers, Cracow 2016, Poland, by D. Ciechańska, L. Kaszuba, J. Kapuśniak H. Żakowska ('Innovative and Functional Products from Biopolymer Row Materials of the Grain-Mill Industry').

Acknowledgements

The research was conducted within the project: "Modification and Functionalization of Biopolymer Materials From Cereal Processing to Develop a new Generation of Biomaterials" No. PB1/A5/22/2012, co-financed by the National Centre of Research and Development within the framework of the 'Programme of Applied Research'.

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Received 15.11.2016 Reviewed 07.12.2016