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# Utilization of Cereal and Milling Industry Products as Raw Materials for the Manufacture of Biopolymer Technical Products

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**Abstract**
*The pressure which is being exerted on manufacturers by the users of consumer goods towards more environmentally friendly applications, favours the use of already existing environmentally friendly raw materials or the search for new ones. One of the promising directions for research is aimed at developing new packaging materials based on biopolymers. Research recently conducted made it possible to use hydrothermally pre-treated starch/protein raw material in the manufacture of a new generation of biopolymer materials. Biopolymer products obtained by various modifications were used to produce an exemplary batches of mouldings and packaging materials (films, corrugated cardboard).*

**Key words:** *cereal milling industry, functional biopolymers, bio-packaging materials, bio-thermoplastics, bio-adhesives.*

## Introduction

The recent development of knowledge concerning environmental protection has highlighted the possibility of negative impact of different products, including polymer products on the various components of the environment, should be considered throughout their whole life cycle. For this reason, the product design, manufacture, use and handling of wastes in accordance with the principles of sustainable development is of the utmost importance.

Many companies operating in the global market use standardized methods of life cycle assessment (LCA) in relation to their products while conducting research of technical and material solutions which could minimize the impact on the environment. LCA evaluation results may shape new product lines taking into account such factors as the sources of raw materials, their suitability for recycling, the use of recycled raw materials and reduction of the emission greenhouse gases (so called "carbon footprint" indicators), etc. [1]. For example, while considerations packaging materials, currently observed trends in environmental protection include the following:

- the search for alternative materials, in particular the use of raw materials derived from renewable sources,
- the use of recycled raw materials for production,
- the use of technologies of favorable "carbon footprint" indicators due to the greenhouse effect
- the use of biodegradable materials that meet the criteria for compostability, which allows for the waste composting and use of organic recycling [2, 3].

Already in the mid of 1990s, guided by the requirements of environmental protection, the implementation of innovative technologies for polymeric materials began based on renewable raw materials, as well as the implementation of production technologies for biodegradable plastics which, in accordance with the definition of the European Bioplastics Association are referred to as bioplastics [4].

Decreasing global petroleum resources have prompted scientists to search for alternative sources of materials. Among different research directions are performed of studies on the production technologies of biodegradable polymers that could replace conventional plastics. These materials should have similar utility and processability properties as the materials used so far. The new biopolymers should be used to produce packaging materials, which could be collected together with organic waste and undergo a process of composting or organic recycling in industrial installations [5, 6].

The main contractor for research which would lead to the development of innovative biopolymer packaging materials and adhesives was the Institute of Biopolymers and Chemical Fibres, Lodz, Poland. The other were asfollows: Jan Dlugosz University, Czestochowa, Poland, COBRO Packaging Research Institute, Warsaw, Poland and the industrial partner Lubella Ltd., Lublin, Poland - a producer of starch-protein raw material branded Q-Farin.

Among the raw materials supplied by the industrial partner and tested in the first stage of the study[I)] two types marked as Q-Farin C1000 & Q-Farin H501 were selected for further research. They consisted of hydrothermically modified flours obtained from wheat (*Triticum aestivum L.*) grains. The selection of the test materials resulted from their best properties in terms of susceptibility to chemical and biochemical modifications. It was also found that the powder form is more suitable for chemical and enzymatic modification than the granular form.

## The aim and scope of the study

The aim of the study was to produce innovative bioplastics for packaging purposes as well as adhesives applicable in the production of corrugated cardboard using as raw material hydrothermally pre-treated starch-protein material derived from the milling of cleaned wheat grains.

The complex study was to determine the characteristics of the starch-protein raw materials, prepare the initial assumptions for chemical and biochemical modification of the raw materials on a laboratory scale, upscale the process, produce a batch of modified starch-protein intermediates and determine their properties, evaluate the applicability of the biomaterials obtained for processing by injection moulding and extrusion, and for the preparation of biopolymer adhesives.

*Table 1. Yields and modification degrees of starch-protein raw materials*

| Modification method | Yield, % | Modification degree (DS/DO) | Maximum (theoretical) DS/DO [18] |
|---|---|---|---|
| 1 | 80 | DS = 0.38 - 2.45 | 3 |
| 2 | 80 | DS = 0.43 - 2.99 | 3 |
| 3 | 50 | DO = 1.00 - 35.5% | 56.3% |
| 4 | 98 | DS = 0.01 - 0.2 | 3 |

## Materials and analytical methods

The evaluation of physical-chemical properties of the starch-protein raw materials, modified intermediates, the experimental batches of biopolymer materials, as well as test method and equipment, and the reagents used were described Ed. notes I - IV.

## Results

In preliminary studies on the modification of starch contained in the starch-protein raw materials, characteristics of the raw materials and modified intermediates were determined. Results of these studies showed which types of raw materials offered by the industrial partner would be suitable for further modifications in terms of the processability and properties of the end products. Among the methods of modification tested the following methods were selected for tests on a large-laboratory scale (presented in ***Table 1***):

1. Sodium hydroxide-activated esterification of starch using acetic anhydride (Mark and Mehltretter) [7].
2. Potassium carbonate-activated esterification of starch using acetic anhydride (Volkert) [7].
3. Cu (II)-catalysed oxidation of hydroxyl groups in starch by hydrogen peroxide to carboxyl and/or aldehyde groups (Zhang et al.) [8 - 10].
4. Enzymatic esterification of starch by fatty acids using lipase as a biocatalyst [11, 12].

The results of the study on the modification of starch-protein raw materials are described in a series of papers published Ed. notes I, II. Moreover, the results of the study on the development new packaging biomaterials are described Ed. note IV.

The methods of starch modification selected on the basis of laboratory testing and the process assumptions developed were the basis for the upscaling and optimisation of the process. As a result of these studies, which types of modified intermediates would be suitable from the point of view of their processing properties were also determined. The yields and degrees of modification of the starch contained in the raw materials obtained (degree of substitution DS or degree of oxidation DO) are shown in ***Table 1***.

Upscaling of the laboratory process allowed to obtain experimental batches of biopolymer materials. It was found that in terms of suitability for processing into consumer products the best results were obtained for the intermediates produced by chemical modification (methods 1 and 2). Material also showed processing good suitability for obtained by enzymatic modification (method 4). It was also established that in view of material processability, the optimal degree of substitution DS should be about 0.7, while the degree of oxidation DO should be around 1.2. In the case of enzymatic modification the resultant degree of substitution DS does not affect the processing capability of the modified biopolymer. Examples of intermediates obtained in various modifications of starch-protein raw materials are shown in ***Figure 1***.

The quantities of intermediates produced were suitable to perform processing tests whereby functional products were obtained in the form of packaging foil, spatial forms, layered compositions and paper adhesives. A study on the intermediate processing was carried out on the basis of the available scientific literature [13 - 15].

The modified intermediates and products obtained were tested for the evaluation of their morphology, physical-chemical and metrological properties, susceptibility to biodegradation and structure. The study was performed in laboratories operating in accordance with the implemented quality management system and certified in Polish Centre for Accreditation (PCA) accreditation. The results obtained are described Ed. notes I - IV.

Production of packaging materials from modified starch-protein raw materials was evaluated in terms of the Life Cycle Assessment (LCA), "carbon footprint" philosophy and the market research aimed at bio-packaging materials and opportunities of implementation of technology developed.

### Study on the processing of selected compositions based on modified biopolymers

***Preparation of starch-protein films***

In order to give the starch compositions hydrophobic and thermoplastic properties they underwent physical modification by extrusion with the addition of glycerol as a plasticizer. A Plasti-Corder® 330 apparatus equipped with a single screw extruder and a slotted die head was used, and the following process parameters were applied:

- the temperature profile of the extruder: 125/125/140/140/135 °C,
- head dimensions: 100 mm orifice diameter 0.35 mm,
- temperature of leading drums: 80 °C,
- take up rate: 0.5 m/min.

The resulting semiproducts were used in further stages of research for producing biopolymer foils and moulded parts.


***Figure 1.*** *Intermediates obtained from modification of starch-protein raw materials: a) chemically esterified intermediate, Q-Farin C1000, DS = 0.7, b) oxidized intermediate Q-Farin C1000, DO = 1.2%, c) enzymatically esterified intermediate Q-Farin C1000, DS = 0.2.*

***Figure 2.*** *Plasti-Corder ® 330 apparatus with a single screw extruder.*

*Figure 3. Foil prepared from modified Q-Farin C1000 starch-protein raw material.*

The experimental setup for foil manufacture is presented in ***Figure 2*** and the foils prepared from modified Q-Farin C1000 starch-protein raw material are presented in ***Figure 3***.

***Preparation of starch-protein moulded parts***

Starch-protein moulded parts were produced using a laboratory injection moulding machine with extruder and temperature-controlled feed zone. The following process parametres were applied:

- screw L/D ratio: 28
- the temperature profile of the extruder: 145/145/150/150 °C,
- injection pressure: 800 kPa,
- injection time: 7 s,
- cooling time: 6 s.

The laboratory injection moulding machine is presented in ***Figure 4*** and the moulded parts prepared from modified Q-Farin C1000 starch-protein raw material are presented in ***Figure 5***.

***Production of functional bio-adhesives***

As part of the research the suitability of the modified biopolymer raw material for the production of functional adhesives for paper processing was determined. Research related to the use of modified biopolymers in the manufacture of a multilayer corrugated board (gluing the individual layers). The production of corrugated cardboard is carried out on special machines called corrugators. The industry uses corrugators of multiple construction solutions, the choice of which depends on, among others, the kind of cardboard manufactured, the feedstock and the cardboard application.

Basic operations during the manufacture of cardboard are:

- paper corrugation
- gluing a corrugated layer with one or two flat layers of liner
- drying the corrugated cardboard and its processing into the final product.

The properties of adhesives used to bind the layers of corrugated board should ensure the correct production process (adhesive application, layers bonding, drying, adhesion durability, use of high speed machines), the right quality of product (depending on the application), low production costs, and minimal environmental impact (recyclability of the products). As the result of research conducted within the framework of the research assumed the formulation of paper adhesive based on Q-Farin H501 was developed as a component used for the production of packaging complying with the requirements of sustainable development. In the first step, the properties of adhesives prepared with the Q-Farin starting material were examined in comparison with the commercial glue currently used.

In the second stage of the work, the new adhesive formulation was developed. Two-ply corrugated boards and a liner gluing tests, were performed using the model glue and Q-Farin H501-based glue. The three-ply boards produced using reference glue and the starch-based glue exhibited comparable properties. For cardboard obtained using Q-Farin H501-based adhesive as compared with that produced using the standard adhesive slightly higher values were observed for puncture resistance (2.64 vs 2.61 J), edgewise crush resistance (4605 vs. 4399 kN/m ) and the bond strength (0.590 vs. 0.504 kN/m). The burst strength was 491 and 542 kPa respectively for the cardboard glued using an adhesive the based on Q-Farin H501 and the reference glue. Physical-mechanical parameters of the corrugated cardboards obtained were evaluated and it was found that boards made with the use of Q-Farin H501-based glue have the same properties as those glued with commercial adhesive. It

***Figure 4.*** *Laboratory injection moulding machine with extruder unit and moulded specimens.*

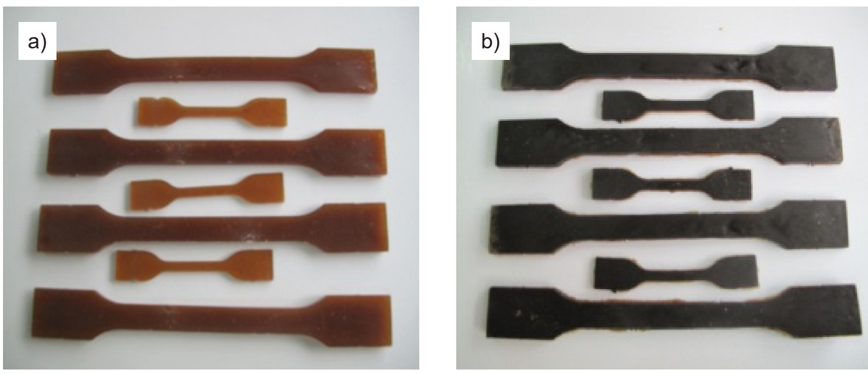


***Figure 5.*** *Injection moulded dumbbell specimens from Q-Farin C1000. A - unmodified, B - chemically modified.*

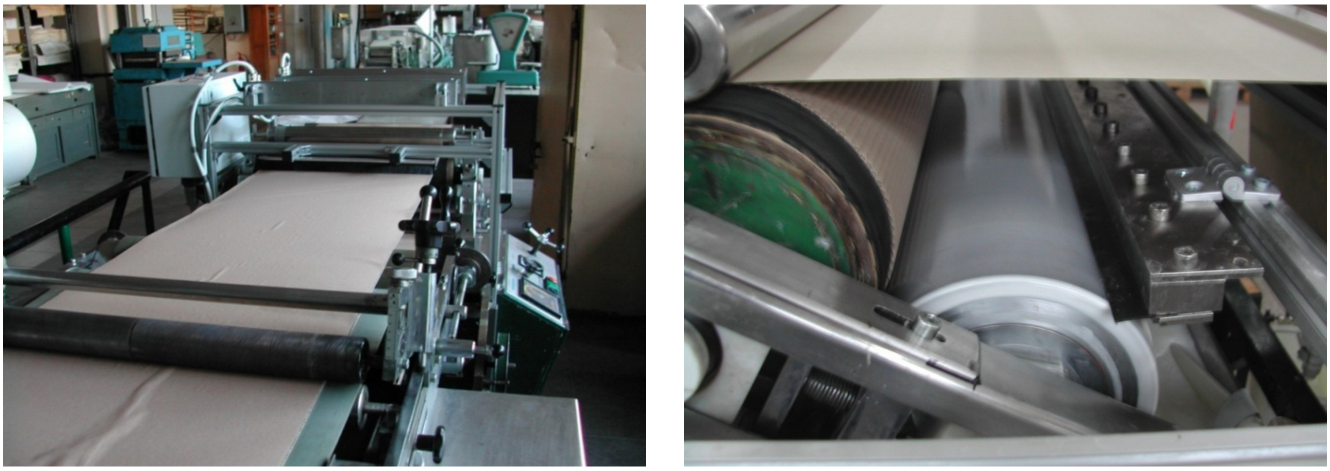

***Figure 6.*** *Experimental setup for the production of corrugated cardboard.*

seems that the adhesives based on functional flour Q-Farin H501 can replace those currently used in the production of corrugated cardboard. The experimental setup for the production of corrugated cardboard is presented in ***Figure 6***.

Samples of corrugated cardboard made with the use of the adhesives developed are presented in ***Figure 7***.

***Market research***

Global production of packaging products from biodegradable materials started in 1995 and since then it has constantly grown. According to European Bioplastics, the global consumption of biodegradable materials in 2007 - 2010 was estimated at 100 - 350 thousand tons. In the years 2013 - 2014 the production capacity increased to 600 thousand tons, and in the years 2017 - 2018 it is forecasted to exceed the level of 1 million tons. Biodegradable packaging concept means that its life cycle ends haveing the complete decomposition of the material by aerobic microorganisms (bacteria and fungi) and as a result of enzymatic reactions occurring in a specified period of time. The domestic market for biodegradable packaging is limited, thus market research conducted as a part of this study involved analysis of the use of new generation biomaterials developed in Polish companies and an inventory of their potential customers.


***Figure 7.*** *Samples of corrugated cardboard made with the use of the adhesives developed.*

The scope of the research included:
1. analysis of the market determinants for market research,
2. discussion of the potential of starch and other plant materials as a raw material for the use in the manufacture of packaging materials,
3. surveys of selected companies producing plastic packaging and enterprises using packaging materials,
4. questionnaire analysis including a database of companies interested in the potential use of innovative biomaterials,
5. analysis of the essential elements of the development of biodegradable packaging market.

The survey involved 91 domestic enterprises: 44% were medium enterprises, 31% - small enterprises and 25% were large enterprises, from which 49% were packaging manufacturers, 36% - packaging users and 14% were both packaging producers and users. Among the respondents, the greatest interest in the new generation of biomaterials was shown by manufacturers of plastic packaging materials, who could possibly be potential recipients of new packaging manufactured on the basis of functional flour Q-Farin. ***Figure 8*** represents the level of interest of the respondents in the introduction of materials of vegetable origin to the market.

Currently, 11% of Polish companies use biodegradable polymers or packaging, 56% declares the introduction of such products in the future, and only 5% intends to use none of them. The reasons affecting application by domestic enterprises of biodegradable polymers in the production of innovative packaging were: price, properties, availability, marketing strategy, regulations, environmental awareness, processing knowledge and implementation of post-consumer packaging collection. The analysis of companies involved in the production of packaging showed that the majority of Polish companies plan to launch a new generation of multi-functional packaging, and only 5% of the respondents completely exclude such action.

***Life cycle assessment and „carbon footprint"***

Life Cycle Assessment was performed using the specialized software - SimaPro which meets the guidelines of Standard PN-EN ISO 14040 [16] using the ReCiPe Endpoint (H) method which is recommended for use in Europe. LCA studies were performed for two representative biopolymer materials: Q-Farin C1000 and Q-Farin H501. Based on the results obtained, it was demonstrated that the greatest environmental effect involved in the production of materials beginning to be used is for wheat flour. According to the method applied, the share of the primary raw material (wheat flour) in all impact categories for Q-Farin H501 and Q-Farin C1000 amounted up to 92.3% and 85.5%, respectively. Other environmental effect

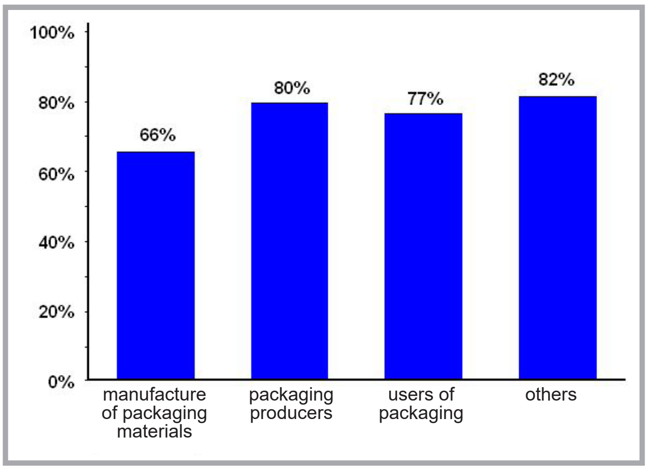


*Figure 8. The percentage of positive responses (rather yes and definitely yes) to the question about increasing the market share of materials of plant origin.*

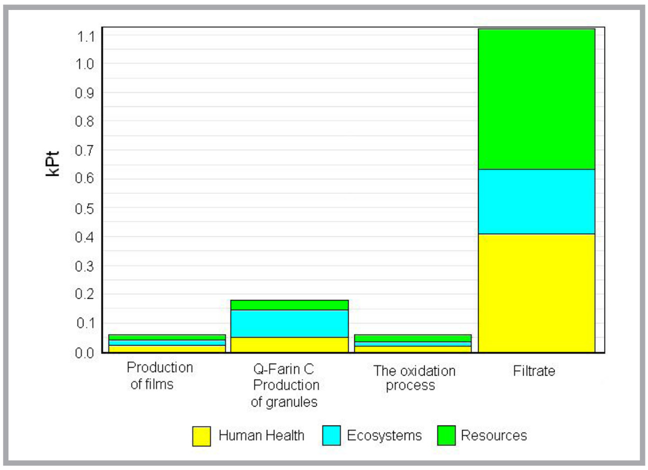


*Figure 10. The shares of individual categories of environmental impact for the production of 1 ton of Q-Farin C-based foil.*

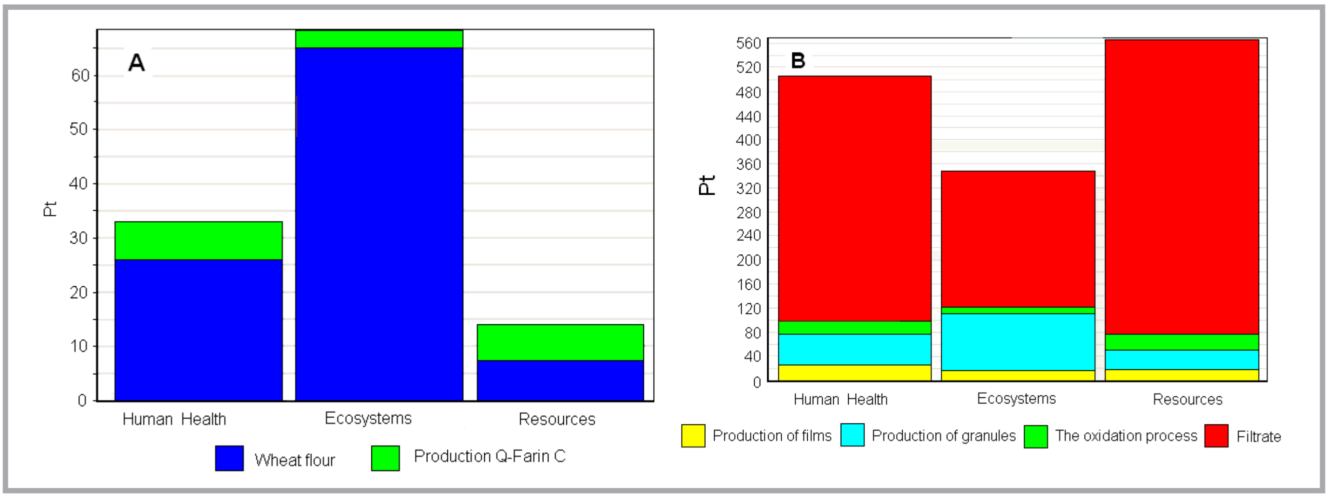


*Figure 9. The shares of individual categories of environmental impact for (A) the production of 1 ton of Q-Farin C and (B) for processing Q-Farin C into pellets and foils.*

result from the production process of the material and, in particular, the hydrothermal treatment process (the significant use of gas and electricity). The most important factor according to the weighted average in the ReCiPe method is the environmental impact related to the use of agricultural land. This impact category is strongly connected with the cultivation of crops, including wheat. Comparative analysis for the production of 1 ton of Q-Farin C1000 and Q-Farin H-501 showed no significant differences in the results obtained, which was due to impact category assessment of the use of agricultural land, which for both types of Q-Farin are virtually identical. Slight differences in other categories influence the result of the technological processes for obtaining these materials.

Foils made from chemically modified flour Q-Farin C1000 were characterized by advanced and complex process modifications. These processes, in the ReCiPe method, accounted for over 83% of the environmental impact associated with the production of the foil. In the modification of the starch method by oxidation, the largest share of the environmental impact was associated with the filtrate resulting from washing operations of the biopolymer materials. The use of glycerol necessary to produce biopolymer pellets as an intermediate for foil production amounted up to 8.2% of the environmental impact. In the foil manufacture from chemically esterified Q-Farin C1000 the most environmentally aggravating step was the use of acetic anhydride in the modification step. The environmental impact resulting from acetic anhydride application amounted to 72% of all environmental impacts related to the production of foils.

Examples of environmental impacts related to individual categories are illustrated ***Figure 9***. ***Figure 9*** shows the shares of the environmental impact for the production of one ton of raw material Q-Farin C and processing it into pellets and foils, ***Figure 10*** presents shares of the environmental impact which is a part, for the production of one ton of Q-Farinu C-based foil.

Comparative analysis performed for the film produced from unmodified Q-Farin C1000 showed that elimination of the complex process of chemical modification significantly increases the environmental impact of glycerol used in the preparation of pellets. In this case the Q-Farin share of the environmental impact amounts to 27%, whereas the effect of glycerin is increased by 10%.

The analysis performed showed that for the preparation of 1 ton of Q-Farin H501-based, the carbon footprint amounts to 169 kg of carbon dioxide equivalent

(CDE), which results from the difference in the values relating to the adhesive and Q-Farin raw material, (CDE 579 kg) and is directly related to the amount of water used to prepare the adhesive. In the manufacture of foils from unmodified Q-Farin C1000, the carbon footprint, expressed in CDE, was 2338 kg. Esterification of Q-Farin caused an increase in CDE to a value of 14894 kg. In turn, the oxidation of starch-protein raw material Q-Farin resulted in an increase in the CDE to a value of 11232 kg. The higher, compared to the manufacture of films from unmodified Q-Farin, carbon footprint results from the complicated modification process, high impact of large amounts of modifying substances used, pellet production granules, and the foil itself. Among the components of the carbon footprint indicator, expressed in CDE, for the foil made of the modified biopolymer material, the largest share was for carbon dioxide coming from fossil and renewable sources and for nitrous oxide, resulting directly from the environmental impact of the filtrate, acetic anhydride and glycerol. In the case of the film obtained from the unmodified biopolymer (only after the initial hydrothermal modification), the largest share of carbon dioxide equivalent in the carbon footprint was from the fossil part, directly resulting from the environmental impact for the production of glycerol and foil.

## Summary

As a result of the study, optimum parameters for producing starch-protein Q-Farin raw materials from wheat were determined. Optimal products of industrial hydrothermal pre-modification were selected for further study. It was concluded that the optimal raw material for chemical and biochemical modification is Q-Farin C1000. This product was used in further research to produce new biodegradable multi-functional packaging materials. It was also concluded that for the preparation of paper adhesives which can be used in the production of corrugated cardboard the most suitable product is Q-Farin H501. Tests performed on a laboratory scale allowed to select methods of chemical and biochemical modifications and also enabled the adoption of the initial assumptions for process upscaling to a large laboratory scale. Within the study the modification processes were optimized and experimental batches of biopolymer materials were prepared in quantities that allowed to check their suitability for the preparation of new generation packaging materials. The biopolymers produced were also tested for their possible use in the production of corrugated cardboard. As part of the research work, technological conditions for the processing of selected thermoplastic compositions developed and demonstration batches of packaging materials were produced. The technologies developed were assessed at the level of technology readiness of TRL 6 relating to the demonstration prototype or model of the system/subsystem technology under realistic conditions. The suitability of selected Q-Farin H501 modified raw material for the production of functional bioadhesives for binding corrugated board was also assessed. In the study the formulation of biopolymer-based paper adhesives was developed. The adhesives prepared were tested in the production of three-ply corrugated cardboard by gluing a two-ply corrugated board and a liner.

## Editorial note

The following articles related to the present review are published in Fibres & Textiles in Eastern Europe (No 6, 2016):

I. Ciechańska D., Kapuśniak J., Kaszuba L, Miecpliński M, Siemion P., Roczkowska M., Arkadiusz Żarski A, Ptak S, Gutowska A.: „Investigation on the Structure and Properties of Modified Products from the Grain-Mill Industry for Use in the Preparation of Biopolymer Technical Materials"
II. Wietecha J., Kazimierczak J., Pałys B., Gutowska A.: „Enzymatic Modification of Starch-protein Raw Material by *Candida antarctica lipase*"
III. Janiga M., Stufka-Olczyk J., Milczarek A., Michniewicz M., Ciechańska D., Tomaszewski W., Gutowska A., Kapusniak J.: „Chemical Modification of Starch--Protein Material Performed in order to Obtain a Half Product for Thermoplastic Processing"
IV. Sulak K., Gutowska A., Pałys B., Rychter P.: „Heat Plasticization of Functional Wheat Flour by Extrusion in the Presence of Plasticizers"

The problems discussed in this article were presented on the Pomerania - Plast 2016 Conference 'Polymer Materials' Międzyzdroje, Poland.

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