Composites containing acetylated wheat B-starch for agriculture applications

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ABSTRACT

Native and acetylated B-starch was used in biodegradable films after blending with either poly-(ε-caprolactone) (PCL) or ethylene vinyl acetate copolymer (EVA). The following mechanical characteristics of prepared films were derived from the stress-strain curves: Young modulus, yield stress, stress-at-break and strain-at-break. Acetylation of starch molecules in the composites reduced the degradation rate in compost. Optical microscopy, combined with the image analysis system NIS-Elements completed with extended depth of focus (EDF) module, was used to study the PCL/starch and EVA/starch films surface morphology during composting. Parameters of the compost used for film exposition were measured.

Keywords: biodegradable plastic; polycaprolactone; ethylene vinyl acetate copolymer; image analysis; green waste compost

Wheat starch has two different types of granules: so-called 'A-starch' and 'B-starch'. A-starch has a larger type of granules (20–30 μm across) and is of lenticular shape. Smaller B-starch spherical granules are 2–8 μm in diameter. Industrially produced B-starch (with higher concentration of proteins, lipids and pentosans) is of lower quality and therefore it is usually used as a cattle feed, as a milk replacer in calf feeds, as a core binder in the foundry industry and in corrugated boards, or as a source for ethanol production (Šárka and Bubník 2010). Challenges for other uses of B-starch were taken up in designs of new technological processes.

Biopolymers based on starch are abundant, inexpensive, renewable, and also biodegradable. In some instances their mechanical properties are relatively poor compared to many petroleum-based plastics due to inherent lower stiffness and strength. Many of them are relatively sensitive to water, with some materials dissolving rapidly and others experiencing a substantial decrease in mechanical strength when they absorb water, especially in moist environment. Starch acetates undergo slower degradation and swelling than native starch. Fringant et al. (1998) used acetylated starch with a degree of substitution (DS) of 3 to improve the resistance of biodegradable materials to moisture. The kinetic measurement of B-starch acetylation and properties of the highly acetylated starch were published earlier (Šárka et al. 2010).

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Poly-(ε-caprolactone) (PCL) is a synthetic polyester with good mechanical properties and is one of the most hydrophobic biodegradable polymers currently available. Ethylene vinyl acetate (EVA) is a copolymer of ethylene and vinyl acetate that approaches elastomeric materials in softness and flexibility. The material has good clarity and gloss, barrier properties, low-temperature toughness, stress-crack resistance, hot-melt adhesive waterproof properties, and resistance to UV radiation. Copolymers of ethylene combined with vinyl acetate were generally used for mulching.

Except poor water resistance, low strength is a limiting factor for the use of materials manufactured from starch. According to Koenig and Huang (1995), blending any kind of starch with PCL increases the modulus and decreases the overall strength compared to the polymer before blending. The biodegradation of PCL/starch compositions begins with starch consumption and continuously increases with the content in natural filler (Singh et al. 2003). According to Bhattacharya (1998), EVA/starch blends display properties similar to rubbery polymer. The modulus of the blends increases as the starch content increases. Swelling in water and water absorption increases with the content of the vinyl acetate group in copolymer macromolecules and starch content in polymer blends. The addition of potato starch to EVA copolymers promotes the biodegradability of polymer blends that might be used for the production of biodegradable materials (Lim et al. 1999).

The aim of the research was to test mechanical characteristics and biodegradability of prepared films based on PCL or EVA and small wheat starch granules. Changes in the compost used for film exposition were measured.

MATERIAL AND METHODS

91.3% of dried wheat B-starch 'Soltex P6' of dry matter (DM) and of mean average diameter 5.9 μm was provided by the Amylon Havlíčkův Brod starch company (Czech Republic). Laboratory preparation of acetylated starch with a high degree of substitution (DS) proceeded at 115–130°C as described earlier (Šárka et al. 2010, 2011).

Commercial grade PCL CAPA 6800 (Perstorp UK Ltd., Warrington, UK) has average molecular weight 80 000, the melt flow index 3 g/10 min (2.16 kg, 160°C) and melting point ranged from 58–60°C.

EVA copolymer resin Escorene Ultra UL04533CC (ExxonMobil Chemical Co., Houston, USA) with 33% wt. of vinyl acetate content and melt index 45 g/10 min (measured at 160°C and 2.16 kg load) was used in combination with native and acetylated starch.

Sample preparation and testing. The composites were prepared by mixing in the melt of the PCL or EVA with 10, 20 and 40% wt. of starch fillers in the W50EHT mixer (Plasti-Corder, Brabender, Duisburg, Germany) at 110°C and at 60 rotations/min for 8 min. Loading of mixer was 54 g. The material removed from the chamber was immediately compression-molded to form 0.5 mm thick films. For tensile testing, the flat shoulder specimens (type 5 – ISO 527 standard) were die-stamped from the compression-moulded films. Tensile tests were performed using an Instron 5800 tensile tester at room temperature and a crosshead speed of 50 mm/min. The following mechanical characteristics were derived from the stress-strain diagrams: Young modulus (E), yield stress (σ_y), stress-at-break (σ_b), and strain-at-break (ε_b). The reported values are averages of at least 5 measurements.

Film incubation in green waste compost. Two composting bins AL-KO K390 (KOBER Ltd., Vrbno pod Pradědem, Czech Republic) were filled with two-year old compost prepared from green municipal waste, white high-moor peat and clayey soil from excavation and then were sieved (10 mm). The formed films were superimposed with composites in five layers. All composites were wetted with a surface emulsion (Supresivit 0.1 g/L; Lignohumate AM 0.1 g/L; Agrisorb 0.1 g/L; Kristalon Start 1 g/L). The first composting bin (A) and the second (B) were opened after 63 days and 147 days (PCL/starch) or 20 and 40 days (EVA/starch), respectively.

To study the surface morphology before and after compost incubation of the EVA/starch films samples, we used optical microscope NIKON Eclipse LV-100 D (Nikon Corporation, Tokyo, Japan) linked with camera Jenoptik ProgRes CT3, (magnification 100–300×) in combination with image analysis system NIS-Elements vs. 3.2 AR complete with extended depth of focus module. The surface morphology of the PCL/starch films was published earlier (Šárka et al. 2011).

The substrate mopped from the composite surface was stored in polypropylene cans (1200 mL at 4°C) for analysis. If the composites were completely destroyed, the substrates were extracted from the space where the remaining composites (incl. metal labels) were found.

DM of compost was determined by the drying of 5 g substrate at 60°C (24 h), pH was measured

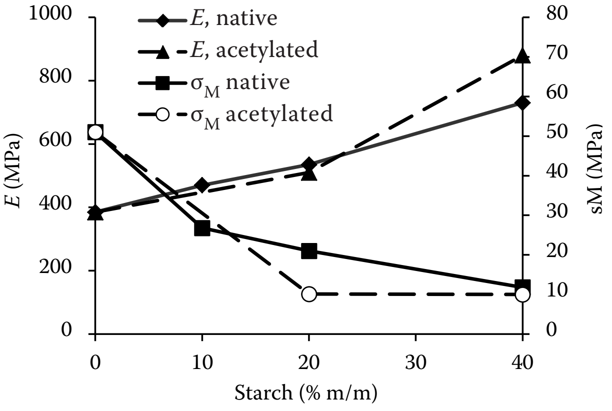

Figure 1. Dependences of Young modulus (*E*) and of tensile strength limit σ_M of PCL/native (acetylated) B-starch composites; DS of acetylated B-starch was 2.0

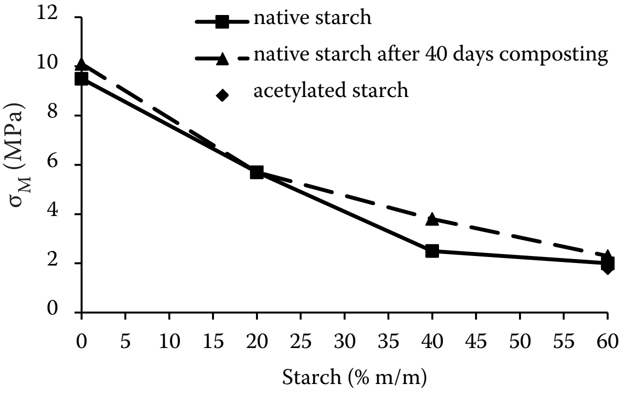

Figure 2. Dependences of tensile strength limit σ_M of EVA/native (acetylated) B-starch composites; DS of acetylated B-starch was 1.5

in the extract of moist substrate using deionized water (3 g/15 mL), shaken with a horizontal shaker (60 min; 250 swings per min) with an electrode by Hanna. Carbon of soil organic matter (C_{org}) was measured using a microwave method with an equivalent amount of moist substrate corresponding to 0.03 g DM (Růžek et al. 2012). Microbial biomass carbon (MBC-MW) was analysed using the microwave irradiation method (Růžek et al. 2009), basal respiration (BR), metabolic quotient (BR/MBC) × 1000, respiratory ratios NR/BR and NGR/BR according to Růžek et al. (2012).

RESULTS AND DISCUSSION

Mechanical behavior. The dependences of physical parameters for the PCL/B-starch and the EVA/B-starch composites on the percentage of the filler are shown in Figures 1–3. The Young modulus increased with increasing B-starch content. On the other hand, the yield stress, stress-at-break and strain-at-break decreased with increasing filler content. The mechanical behavior of the PCL/B-starch composites is comparable with the data of Koenig and Huang (1995) and Rosa et al. (2007). The acetylation of starch significantly affects the macroscopic mechanical behavior of the composites – the Young modulus is markedly increased when acetylated starch is applied.

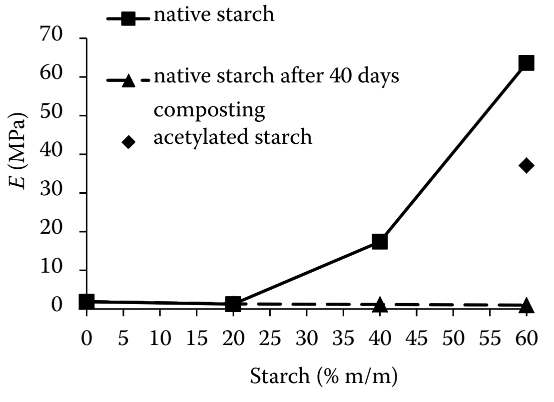

Figure 3. Dependences of Young modulus (*E*) of EVA/native (acetylated) B-starch composites; DS of acetylated B-starch was 1.5

The mechanical properties of the EVA/B-starch and EVA/B-acetylated starch were superior to those with the PCL. Young modulus of EVA/B-acetylated starch was significantly higher compared with EVA/native B-starch. The tensile strength of EVA/B-acetylated starch (60/40) blend was comparable with the strength of the corresponding blend of EVA/B-starch.

Weight loss of PCL-starch composites during composting. The weight loss after 2-months

Table 1. Weight loss of PCL/starch and EVA/starch blends after composting (DS of the acetylated B-starch was 2.0 for PCL/starch and 1.5 for EVA/starch films)

Composite composition	Ratio	Weight loss (%)	
		PCL/ 63 days	EVA/ 40 days
Polymer		7.7	0.0
Polymer/wheat B-starch	90/10	total decomposition	nd
	80/20	total decomposition	0.4
	60/40	total decomposition	14.6
	40/60	nd	38.4
Polymer/acetylated wheat B-starch	90/10	9.0	nd
	80/20	11.1	nd
	60/40	15.2	0.0

DS – degree of substitution; nd – not determined; PCL – poly-(ε-caprolactone); EVA – ethylene vinyl acetate copolymer

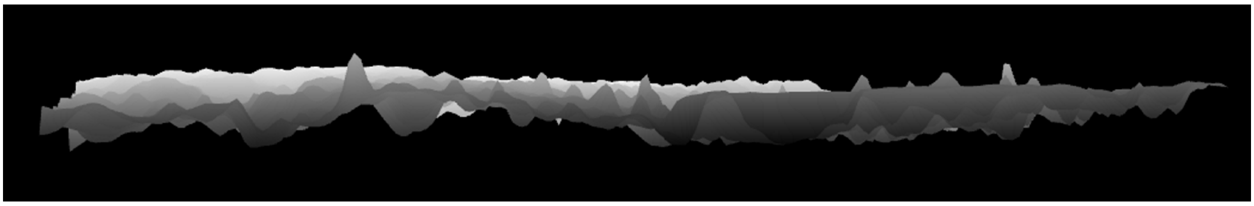

Figure 4. Profile of ethylene vinyl acetate copolymer (EVA)/acetylated B starch (60/40) film after 40 days' storage; degree of substitution (DS) of acetylated B-starch was 1.5

composting of 165 × 245 × 0.5 mm film is shown in Table 1 for the PCL/starch and EVA/starch compositions with starch content lower than or equal to 40% wt. The blends containing native B-starch in PCL were completely dissolved after 63 days. Acetylation reduced the degradation rate. It emerged from the data that PCL undergoes slower degradation compared to the blends with starch in any form. Weight loss of EVA/B-starch blends was always lower than their starch content. The EVA matrix seems to be made intact by the action of soil microorganisms. The EVA/B-acetylated starch blend did not show any substantial signs of decomposition even after 40 days of composting.

Degradation surfaces detected by the EDF module. The results of the image analysis system were 3D images of EVA/starch films which enabled the surface viewing. Figure 4 illustrates the profile of the film. We measured altitude differences (Figure 5) between chosen points (e.g. hill minus valley) and in this way the surface roughness was evaluated. The evaluated data are summarized in Table 2:

- the increased film roughness after 20 days composting;
- the roughness after 20 days did not depend on weight loss (Table 1);
- the percentage of native B-starch in a film increased the roughness after 20 days storage;
- films containing acetylated B-starch was of lower roughness compared with native one.

Changes in surrounding green waste compost. The chemical composition of the compost in which the films were stored was studied at the beginning and the end of the period; the data are shown in Table 3. Substrate properties after films storage showed no deterioration. Substrate was fully suitable for the growth and development of plants, as the soil pH did not decrease greatly. Electrical conductivity during the biodegradation of the films decreased slightly (< 0.3 dS/m), probably because of its dependence on ion immobilization into microbial cells. Surface emulsion also contributes to mitigate the decline of electrical conductivity. Thus, if the substrate is to be used for growing plants after biodegradation, dissolved mineral salts (ions) must be added on a continual basis. Carbon of soil organic matter ranged from 24.8 to 30.4% in the growing substrate, on the surface of films or

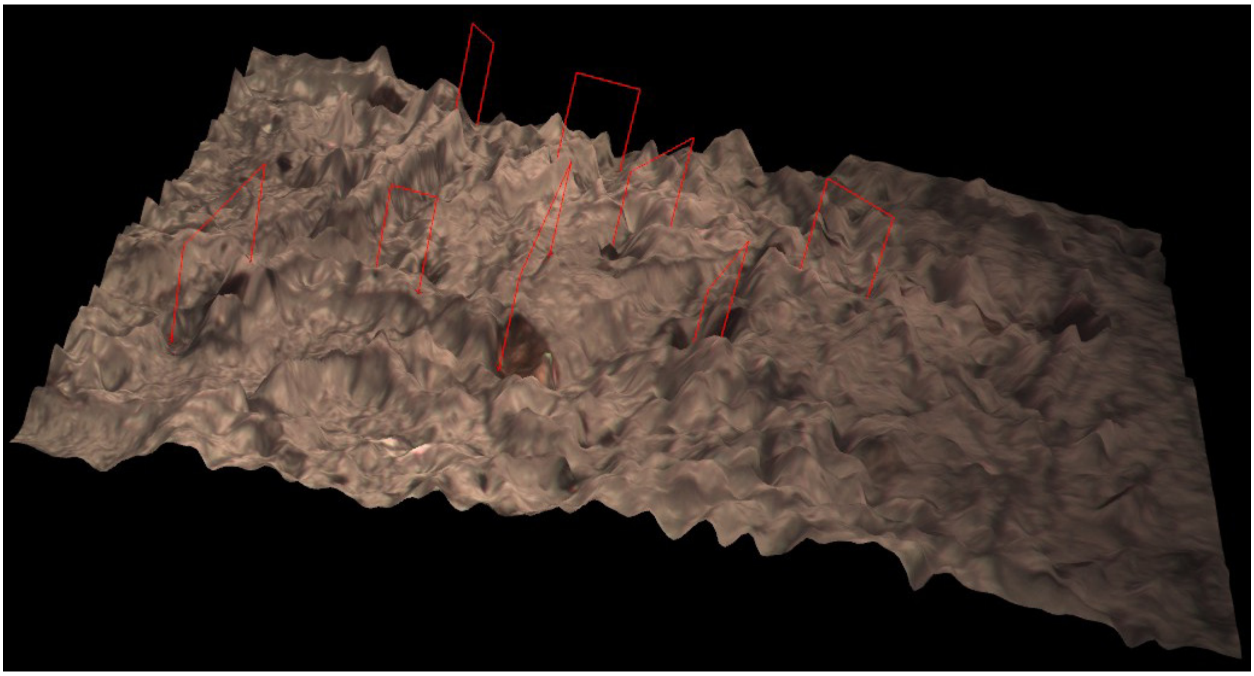

Figure 5. Ethylene vinyl acetate copolymer (EVA) film (100%) after 40 days' storage

Table 2. The roughness of ethylene vinyl acetate copolymer (EVA)/wheat B-starch (BS) and EVA/acetylated wheat B-starch (ABS) film before and after compost incubation

Days	Height difference (µm)				
	EVA 100%	EVA 80%; BS 20%	EVA 60%; BS 40%	EVA 60%; ABS 40%	EVA 40%; ABS 60%
0	13.9 ± 3.3	nd	9.4 ± 3.0	6.2 ± 3.6	nd
20	11.9 ± 1.8	12.8 ± 3.5	19.1 ± 2.3	13.7 ± 5.5	22.2 ± 2.0
40	16.2 ± 3.0	15.8 ± 4.5	17.7 ± 4.9	11.6 ± 4.6	18.8 ± 4.2

nd – not determined

in their immediate vicinity. The fluctuant values correspond the age of the compost. Our data are similar to Adani and Spagnol (2008), who found 41.1% for fresh compost and 22.7% for compost stored 150 days. When biodegradation is successful, a rise in BR and a slight rise in MBC-MW can be seen. The MBC-MW interval of 1896–3144 mg C/kg DM (Table 3) can be viewed as a standard (Šárka et al. 2011). Mondini et al. (2004) analyzing MBC content of fresh compost moist samples after 22, 49, 86, 112, and 149 days found higher values (8000–25 000 mg C/kg DM) for maturing compost. Our data for two-year compost are therefore realistic. BR expresses the mineralization intensity of organic matter (Šárka et al. 2011). In theory, microbial cells respire 80% of received organic carbon as CO_2 and the remaining 20% is immobilized as part of a newly-created biomass. When biodegradation is successful, a rise in BR and a slight rise in MBC-MW can be seen. A more intensive rise in BR thus also leads to a temporary increase in the metabolic quotient. However, this theoretical development is not reflected in Table 3. This is due to the intervals being too long. For both composites with PCL after 63 (147) days and those with EVA after 20 (40) days, biodegradation was far beyond the peak, including PCL 100%. Intensive respiration (38.1 mg C/h/kg DM) is not desirable in this late phase of biodegradation. The limit value of metabolic quotient for composts, 19 mg C/g MBC-MW/h (Šárka et al. 2011) was not achieved. Our values found in the range 2.2–17.4 mg C/g MBC-MW/h are comparable with data of Kuba et al. (2008) which were for composts in the range 12.5–15.6 mg C/g MBC-MW/h. Stable substrates usually reach about 5–7 mg C/g MBC-MW/h. This level protects both organic matter in the substrate against extreme mineralization and the atmosphere against extreme enrichment with CO_2. The minimum value of 2.2 mg C/g MBC-MW/h achieved in the composites with PCL again confirmed that after 63 days, biodegradation was far beyond its peak. The ratio NR/BR signifies the physiological accessibility of nitrogen for microorganisms. The

Table 3. Parameters of compost substrate before and after film storage

	Storage time (days)	DM (%)	Electric conductivity (dS/m)	pH (H_2O)	C_{org} (%)	[1]MBC-MW (mg C/kg DM)	[2]BR	[3]qCO_2	Ratio [4]NR/BR	Ratio [5]NGR/BR
PCL/ B-starch	start	38.27 ± 0.74	1.97 ± 0.05	6.45 ± 0.03	28.03 ± 2.99	3144 ± 376	11.5	3.7	1.56	26.22
	63	39.13 ± 1.90	1.73 ± 0.05	6.38 ± 0.01	26.25 ± 0.76	2405 ± 268	5.2	2.2	1.29	29.24
	147	32.40 ± 0.54	1.73 ± 0.01	6.21 ± 0.01	30.41 ± 2.55	2495 ± 423	38.1	17.4	1.00	7.53
EVA/ B-starch	start	26.89 ± 0.73	1.10 ± 0.05	6.07 ± 0.12	27.29 ± 1.72	2296 ± 1055	31.4	13.7	0.69	7.92
	20	26.36 ± 0.69	0.78 ± 0.03	6.45 ± 0.08	29.55 ± 0.61	1896 ± 779	30.6	16.1	0.88	9.92
	40	26.35 ± 1.71	0.82 ± 0.02	6.42 ± 0.07	24.84 ± 2.35	2890 ± 179	24.9	8.6	1.05	12.77

[1]Microbial biomass-C determined after compost microwave sterilization (800 J/g DM; 600 W, 2 × 67 s, 100 g) and compost extract microwave digestion (800 J/mL; 250 W, 77 s, 24 mL); [2]Basal respiration (BR; mg C/kg DM/h): CO_2 is released by the compost after addition of DW (deionized water); [3]Metabolic quotient (CO_2 carbon released (mg/h) per gram of MBC; (BR/MBC-MW) × 1000; [4]Potential respiration (NR) with ammonium sulfate: CO_2 released after addition of 0.4 mg N-$(NH_4)_2SO_4$/g of moist compost; [5]Potential respiration (NGR) with ammonium sulfate and glucose: CO_2 released after addition of 0.4 mg N-$(NH_4)_2SO_4$ and 4 mg C-glucose/g of moist compost; DM – dry mass of compost (5 g; 60°C; 24 h); PCL – poly-(ε-caprolactone); EVA – ethylene vinyl acetate copolymer

value 1.00 is characteristic for a stable substrate. For biodegradation of the composites with PCL, nitrogen physiologically available in the initial phase of biodegradation was immobilized in microbial cells. Considerable improvement up to the value of 1.00 (day 147) was one cause of extreme basal respiration. However, during the biodegradation of the composites with EVA, value of 1.00 (day 40) caused nitrogen immobilization in microbial cells, as well as a decrease in BR and metabolic quotient. The ratio NGR/BR provides information on organic matter stability, i.e. resistance to microbial decomposition (Šárka et al. 2011). In the biodegradation of the composites with PCL, its level reached the extreme value of 29.24 (day 63) (Table 3), while in the biodegradation of the composites with EVA, the standard value of 12.77 was reached after 40 days. An NGR/BR ratio value below 10 indicates that the soil solution was rich in nutrients, and thus organic matter showed lower stability, i.e. lower resistance to microbial decomposition.

REFERENCES

Adani F., Spagnol M. (2008): Humic acid formation in artificial soils amended with compost at different stages of organic matter evolution. Journal of Environmental Quality, *37*: 1608–1616.

Bhattacharya M. (1998): Stress relaxation of starch/synthetic polymer blends. Journal of Materials Science, *33*: 4131–4139.

Fringant C., Rinaudo M., Gontard N., Guilbert S.E., Derradji H. (1998): A biodegradable starch based coating to waterproof hydrophilic materials. Starch/Stärke, *50*: 292–296.

Koenig M.F., Huang S.T. (1995): Biodegradable blends and composites of polycaprolactone and starch derivatives. Polymer, *36*: 1877–1882.

Kuba T., Tscholl A., Partl C., Meyer K., Insam H. (2008): Wood ash admixture to organic wastes improves compost and its performance. Agriculture Ecosystems and Environment, *127*: 43–49.

Lim S.W., Jung I.K., Lee K.H., Jin B.S. (1999): Structure and properties of biodegradable gluten/aliphatic polyester blends. European Polymer Journal, *35*: 1875–1881.

Mondini C., Fornasier F., Sinicco T. (2004): Enzymatic activity as a parameter for the characterization of the composting process. Soil Biology and Biochemistry, *36*: 1587–1594.

Rosa D.S., Lopes D.R., Calil M.R. (2007): The influence of the structure of starch on the mechanical, morphological and thermal properties of poly(ε-caprolactone) in starch blends. Journal of Materials Science, *42*: 2323–2328.

Růžek L., Růžková M., Voříšek K., Vráblíková J., Vráblík P. (2012): Slit seeded grass-legume mixture improves coal mine reclamation. Plant, Soil and Environment, *58*: 68–75.

Růžek L., Růžková M., Voříšek K., Kubát J., Friedlová M., Mikanová O. (2009): Chemical and microbiological characterization of Cambisols, Luvisols and Stagnosols. Plant, Soil and Environment, *55*: 231–237.

Singh R.P., Pandey J.K., Rutot D., Degee P., Dubios P. (2003): Biodegradation of poly(ε-caprolactone)/starch blends and composites in composting and culture environments: the effect of compatibilization on the inherent biodegradability of the host polymer. Carbohydrate Research, *338*: 1759–1769.

Šárka E., Kruliš Z., Kotek J., Růžek L., Korbářová A., Bubník Z., Růžková M. (2011): Application of wheat B-starch in biodegradable plastic materials. Czech Journal of Food Sciences, *29*: 232–242.

Šárka E., Bubník Z. (2010): Morphology, chemical structure, properties and applications of wheat B-starch. Chemické Listy, *104*: 318–325.

Šárka E., Koláček J., Sikora A., Hrušková K., Prokopová D., Hrabal R., Maixner J., Bubník Z. (2010): Effect of reaction time on the acetylation of wheat B-starch and characterization of the product. In: Proceedings of the 6th International Conference on Polysaccharides-Glycoscience, Prague, 200–205.

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