Effect of Grain Husk Microfibers on Physicochemical Properties of Carboxymethyl Polysaccharides-Based Composite

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Abstract
Preparation of the novel biodegradable composites based on carboxymethylated starch and cellulose matrix containing plant fillers has been described. Adding the natural filler into polysaccharide derivatives allows remaining the biodegradable character of the final composite. As a filler milled cereal husks of various origins: rye, spelt, and rice were used. Rye and spelt fillers have not been used in biocomposite materials so far. Additionally, softwood flour was used for comparison. The grain husks are the waste products, and could be an alternative for popular wood fibers preserving wood resources. Introducing natural filler beneficially affected the mechanical parameters of the CMS/CMC system, as moisture absorption, as well as solubility in water decreased (e.g. by ca. 7% and 6%, respectively for CMS/CMC with rice husk filler when compared to the neat system). Moreover, the mechanical properties, i.e. Young’s modulus, and tensile strength increased. The chemical composition and size of natural fillers are essential factors determining the physicochemical properties of obtained composites, and cereal husks are promising raw materials for filling hydrophilic polysaccharide matrices. The obtained composites met the sustainability requirements as they were made from renewable resources, contributing to a lower environmental footprint.

Keywords Carboxymethyl cellulose · Carboxymethyl starch · Grain husk filler · Microfibers

Introduction
In the twentieth century, many composite systems were based on petroleum-origin components. In the twenty-first century, along with public awareness, great emphasis was placed on the development of biodegradable materials. The composites based on polysaccharide derivatives containing biodegradable fillers may be an alternative to conventional composites [1–4]. Polysaccharides (i.e. cellulose, starch) are widely used in food industry, but also in medical, pharmaceutical, and paper, as well as in coating industries. Chemical modification of polysaccharides widens the areas of their application. Starch and cellulose as renewable, inexpensive, and relatively easy to modification natural polymers, that seem to be the promising raw materials for the biodegradable composite formulations [1–4]. The etherification of starch and cellulose allows to obtain carboxymethyl derivatives which—unlike native polymers—are soluble in cold water. The physicochemical properties of carboxymethyl starch (CMS) and carboxymethyl cellulose (CMC), such as the dissolution rate and viscosity of aqueous solutions, depend greatly on the degree of substitution (DS, average number of substituted hydroxyl groups in the polysaccharide repetitive unit) and their molecular weight [5]. The carboxymethyl derivatives of starch and cellulose have been successfully used for film preparation [3, 6–10].

Introducing filler into the polymer matrix is one of the most common methods of material modification. The compatibility between filler and matrix is essential for effective reinforcement. Adding the natural filler into polysaccharide derivatives allows remaining the biodegradable character of the final composite.

In this paper, the milled cereal husks as the fillers for polysaccharide derivatives-based matrix were proposed. The grain husks are the waste products of food processing (milling). They are available on an annual basis, and could be an alternative for popular wood fibers preserving wood resources [11]. The chemical composition of plant husks depends on their botanical origin, but they contain mostly...
cellulose, hemicellulose, and lignin. In the field of interest are the husks of rye, rice, barley, spelt, coconut, and corncobs. Relatively often plant husks were used for the preparation of nano- or micro-size cellulose crystals [12, 13], however, these methods were cost and time-consuming. Interestingly, unmodified rice husks were used as a macro-filler for cassava starch-based foams for packaging [14]. The other approach was using plant husks for obtaining natural fibers, e.g. corn [15], rice [16–19], brewery spent grain [20], or coffee husks [18] (interestingly, using rye and spelt-based fillers in the composite systems has not been often reported). Subsequently, such biodegradable fillers were applied mainly for thermoplastic starch-based composites [16, 21–23]. Generally, introducing plant fibers resulted in the composite reinforcement effect.

There are many reports on using cereal husks for composites based on synthetic polymers (PE, PP) [11, 24–27]. For nonpolar polymers, enzymatic treatment of plant husks could be beneficial (allowed to remove starch and protein residue) [26]. However, the authors are not familiar with the reports on using milled cereal husks as a reinforcement for carboxymethylated polysaccharide-based material.

The most popular plant filler used both: for biopolymers (e.g. thermoplastic starch [28–31]) and synthetic polymers (e.g. polyolefin [24–27]) was wood flour. It was commercially produced from post-industrial sources such as shavings and sawdust [11]. The scrap wood was sourced for species purity and then grounded to specific particle size distributions. It could be used as a reference for composites containing other plant fillers.

In this paper novel polysaccharide derivatives-based composites were prepared using CMS/CMC matrix and milled cereal husks fillers of various origins: rye, spelt, and rice. Rye and spelt fillers have not been used in biocomposite materials so far. Additionally, the most popular plant filler, i.e. softwood flour was used for comparison. The effect of the polymer matrix, as well as filler type on the physicochemical properties (i.e. moisture absorption, solubility in water, thermal and mechanical properties) of the obtained biodegradable composite films, have been determined.

### Experimental Methods

#### Materials

The potato starch (S) was a product of Nowamyl S.A., Poland. Carboxymethyl cellulose (DS: 0.7, Pollocel AS-2/90) was purchased from Pronicel Sp. o.o. (Poland). Sodium hydroxide (p.a.), chloroacetic acid (p.a.), 2-propanol (p.a.), monohydrate citric acid (CA) (p.a.), copper sulfate pentahydrate, and glycerol (p.a.) were purchased from Chempur, Poland. Murexide and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) were the products of Sigma-Aldrich (Germany). The natural fillers were prepared at the Institute für Lebensmittel und Umweltforschung, Potsdam, Germany, by conditioning and milling spelt, rice husks, and rye brans into particles size smaller than 600 μm. Microfibers made of the industrial-grade softwood flour Jeluxyl Weho500 by Jeluwerk, Germany were used. In Fig. 1 the chemical composition of the fillers was presented.

To determine the cellulose, hemicellulose, and lignin content the neutral detergent dietary fiber (NDF), acid detergent dietary fiber (ADF), and acid detergent lignin (ADL) contents were measured using the method described by Van Soest et al. [32]. The method relied on the application of the alpha-amylase, in order to starch degradation. Dietary fiber was isolated using detergent solutions of acidic, and neutral pH. Hot extractions were performed on a Fibertec apparatus produced by Foss Tecator (Sweden). The hemicellulose fraction was calculated on the basis of the NDF and ADF difference, while the cellulose fraction was calculated using the difference between ADF and ADL.

Starch content was determined according to standard PN-R-64785:1994. This method relied on the dissolution of

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**Fig. 1** The chemical compositions of natural fibers [26, 27]
a sample material using hydrochloric acid and measuring the specific rotation of light in clear extract using polarimeter.

Protein content was determined using the Kjeldahl method, which involved the samples’ mineralization with concentrated sulphuric acid. Subsequently, the amount of ammonia produced in the reaction was measured. To convert the nitrogen content to the protein content, the factor 6.25 was applied in accordance with PN-EN ISO 20483. This was carried out on a Kjeltec device setup by Foss Tecator (Sweden).

**CMS Preparation**

The synthesis of carboxymethyl starch was carried out using the one-step method [33]. In the glass reactor, monochloroacetic acid (35 g) and isopropanol (200 ml) were placed (nitrogen atmosphere), after which the acid was neutralized with an aqueous solution of sodium hydroxide in a molar ratio of 1:1. When the color of reactor content turned opaque white, the system was stirred for 10 min, and subsequently, starch (30 g) and remaining hydroxide were added. The reaction was carried for 2.5 h at 50 °C. Then the mixture was neutralized to pH 6. The product was filtered under reduced pressure and washed five times with 80% methanol solution, and the last one with undiluted methanol. The carboxymethyl starch with a degree of substitution of 0.70 was obtained. DS was measured according to the method described by Kessel [34]. The CMS sample was moisturized by 1 ml of ethanol and dissolved in 50 ml of distilled water. Subsequently, the buffer was added (NH₄Cl aqueous solution, 20 ml), neutral pH was adjusted, and then the whole mixture was poured into a measuring flask (250 ml) with 50 ml of CuSO₄ solution. After 15 min, the measuring flask was filled up with water and the whole content was filtered. The filtrate was titrated with EDTA solution using murexide as an indicator.

**Preparation of Polysaccharide Composites with Plant Fillers**

The CMS/CMC films filled with plant filler were prepared as followed: the aqueous (100 ml) dispersion of plant filler (7 wt.% on a basis of total dry polysaccharide derivatives weight) was prepared and stirred for 30 min at room temperature. Then the 3 g polysaccharide derivatives (CMS/CMC dry mixture 50/50 wt.%) and 2 g glycerol were added to this dispersion and stirred for 30 min. Subsequently, 2 g citric acid was added and mixed until homogeneity. Then the system was poured into PTFE molds (10×10 cm) and placed in a dryer for 48 h at 60 °C. The obtained films (thickness 200–300 μm) were removed from the mold and tested.

**Characterization**

The size, surface morphology, and size distribution of natural fillers were determined using natural fillers were determined using scanning laser microscope KEYENCE, model VK-9700 with equipped with VK Analyzer software.

The FTIR analyses of the natural fillers were performed in Nexus FTIR Spectrometer Thermo Nicolet with Golden Gate ATR attachment. The resulting spectra were converted using the software OMNIC.

The solubility in water of the composites were performed as followed. Three samples (1.5×1.5 cm) were cut from the film and placed in a desiccator to remove moisture (to steady-state). The samples were then weighed, placed in vials, and filled with 50 ml distilled water. After 24 h the samples were removed and dried for about 24 h (60 °C) to steady-state. The dry samples were again weighed. The solubility in water (after 24 h immersion) values were calculated using the following formula [4]:

\[
TSM = \left[ \frac{(M_1 - M_2)}{M_1} \right] \times 100\%
\]

where: TSM (Total Soluble Mater)—solubility in water [%]; M₁—mass of the dry sample [g]; M₂—mass of the sample after drying [g].

For moisture absorption tests of obtained composites, three samples (1.5×1.5 cm) were cut from the film and placed in a desiccator to remove moisture (to steady-state). The samples were then weighed, and placed in a climate chamber (humidity 55 ± 2%, temperature 25 ± 2 °C). The samples were weighed 3, 5, 7, 24, 48, and 72 h after being placed in the climatic chamber. The results obtained in this way were substituted for the formula [7]:

\[
A_t = \left[ \frac{(M_t - M_0)}{M_0} \right] \times 100\%
\]

where: \(A_t\)—sorption of moisture after time t [%]; M₀—mass of the dry sample [g]; Mₜ—sample mass after t time: 3, 5, 7, 24, 48 and 72 h [g].

Tensile strength of the composite films was tested using the INSTRON testing machine equipped with a 1 kN load cell, according to PN-EN ISO 527-3 standard. The initial length of the sample was 100 mm, 10 mm wide, and about 0.2 mm thick. The initial grip separation and cross-head speed were 50 mm and 10 mm/min, respectively. Seven samples of one material type were tested.

Thermal analysis of composites was carried out using the DMTA Q800 (TA Instruments) apparatus in the temperature range – 30–180 °C with a heating rate of 3 °C/min and an amplitude of 15 μm.
Results and Discussion

Plant Fillers

The morphology of plant fillers performed by laser scanning microscopy were presented in Fig. 2. The softwood and spelt fillers exhibited visibly elongated character, whereas rice, and rye fillers were rather irregular. A statistical analysis of LSM images allowed to evaluate the average particle size and aspect ratio of natural fillers, the results were collected in Table 1. It was revealed that softwood and spelt particles exhibited the highest size and aspect ratio (> 270 μm, and > 2.7, respectively). The rye and rice fillers exhibited significantly lower average size (up to ca. 80 μm) and aspect ratio below ca. 2. Thus, bearing in mind the aspect ratio, the applied fillers could be considered as microfibers.

In Fig. 3 the FTIR spectra of plant fillers were presented. For all the plant fillers the absorption bands characteristic...
for starch and cellulose could be observed: the broad band between 3600 and 3000/cm assigned to OH stretching (due to hydrogen bonding involving hydroxyl groups on the starch molecules), and at 2900/cm to CH symmetrical stretching vibrations. The band at ca. 1000/cm is assigned to C-O stretching vibrations, whereas the bands in a range 1650–1750/cm to carbonyls [20]. For the materials with high lignin content, the absorption bands assigned to aromatic rings could be observed at ca. 800/cm. Interestingly, for rice filler an intensive band at ca. 490/cm could be noticed, that could be assigned to the presence of inorganic matter associated with high ash content (Fig. 1) [26]. The band in this area was also noticeable for spelt.

### CMS/CMC Composite Films with Plant Fillers

In Fig. 4 the FTIR spectra of citric acid, neat CMS, and CMC, as well as CMS/CMC film were collected. For unmodified CMS, and unmodified CMC the absorption band between 3600 and 3000/cm, and at 2900/cm could be attributed to hydroxyl groups and to CH stretching vibrations, respectively. The strong peaks at 1415, and 1315/cm were assigned to CH2 scissoring and OH bending vibrations, and at 1060/cm to ether groups, respectively [5, 6]. Protonated carboxylic groups (CA) give a C–O band at about 1700/cm, whereas carboxylate (COO−) of neat CMS and unmodified CMC give strong absorption band at about

| Filler  | Average length [μm] | Aspect ratio (l/d) |
|---------|---------------------|-------------------|
| Rye     | 84 ± 5              | 1.80 ± 0.31       |
| Rice    | 52 ± 3              | 2.03 ± 0.61       |
| Spelt   | 271 ± 21            | 2.71 ± 0.56       |
| Softwood| 293 ± 25            | 2.93 ± 0.64       |

![Fig. 3 FTIR spectra of plant fillers](image-url)
1600/cm [35], however in case of CMS/CMC films the carbonyl group bands are observed at 1720/cm indicating chemical linkages between polysaccharide derivatives and citric acid (crosslinking agent) via ester bonds.

In Fig. 5 the moisture absorption of CMS/CMC composite films containing 7 wt.% of plant filler were presented. Water absorption depends on filler-matrix interphase as well as filler hydrophilic/hydrophobic character [36]. For polyolefin-based composites, it was reported that wood fibers were primarily responsible for water absorption [37]. However, in the case of CMS/CMC-based composites, it was also associated with the type of raw material (i.e. strongly hydrophilic) used for the formation of the polymer matrix. Introducing plant filler resulted in a reduction of moisture absorption of all CMS/CMC composite films. Similar observations were reported for thermoplastic starch composites containing cellulose microfibrils and were attributed to the interactions between fibers and the hydrophilic sites of starch chain, which substituted the starch–water interactions that predominate in films without fibers [38, 39]. However, in the case of rye filler, the moisture absorption decrease was rather low (ca. 2%) when compared to other filler types when the decrease was in a range of 5–7% (after 72 h).

Moisture is mainly absorbed by starch, hemicellulose, and non-crystal cellulose on the microfiber surface [11]. Thus, the probable reason for that was the composition of rye filler, i.e. high starch content (ca. 28%, whereas for others it did not exceed 5%), and hemicellulose (ca. 18%) as well as low lignin content (ca. 4%, and > 12, respectively). Starch exhibits a strongly hydrophilic character—higher than cellulose where the hydrogen bonds hinder the penetration of water molecules into the fibrous structure of the filler [6]—in Fig. 3 the presence of OH groups in fillers’ structure was observed. The formation of hydrogen bonds between COOH and OH groups of biopolymer matrix (starch and CMC) and OH of filler was reported [9]. The results are consistent with the reports on thermoplastic starch-containing wood flour [36].
Solubility in water of CMS/CMC based composites containing various plant origin fillers was collected in Fig. 6. The composite films after solubility test maintained their integrity and did not break apart. That indirectly indicates the successful crosslinking reaction of the polymer matrix. The presence of the filler reduced the solubility of the composite in water. The lowest values of this parameter were recorded for foil filled with softwood, and rice (ca. 57%). The general trend correlates to absorption moisture measurements result, i.e. the composite systems with higher cellulose and lignin content exhibited reduced solubility in water. Similar results, i.e. reduction of solubility in water after wood fiber addition was reported for chayotexile starch-based foams [29, 40]. Such a phenomena were observed also for starch/CMC composites with nanoclay [9], where the cohesiveness of biopolymer matrix was reported as a result of hydrogen bonds formed between hydroxyl and carboxyl groups in biopolymers and OH groups of the filler.

In Fig. 7 the mechanical parameters: elongation at break, Young’s modulus, and tensile strength of the composites based on CMS/CMC containing various plant origin filler have been collected. Adding the plant filler resulted in enhanced mechanical performance of composite: increased tensile strength and Young’s modulus, with elongation at break reduction. The plant fibrous act as mechanical reinforcement of CMS/CMC attributed to well-formed interfacial interaction between the filler and polysaccharide matrix allowing stress transfer from the matrix to the filler [36]. Moreover, reduction of the material flexibility could have occurred due to the formation of the hydrogen bonds between the hydroxyl and carboxyl groups of CMS/CMC and natural particles [9, 41]. Additionally, limiting mobility of CMS and CMC chains could also be affected by crosslinking with CA. These observations strongly correlate with the moisture absorption and solubility in water results.

The highest tensile strength value (ca. 18 MPa) was noted for the composite containing rice fillers. Generally, it could be observed that a higher reinforcing effect was noted for the composites containing smaller particles (rye and rice). The mechanical properties of composites strongly depend on the diameter of the particles [42]. Above a certain diameter value, the possibility of the surface defect and microcracks occur reducing the possibilities of efficient reinforcement [42]. A similar trend, i.e. enhanced mechanical properties with plant fibers addition was observed for the thermoplastic starch-based systems containing walnut [36] or banana leaf fibers [43]. Introducing rice husk filler into thermoplastic starch also resulted in tensile strength increase and reduction of elongation at break [18].

The DMTA measurements were performed to evaluate the loss factor (tan δ) as a function of temperature for
CMS/CMC based composites. The loss factor is sensitive to molecular motion and its peak relates to the glass transition temperature [44]. All the curves of CMS/CMC based composites revealed one broad transition at ca. 40 °C indicating good compatibility between the polymer matrix and the fillers (no phase separation)—Fig. 8. From the chemical point of view, polysaccharide, i.e. cellulose or starch (for rye) is the dominant compound in the fillers, thus compatibility with starch and cellulose derivatives-based matrix is apparent. The Tg noted for the neat CMS/CMC system was 28.4 °C. Introducing natural filler resulted in a slight Tg increase, indicating lowered chain mobility [45] which could be the result of hydrogen bonds formed between hydroxyl and carboxylic groups of CMS/CMC and fillers [9]. However, the value of Tg for all the samples tested was in a narrow range ca. 33—38 °C, which suggested that the filler type had a slight influence on the transition maxima of the composite. Referring to the research carried out on the effect of microcellulose on the thermal transformation of polysaccharide systems, the results are analogous [7, 22].

Conclusions

The novel composites based on CMS/CMC system containing milled cereal husks fillers of various origins: rye, spelt, and rice, as well as softwood flour, have been prepared. Rye and spelt fillers have not been used in biocomposite materials so far. Introducing natural filler beneficially affected the mechanical parameters of the CMS/CMC system, as moisture absorption, as well as solubility in water decreased (e.g. by ca. 7% and 6%, respectively for CMS/CMC with rice husk filler when compared to the neat system). Moreover, the mechanical properties, i.e. Young’s modulus, and tensile strength increased.

It seems that the chemical composition and size of natural fillers are essential factors determining the physicochemical properties of obtained composites.

Bearing the above in mind it could be concluded that cereal husks are promising raw materials for loading into hydrophilic polysaccharide matrices. Moreover, the obtained composites met the sustainability requirements as they were made from renewable resources, contributing to a lower environmental footprint.

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Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.
Consent for Publication
The authors declare consent for publication.

Declarations

Conflict of interest Authors declare that they have no conflict of interest to disclose.

Ethical Approval Not applicable.

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