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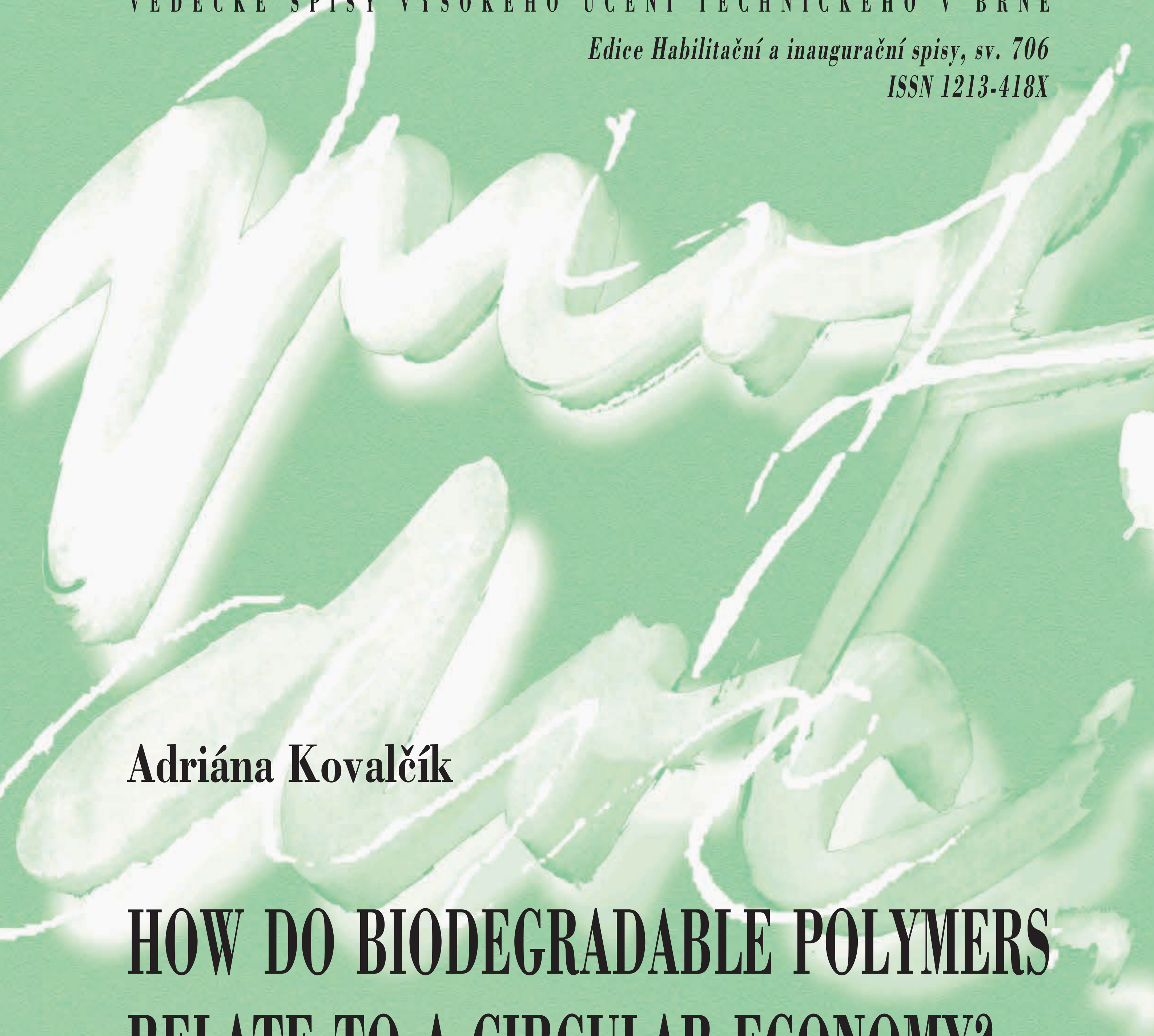

Adriána Kovalčík

HOW DO BIODEGRADABLE POLYMERS RELATE TO A CIRCULAR ECONOMY?

VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ
FAKULTA CHEMICKÁ
ÚSTAV CHEMIE POTRAVIN A BIOTECHNOLOGIÍ

doc. Ing. Adriána Kovalčík, Ph.D.

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JAK SOUVISÍ BIOLOGICKY ROZLOŽITELNÉ POLYMERY S CIRKULÁRNÍ EKONOMIKOU?

Teze přednášky k profesorskému jmenovacímu řízení
v oboru
MAKROMOLEKULÁRNÍ CHEMIE

VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ
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1 INTRODUCTION TO THE TOPIC: THE IMPORTANCE OF PLASTICS

The term “plastic” has a meaning “capable of being shaped or moulded” that comes from the Greek word “plastikos”. Plastic materials have properties that no other material has and found enormous application in our society. It is important to note that crucial discoveries in polymer chemistry in the past helped to make significant progress in many industrial fields. The production of plastics began in the 19th century. Important milestones in plastics technology in the 19th century included producing polystyrene, celluloid, vulcanized rubber, polyvinyl chloride, and polyethylene.

Similarly, the 20th century has brought new polymerization processes and processing technologies. Innovations in polymerization and processing technologies in polymer chemistry supported extended applications of thermoplastics (e.g., polypropylene, polyethylene terephthalate, polycarbonate and nylon) and thermosets (e.g. bakelite, Kevlar, polyurethane, epoxy resins) in many areas. Among the critical industries that use plastics belong industrial machinery, transportation, packaging, building and constructions, textile industry, automotive industry and aerospace, electrical and electronics, toys, agricultural, consumer products and medicine. In the 20th century, in most cases, plastic materials replaced paper and glass (and partially steel). Global plastics production in 2020 reached about 367 million tons [1]. Wide-spread applications of plastic materials are connected with their specific properties such as light in weight, high corrosion resistivity and overall durability, cheap production and large available and cheap polymer processing technologies (e.g. extrusion, injection moulding, blow moulding, rotational moulding, thermoforming, 3D printing methods). No one doubts that plastics have unique user properties, and their application increases the quality and comfort of life. Still, there are several problems with them, such as fossil fuels’ depletion, generated plastic waste (between 1950–2015 was globally generated 6 300 Mt of primary and secondary plastic waste) and greenhouse gas emissions (1.78 Gt. CO_2-eq in 2015) [2, 3]. Most plastic materials have been produced from oil or gas and are classified as fossil fuel-based plastics. Oil and gas fossil fuels are subject to depletion. Some plastic materials are made of renewable biological resources. This is beneficial from the point of reducing CO_2 emissions. Although, nowadays, only “a negligible” amount of plastics are bio-based. It was reported that the global production capacity of bioplastics was 2.1 million tons in 2020 [4]. However, it must be stated that the term bioplastics does not necessarily mean bio-based, as will be explained in the next chapter. The following chapters will also discuss the importance of the transition from the linear (take, make, use and dispose of the used material) to the circular economy (sharing, leasing, reusing, repairing, refurbishing and recycling) model of production and consumption and what properties have biopolymers and bioplastics.

2 PLASTIC DEMAND AND PLASTIC WASTE MANAGEMENT

Geyer et al. estimated that by 2015, it had been globally produced about 8.3 billion tons of virgin plastics. Worldwide, this amount of plastics after the end-of-life was by 2015 managed as follows: 9 % was recycled, 12 % was incinerated, and 79 % was land-filed [2]. In 2019, plastic demand in Europe (EU28+NO/CH) was 50.7 million tons, while the highest consumption of plastics, about 39.6 %, was in the packaging area (Figure 1). The most used polymers include:

- polyethylene (29.8 % - reusable bags, trays/containers, agricultural film, food packaging film, toys, milk bottles, pipes, etc.),
- polypropylene (19.4 % - food packaging, pipes, automotive parts, etc.),
- polyvinylchloride (10 % - window frames, profiles, cable insulation, etc.),

- polyurethanes (7.9 % - building insulation, pillows and mattresses, insulating foams, etc.),
- polyethylene terephthalate (7.9 % - bottles, etc.),
- polystyrene (6.2% - food packaging, building insulation, electrical and electronic equipment, etc.),
- and other thermoplastics and thermosets (18.8 % - touch screens, optical fibres, medical implants, disposable diapers, etc.).

EU data present that in 2018 in the EU28+NO/CH was collected 29.1 million tons of plastic post-consumer waste. From this amount of plastic waste, 32.5% was recycled, 42.6% was used for energy recovery, and 24.9% was landfilled [5]. The current decreased tendency for landfilling plastic waste mainly due to the strict waste policy in the EU is very favourable compared to the previous years. However, zero landfilling worldwide would be optimal, and it requires a transparent plastic value chain from product design to recycling and end-of-life options [6]. In addition to increasing areas for massive landfilling, greenhouse gas emissions and plastic leakage into the environment (oceans, rivers, mountains, etc.) also cause severe problems.

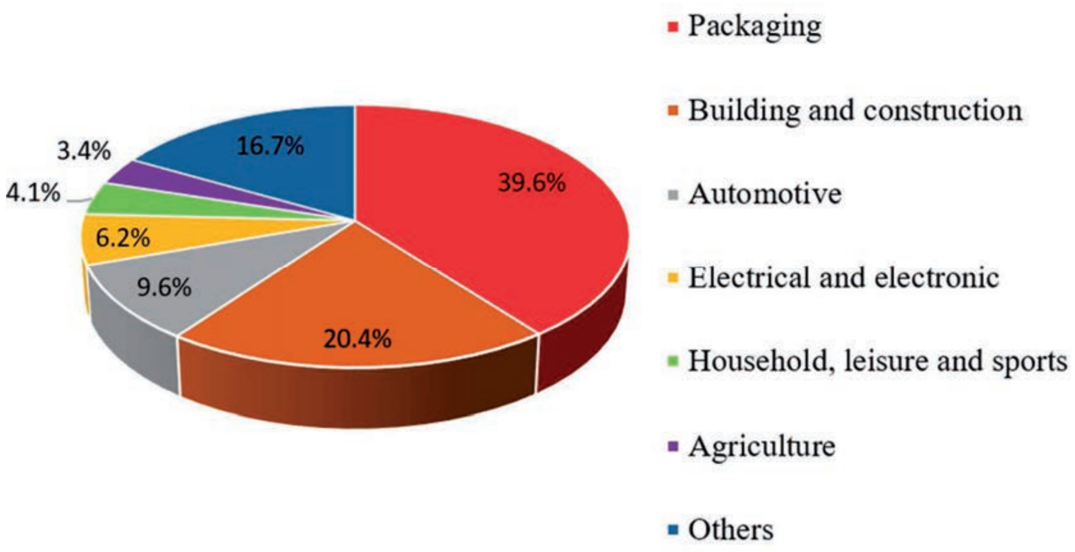

Figure 1: Plastics demanded by segment in 2019. Data were received from PlasticsEurope [5].

2.1 THE CIRCULAR ECONOMY OF PLASTICS

Nowadays, our society understands that the current production and consuming way of life ruin our planet and contribute to the almost irreversible loss of valuable natural resources. At least since 2003, the European Commission has been updating its legislation focused on waste management (e.g., Green Paper "Entrepreneurship" in Europe, Directive on single-use plastics, EU waste management law, Proposal for a new batteries regulation). EU priorities are prevention of pollution, environmental protection, waste recycling and public health. These legislative changes strengthen the necessity of changing the production and consumption linear economy model to the circular economy model to promote an innovative and sustainable way of action being and life. According to the European Union law, a circular economy is a system that maintains the value of products, materials and resources in the economy for as long as possible and minimizes waste generation. It means that the productions of goods should follow the principles of the "6Rs": reduce, redesign, remove, reuse, recycle, recover by extracting chemicals or fuels or by recovering energy [6]. The circular economy action plan was adopted by the European Commission in 2015 [7].

The challenges arising from the circular economy of plastics are connected with circulating material flows that include several strategies but mainly:

1. reuse,
2. collection and sorting,
3. mechanical recycling – it is currently the first option for plastic packaging waste [7], but it plays a minor role in a global waste treatment [2, 3],
4. chemical recycling (refinery feedstock, fuel production, monomer production and chemical upcycling) – a methodology that might help to decrease fossil resource depletion and greenhouse gas emissions [3],
5. composting – the hypothesis and aim are that (bio)degradable plastics would break down in the compost environment to non-toxic compounds and nutrients [6],
6. the development of new effective waste utilization methodologies and approaches covering biotechnological procedures for bio-based economy and production models [8, 9].

The Ellen Macarthur Foundation described its vision for the circular economy of plastics used in packaging, including the following points:

1. elimination of problematic or unnecessary plastic packaging (ban on the single-use plastic products),
2. reuse packaging materials,
3. design of 100% reusable, recyclable or compostable plastic packaging,
4. all plastic packaging is reused, recycled, or compostable in practice,
5. the use of plastic should be fully decoupled from the consumption of finite resources,
6. plastic packaging should be free from hazardous chemicals [10].

3 BIO-BASE RESEARCH AND INNOVATION

The world's leaders and society have agreed that changing from a linear economy to a circular economy is essential to reverse the planet's devastation. The European Commission has approved new ambitious environmental, societal, industrial and climate policy targets for 2050. However, complete sustainability requires combining the circular economy with the bioeconomy and low-carbon economy (the hypothesis is that the new activities could save up to 2.5 billion tons of CO_2 eq. per year by 2030). European Commission has explained that bioeconomy "means using renewable biological resources from land and sea, like crops, forests, fish, animals and micro-organisms to produce food, materials and energy" [11]. The European Commission believes that the European Green Agreement will transform the EU into a modern and competitive resource-efficient economy. Next, the world's leading companies should incorporate these processes into their manufacturing and production processes as well as the company's overall policy. For the fulfilment of new EU and world policy and intention focused on green and circular economy it is critical to find out and establish new methodologies, processes and legal and societal framework.

In order to support the shifting of the production of standard non-sustainable products and techniques to bio-based ones, it is essential to involve and support research, educational institutions, companies, and political organizations [12]. One of the possible concepts of the overview of sustainable materials is depicted in Figure 2.

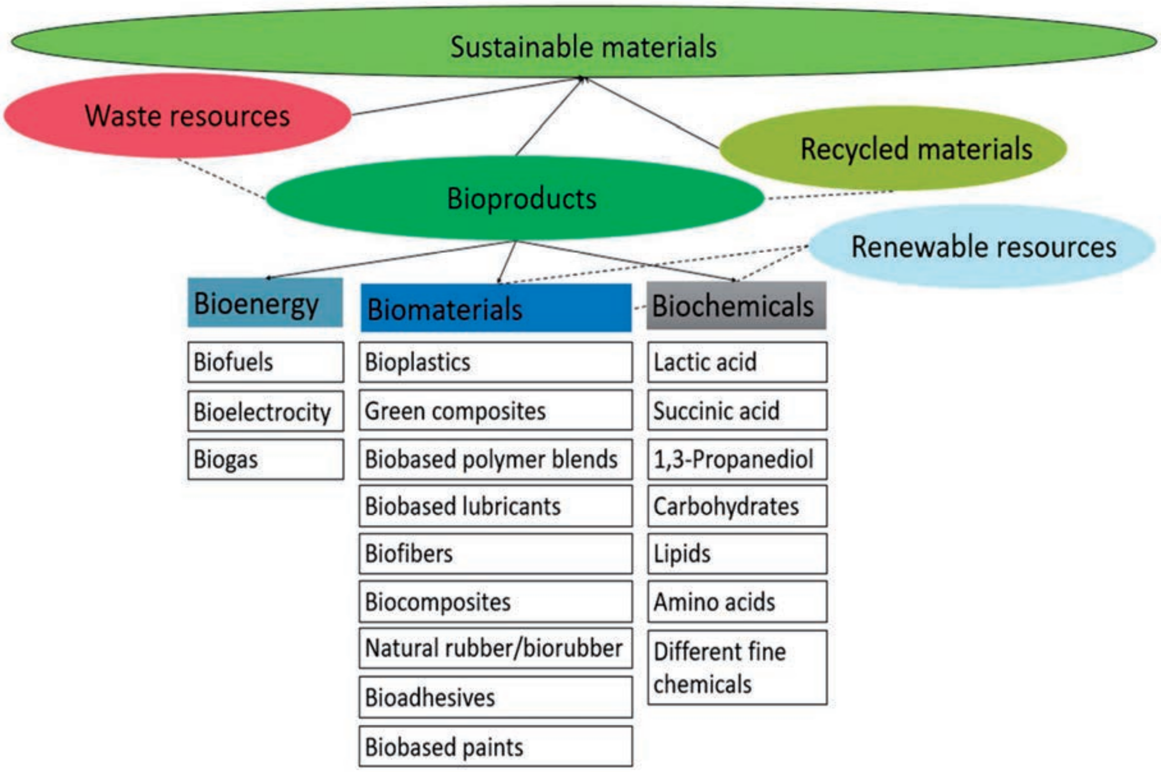

Figure 2: The overview of sustainable materials.

4 BIOPLASTICS

Bioplastics are a group of polymers that are bio-based and/or biodegradable. Classification of bioplastics is shown in Figure 3. Bio-based polymers are termed polymers that carbon building blocks originate from bio-based renewable resources, e.g. lignocellulosic biomass. Bio-based content can be determined, for example, by ASTM D6866 test (ASTM = American Society for Testing and Materials). The advantages of biobased plastics are non-dependency on fossil resources, reducing greenhouse gas emissions, and increasing resource efficiency [13].

Plastic materials can be classified as biodegradable if the tested material is compostable. Compostable plastic is “plastic that undergoes degradation by biological processes during composting to yield CO_2, water, inorganic compounds and biomass at a rate consistent with other known compostable materials and leave no visible, distinguishable or toxic residue” (ISO 17088:2021). The condition is that complete microbial assimilation of the tested material usually occurs within 180 days in a compost environment. However, the ambient testing conditions and timeframe for biodegradation must be specified. The exact testing and analysis methodologies are described in several applicable standards (examples are in Table 1). The biodegradability of plastics depends on their chemical structure and environmental conditions.

There are several certification schemes to prove the biodegradability of materials. However, to prove only that the tested material is "compostable material" is not complete. To avoid misunderstandings, it could also help clarify the type of composting, e.g. industrial compostable, compostable in soil, marine compostable, etc. Promoting the bioeconomy and the circular economy is not enough only at the political level; their real application must be promoted mainly in manufacturing companies, retailers, and consumer society. Creating a functional network of research, teaching, production, and distribution based on these principles is essential for achieving a measurable effect for the most extensive possible range of products.

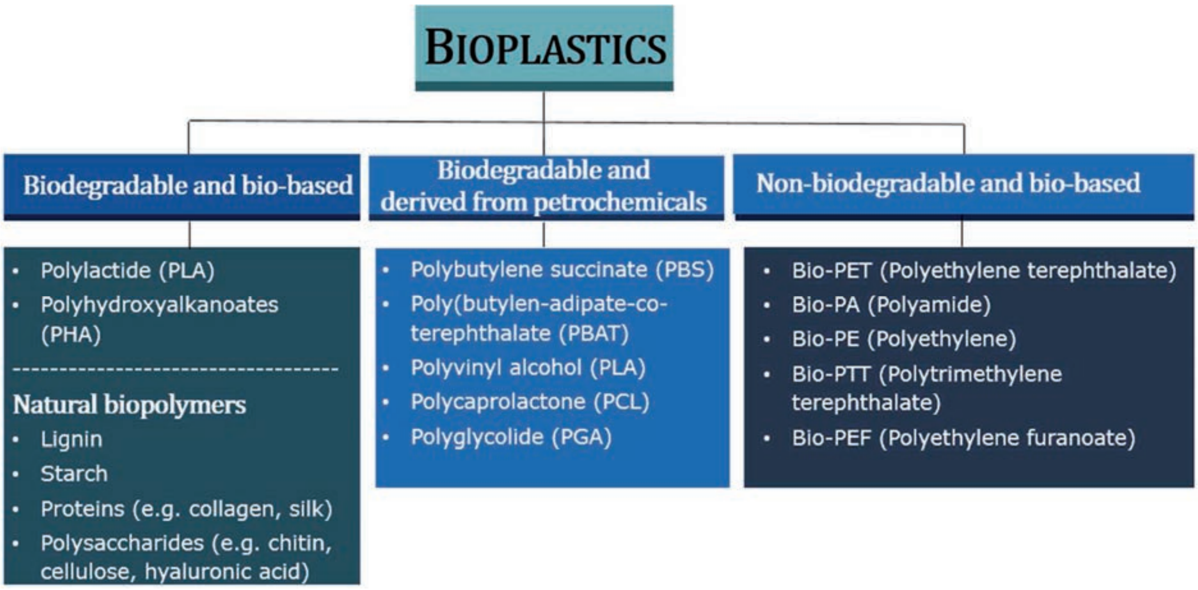

Figure 3: Classification of bioplastics.

Table 1: The selected ASTM and ISO plastic biodegradation standards in compost environment.

Standard	Description
ASTM D6868	Standard specification for labelling of end items that incorporate Plastics and polymers as coatings or additives with paper and other substrates designed to be aerobically composted in municipal or industrial facilities
ASTM D6400	Standard specification for labelling of plastics designed to be aerobically composted in municipal or industrial facilities
ASTM D5988	Standard test method for determining aerobic biodegradation of plastic materials in soil
ISO 16929	Plastics — determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test
ISO 17556	Plastics – determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved
ISO 17088	Specifications for compostable plastics

4.1 BIOBASED BIODEGRADABLE POLYMERS

4.1.1 Polylactide (PLA)

Polylactide (PLA) is a commercial biodegradable polymer produced globally in about 380 000 tons from 2018-2020 [14]. PLA is a semi-crystalline polyester whose monomer, lactic acid (2-hydroxy propionic acid), can be made from annually renewable resources, usually through anaerobic fermentation of carbohydrates. However, lactic acid can also be produced by chemical synthesis. The simplified life cycle of PLA is shown in Fig. 4.

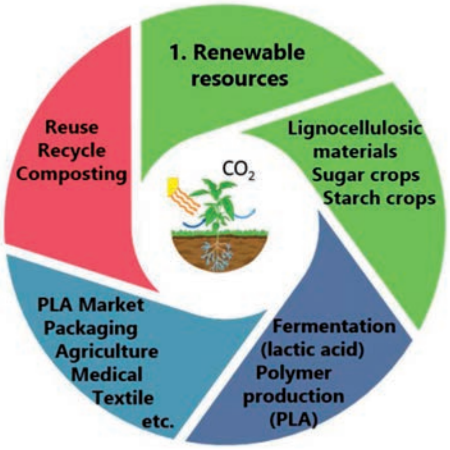

Figure 4: Simplified life cycle of PLA.

Lactic acid occurs in an L (+) isomer or D (–) isomer. The production of PLA by ring-opening polymerization through lactide formation is the favoured synthesis route, which enables the production of high molecular weight PLA on the industrial scale. Figure 5 shows PLA (polylactide) technology according to Prof. Raman Narayan (MSU, USA), who is the developer of PLA technology for Cargill Inc. (Wayzata, MN, USA).

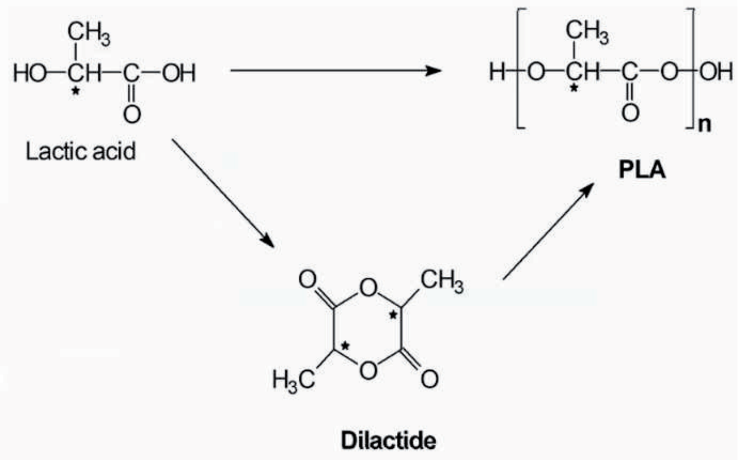

Figure 5: The scheme of PLA (polylactide) technology according to Prof. Raman Narayan, distinguished Professor at Michigan State University (USA).

The Cargill research project on PLA technology was later transformed in NatureWorks (Minnetonka, MN, USA), the current world-leading PLA's supplier.

4.1.1.1 Modification of PLA

The PLA products' physicomechanical properties depend mainly on the composition (the content of stereoisomers and additives, e.g. filler and nucleating agents) and applied thermal processing.

Nucleating agents

The summarized schema of an effect of thermal annealing on the semi-crystalline character of PLA is described in Fig. 6.[1] The crystalline morphology and kinetics of PLA play a significant role in modifying the physical properties of PLA products, such as tensile strength, heat deflection temperature and thermal stability [15]. Some processing technologies such as injection moulding require that polymer melt after cooling crystallizes within a few seconds. The addition of a nucleating agent can achieve the induction of heterogeneous nucleation. This will allow control of PLA's final degree of crystallinity, the crystalline form (ratio of less ordered α' and more ordered form) and the crystallization kinetics. The nucleating agents reduce the surface free energy barrier for nucleation. High nucleation efficiency in PLA have inorganic materials, e.g. talc.[2]

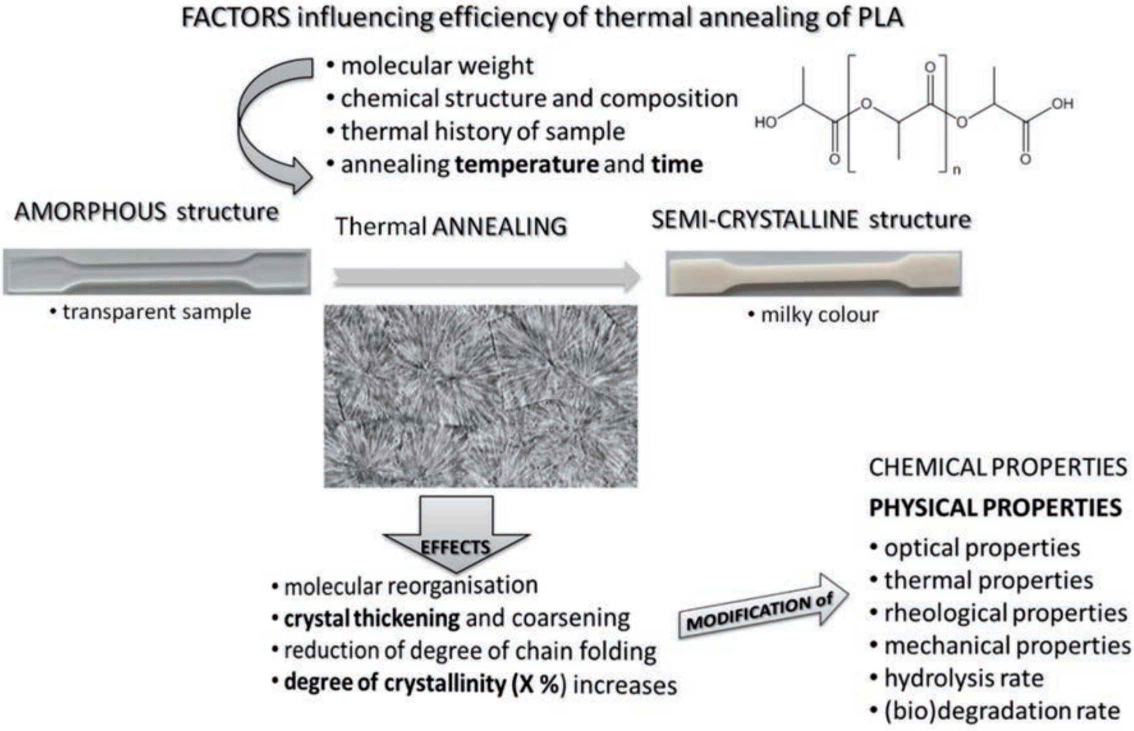

Figure 6: The schema of the influence of thermal annealing processing step on properties of PLA.[1]

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[1] M. Pastorek, A. Kovalcik, Effects of thermal annealing as polymer processing step on poly(lactic acid), Mater. Manuf. Process. 33(15) (2018) 1674-1680. DOI: 10.1080/10426914.2018.1453153

[2] H. Schäfer, A.Kovalcik., Crystallization kinetics of poly(lactic acid) during melt processing, in: M. Koller (Ed.), Current Advances in Biopolymer Processing and Characterization, Nova Science Publishers, Inc., New York, 2018, pp. 205-222

Moreover, the crystallization kinetics of PLA can also be modified by adding renewable organic materials such as lignin.

Lignin has a complex mutative structure consisting of phenylpropane units (Figure 7) with different functional groups.[3]

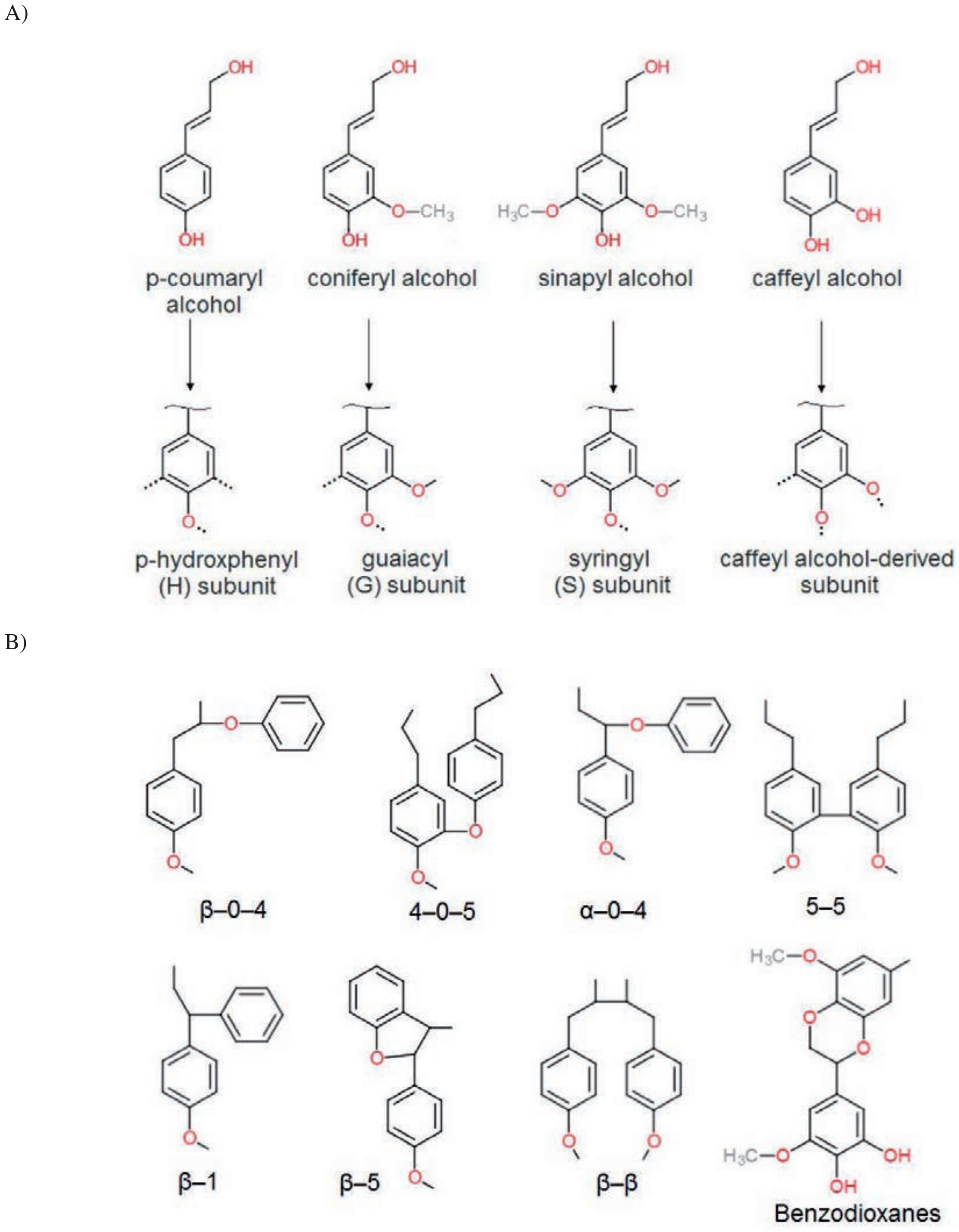

Figure 7: (A) Lignin monomers and their derived subunits. (B) Common linkages found in lignin structure.[5]

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[3] B. Kosikova, P. Alexy, A. Gregorova, Use of lignin products derived from wood pulping as environmentally desirable component of composite rubber materials, Wood Res. 48(1-2) (2003) 62-67

Naturally, lignins have high radical scavenging activity. Some of them have antibacterial properties (they depend on lignin's chemical structure and physical properties).[4] Lignins are heterogeneous polymers in the chemical structure (monomers, functional groups, lignin-carbohydrate complex) as well as in physical properties (such as molecular weight, polydispersity, purity, and solubility).[5] The properties of the isolated lignin sample depend on its origin and applied isolation and modification techniques. Our research shows that sulfur-free lignins with low molecular weight and a narrow polydispersity (Mw about 2000 g mol^{-1}, PDI about 1.2) could be used as a stabilizer for polymers, such as polypropylene, natural rubber, or styrene-butadiene rubber.[3,6]

It is welcome if natural additives are used for the modification of PLA. The advantage of using lignin as a nucleating agent is that the continuity of the intention of the bio-based and biodegradable PLA would be maintained. Our calculations and experimental data showed that both Kraft and Organosolv lignin could reduce the energy barrier for nucleation and growth of spherulites in PLA and therefore are suitable as nucleating agents. The use of industrial lignins as nucleating agents to accelerate PLA crystallization may preserve the biobased and biodegradable character of PLA.[7]

Filler

Our research showed a potential to improve the viscoelastic properties of PLA by reinforcing with organic filler such as wood fibres, wood flour and micro-fibrillated cellulose. The intention is not to impair the biodegradability of the whole composite. However, in the case of the production of PLA/organic filler, it is necessary to pay attention to the natural variability of natural filler and limited interfacial compatibility between the hydrophobic PLA and hydrophilic filler. The surface-chemical structure of organic filler significantly affects the final interfacial compatibility with the PLA matrix. Our data show that micro-fibrillated wood or only partially delignified and subsequently fibrillated beech wood possess much higher interfacial compatibility to PLA than micro-fibrillated cellulose without the presence of lignin and hemicelluloses.[8] Next, the interfacial compatibility between PLA and lignocellulosic filler can be improved, for example, by surface treatment of filler or addition of chain extender in the compound.[9]

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[4] A. Gregorova, Lignin: Antibacterial Properties, in: M. Mishra (Ed.), Encyclopedia of Biomedical Polymers and Polymeric Biomaterials, Taylor & Francis, New York, 2016. pp. 4328-4334.

[5] M. Nar, H.R. Rizvi, R.A. Dixon, F. Chen, A. Kovalcik, N. D'Souza, Superior plant based carbon fibers from electrospun poly-(caffeyl alcohol) lignin, Carbon 103 (2016) 372-383. 10.1016/j.carbon.2016.02.053

[6] (A) A. Gregorova, Z. Cibulkova, B. Kosikova, P. Simon, Stabilization effect of lignin in polypropylene and recycled polypropylene, Polym. Degrad. Stab. 89(3) (2005) 553-558. 10.1016/j.polymdegradstab.2005.02.007; (B) A. Gregorova, (C).K. Kosikova, R. Moravcik, Stabilization effect of lignin in natural rubber, Polym. Degrad. Stab. 91(2) (2006) 229-233. 10.1016/j.polymdegradstab.2005.05.009; (D) A. Gregorova, B. Kosikova, A. Stasko, Radical scavenging capacity of lignin and its effect on processing stabilization of virgin and recycled polypropylene, J. Appl. Polym. Sci. 106(3) (2007) 1626-1631. 10.1002/app.26687; (E) B. Kosikova, A. Gregorova, A. Osvald, J. Krajcovicova, Role of lignin filler in stabilization of natural rubber-based composites, J. Appl. Polym. Sci. 103(2) (2007) 1226-1231. 10.1002/app.24530

[7] A. Kovalcik, R.A. Pérez-Camargo, C. Fürst, P. Kucharczyk, A.J. Müller, Nucleating efficiency and thermal stability of industrial non-purified lignins and ultrafine talc in poly(lactic acid) (PLA), Polym. Degrad. Stab. 142 (2017) 244-254. http://dx.doi.org/10.1016/j.polymdegradstab.2017.07.009

[8] A. Winter, N. Mundigler, J. Holzweber, S. Veigel, U. Muller, A. Kovalcik, W. Gindl-Altmutter, Residual wood polymers facilitate compounding of microfibrillated cellulose with poly(lactic acid) for 3D printer filaments, Philos. Trans. Royal Soc. A 376(2112) (2018). 10.1098/rsta.2017.0046

[9] (A) A. Gregorova, M. Hrabalova, R. Wimmer, B. Saake, C. Altaner, Poly(lactide acid) Composites Reinforced with Fibers Obtained from Different Tissue Types of Picea sitchensis, J. Appl. Polym. Sci. 114(5) (2009) 2616-2623. 10.1002/app.30819;

Furthermore, the higher susceptibility of PLA/wood flour composite to hydrolysis during melt processing (e.g. extrusion, injection moulding) needs to be also addressed. The hydrolysis causes a significant decrease in the molecular weight of the PLA and thus impairs the resulting mechanical properties of the product. In our work, we have shown that the hydrolysis reactions leading to chain scission can be hindered by using 2 wt% of bis(2,6-diisopropylphenyl) carbodiimide.[10]

Functionalization and blending of PLA

The effect of different modifications of PLA in terms of thermal properties was mainly seen as a change in glass transition temperature, crystallization and melting behaviour. Nevertheless, the changes in the thermal stability of PLA regarding the presented synthesis methods, new additives, and blending or polymer processing methods should also be mentioned. Thermal degradation is a complex process depending on harsh conditions such as temperature, time, and kind of environment. The primary mechanism of PLA's thermal degradation at temperatures till 200 °C is considered intramolecular transesterification. Intra- and intermolecular ester exchanges, cis-elimination, radical and non-radical reactions, and Sn-catalyzed depolymerization reactions were identified as main PLA's degradation mechanisms above 200°C [16]. The kind of atmosphere also affects the type of thermal degradation of PLA. Under a nitrogen atmosphere, PLA decomposes to water, short-chain acids, carbon monoxide and carbon dioxide. Under thermo-oxidative atmosphere, acetaldehyde, lactide, carbon monoxide and carbon dioxide were found as degradation products [17]. It is known that the character of functional end groups primarily affects the thermal and hydrolytic sensitivity of PLA. In our research, we have shown that the thermal stability of low-molecular PLA can be improved by modification of functional end groups of PLA by carboxylation with succinic anhydride and L-cysteine within addition-elimination reaction (Figure 8).[11]

Melt blending is another technique to modify the final properties of PLA based materials, for example, morphology, barrier and mechanical properties. Good miscibility and interfacial compatibility between polymers are necessary conditions to receive satisfactory properties of blends. However, the different chemical structure of blended polymers leads to the immiscibility. The final morphology type (dispersed or co-continuous morphology) and mechanical properties of the immiscible blend depend on the concentration of the mixed polymers. The final blend will also have a good apparent contact in the absence of a compatibilizer in the case that a dispersed phase is formed from an amorphous polymer (or polymer with lower crystallinity) as the polymer creating a matrix.

However, at a specific concentration comes a phase inversion, and the co-continuous phase is formed. The blend composition at which a phase inversion occurs causes a co-continuous morphology. Blends with co-continuous morphology are considered promising for various

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[9] (B) M. Hrabalova, A. Gregorova, R. Wimmer, V. Sedlarik, M. Machovsky, N. Mundigler, Effect of Wood Flour Loading and Thermal Annealing on Viscoelastic Properties of Poly(lactic acid) Composite Films, J. Appl. Polym. Sci. 118; (C) (2010) 1534-1540. 10.1002/app.32509; (3) A. Gregorova, M. Hrabalova, R. Kovalcik, R. Wimmer, Surface Modification of Spruce Wood Flour and Effects on the Dynamic Fragility of PLA/Wood Composites, Polym. Eng. Sci. 51(1) (2011) 143-150. 10.1002/pen.21799; (D) A. Gregorova, V. Sedlarik, M. Pastorek, H. Jachandra, F. Stelzer, Effect of Compatibilizing Agent on the Properties of Highly Crystalline Composites Based on Poly(lactic acid) and Wood Flour and/or Mica, J. Polym. Environ. 19(2) (2011) 372-381. 10.1007/s10924-011-0292-6

[10] P. Holcapkova, P. Stloukal, P. Kucharczyk, M. Omastova, A. Kovalcik, Anti-hydrolysis effect of aromatic carbodiimide in poly(lactic acid)/wood flour composites, Compos. Part A Appl. Sci. Manuf. 103 (2017) 283-291. 10.1016/j.compositesa.2017.10.003

[11] K. Berger, A. Gregorova, Thermal Stability of Modified End-Capped Poly(lactic acid), J. Appl. Polym. Sci. 131(22) (2014). 10.1002/app.41105

applications where the controlled release of a bioactive agent (special packaging, possibly medical devices) is required. To process samples with co-continuous morphology, it is necessary to set the proper ratio of polymer blends and mixing conditions to reach optimal properties.

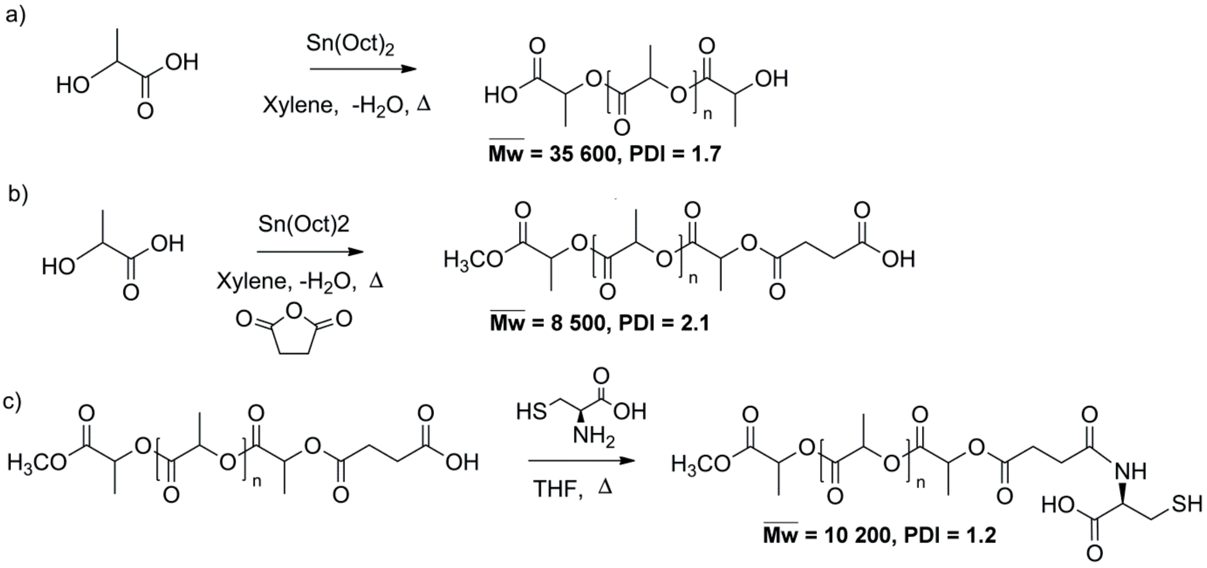

Figure 8: Synthesis of (a) unmodified sample - PLA, (b) sample modified by succinic anhydride - PLA/SA and (c) sample modified in two steps by succinic anhydride and cysteine - PLA/SA/CY.[11]

Our research focused on studying miscibility and properties of a partially biodegradable polymeric blend based on polyamide 6 (PA6) and commercially available co-polyester of polylactide (BioFlex F2110, FKuR Kunststoff GmbH, Willich, Germany). The obtained data revealed the formation of co-continuity for the blends containing 40–60 wt. % of BioFlex (Figure 9). [12]

The interface between PLA and other polymers can be tuned by incorporating reactive compatibilizers (additives that modify thermodynamically immiscible phases and improve the final interactions between polymers), e.g. isocyanates. [13]

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[12] (A) P. Kucharczyk, O. Otgonzul, T. Kitano, A. Gregorova, D. Kreuh, U. Cvelbar, V. Sedlarik, P. Saha, Correlation of Morphology and Viscoelastic Properties of Partially Biodegradable Polymer Blends Based on Polyamide 6 and Polylactide Copolyester, Polymer Plast. Tech. Eng. 51(14) (2012) 1432-1442. 10.1080/03602559.2012.709296; (B) V. Sedlarik, O. Otgonzul, T. Kitano, A. Gregorova, M. Hrabalova, I. Junkar, U. Cvelbar, M. Mozetic, P. Saha, Effect of Phase Arrangement on Solid State Mechanical and Thermal Properties of Polyamide 6/Polylactide Based Co-polyester Blends, J. Macromol. Sci. Phys. 51(5) (2012) 982-1001. 10.1080/00222348.2011.610265

[13] A. Gregorova, E. Riedl, V. Sedlarik, F. Stelzer, Effect of 4,4'-methylenediphenyl diisocyanate on thermal and mechanical properties of Bioflex/lactic acid polycondensate blends, Asia-Pac. J. Chem. Eng. 7(S3) (2012) S317-S323. 10.1002/apj.1650

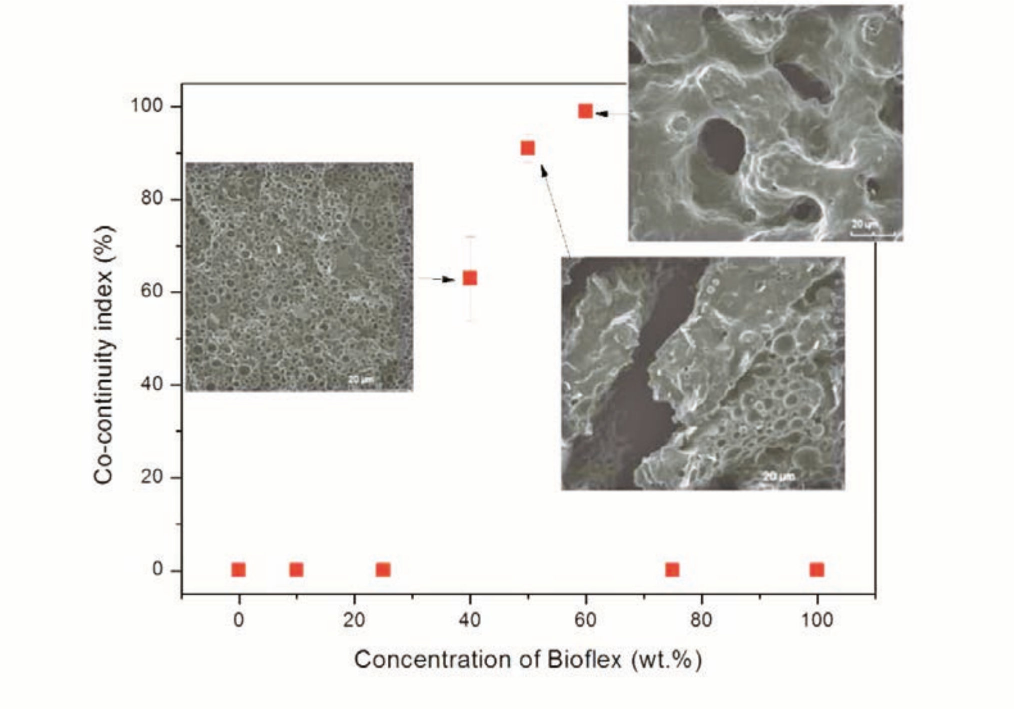

Figure 9: Dependence of co-continuity index on Bioflex concentration presented in the PA6/Bioflex blend.

4.1.2 Polyhydroxyalkanoates (PHA)

Polyhydroxyalkanoates (PHA) are a class of polyesters of natural origin that are accumulated as carbon and energy storage materials in the form of intracellular granules by a wide variety of bacterial strains. Between the PHA producing microorganisms belong most genera of eubacteria and members of the family *Halobacteriaceae* of the *Archea*. The microorganisms producing PHA are cultivated in fermentation media, which contain carbon, nitrogen, phosphorous and minerals. The deposition of PHA granules occurs in the stationary phase of the growth curve of the microorganism under conditions of the carbons source excess and a lack of the nitrogen source in the fermentation medium. PHAs are formed in accumulating microorganisms as an intracellular secondary product in water-insoluble granules and are stored in the cytoplasm. PHAs are unique biopolymers; they are biobased and biodegradable. The PHA lifecycle is shown in Figure 10.

The variability of PHA composition is broad and depends mainly on the production of microorganisms and the composition of fermentation media. So far, over 150 monomers have been identified in structures of biosynthesized PHA. A typical producer of poly(3-hydroxybutyrate) (P3HB) or poly(3-hydroxy-co-3-hydroxyvalerate) (P3HBV) is *Cupriavidus necator*. P3HB and P3HBV belong to the most produced PHA on an industrial scale (e.g., Biomer – Schwalbach, Germany; TianAn Biological Materials – Zhejiang China; Newlight Technologies – Irvine, CA, USA; Nafigate – Prague, Czech Republic; and some others). PHAs are divided into several groups according to the length of the polymer chain: polymers with short-chain length (3-5 carbons, scl-PHA), polymers with medium-chain length (6-14 carbons, mcl-PHA) and polymers with long-chain length (more than 14 carbons, lcl-PHA). P3HB and some of its copolymers belong to the most often produced and investigated PHAs.

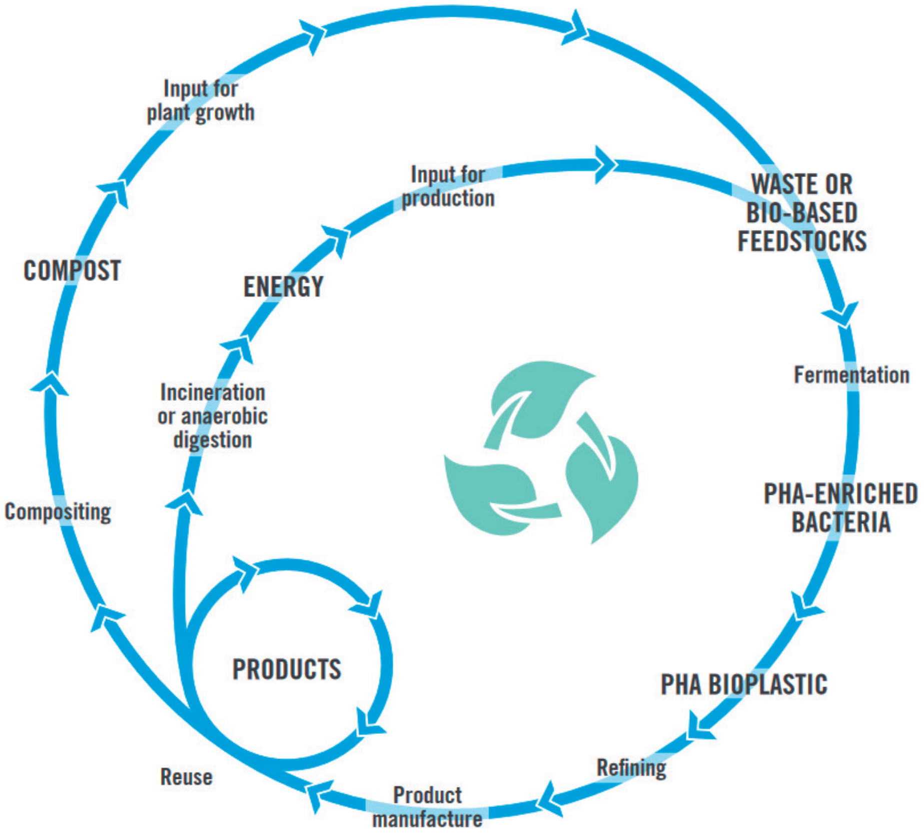

Figure 10: The PHA lifecycle [18].

Thermal, rheological and mechanical properties of PHAs depend on their chemical composition and molecular weight. PHAs, after biosynthesis, may reach molecular weight from 0.5×10^5 to 35×10^5 g mol^{-1} and polydispersity from 1.1 to 6.0 [19]. The physical properties of P3HB are similar to polypropylene, but P3HB is a more rigid and less flexible material. Its melting temperature is in the range of 170 to 180°C. The high brittleness corresponds with a high degree of crystallinity (up to 80%). The lower degree of crystallinity and higher flexibility may be reached by forming copolymers of 3-hydroxybutyrate with 3-hydroxyvalerate (P3HBV), 3-hydroxyhexanoate (P3HB-co-3HHx), or 4-hydroxybutyrate P3HB-co-4HB. The semi-crystalline structure of copolymers differs from P3HB and allows the formation of materials with lower brittleness, lower stiffness and higher elongation at break. Thermal as well as mechanical properties of PHAs are variable and depend on the concentration of monomers in copolymers as well as used additives (Figures 11 and 12).[14]

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[14] A. Kovalcik, Recent Advances in 3D Printing of Polyhydroxyalkanoates: A Review, Eurobiotech Journal 5(1) (2021) 48-55. 10.2478/ebtj-2021-0008

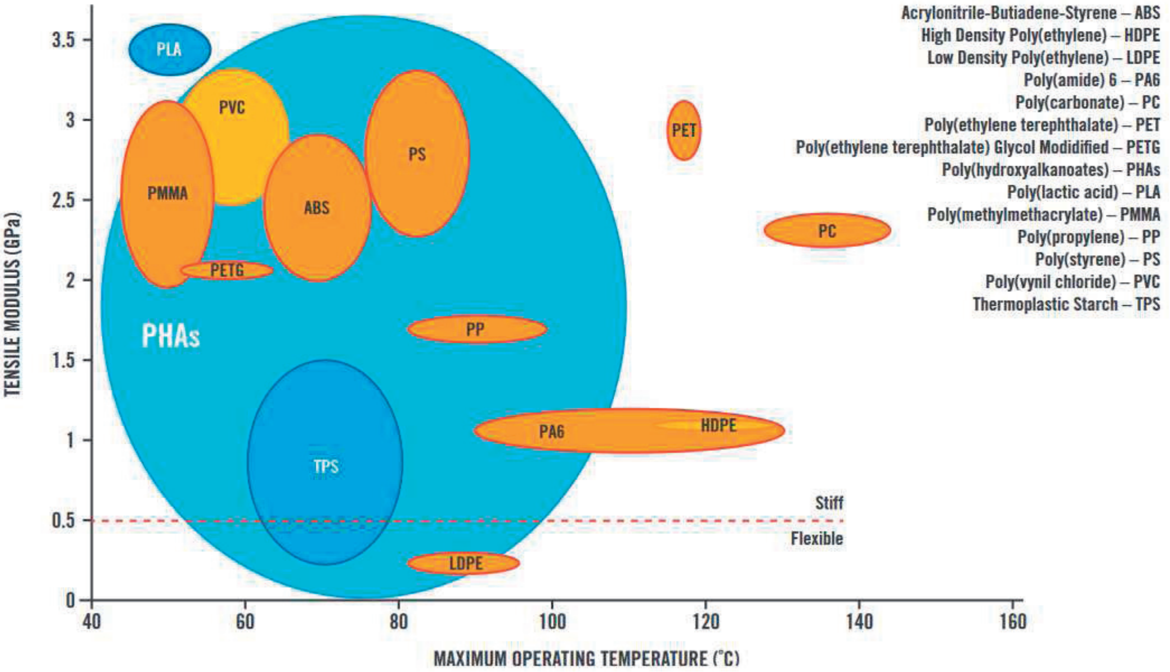

Figure 11: The PHA mechanical design space for tensile modulus against maximum operating temperature (light blue colour). For comparison are added mechanical properties of other oil-based (orange) and bio-based (blue) thermoplastic [18].

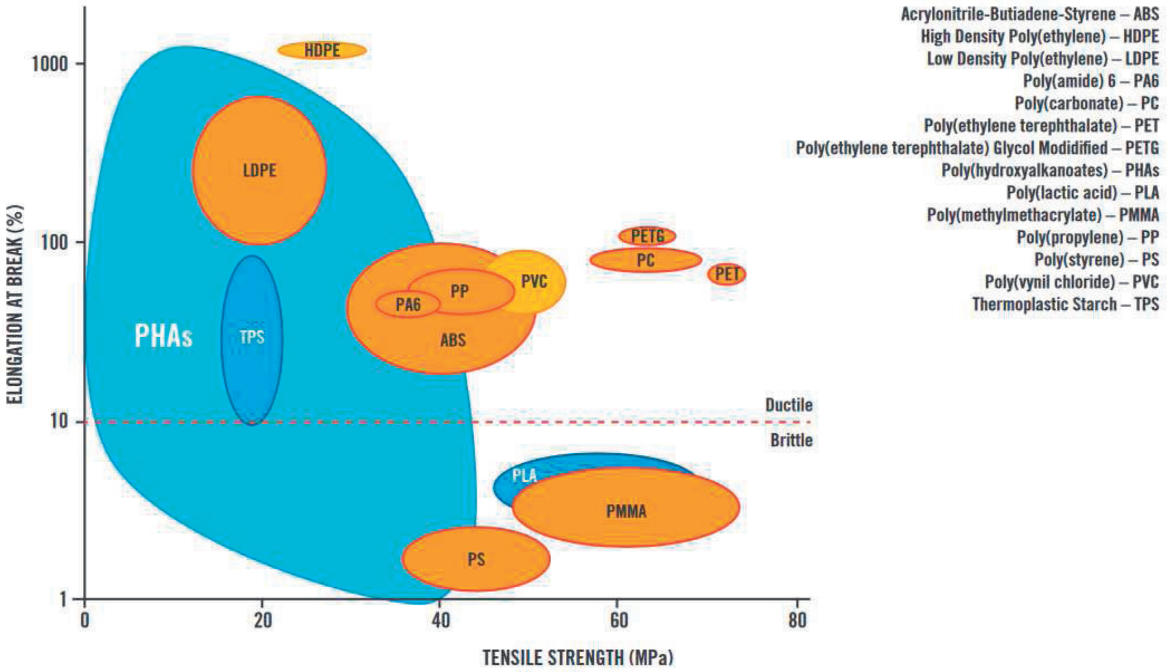

Figure 12: The PHA mechanical design space for elongation at break against tensile strength (light blue colour). For comparison are added mechanical properties of other oil-based (orange) and bio-based (blue) thermoplastic [18].

Commercial available PHAs are mainly used in pharmacy and medicine (tissue engineering, bio-implant patches, surgical applications and drug delivery) [20], cosmetics [21], nanotechnology [22] and additive manufacturing (e.g. fused deposition modelling)[14].

Despite the fantastic potential of PHAs as bio-based and biodegradable polymers, some drawbacks limit the more extensive PHA's applicability:

1. high production cost,
2. limited functionalities,
3. high susceptibility to thermal degradation[15] (Figure 13),
4. too complex biotechnological upstream and downstream technologies[16],
5. incompatibility with some of the conventional thermal processing techniques,
6. and the necessity for modifications to reach the required properties of products[17] or to enable processing by conventional polymer processing technologies.

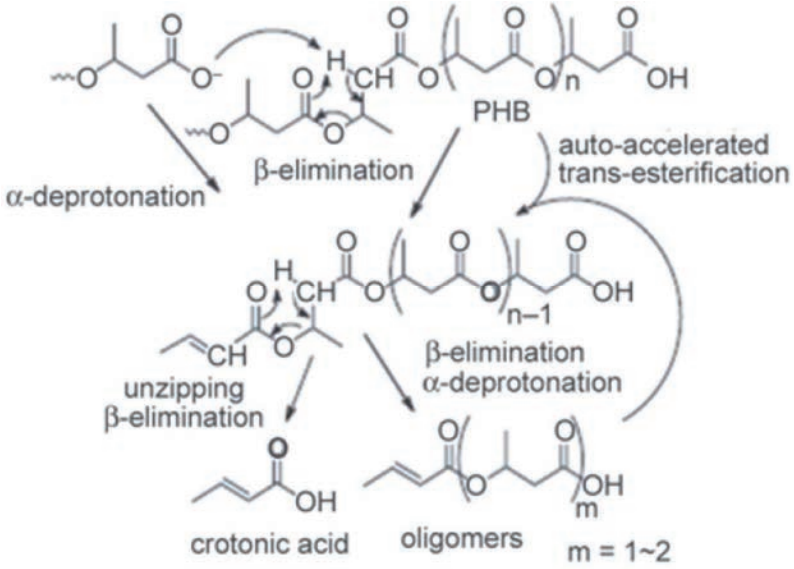

Figure 13: Reaction mechanisms of thermal degradation of P3HB [23].

The great benefit for the environment and targeted waste management is that carbon sources for biotechnological production of PHA can be derived from agro wastes [24], crude vegetable oils or waste frying oils [25]. Especially, the possible valorization of food waste, which is generated 180 kg per capita per year in the EU, is receiving interest. Every year is produced in EU about 88 million tons of food waste [26]. Development of the sustainable technologies, which would contribute to the circular economic use of food waste, is an essential multidisciplinary research task.

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[15] (A) A. Kovalcik, K. Meixner, M. Mihalic, W. Zeilinger, I. Fritz, W. Fuchs, P. Kucharczyk, F. Stelzer, B. Drosg, Characterization of polyhydroxyalkanoates produced by Synechocystis salina from digestate supernatant, Int. J. Biol. Macromol. 102 (2017) 497-504. 10.1016/j.ijbiomac.2017.04.054; (B) A. Kovalcik, L. Sangroniz, M. Kalina, K. Skopalova, P. Humpolíček, M. Omastova, N. Mundigler, A.J. Müller, Properties of scaffolds prepared by fused deposition modeling of poly (hydroxyalkanoates), Int. J. Biol. Macromol. 161 (2020) 364-376.

[16] K. Meixner, J. Jerney, A. Kovalcik, I. Fritz, B. Drosg, Poly(3-hydroxybutyrate) as renewable resource, in: R. Kourist, S. Schmidt (Eds.), The Autotrophic Biorefinery, De Gruyter In press.

[17] (A) A. Gregorova, R. Wimmer, M. Hrabalova, M. Koller, T. Ters, N. Mundigler, Effect of surface modification of beech wood flour on mechanical and thermal properties of poly (3-hydroxybutyrate)/wood flour composites, Holzforschung 63(5) (2009) 565-570. 10.1515/hf.2009.098; (B) A. Kovalcik, M. Machovsky, Z. Kozakova, M. Koller, Designing packaging materials with viscoelastic and gas barrier properties by optimized processing of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with lignin, React. Funct. Polym. 94 (2015) 25-34. 10.1016/j.reactfunctpolym.2015.07.001

In the last 15 years, a broad range of using food waste as carbon sources for PHA production has been described and studied (in September 2021, the Web of Science lists 73 papers/patents containing keywords food waste and PHA).

Since June 2017, when I moved to the Faculty of Chemistry, the Brno University of Technology as Marie Skłodowska-Curie Fellow, bringing the European Project: Bio-3D-MER (this project was funded from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie and co-financed by the South Moravian Region under grant agreement No. 665860, June 2017 – May 2020). The goal of my team's research was to pursue a target leap driven forward to the production of PHA using food waste, namely spent coffee grounds (SCG) and grape pomace (GP) biomass as a cheap carbon feedstock. The challenge of this research intention was to follow the principle of a circular economy and the balanced ecological and economic aspects. SCGs arise as waste products through the production of instant coffee and coffee brewing. As the mixture of skins, seeds, and stems, GP biomass is received from the winery waste streams and is usually undervalued. The Moravian region is known for the production of great wine.

Our research was focused on the valorization of SCG and GP as:

1. the valuable carbon sources for the cultivation of bacteria producing biodegradable and biocompatible PHA,
2. coffee oil and grape seed oil that is beneficial to human health due to their composition,
3. sources of bioactive phenolic compounds usable for food and cosmetic industries,
4. polymer matrices to produce various packaging, drug carriers, and tissue engineering materials.

At the beginning of this research, we reviewed the composition, methods for isolating bioactive compounds, and available methods for SCG. The fractionation of SCG and detoxification of SCG hydrolyzates might help to promote its broader utilization in many industrial sectors by the production of numerous valuable products (Figure 14).[18]

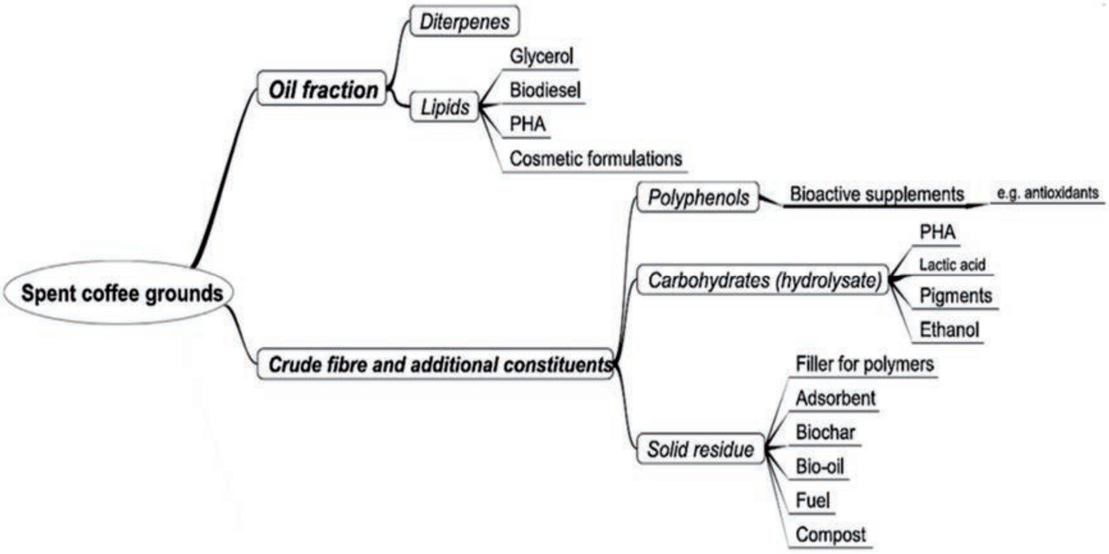

Figure 14: Alternative value-added products derived from spent coffee grounds.[18]

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[18] A. Kovalcik, S. Obruca, I. Marova, Valorization of spent coffee grounds: A review, Food Bioprod. Process. 110 (2018) 104-119. 10.1016/j.fbp.2018.05.002

In our research, we have further shown that detoxified spent coffee ground hydrolysates can be used as a carbon substrate for a variety of bacteria, which accumulate PHA, e.g. *Halomonas halophila* (Figure 15).[19] The suggested detoxification method enabled the elimination of polyphenols from SCG hydrolysates at one side and on the other side isolate substances with high antimicrobial activity.[20]

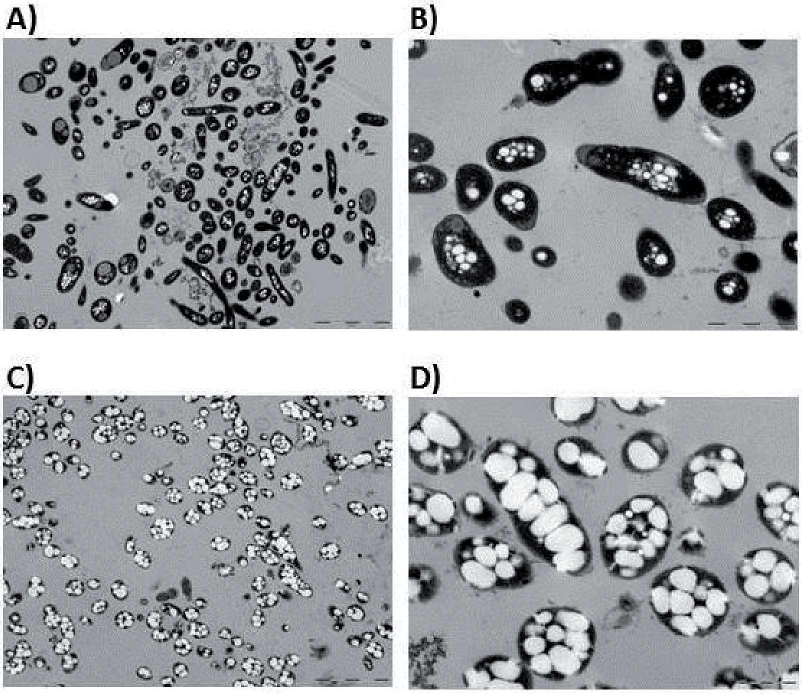

Figure 15: Microphotopgraphs of cells of *H. halophila* cultivated in complex nutrient rich media (A, B) and in mineral media containing glucose as the sole carbon source (C,D).[19A]

Next to the utilization of spent coffee grounds as a valuable by-product, we have proved that from the Moravian region's viewpoint, another valuable carbon source suitable for PHA production could be grape pomace.[21] PHAs can be produced by various bacterial strains,

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[19] (A) D. Kucera, I. Pernicová, A. Kovalcik, M. Koller, L. Mullerova, P. Sedlacek, F. Mravec, J. Nebesarova, M. Kalina, I. Marova, V. Krzyzanek, S. Obruca, Characterization of the promising poly(3-hydroxybutyrate) producing halophilic bacterium Halomonas halophila, Bioresour. Technol. 256 (2018) 552-556. https://doi.org/10.1016/j.biortech.2018.02.062; (B) A. Kovalcik, D. Kucera, P. Matouskova, I. Pernicova, S. Obruca, M. Kalina, V. Enev, I. Marova, Influence of removal of microbial inhibitors on PHA production from spent coffee grounds employing Halomonas halophila, J. Environ. Chem. Eng. 6(2) (2018) 3495-3501. https://doi.org/10.1016/j.jece.2018.05.028

[20] A. Kovalcik, P. Matouskova, D. Kucera, S. Obruca, I. Marova (2019) Why polyphenols present in spent coffee grounds inhibit the growth of bacteria producing polyhydroxyalkanoates? In: Papers, Slide presentations, Posters, European Biomass Conference and Exhibition Proceedings, 26th EUBCE – 2018, ISSN 2282-5819, http://www.etaflorence.it/proceedings/?detail=15436.

[21] (A) A. Kovalcik, I. Pernicova, S. Obruca, M. Szotkowski, V. Enev, M. Kalina, I. Marova, Grape winery waste as a promising feedstock for the production of polyhydroxyalkanoates and other value-added products, Food Bioprod. Process. 124 (2020) 1-10. 10.1016/j.fbp.2020.08.003; (B) A. Kovalcik, S. Obruca, M. Kalina, M. Machovsky, V. Enev, M. Jakesova, M. Sobkova, I. Marova, Enzymatic hydrolysis of poly (3-Hydroxybutyrate-co-3-Hydroxyvalerate) scaffolds, Materials 13(13) (2020) 2992.

and different carbon sources can be used, but the fermentation process needs to be optimized (Figure 16).[15, 22]

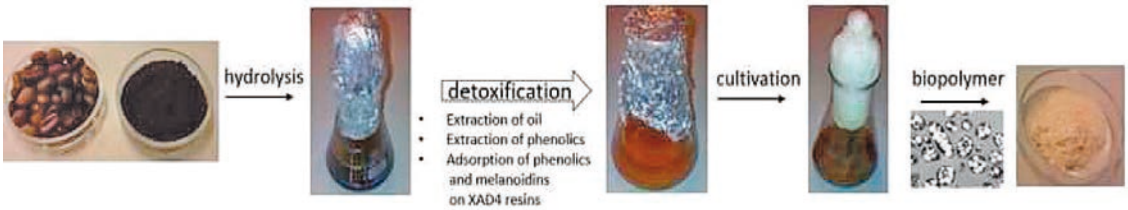

Figure 16: Fermentation of *C.necator* on the base of detoxified SCG hydrolysates.[19B]

4.1.2.1 PHA's applications

The next step in our research was to prepare the high- and low-end applications of PHAs. We have shown that phenolic compounds isolated from grape pomace have high radical scavenging and thermo-oxidation stabilization efficiencies in PHA films.[23] Films and scaffolds for low-end and high-end applications were prepared from isolated as well as commercially available PHAs with different chemical compositions and properties.[24] Furthermore, we have successfully developed and characterized electrospun porous PHB meshes for drug delivery. The results showed that PHB electrospun meshes seem to be efficient drug carriers for antimicrobial agents, and this finding is highly promising for tissue engineering applications.[25] They might contribute to the prevention and treatment of wound and surgical site infections caused by gram-negative bacteria, thus possibly enhancing hygiene/quality of life for citizens in Moravia as well as worldwide.

Our investigations revealed that some types of PHA are suitable for fused deposition modelling (FDM) (Figure 17).

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[22] (A) K. Meixner, A. Kovalcik, E. Sykacek, M. Gruber-Brunhumer, W. Zeilinger, K. Markl, C. Haas, I. Fritz, N. Mundigler, F. Stelzer, M. Neureiter, W. Fuchs, B. Drosg, Cyanobacteria Biorefinery - Production of poly(3-hydroxybutyrate) with Synechocystis salina and utilisation of residual biomass, J. Biotechnol. 265 (2018) 46-53. 10.1016/j.jbiotec.2017.10.020; (B) I. Pernicova, D. Kucera, I. Novackova, J. Vodicka, A. Kovalcik, S. Obruca, Extremophiles-Platform Strains for Sustainable Production of Polyhydroxyalkanoates, Mater. Sci. Forum, Trans Tech Publ, 2019, pp. 74-79; (C) I. Novackova, D. Kucera, J. Porizka, I. Pernicova, P. Sedlacek, M. Koller, A. Kovalcik, S. Obruca, Adaptation of Cupriavidus necator to levulinic acid for enhanced production of P(3HB-co-3HV) copolyesters, Biochem. Eng. J. 151 (2019). 10.1016/j.bej.2019.107350

[23] A. Kovalcik, J. Mierna, P. Vostrejs, M. Kalina, P. Sedlacek, V. Enev, M. Omastova, I. Marova (2019) Packaging materials based on polyhydroxyalkanoates and lignin derived from grape pomace. 27 th European Biomass Conference & Exhibition, Lisbon, Portugal, 27-30 May 2019, Book of abstracts, Session reference 3CO.9.4, Oral presentation – A. Kovalcik.

[24] (A)I. Pernicova, I. Novackova, P. Sedlacek, X. Kourilova, M. Kalina, A. Kovalcik, M. Koller, J. Nebesarova, V. Krzyzanek, K. Hrubanova, J. Masilko, E. Slaninova, S. Obruca, Introducing the Newly Isolated Bacterium Aneurinibacillus sp. H1 as an Auspicious Thermophilic Producer of Various Polyhydroxyalkanoates (PHA) Copolymers–1. Isolation and Characterization of the Bacterium, Polymers 12(6) (2020) 1235; (B) P. Sedlacek, I. Pernicova, I. Novackova, X. Kourilova, M. Kalina, A. Kovalcik, M. Koller, J. Nebesarova, V. Krzyzanek, K. Hrubanova, J. Masilko, E. Slaninova, M. Trudicova, S. Obruca, Introducing the Newly Isolated Bacterium Aneurinibacillus sp. H1 as an Auspicious Thermophilic Producer of Various Polyhydroxyalkanoates (PHA) Copolymers–2. Material Study on the Produced Copolymers, Polymers 12(6) (2020) 1298.

[25] V. Kundrat, N. Cernekova, A. Kovalcik, V. Enev, I. Marova, Drug Release Kinetics of Electrospun PHB Meshes, Materials 12(12) (2019). 10.3390/ma12121924

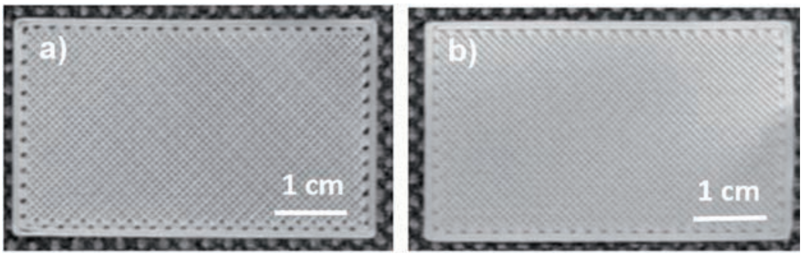

Figure 17: 3D printed (a) PHBH scaffolds and (b) PLA scaffolds.[26]

FDM belongs to modern rapid prototyping techniques for the fabrication of scaffolds. The comparison of thermal and rheological properties of commercially available poly(3-hydroxybutyrate (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(3hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) with poly(lactic acid) (PLA) revealed the massive decrease in viscosity and loss of molecular weight in the case of PHB and PHBV. The thermal stability and mechanical properties of PHBH were comparable to that of PLA. PHBH scaffolds showed no cytotoxicity. Compared to PLA scaffolds, PHBH promoted much higher cell proliferation (Figure 18) and faster abiotic degradation in model digestive fluid. These results illustrated that PHBH could expand the offer of biodegradable polymers used for fused deposition modelling, offering excellent biocompatibility and biodegradability in body fluids. [26]

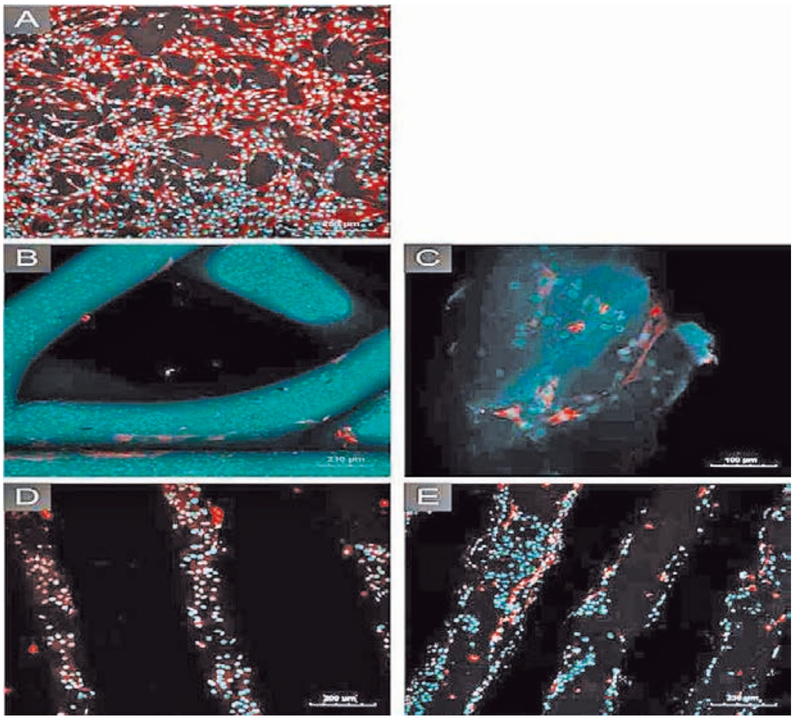

Figure 18: Micrographs of mouse embryonic fibroblast cell line NIH/3T3 cultivated directly on PLA and PHBH scaffolds. A) Reference; B) PLA; C) PLA coated with gelatine; D) PHBH; E) PHBH coated with gelatine.[26]

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[26] A. Kovalcik, L. Sangroniz, M. Kalina, K. Skopalova, P. Humpolíček, M. Omastova, N. Mundigler, A.J. Müller, Properties of scaffolds prepared by fused deposition modeling of poly (hydroxyalkanoates), Int. J. Biol. Macromol. 161 (2020) 364-376.

In addition to the biocompatibility of PHAs, it is also known that they are biodegradable. Despite this hypothesis, once PHA products' composition modifies, biodegradation should be tested. The biodegradability test carried out under a controlled composting environment for 90 days showed that the PHB/PHA blended film with 50 w/w% of amorphous PHA reached the degradability degree of 68.8%. This value was showed about 26.6% higher decomposition than in the case of neat high crystalline PHB film. Next, the degradability degree of PHA films in compost within the tested period reflected the modification of the semi-crystalline character and varied with the incorporated lignin (Figure 19). From the toxicological point of view, the composts obtained after biodegradation of PHA films proved the non-toxicity of PHB/PHA/GS-L materials, and the degradation products showed a positive effect on white mustard (*Sinapis alba* L.) seeds germination.[27]

Figure 19: Active and biodegradable bioplastics originated from grape pomace.[27]

Our research showed that it is possible to prepare PHA-based materials with a wide range of properties with applications in packaging, cosmetics, pharmacy, or medicine. In some cases the composition of PHA has to be modified to withstand the mechanical and thermal stress during melt processing, for example fused deposition modelling.[28]

However, in conclusion, it has been confirmed that PHA materials are thermoplastic materials biodegradable under different conditions and with varying degradation rates and extent concerning the polymer composition, molecular weight and semi-crystalline character.[21B, 24B, 26, 27]

Therefore, it can be stated that PHA is a melt-processable polymer if its viscosity and thermal stability are adjusted according to the requirements of the given processing process.

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[27] P. Vostrejs, D. Adamcova, M.D. Vaverkova, V. Enev, M. Kalina, M. Machovsky, M. Sourkova, I. Marova, A. Kovalcik, Active biodegradable packaging films modified with grape seeds lignin, RSC Adv. 10(49) (2020) 29202-29213. 10.1039/d0ra04074f

[28] A. Kovalcik, J. Smilek, M. Machovsky, M. Kalina, V. Enev, H. Dugova, N. Cernekova, M. Kovacova, Z. Spitalsky, Properties and structure of poly (3-hydroxybutyrate-co-4-hydroxybutyrate) filaments for fused deposition modelling, Int. J. Biol. Macromol. 183 (2021) 880-889. doi.org/10.1016/j.ijbiomac.2021.04.183

5 SUMMARY

The thesis represents a brief overview of 19 years of research, which began with a doctoral study in 2002 focused on isolation and utilization of lignin by Adriana Kovalčík at the Institute of Chemistry, Slovak Academy of Sciences in Bratislava. Lignin is a biopolymer found in the cell walls of plants. The biosphere is estimated to contain 3x10^{11} tons of lignin. Lignin is mainly obtained as a by-product of pulp production. The topic of her dissertation was "Utilization of lignin in polymer mixtures" (2005, Slovak Technical University in Bratislava). This research has shown that lignins have antioxidant, stabilizing and reinforcing properties that can be used to modify rubber and polyolefins. These results were published in 10 scientific impact publications and one book chapter.

The next stage in the Kovalčík research from 2006 to 2016 (University Blaise Pascal, Clermont Ferrand; University of Natural Resources and Applied Life Sciences, Vienna; Graz University of Technology, Graz) focused on the synthesis, modification, processing, and characterisation of chemical and physical properties of biodegradable plastics and composites prepared from them. The main goal of this research was to improve the interfacial compatibility between the inorganic or organic filler and matrices based on biodegradable polyesters. The results of this research were published in 25 scientific impact publications and six book chapters. This period of research and teaching ended in a habilitation in the field of "Macromolecular Chemistry and Technology at TU Graz (2015, Topic: Investigation and modification of thermo-mechanical and viscoelastic properties of biodegradable polymers and biocomposites).

Another significant step in Kovalcik's research occurred in 2017 at the Faculty of Chemistry, the Brno University of Technology. She expanded her work in bioplastics to biotechnology and bioengineering and focused on the circular economy perspective of using agro- and food waste as valuable compounds to produce polyhydroxyalkanoates and other valuable materials with the ability to be compostable. This research continues and has been published in 26 scientific impact publications and one book chapter. This research has brought several new original findings and showed enormous possibilities for the use of renewable resources, especially agro- and food waste, and emphasised that biopolymers and bioplastics belong to important materials with a significant impact on the bioeconomy and society.

6 SHRNUTÍ

Tyto teze představují stručný průřez 19letým výzkumem autorky práce Adriany Kovalčík, který začal doktorským studiem zaměřeným na izolaci a využití ligninu na Chemickém ústavu, Slovenské akademie věd v Bratislavě. Lignin je biopolymer nacházející se v buněčných stěnách rostlin. Odhaduje se, že biosféra obsahuje 3×10^{11} tun ligninu. Lignin se převážně získává jako meziprodukt při výrobě buničiny a papíru. Tématem disertační práce bylo „Využití ligninu v polymerních směsích“ (2005, Slovenská technická univerzita v Bratislavě). Tento výzkum ukázal, že ligniny mají antioxidační, stabilizační a ztužující vlastnosti, které lze využít k modifikaci kaučuku a polyolefinů. Výsledky z uvedené oblasti výzkumu byly publikovány v 10 vědeckých impaktovaných publikacích a v jedné kapitole knihy.

Další etapou v rámci profesní kariéry Adriany Kovalčík byl výzkum zaměřený na syntézu, modifikaci, zpracování a charakterizaci chemických a fyzikálních vlastností biologicky rozložitelných plastů a z nich připravených kompozitů (2006 – 2016; University Blaise Pascal, Clermont Ferrand; University of Natural Resources and Applied Life Sciences, Vienna; Graz University of Technology, Graz). Hlavním cílem bylo zlepšit mezifázovou kompatibilitu mezi anorganickým nebo organickým plnivem a matricemi na bázi biologicky rozložitelných polyesterů. Výsledky uvedené výzkumné etapy byly publikovány v 25 vědeckých impaktovaných publikacích a šesti kapitolách knih. Toto období výzkumu a pedagogických aktivit vyústilo v roce 2015 habilitací v oboru Makromolekulární chemie a technologie na TU Graz (Téma: „Výzkum a modifikace termálních, mechanických a viskoelastických vlastností biologicky rozložitelných polymerů a biokompozitů“).

K dalšímu významnému kroku v profesní historii Adriany Kovalčík došlo v roce 2017, kdy začala pracovat v rámci evropského projektu SoMoPro (JIC + EU) na Fakultě chemické Vysokého učení technického v Brně. Svou práci v rámci bioplastů rozšířila v oblasti biotechnologie a bioinženýrství a zaměřila se na perspektivu využití konceptu cirkulární ekonomiky ke zpracování vybraných odpadních materiálů zemědělsko-potravinářského komplexu jako hodnotných sloučenin k výrobě polyhydroxyalkanoátů a jiných cenných biodegradabilních materiálů, jakož i dalších produktů s vysokou přidanou hodnotou. Tento výzkum průběžně pokračuje a výsledky byly zatím publikovány ve 26 vědeckých impaktovaných publikacích a jedné kapitole v odborné knize. Poslední uvedená etapa výzkumné práce A. Kovalčík přinesla několik nových původních poznatků a poukázala na značný potenciál využití obnovitelných zdrojů, zejména odpadů ze zemědělského a potravinářského průmyslu. Z dosažených výsledků jasně vyplývá, že přírodní biopolymery a bioplasty patří k důležitým materiálům s významným dopadem na biohospodářství a celou společnost.

REFERENCES

[1] I. Tiseo, Annual production of plastics worldwide from 1950 to 2020 2021. https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/.

[2] R. Geyer, J.R. Jambeck, K.L. Law, Production, use, and fate of all plastics ever made, Sci. Adv. 3(7) (2017) e1700782.

[3] R. Meys, F. Frick, S. Westhues, A. Sternberg, J. Klankermayer, A. Bardow, Towards a circular economy for plastic packaging wastes–the environmental potential of chemical recycling, Resour. Conserv. Recycl. 162 (2020) 105010.

[4] I. Tiseo, Production capacity of bioplastics worldwide from 2019 to 2025, by type 2021. https://www.statista.com/statistics/678684/global-production-capacity-of-bioplastics-by-type/.

[5] PlasticsEurope, Plastics - the Facts 2020, PlascticsEurope, Belgium, 2020.

[6] R.A. Sheldon, M. Norton, Green chemistry and the plastic pollution challenge: towards a circular economy, Green Chem. 22(19) (2020) 6310-6322.

[7] https://eur-lex.europa.eu/summary/glossary/circular_economy.html, Glossary of summaries. CIRCULAR ECONOMY, download 26.09.21.

[8] D.K. Bora, Rise of the sustainable circular economy platform from waste plastics: A biotechnological perspective, MRS Energy Sustain. 7 (2020). 10.1557/mre.2020.28.

[9] G. Kaur, K. Uisan, K.L. Ong, C.S.K. Lin, Recent trends in green and sustainable chemistry & waste valorisation: rethinking plastics in a circular economy, Curr. Opini.Green Sustain. chem. 9 (2018) 30-39.

[10] https://ellenmacarthurfoundation.org/, The vision of a circular economy for plastic, 2020.

[11] https://ec.europa.eu/info/research-and-innovation/research-area/environment/bioeconomy_en, Why the EU supports bioeconomy research and innovation, download 28.09.21.

[12] https://ec.europa.eu/info/research-and-innovation/research-area/environment/bioeconomy/bio-based-products-and-processes_en, Bio-based products and processes, download 28.09.21.

[13] https://www.european-bioplastics.org/faq-items/what-are-the-advantages-of-bioplastic-products/, What are the advantages of bioplastic products?, download 27.09.21.

[14] M. Carus, Bio-based Building Blocks and Polymers – Global Capacities, Production and Trends 2020 – 2025, www.renewable-carbon.eu/publications, 2021.

[15] T. Tábi, S. Hajba, J. Kovács, Effect of crystalline forms (α′ and α) of poly (lactic acid) on its mechanical, thermo-mechanical, heat deflection temperature and creep properties, Eur. Polym. J. 82 (2016) 232-243.

[16] F.-D. Kopinke, M. Remmler, K. Mackenzie, M. Möder, O. Wachsen, Thermal decomposition of biodegradable polyesters—II. Poly (lactic acid), Polym. Degrad. Stab. 53(3) (1996) 329-342.

[17] C. Vogel, H.W. Siesler, Thermal Degradation of Poly (ε-caprolactone), Poly (L-lactic acid) and their Blends with Poly (3-hydroxy-butyrate) Studied by TGA/FT-IR Spectroscopy, Macromol. Symp., Wiley Online Library, 2008, pp. 183-194.

[18] W.P. Cambridge Consultants, Polyhydroxyalkanoates: Plastic the way nature intended?, www.CambridgeConsultants.com, download 20.09.2021.

[19] P. Kumar, S.K. Patel, J.-K. Lee, V.C. Kalia, Extending the limits of Bacillus for novel biotechnological applications, Biotechnol. Adv. 31(8) (2013) 1543-1561.

[20] https://www.tepha.com/products/overview/, Tepha Medical Devices, download 29.09.2021.

[21] https://www.nafigatecosmetics.cz, Nafigate cosmetics, (download 29.09.2021).

[22] Z.A. Raza, S. Abid, I.M. Banat, Polyhydroxyalkanoates: Characteristics, production, recent developments and applications, Int. Biodeterior. Biodegrad. 126 (2018) 45-56.

[23] E. Bugnicourt, P. Cinelli, A. Lazzeri, V.A. Alvarez, Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging, Express Polym. Lett. (2014), 10.3144/expresspolymlett.2014.82.

[24] C. Nielsen, A. Rahman, A.U. Rehman, M.K. Walsh, C.D. Miller, Food waste conversion to microbial polyhydroxyalkanoates, Microb. Biotechnol. 10(6) (2017) 1338-1352.

[25] I. Marova, S. Obruca, R. Prikryl, Method of producing polyhydroxyalkanoates (pha) from oil substrate, WO2014032633A1 2014.

[26] European Parliament, Food waste: the problem in the EU in numbers. www.europarl.europa.eu/news/en. (Accessed 12-05-2017.

ABSTRACT

The submitted thesis deals with the importance of bioplastics from the point of view of the circular economy. Bioplastics are a group of polymers that are bio-based and/or biodegradable. The primary attention in the present work is paid to lignin, polylactide and polyhydroxyalkanoates. Lignin is an amorphous natural polymer composed of phenylpropane units with various functional substitutions. Lignins occur in plants and act as a stabilizer against mechanical, biochemical and environmental stress. PLA is a semi-crystalline polyester whose monomer, lactic acid, can be obtained biotechnologically from renewable sources. Polyhydroxyalkanoates are biodegradable thermoplastic biopolymers with high application potential produced by microorganisms. The work aimed to point out how research and applications in the field of bioplastics can help to respect the principles of circular economics and bioeconomy.

ABSTRAKT

Tyto teze pojednávají o významu bioplastů z hlediska cirkulární ekonomiky. Bioplasty jsou materiály na bázi polymerů, které splňují aspoň jedno z kritérií: 1) jsou syntetizovány z obnovitelných zdrojů, 2) jsou biologicky rozložitelné. Hlavní pozornost v předložené práci je věnovaná ligninu, polylaktidu a polyhydroxyalkanoátům. Lignin je amorfní přírodní polymer složený z fenylpropanových jednotek s různými funkčními substitucemi. Ligniny se vyskytují v rostlinách a působí jako stabilizátor proti mechanickému, biochemickému a environmentálnímu stresu. Polylaktid je semikrystalický polyester jehož monomer, kyselinu mléčnou, lze získat biotechnologicky z obnovitelných zdrojů. Polyhydroxyalkanoáty jsou biodegradabilní termoplastické biopolymery s velkým aplikačním potenciálem produkované mikroorganismy. Záměrem práce bylo demonstrovat, jak může výzkum a aplikace v oblasti bioplastů podpořit principy cirkulární ekonomiky a biohospodářství.